

STRONG-FIELD CHIRAL LIGHT - MATTER INTERACTION

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ABSTRACT

The physical world is asymmetric in nature. This broken symmetry manifests itself throughout the micro and macro worlds, ranging from fundamental particles to the realm of molecules, and from biological organisms to spiral galaxies. Therefore, chirality is of interest to physicists, chemists, and biologists alike. The study of chiroptical phenomena requires an interaction between two chiral systems - a chiral reagent with known handedness that can induce a differential response of non-superimposable chiral objects. Chiroptical effects are conventionally performed using Circularly polarized light (CPL) as their chiral probe.

This dissertation presents a conceptually new form of chiroptical detection technique using the helical phase of light as the chiral probe. Structured light beams, also known as helical light beams, can carry Orbital Angular Momentum (OAM) $\pm l\hbar$ which is associated with the dynamical rotation of wavefront structure. The intensity profile of such light is characterized by a phase singularity (optical vortex) and hence a null intensity region at the center of the beam. The handedness of these beams is associated with the twisting of the wavefront undergoing l intertwined rotations in one wavelength. This is analogous to the chiral structure of the electric field associated with CPL. Moreover, helical light can be categorized as symmetrical and asymmetrical OAM beams. The latter is achieved by displacing the phase singularity, resulting in an additional degree of control over these structured beams. Therefore, by using asymmetrical helical light as a chiral probe, two extra degrees of freedom are gained to study chiral interactions. i) The theoretical unbounded l -value, which increases the number of intertwined twists within the helical pitch which in principle could increase the chiral sensitivity with the l -value. ii) The asymmetrical parameter δ , affects the field strength and the field gradient around the optical vortex.

We show that these additional degrees of freedom can influence and control the sensitivity of the chiral signal. The chiral response from the helical light can be classified by two types of Helical Dichroism (HD) signals: HD(Type I) defined as the differential absorption of left- and right-helical light for a specific molecule and HD(Type II) defined as differential absorption between the two chiral objects for a specific helicity and polarization of light. Our observations demonstrate that HD(Type I) is a beam-dominant property where the broken symmetry of the helical light can induce a differential response in randomly orientated molecules or solids with or without structural symmetry. While, HD(Type II) is a material property and is sensitive to both chiral molecular and crystalline structures.

Using absorption spectroscopy, we demonstrated the first direct observation of HD in liquid, solid, and gas phases using linearly polarized asymmetrical helical light as the chiral probe without the use of any intermediary.

- (i) We show that enantio-pure liquids exhibit enantio-selectivity, a phase effect that can be enhanced by the l -value and controlled by the asymmetrical parameter δ . Contrary to conventional beliefs, we found that HD(Type I) occurs even in randomly orientated achiral liquids. These discoveries highlight the benefits of using asymmetrical helical light as the chiral probe and shift the paradigm of chiroptical detection from laser polarization to the optical helical phase.
- (ii) To further solidify the significance of HD as a chiroptical technique, we demonstrated its presence in enantiomeric solutions with varying concentrations, since solvents can alter the structure and properties of biomolecules thereby modifying their function and reactivity.

These chiroptical effects are not exclusive to molecular structures; they can also occur in crystalline structures. In solid-state materials, the higher density combined with the inherent birefringence and macroscopic anisotropies often mask the optical signal of traditional methods.

- (i) We demonstrate that helical light can map crystal symmetry, and differentiate chiral crystals with an HD signal one to two orders of magnitude higher than when using CPL. We also show that achiral crystals exhibit HD(Type I) and the magnitude of the signal is influenced by the bandgap. These results demonstrate that the crystal structure in solid-state matter responds strongly to the optical helical phase compared to CPL.
- (ii) This novel form of solid-state optical dichroism is not limited to crystalline structures. We observe the first existence of intrinsic dichroism in amorphous solids using asymmetrical helical light beams. Such an

effect is typically unexpected in glass materials due to the disorderly state of the medium. Suggesting that HD(Type I) is responsive to the short-range order of amorphous materials. This new development in chiroptical techniques can aid the understanding of the mysterious nature of amorphous materials and the development of various optical applications.

In the gas phase, two techniques are introduced to study chiral systems. Both implement a time-of-flight mass spectrometer (TOFMS) detection scheme; however, we use two different chiral probes.

- (i) Elliptical dichroism using a femtosecond laser mass spectrometer provides a molecular fingerprint of the interaction by measuring the ions and fragments produced during the ionization and recollision process. The chiral recollision yields are influenced by the handedness of the elliptically polarized light. This method overcomes the limitation of needing pure enantiomers or prior chemical separation for measurements. The chiral efficiency is significantly higher than conventional Circular Dichroism (CD) and comparable to Photoelectron circular dichroism (PECD).
- (ii) Orbital angular momentum-dependent strong-field ionization reveals that asymmetrical helical light offers new dimensions to control the strong-field ionization of atoms and molecules. Our findings indicate that the ions and fragments of chiral and achiral molecules are strongly influenced by the handedness, the l -value of the OAM, and can be manipulated by shifting the phase singularity. This allows us to examine the effect of helical light on any element of the molecular composition. Moreover, this differential ionization is not limited to molecules; we show that argon exhibits similar ionization effects.

In a vacuum system, the absence of significant intermolecular interactions and propagation leads to a clean chiroptical signal with high sensitivity compared to the liquid and solid phases. Also, by using asymmetrical helical light the field strength and the field gradient around the optical vortex can be manipulated which can increase the ponderomotive energy and acceleration compared to Gaussian light, and this effect intensifies with an increase in the l -value. These discoveries offer new opportunities in strong-field and plasma physics, potentially creating applications of asymmetrical helical beams in *all* states of matter.

In the liquid phase, we model light-matter interaction by considering multipole expansion in the perturbative regime. We find that HD arises from the coupling of the electric dipole and electric quadrupole terms. In the solid phase, we model HD by considering electron transitions via Multiphoton-Assisted Tunneling (MPAT). This process ensures that electron displacement remains within the short-range order in solids, enabling us to effectively probe intrinsic dichroism. In the gas phase, we extend the model to the non-perturbative tunneling regime and demonstrate that the differential ionization results from the field strength and gradient directly influencing the molecular and atomic potential.

The advantages of using asymmetrical helical phased light as a chiral reagent in all three phases of matter include the ability to tune and precisely control the amplitude of HD(Type I). This can be achieved by (i) shifting the phase singularity in the beam, (ii) superposition of OAM and Gaussian beams, (iii) varying the l -value, and (iv) varying the laser polarization. These unique characteristics, along with the bandgap and ionization potential dependence of HD and differential ionization, distinguish this technique from other existing polarization-based chiroptical methods.

THESIS MOTIVATION

Chiroptical effects were traditionally studied using spectroscopic methods and CPL as their chiral probe. These techniques, which include optical rotatory dispersion (ORD), CD, and Vibrational Circular Dichroism (VCD), rely on the handedness of CPL to induce enantio-sensitive transitions in a chiral molecule. The differential response arises from the coupling of the electric and magnetic dipole matrix elements. The chiral sensitivity is limited by the relative size difference between the molecular dimension and helical pitch of the CPL and scales inversely with the wavelength of light. Consequently, the chiral efficiency of CD is poor, on the order of 0.01 – 1%. Spectroscopic techniques using CPL X-ray gained considerable interest due to the size of the helical pitch being comparable to the molecular size. However, it is still performed in the linear resonant absorption regime and relies on the weak transition moments.

Applications of conventional chiroptical techniques are widespread, from the stereochemistry of both organic and inorganic molecules to the characterization of biomolecules (such as nucleic acids, DNA) and to drug development in the pharmaceutical industry since most drugs are chiral compounds. As the demand for these techniques grows, so does the need for innovative and highly efficient chiroptical techniques that provide detailed insights into the characterization of chiral molecules and their enantio-sensitive interactions.

The advent of high-powered pulsed lasers opened new avenues for investigating chiral effects, leading to improved chiral signals in the nonlinear absorption regime through two-photon CD and nonlinear optical activity. These advancements enabled the development of non-resonant, nonlinear chiroptical techniques with greater enhanced chiral sensitivity due to the intense light fields. To further improve efficiency, we can either rely exclusively on the electric dipole transitions as seen in PECD and synthetic chiral light or redefine a new chiral reagent that can amplify the chiral signal even with higher-order interaction terms. PECD has higher efficiency than CD but is mostly limited to gas phase chiral molecules, and synthetic chiral light has yet to be observed experimentally. Therefore, defining a new chiral reagent is the only path forward for the advancements of chiroptical spectroscopy.

This research introduces a conceptually new form of chiroptical technique using asymmetrical helical light beams to probe and control light-matter interactions in liquid, solid and gas phases. It exhibits high efficiency and control over the chiral signal and can induce differential signal even in achiral matter. This optical probe has potential implications for a variety of fields, including physics, chemistry, and material science. This approach is versatile and can be integrated into existing CD spectrophotometers and can be extended to plasmonic metasurfaces or transparent polymers. This work paves the way for advancements in chiroptical spectroscopy, asymmetric catalysis, molecular electronic devices, chiral sensors, and electron dynamics in attosecond and plasma physics. The efficiency of HD allows for chiral recognition on solid surfaces, a critical aspect in surface and material sciences. It also offers new avenues for developing enantioselective catalysis and asymmetrically synthesizing bioactive molecules.

OVERVIEW

INTRODUCTION TO CHIRALITY

This first chapter provides an introduction to the concept of chirality and its significant role in nature. This sets the stage for an exploration and explanation of traditional chiroptical techniques and the theory used in both liquid and solid phases, such as CD and Optical Rotation (OR). It will also discuss the observation of chiral discrimination in the gas phase, where we present an efficient nonlinear gas phase chiroptical techniques and their mechanisms. These above-mentioned techniques utilize CPL as the chiral probe and will serve as a comparative basis throughout our study. Despite their widespread use, we address the inherent limitations of using CPL as a chiral reagent. Throughout, the chapter we propose a solution to these constraints by employing helical light as a probe, where unexpected findings and additional advantages are observed.

OPTICAL PROBE AND DETECTION SCHEME

The second chapter includes both the theoretical and experimental aspects of the optical probe and the detection schemes. The section on the optical probe describes the fundamentals of femtosecond pulses, their physical properties, and their generation process in a Ti:Sapphire laser system. This discussion will be extended to include structured light such as Laguerre-Gaussian (LG) beams. Additionally, a distinction between symmetric and asymmetric LG beams will be presented both theoretically and experimentally. The second section on the detection scheme will explore the details of two experimental setups: i) a transmission setup used to measure the absorption of light for both liquid and solid samples and ii) a TOFMS used to detect the ions and fragments produced during the interaction.

WEAK- AND STRONG-FIELD LIGHT-MATTER INTERACTION

This chapter sets the theoretical groundwork for our models and results, focusing on light-matter interaction in both weak and strong field regimes. The weak field section provides details on the perturbative approach of light-matter interaction with a weakly perturbing field. It provides an overview of linear absorption, in relation to CD and ORD, and on nonlinear absorption, specifically Multiphoton Absorption (MPA) pursued using both microscopic and macroscopic approaches.

The strong-field section will discuss the non-perturbative approach, used when the light field strength becomes comparable to the atomic potential. It outlines the limitations of the perturbation regime at high intensities and introduces the concept of tunnel ionization as well as different types of strong-field ionization methods. Furthermore, recollision dynamics is analyzed via generated ions (non-sequential double ionization) or emitted high-harmonics of incident light.

LIQUID PHASE - HELICAL LIGHT INTERACTION

This chapter lays the foundation for understanding helical dichroism in the liquid phase, summarizing past experimental and theoretical advancements. It is followed by an outline of two published articles in Nature Photonics and the Journal of Chemical Physics where we elaborate on the uniqueness of our concept, experimental procedures, and key aspects useful for understanding the progression of our findings.

We demonstrate that enantio-pure liquids respond differently to the handedness of the rotating wavefront of the helical light and therefore exhibit enantio-selectivity. It was also found that randomly oriented achiral liquids show a type of dichroism when probed with helical light. Additional information includes experimental checks and procedures to validate our observations. The second study highlights the importance of HD as a chiroptical technique by demonstrating its presence in enantiomeric solutions with varying concentrations, given the crucial role solvents play in many biological processes. Chiroptical effects can be amplified by the l -value and controlled by the asymmetrical parameter δ .

Throughout this chapter, we emphasize the use of asymmetrical helical light as the chiral probe, which adds more control parameters to existing chiroptical detection utilizing laser polarization.

SOLID-STATE PHASE - HELICAL LIGHT INTERACTION

This chapter will shift focus from the liquid phase to the solid-state phase, illustrating that chiroptical effects are also evident in crystalline structures. Initially, we will provide foundational knowledge of multiphoton absorption of Gaussian and helical light, followed by the necessary details to comprehend the physics of the established model.

Using our third article, published in Nature Communications, we reveal that the structural symmetry of the crystal can be mapped by angle-dependent absorption of helical light. Furthermore, the HD signal of both chiral and achiral crystals can be measured at a level one to two orders of magnitude greater than when probed using circularly polarized light. We also show that HD is not limited to crystalline structures. Intrinsic dichroism is present in amorphous solids when probed with asymmetrical helical light beams. This indicates that HD is sensitive to the short-range order of amorphous materials. These observations are explained by a hybrid model between perturbative and tunnel ionization, known as MPAT. A supplementary is included for additional theoretical and experimental results.

GAS PHASE - HELICAL LIGHT INTERACTION

This chapter will focus on the experimental results obtained from a time-of-flight mass spectrometer where ions produced in the interaction region are detected. It will be divided into two gas phase techniques to study molecular and atomic systems in the strong-field regime. The first section will consist of the chiroptical technique, as detailed in our fourth article published in Scientific Reports. Here, we found that the chiral recollision yields of ions and fragments are influenced by the handedness of the elliptically polarized light. This variation in ionization results in an efficiency comparable to PECD and surpasses CD. A detailed section on recollision dynamics lays the foundations for the description of the mechanisms responsible for the chiroptical effects.

The second section focuses on orbital angular momentum-dependent strong-field ionization an article submitted to Nature Physics. In this approach the chiral optical probe is replaced from CPL to asymmetrical helical light, offering new degrees of control over the ionization of atoms and molecules. Our findings indicate that ionization of chiral and achiral molecules are strongly influenced by the handedness, l -value, and can be manipulated by shifting the phase singularity. This observed differential ionization is also shown for atomic systems such as argon. Lastly, by using asymmetrical helical light, the field strength and the field gradient around the optical vortex can be manipulated to increase the ponderomotive energy and force with l -value. A theory section on non-dipole tunnel ionization with asymmetrical LG beam is provided with additional supplementary information.

CONCLUSION AND FUTURE IMPACT

The final chapter of this dissertation will contain the concluding remarks and the future scope of my research. This will include a discussion on the potential impact this research has on the scientific community, such as further advancement in strong-field physics, plasma physics, nonlinear optics, and attosecond dynamics. The findings from this research open many opportunities for future experiments such as High-Harmonics Generation (HHG) with asymmetric LG beam, Photoelectron Helical Dichroism (PEHD), and OAM-dependent Non-Sequential Double Ionization (NSDI). These new ideas followed by their proof of principle are included. This research and future scope should encourage further investigation into the mysterious nature of helical light-matter interaction. The potential for new discoveries and advancements is immense, and the implications of such could be far-reaching.

LIST OF PUBLICATIONS

I contributed to the following peer-reviewed publications during my graduate studies at the University of Ottawa in the department of Physics.

1. **Jean-Luc Bégin**, Maye Alsaawy, & Ravi Bhardwaj. Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry. *Scientific Reports*. **10**, 14074 (2020) DOI: 10.1038/s41598-020-71069-9.
2. **Jean-Luc Bégin***, Ashish Jain*, Andrew Parks, Felix Hufnagel, Paul Corkum, Ebrahim Karimi, Thomas Brabec & Ravi Bhardwaj. Nonlinear helical dichroism in chiral and achiral molecules. *Nature Photonics*. **17**, 82–88 (2023) DOI: 10.1038/s41566-022-01100-0.
3. Ashish Jain*, **Jean-Luc Bégin***, & Ravi Bhardwaj. Helical dichroism in enantiomeric solutions^{EP}. *Journal of Chemical Physics*. **7**, 159, 014504 (2023) DOI: 10.1063/5.0152203.
4. Ashish Jain*, **Jean-Luc Bégin***, Paul Corkum, Ebrahim Karimi, Thomas Brabec & Ravi Bhardwaj. Intrinsic dichroism in amorphous and crystalline solids with helical light. *Nature Communication* **15**, 1350 (2024) DOI: 10.1038/s41467-024-45735-9.
5. **Jean-Luc Bégin**, Ebrahim Karimi, Paul Corkum, Thomas Brabec & Ravi Bhardwaj. Orbital angular momentum control of strong-field physics in gas phase. Under review in *Nature Communication* (2024) DOI: 10.21203/rs.3.rs-4768665/v1.

* These authors contributed equally and are co-first authors for manuscripts 2-4.

^{EP} This article was selected as the Editor’s Pick.

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CONTENTS

ABSTRACT	ii
THESIS MOTIVATION	iv
OVERVIEW	v
LIST OF PUBLICATIONS	vii
ACKNOWLEDGEMENTS	vii
CONTENTS	ix
LIST OF FIGURES	xii
LIST OF TABLES	xvii
LIST OF ABBREVIATIONS	xviii
1 INTRODUCTION TO CHIRALITY	1
1.1 Chirality in the natural world	1
1.1.1 Homochirality	2
1.1.2 Chirality and optical activity	3
1.1.2.1 Chiral molecules and the double well potential	4
1.1.2.2 Optical rotation	6
1.2 Conventional Chriotpical Theory and Techniques	8
1.2.1 Circular dichroism	9
1.2.1.1 Optical chirality	10
1.2.1.2 Rosenfeld equation	11
1.2.1.3 Parity of circular dichroism	14
1.2.1.4 Induced molecular moments	15
1.2.2 Photoelectron circular dichroism	19
1.2.2.1 Mechanism for PECD	20
1.2.2.2 Multiphoton case	23
1.2.3 Chiral High harmonic generation	24
1.2.4 Coulomb explosion imaging	25
2 OPTICAL PROBE AND DETECTION SCHEME	27
2.1 Optical probe and beam representation	27
2.1.1 Paraxial Helmholtz wave equation	27
2.1.2 Gaussian beam	29
2.1.3 Hermite-Gaussian modes	30
2.1.4 Symmetric and Asymmetric Laguerre-Gaussian modes	31
2.1.5 Generating structured light	35
2.1.5.1 Spiral phase plate	36
2.1.5.2 Q-Plates	37
2.1.5.3 OAM and SAM states of light	39
2.2 Experimental setup and detection scheme	41
2.2.1 Temporal and Spectral pulse representation	41

2.2.2	Ti:Sapphire LASER system	42
2.2.3	Mode-locking	44
2.2.4	Pulse stretcher and compressor	46
2.2.5	Single-shot autocorrelation	48
2.2.6	Optical parametric amplifier	50
2.2.7	Time-of-flight mass spectrometer	50
2.2.7.1	Wiley-Mclaren geometry	53
2.2.8	Gas phase experimental setup	54
2.2.9	Transmission experimental setup	56
2.2.10	Beam waist measurement	57
2.2.10.1	Saturated intensity method	57
2.2.10.2	Knife-edge method	58
3	WEAK- AND STRONG-FIELD LIGHT-MATTER INTERACTION	61
3.1	Nonlinear regime	62
3.1.1	Wave equation in absorbing isotropic and anisotropic nonlinear medium	63
3.1.1.1	Time domain	63
3.1.1.2	Frequency domain	65
3.1.2	Linear refractive index	65
3.1.3	Nonlinear refractive index	67
3.1.4	Multiphoton process	68
3.1.4.1	Multiphoton absorption	70
3.2	Extreme nonlinear regime	75
3.2.1	Breakdown of perturbative approach	75
3.2.1.1	Critical intensity	76
3.2.2	Strong-field Ionization	77
3.2.2.1	Multiphoton ionization	79
3.2.3	Tunneling in static field	80
3.2.4	Tunneling in a quasi-static field	81
3.2.5	Keldysh approach: Strong field approximation	82
3.2.5.1	Keldysh exponential	85
3.2.6	Recollision model	86
4	LIQUID PHASE - HELICAL LIGHT INTERACTION	89
4.1	Early developments	90
4.2	Transmission measurements	90
4.3	Parity of helical dichroism	93
4.4	Nonlinear helical dichroism in chiral and achiral molecules	94
4.5	Helical dichroism in enantiomer solutions	118
5	SOLID-STATE PHASE - HELICAL LIGHT INTERACTION	128
5.1	Transmission in crystalline and amorphous SiO ₂ solids	129
5.2	Multiphoton assisted tunneling	130
5.3	Intrinsic dichroism in amorphous and crystalline solids with helical light	131
6	GAS PHASE - HELICAL LIGHT INTERACTION	157
6.1	Recollision dynamics	158
6.2	Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry	160
6.2.1	Chiral-sensitive recollision dynamics	172
6.3	Orbital angular momentum control of strong-field physics in gas phase	176
6.3.1	Advancement in strong-field physics	177
6.3.2	Experimental methods	179
6.3.2.1	Ionization measurements	179
6.3.2.2	Calibration of mass spectrometer, laser intensity and ellipticity	180
6.3.2.3	Generation of OAM beams and displacement of singularity	180
6.3.3	OAM dependent ionization of atom and molecules	181
6.3.4	Simulated OAM dependent ionization of argon	184
6.3.5	Argon strong-field non-dipole ionization amplitude	189
6.3.6	Supplementary information	196

6.3.6.1	Effect of intensity and E1E2 strength on the ionization probability	196
6.3.6.2	Ionization as a function of singularity	197
6.3.6.3	Correlation between intensity variation and differential ionization	197
6.3.6.4	Differential ionization of S(-)- and R(+)-Limonene	198
6.3.6.5	Ellipticity dependence of ionization	200
6.3.6.6	Peak intensity and beam waist for increasing l -value	202
6.3.6.7	Kinetic energy of recollision for asymmetrical Laguerre-Gaussian beam.	202
7	CONCLUSION AND FUTURE IMPACT	204
7.1	Conclusion	204
7.2	Future impact	205
7.2.1	High harmonics and phase matching using asymmetrical OAM beam	206
7.2.2	Photoelectron helical dichroism	210
7.2.2.1	Proof of principle	211
7.2.3	OAM dependent non-sequential double ionization	213
	APPENDICES	217
A	APPENDIX	218
A.1	Multipole expansion of the interacting Hamiltonian	218
A.2	Non-dipole continuum wavefunction	222
	REFERENCES	224

LIST OF FIGURES

1.1	Biological chirality: On the left, we have the types of biomolecules that occur in nature. These include right-handed B-DNA, left-handed Z-DNA, and L-alanine, which is an amino acid. On the right, we have the types of biomolecules that are not typically found in nature. These include left-handed B-DNA, right-handed Z-DNA, and a small amount of D-alanine, another form of the amino acid [1].	3
1.2	Chirality in molecules: Schematic representation of the molecular structure of limonene enantiomers. * represents the chiral centre.	3
1.3	Chirality in crystals: Schematic representation of the crystal structure of α -quartz and its relation to a distinct crystal growth.[2]	4
1.4	Double well potential: Schematic representation of the wavefunction of a single particle in a double well potential. Left:The wave function ψ_+ (blue) with even parity, ψ_- (red) with odd parity. Right: Shows the symmetric, ψ_L (magenta), and anti-symmetric, ψ_R (gray), wavefunction as a linear superposition of ψ_+ , and ψ_- . It represents the particle localization in the left and right well, respectively.	6
1.5	Conventional chiral probe: Schematic representation of left- and right-handed circular polarization. Identifying two elements essential for chiral interaction, the helical pitch and the field strength of the incident light.	7
1.6	Multipole moments: Schematic representation of the Electric-dipole, electric-quadrupole, and magnetic-dipole moments depicting the charge translation and rotation.	13
1.7	Photoelectron circular dichroism technique: Schematic representation of left- and right-handed CPL as the chiral probe interacting with a toy molecule and generating asymmetrical PAD represented by the 2D projection [26].	20
1.8	Triangle condition: Schematic representation of the triangle condition for the Clebsch-Gordon coefficients. J can take any discrete values within the dotted bracket.	23
1.9	Chiral-high harmonic generation technique Measured ellipticity dependence of HHG and time-resolved chiral response. For each harmonic order, the corresponding ellipticity dependence is fitted with a Gaussian function, the central position of which we call a maximizing ellipticity $\varepsilon = 0$. Ellipticity as a function of the harmonic order (top axis) and the emission energy (bottom axis). Red and blue traces correspond to enantiomers of epoxyp propane (the latter is acquired at 1,850 nm, 3×10^{13} W/cm ² . The grey line shows the non-chiral reference (xenon). The experimental errors are the standard deviation and are shown as shaded areas surrounding the solid lines. [28]	24
1.10	Chiral discrimination of CHBrClF: A histogram representation of the cosine of the chiral angle θ shows clear identification of the left- and right-handed enantiomers of a racemic mixture of CHBrClF. The peak at the negative (positive) values of $\cos\theta$ corresponds to the S-enantiomer (R-enantiomer). A clear mirroring effect is observed [33].	26
2.1	Paraxial approximation: Schematic of the transverse spread in (x, y) compared to the propagation distance z	28
2.2	Hermite-Gaussian modes for various order (m, n)	31
2.3	Symmetric Laguerre-Gaussian modes for various order (p, l) . $\mathbf{E}_{0,l}(r, \phi, 0)$ represents only the top row which are the beam profiles used experimentally.	32
2.4	Asymmetric Laguerre-Gaussian modes for various order of (p, l) . $\mathbf{E}_{0,l}(r, \phi, 0)$ represents only the top row which are the beam profiles used experimentally	35
2.5	Beam propagation: a) (c)) display the phase profile for $l = 0, \pm 1, \pm 2$ for a Gaussian and symmetric (asymmetric) LG beam. b) (d)) depicts the propagation and intensity profile for symmetrical (asymmetrical) beams.	36

2.6	Spiral phase plate converts an Gaussian beam ($l = 0$) into a symmetric LG beam ($l = 1$). Transverse profiles are shown on the right, where the dark red (dark blue) represents the maximum (minimum) intensity values [40].	37
2.7	q-plate fabrication is typically performed using a photo-alignment setup. The polarizer and LC cell are mounted on a rotational stage with independent-angular frequencies while the cylinder is fixed in space [43].	38
2.8	q-plate with topological charge $l=2$. A q-plate converts RHC (LHC) polarized Gaussian beam to an OAM beam $-2\hbar$ ($+2\hbar$). This image was created by Dr. Ebrahim Karimi.	39
2.9	Frequency and Time domain: A graphical representation of the driving laser field in time and frequency domain. It demonstrates the real component of the electric field can be obtained through a product with a Heaviside function in the frequency domain. By considering only the positive frequencies we obtain $\text{Re}[\mathcal{E}(t)]$	42
2.10	Time-bandwidth product: Graphical example of the time-bandwidth product for Gaussian beams. Demonstrates that a femtosecond must contain a broad spectrum to allow a short temporal pulse.	43
2.11	Absorption and emission spectra of Ti:Sapphire. Depicts the emission and absorption spectral range for a Ti:Sapphire crystal [49].	43
2.12	Schematic of the femtosecond laser system demonstrating CPA in a regenerative amplifier.	44
2.13	Acoustic-optics modulator inside a laser cavity of length L will generate pulses every round-trip of the cavity.	45
2.14	Chirped pulse: Graphical representation of a) transform limited pulse, b) negative chirped pulse, and c) positive chirped pulse.	46
2.15	4f system used as pulse stretcher or compressor Schematic of pulse stretcher and compressor. By displacing the second grating, G_2 , at a distance smaller than the focal point of the second lens, L_2 , the 4f system stretches the pulse, ($GDD > 0$). The gray grating shows how this setup can be altered to compress a pulse ($GDD < 0$) by displacing the G_2 , further than the focal point of the L_2 . Both a stretcher and compressor are used in chirp pulse amplification.	48
2.16	Single-shot autocorrelator: Every optical element of a hybrid version of a single-shot autocorrelator and a GRENOUILLE used in the laboratory.	49
2.17	Optical parametric amplifier: The signal is the seed to be amplified, the pump is the high-powered light source that provides power to the amplifier, and the idler is an auxiliary wave created by the interaction process due to the conservation laws.	50
2.18	Time-of-flight system: Schematic of simple time-of-flight mass spectrometer. The area between the repeller and ground is defined by d and the L is the length of the flight tube.	51
2.19	Xenon mass calibration: Experimental data used to calibrate the mass-to-charge ratio with the flight time of the ions.	52
2.20	Wiley-McLaren Time-of-flight geometry: Schematic of a double field time-of-flight mass spectrometer depicting two acceleration regions improving the space-charge resolution.	53
2.21	Schematic of the gas phase experimental setup: Identifying all essential experimental components for the gas phase experiment. The voltage on the repeller and extractor was +2000V and +1000V. The negative voltage on the MCP plate was set at -4900V. No mirror after the optics was used during the experiments to not alter the polarization state of the light. It was introduced in the schematic to condense the figure.	55
2.22	Schematic of the transmission setup in the liquid and solid experiments. All essential components are included in the schematic. For the solid transmission experiment, the cuvette was replaced by the $10 \times 10 \times 1\text{mm}$ sample.	57
2.23	Saturation intensity of argon at 800nm. The figure shows the linear fit of a semi-log curve with an x-axis intercept of $9.7\mu\text{J}$. The resulting intensity for $1\mu\text{J}$ is $\sim 2.6 \times 10^{13}\text{W}/\text{cm}^2$ giving rise to an estimated beam waist of $3\mu\text{m}$	59
2.24	Knife edge graphical representation: For a) Gaussian beam ($l = 0$) and b) Laguerre-Gaussian beam ($l = 1$). The black curve is intensity distribution and the blue curve represents the knife edge power curve at the beam waist.	59
2.25	Beam waist measurement: Laguerre-Gaussian beam width $w(z)$ as a function of the z -direction along the beam. The beam waist is located at the minimum with a value $\sim 2\mu\text{m}$. Measurement was performed with an aspherical lens with $\text{NA}=0.3$	60
3.1	Linear transmission: Schematic representation of linear transmission through a liquid sample. I_0 is the incident light and I is the transmitted light, L is the thickness of the cuvette.	66

3.2	Simulated transmission curves for a) various n-photon absorption of Gaussian beam ($l = 0$) and b) for different l -value of LG beam ($l \neq 0$).	71
3.3	Experimental transmission curves of limonene for $l = 0, 1, 3$ depicting the change in the necessary energy for the nonlinear onset.	72
3.4	Experimental and simulated transmission curves. a) Experimental measurement of left-quartz (z-cut) for a Gaussian beam ($l = 0$) in black, for symmetric OAM beam ($l = +1, \delta = 0$) in red, and for asymmetric OAM beam ($l = +1, \delta = \pm 0.3w_0$) in blue and magenta. b) Simulated transmission for a 6-photon process for Gaussian beam ($l = 0$) in black, for symmetric LG beam ($l = +1, \delta = 0$) in red, and for asymmetric LG ($l = +1, \delta = \pm 0.3w_0$) in blue and magenta. $w_0 = 2\mu m$ and is the beam waist at the focus measured by the knife-edge technique.	73
3.5	Quartz six-photon absorption cross-section. a) Experimental measurement (dashed line) and theoretical fit (solid line) of left-quartz (z-cut) for a) symmetric OAM beam ($l = +1, \delta = 0nm$) in red and ($l = -1, \delta = 0nm$) in black and for b) asymmetric OAM beam ($l = +1, \delta = -350nm$) in red and ($l = -1, \delta = -350nm$) in black.	74
3.6	Tunnel ionization: The laser field strength is strong enough to distort the atomic potential and allow the ground state electron's wavefunction to tunnel through the barrier.	77
3.7	Feynman diagrams for a) Multiphoton ionization (MPI), takes an absorption of $(n + 1)\hbar\omega$ to reach the continuum. b) Multiphoton assisted tunneling (MPAT), absorption of n-photon leading to an excited state and subsequent tunneling to the continuum. c) Above-threshold ionization (ATI), absorption of $(n+s)$ -photon leading to ionization with additional photons absorbed. d) Tunneling ionization, the incident field is strong enough to force the electron to tunnel from the ground state to the continuum.	79
3.8	Recollision physics: In the first step, an intense pulse bends the coulomb potential of an atom or molecule. This allows an electron's wavefunction in the ground state to tunnel through the barrier. In the second step, the electron wavepacket propagates in the continuum and gains energy by the driving by laser field. Upon reversal of the laser field, accelerates towards the parent ion. In the third step, the liberated electron wavepacket recollides either elastically or inelastically with the parent ion. Resulting in either higher energy photons or doubly/triply charged ions.	87
4.1	Nonlinear transmission curves for a) Left- and right-circularly polarized Gaussian beam and b) linearly polarized symmetric OAM beam. The inset shows the simulated beam profile and the error bars are the standard variation of three measurements.	91
4.2	OAM dependent transmission curves for a) (b)) Left- and right-linearly polarized OAM beam with the singularity displaced to the positive (negative) x-axis. The inset shows the simulated beam profile and the error bars are the standard variation of three measurements.	91
4.3	Illustration of a limonene enantiomers in a cuvette being irradiated by left- and right-handed asymmetrical helical light. The transmitted light depicts the difference in absorptance.	95
5.1	Quartz and fused-silica transmission curves. a) Experimental measurement for a) Left-handed quartz for asymmetric OAM beam ($l = +1, \delta = 900nm$) in red and ($l = -1, \delta = 900nm$) in black and b) fused-silica for asymmetric OAM beam ($l = +1, \delta = 900nm$) in red and ($l = -1, \delta = 900nm$) in black.	129
5.2	Illustration of a fused silica being irradiated by asymmetrical helical light.	156
6.1	Feynman diagrams for a) non-sequential double ionization (NSDI), b) recollision induced excitation and subsequent ionization (RESI), and c) field induced excitation and subsequent recollision ionization (FESI).	160
6.2	Mass spectrum of R(+)-limonene for opposite helicities. a) Symmetric OAM beam ($\delta = 0$) for $l = -1$ (black) and $l = +1$ (red). b) Asymmetric OAM beam ($\delta = -750 nm$) for $l = -1$ (black) and $l = +1$ (red). c) same as (b) for $\delta = 750 nm$. The laser polarization is linear ($s = 0$) and the wavelength and intensity were 800 nm and $8 \times 10^{13} W/cm^2$, respectively. The insets show the intensity profile of LG beams.	181
6.3	OAM dependent ionization in molecules. Single ionization yields for $l = +1$ (black) and $l = -1$ (red) as a function of displacement of the singularity in a) R(+)-limonene, c) acetone. b),d) shows the difference in the ionization yields between the left- and right-helical light for the respective molecules. The laser polarization was linear ($s = 0$) and the intensity was $8 \times 10^{13} W/cm^2$ and $9 \times 10^{13} W/cm^2$ for limonene and acetone, respectively.	182

6.4	OAM control of ionization of argon atom a) Single ionization yields of argon for $l = +1$ (black) and $l = -1$ (red). b) Difference in ionization between left and right-handed helical light ($l = 1$). c) Single ionization yields of argon for $l = +3$ (black) and $l = -3$ (red). d) left and right-handed helical light ($l = 3$). The laser polarization was linear ($s = 0$) and the intensity for $l = 1$ was 10^{14} W/cm ² and $l = 3$ was 1.5×10^{14} W/cm ²	183
6.5	Simulated differential ionization probability of argon. a) Simulated difference in ionization probabilities of argon between left- and right-helical light for $l = 1$ in black and $l = 3$ in red, respectively. b) Single ionization probability of argon for $l = +1$ ($l = +3$) in black (blue) and $l = -1$ ($l = -3$) in red (magenta). They were obtained by solving Eq.6.20 for vertical polarization and intensity of 10^{14} W/cm ² for $l = 1$ and 1.2×10^{14} W/cm ² for $l = 3$	186
6.6	OAM-dependent ionization in atoms. a) Distortion of atomic potential at peak intensity for a vertically polarized Gaussian beam (black dashed line) and, for $l = -1$ (blue) and $l = +1$ (red) asymmetric LG beams. b) Normalized transverse profiles of ionization probability for symmetric ($\delta = 0\mu\text{m}$) and asymmetric ($\delta = -1\mu\text{m}$) LG beam at an intensity of 10^{14} W/cm ² . The x and y-axis are given in microns. Figure a) was evaluated with the beam coordinates at $(1\mu\text{m}, 0\mu\text{m})$	187
6.7	Tuning the ponderomotive energy and force. Simulation of a) peak ponderomotive energy, and b) average ponderomotive force, at an intensity of 10^{14} W/cm ² , for different positions of the singularity in a linearly polarized OAM beam and for different l -values. The open circles correspond to a Gaussian beam at the same laser intensity. The ponderomotive force was integrated over the beam cross-section at the laser focus.	188
6.8	Influence of laser intensity and the E1E2 strength on the ionization probability. a) Depiction of ionization probability at various intensities. b) ionization probability curves with various E1E2 strength. The behaviour flips for $l = +1$ (not shown).	196
6.9	Ionization map for linearly polarized $l = -1$ beam. Polar contour map of the ionization as a function of displacement of singularity in the x, y -plane within the interaction region.	197
6.10	Differential ionization of singly charged R(+)-limonene as a function of displacement of the singularity for linearly polarized $l = 1$. The insets show the intensity variation of R(+)-limonene for $l = +1$ ($l = -1$) in red (black) at the positions denoted by the blue rectangles.	198
6.11	Differential ionization for single, double and fragment ions of limonene enantiomers for linearly polarized $l = 1$. Parent ion yields ($m/z = 136$), for S(-)-limonene (R(+)-limonene) in blue (green), and doubly charged/fragments ($m/z = 68$), for S(-)-limonene (R(+)-limonene) in black (red). The laser intensity was 8×10^{13} W/cm ²	199
6.12	Single ionization control of limonene for $l = \pm 3$. a) Single ionization yields of R(+)-limonene for $l = +3$ (black) and $l = -3$ (red). b) Difference between left and right-handed helical light ($l = 3$) for singly charged limonene ion yield. The laser intensity was 9×10^{13} W/cm ²	199
6.13	Ionization control of limonene for circularly polarized $l = \pm 3$ beam. a), b) Differential ionization yields of S(-)-limonene and R(+)-Limonene between RHC and LHC for a specific helicity of light; $l = +1, s = \pm 1$ (blue) and $l = -1, s = \pm 1$ (green). Differential ion yields of S(-)-limonene and R(+)-limonene between helicity of light for a specific polarization for singly charged $l = \pm 1, s = -1$ (red), $l = \pm 1, s = +1$ (black). The laser intensity was 8×10^{13} W/cm ²	200
6.14	Ellipticity dependence of single ionization of limonene . a) Difference in single ionization yields of S(-)-limonene for $l = 1$. The insets show the ellipticity variation for S(-)-limonene for $l = +1$ ($l = -1$) in red (black) at the positions denoted by the blue rectangles. The laser intensity was 8×10^{13} W/cm ² . b), c) Simulated ellipticity variation for asymmetrical parameters comparable to the insets in a) . The ionization probability for $l = +1$ ($l = -1$) is denoted by the red (black) curve. The laser intensity was 10^{14} W/cm ²	201
6.15	a) Normalized experimental and simulated ellipticity variation. Single ionization yields of argon for $l = +1$ and $\delta = 0$ in black, $\delta = 1$ in red, and $\delta = -1$ in blue, as a function of laser ellipticity. The solid lines represent the simulated ionization probabilities. The laser intensity was 10^{14} W/cm ² for both experiments and theory. b) Single ionization yields of argon for $l = +3$ (black) and $l = -3$ (red) for $\delta \sim 1\mu\text{m}$. The laser intensity was 1.2×10^{14} W/cm ² . The error bars represent fluctuations in the ion yields over repeated measurements.	201
6.16	Electron recollision in argon for various l-value. The dash (solid) lines represent the long (short) trajectories created when the electron is ionized before (after) the peak located at $\omega_0 t' = 0.05 \times 2\pi = 18^\circ$. The electron will return to the parent ion at $\omega_0 t = 0.7 \times 2\pi = 252^\circ$	203

7.1	Dipole phase for an atom as a function of intensity for short (blue) and long (red) trajectories calculated by classical trajectories (dashed) and quantum orbits (solid) that contribute to the 21st harmonic. For the harmonic plateau, the dipole phase increases linearly with intensity. The slope of the dipole phase of the short trajectories is approximately $\alpha_s = 1.5 \times 10^{14} \text{W/cm}^2$, whereas the slope of the dipole phase for the long trajectories is $\alpha_L = 22 \times 10^{14} \text{W/cm}^2$ [162]	208
7.2	Longitudinal cross-section of the intensity and phase profile of Gaussian (upper row) and a symmetric LG beam (lower row). The Gaussian has a transverse intensity maximum at the beam axis and for the LG beam, it is off-axis located at $R_{l,\text{max}}$. The phase profile of the Gaussian beam shows the phase shift from $\pi/2$ to $-\pi/2$ due to the Gouy phase. The focal phase modifies the phase off-axis. The phase profile of the LG beam has a phase singularity on the propagation axis due to the term $il\phi$. In addition the phase shift caused by the Gouy phase is increased, from π to $-\pi$ [162]	209
7.3	Longitudinal phase profile of Gaussian (a), a symmetric LG beam (b), and asymmetrical LG beam for $\delta = \pm 1$ (c and d). The y-axis represents the the beam waist $w(z)$ in the x-direction and the x-axis represents the Rayleigh range z_R . The white lines are merely a relic of the computation.	210
7.4	Velocity map imaging of the photoelectron angular distribution by ionization of chiral molecules using asymmetrical helical light. The purpose is to enhance the chiral signal by generating larger dichroic contrast and higher-order sidebands compared to PECD. These measurements can also be performed for achiral molecules and atoms. This is an extension of the TOF-MS OAM-dependent ionization, in chapter 6. Analyze the ionization dynamics by imaging the asymmetrical PAD instead of the charged ions and fragments [165].	211
7.5	Ellipticity variation of singly (circles) and doubly (triangles) charged argon as a function of laser ellipticity for $l = 0, \delta = 0 \mu\text{m}$ in red, $l = 1, \delta = 0 \mu\text{m}$ in black, and $l = 1, \delta \sim +1 \mu\text{m}$ in blue. The laser intensity was $1.1 \times 10^{14} \text{ W/cm}^2$ and dashed lines are for visual guidance.	215
7.6	Argon Ion yields as a function of pulse intensity. (1) Single ionization, $\text{Ar} \rightarrow \text{Ar}^+ + e^-$. (2) Dominance of the non-sequential double ionization, $\text{Ar} \rightarrow \text{Ar}^{2+} + 2e^-$, the momentum distribution will show a distinct double peak. (3) the double ionization rate is described by the sequential process, $\text{Ar} \rightarrow \text{Ar}^+ + e^- \rightarrow \text{Ar}^{2+} + 2e^-$, the momentum distribution shows a single peak as for the single ionization. All curves can be simulated by SFA with the Coulomb correction or ADK/PPT.	215

LIST OF TABLES

3.1	Different ionization regime and their respective condition of validity. The parameter are in atomic units.	78
4.1	PT symmetry of quantities used in CD and HD.	93

LIST OF ABBREVIATIONS

ADK	Ammosov, Delone, Krainov	81
aLG	asymmetric Laguerre-Gaussian	33
ATI	Above-Threshold Ionization	77
CD	Circular Dichroism	iii, v, 1
CEI	Coulomb Explosion Imaging	25
cHHG	Chiral-High Harmonic Generation	24
COLTRIMS	Cold Target Recoil Ion Momentum Spectrometer	20
CPA	chirped pulse amplification	44
CPL	Circularly polarized light	ii, 8
DFG	Difference Frequency Generation	50
E1	electric-dipole	13
E1E1	electric dipole-dipole coupling term	13
E1E2	electric-dipole electric-quadrupole coupling term	14
E1M1	electric-dipole magnetic-dipole coupling term	13
E2	electric-quadrupole	13
E2E2	electric quadrupole-quadrupole coupling term	13
ED	Elliptical Dichroism	160
ED-REFLMS	Elliptical Dichroism by recollision-enhanced femtosecond laser mass spectrometry	159
FESI	Field-induced excitation and subsequent recollision ionization	88
GDD	Group Delay Dispersion	47
GRENOUILLE	GRating-Eliminated No-nonsense Observation of Ultrafast Incident Laser Light E-fields	49
GVD	Group-Velocity Dispersion	46
HD	Helical Dichroism	ii, 19
HHG	High-Harmonics Generation	vi
LC	Liquid Crystal	37
LG	Laguerre-Gaussian	v, 27
LHC	left-handed circular	8
M1	magnetic-dipole	13
M1E2	magnetic-dipole electric-quadrupole coupling term	14

M1M1 magnetic dipole-dipole coupling term 13, 14

MCP microchannel plate 52

MPA Multiphoton Absorption v

MPAT Multiphoton-Assisted Tunneling iii

NIR near-infrared 41

NIR-IR Near-Infrared and Infrared 7

NSDI Non-Sequential Double Ionization vi

OAM Orbital Angular Momentum ii

OPA Optical parametric amplifier 50

OPL Optical Path Length 3

OR Optical Rotation v, 1

ORD optical rotatory dispersion iv, 8

PAD Photoelectron Angular Distribution 19

PD photodiode 56

PECD Photoelectron circular dichroism iii, 19

PEHD Photoelectron Helical Dichroism vi

PEPICO photoelectron-photoion coincidence spectroscopy 213

PPT Perelomov, Popov, and Terentev 81

PT parity-time 10

QWP Quarter-Wave Plate 40

RESI Recollision excitation with subsequent ionization 87

RHC right-handed circular 8

SAM Spin Angular Momentum 39

SFA strong-field approximation 82

SHG Group second harmonic-generation 48

SHG-FROG second harmonic generation frequency-resolved optical gating 49

SI sequential ionization 87

SLM Spatial Light Modulator 32

SPP Spiral Phase Plate 35

TOF Time-Of-Flight 25

TOFMS time-of-flight mass spectrometer iii

UV-vis Ultraviolet-visible 7

VCD Vibrational Circular Dichroism iv

VMI velocity map imaging 20

WKB Wentzel–Kramers–Brillouin 80

INTRODUCTION TO CHIRALITY

This first chapter provides an introduction to the concept of chirality and its significant role in nature. This sets the stage for an exploration and explanation of traditional chiroptical techniques and the theory used in both liquid and solid phases, such as CD and OR. It will also discuss the observation of chiral discrimination in the gas phase, where we present an efficient nonlinear gas phase chiroptical techniques and their mechanisms. These above-mentioned techniques utilize CPL as the chiral probe and will serve as a comparative basis throughout our study. Despite their widespread use, we address the inherent limitations of using CPL as a chiral reagent. Throughout, the chapter we propose a solution to these constraints by employing helical light as a probe, where unexpected findings and additional advantages are observed.

1.1 CHIRALITY IN THE NATURAL WORLD

From early on, we as humans have understood that the physical world is not symmetrical. Despite our efforts to create order and symmetry around us, the natural world is inherently asymmetrical, chaotic, and constantly in a state of disorder. Yet, we recognized by manipulating the input of an asymmetrical system, we can control the outcome and achieve our desired tasks. To exploit this asymmetry we first must recognize its presence, understand its mechanics, and then determine how to control it in order to achieve an intended outcome.

We acknowledge a form of asymmetry, known as chirality, in the natural world when we realize that our hands and feet are non-superimposable mirror images of each other, each capable of producing different outcomes. We can refer to this form of chirality as a chiral probe - a chiral object with a known handedness and functionality that can trigger a chiral interaction leading to a unique result.

In our daily lives, we encounter other chiral objects, such as screws and propellers, which have a directionality linked to their rotational dynamics. For instance, a right-threaded screw will have a different direction of linear displacement (angular momentum or torque) depending on the direction of the applied force by our hand (chiral probe) on the screw (chiral object). A counter-clockwise rotation results in a positive displacement, while a clockwise rotation results in a negative displacement. Interestingly, a left-threaded screw with a clockwise rotation will yield the same result as a right-threaded screw with a counter-clockwise rotation. Thus, the combination of i) rotational dynamics generated by the chiral probe (our hands), and ii) the directionality of the linear translation (observed outcome) caused by the chiral interaction are the two types of movement essential for dynamic chirality in the physical world.

1.1.1 HOMOCHIRALITY

Chirality can be examined and scrutinized from the macroscopic level that we encounter daily, to the microscopic level of crystal lattices and biological cells, and even further to the submicroscopic in the realm of molecules. However, it's important to note that macroscopic objects do not necessarily have a microscopic chiral composition and vice versa. Take a screw for example, it is a chiral object on a macroscopic scale, but microscopically its molecular or lattice composition is achiral. As for the biological makeup of our left and right hands, both contain B-DNA in the form of a right-handed double helix, all the proteins in these cells are composed of L-amino acids, and most carbohydrates originate from D-sugars. The molecular composition of living organisms, including DNA, RNA, proteins, and sugars, are all chiral molecules, also referred to as enantiomers and depicted in figure 1.1. Biomolecular chirality, whether in a virus, a primitive bacterium, or a human brain cell, is universally the same. Living organisms composed of left-handed B-DNA, D-amino acids, and L-sugars enantiomeric biomolecules does not exist on Earth. This extraordinary selectivity on earth is known as biological homochirality [1].

From a chemical perspective, a pair of enantiomers are non-superimposing mirror images of each other and have similar physical and chemical properties. Interestingly, under identical external conditions and within an equilibrium state, both enantiomers are expected to have equal energy levels and therefore have an equal probability of existence. However, if one considers the interactions of elementary particles, referred to as parity-violating weak forces, it leads to the conclusion that there must be a small difference in their energy potential thus favouring one chiral form over the other. Therefore, the abundance of one chiral compound is always more prevalent in nature than the other handedness. The question then arises, is the biological homochirality observed on Earth a direct consequence of universal asymmetrical laws of the weak interactions, or is it merely

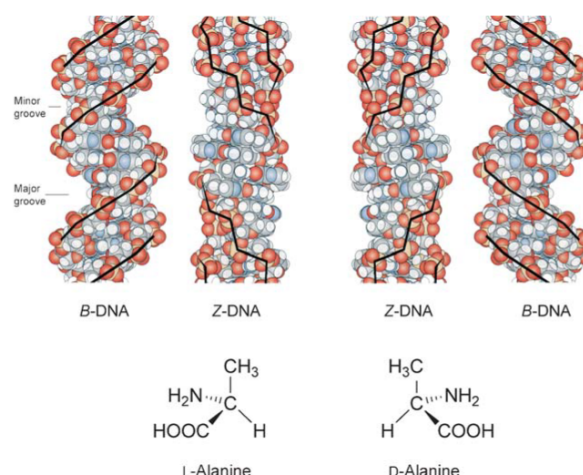


Figure 1.1: **Biological chirality:** On the left, we have the types of biomolecules that occur in nature. These include right-handed B-DNA, left-handed Z-DNA, and L-alanine, which is an amino acid. On the right, we have the types of biomolecules that are not typically found in nature. These include left-handed B-DNA, right-handed Z-DNA, and a small amount of D-alanine, another form of the amino acid [1].

a coincidence?

1.1.2 CHIRALITY AND OPTICAL ACTIVITY

Chirality can manifest itself in two ways: i) within the molecular structure from the lack of the S_n axis of symmetry due to the presence of a chiral center [1], an atom is connected to four different groups of atoms, depicted by figure 1.2. By definition S and R labels are determined by the orientation of the chiral center which is determined by prioritizing the atoms with the largest to the lowest atomic order. ii) Through the crystal lattice, a consequence of the structure created during the arrangement of atoms and molecules. Such a structure can be visualized in figure 1.3, a crystal lattice that is created from achiral molecular composition, SiO_2 , such that it generates a chiral crystal orientation defined as left- and right-quartz.

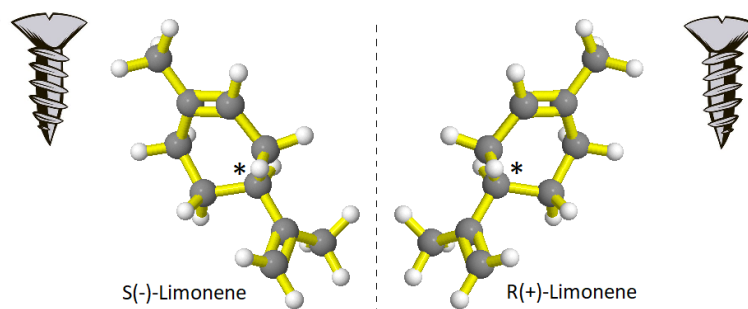


Figure 1.2: **Chirality in molecules:** Schematic representation of the molecular structure of limonene enantiomers. * represents the chiral centre.

In principle, a chiral medium is defined by the degree of rotation of linearly polarized light with respect to the polarization plane, a phenomenon known as optical activity. The angle of rotation is i) a property of the medium and Optical Path Length (OPL) and ii) is inversely related for both chiral compounds. This was first observed

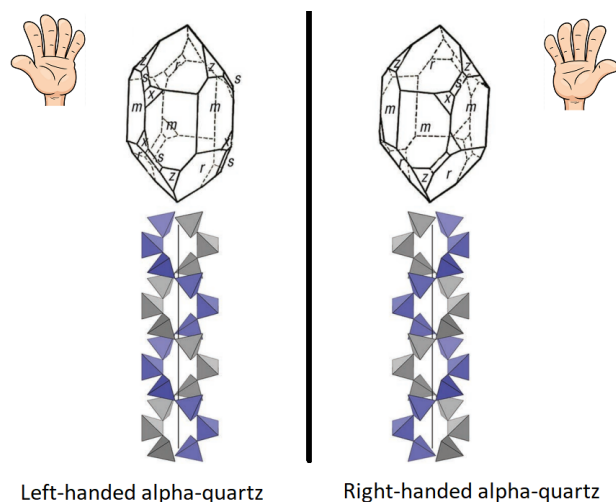


Figure 1.3: **Chirality in crystals:** Schematic representation of the crystal structure of α -quartz and its relation to a distinct crystal growth.[2]

in the early 19th century for left- and right-handed α -quartz, the crystal cut and propagation direction was perpendicular to the crystal axis [1]. It was later demonstrated that optical activity is not exclusive to crystal chirality but can also be observed in a sugar solution, a form of molecular chirality in bulk form.

The angle of rotation is typically measured using a polarizer (the probe), a second adjustable polarizer known as an analyzer, and a detector. By altering the wavelength of the incident light, it is possible to measure optical rotation as a function of light wavelengths, a process referred to as ORD [3]. Therefore, the optical activity of quartz is a result of the crystal's overall structure of the SiO_2 , an achiral molecule, while for the sugar solution, it arises from the individually and randomly orientated chiral molecules.

By convention, chiral compounds are labelled by the sign of their optical rotation. If the plane of linear polarization is rotated clockwise by the chiral sample. It is called *dextrorotatory* (+). On the other hand, if the sample rotates the linearly polarized light counter-clockwise it is said to be *levorotatory* (-). A common chiral molecule is S(-)- and R(+)-Limonene (figure 1.2) can be used to show that chirality plays a pivotal role in our daily life by serving as a chiral reagent for enantio-selectivity. Consider the olfactory receptors in our nose, responsible for the sense of smell, they interact differently with the two limonene enantiomers. For instance, the R(+)-limonene is associated with citrus odours while the S(-)-handed enantiomer is closer to a pine odour [4].

1.1.2.1 CHIRAL MOLECULES AND THE DOUBLE WELL POTENTIAL

Chiral compounds can be described quantum mechanically by a double well potential, where the left- and right-potential is associated to the handedness of the enantiomer [5], see figure 1.13. According to quantum mechanics, there is always a finite probability of an enantiomer converting from one handedness to the other by tunneling through the potential barrier. When the barrier is high compared to the energy of the particle, then

the particle is localized in one or the other of the wells.

In the absence of parity-violating interactions, the 1D double potential well is symmetric with respect to the inversion parity operator $\hat{P}$, $(x, y, z) \rightarrow (-x, -y, -z)$, where the real eigenfunctions of particles in this potential have definite parity, the stationary states are either odd or even with respect to parity. One can designate the symmetric and anti-symmetric wavefunctions corresponding to the left- and right-hand wells by ψ_L and ψ_R , respectively. Then the real wavefunctions to the time-independent Schrodinger equation, are the positive and negative linear combinations of the wavefunctions corresponding to the two separate wells; $\psi_{\pm} = \frac{1}{\sqrt{2}}(\psi_R \pm \psi_L)$. It is also possible to define the left and right eigenfunctions as a superposition of even and odd functions, $\psi_{L/R} = \frac{1}{\sqrt{2}}(\psi_+ \pm \psi_-)$. We define the inversion operator on the states as $\hat{P}[\psi_{L/R}] = \psi_{R/L}$ and $\hat{P}[\psi_{\pm}] = \pm\psi_{\pm}$. Under inversion, the symmetric function becomes anti-symmetric and vice versa due to ψ_+ (ψ_-) being even (odd) under parity.

The evolution of the eigenfunctions behaves accordingly to

$$\psi(x, t)_{L/R} = \frac{1}{\sqrt{2}} \left(\psi_+ e^{-iE_+ t/\hbar} \pm \psi_- e^{-iE_- t/\hbar} \right) = \frac{1}{\sqrt{2}} e^{-iE_+ t/\hbar} \left(\psi_+ \pm \psi_- e^{-i\Delta E t/\hbar} \right) \quad (1.1)$$

where $\Delta E = (E_- - E_+)$ is the tunneling rate between the wells. Let us suppose that at t_0 the state of the system is ψ_L . At a later moment, $t = h/2\Delta E$, the system will be in the pure ψ_R state. The system oscillates between the state ψ_L and ψ_S at angular frequency $\omega = \Delta E/\hbar$. For a very high barrier, tunneling between the wells is negligible, in this case, it is possible to describe the particle as being either in the left or right well. This is clearly the case when the wells are very far apart so that the particle is localized in one of the wells, and this situation is true for stable S- and R-enantiomers. The left and right states are degenerate energy eigenstates but not parity eigenstates. A particle which is localized in one of the wells will remain there forever. Its wave function does not obey the same symmetry as the Hamiltonian, it is a system in broken symmetry.

The ground state energy of both enantiomers will be slightly different due to the superposition of the odd ψ_- and even ψ_+ functions. The Hamiltonian of the system commutes with the parity operator $\hat{P}$, $[\hat{H}, \hat{P}] = 0$. The energy of the state whose wave function ψ_+ has even parity is less than that of the wave function with odd parity ψ_- , the barrier has less effect on the odd wave function because ψ_- has a node at $x = 0$ no matter the height of the barrier, whereas the energy of the even parity wave function decreases as the barrier height decreases. In figure 1.13, the wave functions of a single particle in a double well potential can be visualized by the two chiral molecule.

This broken symmetry discussed for enantiomers can also be extrapolated to the crystal chirality, where the crystal lattice contains the broken symmetry. The solution to the Schrodinger equation in a periodic potential can be expressed by a plane wave modulated by a periodic function. The solution is known as the Bloch wavefunction $\psi(r) = e^{ik \cdot r} u_k(r)$, where r is the position k is the crystal momentum, and $u_k(r)$ is the periodic function with the same periodicity as the crystal.

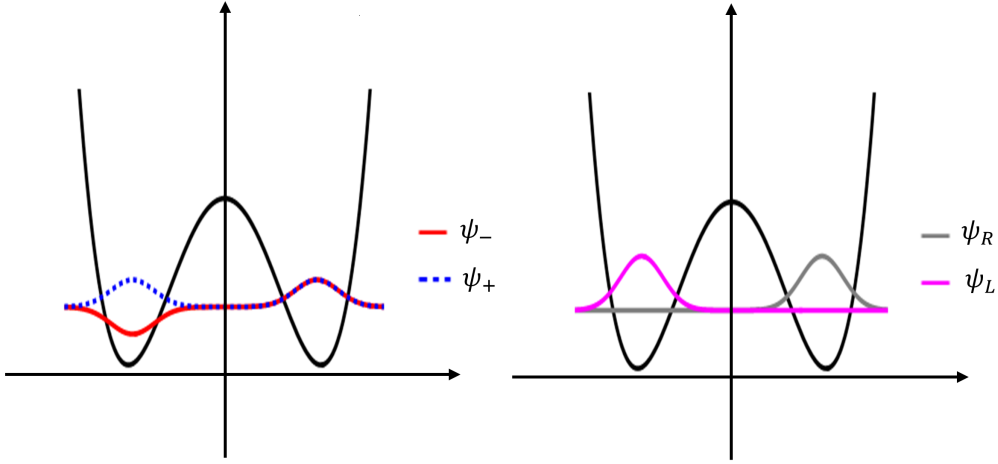


Figure 1.4: **Double well potential:** Schematic representation of the wavefunction of a single particle in a double well potential. Left: The wave function ψ_+ (blue) with even parity, ψ_- (red) with odd parity. Right: Shows the symmetric, ψ_L (magenta), and anti-symmetric, ψ_R (gray), wavefunction as a linear superposition of ψ_+ , and ψ_- . It represents the particle localization in the left and right well, respectively.

For a chiral crystal, the crystal lattice of one handedness is a mirror image of the other, $\hat{P}[u_k^L(r)] = u_k^R(r)$, where the periodicity of the crystal lattice can be expressed as a linear superposition of symmetric and anti-symmetric functions, $u_k^{L/R}(r) = \frac{1}{\sqrt{2}}(u_k^+(r) \pm u_k^-(r))$. However, a plane wave is not an eigenstate of parity because the states $|k\rangle$ and $|-k\rangle$ are degenerate. Nonetheless, a parity eigenstate is formed by a superposition of these two states, $\frac{1}{\sqrt{2}}(|k\rangle \pm |-k\rangle)$. Note, that this function is degenerate in energy but not in momentum. Therefore, we can express the left- and right-handed plane waves as $\langle r|k\rangle_{L/R} = \frac{1}{\sqrt{2}}(\langle r|k\rangle \pm \langle r|-k\rangle)$ which are none other than a cosine (even) and sine (odd) function. Under parity the Bloch wavefunction for a left-handed crystal lattice becomes a right-handed one.

$$\hat{P}[\psi_S] = \hat{P}\left[\frac{1}{\sqrt{2}}(\langle r|k\rangle + \langle r|-k\rangle)\right] \hat{P}[u_k^S(r)] = \frac{1}{\sqrt{2}}(\langle r|k\rangle - \langle r|-k\rangle)u_k^R(r) = \psi_R \quad (1.2)$$

Thus, we can define the left- and right-handed chiral crystal as these Bloch wavefunctions.

$$\psi_S = \frac{1}{\sqrt{2}}[u_k^+(r) + u_k^-(r)] \text{Re}[\langle r|k\rangle]; \quad \psi_R = \frac{1}{\sqrt{2}}[u_k^+(r) - u_k^-(r)] \text{Im}[\langle r|k\rangle] \quad (1.3)$$

The left- and right-handed wavefunctions for enantiomers (1.1.2.1) and chiral crystals (1.1.2.1) are solutions to the Schrodinger equation and are used to solve the transition amplitude for CD and ORD.

1.1.2.2 OPTICAL ROTATION

To elucidate the polarization effect on OR we use the wave theory of light. The electric field of linearly polarized light can be decomposed as a superposition of left and right circularly polarized light with the same frequency

and amplitude but with a phase shift of $\pi/2$.

$$\mathbf{E}_{RHC} = \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y}); \mathbf{E}_{LHC} = \frac{1}{\sqrt{2}} (\hat{x} - i\hat{y}) \quad (1.4)$$

The polarization of the magnetic field can be determine by $\hat{b} = \hat{z} \times \hat{e}$.

$$\mathbf{B}_{RHC} = \frac{1}{\sqrt{2}} (-i\hat{x} + \hat{y}); \mathbf{B}_{LHC} = \frac{1}{\sqrt{2}} (i\hat{x} + \hat{y}) \quad (1.5)$$

where we have decomposed left- and right-circularly polarized light into $\hat{x}$ and $\hat{y}$ unit vectors in the Cartesian coordinate system. The left- and right-handed circular polarized light can be converted from one-handedness to the other via a reflection unitary operator, $\hat{\sigma}_y \hat{\sigma}_y^\dagger = 1$, which acts only on the y-coordinate, $\hat{\sigma}_y \mathbf{E}_{RHC} \hat{\sigma}_y^\dagger = \mathbf{E}_{LHC}$. Figure 1.5 shows the chiral nature of CPL displaying the rotation of the electric field as the light propagates in space.

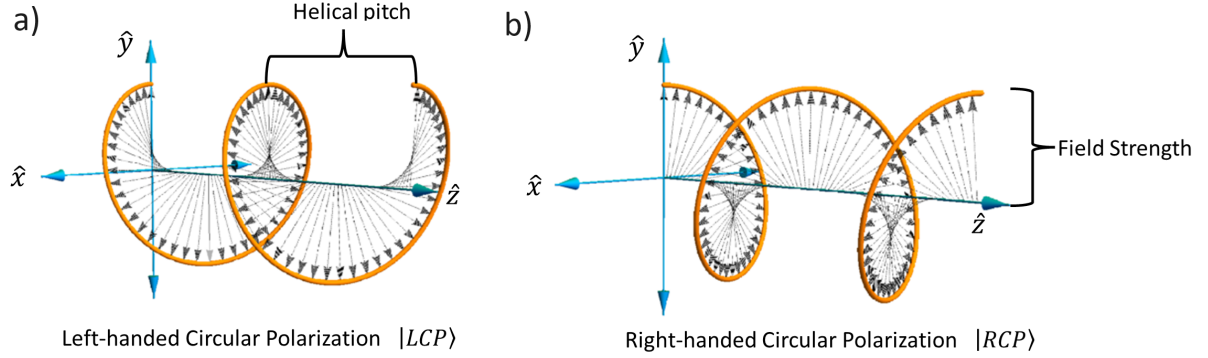


Figure 1.5: **Conventional chiral probe:** Schematic representation of left- and right-handed circular polarization. Identifying two elements essential for chiral interaction, the helical pitch and the field strength of the incident light.

In a chiral medium, the index of refraction for left circularly polarized light n_{LHC} is different from that for right circularly polarized light n_{RHC} [1, 3]. Therefore, the rotation of the plane of linearly polarized light for a given wavelength in an optically active medium can be understood as the difference in the absorption of left- and right-circularly polarized light. For a specific enantiomer, the degree of rotation is proportional to the difference in the index of refraction:

$$\Delta n(\lambda)_{R(+)} = n_{RHC} - n_{LHC} = -(n_{RHC} - n_{LHC}) = -n(\lambda)_{S(-)} \quad (1.6)$$

For any chiral medium, there is an observed wavelength effect on the absorption of polarized light. The strength of such an absorption is measured by the absorption coefficient. The difference in absorption is a result of the specific wavelength of light that is most sensitive to the molecular electronic energy structure in the Ultraviolet-visible (UV-vis) or the ro-vibrational energy structure in the Near-Infrared and Infrared (NIR-IR).

The measured absorption corresponds to a specific electronic or ro-vibronic transition from the ground to an excited state within the molecule. Therefore, the energy difference is thereby measured by the electromagnetic field which is related to the frequency of the exciting light. In chiral compounds, the non-zero difference in the refractive index for the Left-handed circular (LHC) and Right-handed circular (RHC) polarization of light is directly linked to a non-zero difference in absorbance $A(LHC) - A(RHC) \neq 0$ and extinction coefficient $\varepsilon(LHC) - \varepsilon(RHC) \neq 0$. This phenomenon is called CD. Since the index of refraction and absorption are related via the Kramers-Kronig relation [6] in the linear and nonlinear regime so are the ORD and CD spectra.

$$\text{Im} [\chi^{(n)}(\omega)] = -\frac{2\omega}{\pi} \int_0^\infty \frac{\text{Re}[\chi^{(n)}(\omega')]}{\omega'^2 - \omega^2} d\omega'; \text{Re} [\chi^{(n)}(\omega)] = \frac{2}{\pi} \int_0^\infty \frac{\omega' \text{Im}[\chi^{(n)}(\omega')]}{\omega'^2 - \omega^2} d\omega' \quad (1.7)$$

where $\chi^{(n)}$ is the susceptibility, where $n = 1$ for the linear regime and $n \neq 1$ is the nonlinear regime. ω is the frequency of the incident light, $\text{Im} [\chi^{(n)}(\omega)]$ is related to the absorption coefficient and $\text{Re} [\chi^{(n)}(\omega)]$ is related to the refraction index. More details are presented in chapter 3 section 3.1.

From these basic principles, it is evident that chiral interactions are dependent on two elements:

1. The helical pitch, which determines the chiral structure of the probe within the wavelength of light. The helical pitch can be manipulated by altering the wavelength of the light, a shorter wavelength results in stronger chiral interaction, or by increasing the number of intertwined rotations in one wavelength. The latter is not feasible with CPL but can be achieved by switching the chiral probe to structured light, where the chiral structure is incorporated into the wavefront, see chapter 4, 5, 6.
2. The field strength of the incident light. The field strength is governed by the intensity, at high intensities $> 10^6 \text{W/cm}^2$ the interaction regime transitions from linear to the nonlinear regime. At even higher intensities $> 10^{12} \text{W/cm}^2$ the regime is considered extremely nonlinear.

By changing these parameters you can effectively alter the interaction resulting in new and efficient chiral light-matter interactions. These two factors are instrumental in the advancement of new chiroptical methods and will be continuously elaborated upon throughout the dissertation.

1.2 CONVENTIONAL CHIROPTICAL THEORY AND TECHNIQUES

In order to characterize chiral interactions, we examine the impact of chiral light, our probe, on chiral matter. We will explore the physical mechanisms at play behind the pioneering chiroptical methods, using a traditional approach known as single photon or linear absorption.

While it is widely recognized that nonlinear effects can enhance the efficiency of chiral-light matter interactions, they also introduce a new set of challenges. With intense laser pulses, the interactions take place at

varying time and length scales, leading to the presence of other physical processes during the interaction. Future chapters will extend these single photon mechanisms to nonlinear processes.

From an experimental perspective, it is common to use bulk samples, necessitating many-body calculations to account for the large number of atoms involved in the interaction volume. These chiral-sensitive mechanisms do not describe its effect on many-body interactions but rather concentrate on the differential response between matter with broken symmetry. Therefore, a single electron approach is adequate to describe the observed differences.

1.2.1 CIRCULAR DICHROISM

CD is widely used to analyze and discriminate chiral molecules. It is a linear spectroscopic technique that measures the transmission of left- and right-circular polarized light, at some specific wavelength, through a sample. CD is obtained by measuring absorptance, defined as the ratio of transmitted intensity by the incident intensity (I/I_0) or the absorbance, which is the logarithm of the transmittance ($A = -\text{Log}[I/I_0]$) for each polarization or enantiomer and computing the difference gives CD. The first differential measurements were observed using the electronic transitions, and the signal was quite small.

The probability of measuring an enantio-sensitive transition is proportional to the matrix element involving the dipole interference term [7]. The sensitivity of chiroptical techniques that use polarization of the light as the chiral probe is limited by the relative size difference between the molecular dimension and the helical pitch of the circularly polarized electromagnetic field. As a result, sensitivity scales inversely with wavelength of light [8, 9]. Thus, linear techniques in the resonant regime such as VCD that are performed at infrared wavelengths are often two to three orders of magnitude lower than its counterpart, electronic CD [10]. Shorter wavelengths such as X-rays in which the helical pitch is in the same order as the molecular size [11] lead to greater chiral signals.

The mechanism of CD arises due to the coupling of the electric and magnetic dipole transitions resulting in a differential absorption of left- and right-CPL. The E1M1 coupling,

$$\left| \langle \psi_f | \hat{H}_{int} | \psi_i \rangle \right|^2 \propto \frac{1}{3} [\langle \psi_f | \boldsymbol{\mu} \cdot \mathbf{m} | \psi_i \rangle]_M [\mathbf{E}^* \cdot \mathbf{B}]_L + c.c. \quad (1.8)$$

is expressed in terms of electric and magnetic dipoles. It arises from the time-dependent perturbative method and changes sign under parity. Equation 1.8 represents the single photon transition elements between an initial state ψ_i and a final state ψ_f . The transition is dictated by the electric dipole $\boldsymbol{\mu}$ and the magnetic dipole $\mathbf{m}$ within the molecular frame M . The electric $\mathbf{E}$ and magnetic $\mathbf{B}$ fields are expressed in the lab frame L . The factor of 1/3 represents the rotational averaging over all molecular orientations in a bulk sample [12].

The electric-dipole and the electric field are polarvectors having odd parity while the magnetic dipole and the magnetic field are pseudovectors having even parity. In the molecular frame, the electric and magnetic

dipole coupling leads to a pseudoscalar, $\text{Im} [\boldsymbol{\mu}^{fi} \cdot \mathbf{m}^{if}]$ also known as the "Rosenfeld equation" [1, 13]. In the lab frame, the helicity of the circularly polarized light $\text{Im} [\mathbf{E}^* \cdot \mathbf{B}]$ also leads to a pseudoscalar associated with the chiral probe and called "optical chirality" [14–16]. Therefore, the interference term is a product of two pseudoscalars which are sign variant under improper rotations.

1.2.1.1 OPTICAL CHIRALITY

Chiroptical effects are generally small, primarily because the light's wavelength significantly surpasses the size of most molecules and they rely on the magnetic dipole moment. The electromagnetic field experiences a barely noticeable rotation across molecular dimensions. To enhance the coupling with molecular chirality, one could amplify the chirality by augmenting the electromagnetic field's twist.

The local chirality of a circularly polarized electromagnetic field can be described by a quantity called optical chirality, a time-even parity-odd pseudoscalar. It is a fundamental conserved quantity of the electromagnetic field. Optical chirality can be quantified by the optical chirality density C [14–16].

$$C = \frac{\varepsilon_0}{2} \mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu_0} \mathbf{B} \cdot \nabla \times \mathbf{B} \Rightarrow C = \frac{\varepsilon_0}{2} \left(\mathbf{B} \cdot \frac{\partial \mathbf{E}}{\partial t} - \mathbf{E} \cdot \frac{\partial \mathbf{B}}{\partial t} \right) \quad (1.9)$$

where we used the Faraday's law and Ampère-Maxwell law. Using the real valued electric and the magnetic field as $\mathbf{E} = \frac{1}{\sqrt{2}} (\tilde{\mathbf{E}} e^{-i\omega t} + \tilde{\mathbf{E}}^* e^{i\omega t})$ and $\mathbf{B} = \frac{1}{\sqrt{2}} (\tilde{\mathbf{B}} e^{-i\omega t} + \tilde{\mathbf{B}}^* e^{i\omega t})$, the time-averaged form of equation 1.9 yields

$$C = -\frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \quad (1.10)$$

This is known as chirality of light and is odd under Parity-time (PT) symmetry.

$$PT \left\{ -\frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \right\} \rightarrow P \left\{ \frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E} \cdot \mathbf{B}^*] \right\} \rightarrow -\frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E} \cdot \mathbf{B}^*] = \frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \quad (1.11)$$

$$PT \left\{ -\frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \right\} = \frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \quad (1.12)$$

Now that we have defined the chirality of CPL which is in the lab frame. the circular polarization states are defined as $|\text{RHC}\rangle = \frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}]$ and $|\text{LHC}\rangle = -\frac{\omega \varepsilon_0}{2} \text{Im} [\mathbf{E}^* \cdot \mathbf{B}]$.

1.2.1.2 ROSENFELD EQUATION

Optical activity in randomly oriented molecules is described by the optical rotatory parameter. It is known as the Rosenfeld equation and the first mechanism that could explain the selective absorption or optical rotation observed when CPL is transmitted through a sample. This was extensively pursued in the linear regime (single-photon absorption) but can be extended to the nonlinear regime (multiphoton absorption) through higher-order perturbation. The Rosenfeld equation is related to a single-photon rate of absorption obtained from the time-dependent perturbation theory.

When the Hamiltonian does not explicitly contain a time-dependence, then the solution to the Schrodinger equation $H_0|\Psi_n^{(0)}\rangle = E_n^{(0)}|\Psi_n^{(0)}\rangle$ is separable in spatial and temporal contributions $|\Psi_n^{(0)}\rangle = |\psi_n^{(0)}\rangle \exp(-iE_n^{(0)}t/\hbar)$. H_0 is the field-free Hamiltonian with eigenvalue E_n . The introduction of a time-dependent Hamiltonian $H(t)$ will force the system to undergo oscillations. If $H(t)$ changes very slowly in time compared to the natural frequencies $|(\partial H(t)/\partial t)/H(t)| \ll \omega_{nm}$, the method of time-independent perturbation theory, under the adiabatic process, can be used [13]. The system will continuously evolve from one stationary state to another without the absorption of radiation. However, when the perturbation is rapidly oscillating such as a field with its frequency $\omega \sim (\omega_m - \omega_n) = \omega_{mn}$ then the time-dependent perturbation theory must be employed.

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = (H_0 + \lambda V(t)) |\Psi\rangle \quad (1.13)$$

where, λ is the perturbation parameter and $V(t)$ is the interaction Hamiltonian [13]. For the time-dependent Hamiltonian, any wavefunction describing the perturbed system may be expanded in terms of a superposition of stationary states, $|\Psi\rangle = \sum_n c_n(t) |\Psi_n^{(0)}\rangle$ where $c_n(t)$ is the time dependent coefficient for spatial expansion of $|\Psi\rangle$ in terms of $|\Psi_n^{(0)}\rangle$. Substituting $|\Psi\rangle$ in equation 1.13, applying $\langle \Psi_m^{(0)} |$ to both sides and using the orthogonality of $|\Psi_n^{(0)}\rangle$ to eliminate the summation on the left.

$$i\hbar \frac{d}{dt} c_m(t) = \sum_n c_n(t) \langle \Psi_m^{(0)} | V(t) | \Psi_n^{(0)} \rangle \quad (1.14)$$

This is an exact solution and applies to any perturbation. The system is initially in the stationary states $|\Psi_n^{(0)}\rangle$ and set $c_n(t) \sim 1$ since the population is mostly in the ground state. Thus, the general solution is

$$c_m(t) = c_m^{(0)} - \frac{i}{\hbar} \int_{-\infty}^t \langle \Psi_m^{(0)} | V(t') | \Psi_n^{(0)} \rangle dt' \quad (1.15)$$

We can expand the time dependent coefficient $c_m(t)$ in powers of perturbation parameter λ ; $c_m(t) = c_m^{(0)} + \lambda c_m^{(1)}(t) + \lambda^2 c_m^{(2)}(t) + \dots + \lambda^N c_m^{(N)}(t)$. Where different order coefficients can be obtained by comparing powers

of perturbation parameter λ [6].

$$c_m^{(1)}(t) = \left(\frac{1}{i\hbar}\right) \int_{-\infty}^t dt' \langle m|V(t')|n\rangle e^{i\omega_{mn}t'} \quad (1.16)$$

$$c_m^{(2)}(t) = \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \sum_j \langle m|V(t_1)|j\rangle \langle j|V(t_2)|n\rangle e^{i\omega_{mj}t_1} e^{i\omega_{jn}t_2} \quad (1.17)$$

$$c_m^{(3)}(t) = \left(\frac{1}{i\hbar}\right)^3 \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \sum_{j,k} \langle m|V(t_1)|j\rangle \langle j|V(t_2)|k\rangle \langle k|V(t_3)|n\rangle e^{i\omega_{mj}t_1} e^{i\omega_{jk}t_2} e^{i\omega_{kn}t_3} \quad (1.18)$$

and the Nth order process is defined as, $c_m^{(N)}(t) = \left(\frac{1}{i\hbar}\right)^N \sum_n \int_{-\infty}^t dt' \langle m|V(t')|n\rangle c_n^{(N-1)}(t') e^{i\omega_{mn}t'}$.

To include higher order multipoles, such as electric-quadrupole and magnetic-dipole in the interaction Hamiltonian $V(t)$, a multipole expansion must be performed. An overview of the derivation is introduced here and a full derivation is included in Appendix A.1.

In principle, the transition amplitude can be expressed either in velocity or length gauges. Conversion from one gauge to the other can be achieved by using the generating function $\chi(r, R, t) = \int_0^1 \vec{r} \cdot \vec{A}(R + \lambda r, t) d\lambda$ and its resulting unitary operator $e^{-i\chi(r, R, t)}$ [17]. In the velocity gauge, the ground state wavefunction is given by $|\tilde{\psi}_g(t)\rangle = e^{-i\chi(r, R, t)} |\psi_g(t)\rangle$ and the Hamiltonian is given by $\hat{H}(t) = \frac{1}{2} \left(-i\vec{\nabla} + \vec{A}(r', t) \right)^2$ where $|\psi_g(t)\rangle$ is the ground state wavefunction in length gauge, $i\vec{\nabla}$ is the momentum operator and $\vec{A}(r', t)$ is the vector potential. We used the length gauge to derive the transition amplitude.

To introduce higher-order multipoles in the interaction Hamiltonian, we

1. Taylor expanded the vector potential to the second order about a point R in the interaction Hamiltonian as, $\vec{A}(r', t) \approx \vec{A}(R, t) + \vec{r}^T \widehat{\partial \vec{A}}(R, t) \dots$, and in the generating function as, $A(R + \lambda r, t) = A(R, t) + \lambda \vec{r}^T \widehat{\partial A}(R, t)$, where $\vec{r}^T$ is the transpose of position vector and $\widehat{\partial A}$ is the vector potential gradient written as a second rank tensor, see Appendix A.1.
2. Applied the unitary transformation operator $e^{-i\chi(r, R, t)}$ to explicitly express the existence of electric quadrupole and magnetic dipole in length gauge resulting in the non-dipole interaction Hamiltonian $\hat{V}(t') = r_i E_i(R, t') + \frac{1}{2} r_i r_j \widehat{\partial_j E_i}(R, t') + \frac{1}{2} L_i B_i(R, t')$, where $E_i(R, t)$ and $B_i(R, t)$ are the incident electric and magnetic fields, respectively, of the asymmetrical Laguerre-Gaussian laser beam, $r_{i,j}$ is the distance between positive and negative charge in the atomic frame and R represents the coordinates of the laser beam profile. $\widehat{\partial_j E_i}$ represents the field gradient tensor and L_i is the orbital angular momentum of the magnetic dipole transition moment.

Consider an interaction Hamiltonian of the form, $V(t) = V e^{-i\omega t} + V^* e^{i\omega t}$. By implementing the rotating wave approximation, we neglected the complex conjugate of the field because we are only considering absorption and ignoring the stimulated emission (anti-resonant terms) [6]. The probability amplitude can be expressed as $p_m^{(N)}(t) = |c_m^{(N)}(t)|^2$, and the rate of transition is $R_{mg}^{(N)} = \frac{p_m^{(N)}(t)}{t}$. For a single photon process we obtain Fermi's

golden rule, the transition rate for absorption, from ground state $|g\rangle$ to excited state $|m\rangle$.

$$R_{mg}^{(1)} = \frac{d}{dt} P_m(t) = \frac{2\pi}{\hbar^2} |\langle m|V|g\rangle|^2 \delta(\omega_{mg} - \omega) = \frac{2\pi}{\hbar} |\langle m|V|g\rangle|^2 \rho(E_f) \quad (1.19)$$

where $\omega_{mg} = \hbar(E_m - E_g)$ represent the energy difference between the two states and the delta function can be represented by the lineshape function for the resonant absorption $\delta(E_f - E_i - \hbar\omega) \approx \rho(E_f)$. The single photon transition rate for Electric-dipole (E1), Magnetic-dipole (M1) and Electric-quadrupole (E2) moments are

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar} \left| \underbrace{\langle \Psi_m^{(0)} | \boldsymbol{\mu} | \Psi_g^{(0)} \rangle \cdot \mathbf{E}}_{\text{E1}} + \underbrace{\langle \Psi_m^{(0)} | \mathbf{m} | \Psi_g^{(0)} \rangle \cdot \mathbf{B}}_{\text{M1}} + \underbrace{\langle \Psi_m^{(0)} | \mathbf{Q} | \Psi_g^{(0)} \rangle \cdot \widehat{\nabla \mathbf{E}}}_{\text{E2}} \right|^2 \rho(E_f) \quad (1.20)$$

The charge transfer for these higher-order multipoles are depicted in figure 1.6. The electric multipoles represent charge configurations, whereas magnetic multipoles correspond to current sources [18]. Electric-dipole moment and magnetic-dipole moment coupling term is sensitive to polarization and is responsible for CD and ORD while the electric-dipole moment and electric-quadrupole moment coupling term is responsive to the helical phase and give rise to HD.

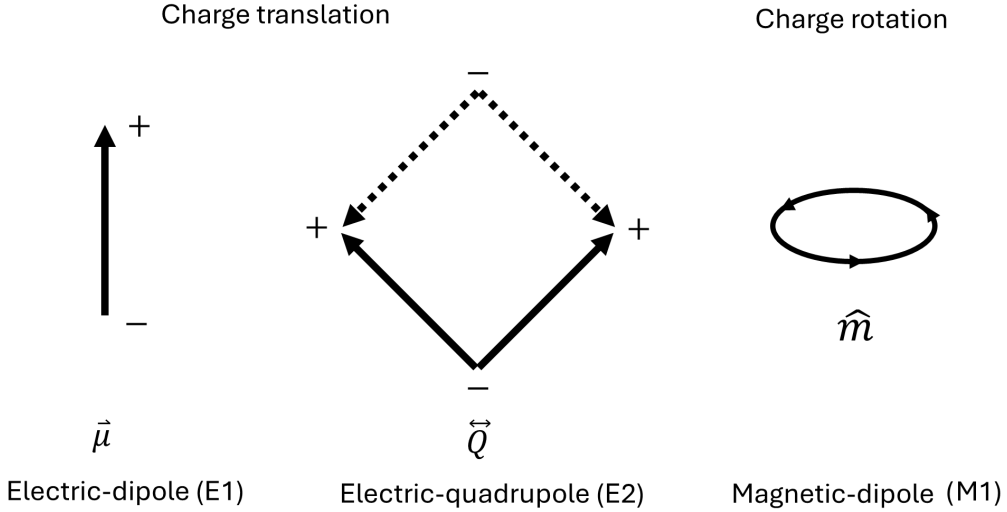


Figure 1.6: **Multipole moments:** Schematic representation of the Electric-dipole, electric-quadrupole, and magnetic-dipole moments depicting the charge translation and rotation.

Optical measurements are often performed on media in which the individual molecules are randomly oriented, such as in liquids or gases. This requires a rotational averaging over all molecular orientation ($\langle \rangle_{\Omega}$). It can be calculated through the use of a direction cosine matrix, Φ [12] which contains the molecular orientation in the laboratory frame. A factor of 1/3 for Electric dipole-dipole coupling term (E1E1), Electric-dipole magnetic-dipole coupling term (E1M1), Magnetic dipole-dipole coupling term (M1M1) and a factor of 1/5 for Electric quadrupole-quadrupole coupling term (E2E2) arises from the rotational averages, $\langle \Phi_i \Phi_j \rangle = \delta_{ij}/3$ and $\langle \Phi_i \Phi_j \Phi_k \Phi_l \rangle = (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})/3*5$ [12]. If the molecules are not in a fixed frame or not partially aligned

by the field (such is the case for linear regime), the Electric-dipole electric-quadrupole coupling term (E1E2) and Magnetic-dipole electric-quadrupole coupling term (M1E2) vanishes upon rotational averaging $\langle \Phi_i \Phi_j \Phi_k \rangle = 0$ [12, 13]. So, for linear absorption in an isotropic liquid, only four terms survive upon rotational averaging and we can further ignore the M1M1 and E2E2 coupling term as they are significantly smaller compared to the other terms.

By using perturbation theory and rotationally averaging over all molecular orientation for an isotropic medium we obtain the average transition rate.

$$\langle R_{mg}^{(1)} \rangle_\Omega = \frac{2\pi}{\hbar} \left(\frac{1}{3} |\boldsymbol{\mu}^{mg}|^2 |\mathbf{E}|^2 + \frac{1}{3} |\mathbf{m}^{mg}|^2 |\mathbf{B}|^2 + \frac{1}{3} \text{Im} [\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}] \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] + \right. \\ \left. \cancel{\langle \boldsymbol{\mu}^{mg} \cdot \mathbf{Q}^{gm} \rangle_\Omega \text{Re} [\widehat{\nabla \mathbf{E}} \cdot \mathbf{E}^*]} \xrightarrow{0} + \cancel{\langle \mathbf{m}^{mg} \cdot \mathbf{Q}^{gm} \rangle_\Omega \text{Im} [\widehat{\nabla \mathbf{E}} \cdot \mathbf{B}^*]} \xrightarrow{0} + \frac{1}{5} |\mathbf{Q}^{mg}|^2 |\widehat{\nabla \mathbf{E}}|^2 \right) \rho(E_f) \quad (1.21)$$

$$\langle R_{mg}^{(1)} \rangle_\Omega = \Gamma_{E_1 E_1} + \cancel{\Gamma_{M_1 M_1}} \xrightarrow{\text{small}} + \left(\Gamma_{E_1 M_1} \right) + \cancel{\Gamma_{E_1 E_2}} \xrightarrow{0} + \cancel{\Gamma_{M_1 E_2}} \xrightarrow{0} + \cancel{\Gamma_{E_2 E_2}} \xrightarrow{\text{small}} \quad (1.22)$$

Where for real quantities, $\mathbf{B} \cdot \mathbf{E}^* - \mathbf{E} \cdot \mathbf{B}^* = -2i \text{Im} [\mathbf{E}^* \cdot \mathbf{B}]$ known as optical chirality, C [14–16], and the molecular chirality is defined by $\langle -i \boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm} \rangle = \text{Im} [\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]$ and is known as the Rosenfeld equation [1, 13]. Both the optical chirality and the molecular chirality term are responsible for ORD and CD. It is important to note here that for an ordered or partially ordered medium the E1E2 coupling term does not vanish and is called optical helicity, Υ and is defined as $\left[\left(\widehat{\nabla \mathbf{E}} \cdot \mathbf{E}^* + \mathbf{E} \cdot (\widehat{\nabla \mathbf{E}})^\dagger \right) \right] = 2 \text{Re} [\mathbf{E}^* \cdot \widehat{\nabla \mathbf{E}}^\dagger] = 2 \text{Re} [\widehat{\nabla \mathbf{E}} \cdot \mathbf{E}^*]$. Optical helicity becomes important for strong-field chiroptical measurement with helical light described in the later chapter 4, 5, 6. These coupling terms can be readily extended to a multiphoton process by introducing the higher perturbation terms (see supplementary of chapter 4).

1.2.1.3 PARITY OF CIRCULAR DICHROISM

Using the PT symmetry we can show the existence of differential absorption of CPL for enantiomers, the molecular response for one molecular handedness is equal to its mirror image. Therefore, it is a time-even parity even scalar.

$$PT \left\{ \text{Im} [\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_R \right\} = \text{Im} [\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_S \quad (1.23)$$

Where we assign the symmetrical ground state Ψ_s to the R-enantiomer and the anti-symmetrical Ψ_{as} to the S-enantiomer. This can be justified as the consequence of the slight asymmetry in the molecular potential, leading to eigenfunctions either symmetrical $\Psi_s^g = 1/\sqrt{2} (\psi_+ + \psi_-)$ or anti-symmetrical $\Psi_{as}^g = 1/\sqrt{2} (\psi_+ - \psi_-)$, where Ψ_+ (Ψ_-) is even (odd) under parity. Therefore, the enantiomer pair is localized in opposite ground states; if R is even, then S is odd or vice versa. The excited states for both enantiomers are assumed to be a

mixed parity state given as $\Psi_m = 1/\sqrt{2} (\psi_+ + i\beta\psi_-)$, where $i\beta$ is a small phase lag factor between even and odd states [1, 19].

The PT symmetry for E1M1 for circularly polarized Gaussian beam is

$$PT\{\Gamma_{E1M1}\} = PT\left\{\frac{1}{3}\text{Im}[\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_R \text{Im}[\mathbf{E}^* \cdot \mathbf{B}]\right\} = -\frac{1}{3}\text{Im}[\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_S \text{Im}[\mathbf{E}^* \cdot \mathbf{B}] \quad (1.24)$$

Therefore, E1M1 transition are odd under PT symmetry. This is known as true chirality because it is parity-odd and time-even pseudoscalar. This can be translated to conventional CD for Gaussian beams.

$$\begin{aligned} PT\{CD_R\} &= PT\left\{\frac{1}{3}\text{Im}[\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_R\right\} PT\left\{\text{Im}[\mathbf{E}^* \cdot \mathbf{B}] - \text{Im}[\mathbf{E} \cdot \mathbf{B}^*]\right\} = \\ &= -\frac{1}{3}\text{Im}[\boldsymbol{\mu}^{mg} \cdot \mathbf{m}^{gm}]_S (\text{Im}[\mathbf{E}^* \cdot \mathbf{B}] - \text{Im}[\mathbf{E} \cdot \mathbf{B}^*]) = -CD_S \end{aligned} \quad (1.25)$$

Therefore, CD is odd under PT symmetry [14, 15]. Therefore, CD can be considered “true chirality” because it is odd under space inversion.

1.2.1.4 INDUCED MOLECULAR MOMENTS

Induced multipole molecular moments are responsible for many optical phenomena as they are related to the polarization and magnetization of the material times the number density N of the atoms. Consider an observable O such as the electric or magnetic dipole moment of a molecule. According to quantum mechanics, the expectation value is defined as $\langle O \rangle_{nn} = \langle \tilde{\Psi}_n^{(0)} | O | \tilde{\Psi}_n^{(0)} \rangle$ where the wavefunction is defined as $|\tilde{\Psi}_n^{(0)}\rangle = |\Psi_n^{(0)}\rangle + \sum_m c_m(t) |\Psi_m^{(0)}\rangle$. We can use the expectation values to calculate the form of the linear and nonlinear susceptibilities. Here we will explicitly derive the induced multipole moments that are commonly used to describe chiroptical interaction and extend to chiro-helical interaction in chapter 4. First, expand the expectation value to explicitly show the time dependence of a $n \rightarrow m$ transition

$$\langle O \rangle_{nn} = \langle \Psi_n^{(0)} | O | \Psi_n^{(0)} \rangle + 2\text{Re} \left[\sum_m c_m(t) \langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle e^{-i\omega_{nm}t} \right] \quad (1.26)$$

Here we expressed the complex conjugate term as a real part for simplicity and the energy difference between the states is defined as $\omega_{nm} = (E_m - E_n)/\hbar$. If our perturbation is a monochromatic wave, the perturbation operator has the form $V(t) = \tilde{V} \cos(\omega t)$ where $\tilde{V}$ is the time-independent interaction Hamiltonian. Substitution of the perturbation $V(t)$ in the time-dependent coefficient represented by equation 1.15 leads to

$$c_m(t) = c_m^{(0)} - \frac{i}{\hbar} \langle \Psi_m^{(0)} | \tilde{V} | \Psi_n^{(0)} \rangle \int \cos(\omega t) e^{i\omega_{nm}t} dt \quad (1.27)$$

and solving the time integral gives

$$c_m(t) = c_m^{(0)} - \frac{i}{\hbar} \langle \Psi_m^{(0)} | \tilde{V} | \Psi_n^{(0)} \rangle e^{i\omega_{nm}t} \left[\frac{(\omega \sin(\omega t) + i\omega_{nm} \cos(\omega t))}{(\omega^2 - \omega_{nm}^2)} \right] \quad (1.28)$$

Substituting the above equation into 1.26 we get

$$\begin{aligned} \langle O \rangle_{nn} = \langle \Psi_n^{(0)} | O | \Psi_n^{(0)} \rangle + 2\text{Re} \sum_m \left[c_m^{(0)} \langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle e^{-i\omega_{nm}t} \right. \\ \left. + \frac{\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \tilde{V} | \Psi_n^{(0)} \rangle}{\hbar(\omega_{nm}^2 - \omega^2)} [(i\omega \sin(\omega t) - \omega_{nm} \cos(\omega t))] \right] \end{aligned} \quad (1.29)$$

The transient term can be eliminated by taking $c_m^{(0)} \sim 0$ [13] and simplifying the real argument, $\text{Re}[ia - b] = -(\text{Re}[b] + \text{Im}[a])$, results in

$$\begin{aligned} \langle O \rangle_{nn} = \langle \Psi_n^{(0)} | O | \Psi_n^{(0)} \rangle - \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\text{Re} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \tilde{V} | \Psi_n^{(0)} \rangle \right] \omega_{nm} \cos(\omega t) \right. \\ \left. + \text{Im} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \Psi_n^{(0)} \rangle \right] \omega \sin(\omega t) \right] \end{aligned} \quad (1.30)$$

Here, we substitute the time-dependent perturbation operator $V(t) = \tilde{V} \cos(\omega t)$ and its rate of change as $\frac{\partial V(t)}{\partial t} = -\omega \tilde{V} \sin(\omega t)$ to obtain an implicit form of the time-dependent transition.

$$\begin{aligned} \langle O \rangle_{nn} = \langle \Psi_n^{(0)} | O | \Psi_n^{(0)} \rangle - \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | V(t) | \Psi_n^{(0)} \rangle \right] \right. \\ \left. - \text{Im} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \frac{\partial V(t)}{\partial t} | \Psi_n^{(0)} \rangle \right] \right] \end{aligned} \quad (1.31)$$

For isotropic medium, the optical activity or circular dichroism arises from the E1 and M1 moments. However, the E2 term becomes significantly important for an ordered environment or for the nonlinear regime when a molecule is irradiated by helical light (shown in chapter 4 and 5). For completeness, we will still perform the derivation with the quadrupole term.

Introducing the higher order multipoles (derived in Appendix A.1) in the perturbation $V(t)$ we can explicitly show the electric-dipole, magnetic-dipole and electric-quadrupole moments in the transition matrix element.

$$\langle \Psi_m^{(0)} | V(t) | \Psi_n^{(0)} \rangle = -\langle \Psi_m^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle \cdot \mathbf{E} - \langle \Psi_m^{(0)} | \mathbf{m} | \Psi_n^{(0)} \rangle \cdot \mathbf{B} - \langle \Psi_m^{(0)} | \mathbf{Q} | \Psi_n^{(0)} \rangle \cdot \widehat{\nabla \mathbf{E}} \quad (1.32)$$

$$\langle \Psi_m^{(0)} | \frac{\partial V(t)}{\partial t} | \Psi_n^{(0)} \rangle = -\langle \Psi_m^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle \cdot \frac{\partial \mathbf{E}}{\partial t} - \langle \Psi_m^{(0)} | \mathbf{m} | \Psi_n^{(0)} \rangle \cdot \frac{\partial \mathbf{B}}{\partial t} - \langle \Psi_m^{(0)} | \mathbf{Q} | \Psi_n^{(0)} \rangle \cdot \frac{\partial \widehat{\nabla \mathbf{E}}}{\partial t} \quad (1.33)$$

Substituting the matrix element 1.32 and 1.33 into equation 1.31 gives rise to an expanded form of the

expectation value of an arbitrary observable $\langle O \rangle_{nn}$.

$$\begin{aligned}
 \langle O \rangle_{nn} = & \langle \Psi_n^{(0)} | O | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle \right] \cdot \mathbf{E} \right. \\
 & + \omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mathbf{m} | \Psi_n^{(0)} \rangle \right] \cdot \mathbf{B} - \omega \text{Im} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle \right] \cdot \frac{1}{\omega} \frac{\partial \mathbf{E}}{\partial t} \\
 & - \omega \text{Im} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mathbf{m} | \Psi_n^{(0)} \rangle \right] \cdot \frac{1}{\omega} \frac{\partial \mathbf{B}}{\partial t} + \omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mathbf{Q} | \Psi_n^{(0)} \rangle \right] \cdot \widehat{\nabla \mathbf{E}} \\
 & \left. - \omega \text{Im} \left[\langle \Psi_n^{(0)} | O | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mathbf{Q} | \Psi_n^{(0)} \rangle \right] \cdot \frac{1}{\omega} \frac{\partial \widehat{\nabla \mathbf{E}}}{\partial t} \right] \quad (1.34)
 \end{aligned}$$

By replacing the observable with the electric-dipole, magnetic-dipole, and electric-quadrupole (ignore the higher order terms such as M1E2 and E2E2) we can express the real induced oscillating multipole moments as

$$\begin{aligned}
 \langle \mu_i \rangle_{nn} = & \langle \Psi_n^{(0)} | \mu_i | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] E_j \right. \\
 & + \omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] B_j - \omega \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial E_j}{\partial t} \\
 & - \omega \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial B_j}{\partial t} + \frac{\omega_{nm}}{3} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \theta_{jk} | \Psi_n^{(0)} \rangle \right] \nabla E_{jk} \\
 & \left. - \frac{\omega}{3} \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \theta_{jk} | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial E_{jk}}{\partial t} \right] \quad (1.35)
 \end{aligned}$$

$$\begin{aligned}
 \langle m_i \rangle_{nn} = & \langle \Psi_n^{(0)} | m_i | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] E_j \right. \\
 & + \omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] B_j - \omega \text{Im} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial E_j}{\partial t} \\
 & \left. - \omega \text{Im} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial B_j}{\partial t} \right] \quad (1.36)
 \end{aligned}$$

$$\begin{aligned}
 \langle \theta_{ij} \rangle_{nn} = & \langle \Psi_n^{(0)} | \theta_{ij} | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{2}{\hbar(\omega_{nm}^2 - \omega^2)} \left[\omega_{nm} \text{Re} \left[\langle \Psi_n^{(0)} | \theta_{ij} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_k | \Psi_n^{(0)} \rangle \right] E_k \right. \\
 & \left. - \omega \text{Im} \left[\langle \Psi_n^{(0)} | \theta_{ij} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_k | \Psi_n^{(0)} \rangle \right] \frac{1}{\omega} \frac{\partial E_k}{\partial t} \right] \quad (1.37)
 \end{aligned}$$

The first term is the induced electric dipole moment, the second is the induced magnetic dipole moment and the third term is the induced quadrupole moment of a molecule in a real oscillating electromagnetic field [20–22]. The introduction of the traceless electric quadrupole moment $\mathbf{Q}_{ij} = \frac{1}{3}\theta_{ij}$ is permissible due to the origin begin far from the external charge distribution [20]. In order to determine the scattering properties of a medium, the observables must be averaged over all orientations. However, for the principle of this derivation let us maintain all the terms and concern ourselves with the isotropic averaging in the latter chapters. The induced electric-dipole, magnetic-dipole and electric quadrupole can be condensed and written in terms of mixed polarizability tensors.

$$\langle \mu_i \rangle_{nn} = \alpha_{ij} E_j + \frac{\alpha'_{ij}}{\omega} \frac{\partial E_j}{\partial t} + G_{ij} B_j + \frac{G'_{ij}}{\omega} \frac{\partial B_j}{\partial t} + \frac{1}{3} A_{i,jk} \nabla_j E_k + \frac{1}{3} \frac{A'_{i,jk}}{\omega} \frac{\partial \nabla_j E_k}{\partial t} \quad (1.38)$$

$$\langle m_i \rangle_{nn} = G_{ji} E_j - \frac{G'_{ji}}{\omega} \frac{\partial E_j}{\partial t} + \chi_{ij} B_j + \frac{\chi'_{ij}}{\omega} \frac{\partial B_j}{\partial t} \quad (1.39)$$

$$\langle \theta_{ij} \rangle_{nn} = A_{k,ij} E_k - \frac{A'_{k,ij}}{\omega} \frac{\partial E_k}{\partial t} \quad (1.40)$$

where α_{ij} is the electric dipole polarizability, χ_{ij} is the magnetic susceptibility, $A_{i,jk}$ is the electric dipole -quadrupole polarizability, and G_{ij} is the electric-magnetic dipole polarizability. These real dynamic molecular tensors are defined as

$$\alpha_{ij} = \sum_{m \neq n} \frac{2\omega_{nm}}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] \quad (1.41)$$

$$\alpha'_{ij} = - \sum_{m \neq n} \frac{2\omega}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mu_j | \Psi_n^{(0)} \rangle \right] \quad (1.42)$$

$$G_{ij} = \sum_{m \neq n} \frac{2\omega_{nm}}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \quad (1.43)$$

$$G'_{ij} = - \sum_{m \neq n} \frac{2\omega}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \quad (1.44)$$

$$A_{i,jk} = \sum_{m \neq n} \frac{2\omega_{nm}}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Re} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \theta_{jk} | \Psi_n^{(0)} \rangle \right] \quad (1.45)$$

$$A'_{i,jk} = - \sum_{m \neq n} \frac{2\omega}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Im} \left[\langle \Psi_n^{(0)} | \mu_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \theta_{jk} | \Psi_n^{(0)} \rangle \right] \quad (1.46)$$

$$\chi_{ij} = \sum_{m \neq n} \frac{2\omega_{nm}}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Re} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \quad (1.47)$$

$$\chi'_{ij} = - \sum_{m \neq n} \frac{2\omega}{\hbar(\omega_{nm}^2 - \omega^2)} \text{Im} \left[\langle \Psi_n^{(0)} | m_i | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | m_j | \Psi_n^{(0)} \rangle \right] \quad (1.48)$$

Note, the order of the indices must be taken under consideration as these are tensors [20], for example, $\text{Re} [\mu_i \mu_j] = \text{Re} [\mu_j \mu_i]$ and $\text{Im} [\mu_i \mu_j] = -\text{Im} [\mu_j \mu_i]$. The real electric and magnetic field are defined as $E_j = \frac{1}{2} [\tilde{E}_j e^{-i\omega t} + \tilde{E}_j^* e^{i\omega t}]$ and $B_j = \frac{1}{2} [\tilde{B}_j e^{-i\omega t} + \tilde{B}_j^* e^{i\omega t}]$.

It is convenient to present the real oscillating induced electric and magnetic multipole moments in a complex form. The complex dynamic molecular tensors [20] are $\tilde{\alpha}_{ij} = \alpha_{ij} - i\alpha'_{ij}$, $\tilde{G}_{ij} = G_{ij} - iG'_{ij}$, $\tilde{A}_{i,jk} = A_{i,jk} - iA'_{i,jk}$ and

$\tilde{\chi}_{ij} = \chi_{ij} - i\chi'_{ij}$ which allows us to express the complex induced oscillating electric and magnetic multipole moments as

$$\begin{aligned}\tilde{\mu}_i &= \tilde{\alpha}_{ij}\tilde{E}_j + \tilde{G}_{ij}\tilde{B}_j + \frac{1}{3}\tilde{A}_{i,jk}\nabla_j\tilde{E}_k + \dots \\ \tilde{m}_i &= \tilde{G}_{ij}^*\tilde{E}_j + \tilde{\chi}_{ij}\tilde{B}_j + \dots \\ \tilde{\theta}_{ij} &= \tilde{A}_{k,ij}^*\tilde{E}_k + \dots\end{aligned}\tag{1.49}$$

The induced electric and magnetic dipole moments are responsible for CD and ORD as can be seen by the presence of the Rosenfeld rotational strength in the mixed electric magnetic dipole tensor G'_{ij} . The future chapters will show that the electric-dipole and quadrupole moments are responsible for the HD.

The force exerted by an electric or magnetic field on a system of charges over a time Δt must be averaged over the oscillation period. This gives rise to the work from the field on a system of charge which is none other than the average energy absorbed. Therefore, the rate of energy absorbed (Γ) from the electromagnetic fields by the induced multipoles is represented by [16, 20]

$$\Gamma = \langle \dot{\mu}_i E_j + \dot{m}_i B_j + \frac{1}{3}\dot{\theta}_{ij} E_{ij} \rangle_t \tag{1.50}$$

1.2.2 PHOTOELECTRON CIRCULAR DICHROISM

PECD has recently emerged as an effective chiroptical imaging technique with an efficiency of two to three times larger than CD [23–25]. This chiral discrimination imaging technique operates strictly in the dipole approximation, the underlying mechanism is an interaction between circularly polarized light and a chiral molecule resulting in a forward and backward asymmetric Photoelectron Angular Distribution (PAD). Thus, the chiral reagent is CPL and the chiral observable is the PAD emitted by the chiral molecule when irradiated by a laser field. The PAD is identical but opposite in sign for both enantiomers. This forward-backwards asymmetry in the angular distribution is caused by a difference of potential felt by the photoelectron as a function of the azimuthal angle. The chiral response is described by the differential cross-section $\sigma_{i \rightarrow f}^{abs}(\omega)$ of the photoelectron emitted into a solid angle Ω for randomly orientated molecules defined in terms of angular distribution function $I(\theta)$ where θ is the angle of emission.

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} I(\theta) \tag{1.51}$$

where the angular distribution $I(\theta)$ is defined as

$$I(\theta) = \sum_{j=0}^2 b_j^{(p)} P_j(\cos(\theta)) = 1 + b_1^{(p)} P_1(\cos(\theta)) + b_2^{(p)} P_2(\cos(\theta)) \tag{1.52}$$

The angular distribution is derived from the differential cross-section for electron emission into a solid-angle Ω . The coefficients $b_1^{(p)}$ and $b_2^{(p)}$ are determined by the photoionization dynamics and are dependent on the incident field polarization p . $p = 0$ represents linearly polarized light and $p = \pm 1$ represents the left- and right-circularly polarized light, respectively. $P_1(\cos\theta)$ and $P_2(\cos\theta)$ are the first and second order Legendre polynomials. θ is defined as the angle between the ejected electrons and the propagation direction of the incident light. The ionized electron exhibits asymmetric behaviour due to momentum conservation during the photoionization process involving circularly polarized

photon and the chiral molecules.

The enantio-selectivity is mainly due to the first order term $b_1^{\{p\}} P_1(\cos\theta)$ in the differential cross-section. This term does not contribute to linearly polarized light or an achiral molecule since $b_1^{\{0\}} = 0$. For circularly polarized light the first order term is anti-symmetric ($b_1^{+1} = -b_1^{-1}$) with the exchange of either the incoming polarized light or the enantiomer leading to forward and backwards asymmetry of the PAD depicted by figure 1.7. The second order term does not give rise to any asymmetry even for circularly polarized light because $b_2^{\{\pm 1\}} = -(1/2)b_2^{\{0\}}$. PECD arise due to pure electric dipole transitions, unlike conventional CD which relies on the coupling of electric and magnetic dipole transitions. Consequently, PECD is a highly efficient gas phase chiroptical technique whereas CD requires a large number density.

The photoelectrons are emitted in a 3D Newton sphere where the electron kinetic energy is encoded in the radial coordinate and the PAD in the angular coordinate. This imaging technique detects the 3D PAD as a 2D projection and is reconstructed using inversion theorems. The experimental observable detects both the ions and the photoelectrons using either Cold Target Recoil Ion Momentum Spectrometer (COLTRIMS) or Velocity map imaging (VMI).

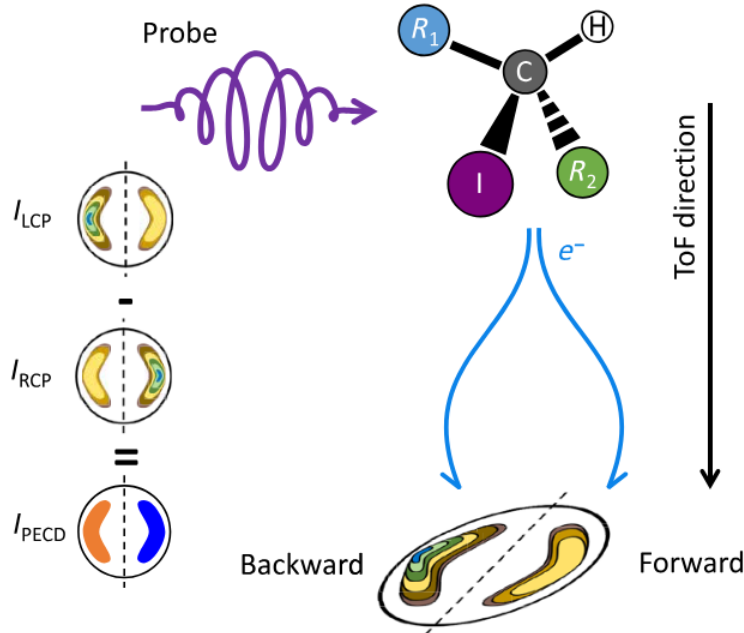


Figure 1.7: **Photoelectron circular dichroism technique:** Schematic representation of left- and right-handed CPL as the chiral probe interacting with a toy molecule and generating asymmetrical PAD represented by the 2D projection [26].

1.2.2.1 MECHANISM FOR PECD

Using time-dependent perturbation theory, as done previously, we can express Fermi's golden rule in terms of the differential cross-section. For single photon, we use the transition rate 1.19 but restrain ourselves to the dipole moment.

$$R_{mg}^{(1)} = \frac{d}{dt} P_m(t) = \frac{2\pi}{\hbar^2} |\langle m | \boldsymbol{\mu} \cdot \mathbf{E} | g \rangle|^2 \delta(\omega_{mg} - \omega) = \frac{2\pi}{\hbar} |\langle m | V | g \rangle|^2 \rho(E_f) \quad (1.53)$$

Our goal is to find the differential cross-section from Fermi's golden rule. To do so, we must find the density of states for scattering into a solid angle $d\Omega$. In three-dimensional k-space, the volume element is $(\frac{2\pi}{a_0})^3$, where a_0 is the Bohr

radius. By treating the k-space as the continuum, we want to find the number of states in the k-space volume $k^2 dk d\Omega$ that corresponds to energy between E and $E + dE$. Thus, $\rho(E)dE = \left(\frac{a_0}{2\pi}\right)^2 k^2 dk d\Omega$ and $\rho(E) = \left(\frac{a_0}{2\pi}\right)^3 \frac{mk}{\hbar^2} d\Omega$ where $E_f = \hbar^2 k^2 / 2m$. The differential cross-section is related to the rate of absorption by multiplying the photon energy $\hbar\omega$ and dividing the incident intensity [27], $I = \frac{1}{2} cn\epsilon_0 |E|^2$.

$$\frac{d\sigma}{d\Omega} = R_{fi}^{(1)} \frac{E_{\hbar\omega}}{I} = \frac{\alpha a_0^2}{2\pi} k E_{\hbar\omega} |\langle \psi_f(\vec{r}) | \hat{e} \cdot \vec{r} | \psi_i(\vec{r}) \rangle|^2 \quad (1.54)$$

where a_0 is the Bohr radius of the atom, $E_{\hbar\omega}$ is the photon energy, k is the wavenumber, α is the fine structure constant in atomic units, and $\hat{e}$ is the polarization direction. This is for the dipole approximation, the result is similar to the first Born approximation scattering amplitude, to first order the Born approximation and Fermi's golden rule coincide.

The bound and continuum wavefunction can be written in terms of partial waves in the Spherical harmonics basis as a product of radial ($R_{nl}(r)$) and angular ($Y_{lm}(\hat{r})$) state

$$\begin{aligned} \psi_i(\vec{r}) &= R_{nl}(r) Y_{lm}(\hat{r}) \\ \psi_f(\vec{r}) &= e^{ik \cdot r} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l e^{-i\delta_l} R_{nl}(kr) Y_{lm}(\hat{k})^* Y_{lm}(\hat{r}) \end{aligned} \quad (1.55)$$

where δ_l is the scattering phase, the Legendre polynomial can be expressed as $P_l(\cos(\theta)) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}(\hat{k})^* Y_{lm}(\hat{r})$, the radial functions can be written as spherical Bessel functions, and the angular function are spherical harmonics. Substituting the initial and final state into the differential cross-section leads to

$$\frac{d\sigma}{d\Omega} \propto \left| 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l (i)^l e^{-i\delta_l} Y_{lm}(\hat{k})^* \underbrace{\langle R_{n'l'}(kr) Y_{l'm'}(\hat{r}) | \hat{e} \cdot \vec{r} | R_{nl}(r) Y_{lm}(\hat{r}) \rangle}_{f_{nlm}} \right|^2 \quad (1.56)$$

The incident polarization can be written as spherical harmonics, $\hat{e}_x \cdot \vec{r} = \sqrt{\frac{4\pi}{3}} r Y_{10}(\hat{r})$ for linear polarization and $(\hat{e}_x \pm i\hat{e}_y) \cdot \vec{r} = \mp \sqrt{\frac{8\pi}{3}} r Y_{1\pm 1}(\hat{r})$ for circular polarization. Thus, the angular and radial parts can be separated. We define the radial part as $\langle R_{n'l'}(kr) | r | R_{nl}(r) \rangle$ and the angular part as $\langle Y_{l'm'}(\hat{r}) | Y_{1(0,\pm 1)}(\hat{r}) | Y_{lm}(\hat{r}) \rangle$. The radial part must be solved numerically, however, the angular part can be solved analytically. For ease of derivation, we label the full transition as f_{nlm} .

The differential cross-section expressed in 1.56 is written in the molecular frame. To describe PAD detected in terms of the laboratory frame we must perform a rotational transform of 1.56 using the Wigner D-matrix which is a unitary square rotational matrix of dimension $2j+1$, $D_{\nu\mu}^j(R) = \langle jm | e^{-i(\alpha J_x + \beta J_y + \gamma J_z)} | jm \rangle$ where $R = (\alpha, \beta, \gamma)$ are Euler angles. The angular momentum projections, ν, μ are defined in the molecular frame but may be transformed to the lab frame by a rotation. This allows us to express the differential cross-section for a specific lab-frame polarization, p , and electron detection direction, $\hat{k}$, as

$$\frac{d\sigma}{d\Omega} \propto \int dR \left| 4\pi \sum_{lm\nu\mu} (i)^l e^{-i\delta_l} \left[D_{\mu m}^j(R) Y_{lm}(\hat{k}) \right]^* D_{p\nu}^1(R) e_{\nu}^1 f_{\nu lm} \right|^2 \quad (1.57)$$

$$\frac{d\sigma}{d\Omega} \propto 16\pi^2 \sum_{lm\nu\mu} \sum_{l'm'\nu'\mu'} (i)^{l-l'} e^{-i(\delta_l-\delta_{l'})} \int dR \left[D_{\mu m}^l(R) Y_{l\mu}(\hat{k}) \right]^* D_{p\nu}^1(R) e_{\nu}^1 f_{\nu lm} \times D_{\mu' m'}^{l'}(R) Y_{l'\mu'}(\hat{k}) \left[D_{p\nu'}^1(R) e_{\nu'}^1 f_{\nu' l' m'} \right]^* \quad (1.58)$$

where e_{ν}^1 is a spherical tensor component of the photon electric polarization vector [23]. The pairs of rotation matrix products can be replaced by the Clebsch-Gordon series.

$$\left[D_{\mu m}^l(R) \right]^* D_{\mu' m'}^{l'}(R) = \sum_k (-1)^{\mu-m} \langle l' \mu', l - \mu | k \mu' - \mu \rangle \langle l' m', l - m | k m' - m \rangle D_{\mu' - \mu, m' - m}^k(R) \quad (1.59)$$

$$D_{p\nu}^1(R) \left[D_{p\nu'}^1(R) \right]^* = \sum_j (-1)^{p-\nu'} \langle 1-p, 1p | j 0 \rangle \langle 1-\nu', 1\nu | j \nu - \nu' \rangle D_{0, \nu-\nu'}^j(R) \quad (1.60)$$

Only two Wigner D-matrix survive the transformation. Substituting these Clebsch-Gordon coefficients into equation 1.56 leads to

$$\begin{aligned} \frac{d\sigma}{d\Omega} \propto 16\pi^2 \sum_{jk} \sum_{lm\nu\mu} \sum_{l'm'\nu'\mu'} (i)^{l-l'} (-1)^{\mu-m} (-1)^{p-\nu'} e^{-i(\delta_l-\delta_{l'})} Y_{l\mu}(\hat{k})^* e_{\nu}^1 f_{\nu lm} Y_{l'\mu'}(\hat{k}) \left[e_{\nu'}^1 f_{\nu' l' m'} \right]^* \langle l' \mu', l - \mu | k \mu' - \mu \rangle \\ \langle l' m', l - m | k m' - m \rangle \langle 1-p, 1p | j 0 \rangle \langle 1-\nu', 1\nu | j \nu - \nu' \rangle \int D_{0, \nu-\nu'}^j(R) D_{\mu' - \mu, m' - m}^k(R) dR \end{aligned} \quad (1.61)$$

To accommodate the randomly orientated molecules, an integration over all orientation must be performed over the remaining two Wigner D-matrices, $\int D_{0, \nu-\nu'}^j(R) D_{\mu' - \mu, m' - m}^k(R) dR = \left((-1)^{\nu'-\nu} \frac{8\pi^2}{(2j+1)} \delta_{jk} \delta_{0, \mu' - \mu} \delta_{\nu' - \nu, m' - m} \right)$. Using the Kronecker delta we can further simplify the rotational averaged differential cross-section to

$$\begin{aligned} \frac{d\sigma}{d\Omega} \propto 128\pi^4 \sum_{lm\nu\mu} \sum_{l'm'\nu'j} \frac{(i)^{l-l'}}{2j+1} (-1)^{\mu-m} (-1)^{p-\nu'} (-1)^{\nu'-\nu} e^{-i(\delta_l-\delta_{l'})} Y_{l\mu}(\hat{k})^* e_{\nu}^1 f_{\nu lm} Y_{l'\mu'}(\hat{k}) \left[e_{\nu'}^1 f_{\nu' l' m'} \right]^* \langle l' \mu', l - \mu | j 0 \rangle \\ \langle l' m', l - m | j m' - m \rangle \langle 1-p, 1p | j 0 \rangle \langle 1-\nu', 1\nu | j \nu - \nu' \rangle \delta_{\nu' - \nu, m' - m} \end{aligned} \quad (1.62)$$

We can eliminate the sum over μ by representing the spherical harmonics in the form of D-rotation matrices and substituted by the Clebsch-Gordan series $Y_{l\mu}(\hat{k})^* Y_{l'\mu'}(\hat{k}) = \frac{\sqrt{(2l'+1)(2l+1)}}{4\pi} (-1)^{l'+l+j} \langle l' 0, l 0 | j 0 \rangle P_j(\cos\theta)$. Finally, the differential cross-section [23] is expressed as

$$\begin{aligned} \frac{d\sigma}{d\Omega} \propto 32\pi^3 \sum_j \sum_{\substack{l'm'\nu'j \\ l'm'\nu'j}} \frac{\sqrt{(2l'+1)(2l+1)}}{2j+1} (i)^{l-l'} (-1)^{\mu-m} (-1)^{p-\nu'} (-1)^{\nu'-\nu} (-1)^{l'+l+j} e^{-i(\delta_l-\delta_{l'})} \langle l' 0, l 0 | j 0 \rangle \\ \langle l' m', l - m | j m' - m \rangle \langle 1-p, 1p | j 0 \rangle \langle 1-\nu', 1\nu | j \nu - \nu' \rangle e_{\nu}^1 f_{\nu lm} \left[e_{\nu'}^1 f_{\nu' l' m'} \right]^* P_j(\cos\theta) \delta_{\nu' - \nu, m' - m} \end{aligned} \quad (1.63)$$

The general expression of PECD, for a single photon process, given by equation 1.51 and 1.52 allows for only three terms due to the angular momentum condition. The b_j^p coefficients represent four inner sums and are Clebsch-Gordon coefficients which are obtained from the Wigner D-matrix. From the triangle condition, $|j_1 - j_2| < j < j_1 + j_2 \rightarrow 0 < j < 2$ (depicted by figure 1.8), the total angular momentum (j) is restricted to 0,1,2 limiting the number of b_j^p coefficients to three, where p is the polarization, and $P_j(\cos\theta)$ are the associated Legendre polynomial. $I(\theta)$ is the angular distribution

and σ is the total cross-section which is obtained by solving the radial portion of the transition matrix element.

The Clebsch-Gordon coefficients can be expressed as a 3j-symbol matrix which is used to determine the restriction on the Clebsch-Gordan coefficients, $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \langle j_1 m_1, j_2 m_2 | j_3 (-m_3) \rangle$. There are three conditions to remember when dealing with the 3-j symbols:

1. $m_1 + m_2 + m_3 = 0$
2. $|j_1 - j_2| < j < j_1 + j_2$
3. $j_1 + j_2 + j_3 = \text{odd or even integer, if even then } m_1 = m_2 = m_3 = 0$

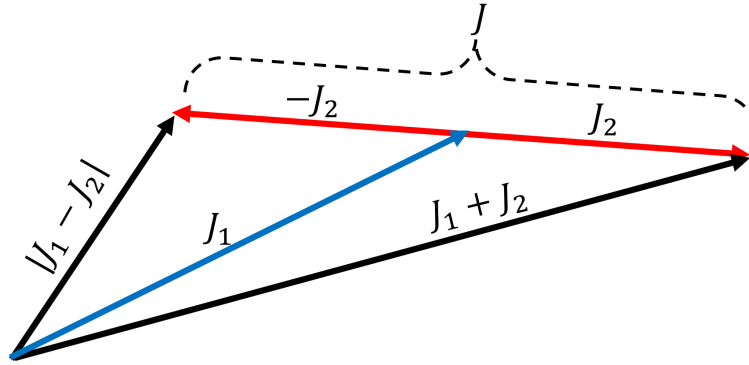


Figure 1.8: **Triangle condition:** Schematic representation of the triangle condition for the Clebsch-Gordan coefficients. J can take any discrete values within the dotted bracket.

For linear polarization $p = 0$, the important term is $\langle 1 - p, 1p | j0 \rangle$ where j cannot be odd due to the third rule $(1 + 1 + j)$, thus j must be even. For linear polarization the angular distribution becomes $I(\theta) = 1 + b_2^{(0)} P_2(\cos\theta)$ for both chiral and achiral molecules [23–25].

For CPL, $p = \pm 1$, the important term is $\langle l'0, l0 | j0 \rangle$ where j can be odd, however the sum $l + l' + j$ must be even. If j is odd, l and l' must be of opposite parity for the coefficient to exist. This restricts the existence of $b_1^{(\pm 1)} P_1(\cos\theta)$ to molecules whose states have indefinite parity, or molecules with the absence of plane symmetry. For chiral molecules the coefficient $b_1^{(+1)} = -b_1^{(-1)}$ which is responsible for the forward-backward photoelectron angular distribution in PECD [23–25].

1.2.2.2 MULTIPHOTON CASE

The concept of PECD can be extended to the multiphoton ionization where the PAD results from n -photon ionization of chiral molecules with CPL. The differential cross-section becomes

$$\frac{d\sigma^{(n)}}{d\Omega} = R_{fi}^{(n)} \frac{n\hbar\omega}{I^n} = \frac{\sigma_{tot}^{(n)}}{4\pi} \sum_{j=0}^{2n} b_j^p P_j(\cos\theta) \quad (1.64)$$

The symmetry properties of the Clebsch-Gordan coefficients for linearly and circularly polarized light are similar to the single photon case. That is, the odd Legendre coefficients change sign when changing the helicity or enantiomer and the even Legendre coefficients remain equal. The difference in the angular distribution measured for left- and right-circularly

polarized light for an enantiomer can be expressed as

$$\begin{aligned} \text{Single-photon} &\rightarrow I_{LCP}(\theta) - I_{RCP}(\theta) = 2_1^{(+1)}(\cos\theta) \\ \text{Multiphoton} &\rightarrow I_{LCP}(\theta) - I_{RCP}(\theta) = \sum_{j=1}^n 2_{2j-1}^{(+1)} P_{2j-1}(\cos\theta) \end{aligned} \quad (1.65)$$

Therefore, for the multiphoton process the difference in the angular distribution contains contributions of Legendre polynomials up to order $(2n - 1)$. For instance, a three-photon ionization will have three coefficients, $b_1^{(+1)}$, $b_3^{(+1)}$, and $b_5^{(+1)}$. All will contribute to the shape of $\Delta I(\theta)$. Depending on the relative size of the odd coefficients the maxima and minima of the function $\Delta I(\theta)$ will be found at various angles θ which can differ from the single-photon case, where the maximum is always at $\theta = 0^\circ$ and $\theta = 180^\circ$ [24].

1.2.3 CHIRAL HIGH HARMONIC GENERATION

Chiral-High Harmonic Generation (cHHG) method [28] use coherent radiation emitted as high-order harmonics of the driving field to differentiate the handedness of the enantiomers. cHHG is an ultrafast all-optical non-resonant detection scheme where the chiral response can be monitored on a sub-femtosecond timescale. In cHHG, the maximum harmonic yield varies with respect to the ellipticity of the driving field and the handedness of the chiral molecule. Figure 1.9 shows the ellipticity at which the harmonic order is maximum for epoxypropane, a chiral molecule, and a xenon, a reference achiral atom. For a pair of enantiomers, the maximum occurs at opposite ellipticity for a similar harmonic order. For example, at the 38th harmonic, the left-handed (right-handed) molecule is maximum for an $\varepsilon = 1$ ($\varepsilon = -1$). The maximum yield of each harmonic order is strongly influenced by the incident ellipticity and depicts a mirroring effect between both enantiomers with respect to the linear polarization ($\varepsilon = 0$).

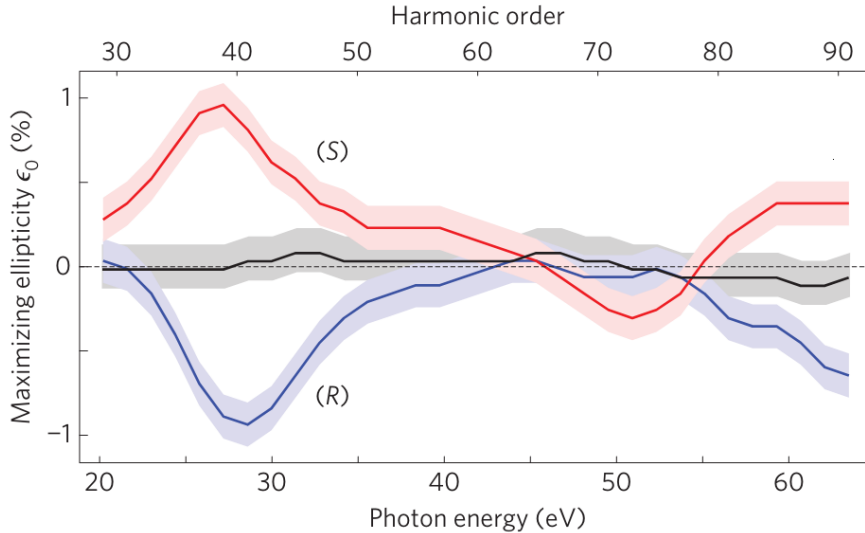


Figure 1.9: **Chiral-high harmonic generation technique** Measured ellipticity dependence of HHG and time-resolved chiral response. For each harmonic order, the corresponding ellipticity dependence is fitted with a Gaussian function, the central position of which we call a maximizing ellipticity $\varepsilon = 0$. Ellipticity as a function of the harmonic order (top axis) and the emission energy (bottom axis). Red and blue traces correspond to enantiomers of epoxypropane (the latter is acquired at 1,850 nm, 3×10^{13} W/cm²). The grey line shows the non-chiral reference (xenon). The experimental errors are the standard deviation and are shown as shaded areas surrounding the solid lines. [28]

For xenon atom, the Harmonic yields exhibit a symmetric Gaussian-like function as a function of ellipticity, with the

maximum for linear polarization ($\varepsilon = 0$). As ellipticity grows, the HHG yield rapidly decreases because the liberated electron gains a lateral drift that intensifies with increasing ellipticity. At higher ellipticity, the electron does not recollide with the parent ion. This results in the suppression of electron-hole recombination, leading to a reduction in the HHG yield. However, the findings indicate that randomly oriented chiral molecules exhibit asymmetrical HHG yields as a function of ellipticity, with the maximum yields localized at a non-zero ellipticity. Therefore, the HHG of a chiral molecule exhibits elliptical dichroism.

The mechanism for cHHG can be explained by the semi-classical three step model [28–30].

1. Ionization of a chiral molecule by strong IR field in the tunneling regime defined by the Keldysh parameter $\gamma < 1$ [31]. For randomly orientated molecules, the laser field will preferentially ionize a subset of them whose molecular axes are aligned with the field.
2. Laser-induced propagation and acceleration of the ionized electron whose trajectory is influenced by the electric and magnetic field of the light. The non-dipole Lorentz force pushes the the liberated electron outside the plane of polarization and acts as a chiral reagent for the recollision dynamics. The maximum energy of the recolliding electron is $3.17U_p$ where U_p is the ponderomotive energy [29, 32].
3. Recombination of the liberated electron with an excited state parent cation due to E1M1 chiral-sensitive excitation from the remnant field during electron propagation in step 2. The excitation pathways for both enantiomers are influenced by their selection rules. The process results in a different emission rate of higher-order harmonics for both enantiomers only for elliptical light.

Chiral high harmonics have poor conversion efficiency due to the ellipticity effect on recollision combined with the need to differentiate different harmonics makes it technically challenging. Therefore, in chapter 6 section 6.2, we show a simpler version of this strong-field method by relying only on the detection of doubly charged ions.

1.2.4 COULOMB EXPLOSION IMAGING

Another efficient gas phase chiroptical technique is Coulomb Explosion Imaging (CEI) [33, 34]. In CEI, the molecule is rapidly ionized by an intense laser pulse and subsequently undergoes fragmentation due to coulomb repulsion. using a Time-Of-Flight (TOF) the time of arrival and position of each fragment is detected. From the momentum of each fragment recorded, the molecular structure is reconstructed. For chiral molecules, the momentum vectors of the fragments are enantio-sensitive as they are equal in magnitude but opposite in sign due to the non-symmetric behaviour of their coulomb potential. The distinction between handedness is expressed in terms of the normalized triple product of the momentum vectors [34].

$$\cos\theta = \frac{\vec{p}_x \cdot (\vec{p}_y \times \vec{p}_z)}{|\vec{p}_x| \cdot |\vec{p}_y \times \vec{p}_z|} \quad (1.66)$$

This pseudoscalar is constructed from coulomb explosion data where all three independent momenta vectors can be expressed in terms of the heaviest fragments of the sample, denoted by (x, y, z) [33, 34]. The momentum gained in the explosion can be retrieved by assuming classical trajectories in the spectrometer. At least three linearly independent vectors are required to differentiate the molecular handedness. The quantity is referred to as $\cos\theta$ because it represents

the angle between $\vec{p}_x$ and the normal vector of the $\vec{p}_y - \vec{p}_z$ plane, see inset in figure 1.10. Additionally, the figure depicts clear chiral discrimination of a racemic mixture of CHBrClF by plotting the ion counts as a function of the chiral parameter ($\cos\theta$). The discrimination is angle-dependent showing two equally populated distinct peaks mirroring each other with respect to the center axis.

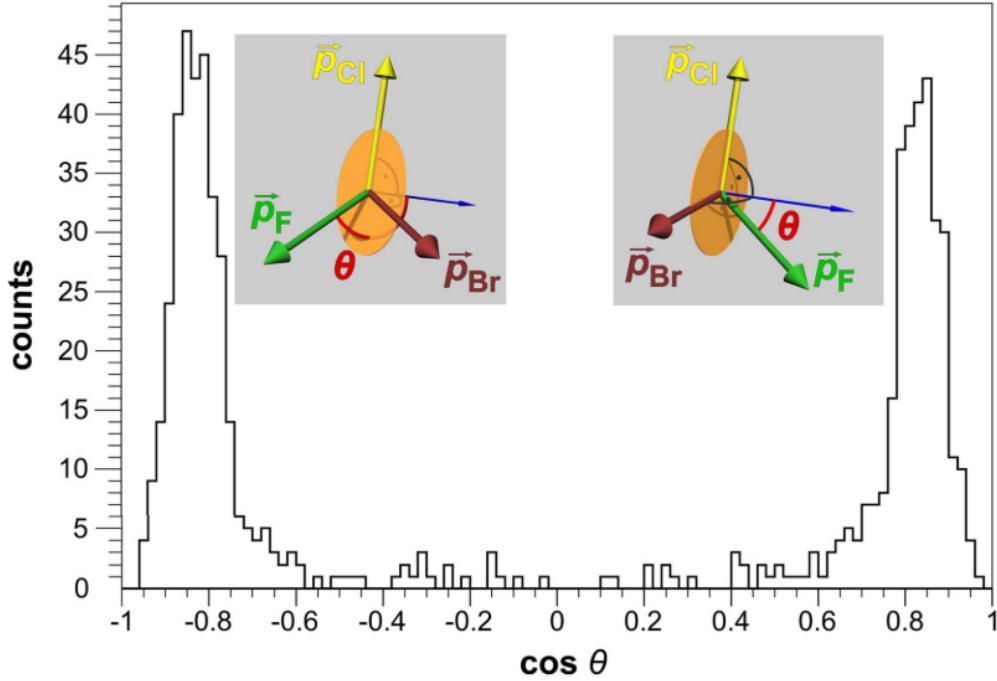


Figure 1.10: **Chiral discrimination of CHBrClF:** A histogram representation of the cosine of the chiral angle θ shows clear identification of the left- and right-handed enantiomers of a racemic mixture of CHBrClF. The peak at the negative (positive) values of $\cos\theta$ corresponds to the S-enantiomer (R-enantiomer). A clear mirroring effect is observed [33].

This technique can identify both enantiomers in a racemic mixture and imaging the absolute configuration of a single chiral molecule. However, it cannot be extended to complicated molecules because (i) the detection efficiency decreases exponentially for the increasing number of fragments and (ii) reconstruction of the molecular structure may not be possible from the kinematic properties of the fragments.

OPTICAL PROBE AND DETECTION SCHEME

The second chapter includes both the theoretical and experimental aspects of the optical probe and the detection schemes. The section on the optical probe describes the fundamentals of femtosecond pulses, their physical properties, and their generation process in a Ti:Sapphire laser system. This discussion will be extended to include structured light such as LG beams. Additionally, a distinction between symmetric and asymmetric LG beams will be presented both theoretically and experimentally. The second section on the detection scheme will explore the details of two experimental setups: i) a transmission setup used to measure the absorption of light for both liquid and solid samples and ii) a TOFMS used to detect the ions and fragments produced during the interaction.

2.1 OPTICAL PROBE AND BEAM REPRESENTATION

2.1.1 PARAXIAL HELMHOLTZ WAVE EQUATION

A paraxial beam is a concept used in optics and is particularly relevant in the field of laser physics. The term “paraxial” refers to light rays that make a small angle with the optical axis, and lie close to the axis throughout the system. This approximation leads to a simplification of the wave equation, making it more manageable and facilitating a more direct analysis of optical systems.

The wave equation governs all electromagnetic radiation. It is obtained from Maxwell’s equation and for free-space

propagation of light we get

$$\nabla^2 \mathbf{E}(r, t) = \varepsilon_0 \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{E}(r, t) \quad (2.1)$$

For an electromagnetic wave, the time variation of the field is sinusoidal of the form $\mathbf{E}(r, t) = \mathbf{E}(r) e^{-i\omega t}$ where ω is the angular frequency and $\mathbf{E}(r)$ is the complex amplitude of the wave. The substitution of this electromagnetic wave into the wave equation results in the time-dependent reduced wave equation (Helmholtz equation)

$$\nabla^2 \mathbf{E}(r) + k^2 \mathbf{E}(r) = 0 \quad (2.2)$$

where $c = 1/\sqrt{\varepsilon_0 \mu_0}$ is the speed of light and $k = \omega/c = 2\pi/\lambda$ is the optical wave number related to the optical wavelength. For optical wave propagation, we can further reduce the Helmholtz equation to the paraxial wave equation by using the paraxial approximation. It is based on the notion that the propagation distance for an optical wave along the z -axis is much greater than the transverse spreading of the wave, $\mathbf{E}(r, t) = \tilde{\mathbf{E}}(r, z) e^{i(k_z z - \omega t)}$ where k_z is the wave vector in the z -propagation and $\tilde{\mathbf{E}}(r, z)$ is the transverse spatial profile of the beam where $r = \sqrt{x^2 + y^2}$.

To understand the paraxial approximation concept, consider two points in space along the propagation direction z , $\mathbf{S} = 0$ as the origin and $\mathbf{R} = (\mathbf{r}, z)$ are the transverse spreading at position $\mathbf{r}$ from the point z as shown in figure 2.1. This creates a right-angle triangle where

$$|\mathbf{R} - \mathbf{S}| = \sqrt{(z^2 + \mathbf{r}^2)} = z \sqrt{\left(1 + \frac{\mathbf{r}^2}{z^2}\right)} \quad (2.3)$$

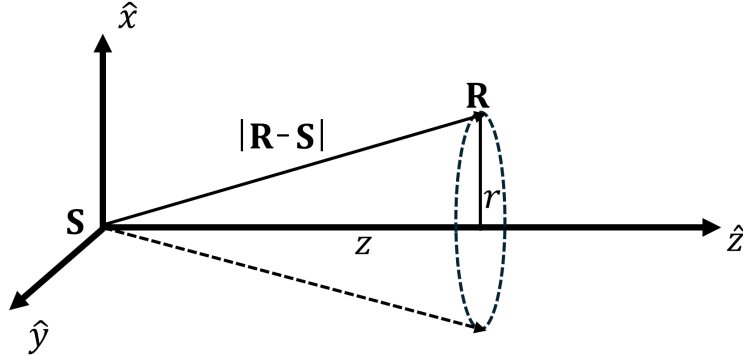


Figure 2.1: **Paraxial approximation:** Schematic of the transverse spread in (x, y) compared to the propagation distance z .

By assuming the transverse distance to be much smaller than the longitudinal propagation distance ($\mathbf{r} \ll z$). Therefore, we can Taylor expand the above equation 2.3 to obtain $|\mathbf{R} - \mathbf{S}| = \left(z + \frac{\mathbf{r}^2}{2z} + \dots\right)$. The first two terms are considered the paraxial approximation. As a consequence, $\left|\frac{\partial^2 \tilde{\mathbf{E}}(r, z)}{\partial z^2}\right| \ll \left|2k \frac{\partial \tilde{\mathbf{E}}(r, z)}{\partial z}\right|$ [35]. This inequality describes the diffraction effects of the optical wave, $\tilde{\mathbf{E}}(r, z)$, which changes slowly with respect to propagation distance z and also with respect to transverse variations due to the finite size of the beam. Therefore, the paraxial wave equation is

$$\nabla_T^2 \tilde{\mathbf{E}}(r, z) + 2ik \frac{\partial}{\partial z} \tilde{\mathbf{E}}(r, z) = 0 \quad (2.4)$$

where $\nabla_T^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$ is the tranverse Laplacian.

2.1.2 GAUSSIAN BEAM

To construct a beam with finite transverse extent into the x - y plane and propagating into the positive z -direction. Consider a superposition of plane waves, the Fourier transform of the propagating field is

$$\mathbf{E}(r, z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{\mathbf{E}}(k_x, k_y) e^{-i(k_x x + k_y y + k_z z)} dk_x dk_y \quad (2.5)$$

where $\tilde{\mathbf{E}}(k_x, k_y)$ is the transverse amplitude for the wave in momentum space. Apply the paraxial approximation in momentum space with respect to the wave vector, $k_z = \sqrt{k^2 - k_x^2 - k_y^2} = k \sqrt{1 - \frac{k_x^2 + k_y^2}{k^2}}$. By assuming the transverse distance to be much smaller than the longitudinal propagation distance ($k_x, k_y \ll k$), we can Taylor expand the above equation.

$$k_z = k \left(1 - \frac{k_x^2 + k_y^2}{2k^2} \right) + \dots \quad (2.6)$$

Substituting this approximation in equation 2.5.

$$\mathbf{E}(r, z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{\mathbf{E}}(k_x, k_y) e^{i \left(\frac{k_x^2 + k_y^2}{2k} \right) z} e^{-ik_x x} e^{-ik_y y} dk_x dk_y e^{-ikz} \quad (2.7)$$

This function is slowly varying in the transverse direction and satisfies the paraxial wave equation. Using a two-dimensional Gaussian for the transverse amplitude distribution in momentum space, $\tilde{\mathbf{E}}(k_x, k_y) = E \exp \left(- \left(\frac{k_x^2 + k_y^2}{2k_T^2} \right) \right)$, also gives a Gaussian in real space (Fourier transform of Gaussian is Gaussian).

$$\tilde{\mathbf{E}}(r, z) = E \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[i \left(\frac{k_x^2 + k_y^2}{2k} \right) (z + iz_R) \right] e^{ik_x x} e^{ik_y y} dk_x dk_y \quad (2.8)$$

where we can extract the Rayleigh range, $z_R = k/k_T^2 = \frac{\pi w_0^2 n}{\lambda}$ [35]. Carrying out the integration we obtain

$$\tilde{\mathbf{E}}(r, z) = \frac{iE}{z + iz_R} \exp \left[-i \frac{k_0}{2} \left(\frac{x^2 + y^2}{z + iz_R} \right) \right] = \frac{E}{q(z)} \exp \left[-i \frac{k_0}{2} \left(\frac{x^2 + y^2}{q(z)} \right) \right] \quad (2.9)$$

this is a shifted paraboloidal wave and is a solution to the paraxial Helmholtz equation because we know that the paraboloidal wave $\frac{A}{z} \exp \left[-ik \frac{r^2}{2z} \right]$ is a solution to the paraxial Helmholtz equation. A paraboloidal wave is the paraxial approximation of the spherical wave when x and y are much smaller than z . Here, we can define the q -parameter as $q(z) = z + iz_R$, a complex beam parameter which describes the Gaussian beam intensity with distance r from the optic axis and the beam curvature of the wavefront which is spherical near the axis. Decomposing the inverse into real and imaginary parts

$$\frac{1}{q(z)} = \frac{1}{z + iz_R} = \frac{z}{z^2 + z_R^2} - i \frac{z_R}{z^2 + z_R^2} = \frac{1}{R(z)} - i \frac{\lambda}{\pi n w^2(z)} \quad (2.10)$$

Substituting into our electric field 2.9 and expressing a complex number as an amplitude times a phase $\frac{1}{z+iz_R} = \left| \frac{z-iz_R}{z^2+z_R^2} \right| e^{i\psi(z)} = \frac{1}{\sqrt{z^2+z_R^2}} e^{i\psi(z)} = \frac{w_0}{z_R w(z)} e^{i\psi(z)}$ we obtain our lowest-order Gaussian beam [36].

$$\mathbf{E}(r, z) = E_0 \frac{w_0}{w(z)} \exp \left[-\frac{r^2}{w^2(z)} \right] \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i\psi(z) \right] \quad (2.11)$$

where the electric amplitude $E_0 = E/z_R$, the wavefront curvature is described by $R(z) = z \left[1 + \left(\frac{\pi w_0^2}{\lambda z} \right)^2 \right]$ and the evolving beam waist is given by this hyperbolic relation $w(z) = w_0 \sqrt{1 + \left(\frac{\lambda z}{\pi w_0^2} \right)^2}$. $\psi(z) = \arctan \left(\frac{z}{z_R} \right)$ represents the complex phase shift associated with the propagation of the light and represents the Gouy phase.

2.1.3 HERMITE-GAUSSIAN MODES

The Gaussian beam is not the only solution to the paraxial Helmholtz wave equation. There are sets of solutions called modes that exhibit non-Gaussian intensities but with the same wavefront of the Gaussian beam. We start with the Gaussian beam complex envelope derived previously

$$\tilde{\mathbf{E}}(r, z) = \frac{E}{q(z)} \exp \left[-i \frac{k_0}{2} \left(\frac{x^2 + y^2}{q(z)} \right) \right] \quad (2.12)$$

Now we consider a Gaussian wave whose complex envelope is modulated in the x and y . For a system with rectangular geometry, such as a laser cavity, we can try this solution with the form

$$\tilde{\mathbf{E}}(r, z) = g \left(\frac{x}{w(z)} \right) \cdot h \left(\frac{y}{w(z)} \right) \cdot \frac{E}{q(z)} \exp \left[-i \frac{k_0}{2} \left(\frac{x^2 + y^2}{q(z)} \right) \right] \quad (2.13)$$

Here g is a function of x and z , and h is a function of y and z . Substituting this ansatz in the paraxial equation 2.4 and after a considerable amount of substitution and simplification we obtain a differential equation for g , a function of $u = x/w(z)$, and h , a function of $v = y/w(z)$, of the form

$$\frac{d^2}{du^2} g(u) - 2u \frac{d}{du} g(u) + 2mg(u) = 0 \quad \frac{d^2}{dv^2} h(v) - 2v \frac{d}{dv} h(v) + 2nh(v) = 0 \quad (2.14)$$

These are Hermite differential equations, their solutions are Hermite polynomials $H_m(u)$ of order m and $H_n(v)$ of order n . The differential equations are satisfied when the modulated function is described by these Hermite polynomials, $g \left(\frac{x}{w(z)} \right) = H_m \left(\sqrt{2} \frac{x}{w(z)} \right)$ and $h \left(\frac{y}{w(z)} \right) = H_n \left(\sqrt{2} \frac{y}{w(z)} \right)$. Therefore, the higher order Gaussian modes are given by [36]

$$\mathbf{E}_{m,n}(r, z) = E_0 \left(\frac{w_0}{w(z)} \right) H_m \left(\sqrt{2} \frac{x}{w(z)} \right) H_n \left(\sqrt{2} \frac{y}{w(z)} \right) \exp \left[-\frac{r^2}{w^2(z)} \right] \times \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i(m+n+1)\psi(z) \right] \quad (2.15)$$

where m and n are the mode numbers. Figure 2.2 depicts the transverse intensity distribution for several orders of Hermite-Gaussian beams and illustrates the dependence of the intensity on $u = \sqrt{2}x/w(z)$ and $v = \sqrt{2}y/w(z)$ for different mode numbers. The higher modes have larger widths, due to the beam waist factor and the width of the beam is proportional to $w(z)$ [36]. The only circularly symmetric order is the TEM_{00} solution which is the lowest

Hermite-Gaussian mode given by equation 2.11.

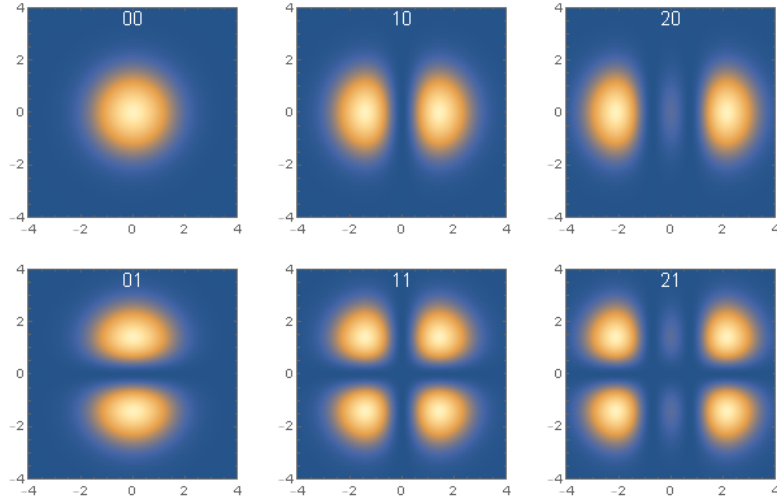


Figure 2.2: **Hermite-Gaussian modes** for various order (m,n).

2.1.4 SYMMETRIC AND ASYMMETRIC LAGUERRE-GAUSSIAN MODES

For a system with cylindrical geometry, the modulation of the complex envelope can generate different mode shapes than conventional Hermite-Gaussian modes. To accommodate for this change of geometry, we perform a change of coordinate system, from rectangular geometry to cylindrical geometry, and express the Cartesian paraxial Helmholtz wave equation 2.4 in terms of cylindrical coordinates.

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) \tilde{\mathbf{E}}(r, \phi, z) + 2ik \frac{\partial}{\partial z} \tilde{\mathbf{E}}(r, \phi, z) = 0 \quad (2.16)$$

Using separation of variable we can easily isolate the contribution of the polar angle ϕ given by $\frac{\partial^2}{\partial \phi^2} \Phi + l^2 \Phi = 0$ which has a solution of the form $\Phi(\phi) = \exp[il\phi]$. Therefore, the solution of the paraxial Helmholtz equation must now allow variation of the electric field as a function of the polar angle ϕ . From our above derivation we can assume a first-order paraboloidal ansatz [36] as

$$\tilde{\mathbf{E}}(r, \phi, z) = g\left(\frac{r}{w(z)}\right) \cdot \frac{E}{q(z)} \exp\left[-i \frac{k_0}{2} \left(\frac{x^2 + y^2}{q(z)}\right) - il\phi\right] \quad (2.17)$$

where the modulation is given by a radial function g . After considerable substitution and simplification we obtain a paraxial equation that is reduced to a differential equation dependent on r and z .

$$g''\left(\frac{r}{w(z)}\right) + \left(\frac{w(z)}{r} - \frac{4r}{w(z)}\right) g'\left(\frac{r}{w(z)}\right) - \left(\frac{w^2(z)l^2}{r^2} - \alpha\right) g\left(\frac{r}{w(z)}\right) = 0 \quad (2.18)$$

Here we defined $\alpha = w^2(z) \left(\frac{2ik}{q(z)}\right)$ and $q(z)$ is the same q -parameter as for a Gaussian beam. The solution obtained has the shape $g\left(\frac{r}{w(z)}\right) = \left(\frac{\sqrt{2}r}{w(z)}\right)^{|l|} L_p^{|l|}\left(\frac{2r^2}{w^2(z)}\right)$ where $L_p^{|l|}(x)$ is the Laguerre polynomial, p and l are the radial and angular

mode numbers and are solution to the Laguerre differential equation.

$$x \frac{d^2}{dx^2} L_p^{(|l|)}(x) + (|l|+1-x) \frac{d}{dx} L_p^{(|l|)}(x) + p L_p^{(|l|)}(x) = 0 \quad (2.19)$$

with $p = -\left(\frac{|l|}{2} - \frac{\alpha}{8}\right) \rightarrow \alpha = 8p + 4|l|$. Collecting all terms we obtain the LG modes given by

$$\mathbf{E}_{p,l}(r, \phi, z) = E_0 \frac{w_0}{w(z)} \left(\frac{\sqrt{2}r}{w(z)} \right)^{|l|} L_p^{(|l|)} \left(\frac{2r^2}{w^2(z)} \right) \exp \left[-\frac{r^2}{w^2(z)} \right] \exp[-il\phi] \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i(|l|+2p+1)\psi(z) \right] \quad (2.20)$$

These beam profiles are circularly symmetric and are a good approximation of the helical light created by an Spatial Light Modulator (SLM) or q-plate, see section 2.1.5 for more details. Experimentally, we generated our OAM beams using q-plates with the radial index $p = 0$, $L_p^{(|l|)} \left(\frac{2r^2}{w^2(z)} \right) = 1$, but with increasing azimuthal index, $l = 0, 1, 2, 3$. Therefore, the electric field used to mimic our experimentally generated symmetrical helical light is given in equation 2.21. Figure 2.3 depicts the transverse intensity distribution of symmetric LG beams. The top row corresponds to the beam profile with increased azimuthal index l and no radial index (equation 2.21), which were used experimentally, and the lower row displays the beam profile for increasing radial and azimuthal index (equation 2.20). The increase in the topological charge l impacts the size of the null intensity relative to the overall size of the annular beam.

$$\mathbf{E}_{0,l}(r, \phi, z) = E_0 \frac{w_0}{w(z)} \left(\frac{\sqrt{2}r}{w(z)} \right)^{|l|} \exp \left[-\frac{r^2}{w^2(z)} \right] \exp[-il\phi] \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i(|l|+1)\psi(z) \right] \quad (2.21)$$

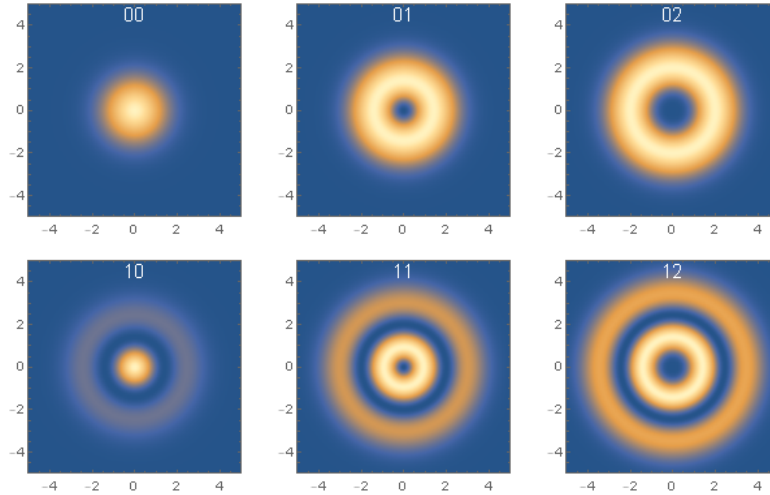


Figure 2.3: **Symmetric Laguerre-Gaussian modes** for various order (p,l) . $\mathbf{E}_{0,l}(r, \phi, 0)$ represents only the top row which are the beam profiles used experimentally.

For the purpose of our research, we must also extend these symmetric LG modes to asymmetrical LG modes. By introducing an asymmetrical parameter δ , the null intensity can be controlled and displaced to create asymmetrical transverse beam profiles. To do so, rewrite the polar angle ϕ of the LG modes to Cartesian coordinate, $r^{|l|} \exp[\pm i|l|\phi] = (x \pm iy)^{|l|}$, where $r = \sqrt{x^2 + y^2}$ and $\phi = \tan^{-1}(y/x)$.

$$r^{|l|} e^{\pm i|l|\phi} = (x^2 + y^2)^{\frac{|l|}{2}} \exp \left[\pm i|l| \tan^{-1} \left(\frac{y}{x} \right) \right] \quad (2.22)$$

$$r^{|l|} e^{\pm i|l|\phi} = (x^2 + y^2)^{\frac{|l|}{2}} \exp \left[-\frac{|l|}{2} \log \left(1 \mp \frac{iy}{x} \right) \right] \exp \left[\frac{|l|}{2} \log \left(1 \pm \frac{iy}{x} \right) \right] \quad (2.23)$$

$$r^{|l|} e^{\pm i|l|\phi} = (x^2 + y^2)^{\frac{|l|}{2}} \left[\frac{(1 \pm \frac{iy}{x})}{(1 \mp \frac{iy}{x})} \right]^{\frac{|l|}{2}} = [(x \pm iy)]^{|l|} \quad (2.24)$$

The handedness of the helical phase is by the $\pm$. Thus, the transverse-electric LG ($p = 0, l$) mode becomes

$$\mathbf{E}_{0,l}(x, y, z) = E_0 \frac{w_0}{w(z)} \left(\frac{\sqrt{2}}{w(z)} \right)^{|l|} [(x \pm iy)]^{|l|} \exp \left[-\frac{r^2}{w^2(z)} \right] \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i\psi(z) \right] \quad (2.25)$$

Now, we can introduce the asymmetrical parameter to displace the singularity and generate asymmetric Laguerre-Gaussian (aLG) beams. Let the beam singularity be shifted by $x_0 = \zeta\delta$ along the x-coordinate and $y_0 = \eta\delta$ along the y-coordinate, where δ is the displacement of singularity that can take negative and positive values and η, ζ are used to displace the singularity anywhere in the x-y plane and are values between 0 and 1. If we consider the singularity arbitrarily in the first quadrant, $[(x + x_0) \pm i(y + y_0)]^{|l|} = [(x \pm i\eta\delta) \pm i(y \mp i\zeta\delta)]^{|l|}$, then the aLG beam in the Cartesian coordinates is

$$\mathbf{E}_{0,l}(x, y, z) = E_0 \frac{w_0}{w(z)} \left(\frac{\sqrt{2}}{w(z)} \right)^{|l|} [(x \pm i\eta\delta) \pm i(y \mp i\zeta\delta)]^{|l|} \exp \left[-\frac{r^2}{w^2(z)} \right] \times \exp \left[ikz - ik \left(\frac{r^2}{2R(z)} \right) + i\psi(z) \right] \quad (2.26)$$

This only introduces an asymmetry in the angular portion of the LG mode. One can also introduce the asymmetry in the radial portion of the mode by inserting the asymmetrical parameter in the Laguerre polynomial, however, this will only be useful when dealing with ($p \neq 0, l$) modes. When the asymmetrical parameter is set to zero ($\delta = 0$) we obtain the symmetric LG beam and when the angular index is set to zero ($l = 0$) the beam reverts back to the lowest order Hermite-Gaussian mode. The left- and right-handed asymmetrical helical light for arbitrary polarization at the focal spot is represented by

$$\begin{aligned} E_x(x, y, 0) &= \alpha u_{(0,l)}^{\pm}(x, y, 0) \\ E_y(x, y, 0) &= \pm i\beta u_{(0,l)}^{\pm}(x, y, 0) \end{aligned} \quad (2.27)$$

where α and β are the polarization factors and are normalized such that $|\alpha|^2 + |\beta|^2 = 1$ and the transverse profile is defined by

$$u_{(0,l)}^{\pm}(x, y, 0) = E_0 \left(\frac{\sqrt{2}}{w_0} \right)^{|l|} [(x \pm i\eta\delta) \pm i(y \mp i\zeta\delta)]^{|l|} \exp \left[-\frac{r^2}{w_0^2} \right] \quad (2.28)$$

As we displace our singularity, the beam does not shift and the average cross-sectional power remains unchanged.

This above beam mimics the experimental transverse beam profile behaviour at the focal spot. For $l=1$, the normalized amplitude was obtained by integrating the intensity over all space ($-\infty$ to $+\infty$) and is given by $E_0 = \sqrt{\frac{2P_0}{\pi w_0^2}} \frac{1}{\sqrt{(\alpha^2 + \beta^2)(2(\delta/w_0)^2(\zeta^2 + \eta^2) + 1)}}$, where P_0 is the total power of the beam.

For tight focusing the longitudinal component of the beam can no longer be ignored. The longitudinal component of the aLG beam is chosen to ensure that the divergence of the total field is zero [37].

$$\nabla \cdot \mathbf{E}(x, y, z) = 0 \rightarrow \alpha \frac{\partial}{\partial x} E_x \pm i\beta \frac{\partial}{\partial y} E_y = -\frac{\partial}{\partial z} E_z \quad (2.29)$$

$$E_z = \frac{i}{k} \left[\alpha \frac{\partial}{\partial x} E_x \pm i\beta \frac{\partial}{\partial y} E_y \right] \quad (2.30)$$

$$E_z(x, y, z) = if \left[(\alpha \pm i\beta) \frac{|l|w_0 [(x \pm i\eta\delta) \pm i(y \mp i\zeta\delta)]}{(x \pm i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_{(0,l)}^\pm(x, y, 0) - \frac{2}{w_0} (\alpha x + \beta y) u_{(0,l)}^\pm(x, y, 0) \right] e^{ikz} \quad (2.31)$$

where $u_{(0,l)}^\pm(x, y, 0)$ is the transverse-electric aLG beam given by equation 2.28. Moreover, the magnetic field can be obtain from $\mathbf{B}(x, y, z) = \hat{z} \times \mathbf{E}(x, y, z)$ and recalling the amplitude to be $B_0 = E_0/c$.

$$\begin{aligned} B_x(x, y, 0) &= \mp i\beta u_{(0,l)}^\pm(x, y, 0) \\ B_y(x, y, 0) &= \alpha u_{(0,l)}^\pm(x, y, 0) \\ B_z(x, y, z) &= if \frac{k}{\omega} \left[(\alpha \pm i\beta) \frac{|l|w_0 [(x \pm i\eta\delta) \mp i(y \mp i\zeta\delta)]}{(x \pm i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_{(0,l)}^\pm(x, y, 0) - \frac{2}{w_0} (\alpha y - \beta x) u_{(0,l)}^\pm(x, y, 0) \right] e^{ikz} \end{aligned} \quad (2.32)$$

It may also be useful to express the aLG beam in cylindrical coordinates for symmetry properties. We first begin with the aLG beam in Cartesian coordinates and group the translation terms ($x_0 = \zeta\delta, y_0 = \eta\delta$) together and the (x, y) coordinates together.

$$u_{(0,l)}^\pm(x, y, 0) = E_0 \left(\frac{\sqrt{2}}{w_0} \right)^{|l|} L_p^{|l|} \left(\frac{2r^2}{w_0^2} \right) [(x \pm iy) + \delta(\zeta \pm i\eta)]^{|l|} \exp \left[-\frac{r^2}{w_0^2} \right] \quad (2.33)$$

Using our above identity, $\text{rexp}(\pm i\phi) = (x \pm iy)$, to convert from cylindrical to Cartesian coordinates. We can extend this identity to the translation terms we can write the translation values (asymmetrical parameter) as $R_\delta \exp(\pm i\theta) = (\zeta \pm i\eta)$ where $R_\delta = \sqrt{\zeta^2 + \eta^2}$ and $\theta = \tan^{-1}(\eta/\zeta)$. Finally, the asymmetrical LG beam in cylindrical coordinates has the form.

$$u_{(0,l)}^\pm(r, \phi, 0) = E_0 \left[\frac{\sqrt{2}}{w_0} \left(r e^{\pm i\phi} + \delta R e^{\pm i\theta} \right) \right]^{|l|} L_p^{|l|} \left(\frac{2r^2}{w_0^2} \right) \exp \left[-\frac{r^2}{w_0^2} \right] \quad (2.34)$$

The signs in front of the ϕ represent the handedness of the OAM value while the sign in front of θ represents the direction of the singularity displacement (positive to negative quadrant or vice versa). Figure 2.4 depicts the transverse intensity profile for an asymmetrical LG mode. The first row mimics our experimental beams where the asymmetry is introduced in the angular portion of the LG beam since the radial index is set to zero, while the second row expresses the asymmetry in both the angular and radial portion of the LG beam.

Figure 2.5 a) shows the phase profile of a Gaussian and a symmetric LG beam. The wavefront for the Gaussian beam is in phase, however, with the presence of a helical phase there is a 2π phase change of the wavefront on any closed path around the propagation axis. For large topological charge, one round trip around the phase surface leads to the

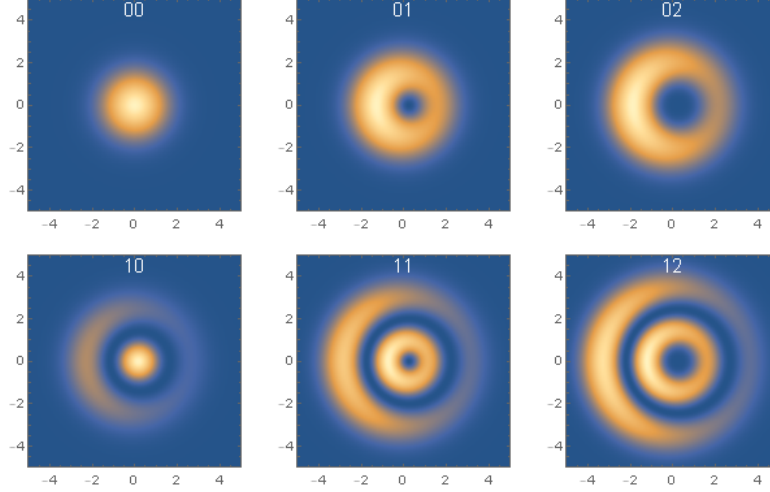


Figure 2.4: **Asymmetric Laguerre-Gaussian modes** for various order of (p, l) . $\mathbf{E}_{0,l}(r, \phi, 0)$ represents only the top row which are the beam profiles used experimentally

next coil with a helical pitch of $l\lambda$, where λ is the wavelength of light and l is the topological charge [38]. Therefore, as the azimuthal index increases, the number of intertwined rotations is increased. The Gaussian beam propagates as a series of planar wavefronts while the wavefront of the symmetric LG beam rotates about the center axis creating a corkscrew pattern, see figure 2.5 b). Consequently, the energy density from the Poynting vector creates a spiral about the center axis of the beam where the maximum intensity is located off-axis and spreads over a larger area. Moreover, the handedness of the corkscrew is determined by the sign of the azimuthal index, with a positive (negative) topological charge l having a clockwise (counter-clockwise) rotating wavefront [38].

For aLG beams, the chiral nature of the wavefront is asymmetric due to the shift of the singularity, see figure 2.5 c). Additionally, the off-axis maximum intensity is increased compared to the symmetric case when the beam power remains identical, see figure 2.5 d). Therefore, the two basic elements that define a chiral probe, the helical pitch and the field strength, can be controlled using asymmetrical helical light and directly influence the chiral interaction. The topological charge controls the handedness and the helical pitch while the displacement of singularity increases the peak field strength.

2.1.5 GENERATING STRUCTURED LIGHT

There are many different ways to generate optical OAM beams using i) a Spiral Phase Plate (SPP), a transparent piece of glass with increasing thickness as a function of azimuthal angle (0 to 2π). ii) Diffraction grating with fork hologram in which an incident Gaussian beam encounters a diffraction grating with a pitch-fork pattern results in several diffraction orders. Each transmitted order carries additional phases, which cause alterations in their wavefront. The Oam value is determined by the dislocation at the center of the grating. iii) Q-plate technique, based on spin-orbit coupling when propagating through a liquid crystal phase plate. The OAM sign is controlled by the incident polarization. iv) Liquid crystal SLM, essentially a hybrid technique which allows full spatial control over the phase either in transmission or reflective geometry. v) Cylindrical mode converters, that convert Hermite-Gaussian beams to LG beams by introducing a phase between the horizontal and vertical polarization by using cylindrical lenses. The section below will concentrate on SPP and q-plates.

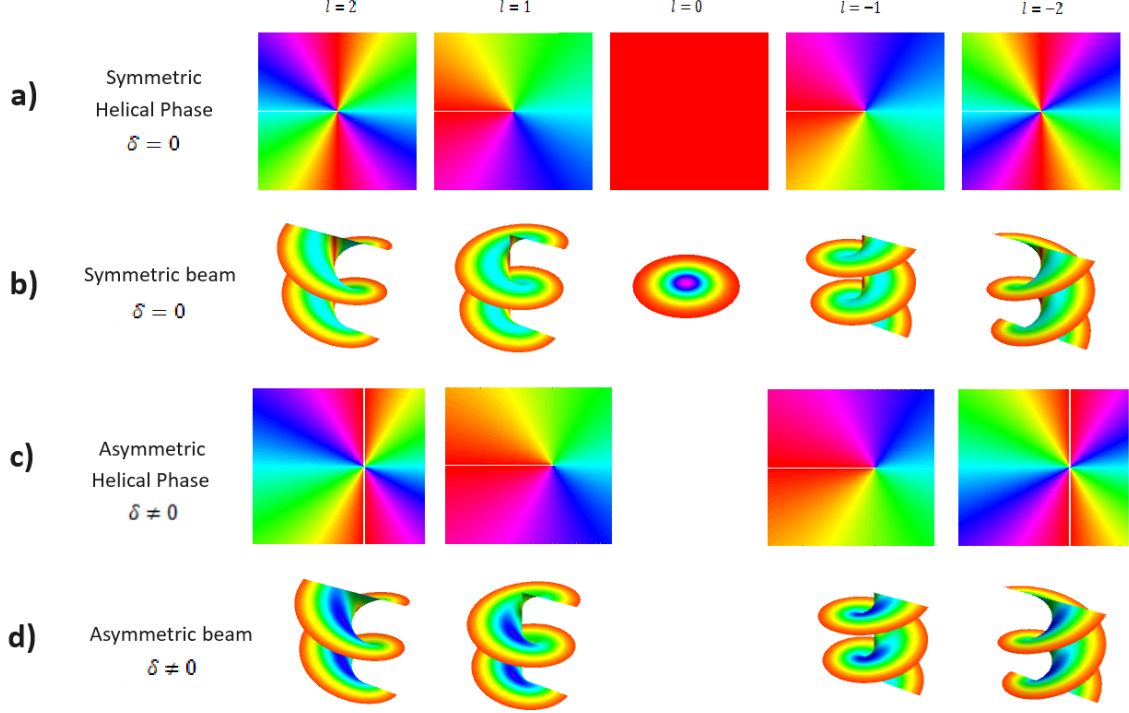


Figure 2.5: **Beam propagation:** **a)** **(c)**) display the phase profile for $l = 0, \pm 1, \pm 2$ for a Gaussian and symmetric (asymmetric) LG beam. **b)** **(d)**) depicts the propagation and intensity profile for symmetrical (asymmetrical) beams.

2.1.5.1 SPIRAL PHASE PLATE

SPP is a transparent plate of refractive index n , whose thickness increases proportionally to the azimuthal angle ϕ around a center point of the plate.

$$h = h_0 + \frac{\phi}{2\pi} h_s \quad (2.35)$$

where h_0 is the base height of the optic and h_s is the step size height increase [39]. When an incident beam, with a planar wavefront, transmits through the SPP, the helical surface imprint a vortex charge of $q = \frac{h_s(n-n_0)}{\lambda}$ resulting in a rotating wavefront illustrated by figure 2.6. A detailed calculation of the inner working of the SPP would necessitate the use of vector diffraction theory. Nonetheless, when dealing with beams of minimal divergence and with a small step height, we stay within the paraxial domain. In this context, the plate's function can be viewed as solely influencing the phase.

When light propagates through a medium of thickness h_0 with an index of refraction n (assuming a homogeneous distribution of the refractive index) it acquires a phase delay $\theta(\omega) = \frac{\omega}{c} \text{OPL}$ compared to free-space propagation, given by $\mathbf{E}(\mathbf{r}, z; t) = E_0(\mathbf{r})e^{i(kz - \omega t)}e^{-i\theta(\omega, z)}$. This additional phase is the result of frequencies having different OPL than in free space, then $\text{OPL} = \int_0^{h_0} n(s)ds = nh_0$ [36]. Then the light transmitted through the medium will gain an extra phase term compared to the incident light.

$$T = \frac{E_0 e^{i(kz - \omega t)} e^{-i\frac{\omega}{c}(nh_0)}}{E_0 e^{i(kz - \omega t)}} = e^{i\frac{\omega}{c}(nh_0)} \quad (2.36)$$

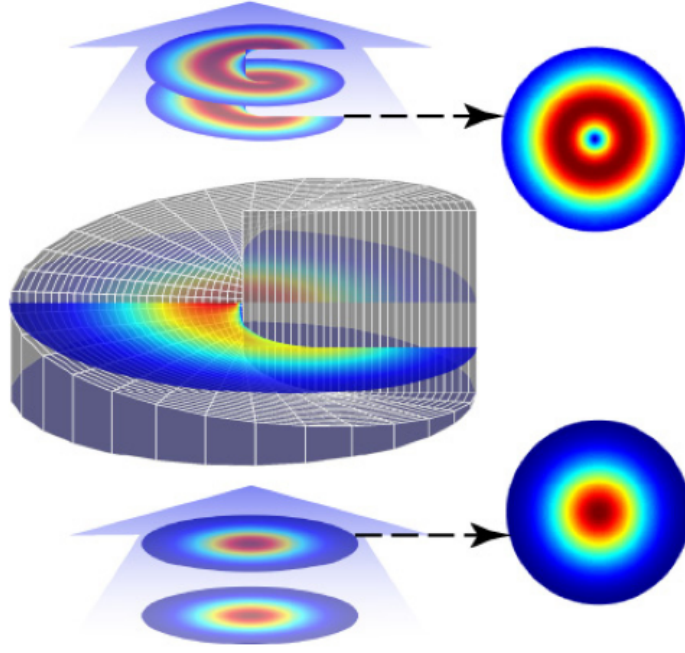


Figure 2.6: **Spiral phase plate** converts an Gaussian beam ($l = 0$) into a symmetric LG beam ($l = 1$). Transverse profiles are shown on the right, where the dark red (dark blue) represents the maximum (minimum) intensity values [40].

Now, instead of a rectangular medium consider the light transmitting through an SPP with thickness h and with the same index of refraction n . If the incident beam is described by the complex amplitude $u(x, y)$, then when light propagates through the variable thickness of the medium, a portion of the wavefront of light will travel through n_0 and the other through n . The resulting light will have a rotating wavefront and carry OAM per photon equal to $q\hbar$.

$$T = \frac{u(x, y, z; t)e^{-i\frac{\omega}{c}nh}}{u(x, y, z; t)} = e^{-i\frac{\omega}{c}nh_0}e^{-i\frac{h_s}{\lambda}(n-n_0)\phi} \quad (2.37)$$

Therefore, the configuration of the SPP yields an azimuthal-dependent optical phase delay.

$$\theta(\phi, \lambda) = \frac{2\pi}{\lambda} \left(\frac{(n - n_0)h_s\phi}{2\pi} + nh_0 \right) \quad (2.38)$$

where the extra phase term results from the varying thickness of the SPP. The vortex charge that such a device imprints on an optical beam can be tuned by modifying either the optical step height $h_s\Delta n$ or the optical wavelength λ .

2.1.5.2 Q-PLATES

OAM light can also be generated using a passive Liquid Crystal (LC) optical element called q-plate. The q-plate is essentially a thin film nematic LC cell sandwiched between two indium-tin-oxide coated glass [41, 42]. LCs are anisotropic, hence birefringent liquids, with a specific molecular orientation defined by the molecular director $\hat{n} = (\sin\theta\cos\alpha, \sin\theta\sin\alpha, \cos\theta)$. Thus, the LC show an azimuthal pattern with respect to the center of the q-plate. Contrary to conventional LC cells, which exhibit a consistent director throughout the plate, a q-plate possesses a distinct azimuthal pattern of $\hat{n}$ within the cell plane. This pattern is defined in relation to a central point, which is considered the origin of

the coordinate system. In the cell plane, the angle α within the molecular director is a function of the azimuthal angle ϕ , defined by $\alpha(\phi) = q\phi + \alpha_0$, where q is the topological charge and α_0 is the angle of the LC director on the reference line [43].

The q-plate is fabricated using a photo-alignment technique which consists of a combination of a polarizer, a cylindrical lens, and two indiumtin oxide (ITO)-coated glass used as the substrate for the LC cell (see figure 2.7) [43–46]. Each glass is spin-coated with a photosensitive solution (sulphonic azo dye). The polarizer and glass cell are placed on a motorized angular rotational stage with angular speeds of ω_p and ω_c . This allows the high-frequency incident light to scan the entire plate and generate a distinct angular pattern on the azo dye layer. The cylindrical lens focuses the polarized light narrowly in one dimension versus the other selecting a narrow angular area on the cell. The ratio of the angular rotations of the polarizer and the cell determines the q -value, given by $q = 1 \pm \omega_p/\omega_c$. The signs correspond to the rotation direction of the polarizer and LC cell if positive (negative) both rotate in the same (opposite) directions [43]. This technique allows for the fabrication of any integer, half-integer, positive or negative value for the topological charge, q . The photo-alignment procedure enables the inscription of any pattern on the plate, provided it possesses azimuthal cylindrical symmetry.

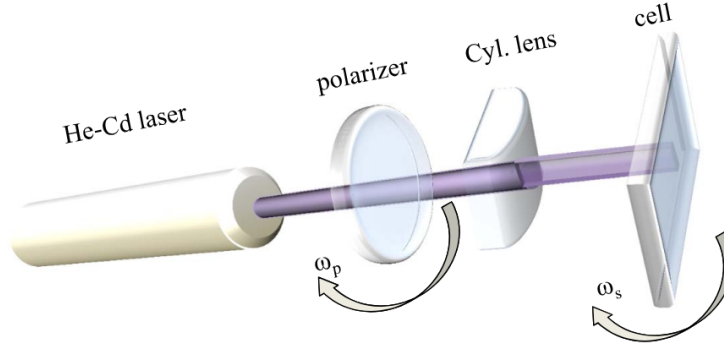


Figure 2.7: **q -plate fabrication** is typically performed using a photo-alignment setup. The polarizer and LC cell are mounted on a rotational stage with independent-angular frequencies while the cylinder is fixed in space [43].

To understand the operating principles of a q -plate on the optical field, it is convenient to adopt a Jones formalism. The Jones matrix for a q -plate is as follows [43, 47]:

$$M_q = R(-\alpha)HWP(\theta)R(\alpha) \quad (2.39)$$

Where R is a 2×2 rotational matrix and HWP is the Jones matrix for a half-wave plate, assuming the fast axis θ with respect to the horizontal axis is zero.

$$M_q = R(-\alpha) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} R(\alpha) \Rightarrow M_q = \begin{pmatrix} \cos(2\alpha) & \sin(2\alpha) \\ \sin(2\alpha) & -\cos(2\alpha) \end{pmatrix} \quad (2.40)$$

This is the Jones matrix for a q -plate which is used to determine the transmitted structure of the beam. When an incident circularly polarized Gaussian beam propagates through the q -plate, it acquires an OAM defined by $l = \pm 2q$. This is known as spin-to-OAM conversion. This is depicted by figure 2.8 where the RHC and LHC polarized Gaussian beam determine the handedness of the helical light. Experimentally, we can measure the efficiency of the conversion

process. To do this we first, transform the linear polarization to circular polarization using a first quarter-wave plate, then imprint OAM onto the CPL by using a q-plate, and then revert back the polarization to linear using a second quarter-wave plate. Lastly, we use a polarizer to split the output into two channels and measure the light intensity of both channels to quantify the amount of converted to non-converted light [43].

$$|V\rangle \longrightarrow \text{QWP}(\pm 45) \xrightarrow[\text{RHC}]{\text{LHC}} \text{Q-plate} \xrightarrow[l_-]{l_+} \text{QWP}(\mp 45) \longrightarrow \text{LP} \xrightarrow[|V\rangle]{|H\rangle} \quad (2.41)$$

If the conversion efficiency is not 100%, as is often the case, the transmitted light will consist of a superposition of Gaussian and LG beams. That is, a portion of the incident Gaussian will be transmitted unaffected and the other part will convert to OAM.

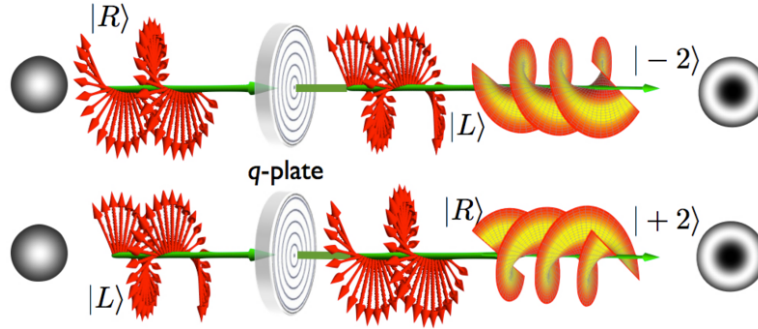


Figure 2.8: **q-plate with topological charge $l=2$** . A q-plate converts RHC (LHC) polarized Gaussian beam to an OAM beam $-2\hbar$ ($+2\hbar$). This image was created by Dr. Ebrahim Karimi.

2.1.5.3 OAM AND SAM STATES OF LIGHT

Light can carry both Spin Angular Momentum (SAM) and OAM. The former is described by the dynamical rotation of the electric field vector around the propagation direction, ($s = \pm\hbar$) and the latter is associated with the dynamical rotation of the wavefront structure, the twisting of the wavefront undergoing l intertwined rotations in one wavelength, $\pm l\hbar$. Using OAM results in an additional degree of freedom to influence the characteristics of light-matter interaction. The total angular momentum of an electromagnetic field can be split into the two forms of rotation via

$$\mathbf{J} = \int \mathbf{r} \times (\varepsilon_0 \mathbf{E} \times \mathbf{B}) d^3r = \underbrace{\int \varepsilon_0 E_i (\mathbf{r} \times \nabla) A_i d^3r}_L + \underbrace{\int \varepsilon_0 \mathbf{E} \times \mathbf{A} d^3r}_S \quad (2.42)$$

where i -subscript denotes the Cartesian vector components, ε_0 is the vacuum permittivity, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field, and $\mathbf{A}$ is the vector potential. However, the splitting is gauge-dependent due to the vector potential. Nonetheless, it gives a good general idea of the light's SAM and OAM.

Using the notion of SAM and OAM we will describe the polarization state and angular momentum of the structured light used experimentally. According to our setup, the incident polarization onto the optical setup is vertically polarized light.

$$|V\rangle \longrightarrow \text{QWP}(\pm 45) \xrightarrow[\text{RHC}]{\text{LHC}} \text{Q-plate} \xrightarrow[l_-]{l_+} \text{QWP}(\mp 45) \longrightarrow \text{QWP}(\theta) \quad (2.43)$$

Vertically polarized light incident onto the first Quarter-Wave Plate (QWP) generates left-CPL (Right-CPL) if the angle of incidence is 45° (-45°) with respect to the horizontal axis. Experimentally, the transmitted light has an ellipticity between 90 – 95% therefore the major and minor axes are not identical. We must take this into account by introducing two variables α and β (such that $|\alpha|^2 + |\beta|^2 = 1$) which are used to vary the ellipticity of the transmitted light that is subsequently incident on the q-plate. Depending on the conversion efficiency of the q -plate, a portion of the light will remain unchanged and the other will acquire an l -value with opposite polarization due to the retardance of π radians. The ratio of Gaussian to LG is determined by the retardation angle ξ . The second QWP was used to generate linearly polarized superimposed Gaussian and OAM beams. The third QWP could be used to produce the desired ellipticities. To determine the polarization state after each optics we will implement the Jones matrices convention for $\text{QWP}(\theta)$ and $\text{HWP}(\theta)$ where θ is the angle with respect to the horizontal axis [36, 48]. We can define the operation of the q -plate by means of a unitary operator M_Q [43, 47]. The handedness of the helical light is determined by the incident circular polarization on the q -plate.

$$\begin{cases} M_q|\text{LHC}\rangle = \cos\left(\frac{\xi}{2}\right)|\text{LHC}\rangle + i\sin\left(\frac{\xi}{2}\right)|\text{RHC}\rangle e^{il\phi} \\ M_q|\text{RHC}\rangle = \cos\left(\frac{\xi}{2}\right)|\text{RHC}\rangle + i\sin\left(\frac{\xi}{2}\right)|\text{LHC}\rangle e^{-il\phi} \end{cases} \quad (2.44)$$

The portion of the light that acquires an l -value also gains a π phase shift between polarization components i.e. the q -plate acts like a HWP with respect to the incident polarization. The output unit vectors of the electromagnetic field can be determined via Jones matrix multiplication of the second and third QWP. By introducing the spatial components of the incident light we can express the electric field for both helicities as

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix}_{l\pm} = \frac{1}{\sqrt{2}} \left[\cos(\xi/2) \begin{pmatrix} \alpha \\ i\beta \end{pmatrix} e^{-\frac{i\pi}{2}} u_g(x, y, z) + \sin(\xi/2) \begin{pmatrix} \beta \\ -i\alpha \end{pmatrix} u_0^\pm(x, y, z) \right] \quad (2.45)$$

The magnetic field can be obtained via the relation $\mathbf{B}(x, y, z) = \hat{z} \times \mathbf{E}(x, y, z)$.

$$\begin{pmatrix} B_x \\ B_y \end{pmatrix}_{l\pm} = \frac{1}{\sqrt{2}} \left[\cos(\xi/2) \begin{pmatrix} \beta \\ i\alpha \end{pmatrix} e^{-i\pi} u_g(x, y, z) + \sin(\xi/2) \begin{pmatrix} i\alpha \\ \beta \end{pmatrix} u_0^\pm(x, y, z) \right] \quad (2.46)$$

These were our OAM and SAM states of light used experimentally. These expressions give us a good understanding of the beam structure at the interaction region.

2.2 EXPERIMENTAL SETUP AND DETECTION SCHEME

2.2.1 TEMPORAL AND SPECTRAL PULSE REPRESENTATION

A pulse of light is described by an optical field of finite time duration. It is convenient to describe a near-infrared (NIR) driving field in the time and frequency domain. For simplicity, consider the one-dimensional case and assume that the NIR laser is a monochromatic light and linearly polarized in the x-direction. The real-valued electric field of a light pulse $E(t)$ with central frequency ω_0 is

$$E(t) = E_0 e^{-\left(\frac{t}{\tau}\right)^2} \cos(\omega_0 t + \phi(t)) \quad (2.47)$$

where E_0 is the amplitude, $\omega_0 = 2\pi/T_0$ is the central frequency and τ is the $1/e$ -width of the pulse, respectively. Now it is useful to represent the pulse in the frequency domain because experimentally the power spectrum is most easily measured through a grating spectrometer, or it can also be converted into electrons and measured by a time-of-flight spectrometer. In the frequency domain, $\omega = 2\pi\nu$. The Fourier transform $E(\omega) = \mathcal{F}[E(t)]$.

$$\begin{aligned} E(\omega) &= \mathcal{F}[E(t)] = \mathcal{F}\left[E_0 e^{-\frac{t^2}{\tau^2}}\right] * \mathcal{F}[\cos(\omega_0 t + \phi(t))] \\ E(\omega) &= \mathcal{F}[E(t)] = E_0 \sqrt{\pi} \tau e^{-\frac{\tau^2 \omega^2}{4}} * \frac{1}{2} \left(\delta(\omega + \omega_0) e^{i\phi(\omega)} + \delta(\omega - \omega_0) e^{-i\phi(\omega)} \right) \\ E(\omega) &= \mathcal{F}[E(t)] = \frac{\tilde{E}_0}{2} \left(e^{-\frac{\tau^2 (\omega + \omega_0)^2}{4}} e^{-i\phi(\omega + \omega_0)} + e^{-\frac{\tau^2 (\omega - \omega_0)^2}{4}} e^{-i\phi(\omega - \omega_0)} \right) \end{aligned} \quad (2.48)$$

where we made use of the Fourier transform scaling and the convolution theorem, and $\tilde{E}_0 = E_0 \sqrt{\pi} \tau$. For a real field we have $E^*(\omega) = E(-\omega)$. It is therefore redundant to keep all the definitions of the field since the negative-frequency component contains the same information as the positive-frequency component. We can neglect the negative frequencies by using a Heaviside function, $\mathcal{E}(\omega) = 2H(\omega)E(\omega) = \tilde{E}_0 \exp\left(-\frac{\tau^2}{4}(\omega - \omega_0)^2\right) \exp(-i\phi(\omega - \omega_0))$, where $\mathcal{E}(t) = \mathcal{F}^{-1}[\mathcal{E}(\omega)]$ and is a complex amplitude. We do not lose any information by considering only the positive frequencies. This is graphically depicted in figure 2.9, where we can reconstruct the initial pulse via the inverse Fourier transform of the positive frequencies.

$$\begin{aligned} \text{Re}[\mathcal{E}(t)] &= \frac{1}{2} [\mathcal{E}(t) + \mathcal{E}^*(t)] \\ \text{Re}[\mathcal{E}(t)] &= \frac{1}{2} \mathcal{F}^{-1} [\mathcal{E}(\omega) + \mathcal{E}^*(-\omega)] \\ \text{Re}[\mathcal{E}(t)] &= \mathcal{F}^{-1} [H(\omega)E(\omega) + H(-\omega)E^*(-\omega)] \end{aligned} \quad (2.49)$$

where $1 - H(\omega) = H(-\omega)$

$$\begin{aligned} \text{Re}[\mathcal{E}(t)] &= \mathcal{F}^{-1} [H(\omega)E(\omega) + (1 - H(\omega))E(\omega)] \\ \text{Re}[\mathcal{E}(t)] &= \frac{1}{2} \mathcal{F}^{-1} [H(\omega)E(\omega) + (1 - H(\omega))E(\omega)] \\ \text{Re}[\mathcal{E}(t)] &= \mathcal{F}^{-1} [E(\omega)] \\ \text{Re}[\mathcal{E}(t)] &= E(t) \end{aligned} \quad (2.50)$$

where $\mathcal{E}(t) = E_0 e^{-\left(\frac{t}{\tau}\right)^2} e^{i\omega_0 t}$ and $E(t) = E_0 e^{-\left(\frac{t}{\tau}\right)^2} \cos(\omega_0 t)$. We can also center the pulse spectrum on the frequency ω instead of zero. The commonly used complex frequency-domain pulse field is

$$\mathcal{E}(\omega) = \sqrt{S(\omega)} e^{-i\phi(\omega)} \quad (2.51)$$

where the spectrum is $S(\omega) = |\mathcal{E}(\omega)|^2$ and the spectral phase is $\phi(\omega) = -\arctan\left(\frac{\text{Im}[\mathcal{E}(\omega)]}{\text{Re}[\mathcal{E}(\omega)]}\right)$.

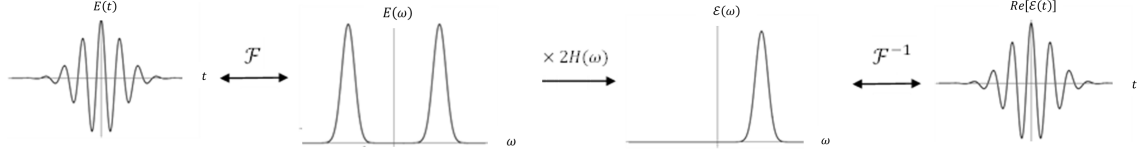


Figure 2.9: **Frequency and Time domain:** A graphical representation of the driving laser field in time and frequency domain. It demonstrates the real component of the electric field can be obtained through a product with a Heaviside function in the frequency domain. By considering only the positive frequencies we obtain $\text{Re}[\mathcal{E}(t)]$.

The broader the bandwidth in the frequency domain, the shorter the τ of the pulse in the time domain. Large bandwidths are required to support femtosecond or attosecond pulses. For example, to support a 40 fs pulse it requires a supporting bandwidth of 11 THz. The bandwidth can be calculated from the time-bandwidth product of a transform-limited Gaussian and is shown in figure 2.10. This relation is derivable through the Fourier transform of a transform-limited Gaussian pulse in the time domain

$$E(\omega) = \mathcal{F}[E(t)] = \mathcal{F}\left[E_0 e^{-\pi\left(\frac{t}{\sqrt{\pi}\tau}\right)^2}\right] = E_0 \sqrt{\pi}\tau e^{-\pi^2\tau^2\nu^2} \quad (2.52)$$

and by finding the FWHM for $|E(t)|^2$ and $|E(\nu)|^2$. The τ is for the 1/e-half-width and can be converted to FWHM by $\tau_{1/e} = \frac{\tau_{FWHM}}{\sqrt{2\ln 2}}$. Solving for t and ν we can obtain the width defined as $\Delta t = \sqrt{2\ln(2)}\tau$ and $\Delta\nu = \frac{\sqrt{2\ln(2)}}{\pi\tau}$. Thus, the product of the FWHM in the time and frequency domain given by the relation

$$\Delta t \Delta\nu = \frac{2\ln(2)}{\pi} = 0.44 \quad (2.53)$$

This is the fundamental relationship between the laser pulse duration width (Δt) and bandwidth ($\Delta\nu$). The frequency bandwidth can be converted to wavelength range via the derivative of the relation between frequency and wavelength.

$$\nu = \frac{c}{\lambda} \Rightarrow \frac{d\nu}{d\lambda} = -\frac{\Delta\nu}{\Delta\lambda} \Rightarrow \Delta\nu = -\frac{c}{\lambda^2} \Delta\lambda \quad (2.54)$$

2.2.2 Ti:SAPPHIRE LASER SYSTEM

Titanium-Sapphire (Ti:Sapphire) laser is a solid-state laser that uses a Ti:Sapphire crystal as its lasing medium. The Ti:sapphire crystal is produced by introducing Ti_2O_3 into a melt of Al_2O_3 , where Ti^{3+} (titanium) ions replace a small percentage of the Al^{3+} (aluminium) ions. A boule of material is then grown from this melt. The Ti^{3+} ion is responsible for the lasing action in Ti:Sapphire. The electronic ground state of the Ti^{3+} ion is split into a pair of vibrationally broaden levels [49]. The absorption transitions occur between 400 to 600nm. The pump laser provides the initial energy

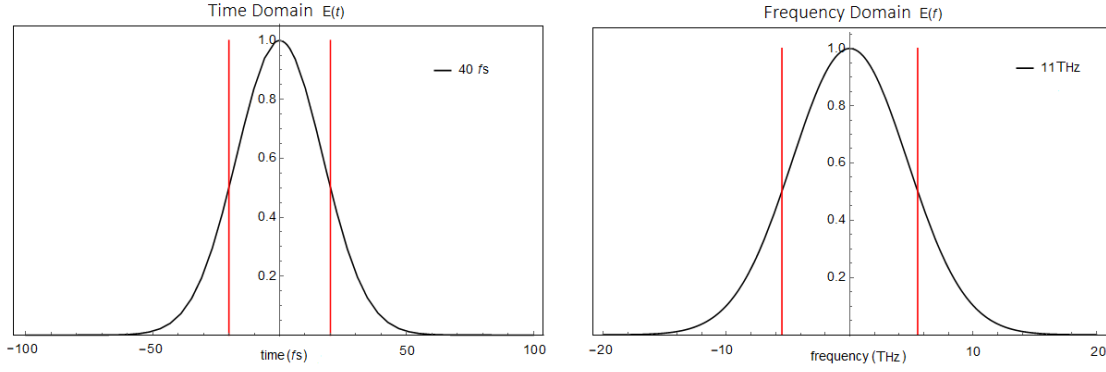


Figure 2.10: **Time-bandwidth product:** Graphical example of the time-bandwidth product for Gaussian beams. Demonstrates that a femtosecond must contain a broad spectrum to allow a short temporal pulse.

needed to excite the Ti^{3+} and create population inversion in the crystal triggering a chain reaction of photon emission through stimulated emission. The strongest absorption is near the wavelength 532nm, therefore a green continuous wave green laser is commonly used.

Fluorescence transitions occur from the lower vibrational levels of the excited state to the upper vibrational levels of the ground state. The resulting emission and absorption spectra are shown in figure 2.11. Although the fluorescence band extends from wavelengths as short as 600 nm to wavelengths greater than 1000 nm, lasing action is only possible at wavelengths longer than 670 nm because the long wavelength side of the absorption band overlaps the short wavelength end of the fluorescence spectrum [49]. Nevertheless, Ti:Sapphire possesses a broad continuous wavelength tuning range. This broad tuning range allows Ti:Sapphire lasers to produce and amplify optical pulses of extremely short duration.

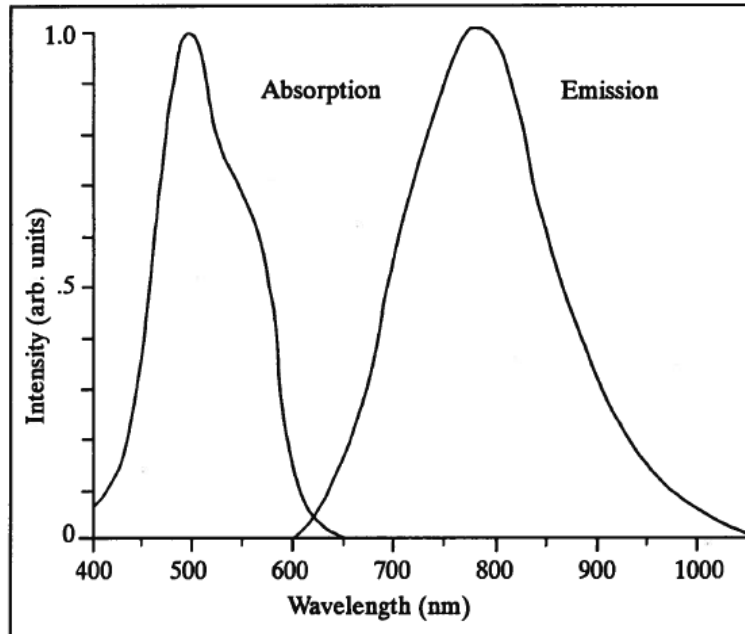


Figure 2.11: **Absorption and emission spectra of Ti:Sapphire.** Depicts the emission and absorption spectral range for a Ti:Sapphire crystal [49].

The Tsunami Ti:Sapphire is an ultrafast oscillator that delivers a range of wavelength and pulse width from 720nm to 1080nm and from picosecond to ~ 100 fs. The typical tsunami output laser parameter obtained experimentally was a

TEM₀₀ mode with 2mm $1/e^2$ beam diameter, an average power of $\sim 400\text{mW}$ at 800nm, with a repetition rate of $\sim 80\text{MHz}$ when pumped by a continuous wave diode-pumped solid-state laser (Millenia Pro) with a 15W power at 532nm.

To increase the peak power of the Tsunami output pulse, the laser system was used in combination with a Spectra-physics Spitfire regenerative amplifier (800nm, 1kHz, $\sim 40\text{fs}$, $\sim 2.5\text{mJ}$). See figure 2.12 for a schematic of the Spitfire laser system. The maximum output energy of a solid-state amplifier is normally limited by the optical damage threshold of the crystalline material used in the system. To generate a high-power optical pulse, the spitfire regenerative amplifier uses the chirped pulse amplification (CPA) technique [50]. The incoming seed pulse is temporally stretched to reduce the peak power by a multi-pass grating and mirror combination. Then, amplified by a Ti:Sapphire gain medium with the help of a high-power pulsed green solid-state pump laser. The Empower laser system is a Q-switched Nd:YLF laser capable of delivering an average output power of 30W near 527nm at a repetition rate of 1kHz to 10kHz. The synchronization and delay generator provides the control to select and capture the pulses from the train of stretched Tsunami pulses and direct them into the amplifier cavity. The selected pulses trapped in a laser resonator pass multiple times through the gain medium to extract all of the energy stored in the amplification medium. It then provides the timing control to direct the amplified pulse to the compressor to temporally compress the pulses to a femtosecond duration. This method allows for increased peak power while avoiding any nonlinear optical damage to the gain medium.

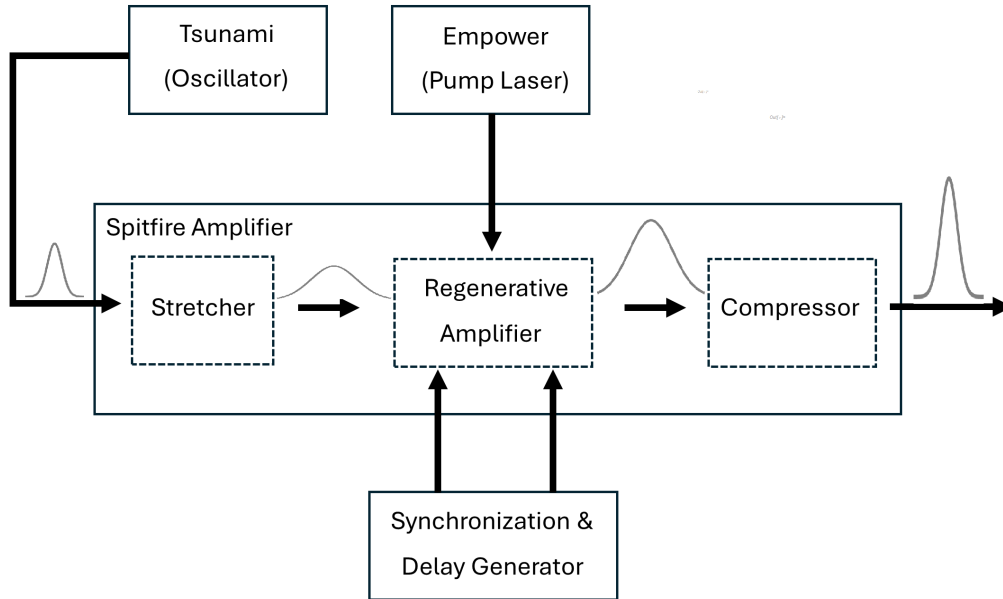


Figure 2.12: **Schematic of the femtosecond laser system** demonstrating CPA in a regenerative amplifier.

2.2.3 MODE-LOCKING

A broadband femtosecond laser such as Ti:Sapphire laser produces a train of short laser pulses, in the time domain. The most common method of passive mode-locking is the Kerr-lens mode locking, which is a nonlinear phenomenon. By placing a nonlinear crystal in the cavity it creates low-loss for high intensities and high-losses for low intensity. Thus, only the high-intensity modes get amplified by the gain medium. As the high-intensity light propagates through the nonlinear crystal it leads to a refractive index gradient, similar to a lens. The Kerr effect can be understood by $n = n_0 + n_2 I$, where n_0 is the initial refractive index of the material, n_2 is the intensity-dependent refractive index, and I is the intensity of

the light. This change in the refractive index only allows the high-intensity light to penetrate a pinhole inside the cavity, as it is focused by the change of the refractive index. Hence, the high-intensity light gets amplified while the low intensity dies out due to its low degree of focusing and is blocked by the same pinhole. The remaining modes in the cavity are locked in phase together, allowing constructive interference to generate a single pulse, in time, inside the cavity. This pulse has a carrier frequency ω_c and circulates in the laser cavity with length L , it gets amplified every time it passes through the gain medium. The output of the laser is a train of pulses, essentially replicas of the oscillating pulse. The output pulses are separated by the repetition time or round-trip time, given by $T = \frac{v_g}{2L} = \frac{1}{\omega_r}$, where v_g is the cavity's mean group velocity and is defined by the round-trip time of the cavity and ω_r represents the repetition rate or repetition frequency. The output pulses are in reality not identical, the carrier frequency shifts with respect to the pulse envelop $E(t)$ every round trip by $\Delta\phi$. The carrier and envelop phase continuously change as the wave packet propagates through the dispersive medium of the cavity. Thus, the difference between the group and phase velocity generates this phase shift $\Delta\phi$. The propagation of a single pulse can be represented as $E(t, z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(\omega) e^{i\omega t} d\omega e^{-ik(\omega)z}$ where the Fourier transform is defined as $E(\omega) = \int_{-\infty}^{\infty} E(t) e^{-i\omega t} dt$. By expansion the frequency-dependent propagation vector in terms of the phase and group velocity we can identify the added phase shift $\Delta\phi$ the output pulse gains $\Delta\phi = \omega_0 \left(\frac{1}{v_g} - \frac{1}{v_p} \right) z = \frac{\omega_0}{\omega_r}$, where ω_0 is the offset frequency and ω_r the repetition rate [51].

In our Ti:Sapphire system we also implement active mode locking, the periodic modulation of the resonator losses or of the round-trip phase change. We have an acoustic-optic modulator inside the laser cavity to generate a train of pulses, see figure 2.13 for visualizing the pulse emission of an acoustic-optic modulator. We set up a standing wave in the Bragg cell with an angular frequency Ω , the diffraction from the Bragg cell causes a loss inside the cavity. The loss is periodic and is only lossless for a short interval of time. Modes with random phases will experience high loss and will not amplify inside the cavity. Only modes whose phases match the modulator phase will be allowed to grow and produce laser output. All modes that survive evolve simultaneously in the cavity. The output is a train of pulse in the time domain.

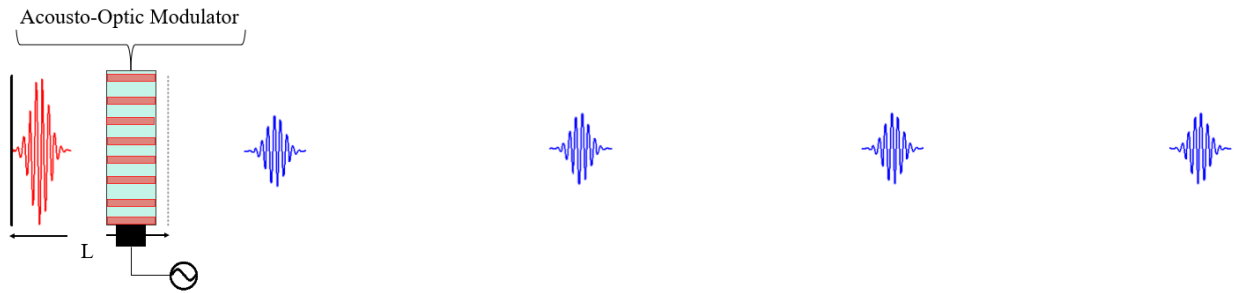


Figure 2.13: **Acoustic-optics modulator** inside a laser cavity of length L will generate pulses every round-trip of the cavity.

The acoustic-optic effect is based on the change in the refractive index of a medium due to the presence of sound waves. Sound waves cause molecular vibrations which alter the medium optical polarizability, acoustic waves perturb the refractive index in a wave-like manner. This creates a refractive index grating in the material that can be used to diffract light. When acoustic waves travel through a medium this causes strain $S(z, t) = S_0 \cos(\Omega t - k_a z)$, where S_0 is the amplitude and k_a is the acoustic wavenumber, in the direction of propagation [36]. The strain causes a sinusoidal perturbation in the optical medium density, altering the refractive index. The medium has a time-varying inhomogeneous

refractive index in the form of a wave, $\Delta n(z, t) = -\frac{1}{2}pn^3S(z, t)$, where p is the photoelastic constant and n is the refractive index. The negative sign indicates that positive strain leads to a reduction in the refractive index, $n(z, t) = n - \Delta n(z, t)$ [36].

Acoustic modulators provide a powerful means to control the frequency, direction, and intensity of a laser beam. The acoustic frequency is much less than the optical frequencies, thus the variation in the index of refraction is relatively slow compared to the optical period. The medium can be treated in the static inhomogeneous medium (adiabatic approach). The acoustic wave propagating in the optical medium can be considered as a sequence of partially reflecting mirrors with separation of the acoustic wavelength and with velocity of sound. In order to have a transition there must be constructive interference between the reflected waves.

2.2.4 PULSE STRETCHER AND COMPRESSOR

A chirped pulse is a frequency-modulated pulse where its instantaneous frequency ($\omega_{inst}(t) = \omega_0 - \frac{d\phi}{dt}$) is time-varying. If the $\omega_{inst}(t)$ increases linearly with time, it is a positively chirped pulse and if the $\omega_{inst}(t)$ decreases linearly with time, the pulse is negatively chirped (see figure 2.14). We can write a linearly chirped Gaussian pulse mathematically as

$$E(t) = \underbrace{E_0 e^{-\left(\frac{t}{\tau}\right)^2}}_{\text{Gaussian amplitude}} \exp \left[i \left(\underbrace{\omega_0 t}_{\text{carrier wave}} + \underbrace{\beta t^2}_{\text{chirp}} \right) \right] \quad (2.55)$$

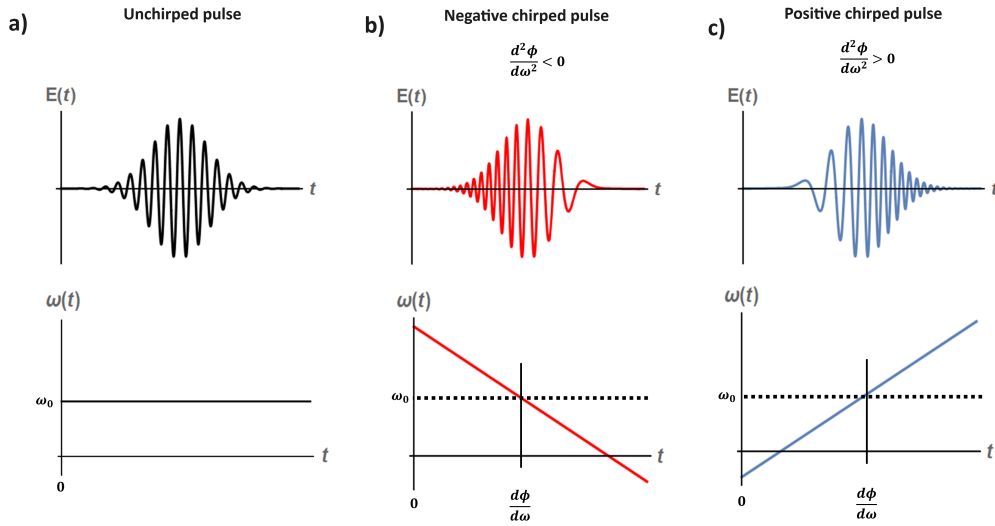


Figure 2.14: **Chirped pulse:** Graphical representation of **a)** transform limited pulse, **b)** negative chirped pulse, and **c)** positive chirped pulse.

Group-Velocity Dispersion (GVD) is used to describe how a medium affects the duration of an optical pulse after propagation. The phase gain due to a medium is $\phi(\omega) = n(\omega)k_0L = k(\omega)L$, where $n(\omega)$ is the frequency-dependent index of refraction, k_0 is the vacuum wave vector and L is the length of the medium. To account for dispersion, we can

Taylor expand the wave vector.

$$k(\omega)L = \underbrace{k(\omega_0)L}_{\text{phase delay}} + \underbrace{\frac{dk(\omega)}{d\omega}\bigg|_{\omega_0}}_{\text{group delay}} L(\omega - \omega_0) + \frac{1}{2} \underbrace{\frac{d^2k(\omega)}{d\omega^2}\bigg|_{\omega_0}}_{\text{group delay dispersion}} L (\omega - \omega_0)^2 + \dots \quad (2.56)$$

We can define the three quantities as $k(\omega_0) = \omega_0/v_p$ where v_p is the phase velocity, $\frac{dk(\omega)}{d\omega}\bigg|_{\omega_0} = 1/v_g$ is the group velocity, and $\frac{d^2k(\omega)}{d\omega^2}\bigg|_{\omega_0} = \frac{d}{d\omega} \left(\frac{1}{v_g} \right)$ is the GVD [51].

Assume a broadband optical pulse incident on a diffraction grating, the pulse will undergo angular dispersion resulting in a different optical path length $OPL(\omega)$ for different frequencies. Moreover, the phase delay for different frequencies, $\phi(\omega)$, is related to the optical path length in terms of $\phi(\omega) = \frac{\omega}{c} OPL(\omega)$. Different spectral components originate from the grating under different angles which results in a cone shape spread. In the diagram of figure 2.15, ω_0 represent the central frequency while ω is an arbitrary frequency within the original optical pulse. The dotted lines are the wavefronts of these frequencies. Wavefronts are surfaces of constant OPL from the initial dispersion point. The angle representing the frequency spread is a frequency-dependent angle $\theta(\omega)$. Each frequency within the initial pulse can be described by the central frequency and the frequency-dependent angle. In our setup, region (1) contains a grating and a convex aberration-free lens separated by L , where L can take a value greater, or smaller, or equal to the focal length f of the lenses. Aberration-free lenses do not cause any spread of light i.e. no dispersion when light propagates through it. The optical path length of the central frequency is $OPL(\omega_0) = L$ while for the arbitrary frequency it is $OPL(\omega) = L \cos(\theta(\omega))$, we can express the phase delay for an arbitrary frequency as $\phi_1(\omega) = \frac{\omega}{c} L \cos(\theta(\omega))$. By differentiating the phase delay of an arbitrary frequency twice and evaluating it at the central frequency ω_0 we obtain the Group Delay Dispersion (GDD) = $\frac{d^2\phi(\omega)}{d\omega^2}\bigg|_{\omega_0}$ of region (1) [51].

$$GDD = \frac{d^2\phi_1(\omega)}{d\omega^2}\bigg|_{\omega_0} \simeq -\frac{\omega_0}{c} L \left(\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0} \right)^2 \quad (2.57)$$

The term $\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0}$ represents the angular dispersion. Notice that the dispersion parameter is always negative independent of the sign of $\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0}$, and increases as L is increased. Therefore, angular dispersion yields negative GDD resulting in a negatively chirped pulse.

Once the incident plane wave propagates through the lens, it becomes a spherical wave converging to a focal plane. The phase delay of the spherical wave in the region (2) is given by $\phi_2(\omega) = \frac{\omega}{c} f \frac{1}{\cos\theta(\omega)}$ [51]. The GDD in region (2) is

$$GDD = \frac{d^2\phi_2(\omega)}{d\omega^2}\bigg|_{\omega_0} \simeq \frac{\omega_0}{c} f \left(\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0} \right)^2 \quad (2.58)$$

Once more, the term $\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0}$ represents the angular dispersion. Notice that this time the dispersion parameter is always positive independent of the sign of $\frac{d\theta(\omega)}{d\omega}\bigg|_{\omega_0}$.

The 4f configuration consists of a pair of confocal lenses and identical gratings (see figure 2.15). One grating is placed in the front focal plane of the first lens, and the other in the back focal plane of the second lens. The black lines describe the pulse path for an arbitrary frequency ω and the central frequency ω_0 . By varying the distance between the second lens and the second grating you can control the GDD of the outgoing pulse.

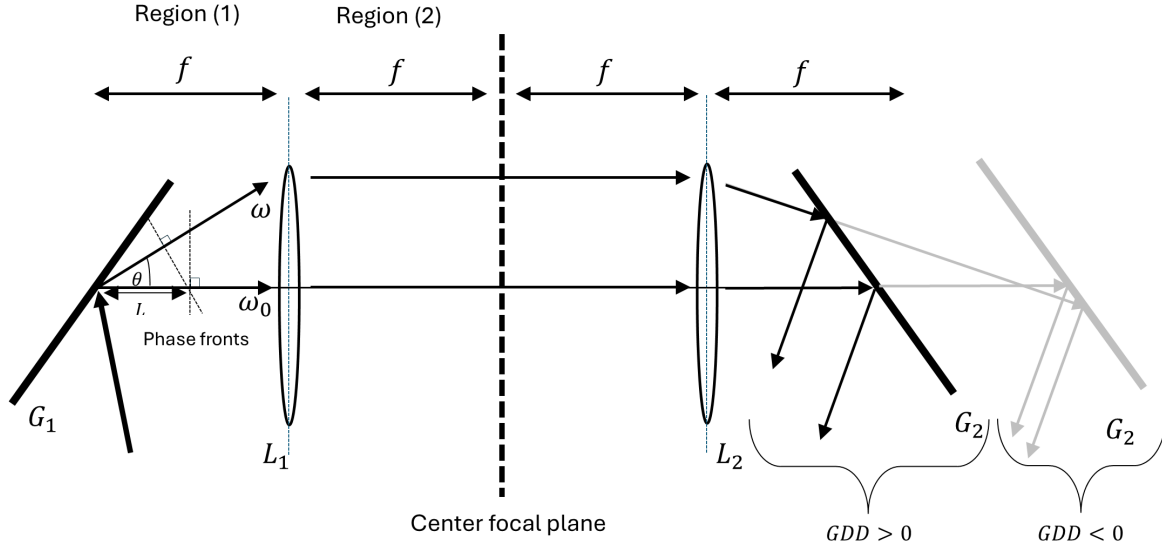


Figure 2.15: **4f system used as pulse stretcher or compressor** Schematic of pulse stretcher and compressor. By displacing the second grating, G_2 , at a distance smaller than the focal point of the second lens, L_2 , the 4f system stretches the pulse, ($GDD > 0$). The gray grating shows how this setup can be altered to compress a pulse ($GDD < 0$) by displacing the G_2 , further than the focal point of the L_2 . Both a stretcher and compressor are used in chirp pulse amplification.

i) If the grating is placed further than the focal length of the lens, $L > f \Rightarrow GDD < 0$, we obtain a negative dispersion (negatively chirped). That is, the lower frequency components of the pulse are delayed, and the blue frequencies travel less than the red frequencies, resulting in a compression of the pulse. In this scenario, our setup acts like a compressor, similar to a pair of parallel gratings (Treacy grating pair). ii) If the grating is placed closer than the focal length of the lens, $L < f \Rightarrow GDD > 0$, which means we obtain a positive dispersion (positively chirped). That is, the higher frequencies of the pulse are delayed, and the blue frequencies travel further than the red frequencies resulting in a stretching of the pulse. In this scenario, our setup acts like a stretcher.

These are the inner workings of a chirp pulse amplification in a Ti:Sapphire femtosecond laser. An incident broadband femtosecond pulse from a tsunami gets stretched by the stretcher to a picosecond in order to amplify the pulse power without damaging the gain medium. After multiple round trips and amplification, the pulse is then compressed back into a femtosecond pulse resulting in increased peak power.

2.2.5 SINGLE-SHOT AUTOCORRELATION

The task of measuring ultrashort laser pulses, the briefest events ever produced, has consistently posed a challenge. To measure a temporal event, a shorter scale is required. For a long time, we could generate ultrashort pulses but lacked the means to directly measure them. Techniques like spectrometry and autocorrelation were used, but they only provided an approximate measure of a pulse. Autocorrelation is a complex measurement to execute. It necessitates the division of the pulse into two duplicates, which are then focused and recombined (overlapped in space and time) in a Group second harmonic-generation (SHG) crystal. This process involves the careful alignment in time and space of three sensitive degrees of freedom, two spatial and one temporal. Moreover, this alignment must be maintained while scanning the delay. The phase-matching-bandwidth condition necessitates a thin SHG crystal, resulting in a weak signal and poor

measurement sensitivity. This issue in alignment makes an autocorrelator setup a labour-intensive and high-maintenance task.

In our laboratory, we used a variant of a single-shot autocorrelator to experimentally measure our pulse duration. This can be seen as a simplified version of the second-harmonic intensity autocorrelator in figure 2.16. Depending on the detector, it can be converted to a GRating-Eliminated No-nonsense Observation of Ultrafast Incident Laser Light E-fields (GRENOUILLE) or a simplified version of second harmonic generation frequency-resolved optical gating (SHG-FROG). This setup includes a cylindrical lens that focuses the beam vertically onto a Fresnel biprism (a prism with an apex angle close to 180°) which divides the beam into two beamlets that cross each other at large angle. This overlap causes the delay to vary across the nonlinear medium, thus mapping delay onto the transverse position. The time delay is a function of transverse position $\tau(x) = 2(x/c)\sin(\theta/2)$, where θ is the angle between the beamlets.

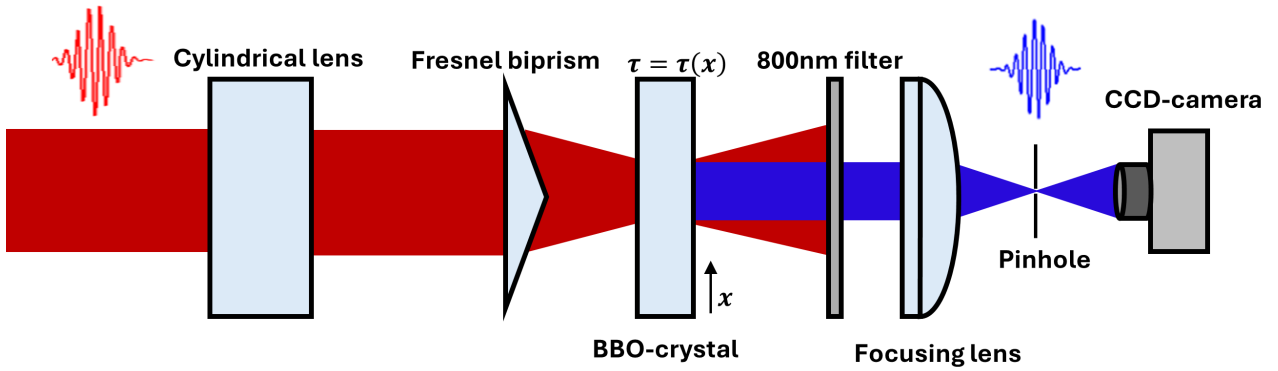


Figure 2.16: **Single-shot autocorrelator:** Every optical element of a hybrid version of a single-shot autocorrelator and a GRENOUILLE used in the laboratory.

The length of the pulse is indicated by the width of the nonlinear-optical signal beam generated by a thick BBO-crystal through a second order nonlinear process. The fundamental light is blocked by a filter, allowing only the second-harmonic to reach the focusing lens. Crossing beams at a large angle and focusing with a cylindrical lens maps delay onto transverse position, yielding the intensity autocorrelation $A^{(2)}(\tau) = \int_{-\infty}^{\infty} I(t)I(t - \tau)dt$ for a single pulse. Crossing beams at an angle is exactly what is required in conventional single-shot autocorrelator and FROG beam geometries, in which the relative beam delay is mapped onto horizontal position at the crystal.

Fresnel biprisms are automatically aligned in space and time, a significant simplification compared to standard single shot autocorrelator as there is no need to vary the time delay. The spatial overlap in the nonlinear crystal provides the time delay. The SHG signal is detected versus the position in the horizontal direction. A pinhole is used for spatial filtering. It is a very simple and inexpensive setup, it is easy to align and hard to misalign. It is a single-shot technique that requires good spatial beam quality. However, Group-velocity dispersion prevents its use for pulses shorter than ~ 20 fs and pulses greater than 250fs cannot be detected due to a lack of sufficient temporal delay between the beams split by the Fresnel biprism.

2.2.6 OPTICAL PARAMETRIC AMPLIFIER

Optical parametric amplifier (OPA) is a nonlinear optical process occurring in second-order nonlinear crystals and involving energy transfer among beams at different frequencies [6], resulting in a variable wavelength output. The nonlinear physical process can be understood through Difference Frequency Generation (DFG) as shown in figure 2.17. This process is described by a nonlinear polarization $P(\omega_1 - \omega_2) = 2\varepsilon_0\chi^{(2)}E_1E_2^*$ and has a conservation of energy, $\omega_3 = \omega_1 - \omega_2$ and momentum conservation $k_3 = k_1 - k_2$ (phase matching condition). The OPA uses three-wave mixing in a nonlinear crystal to provide optical gain. The process is governed by these three coupled equations [6].

$$\text{DFG} = \begin{cases} \frac{dA_1}{dz} = \frac{2id_{eff}\omega_1^2}{k_1c^2}A_3A_2e^{i\Delta kz} \\ \frac{dA_2}{dz} = \frac{2id_{eff}\omega_1^2}{k_2c^2}A_1A_3^*e^{-i\Delta kz} \\ \frac{dA_3}{dz} = \frac{2id_{eff}\omega_1^2}{k_3c^2}A_1A_2^*e^{-i\Delta kz} \end{cases} \quad (2.59)$$

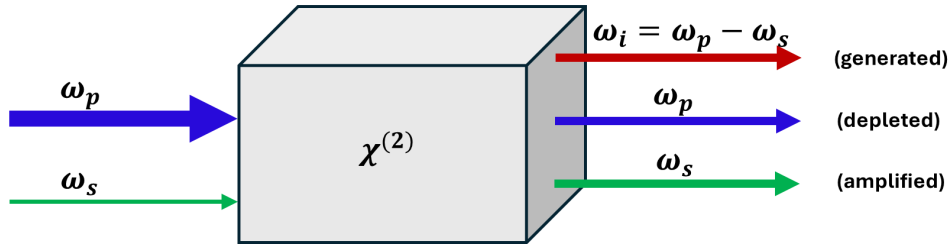


Figure 2.17: **Optical parametric amplifier:** The signal is the seed to be amplified, the pump is the high-powered light source that provides power to the amplifier, and the idler is an auxiliary wave created by the interaction process due to the conservation laws.

Energy is transferred from a high-intensity beam, called the pump beam ($\omega_1 = \omega_p$) to a lower-intensity beam, called the signal beam ($\omega_2 = \omega_s$), thus resulting in an amplification of the signal. During the pump-beam interaction, a third beam is generated, called the idler beam ($\omega_3 = \omega_i$) in order to fulfil energy conservation for the DFG. For a pump frequency higher than the signal and idler frequencies, the conservation rule $\omega_p = \omega_s + \omega_i$. In this case, the OPA systems working in the IR can be used for pumping a parametric process of down conversion into longer wavelengths. Experimentally, TOPAS-OPA from Spectral-Physics was used to extend the wavelength of the spitfire amplifier. It used a white light seeding configuration which provides a consistent, reliable light source for the most demanding applications. The wavelength extension was from $1140nm - 1600nm$ for the signal (vertical polarization), and $1600nm - 2600nm$ for the idler (horizontal polarization). The typical peak energy for the signal and idler is within the range of $250\mu J$.

2.2.7 TIME-OF-FLIGHT MASS SPECTROMETER

A TOFMS is an analytical instrument used to identify different organic or inorganic compounds within a test sample by generating ions and separating them by their mass-to-charge ratio (m/Z). It operates on the principle

that ions of different masses will have different times of flight through a fixed distance when accelerated by an electric field. A TOFMS depicted in figure 2.18 consist of four essential parts: i) the ionization region, ii) acceleration (extraction region), iii) the drift region (sorting of ions), and iv) detection. For optimal resolution and minimal background noise, all stages of a TOF are conducted under low pressure. The necessary vacuum is achieved using rough pumps and turbo pumps, which can create pressures as low as 10^{-5} to 10^{-9} Torr. This low-pressure environment reduces the likelihood of ion collisions and increases the mean-free path of the ions.

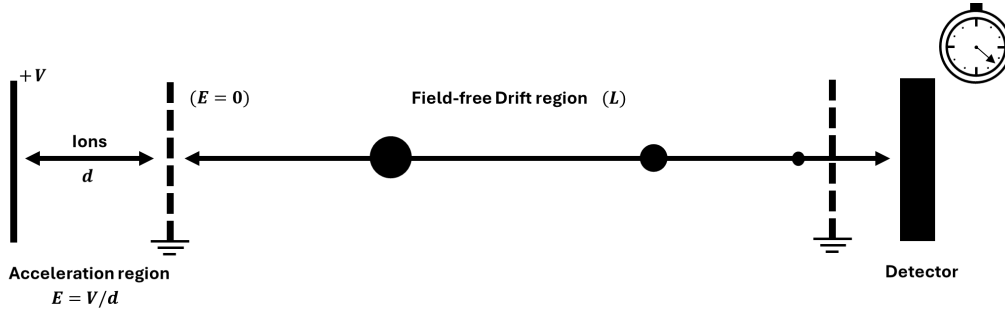


Figure 2.18: **Time-of-flight system:** Schematic of simple time-of-flight mass spectrometer. The area between the repeller and ground is defined by d and the L is the length of the flight tube.

- (i) Ionization: The sample is first ionized, often by a laser field, which removes one or more electrons to form a positive ion (cation).
- (ii) Acceleration: The ions are then accelerated by a static electric field generated by two parallel plates, repeller and extractor, of positive potential. Typically, the repeller has a higher voltage compared to the extractor. This imparts a kinetic energy to the ions that is directly proportional to the charge of the ion.
- (iii) Drift region: The ions then enter a field-free region known as the drift tube. Here, they continue to move at a constant velocity, ions of different mass acquire different velocities and therefore different drift times.
- (iv) Detection: The ions reach a detector at the end of the drift tube. The time taken for the ions to reach the detector is measured and is known as the "time of flight". This time is directly proportional to the square root of the ion's mass-to-charge ratio. Heavier ions will take longer to reach the detector than lighter ones.

The potential energy of a charged particle in an external electric field is $E = q\Delta V$ where q is the charge and ΔV is the electric potential difference. All the potential energy is converted to kinetic energy ($\frac{1}{2}mv^2 = q\Delta V$) where the constant velocity of the ions are $\rightarrow v = \sqrt{\frac{2q\Delta V}{m}}$. The drift time can be extracted from the constant velocity and the length L of the drift tube.

$$t = \left(\sqrt{\frac{L^2}{2\Delta V}} \right) \sqrt{\frac{m}{q}} \quad (2.60)$$

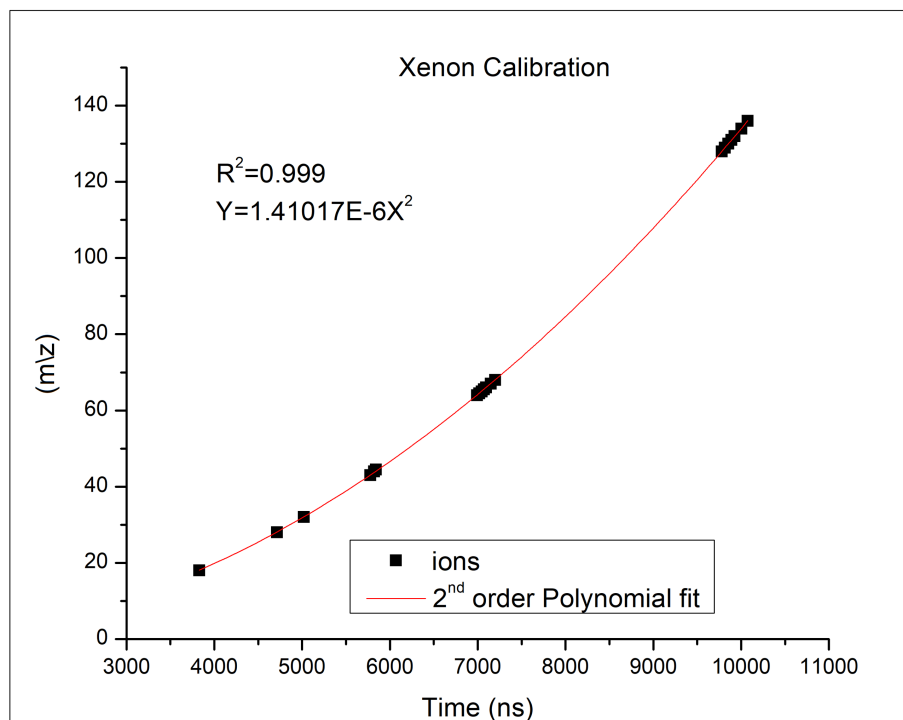


Figure 2.19: **Xenon mass calibration:** Experimental data used to calibrate the mass-to-charge ratio with the flight time of the ions.

By measuring the "time of flight", the mass-to-charge ratio of each ion can be determined through calibration with a known sample. Thus, individual ions and fragments can be identified from a known or unknown substance. This makes the TOFMS a powerful analytical tool allowing for the identification and quantification of a wide range of substances. Its high resolution, fast mass measurements, and suitable for pulsed ionization methods. However, the TOF digital conversion can be difficult due to the fast-changing signal from the ions hitting the detectors in very short time intervals. It requires fast digitizers for time-to-digital conversion. Nevertheless, this instrument is an invaluable instrument for analytical chemistry and physics.

To permit detailed analysis of the ion spectra, molecular mass spectra must be calibrated from the "time-of-flight" values to the mass-to-charge values. Given that precise beam alignment in the x,y and z-axes are normally adjusted at the time of experiment to maximize ion yield, the precise distance from the ionization in the interaction region and the microchannel plate (MCP) detector varies and must therefore be compensated in the conversion of flight time to m/z. Mass calibration shown in figure 2.19 is therefore achieved using known mass spectra obtained from literature such as NIST. Xenon is used for calibration as its ionization spectra are precisely known with the high abundance of isotopes and stable doubly and triply ions permit accurate calibration. It is also useful to use residual molecules such as O_2 , N_2 , and H_2O to extend the fit to lower times.

2.2.7.1 WILEY-MCLAREN GEOMETRY

Ideally, all ions are formed in a plane parallel to the source electrodes and with zero initial velocity, then flight time would be the same for all ions with the same mass-to-charge ratio. Thus, the resolution is limited to the detection equipment. However, in practice, the compounds are introduced in the ionization region through a gas inlet resulting in an initial space and initial kinetic energy distribution. The resolving power of the TOFMS depends on improving the space resolution, the ability to resolve masses despite the initial space distribution, and the energy resolution, reducing the time spread resulting from the initial kinetic energy distribution. Moreover, additional factors that can influence mass resolution are the different starting times, the different initial kinetic energies, the different starting locations, and the different initial directions of motion. Therefore, the improved resolution can be achieved by implementing a Wiley-McLaren TOF geometry [52] shown in figure 2.20.

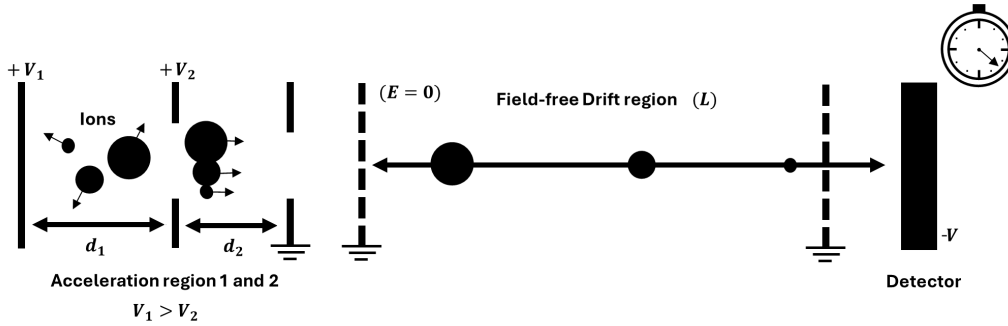


Figure 2.20: **Wiley-McLaren Time-of-flight geometry:** Schematic of a double field time-of-flight mass spectrometer depicting two acceleration regions improving the space-charge resolution.

Assume the initial position x_0 , then the space distribution is $x_0 + \Delta s$. The spatial focusing of ions can be controlled by implementing two parallel plates, a repeller and an extractor with different positive voltages. This generates two acceleration region with different electric fields, E_1 and E_2 with width d_1 and d_2 . This double-field geometry introduces two new parameters which are not present in a single-field source. The spatial focus is controlled by adjusting E_2/E_1 . Moreover, we can further decrease the space distribution, Δs , of the ionization volume - decrease the focal volume by tightly focusing the laser with a parabolic mirror and decrease the time distribution using a short ionization pulse. With these improvements, the Wiley-McLaren geometry is known for its high mass resolution $m/\Delta m$. This high resolution allows for precise identification and differentiation of ions based on their mass-to-charge ratio.

The detector is commonly a MCP with an applied negative voltage. The MCP detects the incident ions via an angular array of micron-sized channel grooves. When an ion collides with the groove wall it generates cascading electrons (electron avalanche). The size of the grooves are $\sim 10\mu\text{m}$ to maintain spatial resolution. The cascade electrons can be amplified by using two or more MCP in a chevron or z-stack geometry. Afterwards, the electrons are detected by an anode and converted to an electronic signal which is amplified and discriminated. The timing discriminator detects the leading and falling edge of the pulse which determines the duration of

acquisition.

Differential pumping is a technique used for vacuum systems to maintain a large difference in pressure between different stages of the system. A small orifice connects two parts of a vacuum system, one with lower pressure than the other. This is particularly important in setups where different sections of the instrument operate at different pressures. Ultra-high vacuum and differential pumping is achieved by using a set of rotary pumps and turbo-molecular pumps. Rotary pumps (rough pumps) are used to bring the system pressure down to roughly 10^{-3} Torr where the Turbo pumps can be activated to bring the system to an ultra-high vacuum $P \leq 10^{-6}$ Torr. They work like a compressor, where the gas is pushed into the lower stages and eventually to the exhaust by fast rotating blades. The mechanical energy from the rotating angled blades is transformed to the molecules (momentum conversion) by collision.

Differential pumping in a TOFMS is crucial for several reasons: i) The background gas pressure in the drift region of the TOFMS must be very low. This is because any collision of an ion with residual background molecules will alter the flight time of the ion and affect the accuracy of its mass-to-charge ratio. ii) Differential pumping ensures that the samples entering the ToF Mass Spectrometer are not contaminated by gases drawn from other regions. iii) Differential pumping helps maintain the kinetic energy of the ions by minimizing collisions with gas molecules. This accounts for free molecular flow where the mean free path is large and limits the amount of contact to the chamber walls or other ions maintaining a good signal resolution. iv) By reducing the number of collisions between ions and gas molecules, differential pumping can enhance the mass resolution of the TOFMS. Differential pumping is important in the operation of a TOFMS, contributing to its accuracy, resolution, and overall performance.

2.2.8 GAS PHASE EXPERIMENTAL SETUP

Near-infrared femtosecond laser pulses are focused by a parabolic mirror with a focal length of 5cm inside a differentially pumped vacuum chamber with a spot size of $3 \pm 0.2\mu\text{m}$. The chamber houses a TOFMS, which operates in a Wiley-McLaren geometry, see figure 2.21. The ions produced in the interaction region are focused and accelerated (denoted by the potential lines between the parallel plates) towards a field-free drift region of 30 cm before they are detected by a MCP (chevron geometry). The ion signal is then amplified, discriminated, and recorded by a time digitizer to generate a TOF mass spectrum. Mass calibration is achieved using Xenon atoms, and the spectrometer has a full width at half maximum mass resolution of 550 at an m/z (mass-to-charge ratio) of 132.

At room temperature, all chemicals and atoms have sufficient vapour pressure to be introduced into the vacuum chamber in the gas phase through a precision leak valve. To minimize contamination of the interaction region, organic compounds like limonene, fenchone or acetone underwent a freeze-and-thaw cycle. The pressure inside the vacuum chamber was maintained at $\sim 1.3 \times 10^{-6}$ Torr. To minimize number density fluctuations in

the interaction region, the samples were kept at 22°C using a temperature bath, and the gas line along with the leak valve was preserved at a positive temperature gradient. This meticulous process ensures the accuracy and reliability of the experiment. All chemicals were purchased from Sigma Aldrich with a purity of greater than 96%, respectively.

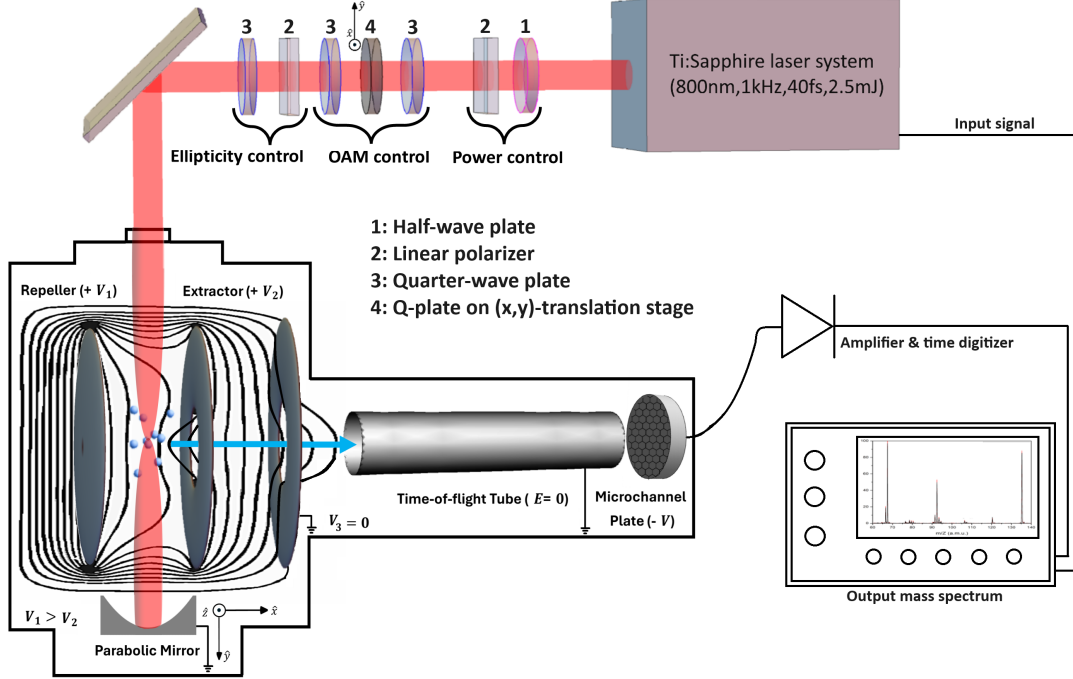


Figure 2.21: **Schematic of the gas phase experimental setup:** Identifying all essential experimental components for the gas phase experiment. The voltage on the repeller and extractor was +2000V and +1000V. The negative voltage on the MCP plate was set at -4900V. No mirror after the optics was used during the experiments to not alter the polarization state of the light. It was introduced in the schematic to condense the figure.

The experiments were conducted at various wavelengths, 800 nm and 1300- 2400nm to ensure adiabatic ionization. The laser pulses used in these experiments were obtained from a Ti:Sapphire laser system (Spitfire, Spectra-Physics) producing ~ 40 fs pulses with a maximum pulse energy of ~ 2.5 mJ and operating at 1 KHz repetition rate. The NIR wavelength was generated from a TOPAS OPA pumped by the Ti:Sapphire laser. The pulse duration in the interaction region was continuously monitored by a single-shot autocorrelator. A combination of a half-wave plate and a polarizer was used to control the pulse energy. To ensure the shortest pulse in the interaction region, a negative chirp was introduced and optimized by maximizing the ion yields of argon. The intensity range for the strong-field measurements was between $\sim 10^{13} - 10^{14}$ W/cm². Moreover, a fast photodiode was employed to continuously monitor the laser pulse energy incident on a 3 mm thick quartz window on the vacuum chamber.

The OAM and ellipticity control consists of a QWP on a motorized rotation stage (with a $\pm 0.005^\circ$ resolution) and was used to generate CPL incident on a LC based phase plate called q-plate. When an incident circularly polarized Gaussian beam propagates through the q-plate with a topological charge q , it acquires an OAM defined by $l = \pm 2q$, with a phase singularity and hence a null intensity region at the centre of the beam, known as an

optical vortex. The wavefront structure of such beams undergoes l intertwined rotations in one wavelength, and the direction of rotation is determined by the handedness of the incident circular polarization. A second QWP was used to generate linearly polarized OAM beams. The conversion efficiencies of the q-plates were $\sim 86 \pm 2\%$ for $l = 1$ and $\sim 88 \pm 2\%$ for $l = 3$. Lastly, a third QWP after a second polarizer controlled the ellipticity, ϵ , of the laser polarization of the helical light incident to the gas chamber. The third QWP was calibrated by measuring the ellipticity dependence of doubly charged argon, and $\epsilon = 0.05$ corresponds to linear polarization. The maximum ellipticity obtained was $\epsilon = \pm 0.96$ corresponding to nearly circular polarization. The uncertainty in ellipticity was ± 0.02 . not all experiments consisted of the OAM control or the ellipticity control.

The q-plate was mounted on a (x, y) -translation stage controlled by micrometre screw gauge with a precision of $10\mu\text{m}$. This extra degree of control allowed us to generate an asymmetrical OAM beam by displacing the null intensity region in the OAM beam. When focused by the parabolic mirror this translation results in nanometer displacement, often of step size of $\sim 330\text{nm}$. The calibration was achieved by measuring the total translation required to displace the singularity to the periphery of the defocused beam and comparing it to the measured spot size of $3 \pm 0.2\mu\text{m}$ obtained by intensity calibration of argon. The helical vortex beams can be further classified into vector and scalar vortex beams. The superposition of vector vortex beams with linear Gaussian leads to the shifting of singularity towards the periphery of the beam for $l = 1$ and splitting of the singularity for higher order l -value [53]. The superposition of linear Gaussian with scalar vortex beam causes the null intensity region to fade and does not lead to the shifting of singularity, which was used in the experiments by detuning the voltage of the q-plate.

2.2.9 TRANSMISSION EXPERIMENTAL SETUP

Ti: Sapphire laser amplifier system, operating in an external trigger mode producing 45 fs, 800 nm pulses with a maximum pulse energy of 2.5 mJ, was used in the transmission measurements, the setup is depicted in figure 2.22. An aspheric objective lens (NA=0.3) was used to focus the femtosecond pulses into a cuvette (10 mm thick) containing liquid samples of chiral or achiral molecules or into a solid samples with typical dimensions of $10 \times 10 \times 1\text{mm}$. A second aspheric objective with the same or higher numerical aperture (NA=0.5) collected and collimated the transmitted light onto a photodiode (PD)2, positioned immediately after the objective. For every laser shot, the transmitted light signal on PD2 was normalized with the incoming light signal on PD1, reflected off a glass plate positioned in the beam path at an angle of $\sim 20^\circ$ to avoid Brewster's angle. The signals generated by PD1 and PD2 were stretched by an electronic pulse stretcher, discretized and recorded by a data acquisition card.

A combination of a half-wave plate and a polarizer was used to vary the pulse energy (power control in Fig. 1a). The incident pulse energies were measured before the objective. During the measurement, for every laser shot, the pulse energy was increased by $\sim 3\text{nJ}$ and the sample was translated by $5\mu\text{m}$ to avoid micro-bubbles in liquids, or to irradiate a fresh sample spot in the solids. To ensure the shortest pulse in the interaction

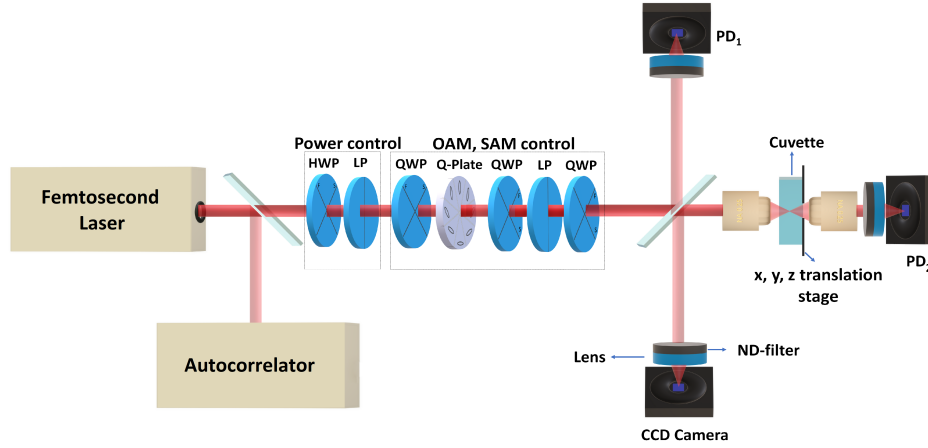


Figure 2.22: **Schematic of the transmission setup in the liquid and solid experiments.** All essential components are included in the schematic. For the solid transmission experiment, the cuvette was replaced by the $10 \times 10 \times 1$ mm sample.

region, a negative chirp was introduced and optimized by measuring the second harmonic generation in a BBO crystal placed at the location of the cuvette. A single-shot autocorrelator then continuously monitored the pulse duration. The pulse duration at the interaction region is about ~ 100 fs. Transmission measurements were always performed in an empty cuvette prior to each experiment to determine and minimize background errors resulting from any discrepancies between the photodiodes. The liquid samples were obtained by Sigma Aldrich and the crystal samples were obtained from MTI Corp., MSE Supplies and chiral quartz from Knight Optical. Fused silica was bought from SPI Supplies. The generation of the asymmetrical OAM beam and the OAM control were performed identically to the gas phase measurements.

2.2.10 BEAM WAIST MEASUREMENT

For our experimental measurements, it is crucial to know the minimum beam waist w_0 at the beam focus. This allows us to determine the fluence or the intensity at the interaction region as well as the displacement of singularity at the focus point. It is also a fundamental beam parameter to determine the beam Rayleigh range and the beam divergence. A common technique when using lenses to focus the laser beam is the knife edge method. However, for gas phase measurements such direct measurement of the focal point is difficult to perform in a gas chamber therefore it is often performed using an intensity calibration of an atom with well-documented saturation intensity such as argon or xenon.

2.2.10.1 SATURATED INTENSITY METHOD

The saturation intensity of argon was performed to determine the focal area in the interaction region. The intensity at which the saturation is reached is determined when the focal area no longer grows proportionally with the ionization count. The saturation can be found by determining the intersection between the ionization

curve slope and the 3/2 slope. the intersection defines the saturation intensity.

Determining accurately where this intersection point is can be difficult therefore the saturation point can be extrapolated more readily by using the linear tangent of the log plot of ionization signal count. The point at which this linear tangent intersects the x-axis is taken and compared with literature. By comparing the saturation energy of argon with its known value from literature, $\text{Ar} = 2.5^{14}\text{W}/\text{cm}^2$ and $\text{Xe} = 1.2 \times 10^{14}\text{W}/\text{cm}^2$, we can calculate the experimental intensity. The saturation point is obtained by the x-axis intercept of the linear fit of the saturation curve of argon. Using the saturation intensity value from literature of argon and comparing it with the inverse log of the saturation energy, we can calibrate the intensity accordingly. In figure 2.23, the linear fit to the semi-log plot is taken between the points with the least uncertainty between them. In this particular case, the curve intercept corresponds to an energy of $9.7 \mu\text{J}$ when the inverse log is taken. This value is used as a ratio with the energy being applied and then multiplied by the intensity value from literature to obtain a calibrated intensity. From the calibration intensity we can determine the beam waist using $I_{sat} = P_{peak}/\pi w_0^2$.

$$\frac{I_{sat}}{I} = \frac{E_{sat}}{E} \Rightarrow I = \frac{I_{sat}}{E_{sat}} E = \frac{2.5 \times 10^{14}\text{W}/\text{cm}^2}{9.7 \times 10^{-6}\text{J}} \times 1 \times 10^{-6}\text{J} = 2.6 \times 10^{13}\text{W}/\text{cm}^2 \quad (2.61)$$

$$I = \frac{E_{avg}}{\pi w_0^2 \Delta t} \Rightarrow w_0 = \sqrt{\frac{E_{avg}}{\pi I \Delta t}} = \sqrt{\frac{1 \times 10^{-6}\text{J}}{\pi(2.6 \times 10^{13}\text{W}/\text{cm}^2)(130 \times 10^{-15}\text{s})}} = 3 \times 10^{-6}\text{m} \quad (2.62)$$

2.2.10.2 KNIFE-EDGE METHOD

The incident Gaussian beam is focused by an aspherical lens of $\text{NA}=0.3$ resulting in a tight focus which can be measured by using a thin tapered blade that is translated across the transverse profile of the beam, in the x or y direction. The maximum power is achieved when the blade does not cover the beam and reaches a minimum when it is fully covered. The power is measured by a PD as a function of transverse position. As it progressively covers the beam the transmitted power decreases monotonically with a dependence related to integration of the power distribution. For a Gaussian,

$$P(x) = \frac{2P}{\pi w(z)^2} \int_{-\infty}^x e^{-\left(\frac{x-x_0}{w(z)}\right)^2} dx \int_{-\infty}^{\infty} e^{-\left(\frac{y}{w(z)}\right)^2} dy \quad (2.63)$$

the fitting function is for $x < x_0$ is $P(x) = P_0 + \frac{P}{2} \left(1 - \text{erf}\left(\frac{\sqrt{2}(x-x_0)}{w}\right)\right)$, where P_0 is a background power, P is the maximum power, x_0 is a position of shift with half of real power, erf is the error function [54]. For a Laguerre-Gaussian beam, the fitting function is similar to that of a Gaussian but with an inflection point at the center due to the singularity. The intensity distribution and the power curve are shown in figure 2.24. However,

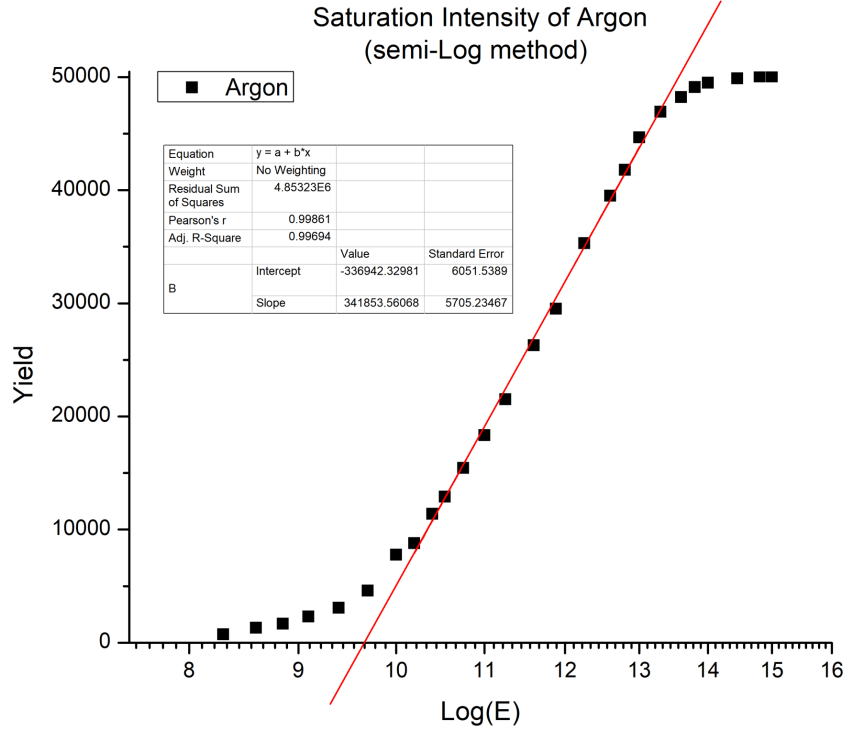


Figure 2.23: **Saturation intensity of argon at 800nm.** The figure shows the linear fit of a semi-log curve with an x-axis intercept of $9.7\mu\text{J}$. The resulting intensity for $1\mu\text{J}$ is $\sim 2.6 \times 10^{13} \text{W}/\text{cm}^2$ giving rise to an estimated beam waist of $3\mu\text{m}$.

the 2D transverse cross-section of the beam still has light transmitting through from the y -component when the knife reaches the null intensity at the x -component. Therefore, depending on the size of the singularity and the step size in x this inflection point could be negligible due to the light from the y -component reaching the detector.

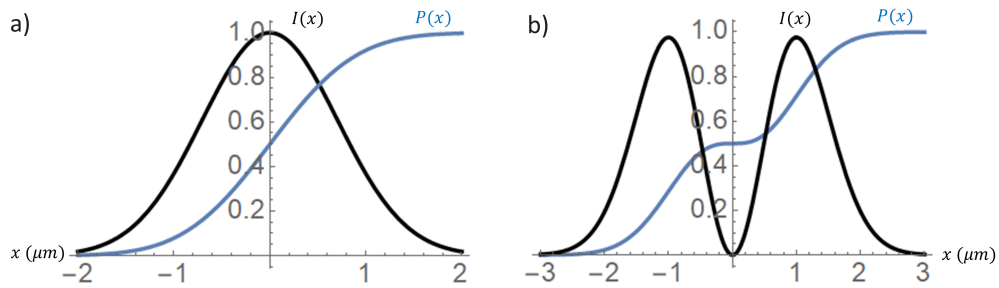


Figure 2.24: **Knife edge graphical representation:** For **a)** Gaussian beam ($l = 0$) and **b)** Laguerre-Gaussian beam ($l = 1$). The black curve is intensity distribution and the blue curve represents the knife edge power curve at the beam waist.

The fitting of this function gives the beam radius $w(z)$. This procedure is performed at various z -position within the Rayleigh range. All the values for the radius $w(z)$ are plotted with respect to the distance z and fitted with the hyperbolic relation between the beam waist and the z -position, given by $w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}$, where z_R is the Rayleigh range. Figure 2.25 shows a knife-edge measurement for an OAM beam with $l = 1$.

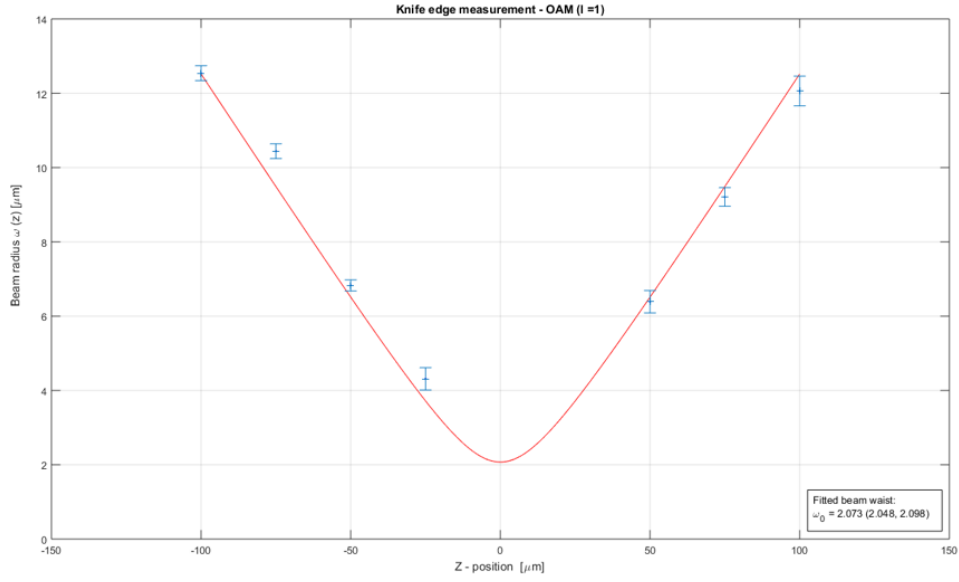


Figure 2.25: **Beam waist measurement:** Laguerre-Gaussian beam width $w(z)$ as a function of the z -direction along the beam. The beam waist is located at the minimum with a value $\sim 2\mu\text{m}$. Measurement was performed with an aspherical lens with $\text{NA}=0.3$.

WEAK- AND STRONG-FIELD LIGHT-MATTER INTERACTION

This chapter sets the theoretical groundwork for our models and results, focusing on light-matter interaction in both weak and strong field regimes. The weak field section provides details on the perturbative approach of light-matter interaction with a weakly perturbing field. It provides an overview of linear absorption, in relation to CD and ORD, and of nonlinear absorption, specifically MPA pursued using both microscopic and macroscopic approaches.

The strong-field section will discuss the non-perturbative approach, used when the light field strength becomes comparable to the atomic potential. It outlines the limitations of the perturbation regime at high intensities and introduces the concept of tunnel ionization as well as different types of strong-field ionization methods. Furthermore, recollision dynamics is analyzed via generated ions (non-sequential double ionization) or emitted high-harmonics of incident light.

3.1 NONLINEAR REGIME

The intense radiation from a laser can induce profound changes in the optical properties of a material. Nonlinear absorption denotes the variation in a material's transmittance based on intensity or fluence. At sufficiently high intensities, the probability of a material absorbing more than one photon before relaxing to the ground state increases significantly. To explain this optical activity, we venture into the field of nonlinear optics. Here, we examine the impact of the electric field on the refractive index and absorption coefficient to understand and describe the differences in transmission measurements between Gaussian and helical light in isotropic and anisotropic samples.

When polarized light with an optical-electrical field strength $\mathbf{E}$ irradiates matter, the electric charge of the molecule and atom oscillate under the influence of the incident electric field. The displacement of charges induces the emission of the electric field which is described by the electric polarization $\mathbf{P}$. For a weak laser field $\sim 10^6$ W/cm², the induced polarization depends linearly on the electric field amplitude, $\mathbf{P} = \varepsilon_0 \chi^{(1)} \cdot \mathbf{E}$. Where $\chi^{(1)}$ is a constant of proportionality known as the linear susceptibility, for an anisotropic medium it is a complex tensor quantity and ε_0 is the permittivity of vacuum.

With the advent of high-power lasers, the intensity of the laser light reached several orders of magnitude higher. The optical response of the material can be described by a generalized induced polarization with higher-order terms. The induced multipole terms derived in Chapter 1 and section 1.2.1.4 are related to the susceptibility via $\mathbf{P}^{(n)} = N \langle O \rangle_{nn} = \varepsilon_0 \sum_j \chi_{ij}^{(n)} E_j(\omega)$, where N is the number density of the atoms, O is the observable i.e. electric-dipole, electric quadrupole etc., $\chi_{ij}^{(n)}$ is the n th order susceptibility, and $E_j(\omega)$ is the electric field with frequency ω . The nonlinear polarization is achieved by expanding the electric polarization into a power series of the field strength [6, 55].

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} \cdot \mathbf{E} + \varepsilon_0 \chi^{(2)} : \mathbf{E}\mathbf{E} + \varepsilon_0 \chi^{(3)} \vdots \mathbf{E}\mathbf{E}\mathbf{E} + \dots \quad (3.1)$$

where $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are the first, second-, and third-order nonlinear susceptibilities, which are known as second-, third-, and fourth-rank tensor quantities, respectively. The symbols $\cdot$, $:$, $\vdots$ are the second-, third-, and fourth-rank tensor multiplication. We can denote the first term as the linear polarization $\mathbf{P}_L$ and the other terms as the higher-order nonlinear polarization $\mathbf{P}_{NL}$. Therefore, the total electric polarization is a sum of the linear and nonlinear terms, $\mathbf{P} = \mathbf{P}_L + \mathbf{P}_{NL}$ [6, 55]. For an isotropic homogeneous medium, the susceptibility can be written as a scalar quantity, then the electric polarization can be expressed as

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E} + \varepsilon_0 \chi^{(2)} |\mathbf{E}| \mathbf{E} + \varepsilon_0 \chi^{(3)} |\mathbf{E}|^2 \mathbf{E} + \dots \quad (3.2)$$

In the linear regime, the polarization of the medium is proportional to the field strength, however, for the

second-order (third-order) nonlinear polarization, the polarization of the medium is proportional to the square (triple) of the field strength and so on. Therefore, in the nonlinear regime, the polarization of the medium is no longer proportional to the field strength and intensity-dependent phenomena can arise. At high field strengths the parameters of the medium become a function of the optical field.

The electromagnetic field also contains a magnetic field which also has a polarization effect on the material known as magnetic polarization of the medium. This effect is often ignored for common materials however its contribution is significant for materials with broken symmetry, namely chiral molecules. The magnetic polarization ($\mathbf{M}$) for an isotropic homogeneous medium is expressed as

$$\mathbf{M} = \mu_0 \chi_m^{(1)} \mathbf{H} + \mu_0 \chi_m^{(2)} |\mathbf{H}| \mathbf{H} + \mu_0 \chi_m^{(3)} |\mathbf{H}|^2 \mathbf{H} + \dots \quad (3.3)$$

where μ_0 is the vacuum permeability, χ_m is the magnetic susceptibility, and the magnetic flux $\mathbf{B}$ is related to the magnetic field strength $\mathbf{H}$ via $\mathbf{B} = \mu_0 \mathbf{H}$ in vacuum.

3.1.1 WAVE EQUATION IN ABSORBING ISOTROPIC AND ANISOTROPIC NONLINEAR MEDIUM

Isotropic materials have optical properties that are uniform in all directions and anisotropic materials display different properties with the orientation of the sample. Gas, liquids and plastic are known to be isotropic where their susceptibility can be written as a scalar while crystalline solids are anisotropic and their susceptibilities are tensor quantities.

3.1.1.1 TIME DOMAIN

To understand the nonlinear absorption we must first describe the form of the wave equation for the propagation of electromagnetic fields through an anisotropic/isotropic nonlinear optical medium. We begin with Faraday's law and Ampere-Maxwell Law.

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{B}}{\partial t} \quad ; \quad \nabla \times \mathbf{B} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \quad (3.4)$$

Rearranging these equations and using the electric displacement, $\mathbf{D} = \hat{\epsilon} \cdot \mathbf{E} + \mathbf{P}_{NL}$, and current density $\mathbf{J} = \sigma \mathbf{E}$ we get

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, t) + \mu_0 \sigma \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} + \mu_0 \hat{\epsilon} \cdot \frac{\partial^2 \mathbf{E}(\mathbf{r}, t)}{\partial t^2} = -\mu_0 \frac{\partial^2 \mathbf{P}_{NL}(\mathbf{r}, t)}{\partial t^2} \quad (3.5)$$

This is the general time-domain wave equation for describing the transmission of the light wave in an absorbing anisotropic nonlinear medium. This equation can be expressed in a more common form by assuming that the nonlinear medium is an absorbent, homogeneous isotropic medium. Let the time and frequency space be related

by the Fourier transform, $\text{FT}[\mathbf{E}(\mathbf{r}, t)] = \mathbf{E}(\mathbf{k}, \omega)$ and denotes the light field strength of the monochromatic transverse plane wave (the component paralleled to $\mathbf{k}$ can be neglected). The wave equation can be reduced to the below differential equation given by

$$\nabla^2 \mathbf{E}(\mathbf{r}, t) - \mu_0 \sigma \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} - \frac{n^2}{c^2} \frac{\partial^2 \mathbf{E}(\mathbf{r}, t)}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \mathbf{P}_{\text{NL}}(\mathbf{r}, t)}{\partial t^2} \quad (3.6)$$

This is a time-domain second-order differential equation obtained by using $\nabla \cdot \mathbf{E} = 0 \rightarrow \nabla \times \nabla \times \mathbf{E} = -\nabla^2 \mathbf{E}$, the tensor quantity $\hat{\varepsilon}$ is written as a scalar ε , and by using the following relations $|\mathbf{k}| = k_0 n$, $k_0 = \omega/c$, $n = \sqrt{\varepsilon/\varepsilon_0}$. In general, it is difficult to solve this differential equation without any approximation. Suppose the variation of field strength incident on an optical medium changes very slowly in time and space compared to the light wavelength and optical frequency. By using the slowly varying envelope approximation, the second-order differential equation will transform into a first-order differential equation. To do so, assume a monochromatic plane wave field propagating along z -direction.

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(z, t) e^{i(kz - \omega t)}; \quad \mathbf{P}_{\text{NL}}(\mathbf{r}, t) = \mathbf{P}_{\text{NL}}(z, t) e^{i(k'z - \omega t)} \quad (3.7)$$

Solving the time component gives us

$$\begin{aligned} \left(\frac{\partial^2}{\partial z^2} + i2k \frac{\partial}{\partial z} - k^2 \right) \mathbf{E}(z, t) e^{i(kz - \omega t)} - \mu_0 \sigma \left(\frac{\partial}{\partial t} - i\omega \right) \mathbf{E}(z, t) e^{i(kz - \omega t)} \\ - \frac{n^2}{c^2} \left(\frac{\partial^2}{\partial t^2} - i2\omega \frac{\partial}{\partial t} - \omega^2 \right) \mathbf{E}(z, t) e^{i(kz - \omega t)} = -\frac{\omega^2}{\varepsilon_0 c^2} \mathbf{P}_{\text{NL}}(z, t) e^{i(k'z - \omega t)} \end{aligned} \quad (3.8)$$

Using the slowly varying envelope approximation condition, $\left| \frac{\partial^2 \mathbf{E}(z, t)}{\partial z^2} \right| \ll \left| k \frac{\partial \mathbf{E}(z, t)}{\partial z} \right|$ and $\left| \frac{\partial^2 \mathbf{E}(z, t)}{\partial t^2} \right| \ll \left| \omega \frac{\partial \mathbf{E}(z, t)}{\partial t} \right|$, equation 3.8 simplifies to get

$$\frac{\partial}{\partial z} \mathbf{E}(z, t) + \frac{1}{\omega} \left(k_0 + i \frac{\alpha_0}{2} \right) \frac{\partial}{\partial t} \mathbf{E}(z, t) + \frac{\alpha_0}{2} \mathbf{E}(z, t) = \frac{i\omega}{2\varepsilon_0 c n} \mathbf{P}_{\text{NL}}(z, t) e^{i\Delta k z} \quad (3.9)$$

where $\alpha_0 = (\mu_0 \sigma c)/n$ is the linear absorption coefficient of the medium and can be written in terms of the complex susceptibility of the material $\varepsilon_0 \chi^{(1)''}(\omega) = \sigma/\omega$. The difference in the wave vector represents the phase matching (momentum conservation) $\Delta k = k' - k$, where k , and k' are the wave vectors of the original light field and polarization field. For an absorbing isotropic medium $\Delta k = 0$. This equation is the time-domain wave equation when the monochromatic plane light wave propagates through an absorbent homogeneous nonlinear medium, and where the optical field strength $\mathbf{E}(z, t)$ satisfies the space and time slowly varying amplitude approximation condition [55].

3.1.1.2 FREQUENCY DOMAIN

It is sometimes easier to work in the frequency domain. To convert the wave equation the optical field $\mathbf{E}(z, t)$ and nonlinear polarization $\mathbf{P}_{NL}(\mathbf{r}, t)$ are represented as a discrete sum of frequency components [6, 55].

$$\text{FT}[\mathbf{E}(\mathbf{r}, t)] = \sum_p \mathbf{E}_p(\mathbf{k}_p, \omega_p) = \sum_p \mathbf{E}_p e^{i(\mathbf{k}_p \mathbf{r} - \omega_p t)}; \quad \text{FT}[\mathbf{P}_{NL}(\mathbf{r}, t)] = \sum_p \mathbf{P}_p^{NL}(\mathbf{k}'_p, \omega_p) = \sum_p \mathbf{P}_p^{NL} e^{i(\mathbf{k}'_p \mathbf{r} - \omega_p t)} \quad (3.10)$$

Substitute the frequency domain electric field and nonlinear polarization in the wave equation 3.6 and omit the sum and ordinal number p , for simplicity.

$$\nabla^2 \mathbf{E}(\mathbf{k}, \omega) + i\omega\mu_0\sigma\mathbf{E}(\mathbf{k}, \omega) + k^2\mathbf{E}(\mathbf{k}, \omega) = -\frac{k_0^2}{\varepsilon_0}\mathbf{P}_{NL}(\mathbf{k}', \omega) \quad (3.11)$$

Applying the spatial derivative, we get

$$\left(\frac{\partial^2}{\partial z^2} + i2k\frac{\partial}{\partial z}\right)\mathbf{E}(z, \omega)e^{ikz} + i\omega\mu_0\sigma\mathbf{E}(z, \omega)e^{ikz} = -\frac{k_0^2}{\varepsilon_0}\mathbf{P}_{NL}(z, \omega)e^{ik'z} \quad (3.12)$$

Once more, the light field satisfies the slowly varying field amplitude approximation condition, $\left|\frac{\partial^2 \mathbf{E}(z, \omega)}{\partial z^2}\right| \ll \left|k\frac{\partial \mathbf{E}(z, \omega)}{\partial z}\right|$. The terms having the second derivative can be omitted, and by combining the exponential factors we get

$$\frac{\partial \mathbf{E}(z, \omega)}{\partial z} + \frac{\alpha}{2}\mathbf{E}(z, \omega) = \frac{i\omega}{2\varepsilon_0 cn}\mathbf{P}_{NL}(z, \omega)e^{i\Delta k z} \quad (3.13)$$

This is the slowly varying amplitude approximation in frequency-domain nonlinear wave equation for absorbent homogeneous medium for the propagation of the monochromatic light wave along the z -direction [55]. Where we have a momentum conservation, phase phase matching condition, $\Delta k = k' - k$. For an absorbing isotropic medium $\Delta k = 0$. Equation 3.13 is used to obtain the multiphoton absorption differential equation used to describe the nonlinear transmission curves in section 3.1.4.

3.1.2 LINEAR REFRACTIVE INDEX

In the linear absorption regime, it is useful to define the linear refractive index and absorption coefficient in order to describe a linear transmission experiment. Consider a monochromatic plane wave with frequency ω propagating in an isotopic medium along an arbitrary direction, $\mathbf{E}(r, t) = \mathbf{E}(r) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + c.c.$, where $\mathbf{k}$ is a complex number known as the wave vector. It can be defined more commonly as $|\mathbf{k}| = \frac{n\omega}{c}$ where n is the index of refraction and is also complex value, $n = (n_0 + i\kappa)$, where n_0 is the real part of the index of refraction and κ is the imaginary part. From these relations, the real part of the wave vector $|\mathbf{k}'|$ is related to the refractive

index n_0 of the material and the its imaginary part $|\mathbf{k}''|$ is related to the absorption coefficient of the material $\alpha_0 = \frac{\omega}{c} \kappa$.

$$|\mathbf{k}| = |\mathbf{k}'| + i |\mathbf{k}''| = k_0 n_0 + i \frac{\alpha_0}{2} \quad (3.14)$$

where $k_0 = \omega/c$ is the vacuum wave vector and α_0 is the absorption coefficient for light intensity, therefore it's divided by 2. The above relation can be confirmed by substituting the complex index of refraction in the plane wave expression.

$$\mathbf{E}(r, t) = \mathbf{E}(r) e^{i \frac{\omega}{c} (n_0 + i \kappa) (\hat{\mathbf{k}} \cdot \mathbf{r}) - \omega t} + c.c. = \mathbf{E}(r) e^{-\frac{\omega}{c} \kappa (\hat{\mathbf{k}} \cdot \mathbf{r})} e^{i \mathbf{k}' \cdot \mathbf{r} - \omega t} + c.c. \quad (3.15)$$

By looking at the intensity of the plane wave, we can derive the Beer-Lambert law in the linear regime.

$$I(r) = I_0 e^{-2 \frac{\omega}{c} \kappa (\hat{\mathbf{k}} \cdot \mathbf{r})} = I_0 e^{-\alpha_0 (\hat{\mathbf{k}} \cdot \mathbf{r})} \quad (3.16)$$

The Beer-Lambert Law is a relationship between the attenuation of light as it propagates through a substance due to the absorption and scattering of light by the substance. The transmittance, T , of the solution is defined as the ratio of the absorbed intensity, I , over the incident intensity, I_0 and takes values between 0 and 1: $T = I/I_0$. The transmitted intensity is equal to the exponentially decaying incident intensity. There is an inherent exponential relationship between the ratio of the intensity of a monochromatic light beam incident on a sample, I_0 , and the transmitted intensity, I . The absorbance, A , of the solution, is related to the transmittance (incident and transmitted intensities) through the following relations: $A = \text{Log}_{10} \frac{I_0}{I} = -\text{Log}_{10} T$. A schematic of a linear transmission setup is shown in figure 3.1.

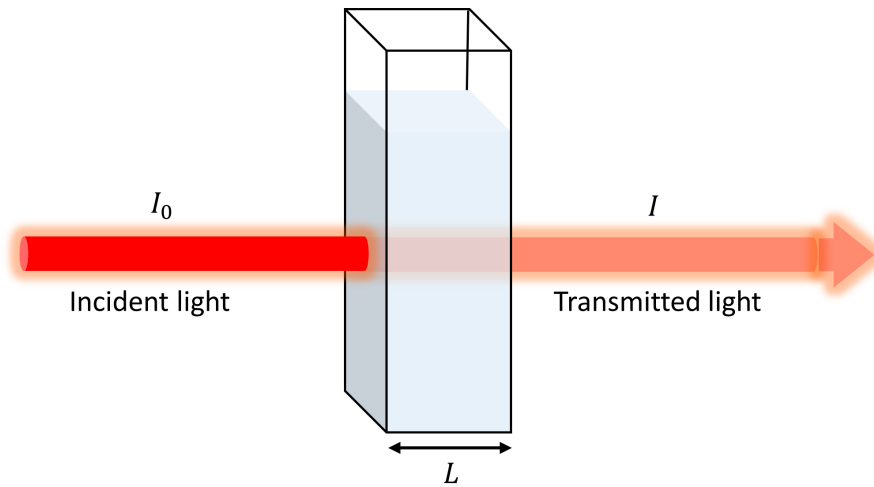


Figure 3.1: **Linear transmission:** Schematic representation of linear transmission through a liquid sample. I_0 is the incident light and I is the transmitted light, L is the thickness of the cuvette.

The linear absorption coefficient α_0 and the refractive index n_0 can be expressed in terms of the real

and imaginary linear susceptibility. This sets the scene for the nonlinear index of refraction and absorption coefficient. To do so, consider the linear polarization in the electric displacement field, $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}_L = \varepsilon_0 (1 + \chi^{(1)}(\omega)) \mathbf{E} = \varepsilon \mathbf{E}$. We can split the linear susceptibility of the medium into the real and imaginary parts: $\chi^{(1)} = \chi^{(1)'}(\omega) + i\chi^{(1)''}(\omega)$ and define the real part of the permittivity as $\varepsilon' = \varepsilon_0(1 + \chi^{(1)'}(\omega))$. Using this and the relation between the permittivity and refractive index, $n_0 = \sqrt{\varepsilon'/\varepsilon_0}$, we obtain

$$\varepsilon = n_0^2 \varepsilon_0 \left(1 + i \frac{\chi^{(1)''}(\omega)}{n_0^2} \right) \quad (3.17)$$

We can further use the complex linear refractive index, $n = \sqrt{\varepsilon/\varepsilon_0}$, and the speed of light, $c = 1/\sqrt{\mu_0 \varepsilon_0}$, to relate the permittivity to the complex wave vector of the medium, $|\mathbf{k}| = k_0 n = \frac{n\omega}{c} = \omega \sqrt{\mu_0 \varepsilon}$. Substituting both above expressions in equation 3.17 for the permittivity, we can obtain an expression for the wave vector in terms of susceptibility, $|\mathbf{k}| = k_0 n_0 \sqrt{1 + i \frac{\chi^{(1)''}(\omega)}{n_0^2}}$. The second term in the square root is much smaller than 1, allowing us to expand the square root as a Taylor's series.

$$|\mathbf{k}| \approx k_0 n_0 \left[1 + i \frac{\chi^{(1)''}(\omega)}{2n_0^2} \right] = k_0 n_0 + i \frac{k_0}{2n_0} \chi^{(1)''}(\omega) \quad (3.18)$$

Therefore, the real and imaginary parts of the wave vector can be expressed in terms of linear susceptibility which we can relate to the real and imaginary parts of the refractive index.

$$|\mathbf{k}'| = k_0 n_0 = \frac{\omega}{c} \sqrt{1 + \chi^{(1)'}(\omega)} \quad \text{and} \quad |\mathbf{k}''| = \frac{\alpha_0}{2} = \frac{k_0}{2n_0} \chi^{(1)''}(\omega) \quad (3.19)$$

The linear absorption coefficient can be extracted and related to Beer-Lambert's Law of transmittance.

$$I(r) = I_0 e^{-\alpha_0(\hat{\mathbf{k}} \cdot \mathbf{r})}, \quad \text{where} \quad \alpha_0 = \frac{\omega}{cn_0} \chi^{(1)''}(\omega) \quad (3.20)$$

The absorption coefficient is related to the imaginary term of linear susceptibility. The absorption coefficient and the index of refraction are related via the Kramers-Kronig relation given by equation 1.7.

3.1.3 NONLINEAR REFRACTIVE INDEX

For a nonlinear absorption process, when two or more photons are absorbed simultaneously, we can define the nonlinear refractive index and absorption coefficient in terms of nonlinear susceptibilities. Let's consider a two-photon absorption, which is a third-order nonlinear process. The nonlinear polarization, $\mathbf{P}_{NL}$ can be expressed as the third-order nonlinear polarization term and is sometimes called the optical Kerr effect.

$$\mathbf{P}^{(3)}(z, \omega) = 3\varepsilon_0 \chi^{(3)}(\omega) |\mathbf{E}(z, \omega)|^2 \mathbf{E}(z, \omega) = 3\varepsilon_0 \left[\chi^{(3)'}(\omega) |\mathbf{E}(z, \omega)|^2 + i\chi^{(3)''}(\omega) |\mathbf{E}(z, \omega)|^2 \right] \mathbf{E}(z, \omega) \quad (3.21)$$

where the complex third-order susceptibility is expanded to explicitly show the real and imaginary contribution for an isotropic medium, $\Delta k = 0$. $\mathbf{E}(\mathbf{r})$ is solved by implementing the slowly varying amplitude approximation nonlinear wave equation, $\frac{\partial \mathbf{E}(z)}{\partial z} = \frac{i\omega}{2\varepsilon_0 cn_0} \mathbf{P}_{NL}(z)$.

$$\frac{\partial \mathbf{E}(z)}{\partial z} = \frac{i3\omega}{2cn_0} \left[\chi^{(3)'}(\omega) |\mathbf{E}(z)|^2 + i\chi^{(3)''}(\omega) |\mathbf{E}(z)|^2 \right] \mathbf{E}(z) \quad (3.22)$$

Using the expression for intensity $I = \frac{1}{2}\varepsilon_0 cn_0 |\mathbf{E}(z)|^2$. The solution of the nonlinear differential equation becomes

$$\frac{\partial \mathbf{E}(z)}{\partial z} = i|\mathbf{k}_{NL}| \mathbf{E}(z) \Rightarrow \mathbf{E}(z) = \mathbf{E}(0)e^{i|\mathbf{k}_{NL}|z} \quad \text{where} \quad |\mathbf{k}_{NL}| = 3k_0 \frac{\chi^{(3)'}(\omega)}{\varepsilon_0 cn_0^2} I + i3 \frac{\omega \chi^{(3)''}(\omega)}{\varepsilon_0 c^2 n_0^2} I \quad (3.23)$$

Where the total wave vector is $|\mathbf{k}_T| = |\mathbf{k}| + |\mathbf{k}_{NL}|$ and can be divided into the real and imaginary part corresponding respectively to the total refractive index n and the absorption α . The total refractive index and the total absorption coefficient can be divided into linear and nonlinear terms.

$$|\mathbf{k}_T| = |\mathbf{k}'_T| + i|\mathbf{k}''_T| = k_0 n + i\frac{\alpha}{2} \quad \text{where} \quad n = n_0 + \Delta n, \quad \alpha = \alpha_0 + \Delta \alpha \quad (3.24)$$

Using the expression for $|\mathbf{k}_T|$ and substituting all expression for the linear and nonlinear index of refraction as well as absorption coefficient we obtain, $|\mathbf{k}_T| = k_0 n_0 + k_0 \Delta n + i\frac{\alpha_0}{2} + i\frac{\Delta \alpha}{2}$.

$$|\mathbf{k}_T| = \underbrace{k_0 n_0 + i\frac{\alpha_0}{2}}_{|\mathbf{k}|} + \underbrace{3k_0 \frac{\chi^{(3)'}(\omega)}{\varepsilon_0 cn_0^2} I + i3 \frac{\omega \chi^{(3)''}(\omega)}{\varepsilon_0 c^2 n_0^2} I}_{|\mathbf{k}_{NL}|} \quad (3.25)$$

where we obtain the nonlinear terms for refractive index and absorption coefficient

$$\Delta n = \frac{3}{\varepsilon_0 cn_0^2} \chi^{(3)'}(\omega) I \quad \text{and} \quad \Delta \alpha = \frac{6\omega}{\varepsilon_0 c^2 n_0^2} \chi^{(3)''}(\omega) I \quad (3.26)$$

3.1.4 MULTIPHOTON PROCESS

Nonlinear absorption can be described by MPA where two or more photons are simultaneously absorbed by the nonlinear medium. To start, consider a two-photon absorption, a third-order nonlinear optical effect in an absorbent nonlinear isotropic medium, let $\Delta k = k' - k = 0$. This nonlinear process is described by the nonlinear wave equation defined by equation 3.13.

$$\frac{\partial \mathbf{E}(z, \omega)}{\partial z} + \frac{\alpha}{2} \mathbf{E}(z, \omega) = \frac{i\omega}{2\varepsilon_0 cn} \mathbf{P}^{(3)}(z, \omega) \quad (3.27)$$

If the intensity of a monochromatic beam with frequency ω is sufficient for two-photon absorption, then the

wave equation is given by

$$\frac{\partial \mathbf{E}(z, \omega)}{\partial z} + \frac{\alpha}{2} \mathbf{E}(z, \omega) = \frac{i3\omega}{2cn_0} \chi^{(3)}(\omega) |\mathbf{E}(z, \omega)|^2 \mathbf{E}(z, \omega) \quad (3.28)$$

By multiplying both LHS and RHS of equation 3.28 with the conjugate of the complex electric field, and using the intensity relation $I = \frac{1}{2} c \varepsilon_0 n_0 |\mathbf{E}|^2$ as well as the imaginary part of the third-order susceptibility we obtain the two-photon differential equation for absorption expressed in terms of intensity.

$$\frac{\partial I(z)}{\partial z} = -\frac{1}{2} \left[\alpha_0 + \frac{6\omega}{\varepsilon_0 c^2 n_0^2} \chi^{(3)''}(\omega) I(z) \right] I(z) \quad (3.29)$$

This is an extension to the Beer-Lambert law as it includes the first order nonlinear absorption coefficient $\alpha_2 = \frac{6\omega}{c^2 n_0^2 \varepsilon_0} \chi^{(3)''}(\omega)$ written in terms of the third order susceptibility, derived earlier in equation 3.26. The two-photon differential absorption equation is now expressed as

$$\frac{dI(z)}{dz} = -\alpha_0 I(z) - \alpha_2 I(z)^2 \quad (3.30)$$

We can generalize the above equation to multiphoton absorption, by considering higher-order MPA such as three-photon absorption which is a fifth-order nonlinear process and so on so forth [6, 56].

$$\frac{dI(z)}{dz} = -\sum_{n=1} \alpha_n I^n(z) = -\alpha_1 I(z) - \alpha_2 I^2(z) - \alpha_3 I^3(z) - \dots \quad (3.31)$$

The summation is over the number of photons absorbed by the nonlinear medium and $\alpha_1, \alpha_2, \alpha_3 \dots$ are the absorption coefficient for $(1, 2, 3 \dots) \hbar\omega$ simultaneous photon absorption. We can use this nonlinear Beer Lambert's law to describe the experimental nonlinear transmission curves which can be used to determine the absorption coefficient of the material and extract the n-photon cross-section of the material.

In the case of a pulse of light propagating through a medium, there is absorption as well as an additional phase delay, $\theta(\omega) = n(\omega)k_0L$, to the transmitted light due to the difference in optical path length between the frequencies, $\tilde{\mathbf{E}}(z, \omega) = \mathbf{E}(z, \omega)e^{-i\theta(\omega, z)}$. Therefore, the frequency-domain wave equation can be split into the nonlinear absorption part given by equation 3.28 and the nonlinear phase delay given by

$$\frac{\partial \theta(z)}{\partial z} = \frac{\omega}{2cn_0} \chi^{(1)'} + \frac{3\omega}{2cn_0} \chi^{(3)'}(\omega) |\mathbf{E}(z, \omega)|^2 \rightarrow \frac{\partial \theta(z)}{\partial z} = \frac{\omega}{2cn_0} \chi^{(1)'} + \frac{3\omega}{\varepsilon_0 c^2 n_0^2} \chi^{(3)'}(\omega) I(z) = \frac{\omega}{c} n_1 + \frac{\omega}{c} n_2 I(z) \quad (3.32)$$

where $n_2 = \frac{3}{\varepsilon_0 c n_0^2} \chi^{(3)'}(\omega)$ is the two-photon nonlinear index of refraction. For the multiphoton process, we can

generalize the above phase delay expression 3.32 to an n -photon process [56].

$$\frac{d\theta(z)}{dz} = \frac{\omega}{c} \sum_{n=1} n_n I^{n-1}(z) = \frac{\omega}{c} [n_1 + n_2 I(z) + n_3 I^2(z) - \dots] \quad (3.33)$$

Therefore, we have two differential equations describing the nonlinear process, one for absorption and another for phase delay.

3.1.4.1 MULTIPHOTON ABSORPTION

The subject of MPA has been pursued theoretically using both microscopic and macroscopic approaches. In the former, one calculates the MPA coefficients from the multiphoton-induced electronic transition probabilities. This is the general approach and was used for our article on nonlinear helical dichroism given in section 4 and 5. In the latter approach, the MPA coefficients are obtained from the imaginary parts of the higher-order nonlinear susceptibilities and are a common method to describe nonlinear absorption. In this section, the macroscopic approach is briefly shown to compare the nonlinear absorption of Gaussian and OAM light validate our experimental transmission curves as well as identify certain key features.

By integrating the n -photon absorption equation of 3.31 we get an expression for the transmitted intensity as

$$I(z) = \frac{I_0(z)}{\left(1 + (n-1)\alpha_n L(1-R)^{(n-1)}I_0^{(n-1)}\right)^{\frac{1}{(n-1)}}} \quad (3.34)$$

where n is the number of photons, L is the sample thickness and R represents the sum of the Fresnel reflection losses at the surface of the sample. This expression is true when the simultaneous absorption of n -photon is described by a plane wave with optical path length z . However, our experiments are performed for pulsed Gaussian or OAM beam profiles. So, we must explicitly take into account the variation of the incident intensity profile in time and space, $I(x, y; t)$. Therefore, an integration over all time and space is required to get the transmitted pulse energy.

The transmission T of the sample is given by the ratio of the transmitted intensity I and incident intensity I_0 : $T = I/I_0$. An important consequence is the change of intensity inside the sample. The intensity inside the sample I' is related to the free-space intensity $I = (1-R)I'$ where R is the Fresnel reflectivity given by $R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$ and where n and κ are the real and imaginary parts of the refractive index [57–59]. The transmission expression for a light pulse with a beam profile is

$$T = \frac{(1-R)^2}{E_0} \int_{-\infty}^{\infty} 2\pi \int_0^{\infty} \frac{I_0(r, t)}{\left(1 + (n-1)\alpha_n L(1-R)^{(n-1)}I_0^{(n-1)}(r, t)\right)^{\frac{1}{(n-1)}}} r dr dt \quad (3.35)$$

In our experiments, the incident pulse shape, $I_0(r, t)$, was either a Gaussian or a LG ($l, p = 0$) beam in space

and a hyperbolic secant squared in time [57, 58]. The beam profile has the form

$$\underbrace{I_0(r, t) = I_0 e^{-4\ln 2 \frac{r^2}{w_0^2}} \operatorname{sech}^2 \left(2\ln(1 + \sqrt{2}) \frac{t}{t_p} \right)}_{\text{Gaussian beam}(l=0)} \quad \text{or} \quad \underbrace{I_0(r, t) = I_0 \frac{1}{|l|!} \left(\frac{r\sqrt{2}}{w_0} \right)^{2|l|} e^{-4\ln 2 \frac{r^2}{w_0^2}} \operatorname{sech}^2 \left(2\ln(1 + \sqrt{2}) \frac{t}{t_p} \right)}_{\text{Laguerre-Gaussian beam}(l \neq 0)} \quad (3.36)$$

where w_0 is the FWHM beam waist, $I_0 = 2P_l/\pi w_0^2$ is the peak intensity and P_l is the peak power for $l = 0, 1, 2, \dots$, and t_p is the pulse duration at FWHM. Details of these beams were given in Chapter 2 section 2.1. The total energy E_0 contained in the pulse can be obtained by integrating the pulse over time and space. The relation between peak intensity and pulse energy for a Gaussian ($l = 0$) is given by $I_0 = E_0(l = 0) \frac{4\ln 2 \ln(1 + \sqrt{2})}{\pi w_0^2 t_p}$ and for a Laguerre-Gaussian beam of order ($l = 1, p = 0$) by $I_0 = E_0(l = 1) \frac{4\ln 2 \ln(1 + \sqrt{2})}{\pi w_0^2 t_p} e^{-1}$, where $E_0(l = 0, 1)$ represents their respective incident energies.

Figure 3.2 a) shows simulated curves of nonlinear absorption with a Gaussian beam for various multiphoton processes. Higher incident pulse energy is required to kick start the nonlinear absorption as the number of photons absorbed increases. That is, higher pulse energy is required to reach the threshold for nonlinear onset as you increase the number of photon absorption. This was also observed experimentally (not shown).

Figure 3.2 b) depicts the difference between the nonlinear absorption of a Gaussian and a symmetric LG beam with different l -value for a six-photon process. For a beam with orbital angular momentum the threshold for nonlinear onset is also reached at higher pulse energies. Moreover, this effect increases as the OAM value increases. This was also observed experimentally, see the transmission curves of Limonene for $l = 0, 1, 3$ in figure 3.3. It also depicts the influence of the left- and right-handed asymmetrical OAM beams on the nonlinear absorption which is the cause of helical dichroism. More information is given in Chapter 4 section 4.2, transmission measurement of OAM beams.

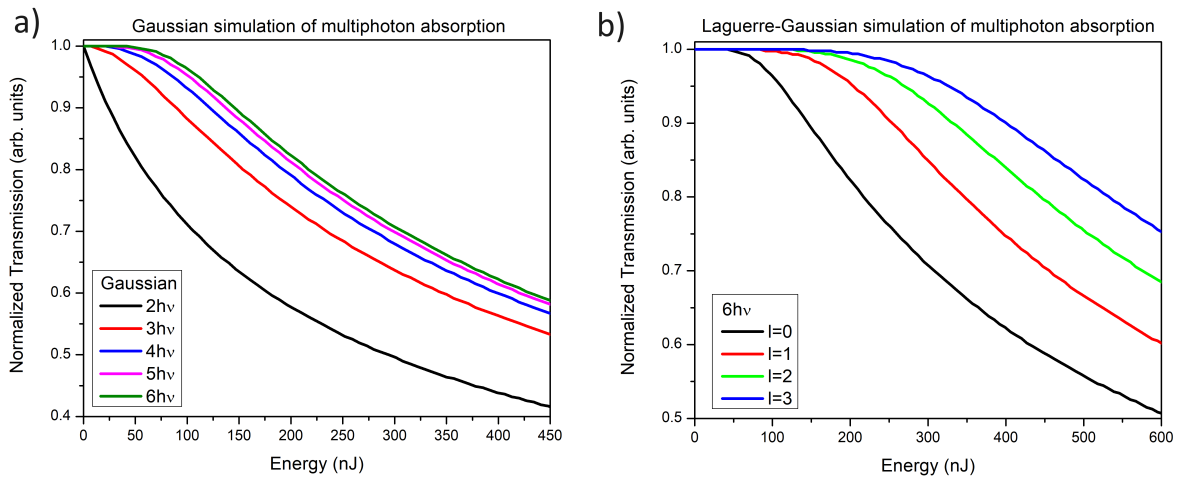


Figure 3.2: **Simulated transmission curves** for a) various n-photon absorption of Gaussian beam ($l = 0$) and b) for different l -value of LG beam ($l \neq 0$).

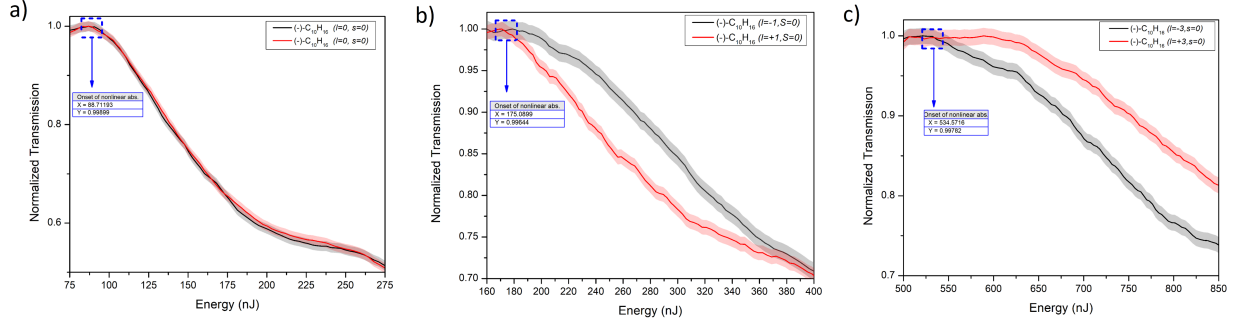


Figure 3.3: **Experimental transmission curves** of limonene for $l = 0, 1, 3$ depicting the change in the necessary energy for the nonlinear onset.

It is important to note that for LG beams the size of the null intensity region increases with increasing l -value. Consequently, for the same spot size higher pulse energies are required to reach the threshold for the onset of nonlinear absorption. However, the peak fluence and intensity remain the same for all l -values. From the threshold energies and peak power, the l -dependent peak fluence and the intensity can be calculated based on the following equations [60]:

$$F_l \left[\frac{J}{cm^2} \right] = \frac{2^{(|l|+1)} r^{2|l|} e^{\frac{-2r^2}{w(z)^2}}}{|l|! \pi w(z)^{2(|l|+1)}} E_l [J] \quad I \left[\frac{W}{cm^2} \right] = \frac{2^{(|l|+1)} r^{2|l|} e^{\frac{-2r^2}{w(z)^2}}}{|l|! \pi w(z)^{2(|l|+1)}} P_l [W] \quad (3.37)$$

where $l = 0; \pm 1; \pm 2; \pm 3 \dots$ is the orbital angular momentum value, r is the radial direction, $w(z)$ is the radius of a beam evaluated at z and E_l is the threshold pulse energy, and P_l is the peak power for different l -values. The peak fluence can be obtained by evaluating the radial parameter r at the maxima of the intensity profile, which occurs when $r_l^2 = w_0^2 |l|/2$. So, for a Gaussian beam ($l = 0$) $r = 0$, and at for OAM beam with $l = 1$ $r_1 = \pm \frac{w_0}{\sqrt{2}}$ and so on.

These transmission calculations can be performed using aLG beams and compared with experimental measurements of quartz. Figure 3.4 a) and b) are the experimental transmission curves and the simulated curves for a linearly polarized Gaussian beam, symmetric LG beam and a positive and negative displacement of the singularity of an aLG beam. It depicts the change in the transmission due to the l -value and the displacement parameter δ . However, the difference between the left- and right-handed helicity for a specific δ -position cannot be directly observed due to the intensity profile being independent of the handedness.

Nonetheless, the absorption coefficient for left- and right-displacement of singularity or handed helical light can be extracted from a material provided you fit the theoretical transmission curve to the experimental data in figure 3.5. By fitting the curve to quartz data it is possible to extract the 6-photon cross-section through the relation of the macroscopic and microscopic approach of MPA.

The absorption coefficient is extracted by relating the macroscopic and microscopic approach of MPA via the n -photon absorption coefficient α_n and is related to the n -photon transition rate per unit volume $W_{mg}^{(n)}$ through $\frac{dI}{dt} = \frac{dN_{ph}}{dt} \hbar\omega = \alpha_n I^n \rightarrow \frac{dN_{ph}}{dt} = \frac{\alpha_n}{\hbar\omega} I^n$ [61]. The n -photon absorption cross-section σ_n is related to the

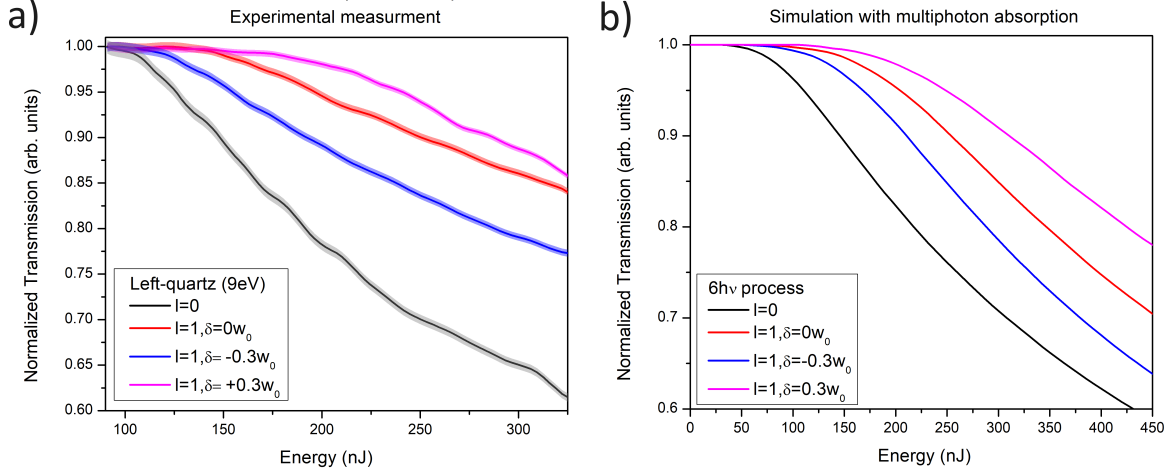


Figure 3.4: **Experimental and simulated transmission curves.** **a)** Experimental measurement of left-quartz (z-cut) for a Gaussian beam ($l = 0$) in black, for symmetric OAM beam ($l = +1, \delta = 0$) in red, and for asymmetric OAM beam ($l = +1, \delta = \pm 0.3w_0$) in blue and magenta. **b)** Simulated transmission for a 6-photon process for Gaussian beam ($l = 0$) in black, for symmetric LG beam ($l = +1, \delta = 0$) in red, and for asymmetric LG ($l = +1, \delta = \pm 0.3w_0$) in blue and magenta. $w_0 = 2\mu\text{m}$ and is the beam waist at the focus measured by the knife-edge technique.

n -photon absorption coefficient via $\alpha_n = N\sigma_n$ where N is the atomic number density. Using

$$\sigma_{mg}^{(n)} = \left(\frac{\hbar\omega}{I} \right)^n W_{mg}^{(n)} \quad (3.38)$$

we can calculate the n -photon cross-section and compare it with the experimental values. The incident radiation intensity is given by $I = \frac{1}{2}n\varepsilon_0 c |E|^2$, $\hbar\omega$ is the photon energy, and $W_{mg}^{(n)}$ is the n -photon transition rate from ground state ($|g\rangle$) to final state ($|m\rangle$). The non-dipole transition rate for n -photon can be obtained from time-dependent perturbation theory and is shown in the supplementary of "nonlinear helical dichroism in chiral and achiral molecules", chapter 3 section 4.4. However, in this case, we extract the absorption coefficient by considering only the dominant interaction to the cross-section.

$$W_{mg}^{(n)} = 2\pi \left| \sum_p \sum_l \dots \sum_r \sum_k \frac{\mu_{\alpha}^{mp} \mu_{\alpha}^{pl} \dots \mu_{\alpha}^{rk} \mu_{\alpha}^{kg} |E_{\alpha}|^n}{\hbar^n (\omega_{pl} - (n-1)\omega) \dots (\omega_{rk} - 2\omega) (\omega_{kg} - \omega)} \right|^2 \rho(\omega_{mg} = n\omega) \quad (3.39)$$

where the n -photon cross-section is defined as

$$\sigma_{mg}^{(n)} = 2\pi \left| \sum_p \sum_l \dots \sum_r \sum_k \frac{\mu_{\alpha}^{mp} \mu_{\alpha}^{pl} \dots \mu_{\alpha}^{rk} \mu_{\alpha}^{kg}}{\hbar^n (\omega_{pl} - (n-1)\omega) \dots (\omega_{rk} - 2\omega) (\omega_{kg} - \omega)} \right|^2 \left(\frac{2\hbar\omega}{n\varepsilon_0 c} \right)^n \rho(\omega_{mg} = n\omega) \quad (3.40)$$

We can perform a numerical estimate of $\sigma_{mg}^{(6)}$ of quartz for a symmetric and asymmetric OAM beam. By assuming the photon transition is highly non-resonant ($\omega_{ij} - \omega \approx \omega$), where ij represents the virtual states. We also assume the laser frequency is tuned to the peak of the six photon resonance, so that $\rho(\omega_{mg} = n\omega) \approx (2\pi\Gamma_m)^{-1}$, where $\Gamma_m \approx 2\pi \times 10^{13} \text{ rad/sec}$ is the width of level $|m\rangle$ [6]. The dipole moments are of order $ea_0 = 8 \times 10^{-30} \text{ Cm}$. These

values were used to calculate the two-photon absorption cross-section, $\sigma_{mg}^{(2)} \approx 2.1 \times 10^{-58} \frac{m_s^4}{\text{photon}^2}$ [6] and was experimentally measured to be 1.1×10^{-54} [62]. Following this similar approach, we obtain $\sigma_{mg}^{(6)} \approx 3 \times 10^{-205}$ for the six-photon cross-section which does not have an l -dependence because we considered only the dipole moment. Nonetheless, it can serve as a comparison to the measure experiment results of figure 3.5.

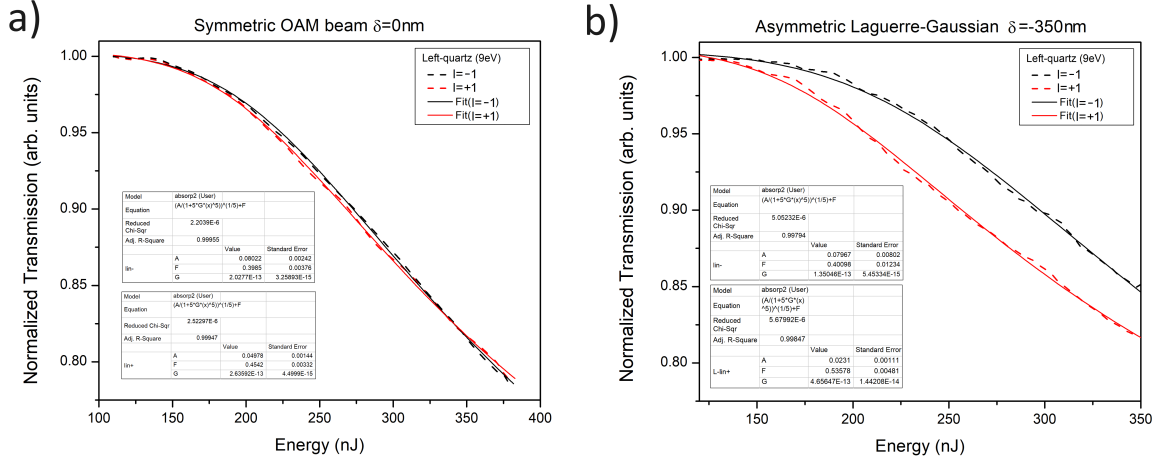


Figure 3.5: **Quartz six-photon absorption cross-section.** **a)** Experimental measurement (dashed line) and theoretical fit (solid line) of left-quartz (z-cut) for **a)** symmetric OAM beam ($l = +1, \delta = 0nm$) in red and ($l = -1, \delta = 0nm$) in black and for **b)** asymmetric OAM beam ($l = +1, \delta = -350nm$) in red and ($l = -1, \delta = -350nm$) in black.

The experimental six-photon cross-section can be extracted from the transmitted intensity fit of figure 3.35 for a symmetric (a) and asymmetric (b) LG beam of order ($l = 1$). According to our fit, the six-photon absorption cross-section is defined as $\sigma^{(6)} = G(\pi w_0 \Delta t)^5 (\hbar \omega)^5 = G (\hbar \omega)^5 \times 10^{-100}$, where w_0 is the beam waist and Δt is the pulse duration. The fitting parameter G for a symmetric left- and right-handed OAM beam is $G(\delta = 0nm)_{l=\pm 1} \approx 2 \times 10^{-13}$ and for the left- and right-handed asymmetric OAM beam are $G(\delta = -350nm)_{l=-1} \approx 1 \times 10^{-13}$ and $G(\delta = -350nm)_{l=+1} \approx 5 \times 10^{-13}$. With these fitting parameters, we can determine the six-photon cross-section. For a symmetric OAM beam, the cross-section is roughly $\sigma_{l=\pm 1}^{(6)}(\delta = 0nm) \approx 2 \times 10^{-206}$ for both handedness (no difference in absorption is observed) and for an asymmetrical OAM beam the cross-sections of $l = -1$ and $l = +1$ are different, $\sigma_{l=-1}^{(6)}(\delta = -350nm) \approx 9 \times 10^{-207}$ and $\sigma_{l=+1}^{(6)}(\delta = -350nm) \approx 4.5 \times 10^{-206}$. Note, the measured cross-sections are near the estimated value $\sigma_{mg}^{(6)} \approx 3 \times 10^{-205}$ obtained from equation 3.40. These are just approximations of the cross-sections however, they serve the purpose of showing that the rate of absorption for left- and right-handed asymmetric OAM beams are different while similar for a symmetric OAM beam.

Although there is a difference in the six-photon absorption cross-sections for left- and right-handed asymmetric OAM beam their values are quite small. At these experimental intensities, it becomes more and more unlikely that this process is purely in the multiphoton perturbative regime. At the experimental intensity range, it is hard to distinguish between multiphoton and tunnel ionization, in fact, the most dominant term is a product of both [63, 64]. Moreover, the intensity profile of LG beams does not show l -dependence, therefore the macroscopic approach might become extensively difficult to explain the physical process of helical phase-

dependent absorption if one relies only on the extraction of the multiphoton absorption coefficient. Additionally, the macroscopic approach describes some features in the intensity-dependent absorption but does not explain the physical cause of this chiroptical effect nor does it allow to directly simulate the helical dichroism. Therefore, the future work in chapter 4 and 5 will focus on the multiphoton absorption rate via the microscopic approach in the perturbative and non-perturbative regimes.

3.2 EXTREME NONLINEAR REGIME

Irradiation of an atom or a molecule by an intense laser pulse can cause the valence electron to overcome or tunnel through the potential barrier and transition into the continuum, leading to ionization. This process occurs when the laser field strength is comparable to the Coulomb field of the atom or molecule and directly interacts with the molecular potential. This non-resonant strong field ionization is significantly impacted by the peak of the laser field and the incident wavelength.

3.2.1 BREAKDOWN OF PERTURBATIVE APPROACH

When the laser field intensity reaches a level such that the ponderomotive potential of an electron within that field approaches the atomic and molecular Coulomb potential, the fundamental assumption of perturbation theory breaks down. Essentially, perturbation theory assumes that an atom or molecule will be only slightly disturbed by an external force. When perturbation fails, the concept of n th-order transitions describing the transition from an initial to a final state via intermediate states must be abandoned. Although in some strong-field theories, the notion of n -photon absorption is still assumed but is only useful when the incident intensity is within the indeterminate regime between multiphoton and tunnel ionization.

In a strong and low-frequency laser field, it is practical to think of ionization as a bending of the atomic potential by the quasi-static electric field of the laser. The electron can then pass over the suppressed atomic potential, or tunnel through the barrier. For strong-fields this mechanism for ionization replaces the common concept of the absorption of a discrete number of photons by the atom through the excited electronic states.

Most nonlinear phenomena assume that the material polarization can be expanded as a power series in the applied complex electric field amplitude as mentioned in section 3.1.

$$\tilde{P}(t) = \chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}(t)^2 + \chi^{(3)} \tilde{E}(t)^3 + \dots \quad (3.41)$$

At significantly large field strengths, this power series expansion does not converge. This perturbation breakdown occurs if the laser field strength is comparable to or larger than the atomic field strength resulting in a value greater than the power series radius of convergence. To elucidate this concept, consider the simplest power

series, a geometric series that converges when $|x| < 1$ and diverges when $|x| > 1$.

$$f(x) = \sum_{n=0}^{\infty} x^n \Rightarrow \frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots, |x| < 1 \quad (3.42)$$

Therefore, the accuracy of the answer will increase as the value of n increases, as long as it is within the radius of convergence [65]. While outside the radius of convergence, the left-hand side, $1/(1-x)$, will yield negative values while the right-hand side of the equality will exhibit positive values. Hence, this series will no longer converge. Extending this concept to the nonlinear polarization expansion we can determine when the series no longer converges.

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}(t)^2 + \chi^{(3)}\tilde{E}(t)^3 + \dots = \sum_{n=0}^{\infty} \chi^{(n+1)}\tilde{E}(t)^{(n+1)} \quad (3.43)$$

The n th term of the series goes to zero as $n \rightarrow \infty$. Therefore, there exist an integer N such that $|\chi^{(n+1)}\tilde{E}(t)^{(n+1)}| \leq 1$ for all $n \geq N$. The series converges for all x such that $|x| \leq |R|$, where R is a real number. For a geometric series $\sum_{n=N}^{\infty} |\frac{\tilde{E}(t)}{R}|^{n+1}$ the convergence is $|\frac{\tilde{E}(t)}{R}| \leq 1$. Thus, the power series of the nonlinear polarization converges for $|\tilde{E}(t)| \leq |R|$, where R represents the atomic field strength of the perturbed atom or molecule. That is, when $\tilde{E}(t) \sim E_{at} = \frac{1}{4\pi\epsilon_0} \frac{e}{a_0}$ the power series approximation breaks down.

3.2.1.1 CRITICAL INTENSITY

In a quasi-static external field of magnitude E_0 in the x -direction, the total potential energy for a hydrogenic electron is $V(x) = -\frac{e^2}{4\pi\epsilon} \frac{1}{x} - exE_0 \sin(\omega t)$. The external field has its greatest influence when $\sin(\omega t) = 1$. The potential gets bent by the electric field resulting in a saddle point located at distance x and energy V_0 . The position and value of this energy is found by $\partial V / \partial x = 0$, where $x = \sqrt{\frac{e^2 Z}{4\pi\epsilon_0}} \sqrt{\frac{1}{E_0}}$, where Z is the nuclear charge number. The energy at this point is $V = -2\sqrt{\frac{e^3 Z E_0}{4\pi\epsilon_0}}$. We can determine the "critical" field strength needed to ionize the atom by considering the situation where the external field pushes the saddle point down to the level of the ground state, therefore the energy of the saddle point is now equal to the binding energy $|V_0| = I_p$. For a hydrogen atom ($Z = 1$) the binding expression is known as $I_p = \frac{me^4 Z^2}{2n^2 \hbar^2 (4\pi\epsilon_0)^2}$. The critical field strength is $E_{cr} = \frac{I_p^2}{4} \frac{4\pi\epsilon_0}{e^3 Z}$. After simplification for a hydrogen atom, the critical field strength is 1/16 of the atomic field strength [65].

$$E_{cr} = \frac{e}{4\pi\epsilon_0} \frac{1}{16a_0^2} = \frac{1}{16} E_{at} \quad (3.44)$$

This means that a field strength of only one-sixteenth of the binding Coulomb field is sufficient to create a saddle point low enough for an electron to easily escape. This results in a critical intensity of $I_{cr} \sim 1.4 \times 10^{14} \text{ W/cm}^2$, an intensity far below the atomic intensity $I_{at} \sim 3.5 \times 10^{16} \text{ W/cm}^2$ of hydrogen. Thus, the atomic structure can be significantly distorted resulting in an interaction too strong to be treated as perturbatively. Therefore,

a ground state electron can tunnel through the barrier and reach the continuum see figure 3.6.

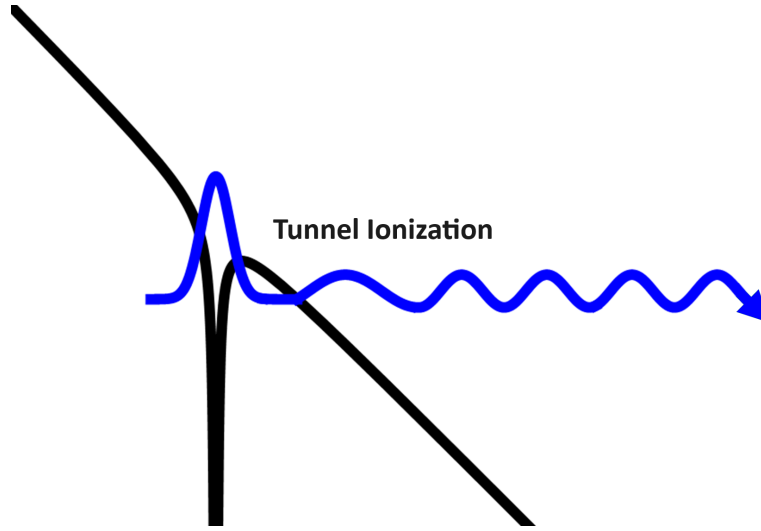


Figure 3.6: **Tunnel ionization:** The laser field strength is strong enough to distort the atomic potential and allow the ground state electron's wavefunction to tunnel through the barrier.

Strong-field physics originates from three main experimental observations that could not be properly explained using the common perturbative approach. i) The plateau of high-order harmonics and the drastic cutoff. ii) The non-sequential double ionization mainly the knee shape in the intensity dependence of the double ionization yield of rare gases. iii) The plateau in the high-order Above-Threshold Ionization (ATI) spectrum, the first-order peak suppression, and the separation between peaks not equal to the photon energy. These phenomena can be explained by a non-perturbative approach and an extension to recollision dynamics through classical electron trajectories.

Experimentally, many interesting multiphoton phenomena arise when atoms and molecules are exposed to an intense laser field, such as ATI, HHG, and NSDI. These phenomena are prevalent at intensities greater than $\sim 10^{13} \text{W/cm}^2$.

3.2.2 STRONG-FIELD IONIZATION

The interaction of an intense laser pulse with matter can result in electrons tunneling from the atom or molecule to the continuum. This ionization process describes the case when the electron penetrates the potential barrier as it does not have sufficient energy to overcome the barrier.

The two main ionization processes for atoms and molecules with an electromagnetic field are: i) The linear regime, the atom or molecule absorbs a photon with energy greater than the ionization potential I_p , the atom is ionized and the electron is liberated. ii) In the nonlinear regime, the ionization potential is greater than the photon energy which results in various ionization mechanisms dependent on the laser intensity and frequency.

Keldysh presented a parameter γ which allows to separate the perturbative multiphoton regime from the non-perturbative regime [31]. The adiabatic parameter is the ratio of the laser frequency ω to the tunneling

frequency ω_{tun} of the valence electron. In the low frequency and high intensity, $\gamma < 1$, it is considered the tunneling regime (non-perturbative regime), when $1 < \gamma < 2$ it is the hybrid regime where multiphoton and tunneling are hard to distinguish and can occur simultaneously as multiphoton assisted tunneling (MPAT). Lastly, in the high-frequency and relatively low intensity, when $\gamma > 2$ the multiphoton ionization process dominates (perturbative regime).

The Keldysh parameter can be derived as a ratio between the time it takes the electron to tunnel through the potential barrier $\times$ the frequency of the incident laser field [31, 32].

$$\gamma = \frac{\omega}{\omega_{tun}} = \omega t_{tun} \quad (3.45)$$

The ratio measures the rate of the barrier oscillations compared to the time it takes for the electron to tunnel ionize. It assumes the electron moves back and forth along the width of the potential well with kinetic energy equal to the binding energy before the electric field is applied. Thus, the outward velocity is $v_{gr} = \sqrt{\frac{2I_p}{m}}$. When the external field is applied the electron travel through this barrier with velocity v_{gr} through a width of $\Delta x = \frac{I_p}{eE}$. The tunneling time can be obtained from the ground state velocity and the width of the barrier [32].

$$\gamma = \omega t_{tun} = \frac{\Delta x}{v_{gr}} = \frac{\omega \sqrt{2mI_p}}{eE} = \sqrt{\frac{I_p}{2U_p}} \quad (3.46)$$

where tunneling time occurs only at half of the period of the laser field. The ponderomotive energy U_p describes the average oscillation energy, quiver motion, that is acquired by a free electron in the radiation field of the laser pulse. The ponderomotive scales linearly with the laser intensity and quadratically with the wavelength [32].

$$U_p(eV) = \frac{e^2 E^2}{4m\omega^2} = 9.33 \times 10^{-14} I(W/cm^2) \lambda^2(\mu m) \quad (3.47)$$

The table 3.1 below shows various types of ionization regime and their conditions of validity, which are dependent on the laser pulse properties, the photon energy ω , the ionization potential I_p , the ponderomotive energy U_p , and the critical field strength for barrier suppression E_{crit} , respectively. Figure 3.7 depicts Feynman diagrams for a few of the ionization mechanisms described below.

Ionization regime	Condition	Keldysh parameter
Single-photon	$U_p \ll I_p < \omega$	$\gamma \gg 2$
Multiphoton	$U_p \ll \omega < I_p$	$\gamma > 2$
Multiphoton assisted tunneling	$\omega \lesssim U_p < I_p$	$1 < \gamma < 2$
Above-Threshold	$\omega < U_p < I_p$	$1 < \gamma < 2$
Tunneling	$\omega < I_p < U_p$	$\gamma < 1$
Barrier suppression	$E_{crit} < E$	$\gamma \ll 1$

Table 3.1: Different ionization regime and their respective condition of validity. The parameter are in atomic units.

1. **Single-photon ionization:** Absorption of a photon with energy greater than the ionization potential I_p .
2. **Multiphoton ionization:** Simultaneously absorption of n -photon with energy lower than the binding potential. The combined efforts of all the photons surpass the binding energy.
3. **Multiphoton assisted tunneling:** Absorption of n low energy photons resulting in an excited electronic state with higher energy and larger distance from the nucleus. Subsequent ionization by tunneling through the suppressed potential of such extended and weakly bond states.
4. **Above-Threshold ionization:** Absorption of more than the energetically required number of photons to ionize. Liberating an electron with additional energy than the binding energy.
5. **Tunnel ionization:** The incident laser field strength is proportional to the atomic field strength partially bending the atomic potential and allowing the electron to penetrate through the thin barrier.
6. **Barrier suppression:** The laser field strength is greater than the critical field strength of the atom. Full suppression of the atomic potential results in the electron to "leak out".

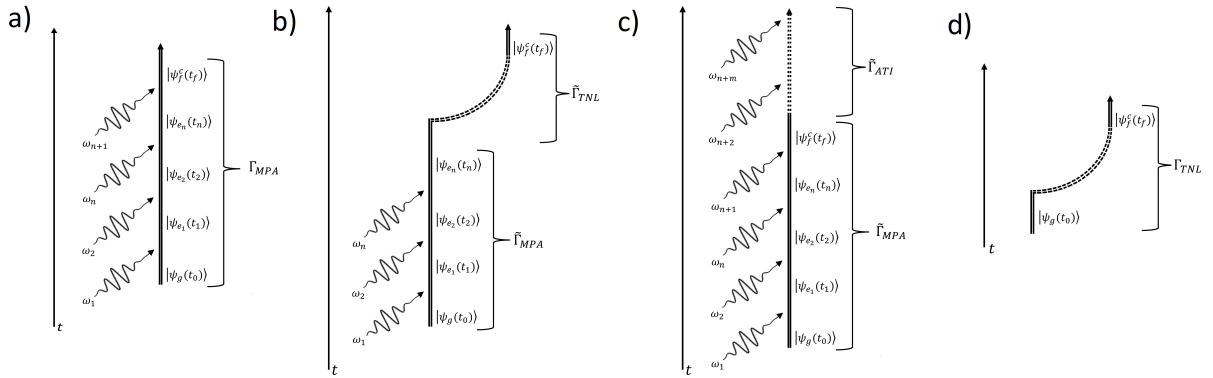


Figure 3.7: **Feynman diagrams** for **a)** Multiphoton ionization (MPI), takes an absorption of $(n + 1)\hbar\omega$ to reach the continuum. **b)** Multiphoton assisted tunneling (MPAT), absorption of n -photon leading to an excited state and subsequent tunneling to the continuum. **c)** Above-threshold ionization (ATI), absorption of $(n+s)$ -photon leading to ionization with additional photons absorbed. **d)** Tunneling ionization, the incident field is strong enough to force the electron to tunnel from the ground state to the continuum.

3.2.2.1 MULTIPHOTON IONIZATION

When the ionization potential I_p is greater than the photon energy with high laser frequency and low intensity ($I < 10^{13} \text{W/cm}^2$), the multiphoton is dominant. This process necessitates the absorption of multiple photons for ionization, the electron can be transferred to the continuum via multiphoton absorption. The electron kinetic energy in the continuum states will be $K \approx N\hbar\omega - I_p$ which is an extrapolation of the Einstein photoelectric effect. This picture is valid when the strength of the electric field is much smaller than the atomic electric field. The condition allows to treat the external potential as a small perturbation of the Coulomb potential. The

n -photon ionization rate Γ_n is a function of generalized n -photon ionization cross-section σ_n and laser intensity

$$\Gamma_n = \sigma_n \left(\frac{I}{\hbar\omega} \right)^n \quad (3.48)$$

The cross-section decreases quickly as the number of photons increases. At high laser frequencies and low intensities, the tunneling time is larger than the laser period (field oscillation) such that the electric field will change its direction while the electron is still confined within the barrier. Therefore, tunnel ionization is completely suppressed and the ionization may happen via the absorption of an integer number of single photons (small vertical arrows in Fig. 2.2b) within the lifetime of intermediate states (real or virtual). So, high photon densities will also be necessary, which have become available after the development of intense laser pulses.

3.2.3 TUNNELING IN STATIC FIELD

The tunneling ionization process is dominant at low frequency and high intensity. The laser period is greater than the tunneling time allowing us to treat this semi-classically. The external electric field distorts the Coulomb potential to an extent where a bound electron can tunnel through the potential barrier to the continuum. The ionization rate is determined from the width of the barrier tunneling time and tunneling time. The electron does not scatter but escapes by tunneling. Unlike multiphoton ionization when the electron transitions between different energy states the tunneling process is a transition from the ground state to the continuum with the same total energy.

For a static electric field Landau and Lifshitz derived the ionization rate for ground state hydrogen $1S$ -state in a strong electric field [66] and can be extended to hydrogen-like ions.

$$\Gamma(E) = \frac{4}{E} e^{-\frac{2}{3E}} \Rightarrow \Gamma(E) = \frac{4(2I_p)^{5/2}}{E} \exp \left(-\frac{2(2I_p)^{3/2}}{3E} \right) \quad (3.49)$$

The exponential seen in most tunneling ionization rates means that at low field strength, the ionization rate is low and is increasing as the field increases. The solution was performed semi-classically by separating the Schrodinger equation in parabolic coordinates (ζ, η, ϕ) in the presence of a static external electric field. The Schrodinger equation was decoupled into an uphill and downhill potential. Considering only the downhill potential representing the distorted potential, one can use the Wentzel–Kramers–Brillouin (WKB) approximation to get the semi-classical wavefunction for the left and right side of the barrier (a treatment similar to a one-sided finite potential well). They neglected the disagreement between the left and right function at the point where the electron emerges from the barrier.

3.2.4 TUNNELING IN A QUASI-STATIC FIELD

Based on a similar idea as Landau and Lifshitz, a general formula for field ionization of atoms was derived by Perelomov, Popov, and Terentev (PPT) [67–69] and also Ammosov, Delone, Krainov (ADK) [70, 71] from the stitching of the field-free atomic state with the WKB solutions at a point under the tunnel barrier. Only the initial state and final states are significant for tunneling. The intermediate states play no role, unlike the multiphoton ionization. The second assumption is a quasi-static field where the static field is replaced by $E\cos(\omega t)$ and integrated over the period T . Below are the six major steps in deriving the ionization rate [72].

i) Separating the Schrodinger equation in parabolic coordinates $\psi(\zeta, \eta, \phi) = \frac{\chi_1(\zeta)}{\sqrt{\zeta}} \frac{\chi_2(\eta)}{\sqrt{\eta}} \frac{e^{im\phi}}{\sqrt{2\pi}}$ in the presence of a static external electric field by using, where they decoupled the Schrodinger equation into an uphill $V(\zeta)$ and downhill $V(\eta)$ potential where $\frac{\chi_1(\zeta)}{\sqrt{\zeta}}$ and $\frac{\chi_2(\eta)}{\sqrt{\eta}}$ are the uphill and downhill functions. In the parabolic coordinate, ionization happens w.r.t. the η -coordinate, where $V(\eta)$ displays the barrier and $V(\zeta)$ describes the bound motion, the electron remains confined in the ζ -coordinate.

$$V(\zeta) = -\frac{1}{2} \left(\frac{\tilde{Z}_1}{\zeta} - \frac{m^2-1}{4\zeta^2} - \frac{E\zeta}{4} \right); \quad V(\eta) = -\frac{1}{2} \left(\frac{\tilde{Z}_2}{\eta} - \frac{m^2-1}{4\eta^2} + \frac{E\eta}{4} \right) \quad (3.50)$$

The downhill and uphill potential are obtained from the potential $V = -\frac{Z}{r} + Ez$, where $\tilde{Z}_1 + \tilde{Z}_2 = Z$ is the nucleus charge, and E is the electric field along z direction are the field strength.

ii) Find the asymptotic Coulomb wavefunction by finding the asymptotic solution for the radial and angular part of the wavefunction.

$$\psi_c \sim Q(l, m) \frac{2^{-(Z/\kappa)+1}}{|m|!} \zeta^{|m|/2} e^{-\kappa\zeta/2} \eta^{(Z/\kappa)-(|m|/2)-1} e^{-\kappa\eta/2} \frac{e^{im\phi}}{\sqrt{2\pi}} \quad (3.51)$$

where $Q(l, m) = (-1)^{(m+|m|)/2} \sqrt{\frac{2l+1}{2} \frac{(l+|m|)!}{(l-|m|)!}}$ comes from the spherical harmonics part of the asymptotic Coulomb wave function with energy $E = -\kappa^2/2$ where $\kappa = \sqrt{2I_p}$.

iii) Express the ionization rate in terms of the wavefunction outside the barrier $\chi_2(\eta)$. The ionization rate is found by integrating the probability current density.

$$W = \frac{1}{2} \frac{|m|!}{\kappa^{|m|+1}} \left[\chi_2 \frac{d\chi_2^*}{d\eta} - \chi_2^* \frac{d\chi_2}{d\eta} \right] \quad (3.52)$$

iv) Obtain a semi-classical expression for the wavefunction outside the barrier and in the classically forbidden region (under the barrier). Relate the semi-classical solution in the classically allowed ($\eta > \eta_0$) and the forbidden region ($\eta < \eta_0$). Tunneling via WKB approximation.

v) Write the rate in terms of semi-classical wavefunction outside the barrier, the function under the barrier must match the asymptotic coulomb wavefunction. The rate is then described completely by parameters

characterizing the asymptotic Coulomb wave function.

$$W = \frac{Q(l, m)^2}{2^{|m|} |m|!} \frac{1}{\kappa^{2Z/\kappa-1}} \left(\frac{2\kappa^3}{E} \right)^{2Z/\kappa-|m|-1} e^{-\frac{2}{3} \frac{\kappa^3}{E}} \quad (3.53)$$

vi) Perform a time averaging of the ionization rate for $E(t) = E_0 \cos(\omega t)$ to obtain the rate in the low-frequency laser field. Ignore the time dependence of the pre-exponential factor because the exponential is much more rapidly changing.

$$\overline{W} = \frac{1}{\pi} \int_{-\infty}^{\infty} W_{static} \exp \left(-\frac{2}{3} \frac{(2I_p)^{3/2}}{E_0 \cos(\omega t)} \right) d(\omega t) = W_{static} \left(\frac{3E_0}{\pi(2I_p)^{3/2}} \right)^{1/2} e^{\left(-\frac{2}{3} \frac{(2I_p)^{3/2}}{E_0} \right)} \quad (3.54)$$

Therefore, the total ionization rate is

$$\overline{W} = \frac{Q(l, m)^2}{2^{|m|} |m|!} \frac{1}{\kappa^{2Z/\kappa-1}} \left(\frac{2(2I_p)^{3/2}}{E} \right)^{2Z/\kappa-|m|-1} \left(\frac{3E_0}{\pi(2I_p)^{3/2}} \right)^{1/2} e^{\left(-\frac{2}{3} \frac{(2I_p)^{3/2}}{E_0} \right)} \quad (3.55)$$

This rate of ionization is identical to PPT model when $\gamma < 1$ [67–69] and to ADK model when $\gamma < 0.5$ [70, 71]. The rate of ionization calculated by PPT model can describe both multiphoton and tunneling ionization. The rate calculated by ADK is simpler than PPT and both rates are identical for $\gamma \ll 1$.

PPT rate is a formula for an atom in the short-range potentials, the photoionization rate is applicable for hydrogen atoms with initial ground state with orbital angular momentum l and magnetic quantum number m . The theory was extended to arbitrary complex atoms by including the effective principle quantum number $n^* Z / \sqrt{2I_p}$ and the effective orbital quantum number $l^* = n^* - 1$ in the ADK theory. The PPT model was derived for short-range potential and includes the effect of the long-range Coulomb interaction through a first-order correction in the quasi-classical approximation. It does not consider discrete binding states, only the ground state and was extended to linearly and elliptically polarized light. Recently, both models have been extended for molecular ionization in molecular-PPT and molecular-ADK [73].

3.2.5 KELDYSH APPROACH: STRONG FIELD APPROXIMATION

The standard Strong-field approximation (SFA) is a widely used non-perturbative approach proposed by Keldysh. The electromagnetic interaction is described in the length gauge and the continuum state is replaced by the Gordon-Volkov wavefunction, the free-electron state in the presence of the laser field. SFA is an approximation for the ionization of an electron from a bound state by a strong, low-frequency oscillating electric field. The three main assumptions of SFA are [31]:

- (i) The laser field does not couple with any bound state beyond the ground state. Only the ground state and the continuum are considered in the dynamics.
- (ii) The effect of the coulomb potential on the free electron is neglected. The electron is treated as a free

particle moving in the laser field.

(iii) The depletion of the ground state can be neglected.

The time-dependent Schrodinger equation for a single active electron system is

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle = [H_0 + V(t)] |\Psi(t)\rangle \quad (3.56)$$

where we can express the total Hamiltonian as a combination of the unperturbed system and the perturbation from the laser field. The total wavefunction can be written as a combination of a homogeneous and the inhomogeneous solution of the form, $|\Psi(t)\rangle = |\phi(t)\rangle + |\Delta\Psi(t)\rangle$ [74]. The solution to the homogeneous equation is obtained from the unperturbed Schrodinger equation, $(i \frac{\partial}{\partial t} - H_0) |\phi(t)\rangle = 0$, where H_0 is the unperturbed Hamiltonian.

$$\phi(t) = e^{-i \int_{t_0}^t H_0 d\tau} |\phi_g\rangle = e^{-i H_0(t-t_0)} |\phi_g\rangle = \hat{U}_0(t, t_0) |\phi_g\rangle \quad (3.57)$$

where the time propagator $\hat{U}_0(t, t_0)$ is related to the Green's function from the homogeneous equation defined by $(i \frac{\partial}{\partial t} - H_0) G_0(t, t') = \delta(t - t')$. The inhomogeneous equation is readily solvable using a Green's function $G(t, t')$ [75]

$$\left(i \frac{\partial}{\partial t} - H_0\right) |\Psi(t)\rangle = V(t) |\Psi(t)\rangle \rightarrow \left(i \frac{\partial}{\partial t} - H_0 - V(t)\right) G(t, t') = \delta(t, t') \quad (3.58)$$

$$|\Delta\Psi(t)\rangle = \int_{-\infty}^t G(t, t') V(t') |\Psi(t')\rangle dt' \quad (3.59)$$

The total solution of the Schrodinger equation is a linear combination of the homogeneous and inhomogeneous solution and is written in terms of time propagator $U(t, t')$. The relationship between Green's function and time operator is given by $G(t, t') = -i\Theta(t-t')\hat{U}(t, t')$ [75–77]. Using the Born approximation where the perturbation acts only on the ground state, we can set $|\Psi(t')\rangle \rightarrow |\phi(t')\rangle$. Finally, the total wavefunction of the time-evolved ground state is expressed as

$$|\Psi(t)\rangle = \hat{U}_0(t, t_0) |\phi_g\rangle - i \int_{t_0}^t \Theta(t-t') \hat{U}(t, t') V(t') \hat{U}_0(t', t_0) |\phi_g\rangle dt' \quad (3.60)$$

Moreover, the formal solution can also be obtained directly via the evolution operator in the interaction picture and following Dyson equations. The transition amplitude, is given by $M_{fi} = \lim_{t \rightarrow \infty} \langle \phi_f(t) | \Psi(t) \rangle$, defined as a projection of non-interacting state to a fully evolved state at large times [40, 65, 77], where the Heaviside identity is taken care of when projecting the non-interacting state onto the fully evolved state at $t \rightarrow \infty$ by

using the fact $\lim_{t \rightarrow \infty} \Theta(t - \tau) = 1$ [65] The initial state, $\phi_i(t)$, and final state, $\phi_f(t)$, are represented by a bound state and the continuum state where the electron is in the presence of the laser field. $|\Psi(t)\rangle$ is the total wave function evolve from the state $|\phi_g(t')\rangle$ when the laser is turned on at t' and the system interacts with the laser field through $V(t')$.

$$M_{fi} = -i \int_{t_0}^t dt' \langle \phi_f(t) | \hat{U}(t, t') V(t') \hat{U}_0(t', t_0) | \phi_g \rangle \quad (3.61)$$

Lastly, we can make the approximation that the final state is represented by the Gordon-Volkov wavefunction (a plane wave solution modulated by the electric field), $\langle \phi_f(t) | \hat{U}(t, t') \rightarrow \langle \phi_f^V(t') |$. This is also known as the Keldysh-Faisal-Reiss (KFR) amplitude

$$M_{fi} = -i \int_{t_0}^t dt' \langle \phi_f^V(t') | V(t') | \phi_g(t') \rangle \quad (3.62)$$

Where $|\phi_f^V(t')\rangle$ can be derived directly from the velocity gauged Schrodinger equation in the dipole approximation $\mathbf{A}(\mathbf{r}, t) \approx \mathbf{A}(t)$. Using SFA, we ignore the coulomb potential $V(\mathbf{r}) = 0$.

$$i \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[\frac{1}{2} (-i \nabla - \mathbf{A}(t))^2 - \frac{1}{r} \right] \psi(\mathbf{r}, t) \quad (3.63)$$

To solve this differential equation we can make use of the commutation principles. The Hamiltonian commutes with the momentum operator $\mathbf{p} = -i \nabla$ and since $\exp(i\mathbf{k} \cdot \mathbf{r})$ is an eigenfunction of $\mathbf{p}$ corresponding to eigenvalue $\hbar \mathbf{k}$, we can look at a solution of the form of a plane wave modulated by the electric field.

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = \frac{1}{2\pi^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r}} f_{\mathbf{k}}(t) \quad (3.64)$$

Plugging this transform in the Schrodinger equation 3.63 leads to

$$i\hbar \frac{\partial}{\partial t} f_{\mathbf{k}}(t) = \left[\frac{1}{2} (\mathbf{k} - \mathbf{A}(t))^2 \right] f_{\mathbf{k}}(t) \Rightarrow f_{\mathbf{k}}(t) = C e^{-\frac{i}{2} \int_{t_0}^t (\mathbf{k} - \mathbf{A}(\tau))^2 d\tau} \quad (3.65)$$

therefore, the Gordon-Volkov wavefunction is in the velocity gauge

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r}} e^{-\frac{i}{2} \int_{t_0}^t (\mathbf{k} - \mathbf{A}(\tau))^2 d\tau} \quad (3.66)$$

where we set the constant $C = 1$ in order for the wavefunction to be normalized according to $\langle \psi_{\mathbf{k}'}(\mathbf{r}, t) | \psi_{\mathbf{k}}(\mathbf{r}, t) \rangle = \delta(\mathbf{k} - \mathbf{k}')$. A gauge transformation can be performed $\psi_L(\mathbf{r}, t) = e^{-i\mathbf{A} \cdot \mathbf{r}} \psi_V(\mathbf{r}, t)$ to the Gordon-Volkov wavefunction from velocity gauge to length gauge.

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}} e^{i(\mathbf{k} - \mathbf{A}(t)) \cdot \mathbf{r}} e^{-\frac{i}{2} \int_{t_0}^t (\mathbf{k} - \mathbf{A}(\tau))^2 d\tau} \quad (3.67)$$

When dealing with higher-order multipole interaction, the Gordon-Volkov wavefunction can be expanded to include the higher-order multipoles. A full expansion is given in the gas phase chapter (non-dipole Gordon-Volkov wavefunction).

3.2.5.1 KELDSYH EXPONENTIAL

In the dipole approximation and for linearly polarized light we can derive the Keldysh probability of ionization. Using the transition amplitude

$$M_{fi} = -i \int_{t_0}^t dt' \langle p + A(t') | \hat{V}(t') | \phi_g(t') \rangle e^{-\frac{i}{2} \int_{t'}^t (p + A(\tau))^2 d\tau} e^{i(t' - t_0)I_p} = -i \int_{t_0}^t dt' \langle p + A(t') | \hat{V}(t') | \phi_g(t') \rangle e^{-iS(p, t, t')} \quad (3.68)$$

Where the plane wave accumulates a phase $S(p, t, t')$ from the laser field. The physical interpretation of this transition amplitude is as follows. The process starts at t_0 which represents the electron located in the ground state in the absence of the field. At time t' the laser field kicks the electron to the continuum and exits with momentum $\vec{p}$. Between t' and t the electron oscillates in the laser field and gains energy until it reaches the detector and gets recorded at time t . The dominant component of the transition amplitude is the exponential phase, which is

$$M_{fi} \propto -i \int_{t_0}^t \exp(-iS(p, t, t')) dt' \quad (3.69)$$

Let the laser polarization be along $\hat{x}$ and the vector potential is $\vec{A}(t) = \frac{E_0}{\omega} \sin(\omega t) \hat{x}$. Using the saddle approach we solve the exponential. The saddle point is defined as $\frac{d}{dt'} S(p, t, t')|_{t^*} = 0$ and where $\gamma = \frac{\omega}{E_0} \sqrt{2I_p}$

$$0 = \frac{1}{2} \left(p_x + \frac{E_0}{\omega} \sin(\omega t^*) \right)^2 + I_p = \frac{E_0^2}{2\omega^2} \left(\frac{p_x \omega}{E_0} + \sin(\omega t^*) \right)^2 + I_p \quad (3.70)$$

$$0 = \left(\frac{p_x \omega}{E_0} + \sin(\omega t^*) \right)^2 + \gamma^2 \quad (3.71)$$

Let's look at the special case where the exit momentum is zero ($p_x = 0$). The ionization happens when the field is strong enough $\omega t^* \ll 1$ therefore $\sin(\omega t^*) \approx \omega t^*$. The dominant contribution to ionization begins at an imaginary time, $t^* = \pm i \frac{\gamma}{\omega} = \pm i \frac{\sqrt{2I_p}}{E_0}$. Therefore, the probability of ionization is proportional to the tunneling phase $S(p, t, t^*)$.

$$P(p_x = 0, t) = |M_{fi}|^2 \propto \left| -i \int_0^t e^{-iS(p, t, t')} dt' \right|^2 \approx_{\text{SFA}} \left| e^{-iS(p, t, t^*)} \right|^2 \quad (3.72)$$

$$\begin{aligned}
P(p_x = 0, t = 0) &= \left| \exp \left[-i \left(\frac{1}{2} \int_{t^*}^0 d\tau \left(\frac{E_0}{\omega} \sin(\omega\tau) \right)^2 - I_p t^* \right) \right] \right|^2 \\
&= \left| \exp \left[-i \left(\frac{1}{2} \frac{E_0^2}{\omega^2} \int_{t^*}^0 d\tau (\omega\tau)^2 - I_p t^* \right) \right] \right|^2 \quad (3.73)
\end{aligned}$$

$$P(p_x = 0, t = 0) = \left| \exp \left[-i \left(-\frac{E_0^2}{2} \frac{(t^*)^3}{3} - I_p t^* \right) \right] \right|^2 = \left| \exp \left[\left(\frac{1}{2} \frac{(2I_p)^{3/2}}{E_0} \left(\frac{1}{3} - 1 \right) \right) \right] \right|^2 \quad (3.74)$$

$$P(p_x = 0, t = 0) \propto \exp \left[-\frac{2(2I_p)^{3/2}}{3E_0} \right] \quad (3.75)$$

This is the probability of ionization at the peak of the field, with zero momentum, to exponential accuracy. This is also identical to the exponential factor for Landau-Lifshitz, PPT, and ADK.

By solving the pre-exponent in the dipole approximation and using the saddle-point method to solve the time integration one can obtain the Keldysh ionization rate.

$$W_K = \frac{\sqrt{6\pi} I_p}{2^{5/4}} \left(\frac{E_0}{(2I_p)^{3/2}} \right)^{1/2} e^{\left(-\frac{2}{3} \frac{(2I_p)^{3/2}}{E_0} \right)} \quad (3.76)$$

3.2.6 RECOLLISION MODEL

High harmonic generation, above-threshold ionization, and recollision-induced double and triple ionization are extremely high-order nonlinear processes and can be characterized by the recollision model. This semi-classical model describes the above-mentioned nonlinear processes that occur when an intense laser pulse interacts with an atom or molecule. The first step involves the tunnel ionization of an electron, where the electron's wavefunction escapes from the atomic potential due to the strong laser field directly interacting with the potential, thus distorting it and creating a potential barrier. In the second step, the freed electron wavepacket propagates in the continuum and is accelerated by the laser field, acquiring energy as it moves away from its parent ion. Upon the reversal of the oscillating field, the electron is driven back towards the vicinity of the parent ion with a broaden wavepacket. The third and final step is the recollision, under the right phase matching conditions, the electron can recombine with the ion, releasing its energy in the form of a high-energy photon. The recombination produces spatially and temporally coherent light known as the generation of HHG. These photons can be in the extreme ultraviolet or X-ray range. It is also capable of generating extremely short attosecond pulses. The three-step model depicted in figure 3.8, is not only pivotal in understanding HHG and attosecond physics but also in exploring ultrafast phenomena such as rescattering and correlated doubly and triply charged ions.

The broaden electron wavepacket is driven back to the parent ion where it can undergo either forward or

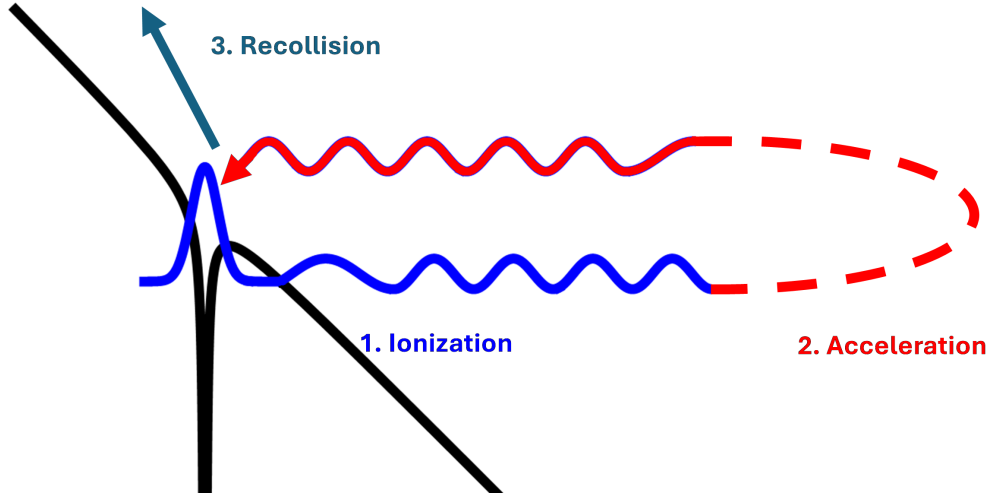


Figure 3.8: **Recollision physics:** In the first step, an intense pulse bends the coulomb potential of an atom or molecule. This allows an electron's wavefunction in the ground state to tunnel through the barrier. In the second step, the electron wavepacket propagates in the continuum and gains energy by the driving by laser field. Upon reversal of the laser field, accelerates towards the parent ion. In the third step, the liberated electron wavepacket recollides either elastically or inelastically with the parent ion. Resulting in either higher energy photons or doubly/triply charged ions.

backward scattering resulting in low- vs high- momentum transfer. The rescattering can lead to high-energy electrons. For linearly polarized light the photoelectron kinetic energy spectrum manifests itself as a plateau that extends from $2U_P$ to $10U_P$ [78, 79]. This plateau is equivalent to the plateau structure of HHG with a cutoff at $3.17U_P$ [29, 80]. The forward scattering provides a means to explore the impact of long-range Coulomb interactions, while backward scattering offers a window into the atomic or molecular structure of the parent ion [81, 82]. This structure can be examined with sub-angstrom spatial resolution and sub-femtosecond temporal resolution.

One of these strong ionization processes is NSDI, an extreme nonlinear process where two electrons are ejected from an atom or molecule without a sequential time order. This phenomenon occurs under the influence of a strong laser field. The recollision model is a widely accepted explanation for NSDI. It suggests that an electron, after being ejected from an atom by the laser field, can be driven back by the oscillating field to inelastically collide with its parent ion. This collision can transfer enough energy to eject a second electron. However, for sequential ionization (SI), the threshold intensity has to be strong enough to ionize two or more electrons in succession. The onset for a charge state is determined by the appearance intensity I_{app} [83, 84] and is given by $I_{app}(\text{W}/\text{cm}^2) = \frac{4 \times 10^9 [I_P(\text{eV})^4]}{Z^2}$ where $I_P(\text{eV})$ is the ionization energy, and Z is the charge state after ionization.

NSDI can occur through a few different mechanisms:

1. Direct impact ionization: The liberated electron is driven back to the parent ion with sufficient energy (higher than the I_p) to directly eject a second electron.
2. Recollision excitation with subsequent ionization (RESI): At intensities below the recollision threshold,

the recolliding electron does not have enough energy to directly ionize the second electron. However, the collision excites a bound electron to an excited state where it is then ionized after the laser field's peak intensity by a remnant laser field (subsequent half-cycle).

3. Shake off ionization: The liberated electron is driven back to the parent ion with kinetic energy lower than the ionization potential of the parent ion. Upon collision, the second electron is populated into an excited state where the ion undergoes reconfiguration which leads to a second electron being ionized.
4. Field-induced excitation and subsequent recollision ionization (FESI): During the propagation of the first electron in the continuum, the second electron gets populated in an excited state by a remnant half-cycle field. Upon field reversal, the first electron collides with the excited state cation with sufficient energy to eject the second electron.

Understanding these interactions is crucial for controlling electron dynamics in atoms and molecules, which has implications for the development of attosecond physics and spectroscopy. Further details on recollision dynamics such as transition amplitude and chiral interactions are given in Chapter 6 section 6.1.

LIQUID PHASE - HELICAL LIGHT INTERACTION

This chapter lays the foundation for understanding helical dichroism in the liquid phase, summarizing past experimental and theoretical advancements. It is followed by an outline of two published articles in Nature Photonics and the Journal of Chemical Physics where we elaborate on the uniqueness of our concept, experimental procedures, and key aspects useful for understanding the progression of our findings.

We demonstrate that enantio-pure liquids respond differently to the handedness of the rotating wavefront of the helical light and therefore exhibit enantio-selectivity. It was also found that randomly oriented achiral liquids show a type of dichroism when probed with helical light. Additional information includes experimental checks and procedures to validate our observations. The second study highlights the importance of HD as a chiroptical technique by demonstrating its presence in enantiomeric solutions with varying concentrations, given the crucial role solvents play in many biological processes. Chiroptical effects can be amplified by the l -value and controlled by the asymmetrical parameter δ .

Throughout this chapter, we emphasize the use of asymmetrical helical light as the chiral probe, which adds more control parameters to existing chiroptical detection utilizing laser polarization.

4.1 EARLY DEVELOPMENTS

Chiral interaction with helical light has been a topic of interest for over a decade in various disciplines, including atomic and molecular physics, and quantum electrodynamics. Conventionally, a Gaussian beam with SAM is employed to investigate chiral interactions. Light can also possess a handedness embedded in its rotating wavefront, referred to as structured light. It was not clear if the phase of helical light could interact with chirality and exhibit similar effects as CPL with chiral matter.

Early developments to observe a chiral response with structured light were not successful. These experiments were carried out in the linear absorption regime and depended solely on electric-magnetic dipole coupling. However, subsequent studies have unveiled surprising effects by employing nanoparticles and leveraging local field effects. This approach amplifies the field strength in the interaction region, facilitating the emergence of higher-order multipole as the origin of this phenomenon. However, direct observation of HD in bulk samples has been elusive [85] ever since the helical beams were generated nearly two decades ago. HD, defined as differential absorption of left- and right-helical light, was observed only in the presence of intermediaries such as nanoparticle aggregates [86] and/or chiral meta-surfaces [87].

4.2 TRANSMISSION MEASUREMENTS

It is well known that for low-intensity radiation $< 10^6 \text{W}/\text{cm}^2$, many molecular liquids are transparent in the UV-vis and NIR optical range. However, when high-power picosecond or femtosecond laser pulses are used, liquid samples absorb efficiently via a multiphoton absorption mechanism. Knowing this, we performed liquid transmission measurements of limonene using a circularly polarized 800nm femtosecond pulse to observe the effect of multiphoton absorption (nonlinear regime) on CD. The experimental transmission curve for the Gaussian beam is represented in figure 4.1 a), the distinct linear absorption regime is located at low pulse energies and exhibits no absorption (represented by the flat portion of the curve). The intensity is too low for the multiphoton absorption threshold and the photon energy is also too low to significantly alter the transmission. Moreover, no visible difference between the absorption of left- and right-handed light beyond the experimental error is observed in this regime. However, the absorption of the circularly polarized Gaussian increases when the nonlinear threshold is reached at $\sim 90 \text{nJ}$. At higher pulse energy, a slight difference between CPL is visible, although it is still mostly within the error of the measurement.

Enhancing the strength of the incident field shows strong effects on the transmission, this combined with the new chiral probe could be a promising pathway to increase the chiral signal. As we know, light also carries orbital angular momentum of $\pm l\hbar$ per photon, in which the handedness is associated by the left or right twisting of the wavefront undergoing l intertwined rotations in one wavelength. These helical beams have a chiral structure analogous to CPL. However, these beams have an additional chiral parameter of control, they can generate a

chiral structure in the rotation of the electric and magnetic field vectors or with the rotation of the wavefront. In addition, the number of intertwined twists within the helical pitch can be increased by increasing the l -value. This in principle, could increase the chiral sensitivity with the l -value. Then naturally the question arises, is it possible to enhance the efficiency of the chiral signal by replacing the chiral probe from CPL to helical light ($l = 1, s = 0$)?

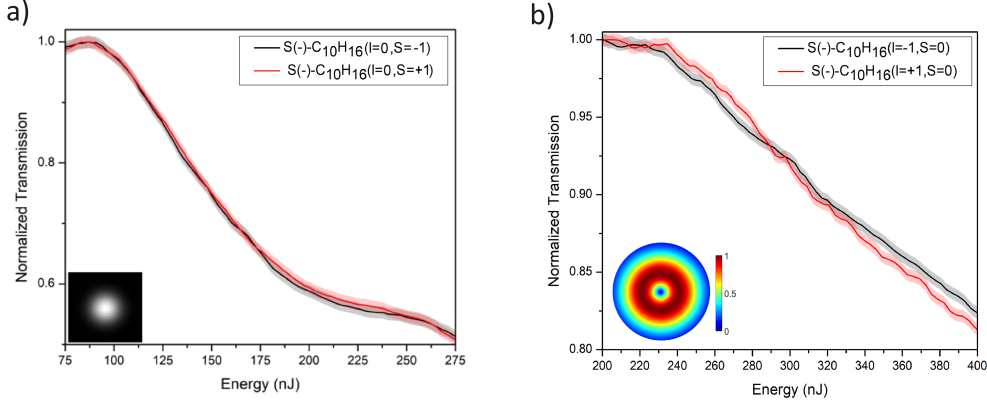


Figure 4.1: **Nonlinear transmission curves** for a) Left- and right-circularly polarized Gaussian beam and b) linearly polarized symmetric OAM beam. The inlet shows the simulated beam profile and the error bars are the standard variation of three measurements.

Indeed, our preliminary measurements do show a variation in the absorption of linearly polarized left- and right-handed helical light, as seen in figure 4.1 b). This variation is only noticeable beyond the onset of nonlinearity. However, when the transmission is averaged over a range of pulse energies, this difference vanishes due to the cross-over in the transmission. Multiple measurements, under identical conditions, were performed with similar results.

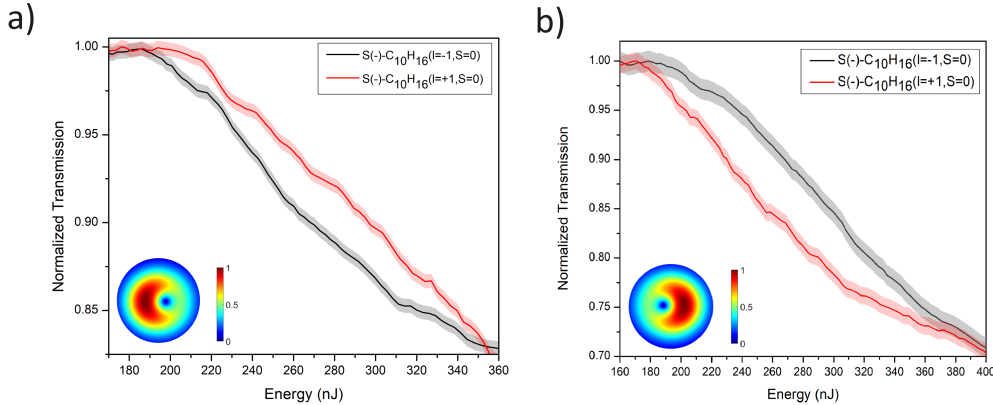


Figure 4.2: **OAM dependent transmission curves** for a) (b)) Left- and right-linearly polarized OAM beam with the singularity displaced to the positive (negative) x-axis. The inlet shows the simulated beam profile and the error bars are the standard variation of three measurements.

The variation in the differential absorption was eventually determined to be a consequence of the position of the singularity. The intensity profile of helical light is characterized by a phase singularity (optical vortex) and hence a null intensity region at the center of the beam. As shown previously, helical light can be categorized as

symmetrical and asymmetrical OAM beams. The latter is achieved by displacing the phase singularity, resulting in an extra degree of control to structured light in addition to the helical phase. By using asymmetrical helical light as a chiral probe, two extra degrees of freedom are gained to study chiral interactions:

1. The theoretical unbounded l -value, which increases the number of intertwined twists within the helical pitch which in principle could increase the chiral sensitivity with the l -value.
2. The asymmetrical parameter δ , affects the field strength and the field gradient around the optical vortex.

By displacing the singularity of the left- and right-handed helical light, the absorption difference between the light's handedness can be stabilized, leading to a non-zero differential absorption across a range of pulse energies, but only beyond the nonlinear onset. Furthermore, the behaviour in the differential absorption was observed to flip as the δ -position traverses the origin (see figure 4.2). The differential absorption was also found to be present in achiral molecules, due to the additional broken symmetry in the OAM beam.

We define two types of helical dichroism by using helical light as the optical probe.

1. **HD(Type I)** is the difference in absorptance of left and right-handed helical light for a fixed sample (chiral, achiral). This is analogous to a typical CD.

$$\text{HD}(\text{Type I}) = A(+l, \pm s, \pm \delta) - A(-l, \pm s, \pm \delta) \quad (4.1)$$

2. **HD(Type II)** is the difference in absorptance between two chiral materials for a specific handedness of the helical light.

$$\text{HD}(\text{Type II}) = \frac{A_R(\pm s, \pm \delta) - A_S(\pm s, \pm \delta)}{A_R(\pm s, \pm \delta) + A_S(\pm s, \pm \delta)} \quad (4.2)$$

According to our results, the two main terms contributing to any form of dichroism are E1M1 and E1E2 coupling terms. These multipole interaction terms are expressed in terms of the electric-magnetic dipole coupling and the optical chirality $E_1M_1 \propto \text{Im}[\mu_\alpha^{mg} m_\alpha^{gm}] \text{Im}[\mathbf{E}^* \cdot \mathbf{B}]$ which is used to describe conventional CD. And, the electric dipole-quadrupole coupling combined with the optical helicity $E_1E_2 \propto \langle \mu_\alpha^{mg} \theta_{\alpha\beta}^{gm} \rangle_\rho \text{Re}[\widehat{\nabla} \mathbf{E} \cdot \mathbf{E}^*]$ which is used to describe HD. These are written for a single photon transition but can be expanded to multiphoton absorption, see supplementary of "nonlinear helical dichroism of chiral and achiral molecules". To describe the bulk response of the isotropic medium, the E1M1 and E1E2 coupling terms must be averaged over all degrees of molecular orientation. For partial orientation of the molecules, due to the laser-induced dipole force (see article), we consider anisotropic averaging $\langle \rangle_\rho$ where ρ is an orientation-dependent weighting factor influenced by the degree of molecular alignment.

For a weak field, the E1E2 does not contribute to differential absorption due to the rotational averaging killing the term $\left(\mu_\alpha^{mg} \theta_{\alpha\beta}^{gm}\right)$. The field is not strong enough to partially align a subset of molecules.

Additionally, the E1E2 term also does not contribute to differential absorption for nonlinear absorption of circularly polarized Gaussian beams due to the $\text{Re} [\widehat{\nabla} \mathbf{E} \cdot \mathbf{E}^*]$ being identical for both left- and right-handed CPL and additionally the dipole force averages to zero over the interaction region. This is also the case for the transmission of strong-field symmetrical OAM beam, even though the field gradient is not identical for left- and right-handed helical light, the dipole force is symmetric and also averages to zero over the interaction region (see supplementary section on optical dipole force).

However, for the nonlinear transition of asymmetrical helical light, the $\text{Re} [\widehat{\nabla} \mathbf{E} \cdot \mathbf{E}^*]$ term survives due to the presence of the helical phase and asymmetrical parameter in the electric field. The gradients are not identical for left- and right-handed and the dipole force does not average to zero and gives rise to HD. Therefore, within this intensity regime, the E1E2 term survives only for nonlinear absorption of left- and right-handed asymmetric OAM beams.

4.3 PARITY OF HELICAL DICHROISM

Parity-time symmetry can beautifully describe the symmetry properties of the problem and is the traditional approach for chiral-matter interaction. However, it does not fully describe our experimental observation. Nonetheless, it gives a quick qualitative understanding of the importance of E1E2 to HD. Table 4.3 shows the space and time parity of electromagnetic quantities [88].

Quantities	Time parity	Space parity
Electric field	+1	-1
Electric field (Gaussian mode)	+1	-1
Electric field (LG mode)	+1	$(-1)^{ l +1}$
Electric dipole	+1	-1
Electric quadrupole	+1	+1
Magnetic field	-1	+1
Magnetic field (Gaussian mode)	-1	+1
Magnetic field (LG mode)	-1	$(-1)^{ l }$
Magnetic dipole	-1	+1
Gradient	+1	-1
Complex number	-1	+1

Table 4.1: PT symmetry of quantities used in CD and HD.

First, recall the PT symmetry for the E1M1 transition for a circularly polarized Gaussian beam incident on a chiral system.

$$PT \left\{ \Gamma_{E_1 M_1} \right\} = PT \left\{ \frac{1}{3} \text{Im} [\mu_\alpha^{mg} m_\alpha^{gm}]_R \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \right\} = -\frac{1}{3} \text{Im} [\mu_\alpha^{mg} m_\alpha^{gm}]_S \text{Im} [\mathbf{E}^* \cdot \mathbf{B}] \quad (4.3)$$

Therefore, E1M1 transition are odd under PT symmetry. This is known as true chirality because it is parity-odd and time-even pseudoscalar. Therefore, the PT symmetry of conventional CD for Gaussian beams,

$PT\{CD_R\} = -CD_S$, is odd under parity-time symmetry [14]. CD is odd under space inversion; therefore, it can be considered “true chirality”.

The PT symmetry for E1E2 transition for an asymmetrical helical light beam

$$PT\{\Gamma_{E_1E_2}\} = PT\left\{\langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho \text{Re}\left[\widehat{\nabla\mathbf{E}}(\pm l, \pm\delta) \cdot \mathbf{E}^*(\pm l, \pm\delta)\right]\right\} = \langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho \text{Re}\left[\widehat{\nabla\mathbf{E}}(\mp l, \mp\delta) \cdot \mathbf{E}^*(\mp l, \mp\delta)\right] \quad (4.4)$$

where for an achiral system is $PT\{\langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho\} = -\langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho$ and for a chiral system is $PT\{\langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho^R\} = -\langle\mu_\alpha^{mg}\theta_{\alpha\beta}^{gm}\rangle_\rho^S$. The time reversal changes the sign of the OAM value, and the parity changes the displacement of singularity for asymmetrical LG beams. Therefore, the optical helicity is odd under PT symmetry and the E1E2 transition is even under PT symmetry. From the PT symmetry of E1E2, we can conclude that HD(Type I) is odd under parity and time symmetry. Since the optical helicity changes under time reversal and space inversion, this could be considered as “false chirality”. Additionally, HD(Type II) is odd under time-parity symmetry. This is purely due to the space inversion of the material and could be considered “true chirality”.

4.4 NONLINEAR HELICAL DICHROISM IN CHIRAL AND ACHIRAL MOLECULES

Here we demonstrate, the first direct observation of HD in both chiral and achiral molecules in the liquid phase without the use of any intermediary. Our approach is based on probing helicity-dependent nonlinear absorption of asymmetric helical light beams propagating through the liquid sample. We show that enantio-selectivity is a phase effect that scales linearly with the OAM value. We model light-matter interactions by considering induced multipole moments, through the averaged energy absorbed, and time-dependent perturbation theory, through the rate of absorption, to show that HD arises from the coupling of electric dipole and quadrupole terms, and can be tuned. The supplementary includes additional experimental results and a series of experimental checks to validate our observation (the measured single-shot beam profile, pulse spectrum, OAM value after transmission through the samples, transmission in the absence of the sample). It also includes optical dipole force calculation, fluence calculation and the extension to multiphoton absorption. The major advances of our work are:

- (i) We introduce a conceptually new form of chiroptical detection based on the nonlinear absorption of polarized asymmetric helical light beams in the liquid phase.
- (ii) HD(Type I) is tunable by displacing the singularity present in an OAM beam. This allowed us to make the first observation of helicity-dependent absorption in achiral systems.
- (iii) HD signal scales with the OAM value, which in principle has no upper bound, and can be further controlled by varying the laser ellipticity. This unique feature does not exist in chiroptical techniques, such as CD, that exploit only laser polarization as a chiral probe.

- (iv) HD does not require tuning the laser wavelength to specific resonances, applied external static electric or magnetic fields, and sample preparation.
- (v) The underlying principle is general and applicable to a large variety of molecules, irrespective of their structural symmetry. It is also extendable to different phases of matter.

Our work shifts the paradigm of chiroptical detection from using laser polarization to the optical helical phase. It opens a new, so far unexplored direction of research in next-generation chiroptical spectroscopy.

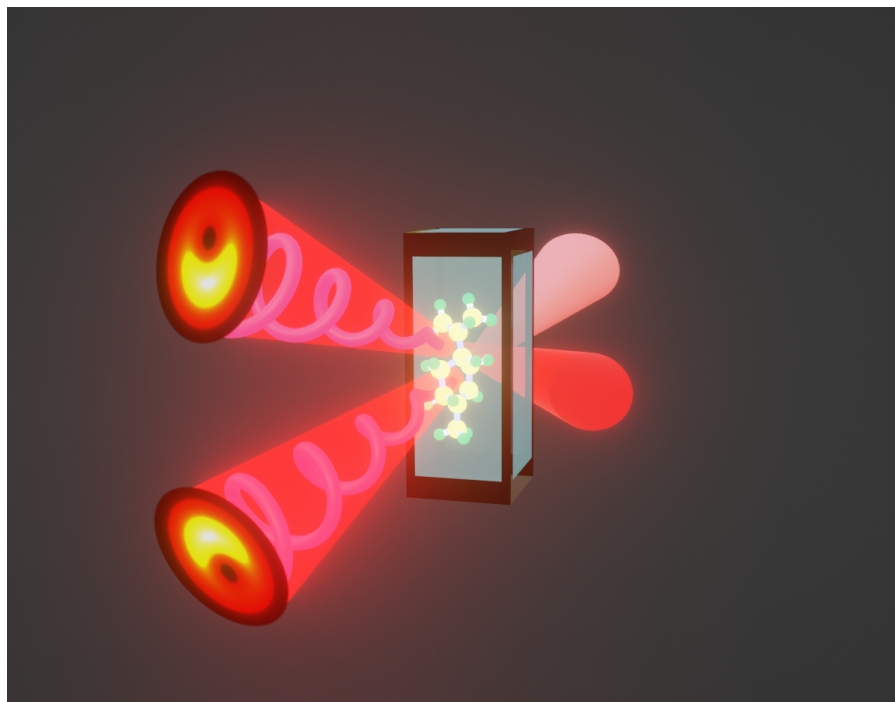


Figure 4.3: **Illustration** of a limonene enantiomers in a cuvette being irradiated by left- and right-handed asymmetrical helical light. The transmitted light depicts the difference in absorbance.

Authors contribution: My colleague Ashish Jain and I contributed equally to this work. The contributions spanned all aspects of the research, experimental measurements, and theoretical advancements including the conception and design of the study, data collection and analysis, manuscript preparation and revision. Therefore, both should be considered as co-first authors.

Nonlinear helical dichroism in chiral and achiral molecules

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Chiral interactions are prevalent in nature, driving a variety of biochemical processes. Discerning the two non-superimposable mirror images of a chiral molecule, known as enantiomers, requires interaction with a chiral reagent with known handedness. Circularly polarized light beams are often used as a chiral reagent. Here we demonstrate efficient chiral sensitivity with linearly polarized helical light beams carrying an orbital angular momentum of $\pm\hbar$, in which the handedness is defined by the twisted wavefront structure tracing a left- or right-handed corkscrew pattern as it propagates in space. By probing the nonlinear optical response, we show that helicity-dependent nonlinear absorption occurs even in achiral molecules and can be controlled. We model this effect by considering induced multipole moments in light–matter interactions. Design and control of light–matter interactions with helical light may open new opportunities in chiroptical spectroscopy, light-driven molecular machines, optical switching and in situ ultrafast probing of chiral systems and magnetic materials.

Our understanding of light–matter interactions is mainly based on the propagation of homogeneously polarized light and the dominance of the dipole-active transitions between different quantum states of matter. Higher-order multipole effects are often ignored. The strength of dipole transitions is governed by the frequency, intensity and polarization of the incident light. The optical phase, represented by the wavefront of the light beam, plays a minimal role in such transitions. Within the dipole approximation, chiral systems are often studied using circularly polarized light (CPL), in which the dynamical rotation of the electric-field vector around the propagation direction yields an effective spin angular momentum (SAM) $\pm\hbar$, and therefore the handedness.

Two correlated optical techniques are widely used to probe chiral systems based on the propagation of polarized light through a chiral sample: circular dichroism (CD) and optical rotation (OR). In CD, left-CPL and right-CPL are absorbed differently in the two enantiomers, leading to differential absorption^{1,2}. In OR, on the other hand, left-CPL and right-CPL travel with unequal velocities in the two enantiomers, leading to polarization rotation^{3,4}. The chiral sensitivity of CD is poor, on the order of 0.01–1% (ref. 5), because it involves coupling of electric and magnetic dipole transitions. CD can be enhanced by

employing super chiral light⁶, plasmonic structures^{7,8} and strong field techniques using elliptically polarized light^{9,10}. A distinct gas-phase chiroptical technique that has emerged in recent years is photo-electron circular dichroism (PECD). In PECD, photo-ionization of a chiral molecule results in an asymmetric photo-electron angular distribution for the two enantiomers¹¹. PECD is due to pure electric dipole transitions, so its efficiency is one to two orders of magnitude larger than that of CD^{5,12}.

Light can also carry orbital angular momentum (OAM) of $\pm\hbar$ associated with dynamical rotation of the wavefront structure^{13–15}. The handedness of such helical light beams is defined by the twisting of the wavefront undergoing l intertwined rotations in one wavelength. This additional degree of freedom influences the characteristics of light–matter interactions. The angular distribution¹⁶, time delay¹⁷ and dynamics of photo-electrons^{18,19} can be modified during the photo-ionization of atoms and molecules. Also, the OAM of light can be transferred to matter either externally by exerting a torque (as in optical tweezers²⁰ and Bose–Einstein condensates^{21,22}) or internally by rotating the electron distribution and resulting in modified selection rules for transitions that depend on the topological charge l (refs. 23,24).

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The possibility of no upper bound on the l value, while SAM can assume only two defined values, has generated substantial interest in using helical light beams carrying OAM as a chiral reagent. Early studies on chirality with twisted photons were not promising. Most experiments were performed in the linear absorption regime^{25,26}, whereas theory focused solely on the coupling of the electric and magnetic dipole transition moments responsible for conventional CD²⁷. Helical dichroism (HD), analogous to CD, was demonstrated by exploiting local field effects in molecules adsorbed on nanoparticle aggregates²⁸, chiral metasurfaces²⁹ and non-chiral nanostructures³⁰. Coupling of the OAM of light with a material's chirality without any intermediary was recently shown to require higher-order transition moments to be engaged along with SAM to observe any chiroptical effects^{31,32}.

In this Article we introduce a conceptually new form of chiroptical detection technique based on nonlinear absorption of linearly polarized helical light beams in the liquid phase. We first demonstrate enantioselectivity in chiral molecules, directly without any intermediary, by probing the differential absorption between the two enantiomers for a specific helical light—we call this HD(Type II). Second, we show the differential absorption of left- and right-helical light in isotropic achiral and chiral molecules—HD(Type I)—which can be precisely controlled by displacing the singularity present in an OAM beam. Third, we reveal that HD(Type I) is scalable by changing the OAM value and that it can be further controlled by varying the laser polarization. This feature does not exist in polarization-based chiroptical techniques, such as CD. Finally, we show that HD(Type I, II) is a phase effect and does not necessarily require CPL. To understand HD, we model the light–matter interaction by considering multipole expansion. We find that HD arises from coupling of the electric dipole and electric quadrupole terms, and that it can be tuned by changing the laser polarization in addition to the OAM value.

To probe the dichroism, we measured the absorption of loosely focused femtosecond Gaussian and helical light pulses propagating through a liquid sample contained in a cuvette, as shown in Fig. 1a. A q -plate converted incident Gaussian light to an optical vortex beam (OVB) carrying an OAM value that is two times the topological charge, q (refs. 33,34). Further experimental details are provided in the Methods. Normalized transmission of left- and right-circularly polarized ($s = \pm 1$) helical light ($l = \pm 1$) is shown in Fig. 1b as a function of the peak laser fluence in $S(+)$ -fenchone, $C_{10}H_{16}O$. For each successive laser pulse, the energy was varied using a combination of half-wave plate (HWP) and polarizer, and a fresh sample region was irradiated by translating the cuvette. Each curve in the figure is an average of three independent measurements, and the colour band represents the statistical standard error. At low peak laser fluences, absorption is negligible and all curves overlap. The laser fluence is not sufficient to induce multiphoton transitions. At the onset of multiphoton absorption ($\sim 1.4 \text{ J cm}^{-2}$), the transmission starts to decrease monotonically. For a given helicity, transmission is nearly identical for left- and right-CPL, except at fluences greater than $\sim 2.2 \text{ J cm}^{-2}$.

The normalized chiral signal in fenchone, defined as HD (Type II; $\pm l$; $\pm s$) = $2 \frac{D(\pm l; \pm s) - L(\pm l; \pm s)}{D(\pm l; \pm s) + L(\pm l; \pm s)}$ (see Methods for notation), is shown in Fig. 1c (solid lines). For a Gaussian beam ($l = 0$), the chiral signal is less than 1% (dashed lines). Overlap of the signal with the error bands represents the sensitivity of our experiment. The chiral signal is enhanced significantly when the helical phase is introduced to the incident beam by switching from a Gaussian beam to an OAM beam. For $l = \pm 1$, HD(Type II) is $\sim 5\%$. However, SAM associated with light polarization appears to play a minimal role. For a given helicity, the chiral signals for left- and right-CPL nearly overlap with each other within experimental error, similar to the Gaussian beam.

To isolate the role of SAM and OAM, we performed experiments with linearly polarized ($s = 0$) helical ($\pm l$) and Gaussian beams. It is worth noting that multiphoton absorption cross-sections depend

on the laser polarization and are typically higher for linear than circular polarization^{35–37}. Figure 2a,b shows HD(Type II) in fenchone as a function of peak laser fluence for $l = \pm 1$ and $l = \pm 2$, respectively. The results for limonene ($C_{10}H_{16}$) are shown in Supplementary Section 1. Also shown in Fig. 2a is the differential absorption of two orthogonal linearly polarized Gaussian beams (dashed lines). The chiral signal in fenchone increases with laser fluence, reaching a maximum of $\sim 4\text{--}6\%$, and also increases with the helicity (l value) of the beam (Fig. 2a,b). For $l = 2$, the onset of nonlinear absorption occurs at higher pulse energies. In experiments with different l values, the pulse energies were always varied from below the threshold for the onset of nonlinear absorption to approximately twice the threshold value, as shown in Fig. 1b. This ensured that the nonlinear response regime we investigated remained the same ($\sim 10^{13} \text{ W cm}^{-2}$), even though the peak fluence of OAM beams depends on the l value³⁸ (Supplementary Section 8). Chiral discrimination with linearly polarized helical light beams demonstrates the prominent role of the optical phase associated with the OAM of light.

Generally, differential absorption defined by HD(Type I) = $A(+l, s) - A(-l, s)$ is not expected in isotropic achiral molecules with CPL. This is also true even with helical light²⁹. We did not observe any differential absorption of linearly polarized helical light with symmetric OAM beams where the null intensity region is at the centre of the beam. However, when the singularity in the OAM beam is displaced from the centre, achiral molecules with different point group symmetries exhibit dichroism (Fig. 3). The singularity within the focal region of a focused OAM beam can be shifted either by (1) detuning the q -plate, leading to a superposition of the incident Gaussian beam with the converted OAM beam³⁹, or (2) physically shifting the centre of the q -plate with respect to the incident beam. We used the latter technique, because the former gives rise to a Gaussian component in the transmitted beam. The resultant asymmetric OAM beam introduces an asymmetry in the intensity profile in the focal region, as shown in Fig. 3a. The orientation of the laser polarization is perpendicular to the displacement of the singularity. In the experiment, alignment of the singularity at the centre of the OAM beam can only be defined before the objective, which translates to an uncertainty $\sim \pm 100 \text{ nm}$ at the focus (see Methods for calibration details).

Figure 3b presents the differential absorption of linearly polarized helical light ($l = \pm 1$) in achiral molecules, HD(Type I), with no inversion symmetry—acetone (C_3H_6O), methanol (CH_3OH) and air—for different positions of the singularity in the focused OAM beam. The differential absorption is averaged over a fluence range from the onset of nonlinear absorption (which depends on the ionization potential) in the normalized transmission curve to $\sim 2 \text{ J cm}^{-2}$. In acetone (blue curve) and methanol (red curve), differential absorption exhibits a sinusoidal behaviour, with a change in sign as the singularity traverses the zero position from $-1.8 \mu\text{m}$ to $1.8 \mu\text{m}$. The small variation in the zero-crossing point for the two molecules ($\sim 100 \text{ nm}$) is due to uncertainty in the position of the singularity. Helicity-dependent absorption does not exist in air (empty cuvette in the experiment) and is independent of the position of the singularity (black curve). This represents the background noise introduced by our experimental set-up (Supplementary Section 5). Helicity-dependent absorption in benzene (C_6H_6), a molecule with inversion symmetry, is shown in Fig. 3c (black curve). The observed behaviour is similar to that of non-centrosymmetric molecules (Fig. 3b), suggesting that the HD signal does not appear to depend on molecular symmetry.

To disentangle the roles of phase and field gradients in an asymmetric OAM beam, we studied the differential absorption of a circularly polarized, non-OAM, annular beam that mimics the profile of a Laguerre–Gaussian (LG) beam with zero OAM value (Supplementary Section 6). Dichroism in $R(-)$ -fenchone (green curve), $S(+)$ -fenchone (red curve) and acetone (blue curve) is independent of the position of the singularity and is less than 1%, within the standard error. Absence of differential absorption confirms that helicity-dependent absorption in achiral molecules is a phase effect and not only due to field gradients.

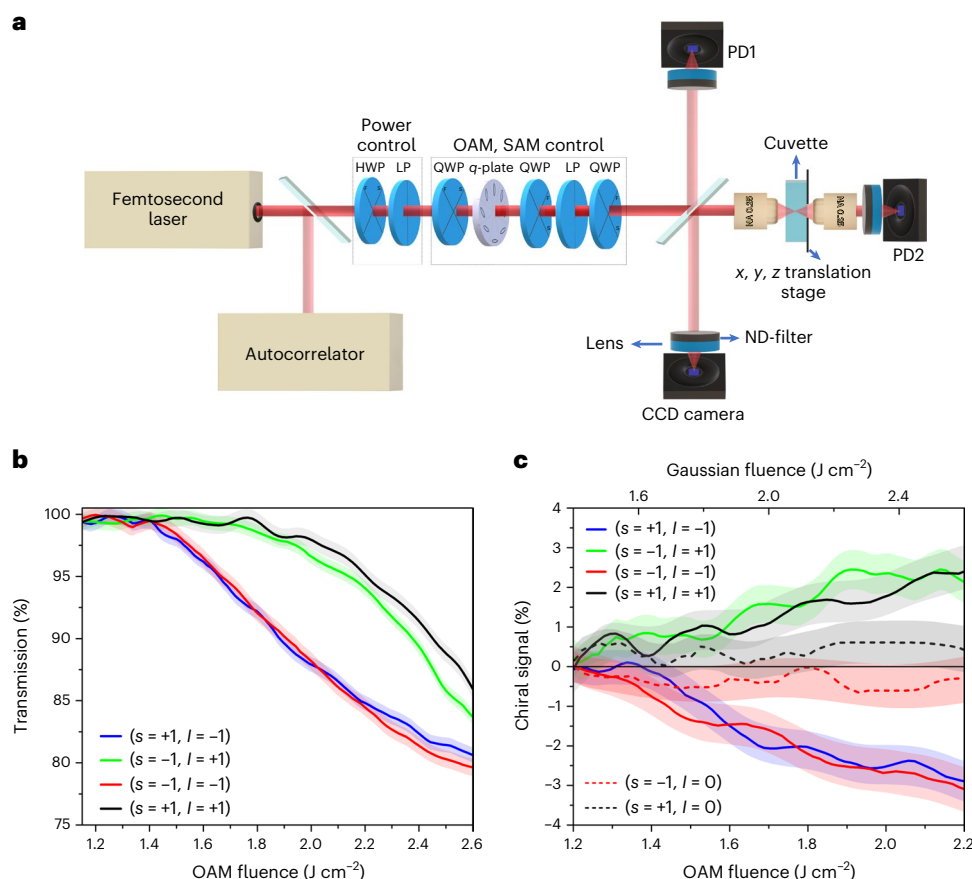


Fig. 1 | Transmission of circularly polarized ($s = \pm 1$) femtosecond vortex pulses in fenchone. a, Schematic of the experimental set-up, which consists of a combination of a half-wave plate (HWP) and quarter-wave plates (QWPs), linear polarizer (LP), a birefringent liquid-crystal-based phase plate called a *q*-plate (see Methods for details), photodiodes (PDs), neutral-density (ND) filters and a charged-coupled device (CCD) camera. **b**, Transmission of left- and right-circularly polarized helical light with $l = \pm 1$ in S(+)-fenchone, as a function

of peak laser fluence. **c**, Chiral signal with circularly polarized Gaussian ($l = 0$, dashed lines) and OAM ($l = \pm 1$, solid lines) beams in fenchone as a function of peak laser fluence. Each curve in **b** is an average of three independent measurements (sample size) and the colour bands represent the statistical standard error. The colour bands in **c** represent the propagation error of the chiral signal. These experimental results were reproduced multiple times under identical conditions.

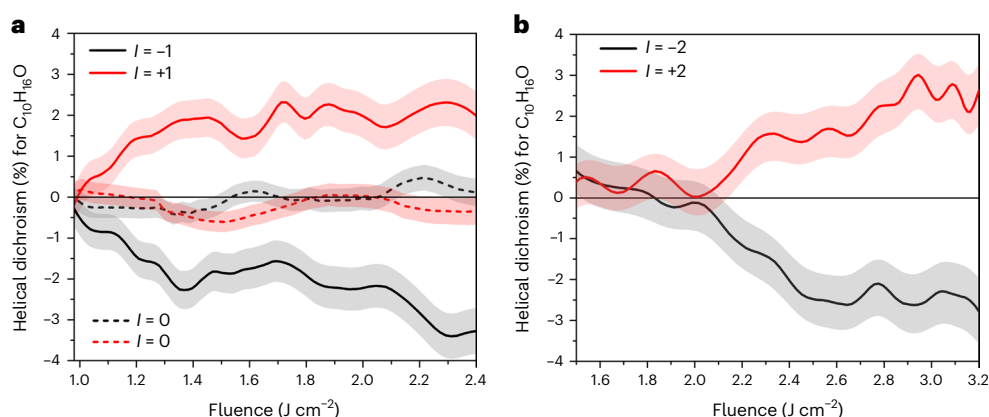


Fig. 2 | Helical dichroism (Type II) in fenchone with linearly polarized light ($s = 0$) as a function of peak laser fluence. a, HD in fenchone for $l = \pm 1$ (solid lines) and Gaussian ($l = 0$, dashed lines) beams. The bottom abscissa shows the peak laser fluence for the OAM and Gaussian beams. **b**, HD in fenchone for $l = \pm 2$

beams. The colour bands represent the propagation error of the chiral signal for three independent measurements (sample size). These experimental results were reproduced multiple times under identical conditions.

Figure 4a presents the HD (Type I) signal in limonene enantiomers for different positions of the singularity in an OAM beam. The spatial variation of HD (Type I) exhibits the same behaviour as achiral molecules (Fig. 3b,c). The key difference is that with asymmetric OAM beam,

the helicity-dependent absorption in the two enantiomers is different, resulting in non-zero chiral signal given by HD (Type II). Figure 4b,c show that the HD (Type II) signal in limonene as a function of peak laser fluence is weakly dependent on the position of the singularity

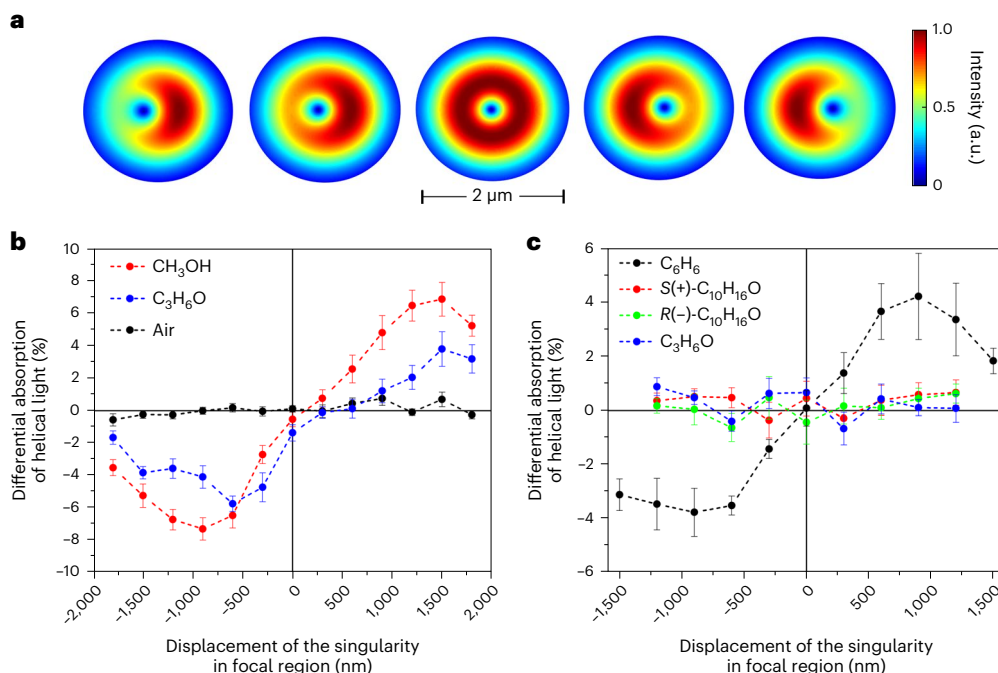


Fig. 3 | Helicity-dependent absorption, HD(Type I), in achiral molecules.

a, Simulated intensity profiles of asymmetric OAM beams obtained by shifting the position of the q -plate with respect to the incident beam. **b,c**, Differential absorption of linearly polarized left- and right-helical light ($l = \pm 1$) as a function of displacement of the singularity in the focal region. **(b)** Air (black) and achiral molecules with no inversion symmetry (acetone (blue), methanol (red)). **(c)** Benzene (black), an achiral molecule with inversion symmetry. Also shown in

c is the differential absorption of a circularly polarized non-OAM beam ($l = 0$) with a singularity at the centre in acetone (blue) and R(-) and S(+)-fenchone (green and red). The dashed lines connecting the discrete experimental points are for visualization only. The error bars represent the propagation error of the chiral signal for three independent measurements (sample size). These experimental results were reproduced multiple times under identical conditions.

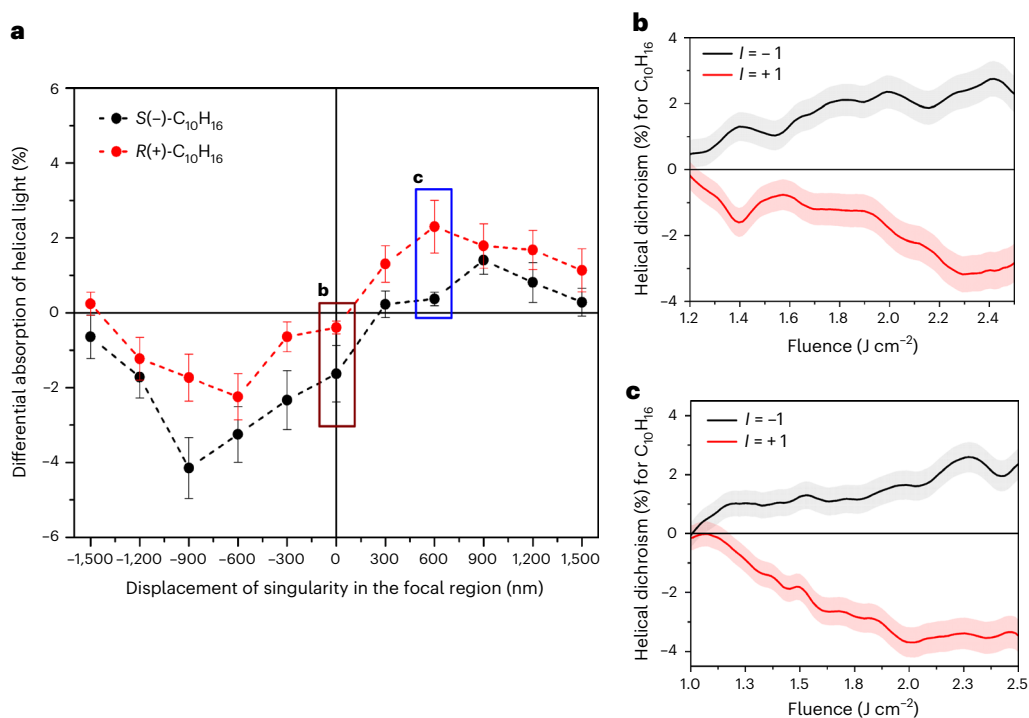


Fig. 4 | Helical dichroism with linearly polarized asymmetric OAM beams ($l = \pm 1$) in limonene. **a**, HD(Type I) as a function of the position (or displacement) of the singularity in the OAM beam. **b,c**, HD(Type II) as a function of peak laser fluence when the singularity is at the positions marked by the maroon (**b**)

and blue (**c**) rectangles in **a**. The error bars and colour bands represent the propagation error of the chiral signal for three independent measurements (sample size).

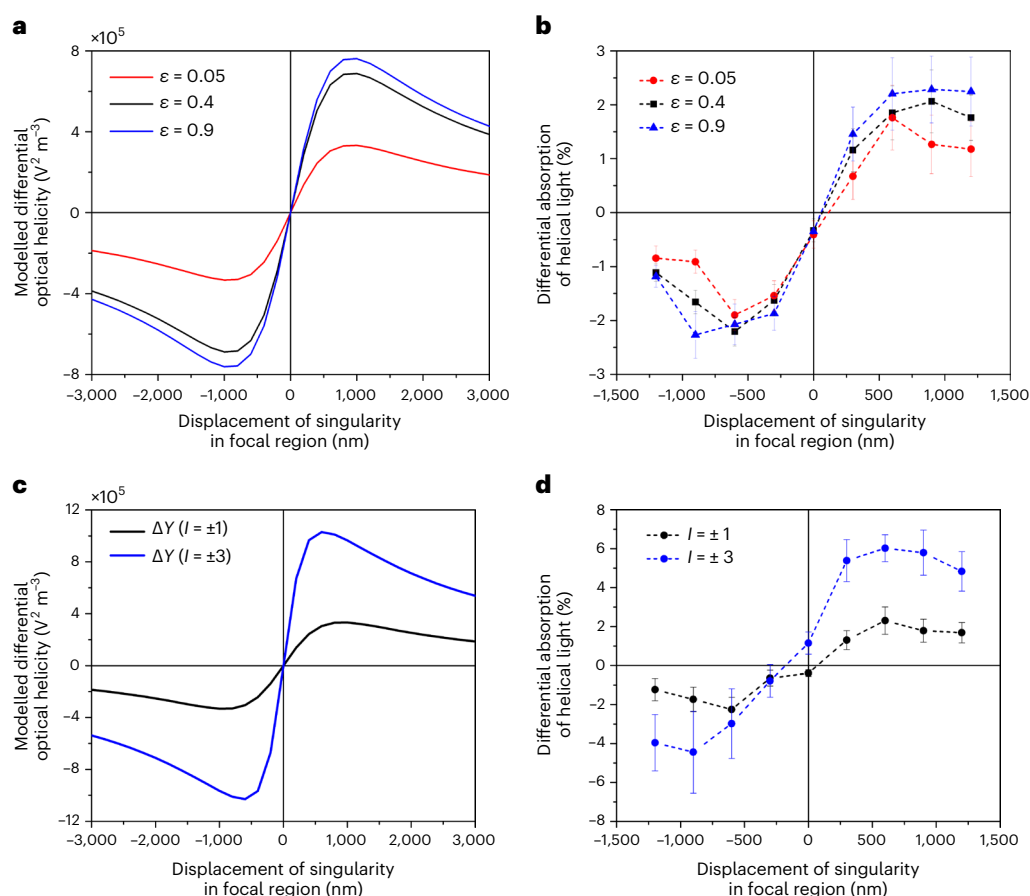


Fig. 5 | Helical dichroism (Type I) with asymmetric OAM beams in R(+)-limonene. Modelled (a,c) and measured (b,d) differential absorption as a function of the displacement of singularity for $l = \pm 1$ and different ellipticities (a,b) and for 95% linearly polarized helical light for $l = \pm 1, \pm 3$ (c,d). Differential absorption was modelled by the relation $\Delta W \approx A'' \Delta \mathcal{H}$, where

$\Delta \mathcal{H} = \int_{-\omega_0}^{\omega_0} [\gamma^+ - \gamma^-] dx dy$ is the differential optical helicity representing the E1E2 coupling term (see main text for details). The error bars represent the propagation error of the chiral signal for three independent measurements (sample size).

within the OAM beam. They were obtained when the singularity is at the positions marked by solid rectangles in Fig. 4a. Similar results were obtained for fenchone (Supplementary Section 1). HD (Type II) signals in limonene (Supplementary Fig. 1) and fenchone (Fig. 2) are of opposite sign (Methods). Although the HD (Type II) signal is not affected by the location of the phase singularity, it is much more stable with an asymmetric OAM beam. The results were also found not to depend on the laser focus position inside the cuvette. The effects of propagation of intense light pulses through the sample were negligible (Supplementary Sections 2 and 4).

To understand the chiral light–matter interaction, we modelled the rate of excitation (I) of the molecule using time-averaged induced multipoles (Methods). The coupling terms involving the electric–magnetic dipole (E1M1) and electric dipole–quadrupole (E1E2) moments (equation (8)) are pseudoscalars, so they change sign under improper rotation, contributing to HD (Type I, II) (equations (10) and (11)). HD (Type I) was modelled by evaluating equations (9) and (10), assuming full alignment, using the experimental parameters (equations (12)–(19); $\omega = 2.35 \times 10^{15}$ Hz, $\omega_0 = 2$ μ m) and approximating the response tensors G' and A'' with scalars (or pseudoscalar)⁴⁰. The E1M1 term vanishes because we take the difference between left and right-helical beams for the same polarization. Hence, the E1E2 term is the major contributor to the HD (Type I) for asymmetric OAM beams.

Figure 5a depicts the modelled E1E2 term (described in terms of differential optical helicity $\Delta \mathcal{H}$) for different polarizations, described by ellipticity ϵ . The magnitude of differential absorption is maximal

for circular polarization ($\epsilon = 1$), decreases with ellipticity and goes to zero for perfect linear polarization ($\epsilon = 0$). This is in agreement with the experimentally observed sinusoidal behaviour of HD (Type I) for the chiral molecule shown in Fig. 5b and the achiral molecules shown in Fig. 3b,c. The minimum ϵ value achieved experimentally was 0.05. In the experiments, the displacement of singularity is restricted by the focal spot, whereas the modelling of the E1E2 term does not include such boundary effects. As a result, at the extreme positions of the singularity in the experiment, the intensity profile mimics a symmetric Gaussian, leading to zero gradient force (Supplementary Section 9) and subsequently no differential absorption. However, in the modelling, the intensity profile does not converge to a symmetric Gaussian.

For asymmetric LG beams, the modelled E1E2 term predicts a higher magnitude of differential absorption for higher values of l , as shown in Fig. 5c. Figure 5d shows experimental HD (Type I) for asymmetric LG beams in limonene for two different OAM values of $l = \pm 1, \pm 3$. The magnitude of HD increases with the l value, in agreement with the modelled E1E2 term, where the limonene response tensor is approximated as a scalar quantity. The E1E2 term is non-zero even for asymmetric non-OAM annular beams. However, because there is no l dependence, HD (Type I) does not exist, as shown in Fig. 3c for the non-OAM, annular beam obtained through Fresnel diffraction.

The contribution of the E1E2 term to the HD signal also depends on the laser fluence. This vanishes at low laser intensity where the degree of molecular alignment is negligible. The extent of molecular alignment with an ~100-fs laser pulse depends on (1) the laser intensity

($\sim 10^{13}$ W cm $^{-2}$), (2) the molecular polarizability and (3) the temperature and/or solute effects^{41–45}. As the laser intensity increases, any degree of alignment in an asymmetric OAM beam is sufficient for the EIE2 term to be non-zero, and its contribution to the HD signal increases, as observed in the experiments (Figs. 3 and 4).

Our technique affords tunability of OAM-dependent differential absorption in both chiral and achiral systems by (1) changing the ellipticity of the laser polarization (Fig. 5a,b), (2) varying the l value (Fig. 5c,d), (3) superimposing Gaussian and OAM beams to manipulate the field distributions and (4) shifting the singularity. The technique is quite general and can be extended to chiral and achiral transparent solids, plasmonic metasurfaces and gas-phase molecules. The OAM of light offers an additional degree of freedom to control light–matter interactions. This opens new opportunities in next-generation chiroptical spectroscopy, asymmetric catalysis and light-driven molecular machines, where ultrashort light pulses can trigger interconversion of enantiomers for dynamic control of chirality.

A key advantage of using helical light is that the HD signal scales linearly with the l value, as predicted by our qualitative model. In Fig. 5, a linear increase in differential absorption was observed by changing from $l = 1$ to $l = 3$. Our model predicts a linear behaviour until $l \approx 15$, therefore, an increase in differential absorption by a factor of 15 relative to $l = 1$. However, at very high l values, saturation behaviour can be expected, as observed recently in chiral nanostructures²⁹, due to the increase in the size of the singularity and the finite beam waist determined by the focusing geometry. The enhanced differential absorption with asymmetric OAM beams at higher l values can be utilized in molecular optical switching for digital processing, in which light transmission can be controlled with helicity.

Another unique feature of the scaling behaviour of the HD signal is that it leads to higher chiral sensitivity. In contrast, the sensitivity of current chiroptical techniques that rely on light polarization is predetermined by the nature of the light–matter interaction, which is not scalable. In fenchone, the chiral signal increased from ~4% to ~6% when l was varied from 1 to 2 (Fig. 2). However, the chiral signal in limonene did not show such dependence. Although the l dependence of the chiral signal needs further investigation, the sensitivity of our technique is comparable to PECD and two-photon absorption CD⁴⁶.

The demonstrated differential absorption in liquids suggests a degree of control over the ionization of gas-phase molecules when irradiated with an intense helical light beam. In addition to polarization and magnetic field, the OAM of light represents another parameter to control the continuum trajectory of ionized electrons. The OAM of light, together with a transverse magnetic field and longitudinal electric field, generate chiral continuum electrons scalable with the l value. In contrast to single-photon ionization, chiral electron trajectories generated by tunnel ionization have attosecond resolution and can be used to probe chiral dynamics with attosecond precision.

Finally, the chiral motion of free electrons also results in a magnetic field along the laser propagation axis that can be controlled via the optical OAM. The magnetic field will be dominant around the singular part of the beam where the electric field is weak. For OAM single-cycle pulses, the magnetic field can be switched on a timescale of ~1 fs. This opens a potentially new way to in situ, ultrafast probing of magnetic materials.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41566-022-01100-0>.

References

- Caldwell, D. J. & Eyring, H. *The Theory of Optical Activity* (Univ. of Utah, 1971).
- Nakanishi, K., Berova, N. & Woody, R. *Circular Dichroism: Principles and Applications* (Wiley, 2000).
- Castiglioni, E., Abbate, S. & Longhi, G. Experimental methods for measuring optical rotatory dispersion: survey and outlook. *Chirality* **23**, 711–716 (2011).
- Kuball, H.-G. in *Encyclopedia of Analytical Science* 2nd edn (eds Worsfold, P. et al.) 60–79 (Elsevier, 2005).
- Janssen, M. H. M. & Powis, I. Detecting chirality in molecules by imaging photoelectron circular dichroism. *Phys. Chem. Chem. Phys.* **16**, 856–871 (2014).
- Tang, Y. & Cohen, A. E. Enhanced enantioselectivity in excitation of chiral molecules by superchiral light. *Science* **332**, 333–336 (2011).
- Collins, J. T. et al. Chirality and chiroptical effects in metal nanostructures: fundamental and current trends. *Adv. Opt. Matter* **5**, 1700182 (2017).
- Wang, X. & Tang, Z. Circular dichroism studies on plasmonic nanostructures. *Small* **13**, 1601115 (2017).
- Cireasa, R. et al. Probing molecular chirality on a sub-femtosecond timescale. *Nat. Phys.* **11**, 654–658 (2015).
- Bégin, J.-L., Alsaawy, M. & Bhardwaj, R. Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry. *Sci. Rep.* **10**, 14074 (2020).
- Lux, C. et al. Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses. *Angew. Chem. Int. Ed.* **51**, 5001–5005 (2012).
- Powis, I. Photoelectron circular dichroism of the randomly oriented chiral molecules glyceraldehyde and lactic acid. *J. Chem. Phys.* **112**, 301 (2000).
- Allen, L. et al. Orbital angular momentum of light and the transformation of Laguerre-Gaussian laser modes. *Phys. Rev. A* **45**, 8185–8189 (1992).
- Torres, J. P. & Torner, L. *Twisted Photons: Applications of Light with Orbital Angular Momentum* (Wiley, 2011).
- Andrews, D. L. & Babiker, M. *The Angular Momentum of Light* (Cambridge Univ. Press, 2013).
- Surzhykov, A., Seipt, D. & Fritzsche, S. Probing the energy flow in Bessel light beams using atomic photoionization. *Phys. Rev. A* **94**, 033420 (2016).
- Wätzel, J. & Berakdar, J. Discerning on a sub-optical-wavelength the attosecond time delays in electron emission from magnetic sublevels by optical vortices. *Phys. Rev. A* **94**, 033414 (2016).
- Picón, A. et al. Transferring orbital and spin angular momenta of light to atoms. *New J. Phys.* **12**, 083053 (2010).
- Peshkov, A. A., Fritzsche, S. & Surzhykov, A. Ionization of H₂⁺ molecular ions by twisted Bessel light. *Phys. Rev. A* **92**, 043415 (2015).
- Franke-Arnold, S., Allen, L. & Padgett, M. Advances in optical angular momentum. *Laser Photon. Rev.* **2**, 299–313 (2008).
- Andersen, M. F. et al. Quantized rotation of atoms from photons with orbital angular momentum. *Phys. Rev. Lett.* **97**, 170406 (2006).
- He, H. et al. Direct observation of transfer of angular momentum to absorptive particles from a laser beam with a phase singularity. *Phys. Rev. Lett.* **75**, 826–829 (1995).
- Schmiegelow, C. T. et al. Transfer of optical orbital angular momentum to a bound electron. *Nat. Commun.* **7**, 129998 (2016).
- Picón, A. et al. Photoionization with orbital angular momentum beams. *Opt. Express* **18**, 3660–3671 (2010).

25. Löffler, W., Broer, D. J. & Woerdman, J. P. Circular dichroism of cholesteric polymers and the orbital angular momentum of light. *Phys. Rev. A* **83**, 065801 (2011).
26. Araoka, F. et al. Interactions of twisted light with chiral molecules: an experimental investigation. *Phys. Rev. A* **71**, 055401 (2005).
27. Andrews, D. L., Romero, L. D. & Babiker, M. On optical vortex interactions with chiral matter. *Opt. Commun.* **237**, 133–139 (2004).
28. Brulot, W. et al. Resolving enantiomers using the optical angular momentum of twisted light. *Sci. Adv.* **2**, 150134 (2016).
29. Ni, J. et al. Giant helical dichroism of single chiral nanostructures with photonic orbital angular momentum. *ACS Nano* **15**, 2893–2900 (2021).
30. Zambrana-Puyalto, X., Vidal, X. & Molina-Terriza, G. Angular momentum-induced circular dichroism in non-chiral nanostructures. *Nat. Commun.* **5**, 4922 (2014).
31. Forbes, K. A. & Andrews, D. L. Spin-orbit interactions and chiroptical effects engaging orbital angular momentum of twisted light in chiral and achiral media. *Phys. Rev. A* **99**, 023837 (2019).
32. Forbes, K. A. & Andrews, D. L. Optical orbital angular momentum: twisted light and chirality. *Opt. Lett.* **43**, 435–438 (2018).
33. Marrucci, L., Manzo, C. & Paparo, D. Optical spin-to-orbital angular momentum conversion in inhomogeneous anisotropic media. *Phys. Rev. Lett.* **96**, 163905 (2006).
34. Hugo, L. et al. Arbitrary optical wavefront shaping via spin-to-orbit coupling. *J. Opt.* **18**, 124002 (2016).
35. Temnov, V. V. et al. Multiphoton ionization in dielectrics: comparison of circular and linear polarization. *Phys. Rev. Lett.* **97**, 237403 (2006).
36. Vivas, M. G. et al. Polarization effect on the two-photon absorption of a chiral compound. *Opt. Express* **20**, 18600–18608 (2012).
37. Gong, S.-H. & Penzkofer, A. Two-photon absorption and two-photon-induced absorption of some organic liquids at 347.15 nm. *Opt. Quantum Electron.* **31**, 269–290 (1999).
38. Oosterbeek, R., Ashforth, S., Bodley, O. & Simpson, M. Measuring the ablation threshold fluence in femtosecond laser micromachining with vortex and Bessel pulses. *Opt. Express* **26**, 34558–34568 (2018).
39. Rahimian, M. G. et al. Spatially controlled nano-structuring of silicon with femtosecond vortex pulses. *Sci. Rep.* **10**, 12643 (2020).
40. Tang, Y. & Cohen, A. E. Optical chirality and its interaction with matter. *Phys. Rev. Lett.* **104**, 163901 (2010).
41. Ohkubo, J. et al. Molecular alignment in a liquid induced by a nonresonant laser field: molecular dynamics simulation. *J. Chem. Phys.* **120**, 9123–9132 (2004).
42. Dooley, P. W. et al. Direct imaging of rotation wave-packet dynamics of diatomic molecules. *Phys. Rev. A* **68**, 023406 (2003).
43. Fleischer, S. et al. Molecular alignment induced by ultrashort laser pulses and its impact on molecular motion. *Is. J. Chem.* **52**, 414–437 (2012).
44. Leibscher, M., Averbukh, I. S. & Rabitz, H. Molecular alignment by trains of short laser pulses. *Phys. Rev. Lett.* **90**, 213001 (2003).
45. Leibscher, M., Averbukh, I. S. & Rabitz, H. Enhanced molecular alignment by short laser pulses. *Phys. Rev. A* **69**, 013402 (2004).
46. Toro, C. et al. Two-photon absorption circular dichroism: a new twist in nonlinear spectroscopy. *Chem. Eur. J.* **16**, 3504–3509 (2010).

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Methods

Differential absorption measurements

A Ti:sapphire laser amplifier system, operating in an external trigger mode and producing 45-fs, 800-nm pulses with a maximum pulse energy of 2.5 mJ, was used in the transmission measurements. An aspheric objective lens (numerical aperture (NA) of 0.3) was used to focus the femtosecond pulses into a cuvette (10-mm thick) containing liquid samples of chiral or achiral molecules. A second aspheric objective with the same or higher NA (0.5) collected and collimated the transmitted light onto a photodiode (PD2), positioned immediately after the objective. For every laser shot, the transmitted light signal on PD2 was normalized with the incoming light signal on PD1, reflected off a glass plate positioned in the beam path at an angle of -20° to avoid Brewster's angle. The signals generated by PD1 and PD2 were stretched by an electronic pulse stretcher, discretized, and recorded by a data acquisition card. A combination of an HWP and a polarizer was used to vary the pulse energy (power control in Fig. 1a). The incident pulse energies were measured before the objective. During the measurement, for every laser shot, the pulse energy was increased by ~ 3 nJ and the sample was translated by $5 \mu\text{m}$ to avoid microbubbles. Multiple transmission curves similar to those in Fig. 1a were obtained for each sample, to be averaged and smoothed. The difference in the normalized transmission of left- and right-helical light ($l = \pm 1$) is proportional to HD (Type I) (that is, differential absorption). To ensure a shortest pulse in the interaction region, a negative chirp was introduced and optimized by measuring the second harmonic generation in a barium borate crystal placed at the location of the cuvette. A single-shot autocorrelator then continuously monitored the pulse duration. The pulse duration at the interaction region is ~ 100 fs. Transmission measurements were always performed in an empty cuvette before each experiment to determine and minimize background errors resulting from any discrepancies between the PDs (Supplementary Section 5). In addition, the measured single-shot beam profile, pulse spectrum and OAM value remained unchanged after transmission through the samples (Supplementary Sections 2–4).

Sign dependence of HD in chiral molecules

We used conventional labelling of a chiral molecule by the sign of the direction of rotation of polarized light, dextrorotatory (D; +) and levorotatory (L; -). Chiral molecules are also labelled as (S)- and (R)- based on their absolute chemical configuration, representing the left- and right-handed isomers. This labelling refers to the spatial orientation of groups at the chiral centre and not to the optical rotation of polarized light. As a result, it is possible for an isomer to be S(+), S(-), R(+) and R(-). The sign dependence of the HD signals arises from optical rotation by an enantiomer. HD (Type II) signals in fenchone (Fig. 2) and limonene (Fig. 4b,c) are of opposite signs because they rotate the plane of linear polarization in opposite directions. R(+)-limonene and S(+)-fenchone rotate the plane of polarization clockwise, and S(-)-limonene and R(-)-fenchone rotate counterclockwise.

Generation of OAM beams

Light beams carrying orbital and/or spin angular momentum were generated and controlled by an OAM/SAM unit (Fig. 1a) consisting of a combination of a HWP and quarter-wave plates (QWPs), a linear polarizer (LP) and a birefringent liquid-crystal-based phase plate called a q -plate³³. When an incident Gaussian beam propagates through the q -plate with a topological charge q , it acquires an OAM defined by $l = \pm 2q$, with a phase singularity and hence a null intensity region at the centre of the beam—an optical vortex. The wavefront structure of such beams undergoes l intertwined rotations in one wavelength, and the direction of rotation is determined by the sign of the input polarization. The conversion efficiencies of the q -plates were $91 \pm 2\%$ for $l = 1, 3$ and $\sim 80 \pm 2\%$ for $l = 2$. Circularly (linearly) polarized Gaussian beams were produced by a QWP. The ellipticity of CPL at the sample was $97 \pm 2\%$. Circularly (linearly) polarized OAM light $s = \pm 1$, $l = \pm 1$ ($s = 0$, $l = \pm 1$) was

generated using a combination of QWP, q -plate, QWP, LP and QWP. The ellipticity of circularly (linearly) polarized OAM light reaching the sample was $95 \pm 2\%$ ($5 \pm 2\%$).

Generation of annular beams and displacement of singularity

An annular light beam with no OAM ($l = 0$) was generated by a circular aperture and exploiting the Fresnel diffraction of the incident Gaussian beam to produce an Airy pattern beam with a null region in the centre of the beam (Supplementary Section 6). A Galilean beam expander and QWP were used to magnify the beam by a factor of four and produce circular polarization. The singularity/null intensity region in the OAM (non-OAM beam) beam was displaced by translating the q -plate (circular aperture), mounted on a x, y -stage, with a step size of $250 \pm 40 \mu\text{m}$. When focused by the objective, this translated to a displacement step size of 300 ± 20 nm with respect to the centre of the beam. The calibration was achieved by measuring the total translation required to displace the singularity to the periphery of the defocused beam and comparing it to the measured spot size of $2 \pm 0.2 \mu\text{m}$ obtained by knife-edge measurements.

Multipole expansion of the light–matter interaction

We consider a monochromatic electromagnetic field incident on a molecule. The resultant time-harmonic charge and current distributions are described by a multipole expansion. The single-photon rate of excitation of the molecule was expressed in terms of time-averaged induced multipoles.

The induced electric-dipole $\tilde{\mu}$, electric quadrupole $\tilde{\theta}$ and magnetic dipole $\tilde{m}$, are expressed in multipole expansion terms as^{47,48}

$$\begin{aligned}\tilde{\mu}_\alpha &= \sum_\beta \tilde{\alpha}_{\alpha\beta} \tilde{E}_\beta + \sum_\beta \tilde{C}_{\alpha\beta} \tilde{B}_\beta + \frac{1}{3} \sum_{\beta\gamma} \tilde{A}_{\alpha\beta\gamma} \tilde{E}_{\beta\gamma}; \\ \tilde{\theta}_{\alpha\beta} &= \sum_\gamma \tilde{a}_{\gamma\alpha\beta} \tilde{E}_\gamma; \\ \tilde{m}_\alpha &= \sum_\beta \tilde{\chi}_{\alpha\beta} \tilde{B}_\beta + \sum_\beta \tilde{g}_{\alpha\beta} \tilde{E}_\beta\end{aligned}\quad (1)$$

where the Greek alphabet represents the Cartesian indices. $\tilde{\alpha}_{\alpha\beta}$ is the electric dipole polarizability, $\tilde{\chi}_{\alpha\beta}$ is the magnetic susceptibility, $\tilde{A}_{\alpha\beta\gamma}$ is the electric dipole–quadrupole polarizability, where $\tilde{A}_{\alpha\beta\gamma} = \tilde{a}_{\gamma\alpha\beta}$, and $\tilde{C}_{\alpha\beta}$ is the electric–magnetic dipole polarizability, where $\tilde{C}_{\alpha\beta} = -\tilde{g}_{\alpha\beta}$. The field gradient $\nabla_\beta \tilde{E}_\gamma$ is defined by $\tilde{E}_{\beta\gamma}$ (refs. 47–49). The complex electric and magnetic fields are defined as $\tilde{E}(t) = \tilde{E}_0 e^{-i\omega t}$ and $\tilde{B}(t) = \tilde{B}_0 e^{-i\omega t}$, where $\tilde{E}_0$ and $\tilde{B}_0$ are arbitrary complex vectors and ω is the frequency of the incident light. The terms with tilde are complex quantities $\tilde{\alpha}_{\alpha\beta} = \alpha'_{\alpha\beta} + i\alpha''_{\alpha\beta} = \tilde{\alpha}^*_{\beta\alpha}$, $\tilde{A}_{\alpha\beta\gamma} = A'_{\alpha\beta\gamma} + iA''_{\alpha\beta\gamma} = \tilde{A}^*_{\gamma\alpha\beta}$ and $\tilde{C}_{\alpha\beta} = G'_{\alpha\beta} + iG''_{\alpha\beta}$.

The dynamic multipole interaction Hamiltonian^{47,48} is given by

$$H_{\text{int}} = -\mu_\alpha E_\alpha - \frac{1}{3} \theta_{\alpha\beta} E_{\alpha\beta} - m_\alpha B_\alpha - \dots \quad (2)$$

The rate of change of the Hamiltonian gives the rate of energy absorption by the induced multipoles^{47,48}, that is, energy absorbed from the EM fields, expressed in terms of time average:

$$\Gamma = \left\langle \dot{\mu}_\alpha E_\alpha + \dot{m}_\alpha B_\alpha + \frac{1}{3} \dot{\theta}_{\alpha\beta} E_{\alpha\beta} \right\rangle_t \quad (3)$$

where $\dot{\mu}$, $\dot{m}$, $\dot{\theta}$, $E_\alpha = \frac{1}{2} (\tilde{E}_\alpha e^{-i\omega t} + \tilde{E}_\alpha^* e^{i\omega t})$ and $B_\alpha = \frac{1}{2} (\tilde{B}_\alpha e^{-i\omega t} + \tilde{B}_\alpha^* e^{i\omega t})$ are real quantities. By considering the component of dipole moment along the electric field direction, we replace β with α (ref. 47) to get

$$\Gamma_{E1-E1} = \frac{\omega}{4} \alpha''_{\alpha\alpha} (\tilde{E}_\alpha^* \tilde{E}_\alpha + \tilde{E}_\alpha \tilde{E}_\alpha^*) \rightarrow \Gamma_{E1-E1} = \frac{\omega}{2} \alpha''_{\alpha\alpha} [\tilde{E}_\alpha \tilde{E}_\alpha^*] \quad (4)$$

Magnetic dipole–dipole excitation (M1–M1) is given by

$$\Gamma_{M1-M1} = \frac{\omega}{4} \chi''_{\alpha\alpha} (\tilde{B}_\alpha^* \tilde{B}_\alpha + \tilde{B}_\alpha \tilde{B}_\alpha^*) \rightarrow \Gamma_{M1-M1} = \frac{\omega}{2} \chi''_{\alpha\alpha} [\tilde{B}_\alpha \tilde{B}_\alpha^*] \quad (5)$$

Electric–magnetic dipole excitation (E1–M1) results in the interaction of the electric field with the electric dipole moment induced by the magnetic field and vice versa. The expression is given by

$$\Gamma_{E1-M1} = \frac{i\omega}{4} \langle G'_{\alpha\beta} \rangle_{\rho} (\tilde{B}_{\beta} \tilde{E}_{\alpha}^* - \tilde{E}_{\alpha} \tilde{B}_{\beta}^*) \rightarrow \Gamma_{E1-M1} = \frac{\omega}{2} \rho G'_{\alpha\alpha} \text{Im} [\tilde{E}_{\alpha}^* \tilde{B}_{\alpha}] \quad (6)$$

To describe the bulk response, the tensor quantity $G'_{\alpha\beta}$ must be averaged over all degrees of molecular orientation. For partial orientation of molecules, due to the laser induced dipole force (see below), we consider anisotropic averaging $\langle G'_{\alpha\beta} \rangle_{\rho} \rightarrow \rho G'_{\alpha\alpha}$ where ρ is an orientation-dependent weighting factor influenced by the degree of molecular alignment^{50,51}.

Electric dipole–quadrupole excitation (E1–E2) arises from two contributions: (1) the interaction of the electric field with the electric dipole moment induced by the field gradient and (2) the interaction of the field gradient with the quadrupole moment induced by the electric field. The expression is given by

$$\Gamma_{E1-E2} = \frac{\omega}{6} \langle A''_{\alpha\beta\gamma} \rangle_{\rho} [\nabla_{\beta} \tilde{E}_{\gamma} \tilde{E}_{\alpha}^* + \tilde{E}_{\alpha} \nabla_{\beta} \tilde{E}_{\gamma}^*] \rightarrow \Gamma_{E1-E2} = \frac{\omega}{3} \rho A''_{\alpha\alpha\gamma} \text{Re} [\tilde{E}_{\alpha}^* \nabla_{\alpha} \tilde{E}_{\gamma}] \quad (7)$$

We consider anisotropic averaging $\langle A''_{\alpha\beta\gamma} \rangle_{\rho} \rightarrow \rho A''_{\alpha\alpha\gamma}$, where ρ is an orientation-dependent weighting factor influenced by the degree of molecular alignment. For complete alignment ($\rho = 1$), considering the principal molecular axis is oriented along the propagation axis (γ), the tensor quantity can be expressed as $\langle A''_{\alpha\beta\gamma} \rangle_{\rho} \rightarrow (A''_{\alpha\alpha\gamma} + A''_{\beta\beta\gamma})$ (ref. 47). Because the dominant contribution to the dipole moment is along the electric field direction (α), we limit to $A''_{\alpha\alpha\gamma}$. This tensor quantity vanishes for randomly oriented molecules, $\rho = 0$ (isotropic averaging). The higher multipole transitions such as E1M2, E2M1 and E2E2 are ignored because the molecular response tensor for these transitions is very small. The total rate of excitation is a sum of all four absorption rates for an asymmetric LG beam:

$$\Gamma_{\delta}^{\pm} = \frac{\omega}{2} \left\{ \underbrace{\rho'' |\tilde{E}_{\delta}^{\pm}|^2}_{\text{EIE1}} + \underbrace{\chi'' |\tilde{B}_{\delta}^{\pm}|^2}_{\text{MIM1}} + \underbrace{\rho G' \text{Im} [(\tilde{E}_{\delta}^{\pm})^* \cdot \tilde{B}_{\delta}^{\pm}]}_{\text{EIM1}} + \underbrace{\frac{2}{3} \rho A'' \text{Re} [(\tilde{E}_{\delta}^{\pm})^* \cdot \nabla \tilde{E}_{\delta}^{\pm}]}_{\text{EIE2}} \right\} \quad (8)$$

The δ is the asymmetrical parameter, $\delta = 0$ for a symmetric LG beam and $\delta \neq 0$ for an asymmetric LG beam. The sign in $\Gamma^{\pm}$ represents the sign of the OAM. The above equation is generalized to multiphoton absorption (Supplementary Section 10). E1 and M1 are the electric and magnetic dipoles, respectively, and E2 is the electric quadrupole. The coupling terms E1M1 and EIE2 are pseudoscalars and change sign under improper rotation. For a specific chiral system, the sign change of these quantities upon reflection would lead to non-zero differential absorption, defined as

$$\Delta W = \int_{-\omega_0}^{\omega_0} \text{HD (Type I, II)} dx dy \quad (9)$$

and integrated over the beam cross-section. HD (Type I) is defined as the difference between the absorption of left- and right-handed helical light for the same molecule (Figs. 3 and 4a):

$$\text{HD}_{\delta} (\text{Type I}) = \Gamma_{\delta}^{+} - \Gamma_{\delta}^{-} = G' [C^{+} - C^{-}] + A'' [\gamma^{+} - \gamma^{-}] \quad (10)$$

HD (Type II) is defined as the difference in absorption between the two enantiomers for a specific helicity and polarization (Figs. 2 and 4b,c):

$$\text{HD}_{\delta}^{\pm} (\text{Type II}) = \Gamma_R^{\pm} - \Gamma_S^{\pm} = C^{\pm} [G'_R - G'_S] + \gamma^{\pm} [A''_R - A''_S] \quad (11)$$

where R and S represent the two enantiomers. The parameter $C^{\pm} = 2\omega \text{Im} [(\tilde{E}_{\delta}^{\pm})^* \cdot \tilde{B}_{\delta}^{\pm}]$ in equations (3) and (4) is called optical chirality,

a local measure of the degree of circular polarization, and we define $\gamma^{\pm} = \frac{2\omega}{3} \text{Re} [(\tilde{E}_{\delta}^{\pm})^* \cdot \nabla \tilde{E}_{\delta}^{\pm}]$ as optical helicity. Both are time-even pseudoscalars. Optical chirality is often used to describe the phenomenon of CD in molecules^{6,47,52} and metasurfaces^{29,53,54}. Optical helicity, γ , is a quantity describing the handedness of helical light. It contains the gradient of the electric field, giving rise to a linear l dependence. The above equations, assuming full molecular alignment, show that the chiral light–matter interaction depends on both molecular transitions (contained in G' and A'') and optical chirality C , and optical helicity, γ . The contribution of the EIE2 term was modelled in Fig. 5 by considering the optical helicity term γ' (dominant component defined by approximating A'' as a scalar).

The following qualitative behaviour emerges by evaluating equations (9) and (10) for HD (Type I) and equations (9) and (11) for HD (Type II):

- HD (Type I) is a beam-dominated property and does not exist for symmetric LG beams. For asymmetric LG beams, the E1M1 term vanishes (because we take the difference between the left- and right-helical beams for the same polarization) and the EIE2 coupling term is non-zero. For a circularly polarized Gaussian beam, the E1M1 term is non-zero and gives rise to conventional CD.
- HD (Type II) is a material-dominated property where both E1M1 and EIE2 coupling terms contribute to differential absorption for asymmetric LG beams. For symmetric LG beams, the EIE2 term averages out to zero, but the E1M1 term is non-zero and can contribute to HD. E1M1 and EIE2 are of similar magnitudes^{47,55}. For asymmetric LG beams with the same polarization but different helicities, the EIE2 term is responsible for the change in the sign of the HD curves. Because the E1M1 term changes sign only with polarization, its finite magnitude leads to an offset in the HD curves (Fig. 4b,c).

The EIE2 coupling term is often ignored because it vanishes for a random orientation of molecules due to rotational isotropic averaging. However, if the molecules are preferentially aligned, the quadrupolar interactions containing A'' cannot be neglected⁵⁶. This is the case for asymmetric LG beams, in which the spatial inhomogeneity in the intensity profile at the interaction region gives rise to an optical dipole force defined by $\mathbf{F} = \alpha \frac{1}{2} \nabla E^2 + \alpha \frac{d}{dt} (\mathbf{E} \times \mathbf{B})$, where the first term defines the gradient force and the second term the scattering force, which can be neglected when the Poynting vector remains constant over an optical cycle. A net non-zero force is exerted on the induced dipoles directed towards the extrema of the radiation field (Fig. 3a). The resultant torque preferentially aligns the molecular axis parallel to the polarization plane⁵⁷, leading to a non-zero averaged EIE2 contribution to HD. The EIE2 contribution to HD vanishes for symmetric LG beams because the gradient force is zero. The E1M1 term is non-zero even for randomly oriented molecules.

Asymmetric LG beams

We introduced an asymmetry parameter, δ , into the symmetric LG beam to obtain an asymmetric LG beam. We also consider the longitudinal component of the field (E_z) as a correction to the paraxial regime^{58,59} to take into account its finite l (OAM) contribution. The importance of the longitudinal component in the light–matter interaction has been recently demonstrated in differentiating nanoparticle aggregates using helical light²⁸. When light is focused tightly using a higher-NA objective, the contribution of the longitudinal component becomes significant.

For arbitrary polarization in the paraxial regime, the field components can be written as

$$u_{\delta}^{\pm}(x, y, z) = E_0 \exp[ikz] \left(\frac{\sqrt{2}((x \mp i y \delta) \pm i(y \mp i x \delta))}{\omega_0} \right)^{|l|} \exp\left(-\frac{(x^2 + y^2)}{\omega_0^2}\right) L_{p-j}^{(|l+j|)} \left(\frac{2\rho^2}{\omega_0^2} \right) \quad (12)$$

$$E_x^\pm(x, y, z) = \alpha_x u_0^\pm(x, y, z) \quad (13)$$

$$E_y^\pm(x, y, z) = \beta_z u_0^\pm(x, y, z) \quad (14)$$

$$E_z^\pm(x, y, z) = if \left[(\alpha_z \pm i\beta_z) \frac{|l|\omega_0((x \mp i\eta\delta) \mp i(y \mp i\zeta\delta))}{(x \mp i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_0^\pm(x, y, z) - \frac{2}{\omega_0} (\alpha_z(x) + \beta_z(y)) u_0^\pm(x, y, z) \right] \quad (15)$$

$$B_x(x, y, z) = -\beta_z \frac{k}{\omega} u_0^\pm(\mathbf{r}), \quad (16)$$

$$B_y(x, y, z) = \alpha_z \frac{k}{\omega} u_0^\pm(\mathbf{r}) \quad (17)$$

$$B_z(x, y, z) = if \frac{k}{\omega} \left[(\alpha_z \pm i\beta_z) \frac{|l|\omega_0((y \mp i\zeta\delta) \pm i(x \mp i\eta\delta))}{(x \mp i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_0^\pm(\mathbf{r}) - \frac{2}{\omega_0} (\alpha_z(y) - \beta_z(x)) u_0^\pm(\mathbf{r}) \right] \quad (18)$$

where $f = \lambda/2\pi\omega_0$, $\rho = \sqrt{x^2 + y^2}$ and ω_0 is the beam waist. Also, E_0 is the normalization factor obtained by integrating the intensity over all space ($-\infty$ to $+\infty$), and for ($l=1$) it is given as:

$$E_0 = \sqrt{\frac{2k^2\omega_0^2}{\pi(\alpha^2 + \beta^2)(2\omega_0^2 + k^2\omega_0^4 + 2(\zeta^2 + \eta^2)\delta^2(1 + k^2\omega_0^2))}} \quad (19)$$

In our case, there is no radial node, hence $p=0$. The $\pm$ represents the rotational direction of l . The polarization factors α and β are normalized such that $|\alpha_z|^2 + |\beta_z|^2 = 1$. Displacement of the singularity in the x - y plane can be achieved by varying η and ζ . For generalization, we substituted $\eta = 1/4$ and $\zeta = 1$, considering the movement of the singularity is slightly displaced from the axial direction experimentally.

Data availability

The minimum dataset necessary to interpret the results can be obtained from the corresponding authors upon reasonable request.

Code availability

The simulation data were obtained by evaluating the equations using standard technical software. The code is available upon reasonable request to the corresponding authors.

References

- Yang, N. & Cohen, A. E. Local geometry of electromagnetic fields and its role in molecular multipole transitions. *J. Phys. Chem. B* **115**, 5304–5311 (2011).
- Barron, L. D. *Molecular Light Scattering and Optical Activity* (Cambridge Univ. Press, 2004).
- Buckingham, A. D. & Dunn, M. B. Optical activity of oriented molecules. *J. Chem. Soc. A* **1971**, 1988–1991 (1971).
- Andrews, S. S. Using rotational averaging to calculate the bulk response of isotropic and anisotropic samples from molecular parameters. *J. Chem. Educ.* **81**, 877 (2004).

- Andrews, D. L. & Allcock, P. *Optical Harmonics in Molecular Systems: Quantum Electrodynamical Theory* (Wiley, 2005).
- Lipkin, D. Existence of a new conservation law in electromagnetic theory. *J. Math. Phys. (N.Y.)* **5**, 696–700 (1964).
- Wang, Z. et al. A novel chiral metasurface with controllable circular dichroism induced by coupling localized and propagating modes. *Adv. Opt. Mater.* **4**, 883–888 (2016).
- Guo, Y. et al. Orbital angular momentum dichroism caused by the interaction of electric and magnetic dipole moments and the geometrical asymmetry of chiral metal nanoparticles. *Phys. Rev. A* **102**, 033525 (2020).
- Loudon, R. *The Quantum Theory of Light* (Oxford Univ. Press, 2003).
- Forbes, K. A. & Andrews, D. L. Orbital angular momentum of twisted light: chirality and optical activity. *J. Phys. Photon.* **3**, 022007 (2021).
- Bradshaw, D. S. & Andrews, D. L. Manipulating particles with light: radiation and gradient forces. *Eur. J. Phys.* **38**, 034008 (2017).
- Cerjan, A. et al. Orbital angular momentum of Laguerre-Gaussian beams beyond the paraxial approximation. *J. Opt. Soc. Am. A* **28**, 2253–2260 (2011).
- Forbes, K. A. et al. Relevance of longitudinal fields of paraxial optical vortices. *J. Opt.* **23**, 075401 (2021).

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Author contributions

J.-L.B., A.J. and R.B. conceived the experiments. J.-L.B., A.J. and R.B. designed and planned the experiments. J.-L.B. and A.J. conducted the experiments and analysed the results. J.-L.B., A.J., A.P., T.B. and R.B. worked on the theory and conducted numerical simulations. F.H. fabricated the q -plates, P.C., E.K. and R.B. supervised the project. J.-L.B., A.J., T.B. and R.B. prepared the first draft, and all authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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Supplementary materials: Nonlinear helical dichroism in chiral and achiral molecules

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Contents

1	HD(Type I, II) in limonene and fenchone	1
2	Intensity profile of OAM beams before and after the sample	2
3	Measuring the transmitted l value of an OAM beam	3
4	Single shot transmitted spectrum measurement	4
5	Transmission measurements in air in the absence of sample	5
6	Differential absorption with non-OAM beams	6
7	Spatial Mapping of singularity	7
8	Fluence calculations	7
9	Optical dipole force	8
10	Extension of theory to multiphoton case using time-dependent perturbation theory	9
	References	12

1 HD(Type I, II) in limonene and fenchone

Figures S1 shows HD(Type II) in limonene as a function of fluence for $l = \pm 1$ (Fig.S1a) and ± 3 (Fig.S1b), respectively for linearly polarized helical light. The chiral signal increases with laser fluence and reaches a maximum of ~ 6 -7%. The chiral signals in limonene and fenchone are of opposite signs (black curve and red curves are flipped) because they rotate the plane of linear polarization in opposite directions (*see Methods*). The chiral signal did not increase with l -value in limonene.

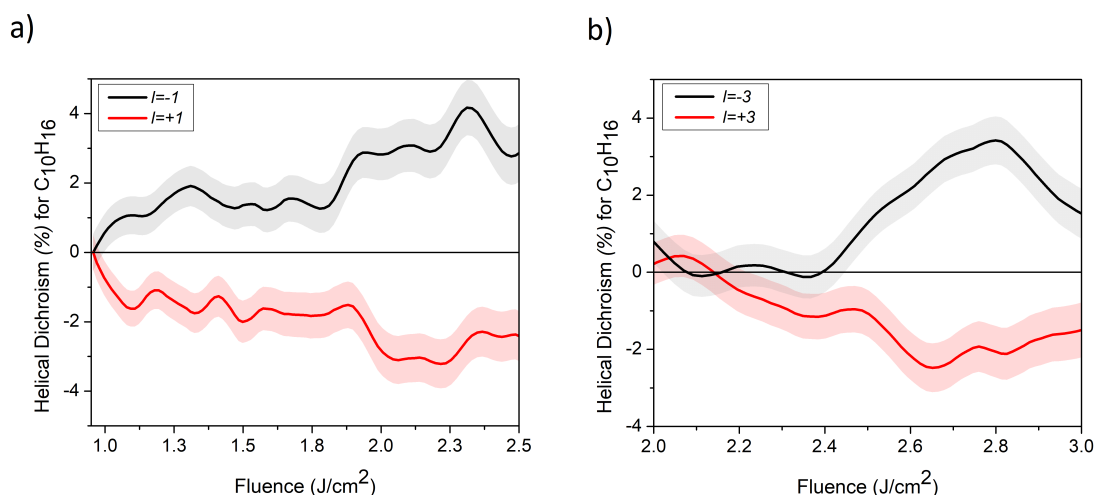


FIG. S 1. HD(Type II) in limonene with linearly polarized light ($s = 0$) as a function of peak laser fluence. **(a)** $l = \pm 1$. **(b)** $l = \pm 3$. The colour bands represent the propagation error of the chiral signal for three independent measurements (sample size).

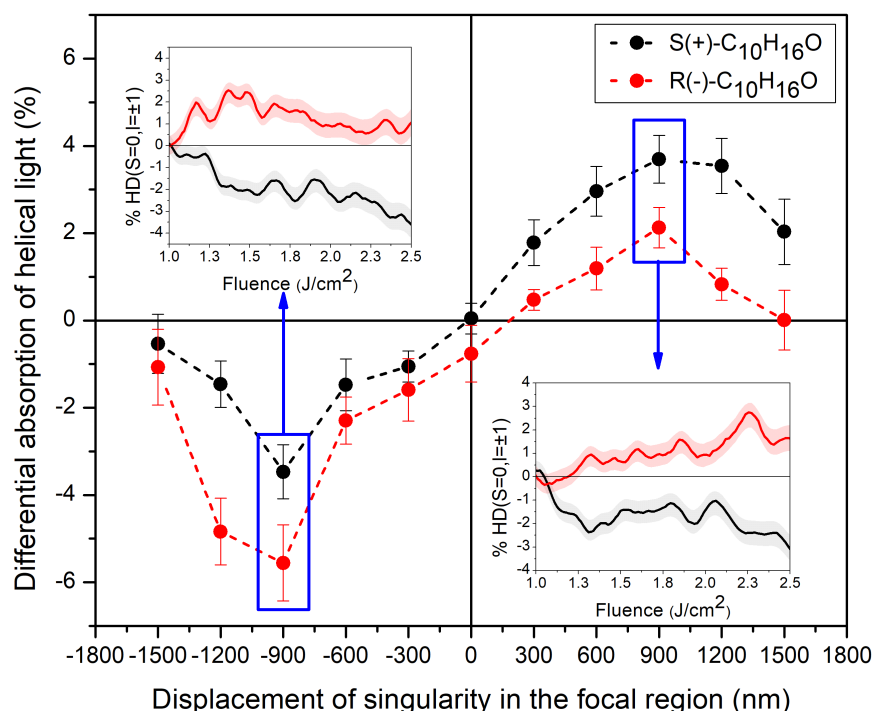


FIG. S 2. Helical dichroism with asymmetric OAM beams in fenchone. Differential absorption of linearly polarized helical light $l = \pm 1$ as a function of the position (or displacement) of the singularity in the OAM beam. The insets show helical dichroism as function of peak laser fluence when the singularity is at the positions marked by solid rectangles. The error bars and colour bands represent the propagation error of the chiral signal for three independent measurements (sample size).

Figure. S2 shows that HD signal in fenchone. The spatial variation of differential absorption, HD(Type I), of linearly polarized helical light in fenchone enantiomers exhibits the same behaviour as achiral molecules (Fig. 3b) as well as limonene enantiomers (Fig. 4). The insets of Fig. S2 represent HD(Type II) as a function of peak laser fluence when the singularity was at the positions marked by solid rectangles.

2 Intensity profile of OAM beams before and after the sample

To ensure that the beam profile is not influenced by nonlinear propagation effects at the interaction region we took single shot images of the beam profile with and without the sample as shown in fig. S3. A pulse energy of 350 nJ for $l = \pm 1$ was chosen because the magnitude helical dichroism (see main article) is largest around that energy region. There was no change in the beam profile after propagating through the sample. This suggests the nonlinear absorption is not influenced by any propagation effects.

Single shot OAM mode imaging at 350 nJ for $l = -1$

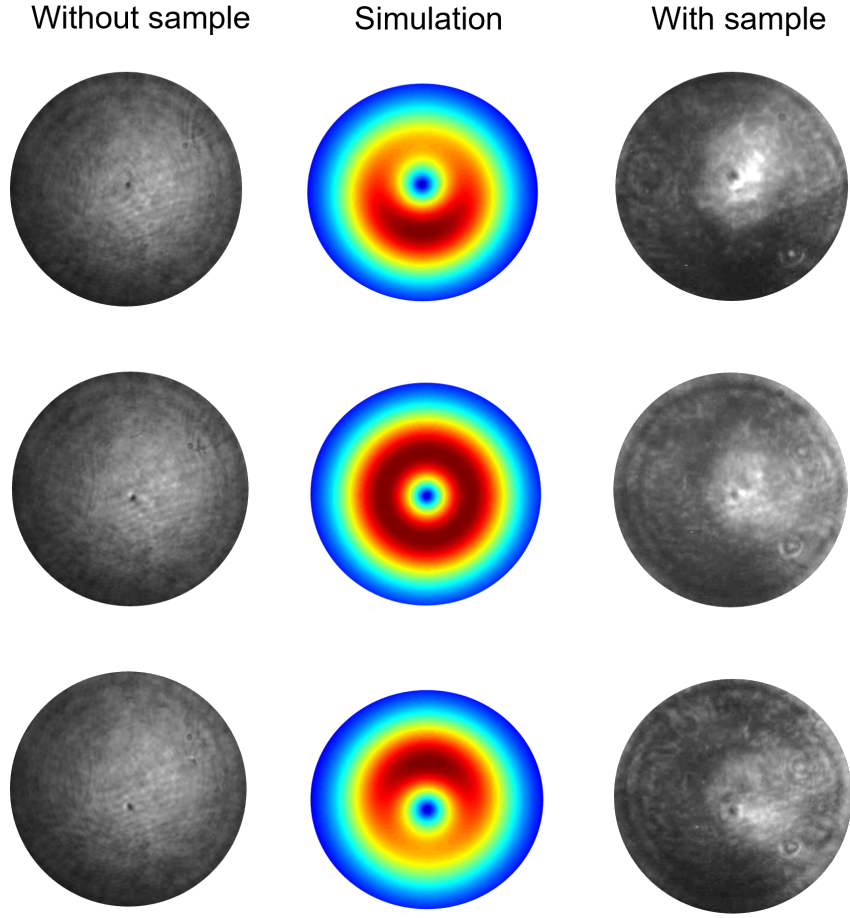


FIG. S 3. Single shot beam profiles of $l = -1$ for a symmetrical LG (center row) and asymmetrical LG (top and bottom rows) beams. The left (right) column shows the beam profiles without(with) the sample. The central column shows the simulated intensity profiles.

3 Measuring the transmitted l value of an OAM beam

To ensure the l value remained unchanged after propagating through the sample, we performed a set of interference experiments involving Gaussian and OAM beams to observe the signature fork patterns. Fig. S4 depicts simulated and measured single-shot fork patterns for $l = -1$ in air (a,b), $l = +3$ in sample (c,d). Fig. S4 e,f shows the measured patterns for $l = \pm 1$ in the sample. Though the contrast of the interference patterns is poor in the sample due to single-shot measurement, they are in agreement with the expected signature patterns. Results indicate no change in the angular momentum value of the light when propagating through the sample.

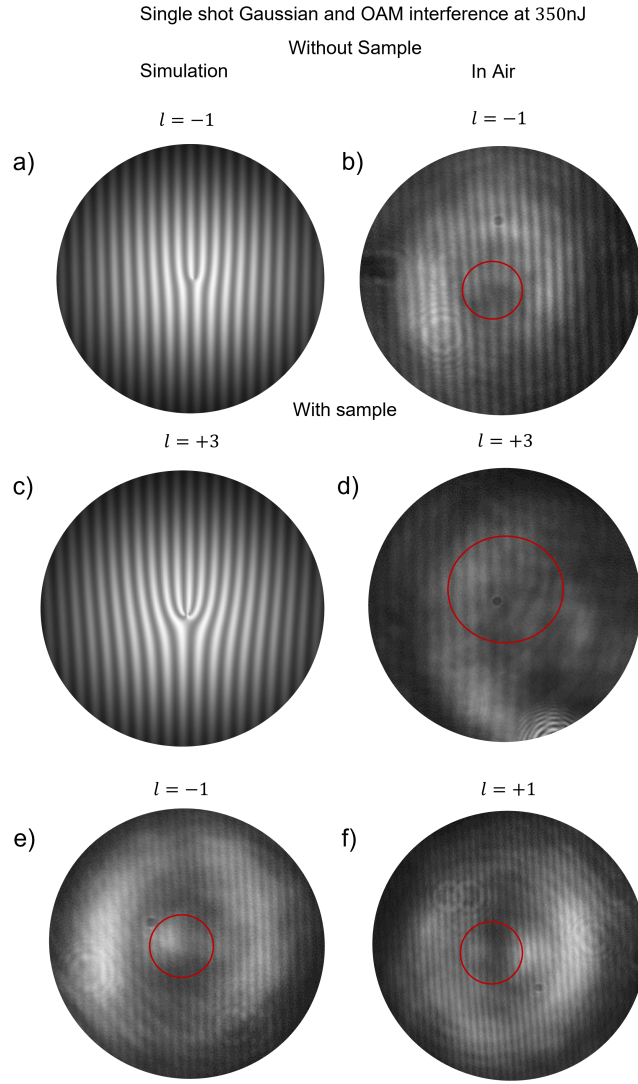


FIG. S 4. Simulated and measured (a,b) two pronged fork pattern for $l = -1$ in air, (c,d) four pronged fork pattern for $l = +3$ in sample. (e,f) measured two pronged fork pattern for $l = \pm 1$ in sample.

4 Single shot transmitted spectrum measurement

Nonlinear affects such as self-phase modulation can influence the propagation of incident light through the sample over the range of pulse energies used in the experiment. Fig. S5 shows set of single-shot spectra (a) of Ti: Sapphire laser used as a reference (black curve), (b) after the power and OAM/SAM control optics (magenta curve) with no sample, and (c) after propagating through (-)-fenchone and (+)-fenchone for linearly polarized helical light, $+l$ (cyan and green curves, respectively) and $-l$ (red and blue curves, respectively). There is no considerable change in the spectral shape after propagating through the sample suggesting nonlinear affects are negligible. Compared to the reference spectrum, the spectrum of light incident on the sample is altered due to numerous optics in the beam path.

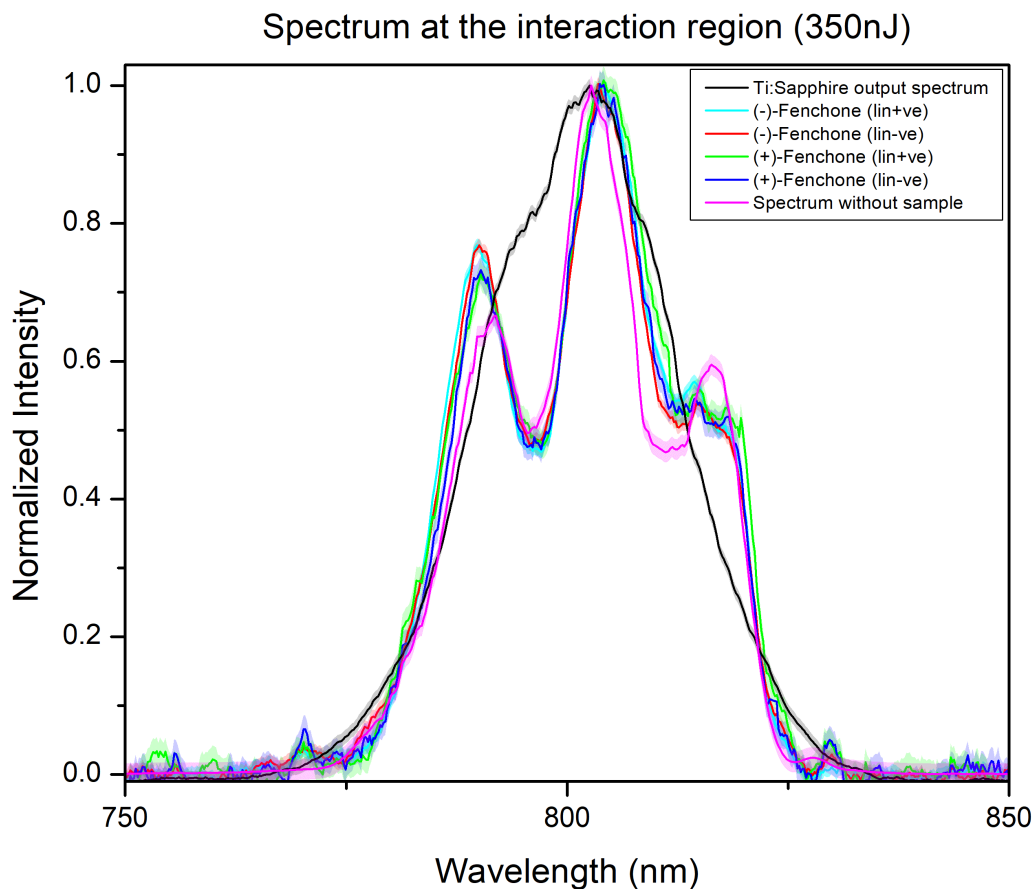


FIG. S 5. Single-shot measurement of transmitted spectra. The reference spectrum (black curve) corresponds to Ti:sapphire laser, spectrum after the power and OAM/SAM control but with no sample (magenta curve). The cyan (green) and red (blue) curves are the spectrum of linearly polarized $l = +l$ (lin +ve) and $l = -l$ (lin -ve) after propagating through (-)-fenchone ((+)-fenchone).

5 Transmission measurements in air in the absence of sample

In the absence of a sample, transmission measurements conducted in air ensure that the photodiodes detect identical signals when changing the incoming linearly polarized light from $+l$ to $-l$. Fig. S6 a) and b) show transmission of a symmetrical and an asymmetrical LG beams through air. The red (black) curves represent the difference between the PD1 (PD2) signal for linearly polarized $+l$ and $-l$. Both signals are centered about zero with a fluctuation of $\pm 0.05V$. Moreover, the red and black curves nearly overlap over the entire energy range, demonstrating no signal change between PD1 (incident light) and PD2 (transmitted light) as the OAM value changed. This indicates there is no arbitrary signal/noise introduced by the experimental setup to the observed differential absorption in chiral and achiral molecules. Transmission measurements in air were performed before every experimental run and for every position of the displaced singularity.

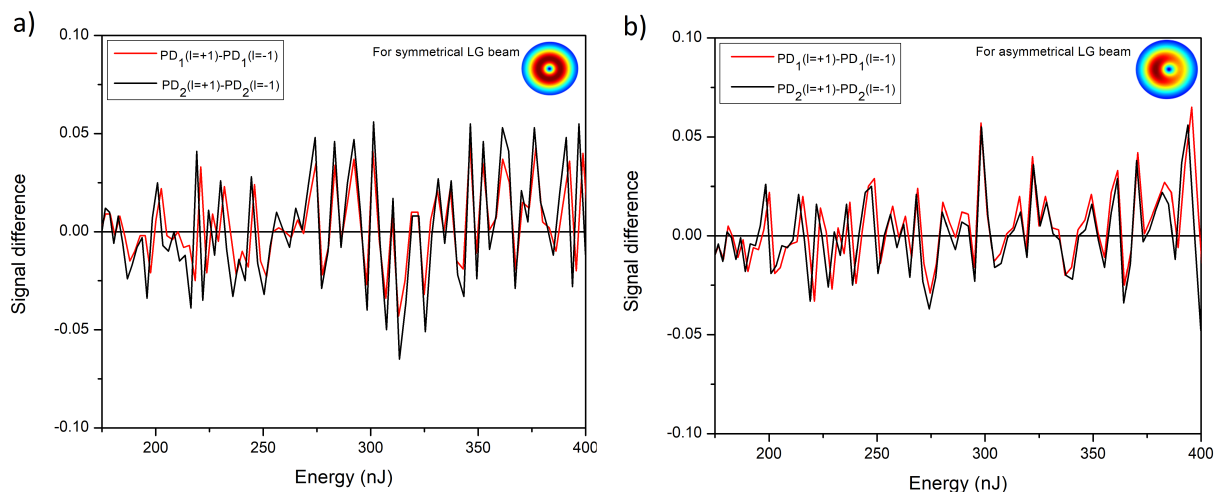


FIG. S 6. Transmission linearly polarized helical light in air (no sample) (a) for a symmetrical and (b) asymmetrical LG beams. The red (black) curve represents the difference between the PD1 signal for $+l$ and $-l$ (PD2 monitoring the transmitted light).

6 Differential absorption with non-OAM beams

Figure S7a shows normalized transmission of a linearly polarized Gaussian beam propagating through left- and right-handed chiral molecule. Both in the linear and the nonlinear regimes, the two curves overlap exhibiting no differential absorption. Similar transmission measurements were conducted for S(-)-limonene with left- and right-circularly polarized annular beam resembling an Airy pattern obtained through Fresnel diffraction (Fig. S7b). In absence of phase, which is responsible for orbital angular momentum, there is no differential absorption in a chiral molecule for a beam with a null intensity at the center. The results remained the same even when the null intensity regions was displaced from the center (fig 3c of the main article). This suggests that differential absorption is not purely due to the field gradient. Helical phase plays a crucial role.

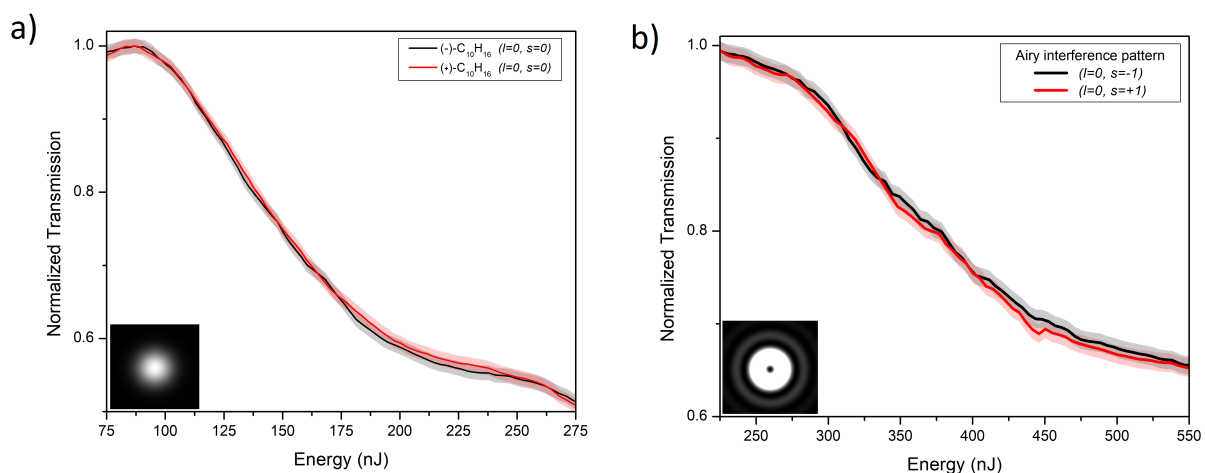


FIG. S 7. (a) Transmission of linearly polarized Gaussian in left- and right-handed limonene. (b) Transmission of left- and right-circularly polarized annular non-OAM beam for S(-)-limonene. Insets show the beam profiles. The colour bands represent the propagation error of the chiral signal for three independent measurements (sample size).

7 Spatial Mapping of singularity

Fig. S8 shows 2D contour map of differential absorption of linearly polarized ($\epsilon = 0.09$) left and right handed OAM ($l = \pm l$) for (+)-fenchone, obtained by displacing the singularity in the xy plane. The results presented in Fig.3, 4 (main text) and Fig. S2 are a line scan along one axial direction. The sinusoidal behaviour of differential absorption becomes asymmetric as we displace our singularity off-axis. This behaviour is likely due to the relative angle between the polarization direction and the direction of displacement of the singularity.

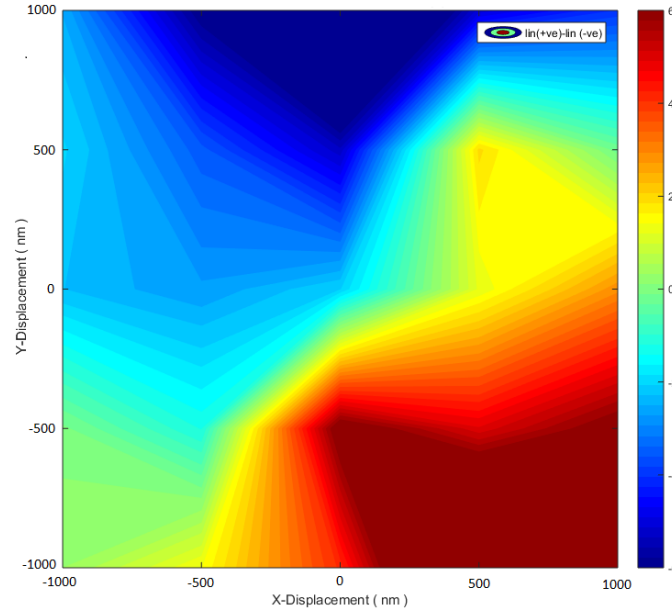


FIG. S 8. Differential absorption of linearly polarized helical light ($l = \pm l$) in (+)-fenchone as a function of the displacement of the singularity in the XY-plane.

8 Fluence calculations

In LG beams with increasing l -value, the size of the null intensity region at the center increases. Consequently, for the same spot size higher pulse energies are required to reach the threshold for the onset of nonlinear absorption. This can be seen from the transmission curves shown in Fig. S9 for $l = 1$ (left) and $l = 3$ (right) plotted as a function of laser pulse energy in fenchone.

From the threshold energies, the peak fluence is calculated based on the below equation¹:

$$F_l \left[\frac{J}{cm^2} \right] = \frac{2^{(|l|+1)} r^{2|l|} e^{\frac{-2r^2}{\omega(z)^2}}}{|l|! \pi \omega(z)^{2(|l|+1)}} E_l^{th} [J]$$

where $l = 0; \pm 1; \pm 2; \pm 3 \dots$ is the orbital angular momentum value, r is the radial direction, $\omega(z)$ is the radius of a beam evaluated at $z=0$ and E_l is the threshold pulse energy for different l -values.

For peak fluence, radial parameter r is evaluated at the maxima of the intensity profile. For Gaussian beam ($l = 0$) maxima occurs at $r = 0$, for OAM beam with $l = 1$ at $r_{pk} = \pm \frac{w_0}{\sqrt{2}}$ and subsequently for higher order l values at the position of their respective maxima.

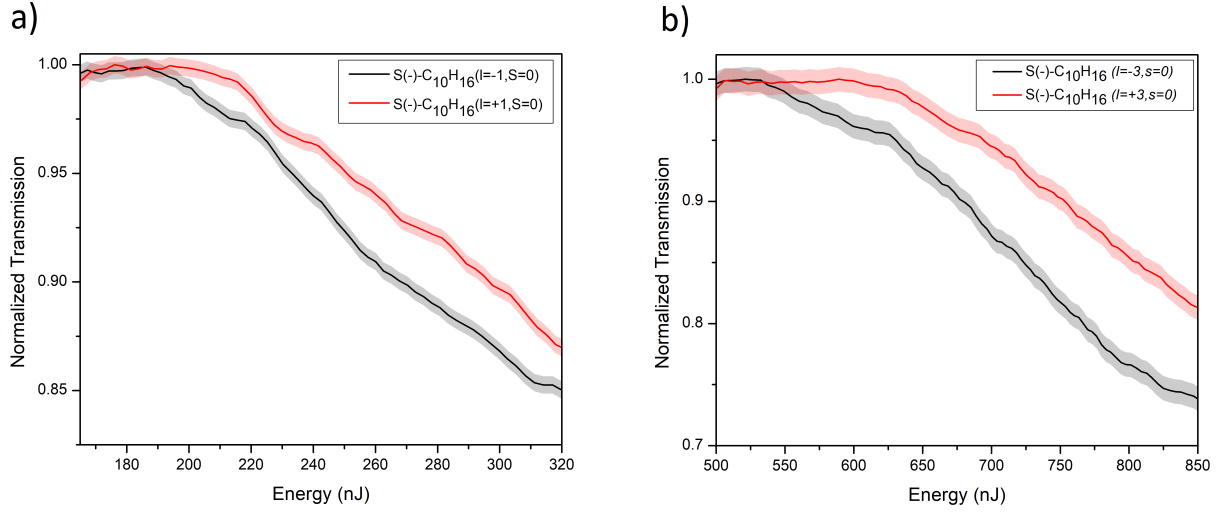


FIG. S 9. Transmission curves of limonene with linearly polarized light ($s = 0$) as a function of pulse energy. **(a)** $l = \pm 1$. **(b)** $l = \pm 3$. The colour bands represent the propagation error of the chiral signal for three independent measurements (sample size).

Substituting the above values for radial parameter, we get

$$\text{For } l = 0 \text{ beam : } F_0(r_{pk}) = 2 \frac{E_0^{th}}{\pi w_0^2}$$

$$\text{For } l = 1 \text{ beam : } F_1(r_{pk}) = 2e^{-1} \frac{E_1^{th}}{\pi w_0^2}$$

One can obtain similar equations for higher order OAM beams from which the peak laser fluences were calculated for the presented results.

9 Optical dipole force

Here we show that optical gradient forces are non-zero for asymmetric LG beams. The total force acting on a dipole can be written as²

$$\mathbf{F} = (\boldsymbol{\mu} \cdot \nabla) \mathbf{E} + \dot{\boldsymbol{\mu}} \times \mathbf{B} + \dot{\mathbf{r}} \times (\boldsymbol{\mu} \cdot \nabla) \mathbf{B} \quad (1)$$

where $\boldsymbol{\mu}$ is the dipole moment. Here first term on the RHS containing the inner product $(\boldsymbol{\mu} \cdot \nabla)$ represents the dipole force due to inhomogeneity in the fields. Second term is the expression of standard Lorentz force and third term represents particle movement in the inhomogeneous magnetic field. The above equation was obtained by assuming dipoles does not change the incident fields. For non relativistic speeds ($\dot{r} \ll c$), third term can be neglected as it is much smaller in comparison to first two terms. Substituting $\boldsymbol{\mu} = \alpha(\omega) \mathbf{E}(\mathbf{r})$ where α is atomic polarizability, we get,

$$\mathbf{F} = \alpha(\mathbf{E} \cdot \nabla) \mathbf{E} + \alpha \left(\frac{d\mathbf{E}}{dt} \times \mathbf{B} \right) \quad (2)$$

Using vector identity $(\mathbf{E} \cdot \nabla) \mathbf{E} = \frac{1}{2} \nabla (E^2) - \mathbf{E} \times (\nabla \times \mathbf{E})$ and second maxwell equation we get,

$$\mathbf{F} = \alpha \frac{1}{2} \nabla E^2 + \alpha \frac{d}{dt} (\mathbf{E} \times \mathbf{B}). \quad (3)$$

Here, first term defines the gradient force and second term is the scattering force which can be neglected when the poynting vector does not change over an optical cycle. Fig. S10 shows the gradient force component (F_x) integrated over the beam

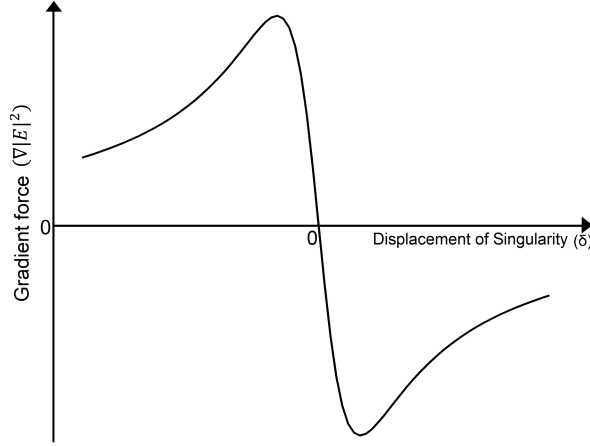


FIG. S 10. Optical gradient force as a function of displaced position of singularities. Optical gradient force is zero for symmetric LG beam and maximum at the position of displaced singularity. Force converges towards zero for the extreme displacement in singularity where beam profile mimics gaussian profile.

cross-section as a function of displaced position of the singularity. For linearly polarized light one of the transverse components will be dominant. The F_y component would be smaller in magnitude however exhibits similar behaviour. The gradient force is zero for the symmetric LG beam for which the singularity is at the center. When the singularity is displaced, the gradient forces initially increases and then decreases to zero for large displacement. A non-zero gradient force would give rise to a torque which preferentially aligns the molecular axis parallel the polarization plane³. Such alignment of molecules in an asymmetric LG beams will lead to non-zero averaged E1E2 dipole-quadrupole contribution to HD. Therefore, the HD signal, shown in Fig. 5 of the main text, is zero for symmetric LG beams, increases with the displacement of the singularity reaching a maximum and then decreases when the singularity reaches the beam periphery.

10 Extension of theory to multiphoton case using time-dependent perturbation theory

Using perturbation theory, a generic time-dependent wavefunction

$$|\Psi\rangle = |\Psi\rangle^{(0)} + \sum_m c_m(t) |\Psi_m\rangle^{(0)} \quad (4)$$

satisfies the Schrodinger equation

$$(H_0 + \lambda V(t)) |\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle \quad (5)$$

where, λ is the perturbation parameter and

$$V(t) = -\mu_\alpha E_\alpha - \frac{1}{3} \theta_{\alpha\beta} \nabla_\alpha E_\beta - m_\alpha B_\alpha - \dots \quad (6)$$

is the interaction Hamiltonian^{4,5}. The corresponding multipoles and fields are complex quantities. $|\Psi\rangle^{(0)} = |\psi\rangle^{(0)} e^{-iE_n^{(0)}t/\hbar}$ are the stationary states satisfying

$$H_0 |\Psi\rangle^{(0)} = i\hbar \frac{\partial}{\partial t} |\Psi\rangle^{(0)} \quad (7)$$

We can expand the time dependent coefficient $c_m(t)$ in powers of perturbation parameter λ .

$$c_m(t) = c_m^{(0)} + \lambda c_m^{(1)}(t) + \lambda^2 c_m^{(2)}(t) + \dots + \lambda^n c_m^{(n)}(t) \quad (8)$$

where different order coefficients can be obtained by comparing powers of perturbation parameter λ

$$c_m^{(0)}(t) = \left(\frac{1}{i\hbar} \right) \int_{-\infty}^t dt' \langle m|V(t')|g \rangle e^{i\omega_{mg}t'} \quad (9)$$

and nth order is defined as,

$$c_m^{(n)}(t) = \left(\frac{1}{i\hbar} \right)^n \sum_l \int_{-\infty}^t dt' \langle m|V(t')|l \rangle c_l^{(n-1)}(t') e^{i\omega_{ml}t'} \quad (10)$$

Now, we calculate the single photon absorption rate and generalize it to multiphoton absorption⁶ Considering a interaction Hamiltonian of the form

$$V(t) = V e^{-i\omega t} + V^* e^{i\omega t} \quad (11)$$

By implementing the rotating wave approximation, we neglected the complex conjugate of the field because we are only considering absorption and ignore the stimulated emission (anti-resonant terms). The probability amplitude can be expressed as

$$p_m^{(n)}(t) = |c_m^{(n)}(t)|^2 \quad (12)$$

and the rate of transition

$$R_{mg}^{(n)} = \frac{p_m^{(n)}(t)}{t} \quad (13)$$

therefore, for single photon we obtain Fermi's golden rule

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} |\langle m|V|g \rangle|^2 \delta(\omega_{mg} - \omega) \quad (14)$$

Single photon transition rate is proportional to absorption cross-section⁶ which is proportional to the rate of energy absorption (Γ) derived in the main text. Substituting the interaction Hamiltonian into the rate expression, we get

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} \left| -\mu_\alpha^{mg} E_\alpha - \frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta - m_\alpha^{mg} B_\alpha \right|^2 \delta(\omega_{mg} - \omega) \quad (15)$$

For physical situations, the delta function can be replaced by a lineshape function

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} \left| -\mu_\alpha^{mg} E_\alpha - \frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta - m_\alpha^{mg} B_\alpha \right|^2 \rho(\omega_{mg} = \omega) \quad (16)$$

$$\begin{aligned} R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} & \left((\mu_\alpha^{mg} E_\alpha) (\mu_\alpha^{mg} E_\alpha)^* + (\mu_\alpha^{mg} E_\alpha) (m_\alpha^{mg} B_\alpha)^* + (\mu_\alpha^{mg} E_\alpha) \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right)^* + (m_\alpha^{mg} B_\alpha) (\mu_\alpha^{mg} E_\alpha)^* \right. \\ & + (m_\alpha^{mg} B_\alpha) \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right)^* + (m_\alpha^{mg} B_\alpha) (m_\alpha^{mg} B_\alpha)^* + \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right) (\mu_\alpha^{mg} E_\alpha)^* + \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right) (m_\alpha^{mg} B_\alpha)^* \\ & \left. + \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right) \left(\frac{1}{3} \theta_{\alpha\beta}^{mg} \nabla_\alpha E_\beta \right)^* \right) \rho(\omega_{mg} = \omega) \end{aligned}$$

Ignoring the M1M1, M1E2 and the E2E2 coupling terms and applying the anisotropic averaging, we get

$$\begin{aligned} R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} & \left[|\mu_\alpha^{mg}|^2 |E_\alpha|^2 + |m_\alpha^{mg}|^2 |B_\alpha|^2 + \langle \mu_\alpha^{mg} m_\alpha^{mg*} \rangle_\rho (E_\alpha B_\alpha^*) + \langle m_\alpha^{mg} \mu_\alpha^{mg*} \rangle_\rho (B_\alpha E_\alpha^*) \right. \\ & \left. + \frac{1}{3} \left(\langle \theta_{\alpha\beta}^{mg} \mu_\alpha^{mg*} \rangle_\rho (\nabla_\alpha E_\beta \cdot E_\alpha^*) + \langle \mu_\alpha^{mg} \theta_{\alpha\beta}^{mg*} \rangle_\rho (E_\alpha \nabla_\alpha E_\beta^*) \right) \right] \rho(\omega_{mg} = \omega) \end{aligned}$$

Here ρ is the orientation-dependent weighting factor arising from the anisotropic averaging ($\rho = 0$ for random orientations and $\rho = 1$ for full alignment of molecules). The dipole transition μ is a real quantity, magnetic transition dipole m is imaginary⁷. Approximating the response of the quadrupole tensor as a scalar we can rewrite the above expression as:

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} \left[|\mu_\alpha^{mg}|^2 |E_\alpha|^2 + |m_\alpha^{mg}|^2 |B_\alpha|^2 + \langle \mu_\alpha^{mg} m_\alpha^{gm} \rangle_\rho (B_\alpha E_\alpha^* - E_\alpha B_\alpha^*) \right. \\ \left. + \frac{1}{3} \left(\langle \mu_\alpha^{mg} \theta_{\alpha\beta}^{gm} \rangle_\rho \left(\nabla_\alpha E_\beta E_\alpha^* + E_\alpha \nabla_\alpha E_\beta^* \right) \right) \right] \rho (\omega_{mg} = \omega)$$

Since $B_\alpha E_\alpha^* - E_\alpha B_\alpha^* = -2i \text{Im} [E_\alpha^* B_\alpha]$ and, $(E_\alpha^* \nabla_\alpha E_\beta + E_\alpha \nabla_\alpha E_\beta^*) = 2 \text{Re} [E_\alpha^* \nabla_\alpha E_\beta]$ we can rewrite the above expression as

$$R_{mg}^{(1)} = \frac{2\pi}{\hbar^2} \left[\underbrace{|\mu_\alpha^{mg}|^2 |E_\alpha|^2}_{\text{E1E1}} + \underbrace{|m_\alpha^{mg}|^2 |B_\alpha|^2}_{\text{M1M1}} + \underbrace{2 \langle \mu_\alpha^{mg} m_\alpha^{gm} \rangle_\rho \text{Im} [E_\alpha^* B_\alpha]}_{\text{E1M1}} + \underbrace{\frac{2}{3} \langle \mu_\alpha^{mg} \theta_{\alpha\beta}^{gm} \rangle_\rho \text{Re} [E_\alpha^* \nabla_\alpha E_\beta]}_{\text{E1E2}} \right] \rho (\omega_{mg} = \omega) \quad (17)$$

This is the single photon transition rate and resembles equation (8) of main text. $\text{Im} [E_\alpha^* B_\alpha]$ and $\text{Re} [E_\alpha^* \nabla_\alpha E_\beta]$ correspond to optical chirality $\mathcal{C}$ and helicity Υ , respectively.

The transition rate for two photon process (transition states: $g \rightarrow k \rightarrow m$) is

$$R_{mg}^{(2)} = 2\pi \left| \sum_k \frac{V_{mk} V_{kg}}{\hbar^2 (\omega_{kg} - \omega)} \right|^2 \rho (\omega_{mg} = 2\omega) \quad (18)$$

$$R_{mg}^{(2)} = 2\pi \left| \sum_k \frac{(\mu_\alpha^{mk} E_\alpha + \frac{1}{3} \theta_{\alpha\beta}^{mk} \nabla_\alpha E_\beta + m_\alpha^{mk} B_\alpha) (\mu_\alpha^{kg} E_\alpha + \frac{1}{3} \theta_{\alpha\beta}^{kg} \nabla_\alpha E_\beta + m_\alpha^{kg} B_\alpha)}{\hbar^2 (\omega_{kg} - \omega)} \right|^2 \rho (\omega_{mg} = 2\omega) \quad (19)$$

$$R_{mg}^{(2)} = 2\pi \left| \sum_k \frac{(\mu_\alpha^{mk} E_\alpha)(\mu_\alpha^{kg} E_\alpha) + (m_\alpha^{mk} B_\alpha)(\mu_\alpha^{kg} E_\alpha) + (\mu_\alpha^{mk} E_\alpha)(m_\alpha^{kg} B_\alpha) + (\frac{1}{3} \theta_{\alpha\beta}^{mk} \nabla_\alpha E_\beta)(\mu_\alpha^{kg} E_\alpha) + (\mu_\alpha^{mk} E_\alpha)(\frac{1}{3} \theta_{\alpha\beta}^{kg} \nabla_\alpha E_\beta)}{\hbar^2 (\omega_{kg} - \omega)} \right|^2 \rho (\omega_{mg} = 2\omega) \quad (20)$$

Ignoring the higher order terms involving M1 and E2 we get

$$R_{mg}^{(2)} = 2\pi \sum_k \frac{1}{\hbar^4 (\omega_{kg} - \omega)^2} \left\{ |\mu_\alpha^{mk} E_\alpha|^2 |\mu_\alpha^{kg} E_\alpha|^2 + |\mu_\alpha^{kg} E_\alpha|^2 \left[(\mu_\alpha^{mk} E_\alpha) (m_\alpha^{mk} B_\alpha)^* + (m_\alpha^{mk} B_\alpha) (\mu_\alpha^{mk} E_\alpha)^* \right] \right. \\ \left. + |\mu_\alpha^{kg} E_\alpha|^2 \left[(\mu_\alpha^{mk} E_\alpha) \left(\frac{1}{3} \theta_{\alpha\beta}^{mk} \nabla_\alpha E_\beta \right)^* + \left(\frac{1}{3} \theta_{\alpha\beta}^{mk} \nabla_\alpha E_\beta \right) (\mu_\alpha^{mk} E_\alpha)^* \right] + |\mu_\alpha^{mk} E_\alpha|^2 \left[(\mu_\alpha^{kg} E_\alpha) (m_\alpha^{kg} B_\alpha)^* + (m_\alpha^{kg} B_\alpha) (\mu_\alpha^{kg} E_\alpha)^* \right] \right. \\ \left. + |\mu_\alpha^{mk} E_\alpha|^2 \left[(\mu_\alpha^{kg} E_\alpha) \left(\frac{1}{3} \theta_{\alpha\beta}^{kg} \nabla_\alpha E_\beta \right)^* + \left(\frac{1}{3} \theta_{\alpha\beta}^{kg} \nabla_\alpha E_\beta \right) (\mu_\alpha^{kg} E_\alpha)^* \right] \right\} \rho (\omega_{mg} = 2\omega)$$

Implementing anisotropic averaging, we get

$$R_{mg}^{(2)} = 2\pi \sum_k \frac{1}{\hbar^4 (\omega_{kg} - \omega)^2} \left\{ |\mu_\alpha^{mk} \mu_\alpha^{kg}|^2 |E_\alpha E_\alpha|^2 + |\mu_\alpha^{kg}|^2 |E_\alpha|^2 \left[\langle \mu_\alpha^{mk} m_\alpha^{mk*} \rangle_\rho (E_\alpha B_\alpha^*) + \langle m_\alpha^{mk} \mu_\alpha^{mk*} \rangle_\rho (B_\alpha E_\alpha^*) \right] \right. \\ \left. + |\mu_\alpha^{kg}|^2 |E_\alpha|^2 \left[\langle \mu_\alpha^{mk} \frac{1}{3} \theta_{\alpha\beta}^{mk*} \rangle_\rho (E_\alpha \nabla_\alpha E_\beta^*) + \langle \frac{1}{3} \theta_{\alpha\beta}^{mk} \mu_\alpha^{mk*} \rangle_\rho (\nabla_\alpha E_\beta E_\alpha^*) \right] + |\mu_\alpha^{mk}|^2 |E_\alpha|^2 \left[\langle \mu_\alpha^{kg} m_\alpha^{kg*} \rangle_\rho (E_\alpha B_\alpha^*) + \langle m_\alpha^{kg} \mu_\alpha^{kg*} \rangle_\rho (B_\alpha E_\alpha^*) \right] \right. \\ \left. + |\mu_\alpha^{mk}|^2 |E_\alpha|^2 \left[\langle \frac{1}{3} \mu_\alpha^{kg} \theta_{\alpha\beta}^{kg*} \rangle_\rho (E_\alpha \nabla_\alpha E_\beta^*) + \langle \frac{1}{3} \theta_{\alpha\beta}^{kg} \mu_\alpha^{kg*} \rangle_\rho (\nabla_\alpha E_\beta E_\alpha^*) \right] \right\} \rho (\omega_{mg} = 2\omega) \\ R_{mg}^{(2)} = 2\pi \sum_k \frac{1}{\hbar^4 (\omega_{kg} - \omega)^2} \left\{ |\mu_\alpha^{mk} \mu_\alpha^{kg}|^2 |E_\alpha E_\alpha|^2 + 2 \left(|\mu_\alpha^{kg}|^2 |E_\alpha|^2 \langle \mu_\alpha^{mk} m_\alpha^{km} \rangle_\rho + |\mu_\alpha^{mk}|^2 |E_\alpha|^2 \langle \mu_\alpha^{kg} m_\alpha^{gk} \rangle_\rho \right) \text{Im} [E_\alpha^* B_\alpha] \right. \\ \left. + \frac{2}{3} \left(|\mu_\alpha^{kg}|^2 |E_\alpha|^2 \langle \mu_\alpha^{mk} \theta_{\alpha\beta}^{km} \rangle_\rho + |\mu_\alpha^{mk}|^2 |E_\alpha|^2 \langle \mu_\alpha^{kg} \theta_{\alpha\beta}^{gk} \rangle_\rho \right) \text{Re} [E_\alpha^* \nabla_\alpha E_\beta] \right\} \rho (\omega_{mg} = 2\omega)$$

Generalizing for n-photon case, where m is the final state and g is the ground state state

$$R_{mg}^{(n)} = 2\pi \left[\sum_p \sum_l \dots \sum_r \sum_k \frac{|\mu_\alpha^{mp} \mu_\alpha^{pl} \dots \mu_\alpha^{rk} \mu_\alpha^{kg}|^2 |E_\alpha|^{2n}}{\hbar^{2n} (\omega_{pl} - (n-1)\omega)^2 \dots (\omega_{rk} - 2\omega)^2 (\omega_{kg} - \omega)^2} \rho(\omega_{mg} = n\omega) \right] \quad (21)$$

$$+ 2 \sum_p \sum_l \dots \sum_r \sum_k \frac{|\mu_\alpha^{mp}|^2 |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{rk}|^2 \text{Im} [\mu_\alpha^{kg} m_\alpha^{gk}] + |\mu_\alpha^{mp}|^2 |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{kg}|^2 \langle \mu_\alpha^{rk} m_\alpha^{kr} \rangle_\rho + \dots +}{\hbar^{2n} (\omega_{pl} - (n-1)\omega)^2 \dots (\omega_{rk} - 2\omega)^2 (\omega_{kg} - \omega)^2} \quad (22)$$

$$\dots + \frac{|\mu_\alpha^{mp}|^2 \dots |\mu_\alpha^{rk}|^2 |\mu_\alpha^{kg}|^2 \text{Im} [\mu_\alpha^{pl} m_\alpha^{lp}] + |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{rk}|^2 |\mu_\alpha^{kg}|^2 \langle \mu_\alpha^{mp} m_\alpha^{pm} \rangle_\rho}{\hbar^{2n} (\omega_{pl} - (n-1)\omega)^2 \dots (\omega_{rk} - 2\omega)^2 (\omega_{kg} - \omega)^2} |E_\alpha|^{2(n-1)} \text{Im} [E_\alpha^* B_\alpha] \rho(\omega_{mg} = n\omega) \quad (23)$$

$$+ \frac{2}{3} \sum_p \sum_l \dots \sum_r \sum_k \frac{|\mu_\alpha^{mp}|^2 |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{rk}|^2 \text{Im} [\mu_\alpha^{kg} \theta_{\alpha\beta}^{gk}] + |\mu_\alpha^{mp}|^2 |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{kg}|^2 \langle \mu_\alpha^{rk} \theta_{\alpha\beta}^{kr} \rangle_\rho + \dots +}{\hbar^{2n} (\omega_{pl} - (n-1)\omega)^2 \dots (\omega_{rk} - 2\omega)^2 (\omega_{kg} - \omega)^2} \quad (24)$$

$$\dots + \frac{|\mu_\alpha^{mp}|^2 \dots |\mu_\alpha^{rk}|^2 |\mu_\alpha^{kg}|^2 \text{Im} [\mu_\alpha^{pl} \theta_{\alpha\beta}^{lp}] + |\mu_\alpha^{pl}|^2 \dots |\mu_\alpha^{rk}|^2 |\mu_\alpha^{kg}|^2 \langle \mu_\alpha^{mp} \theta_{\alpha\beta}^{pm} \rangle_\rho}{\hbar^{2n} (\omega_{pl} - (n-1)\omega)^2 \dots (\omega_{rk} - 2\omega)^2 (\omega_{kg} - \omega)^2} |E_\alpha|^{2(n-1)} \text{Re} [E_\alpha^* \nabla_\alpha E_\beta] \rho(\omega_{mg} = n\omega) \quad (25)$$

Neglecting the higher order cross terms, we therefore obtain similar expressions involving E1E1, E1M1 and E1E2 expressed in terms of optical chirality C and helicity Y. The above expressions were obtained in a scalar approximation regime where tensor properties are restricted to a dominant component for oriented molecules. However, when the tensor nature of molecular response is considered there will be multitude of cross terms that arise in case of n-photon transitions whose *l*-dependence needs to be investigated further. We considered n-photon transition rates because in our experiments, for example, interaction of Ti:Sapphire femtosecond laser with limonene ($I_P = 8.3$ eV) is a 6 photon process.

References

1. Oosterbeek, R., Ashforth, S., Bodley, O., & Simpson, M., Measuring the ablation threshold fluence in femtosecond laser micromachining with vortex and Bessel pulses. *Opt. Express* **26**, 34558-34568 (2018).
2. Novotny, L., & Hecht, B., *Principles of Nano-Optics (2nd ed.)* (Cambridge University Press., 2012).
3. Bradshaw, D. S., & Andrews, D. L., Manipulating particles with light: radiation and gradient forces. *Eur. J. Phys.* **38**, 034008 (2017).
4. Jackson, J. D., *Classical Electrodynamics* (International Adaptation, ISBN: 978-1-119-77077-0, 2021).
5. Barron, L.D., *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, England, 2004).
6. Boyd, R.W., *Nonlinear Optics (3rd ed.)* (Academic Press, 2020).
7. Craig, D. P., & Thirunamachandran, T., *Molecular Quantum Electrodynamics: An introduction to radiation molecule interactions* (Academic Press Inc. London, 1984).

4.5 HELICAL DICHROISM IN ENANTIOMER SOLUTIONS

In this article, we demonstrate, a direct observation of HD in enantiomeric solutions without the use of any intermediary. Our approach is based on probing helicity-dependent nonlinear absorption of asymmetric helical light beams propagating through enantio-pure powders of alanine and camphor dissolved in an achiral solvent. Alanine is an α -amino acid that is used in biosynthesis of proteins and is common in the natural world forming of our biological makeup [1, 89]. The proteins produced by nature are made up of the L-type. It is often used in biology to study homochirality on earth and to understand how the evolution of organisms came to utilize L-amino acids[mystery left-handed] [90, 91].

We show that enantio-selectivity is a phase effect and can be tuned by varying the position of null intensity in helical beams. We describe the chiral response of enantiomers by considering the parity violation of the enantiomeric ground states. The discriminating response of enantiomers arises due to the difference in absorption rates of helical light.

The key advantages of our work:

- (i) We extend the chiroptical detection of enantiopure samples based on nonlinear absorption of linearly polarized, asymmetric helical light beams to enantiomeric solutions with varying concentrations.
- (ii) Our technique is nonlinear non-resonant and does not require tuning of the laser wavelength to specific resonances.
- (iii) We show the differential absorbance of helical light to be an order of magnitude higher relative to conventional resonant linear techniques.
- (iv) HD signal is tunable by displacing the phase singularity present in an OAM beam. This unique feature does not exist in chiroptical techniques, such as linear and nonlinear circular dichroism, that exploit only laser polarization as a chiral reagent.
- (v) The ability to differentiate enantiomeric solution adds an additional benefit for bio-relevant molecules which are often in powder form. This opens new opportunities to study bio-relevant molecules with helical light.

Authors contribution: My colleague Ashish Jain and I contributed equally to this work. The contributions spanned all aspects of the research, experimental measurements, and theoretical advancements including the conception and design of the study, data collection and analysis, manuscript preparation and revision. Therefore, both should be considered as co-first authors.

Helical dichroism in enantiomeric solutions

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ABSTRACT

A novel chiroptical sensing technique was recently introduced that utilized the helical phase of the structured light as a chiral reagent instead of polarization of light to differentiate enantiopure chiral liquids. The unique advantage of this non-resonant, nonlinear technique is that the chiral signal can be scaled and tuned. In this paper, we extend this technique to enantiopure powders of alanine and camphor by dissolving them in solvents of varying concentrations. We show the differential absorbance of helical light to be an order of magnitude higher relative to conventional resonant linear techniques and is comparable to nonlinear techniques that use circularly polarized light. The origin of helicity dependent absorption is discussed in terms of induced multipole moments in nonlinear light-matter interaction. These results opens up new opportunities in using helical light as a primary chiral reagent in nonlinear spectroscopic techniques.

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INTRODUCTION

Chirality is often investigated by a variety of linear spectroscopic methods, such as Electronic or Vibrational Circular Dichroism (ECD^{1,2} or VCD³),⁴ optical rotatory dispersion,⁵ and Raman optical activity.⁶ It can also be investigated in the nonlinear absorption regime through two-photon CD⁷ and nonlinear optical activity.⁸ Most spectroscopic techniques are performed using circularly polarized light as the chiral reagent. The chiroptical response is proportional to the difference between the rate of excitation by right- and left-circularly polarized (RCP and LCP) light. In CD, enantio-sensitive transitions in a chiral molecule arise due to the coupling of the electric and magnetic dipole matrix elements (E1M1).⁹

The sensitivity of chiroptical techniques that use polarization of the light as the chiral reagent is limited by the relative size difference between the molecular dimension and the helical pitch of the circularly polarized electromagnetic field. As a result, sensitivity scales inversely with the wavelength of light.^{10,11} Thus, linear techniques in the resonant regime, such as VCD, that are performed at infrared wavelengths are often two to three orders of magnitude lower than its counterpart, ECD.¹² Shorter wavelengths, such as x rays, in which the helical pitch is on the same order as the molecular size¹³ lead to a greater chiral signal.

Pulsed lasers led to the development of non-resonant, nonlinear chiroptical techniques with enhanced chiral sensitivity due to the intense light fields.¹⁴ Further improvements in efficiency require either to rely exclusively on the electric dipole transitions such as

in Photoelectron circular dichroism (PECD) or to redefine a chiral reagent that can increase the chiral signal even with weaker higher order interaction terms. In PECD, ionization of a chiral molecule with circularly polarized light leads to an asymmetry in electron angular distribution.^{15,16} PECD has higher efficiency than CD since it relies on electric dipole transitions rather the weaker electric and magnetic dipole coupling term. However, this technique is mostly limited to gas-phase chiral molecules.^{17,18}

A conceptually new form of the chiroptical detection technique was recently introduced using the helical phase of the structured light beam as a chiral reagent instead of circular polarization.¹⁹ Such helical light beams, uniquely identified by a phase singularity resulting in a null intensity region in the center, carry an orbital angular momentum of $\pm\hbar$.²⁰ Displacing the singularity can induce a chiral sensitive response in bulk liquids due to the multipole interference terms, such as electric-magnetic dipole and electric dipole-quadrupole excitation.¹⁹

Chiral response with the use of helical light resulted in two types of helical dichroism (HD) signals; HD (Type I) in isotropic chiral and achiral liquids and HD (Type II) in chiral molecules. The former is defined as the differential absorption of left- and right-helical light for the specific enantiomer (analogous to CD), and the latter is differential absorption between the two enantiomers for a specific helicity and polarization of light. HD (Type I) was shown to scale with the l value and tuned by displacing the singularity.¹⁹ HD (Type I and II) was demonstrated in enantiopure liquids, such as limonene and fenchone. However, many chiral systems that have

biological significance exist in the powder form, which needs to be dissolved in a solvent.

In this article, we extend the helical dichroism technique from an enantiopure sample to an enantiomeric solution (chiral solute diluted in an achiral solvent). First test case is alanine, an amino acid used to make proteins, diluted in a water solvent. Second test case is camphor, a terpenoid dissolved in chloroform. Solvents play a crucial role in many biological processes as they can influence the structure and properties of the biomolecules by changing their function and reactivity.²¹ Chiral response of an enantiomeric solution is often difficult to observe due to strong influence of solvent–solute interaction.²² We demonstrate that both enantiomeric solutions exhibit HD (Type I and II) via the differential absorption of left- and right-helical light with an efficiency in absorbance [$\Delta A(\pm l) = \log_{10} \frac{T(-l)}{T(+l)}$] of $\Delta A \approx 0.05$ for camphor and alanine solution. In comparison, the efficiency of linear CD is $\Delta A \approx 0.0076$ for alanine²³ and $\Delta A \approx 6.5 \times 10^{-6}$ for camphor (VCD).²⁴ The efficiency of existing nonlinear techniques is $\Delta A \approx 0.03$ for alanine (two-photon CD)²⁵ and $\Delta A \approx 0.085$ for camphor (PECD).²⁶

METHODS

Light can carry Orbital Angular Momentum (OAM) of $\pm \hbar l$ associated with dynamical rotation of the wavefront structure.²⁰ Such beams are also called helical light beams whose handedness is defined by the twisting of the wavefront undergoing l intertwined rotations in one wavelength, tracing a left- or right-handed corkscrew pattern while propagating in space. In addition, light also carries Spin Angular Momentum (SAM) associated with the dynamical rotation of the electric field vector around the propagation direction, which is often used as a chiral reagent. The polarization of the light is defined as the intrinsic spin degree of freedom. For circularly polarized light, photons carries a spin angular momentum (SAM) of $\pm \hbar$, where $\hbar$ is the reduced Planck constant and the $\pm$ sign represents left- and right-circular polarizations. For linear polarization, SAM is zero.

Helical beams are theoretically modeled using the Laguerre–Gaussian (LG) beams, which are uniquely identified by a phase singularity, a null intensity region, in the center of the beam cross section.²⁰ However, the singularity can be displaced to generate asymmetrical LG beams either by superimposing a Gaussian²⁷ or by translating the phase plate.¹⁹ The asymmetrical LG beam with displaced singularity is shown in Fig. 1 and can be plotted using the following equation:

$$E^{\pm}(r, \theta, z) = E_0 \left(\frac{\sqrt{2}}{\omega_0} (r \exp(\pm i\theta) \mp i\delta r_{\delta} \exp(\pm i\Theta)) \right)^{|l|} \times \exp\left(-\frac{r^2}{\omega_0^2}\right) L_{p-j}^{|l+j|} \left(\frac{2r^2}{\omega_0^2} \right) \exp[ikz], \quad (1)$$

where $r = \sqrt{x^2 + y^2}$, $r_{\delta} = \sqrt{\zeta^2 + \eta^2}$, $\theta = \tan^{-1}(y/x)$, and $\Theta = \tan^{-1}(\eta/\zeta)$. Here, η and ζ correspond to the displacement of singularity in x - y plane. In addition, E_0 is the normalization

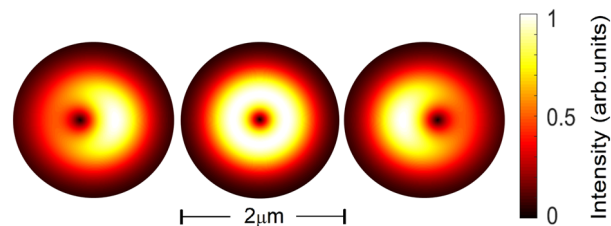


FIG. 1. Simulated intensity profiles of symmetric and asymmetric Laguerre–Gaussian beams. The beam size is defined at the focal region.

factor obtained by integrating the intensity over all space ($-\infty$ to $+\infty$); for ($l = 1$), it is given as:

$$E_0 = \sqrt{\frac{p!}{(p+1)!}} \sqrt{\frac{\omega_0^2}{\pi((\zeta^2 + \eta^2) + \omega_0^2)}}. \quad (2)$$

The above-mentioned beam equation can also be extended to the longitudinal component of the field as a correction to the paraxial regime.¹⁹

The linearly polarized OAM beam was generated by a combination of a quarter-wave plate, a linear polarizer, and a birefringent liquid-crystal-based phase plate called a q-plate.^{28–30} When an incident circularly polarized Gaussian beam propagates through the q-plate with a topological charge q , it acquires an OAM defined by $l = \pm 2q$ with a phase singularity at the center of the beam. The conversion efficiency of the q-plate was $91\% \pm 2\%$ for $l = 3$ beam. The singularity in the OAM beam was displaced by translating the q-plate, mounted on a x , y -stage, with a step size of $250 \pm 40 \mu\text{m}$. When focused by the objective, this translated to a displacement step size of $300 \pm 20 \text{ nm}$ with respect to the center of the beam. The calibration was achieved by measuring the total translation required to displace the singularity to the periphery of the defocused beam and comparing it to the measured spot size of $2 \pm 0.2 \mu\text{m}$.

Transmission experiments were performed by propagating a single femtosecond pulse focused by an aspheric objective ($\text{NA} = 0.3$) into an enantiomeric solution contained in a cuvette (10 mm thick and 3.5 ml volume). A second aspheric objective with the same numerical aperture collimated the transmitted light onto a photodiode (PD2), positioned immediately after the objective. The incident pulse energy was monitored by deflecting a fraction of the incident beam onto another photodiode (PD1). The signals generated by PD1 and PD2 were stretched by an electronic pulse stretcher, discretized and recorded by a data acquisition card.

For every single laser shot, the transmitted light signal on PD2 was normalized with the incoming light signal on PD1 to produce a transmission curve. These curves, as shown in Fig. 2, are plotted as a function of incident pulse energies, which were varied using a combination of a half-wave plate and a polarizer. The incident pulse energies were measured after the first objective, i.e., energy reaching the sample, by defocusing the incident light. During the measurement, for every laser shot, the sample was translated by $4 \mu\text{m}$ to avoid micro-bubbles, and the pulse energy was increased in the steps of $\sim 3 \text{ nJ}$. Multiple transmission curves similar to Fig. 2 were obtained for each sample to be averaged and smoothed, producing the normalized transmission curves of left- and right-helical light ($l = \pm 3$).

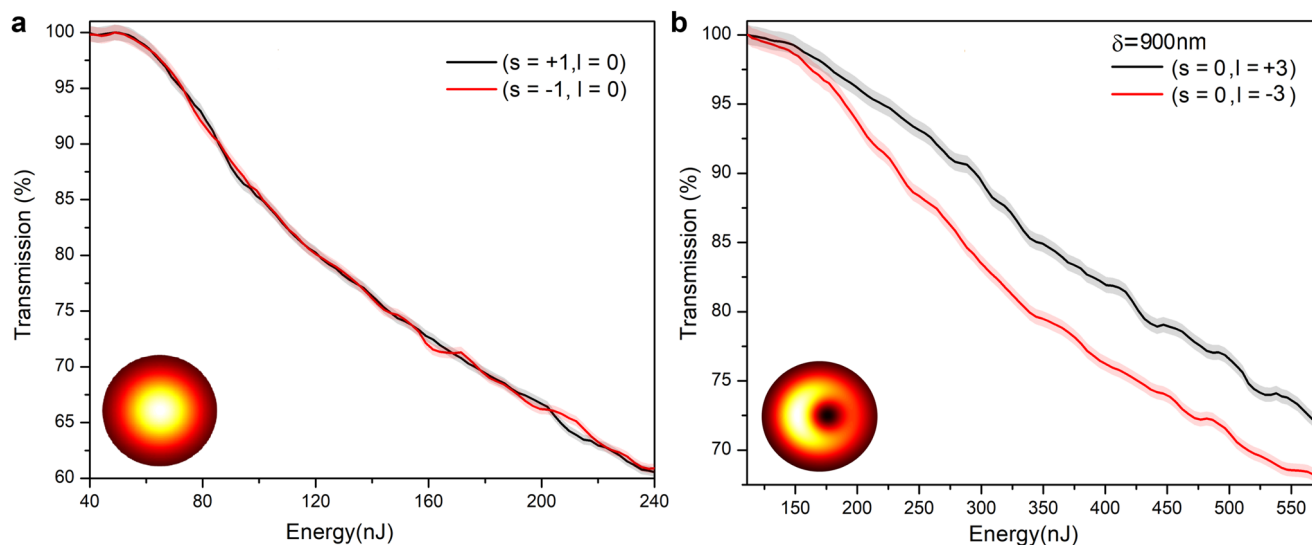


FIG. 2. Transmission curves for 0.5 g of S(–)-camphor diluted in 3.5 ml of chloroform (a) LCP and RCP Gaussian beam ($s = \pm 1$) and (b) linearly polarized helical light $s = 0, l = \pm 3, \delta = 900$ nm, where $\pm$ is for different helicities. The error bands represent the standard error of multiple independent transmission measurements. These experimental results were reproduced multiple times under identical conditions.

Helical dichroism is calculated by taking an average of the difference in transmission from the onset of nonlinear absorption to about two times the threshold value.

Femtosecond pulses were produced by a Ti: sapphire laser amplifier system (45 fs, 800 nm, 1 kHz, 2.5 W) operating in an external trigger mode. The pulse duration at the interaction region is about 100 fs and was continuously monitored using the single-shot autocorrelator. To ensure a shortest pulse in the interaction region, a negative chirp was introduced and optimized by measuring the second harmonic generation in a β -barium borate (BBO) crystal placed at the location of the cuvette. To minimize background noise resulting from any discrepancies between the photodiodes, transmission measurements were always performed in an empty cuvette prior to each experiment. In addition, the measured single-shot beam profile, pulse spectrum, and OAM value remained unchanged after transmission through the samples.¹⁹ All the chemical samples used in the experiment were purchased from Sigma-Aldrich, Inc. The purity as specified by the supplier of R(–)- and S(+)-alanine was 98%. For R(+)-camphor, the purity was 98%, and for S(–)-camphor, the purity was 95%.

RESULTS AND DISCUSSION

To compare the role of SAM and OAM of light as a chiral reagent, we measured absorbance of a single femtosecond pulse in S(–)-camphor (0.5 g diluted in 3.5 ml of chloroform). Figure 2 shows normalized transmission as a function of incident pulse energy for (a) circularly polarized Gaussian ($s = \pm 1, l = 0$) and (b) linearly polarized helical beams ($s = 0, l = \pm 3$). The near overlap of both LCP and RCP transmission curves in Fig. 2(a) represents a conventional CD signal with $\Delta A \approx 0.005$. This signal is considered negligible for enantiomeric solutions due to overlapping error bands.

The transmission curves for both beams uniquely identify two absorption regimes i.e., linear and nonlinear absorption. When the energy of the incident laser pulse is below a certain threshold [≈ 60 nJ for Gaussian and 140 nJ for helical beams in S(–)-camphor], the incident light is not absorbed (transmission = 100%) by the enantiomeric solution because the ionization potential is greater than the photon energy 1.55 eV (800 nm). Above the threshold energy, nonlinear multiphoton absorption sets in leading to a decrease in transmission with increasing pulse energy. The threshold energies are different for the two types of beams. In OAM beams, due to the presence of the null intensity region, higher pulse energies (photon density) are required to reach the threshold for the onset of nonlinear absorption (to maintain similar photon flux) in comparison to Gaussian for the same spot size.³¹ However, the response regime we investigated remained the same, where the pulse energies were always varied from below the threshold for onset of nonlinear absorption to approximately twice the threshold value.

In contrast to Fig. 2(a), significant difference in absorbance of left- and right-helical light was observed, as shown in Fig. 2(b). This differential absorbance ($\Delta A \approx 0.04$) in S(–)-camphor represents the HD (Type I) signal that is an order of magnitude higher than conventional CD. The HD (Type I) signal is only non-zero for the displaced position of the singularity, i.e., asymmetric beams (Fig. 1), and vanishes for symmetric beams. The above curves in Fig. 2(b) are obtained for $\delta = 900$ nm position of singularity.

To discern the effect of the achiral solvent on the HD signal, we performed transmission measurements in a control sample (achiral solvent in black) and in enantiomeric solution (in red) under identical conditions, as shown in Fig. 3 for asymmetric linearly polarized helical light ($s = 0, l = -3$) for (a) chloroform and 0.5 g of R(+)-camphor diluted in 3.5 ml of chloroform and (b) water and 0.5 g of R(–)-alanine diluted in 3.5 ml of water.

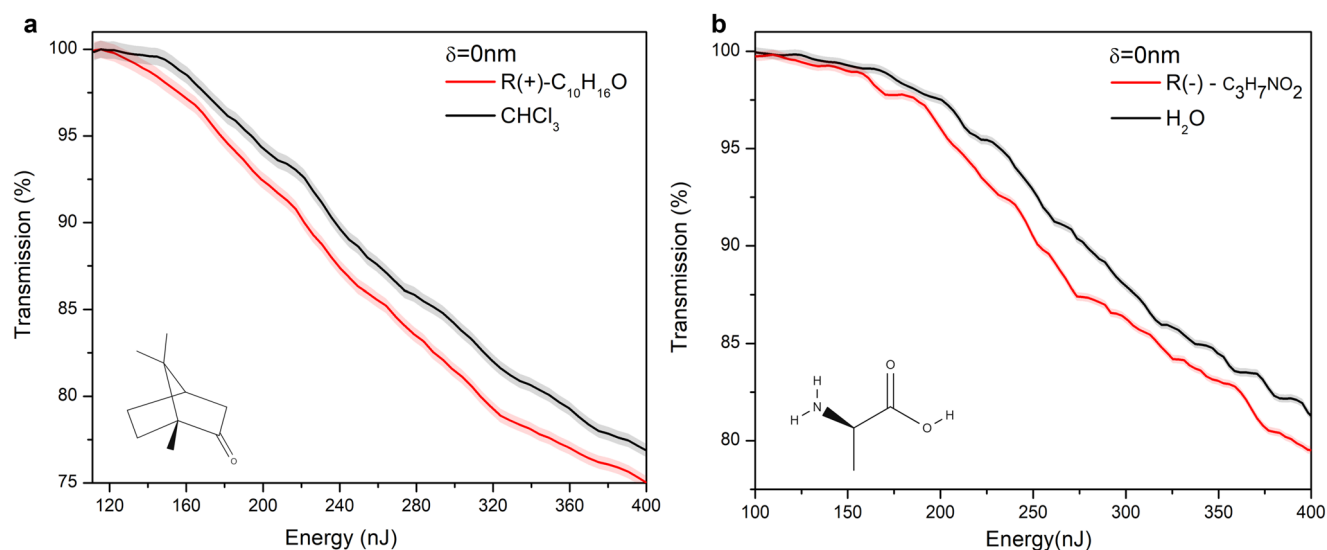


FIG. 3. Transmission curves of linearly polarized helical light ($l = -3$, $\delta = 0$) nm for (a) chloroform and 0.5 g of R(+)-camphor diluted in 3.5 ml of chloroform and (b) H₂O and 0.5 g of R(-)-alanine diluted in 3.5 ml of H₂O. The threshold dependence is independent of the singularity position. The error bands represent the standard error of multiple independent transmission measurements. These experimental results were reproduced multiple times under identical conditions.

Both plots show a lower onset of nonlinear absorption for chiral compounds relative to their respective achiral solvents. This behavior arises because multiphoton absorption depends on the ionization potential of a molecule, which is higher for achiral solvent. This signature property of the nonlinear multiphoton absorption makes it possible to differentiate the HD signal of chiral molecules with minimal interference from achiral molecules. This is crucial as achiral molecules also exhibit helical dichroism.¹⁹ When the handedness of the helical light is changed the threshold energies remain the same. However, the amount of nonlinear absorption in chiral molecules as a function of pulse energy is slightly different, giving rise to differential absorption, HD (Type I).

Any chiroptical technique should be able to differentiate relatively low concentrations of enantiomeric solution as long as the solute's chiral center is maintained. Figure 4 shows HD (Type I) as a function of displacement of the phase singularity in the focal region in camphor and alanine at different concentrations. Figure 4(a) shows two concentration of R(+)-camphor (0.25 and 0.5 g) diluted in 3.5 ml of chloroform. For the lowest concentration, we also show results for S(-)-camphor to demonstrate the differences in the chiral signal between the enantiomers. In our case, the solubility of camphor is 1 g/ml; therefore, the concentrations (0.14 and 0.07 g/ml) in Fig. 4(a) are much below the solubility. The magnitude of the HD (Type I) signal increases with concentration up to ~0.3 g/ml (not shown) beyond which it decreased possibly due to increased solute-solvent interactions.²²

HD (Type I) does not exist in a symmetric Laguerre-Gaussian beam as shown for zero displacement of the singularity ($\delta = 0$). Displacing the phase singularity leads to an asymmetric Laguerre-Gaussian beam [as depicted in Fig. 1 and described by Eq. (1)], resulting in differential absorption of left- and right-linearly polarized helical light. HD (Type I) increases with the

displacement of the singularity, reaches a maximum at ≈ 1000 nm, and decreases with further displacement of the singularity. At extreme displacement of the singularity relative to the center of the focal region, the intensity profile of the OAM beam mimics a Gaussian beam. As a result, the HD (Type I) approaches the behavior of a Gaussian beam as shown in the transmission curves of Fig. 2(a).

Figure 4(b) shows HD (Type I) for S(+)- and R(-)-alanine, an amino acid dissolved in 3.5 ml of water (concentration of 0.14 g/ml). In contrast to Fig. 4(a) where the concentrations are an order of magnitude lower than the saturation value, Fig. 4(b) shows HD (Type I) for a concentration that is near the solubility of alanine 0.167 g/ml. While HD (Type I) exists, there are higher fluctuations in the signal for negative vs positive displacement of singularity between the two enantiomers in comparison to camphor [Fig. 4(a)]. This fluctuation can be attributed to the higher solute concentration (84% reference to solubility) in Fig. 4(b). In comparison, fluctuations are minimal at lower concentrations of 14% and 7% with respect to solubility as seen in Fig. 4(a). Fluctuations at higher concentrations could be due to intense laser-induced nucleation in saturated solutions and nonlinear propagation effects.

In addition, amino acid in an aqueous solution can exist as zwitterion forms. The concentration of zwitterion forms is dependent on the pH value of the enantiomeric solution. The change in pH between enantiomers can introduce spectroscopic differences in the chiroptical response. In our experiments, the measured pH value of R(-)-alanine [S(+)-alanine] solution is 5.80 ± 0.01 [5.85 ± 0.01] with water solvent [pH 5.36 ± 0.01]. However, such small difference in pH value does not affect the HD signal. In addition, the presence of HD in non-zwitterion solution of camphor and enantiopure liquids¹⁹ suggests that zwitterion forms of alanine do not play a major role.

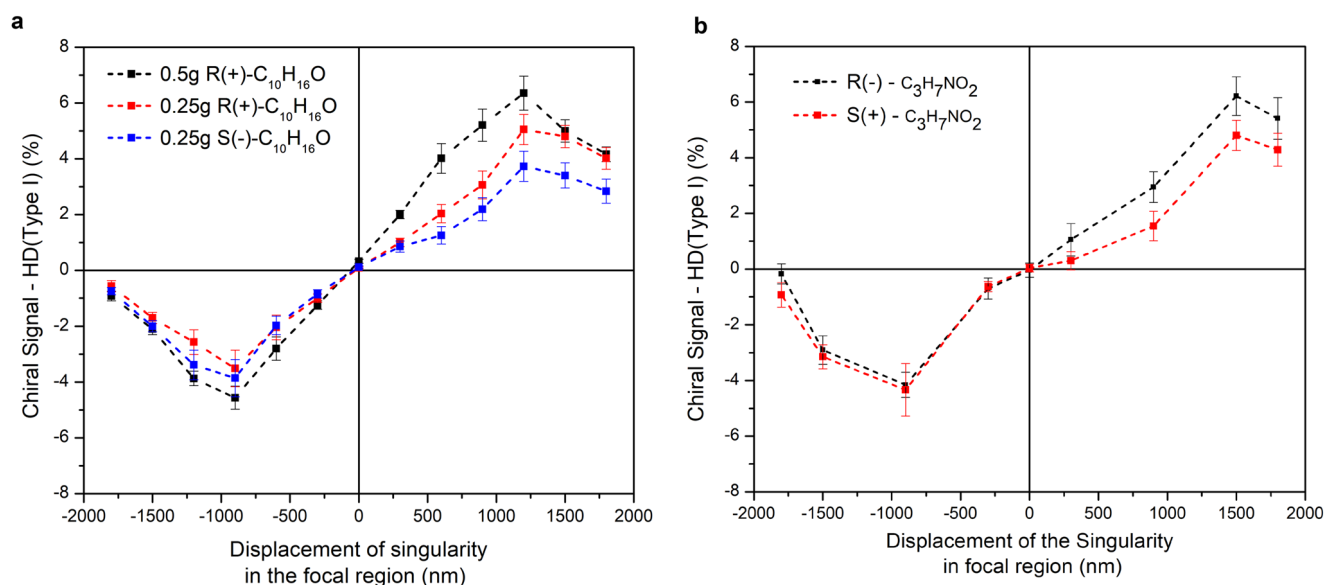


FIG. 4. Helical dichroism (Type I) of linearly polarized left- and right-helical light ($l = \pm 3$) as a function of displacement of the singularity in the focal region. (a) Camphor diluted in 3.5 ml of chloroform. Black curve represents 0.5 g of R(+)-camphor, and the red and blue curves represent 0.25 g of R(+)-camphor and S(-)-camphor. (b) 0.5 g of left- and right-handed alanine diluted in 3.5 ml of water. The dashed lines connecting the discrete experimental points are for visualization only. The error bars represent the standard error over the average energy range starting from the onset of nonlinear absorption to about two times the threshold value.

The helicity dependent differential absorption was described in terms of energy absorbed from the fields at an average rate as shown in the following [Eq. (3)].^{19,32} This energy absorbed is proportional to absorption transition rates based on perturbation theory for single photon absorption^{19,33} and extended to the multiphoton case,¹⁹

$$\Gamma_{\delta}^{\pm} = \frac{\omega}{2} \left\{ \underbrace{\alpha'' |\tilde{E}_{\delta}^{\pm}|^2}_{\text{E1E1}} + \underbrace{\chi'' |\tilde{B}_{\delta}^{\pm}|^2}_{\text{M1M1}} + \underbrace{\rho G' \text{Im}[(\tilde{E}_{\delta}^{\pm})^* \cdot \tilde{B}_{\delta}^{\pm}]}_{\text{E1M1}} + \underbrace{\frac{2}{3} \rho A'' \text{Re}[(\tilde{E}_{\delta}^{\pm})^* \cdot \nabla \tilde{E}_{\delta}^{\pm}]}_{\text{E1E2}} \right\}, \quad (3)$$

where ω is the frequency of incident light, E and B are incident electric and magnetic fields, α'' represents the electric polarizability, χ'' is the magnetic susceptibility, G' represents the isotropic mixed electric-magnetic dipole polarizability, A'' is the mixed electric dipole-electric quadrupole polarizability, and ρ is the orientation-dependent weighting factor for anisotropic averaging. δ is the asymmetrical parameter, $\delta = 0$ for a symmetric LG beam and $\delta \neq 0$ for an asymmetrical LG beam. The sign in $\Gamma^{\pm}$ represents the sign of OAM. E1 and M1 are electric and magnetic dipole, respectively, and E2 is the electric quadrupole. The coupling terms E1M1 and E1E2 are pseudoscalars and change sign under improper rotation.

HD (Type I) $= \Gamma(+l, s) - \Gamma(-l, s)$, defined as differential absorption between right- and left-helical light having identical polarization. The electric-magnetic dipole term (E1M1), responsible for conventional CD, vanishes because we take the difference between

left- and right-helical beams for the same polarization. For symmetric LG beams, the E1E2 coupling term also vanishes due to isotropic averaging of random oriented molecules. The finite HD signal in chiral molecules arises from multipole coupling terms only in the case of asymmetric LG beams. The electric-magnetic dipole term (E1M1), responsible for conventional CD, also vanishes because we take the difference between left- and right-helical beams for the same polarization. The only non-zero contribution to the HD (Type I) signal arises from the electric dipole-quadrupole coupling (E1E2). This term survives isotropic averaging due to the preferential alignment of randomly orientated molecules along the light polarization as a consequence of dipole forces. Such alignment is dependent on the gradient of the light intensity. In our experiments, the laser intensity ranged from 8×10^{12} to 3×10^{13} W/cm². At these intensities, the nonlinear absorption regime is dominated by both multiphoton and multiphoton assisted tunneling since the Keldysh parameter³⁴ ~ 1.5 . In both regimes, the contribution to HD comes from the induced electric dipole and quadrupole moments. In the case of elliptically polarized light, E1M1 term is non-zero and therefore can contribute to the HD signal along with the E1E2 term.

The HD (Type I) chiral signal for R/S enantiomers (Fig. 4) does not mirror each other. In contrast, all polarization based chiroptical techniques, such as CD and PECD, display mirroring behavior i.e., equal magnitude but opposite in sign. In CD, mirroring behavior arises due to the E1M1 coupling term, whereas in PECD, it arises from change in the sign of the photoelectron angular distribution (b_1 coefficient). The HD signal was obtained for the same polarization but opposite helicities; therefore, polarization dependent E1M1 does not contribute. HD arises due to the coupling E1E2 term, which is dependent on the phase (l value) of the beam. Therefore, HD does

not exhibit the same symmetry properties as those arising from the polarization effects.

Figure 4(b) also exhibits a small difference in magnitude of HD (Type I) between the two enantiomers with respect to the displacement of singularity. This can be understood in terms of a slight energy difference between the ground states of the enantiomers due to an asymmetry in the molecular potential, resulting in symmetric (s) and antisymmetric (as) wavefunctions for the two enantiomers.³⁵ As a result, the enantiomeric transition rates can be shown as (see the Appendix)

$$R_{m(as/s)}^{S/R} = \frac{\pi}{3\hbar^2} [\mathcal{D} \mp \mathcal{E}] \operatorname{Re}[E_{\alpha}^* \nabla_{\alpha} E_{\beta}] \rho(\omega_{m(as/s)} - \omega), \quad (4)$$

where $R_{m(as/s)}^{S/R}$ is the single photon transition rate (initial to final state m) for S- and R-enantiomer, which is proportional to the energy absorbed ($\Gamma_{\delta}^{\pm}$) shown in Eq. (3). The $\mathcal{E}$ and $\mathcal{D}$ terms represent the mixed electric dipole–quadrupole response tensors (transition moments) coupled with the electric field gradient dependence of the beam. The above equation represents the E1E2 coupling term of Eq. (3) expanded in case of enantiomer pairs. This expression shows that the transition rate for the R-enantiomer is of the form $\mathcal{D} + \mathcal{E}$ and for the S-enantiomer is of the form $\mathcal{D} - \mathcal{E}$, where $\mathcal{D}$ is bigger than $\mathcal{E}$ (see the Appendix for further details). Therefore, the above transition rates for enantiomers give rise to the difference in the magnitude of the HD signal. The analysis presented in the Appendix is only qualitative. A quantitative analysis of the HD magnitude further requires information about molecular response tensors and wavefunctions.

The key result of Fig. 4 is the tunability of the HD (Type I) signal with the displacement of the singularity. This is the inherent advantage of our technique in comparison to the conventional CD techniques that lack any sort of tunability. In addition, our technique is non-resonant, allowing measurements to be made at a single wavelength of light. In contrast conventional CD is a resonant process often requiring a tunable light source.

Another observable is HD (Type II: $\pm l; \pm s$) = $2 \frac{R(\pm l; \pm s) - S(\pm l; \pm s)}{R(\pm l; \pm s) + S(\pm l; \pm s)}$ defined as differential absorption between the two enantiomers for a specific helicity and polarization. It is a material-dominated property arising due to collective contributions from both E1M1 and E1E2 coupling terms in the case of asymmetric LG beams. For symmetric LG beams, the E1E2 term isotropically averages out to zero, but the E1M1 term is non-zero and can contribute toward the HD signal.

Figure 5 shows HD (Type II) signal for (a) camphor and (b) alanine as a function of incident laser energy (η). The chiral signal in both compounds is for different handedness values of an asymmetric Laguerre–Gaussian beam ($l = \pm 3$). For both chiral compounds, the position of the phase singularity was 900 nm, and the concentration was 0.14 g/ml in their respective achiral solvents, chloroform and water. In both cases, after the onset of nonlinear absorption, the relative magnitude of HD (Type II) for different helicities increases with pulse energy and reaches a maximum of $\approx 4\%$. For comparison, we show the chiral signal for circularly polarized Gaussian beam (dashed-dotted line) with a relative magnitude of $\sim 1\%$, mostly overlapped within the statistical error bands. The HD (Type II) signal is of opposite sign for S(–)- and R(+)-camphor

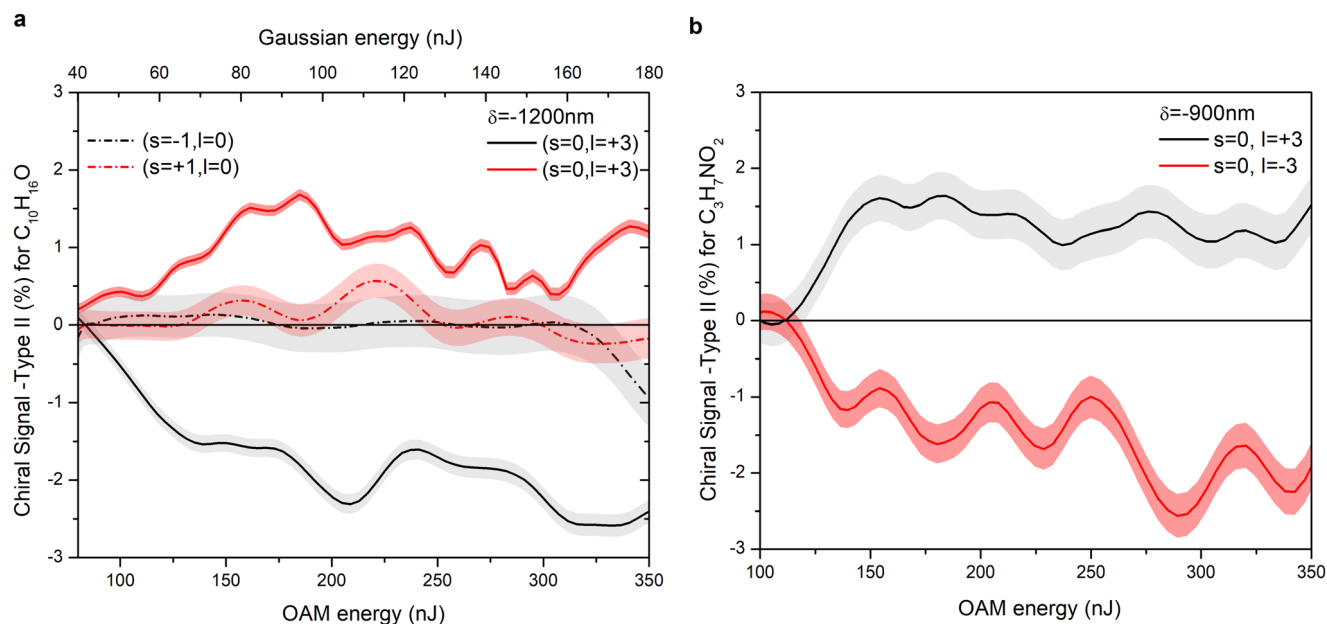


FIG. 5. (a) Chiral signal (Type II) for 0.5 g of camphor diluted in 3.5 ml of chloroform. Dashed-dotted lines are the chiral signal for the circularly polarized Gaussian ($l = 0$), and solid lines are for the linearly polarized helical light ($l = \pm 3$, $\delta = -1200$ nm) as a function of energy. (b) HD (Type II) for 0.5 g of alanine dissolved in 3.5 ml of water as a function of average energy of linearly polarized helical light ($l = \pm 3$, $\delta = -900$ nm). The error bands represent the propagation error of the chiral signal for three independent measurements (sample size). These experimental results were reproduced multiple times under identical conditions.

and S(+)- and R(-)-alanine because they rotate plane polarized light in opposite direction. The HD (Type II) signal is not influenced by the displacement of singularity although it is more stable at higher displacements.

CONCLUSION

Helical dichroism is a non-resonant, nonlinear chiroptical technique that is not limited to enantiopure samples but can also be extended to enantiomeric solutions. The differential absorbance between left- and right-handed helical light reached a high of 5% for 0.14 g/ml of camphor and alanine in achiral solvents. Despite the influence of concentration on the chiral signal, the observed signal efficiency is higher than ECD by an order of magnitude and VCD by a few orders of magnitude. Moreover, ECD and VCD are resonant linear optical techniques and therefore require a tunable light source for measurement. In contrast, HD measurements can be performed at fixed wavelengths by exploiting the nonlinear properties of the material. Other nonlinear chiroptical techniques, such as PECD, has efficiencies comparable to HD. However, PECD is primarily a gas-phase technique but has been recently extended to liquid micro-jets.¹⁸ The ability of HD to differentiate enantiomeric solution adds an additional benefit for bio-relevant molecules, which are often in the powder form. This opens new opportunities to study bio-relevant molecules with helical light. HD (Type I) can also be tuned by displacing the phase singularity, an advantage over other chiroptical techniques that employ circularly polarized light as their chiral reagent. Finally, we have shown that chiral efficiencies for enantiomeric solutions can be enhanced by using an alternative chiroptical reagent that exploits the non-dipole regime.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

A.J. and J.-L.B. contributed equally to this work.

A.J., J.-L.B., and R.B. conceived, designed, and planned the experiments. A.J. and J.-L.B. conducted the experiments and analyzed the results. A.J., J.-L.B., and R.B. worked on the theory. All authors prepared the manuscript.

Ashish Jain: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal);

Project administration (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jean-Luc Bégin:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Ravi Bhardwaj:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: RATE OF ABSORPTION IN CASE OF ENANTIOMERS

The difference in the magnitude of HD (Type I) between the two enantiomers can be qualitatively understood in terms of parity violation arguments. The lack of the “perfect” symmetry state in enantiomers leads to a slight energy difference $\Delta_{pv}E$ between the ground states of the enantiomers, $(\Delta_{pv}E = E_R^g - E_S^g)$.³⁵ This type of broken symmetry condition is often referred to as *de lege* (“lawlike”).³⁵

For single photon absorption transition rate, the Fermi’s golden rule can be written as³⁶

$$R_{m(s/as)} = \frac{2\pi}{\hbar^2} |\langle \Psi_m | V | \Psi_{s/as}^g \rangle|^2 \delta(\omega_{m(s/as)} - \omega), \quad (A1)$$

where $\Psi_{s/as}^g$ represents the symmetric/antisymmetric ground state of the enantiomer pair. We assign the symmetrical ground state Ψ_s to the R-enantiomer and the antisymmetrical Ψ_{as} to the S enantiomer. This can be justified as the consequence of the slight asymmetry in the molecular potential, leading to eigenfunctions either symmetrical $\Psi_s^g = \frac{1}{\sqrt{2}}(\psi_+^g + \psi_-^g)$ or antisymmetrical $\Psi_{as}^g = \frac{1}{\sqrt{2}}(\psi_+^g - \psi_-^g)$, where Ψ_+ (Ψ_-) is even (odd) under parity. Therefore, the enantiomer pair is localized in opposite ground states; if R is even, then S is odd or vice versa. The excited states for both enantiomers are assumed to be a mixed parity state given as $\Psi_m = \frac{1}{\sqrt{2}}(\psi_+ + i\beta\psi_-)$, where $i\beta$ is a small phase lag factor between even and odd states.^{37,38}

The single photon transition rate is proportional to the absorption cross section,³⁶ which is, in turn, proportional to the time averaged energy absorption $[\Gamma_\delta^\pm$ in Eq. (3)]. Since the HD (Type I) is defined as the difference between handedness of helical light for identical polarization, the E1M1 coupling term cancels out; therefore, the magnetic dipole term is neglected, leaving only the electric dipole and quadrupole terms in the interaction Hamiltonian, $V = -\mu_\alpha E_\alpha - \frac{1}{3}\theta_{\alpha\beta}\nabla_\alpha E_\beta$. Substituting above expression in (A1), we get

$$R_{m(s/as)}^{R,S} = \frac{2\pi}{\hbar^2} |\langle \Psi_m | \pm \mu_\alpha E_\alpha + \frac{1}{3}\theta_{\alpha\beta}\nabla_\alpha E_\beta | \Psi_{s/as}^g \rangle|^2 \delta(\omega_{m(s/as)} - \omega), \quad (A2)$$

$$R_{m(s/as)}^{R,S} = \frac{2\pi}{\hbar^2} |\langle \Psi_m | \pm \mu_\alpha E_\alpha + \frac{1}{3} \theta_{\alpha\beta} \nabla_\alpha E_\beta | \Psi_{s/as}^g \rangle| \times |\langle \Psi_{s/as}^g | \pm \mu_\alpha E_\alpha^* + \frac{1}{3} \theta_{\alpha\beta} \nabla_\alpha E_\beta^* | \Psi_m \rangle| \delta(\omega_{m(s/as)} - \omega), \quad (A3)$$

where corresponding fields are complex quantities in the lab frame and multipole moments (dipole μ and quadrupole θ) are real quantities in the molecular frame,^{6,39} which is considered in writing the above expression. The sign $\pm$ in the equation defines the direction of the intrinsic dipole, which is opposite for each enantiomer.⁴⁰

The above expression was evaluated using the following properties: (i) $(E_\alpha^* \nabla_\alpha E_\beta + E_\alpha \nabla_\alpha E_\beta^*) = 2 \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta]$; (ii) symmetry property of an inner product, i.e., $\int \psi_\pm^* \mu \psi_\pm d^3r = 0$, $\int \psi_\pm^* \theta \psi_\pm d^3r = 0$ since μ is odd and θ is even under parity conversion; (iii) neglecting the β^2 term since it is small, and (iv) replacing the delta function by a lineshape function (ρ) to represent a physical system.

For the R-enantiomer,

$$R_{ms}^R = \frac{\pi}{3\hbar^2} \left(i\beta [\langle \psi_+ | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_- \rangle - \langle \psi_- | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_+ \rangle] \times \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] + \frac{1}{2} [\langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle + \langle \psi_+ | \mu_\alpha | \psi_-^g \rangle \langle \psi_-^g | \theta_{\alpha\beta} | \psi_+ \rangle] \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] \right) \times \rho(\omega_{ms} - \omega). \quad (A4)$$

The last two terms in the above expression contain inner products that are complex conjugate of each other. Since the multipole moments are real quantities, we can therefore write $\langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle [E_\alpha^* \nabla_\alpha E_\beta] + \langle \psi_+ | \mu_\alpha | \psi_-^g \rangle \langle \psi_-^g | \theta_{\alpha\beta} | \psi_+ \rangle [E_\alpha \nabla_\alpha E_\beta^*] = 2 \langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle \operatorname{Re}[E_\alpha \nabla_\alpha E_\beta^*]$.

Therefore, we get

$$R_{ms}^R = \frac{\pi}{3\hbar^2} \left[\underbrace{i\beta [\langle \psi_+ | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_- \rangle - \langle \psi_- | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_+ \rangle]}_{\mathcal{E}} + \underbrace{\langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle}_{\mathcal{D}} \right] \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] \rho(\omega_{ms} - \omega) \quad (A5)$$

for the S-enantiomer,

$$R_{m(as)}^S = \frac{\pi}{3\hbar^2} \left(-i\beta [\langle \psi_+ | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_- \rangle - \langle \psi_- | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_+ \rangle] \times \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] + \frac{1}{2} [\langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle + \langle \psi_+ | \mu_\alpha | \psi_-^g \rangle \langle \psi_-^g | \theta_{\alpha\beta} | \psi_+ \rangle] \operatorname{Re}[E_\alpha \nabla_\alpha E_\beta^*] \right) \times \rho(\omega_{m(as)} - \omega). \quad (A6)$$

Solving further for the last term as above, we get

$$R_{m(as)}^S = \frac{\pi}{3\hbar^2} \left[\underbrace{-i\beta [\langle \psi_+ | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_- \rangle - \langle \psi_- | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_+ \rangle]}_{\mathcal{E}} + \underbrace{\langle \psi_+ | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_-^g | \mu_\alpha | \psi_+ \rangle}_{\mathcal{D}} \right] \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] \rho(\omega_{m(as)} - \omega), \quad (A7)$$

where the terms $\langle \psi_- | \mu_\alpha \dots \theta_{\alpha\beta} | \psi_+ \rangle \operatorname{Re}[E_\alpha^* \nabla_\alpha E_\beta] = \frac{1}{2} \langle \psi_- | \mu_\alpha | \psi_+^g \rangle \langle \psi_+^g | \theta_{\alpha\beta} | \psi_+ \rangle [E_\alpha^* \nabla_\alpha E_\beta] + \frac{1}{2} \langle \psi_- | \theta_{\alpha\beta} | \psi_+^g \rangle \langle \psi_+^g | \mu_\alpha | \psi_+ \rangle [E_\alpha \nabla_\alpha E_\beta^*]$ are written using rotational average over symmetric and antisymmetric parity states. In addition, due to the presence of i in the expression, only the imaginary part of $(\mu_\alpha \theta_{\alpha\beta})$ mixed tensor contributes to the transition rate.

Hence, the transition rate for the R-enantiomer is of the form $\mathcal{D} + \mathcal{E}$ and for the S-enantiomer is of the form $\mathcal{D} - \mathcal{E}$, where $\mathcal{D}$ is bigger than $\mathcal{E}$ since the phase lag factor β is small.³⁷ This difference in the transition rates for the R- and S-enantiomers leads to the observed difference in the magnitude of HD (Type I) as shown in Fig. 4.

REFERENCES

1. I. Warnke and F. Furche, "Circular dichroism: Electronic," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 150 (2011).
2. A. Cotton, *C. R. Acad. Sci.* **120**, 989 (1895).
3. P. J. Stephens, "Theory of vibrational circular dichroism," *J. Phys. Chem.* **89**, 748 (1985).
4. J. Neugebauer, "Induced chirality in achiral media—How theory unravels mysterious solvent effects," *Angew. Chem., Int. Ed.* **46**, 7738 (2007).
5. W. Moffitt, "Optical rotatory dispersion of helical polymers," *J. Chem. Phys.* **25**, 467 (1956).
6. L. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, 2004), Vol. 1.
7. E. A. Power, "Two-photon circular dichroism," *J. Chem. Phys.* **63**, 1348 (1975).
8. T. Verbiest, M. Kauranen, A. Persoons, M. Ikonen, J. Kurkela, and H. Lemmetyinen, "Nonlinear optical activity and biomolecular chirality," *J. Am. Chem. Soc.* **116**, 9203 (1994).
9. A. F. Ordóñez and O. Smirnova, "Generalized perspective on chiral measurements without magnetic interactions," *Phys. Rev. A* **98**, 063428 (2018).
10. D. Ayuso, A. F. Ordóñez, and O. Smirnova, "Ultrafast chirality: The road to efficient chiral measurements," *Phys. Chem. Chem. Phys.* **24**, 26962 (2022).
11. K. J. Chau, "Investigation of the chiral origins of electromagnetic activity," *Opt. Lett.* **35**, 1187–1189 (2010).
12. H. Sato, "A new horizon for vibrational circular dichroism spectroscopy: A challenge for supramolecular chirality," *Phys. Chem. Chem. Phys.* **22**, 7671 (2020).
13. R. D. Peacock and B. Stewart, "Natural circular dichroism in X-ray spectroscopy," *J. Phys. Chem.* **105**, 351 (2001).
14. J.-L. Bégin, M. Alsaawy, and R. Bhardwaj, "Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry," *Sci. Rep.* **10**, 14074 (2020).
15. I. Powis, "Photoelectron circular dichroism of the randomly oriented chiral molecules glyceraldehyde and lactic acid," *J. Chem. Phys.* **112**, 301 (2000).
16. M. H. M. Janssen and I. Powis, "Detecting chirality in molecules by imaging photoelectron circular dichroism," *Phys. Chem. Chem. Phys.* **16**, 856 (2014).

- ¹⁷C. Lux *et al.*, “Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses,” *Angew. Chem., Int. Ed.* **51**, 5001 (2012).
- ¹⁸M. N. Pohl *et al.*, “Photoelectron circular dichroism in angle-resolved photoemission from liquid fenchone,” *Phys. Chem. Chem. Phys.* **24**, 8081 (2022).
- ¹⁹J.-L. Bégin, A. Jain, A. Parks *et al.*, “Nonlinear helical dichroism in chiral and achiral molecules,” *Nat. Photonics* **17**, 82 (2023).
- ²⁰L. Allen, M. W. Beijersbergen, R. J. C. Spreeuw, and J. P. Woerdman, “Orbital angular momentum of light and the transformation of Laguerre-Gaussian laser modes,” *Phys. Rev. A* **45**, 8185 (1992).
- ²¹V. Vaquero *et al.*, “Alanine water complexes,” *J. Phys. Chem. A* **118**, 2584 (2014).
- ²²G. Gottarelli, M. A. Osipov, G. P. Spada, O. Bodley, and M. Simpson, “A study of solvent effect on the optical rotation of chiral biaryls,” *J. Phys. Chem.* **95**, 3879 (1991).
- ²³U. J. Meierhenrich, J.-J. Filippi, C. Meinert, J. H. Bredehöft, J.-i. Takahashi, L. Nahon, N. C. Jones, and S. V. Hoffmann, “Circular dichroism of amino acids in the vacuum-ultraviolet region,” *Angew. Chem., Int. Ed.* **49**, 7799 (2010).
- ²⁴G. Longhi, S. Abbate, R. Gangemi, E. Giorgio, and C. Rosini, “Fenchone, camphor, 2-methylenefenchone and 2-methylenecamphor: A vibrational circular dichroism study,” *J. Phys. Chem. A* **110**, 4958 (2006).
- ²⁵B. Jansík, A. Rizzo, and H. Ågren, “Ab initio study of the two-photon circular dichroism in chiral natural amino acids,” *J. Phys. Chem. B* **111**, 446 (2007).
- ²⁶C. S. Lehmann, N. B. Ram, I. Powis, and M. H. M. Janssen, “Imaging photoelectron circular dichroism of chiral molecules by femtosecond multiphoton coincidence detection,” *J. Chem. Phys.* **139**, 234307 (2013).
- ²⁷M. G. Rahimian *et al.*, “Spatially controlled nano-structuring of silicon with femtosecond vortex pulses,” *Sci. Rep.* **10**, 12643 (2020).
- ²⁸L. Marrucci, C. Manzo, and D. Paparo, “Optical spin-to-orbital angular momentum conversion in inhomogeneous anisotropic media,” *Phys. Rev. Lett.* **96**, 163905 (2006).
- ²⁹E. Karimi, B. Piccirillo, E. Nagali, L. Marrucci, and E. Santamato, “Efficient generation and sorting of orbital angular momentum eigenmodes of light by thermally tuned *q*-plates,” *Appl. Phys. Lett.* **94**, 231124 (2009).
- ³⁰F. Cardano, E. Karimi, S. Slussarenko, L. Marrucci, C. de Lisio, and E. Santamato, “Polarization pattern of vector vortex beams generated by *q*-plates with different topological charges,” *Appl. Opt.* **51**, C1–C6 (2012).
- ³¹R. N. Oosterbeek, S. Ashforth, O. Bodley, and M. C. Simpson, “Measuring the ablation threshold fluence in femtosecond laser micromachining with vortex and Bessel pulses,” *Opt. Express* **26**, 34558 (2018).
- ³²N. Yang and A. E. Cohen, “Local geometry of electromagnetic fields and its role in molecular multipole transitions,” *J. Phys. Chem. B* **115**, 5304–5311 (2011).
- ³³K. A. Forbes and D. L. Andrews, “Optical orbital angular momentum: Twisted light and chirality,” *Opt. Lett.* **43**, 435–438 (2018).
- ³⁴L. V. Keldysh, “Ionization in the field of a strong electromagnetic wave,” *Sov. Phys. JETP* **20**, 1307 (1965).
- ³⁵M. Quack, G. Seyfang, and G. Wichmann, “Perspectives on parity violation in chiral molecules: Theory, spectroscopic experiment and biomolecular homochirality,” *Chem. Sci.* **13**, 10598 (2022).
- ³⁶R. Boyd, *Nonlinear Optics*, 4th ed. (Academic Press, 2020).
- ³⁷G. Wagnière, *On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image* (John Wiley and Sons, 2007), p. 1.
- ³⁸H. B. Tran Tan, D. Xiao, and A. Derevianko, “Parity-mixed coupled-cluster formalism for computing parity-violating amplitudes,” *Phys. Rev. A* **105**, 022803 (2022).
- ³⁹D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics: An Introduction to Radiation Molecule Interactions* (Academic Press, Inc., 1984), Vol. 1.
- ⁴⁰D. Patterson, M. Schnell, and J. M. Doyle, “Enantiomer-specific detection of chiral molecules via microwave spectroscopy,” *Nature* **497**, 475 (2013).

SOLID-STATE PHASE - HELICAL LIGHT INTERACTION

This chapter will shift focus from the liquid phase to the solid-state phase, illustrating that chiroptical effects are also evident in crystalline structures. Initially, we will provide foundational knowledge of multiphoton absorption of Gaussian and helical light, followed by the necessary details to comprehend the physics of the established model.

Using our third article, published in Nature Communications, we reveal that the structural symmetry of the crystal can be mapped by angle-dependent absorption of helical light. Furthermore, the HD signal of both chiral and achiral crystals can be measured at a level one to two orders of magnitude greater than when probed using circularly polarized light. We also show that HD is not limited to crystalline structures. Intrinsic dichroism is present in amorphous solids when probed with asymmetrical helical light beams. This indicates that HD is sensitive to the short-range order of amorphous materials. These observations are explained by a hybrid model between perturbative and tunnel ionization, known as MPAT. A supplementary is included for additional theoretical and experimental results.

5.1 TRANSMISSION IN CRYSTALLINE AND AMORPHOUS SiO_2 SOLIDS

Fused silica is an amorphous material with similar chemical and physical properties to crystalline quartz; i) molecular composition SiO_2 , ii) bandgap $9 - 9.5\text{eV}$ [92, 93], and iii) index of refraction of ~ 1.45 at 800nm . The major difference lies in the structure of the solid, the arrangement of the SiO_2 molecules. Quartz has long-range order while fused silica has long-range disorder. To elucidate the cause of this helical phase-dependent absorption in solids it was necessary to compare both samples.

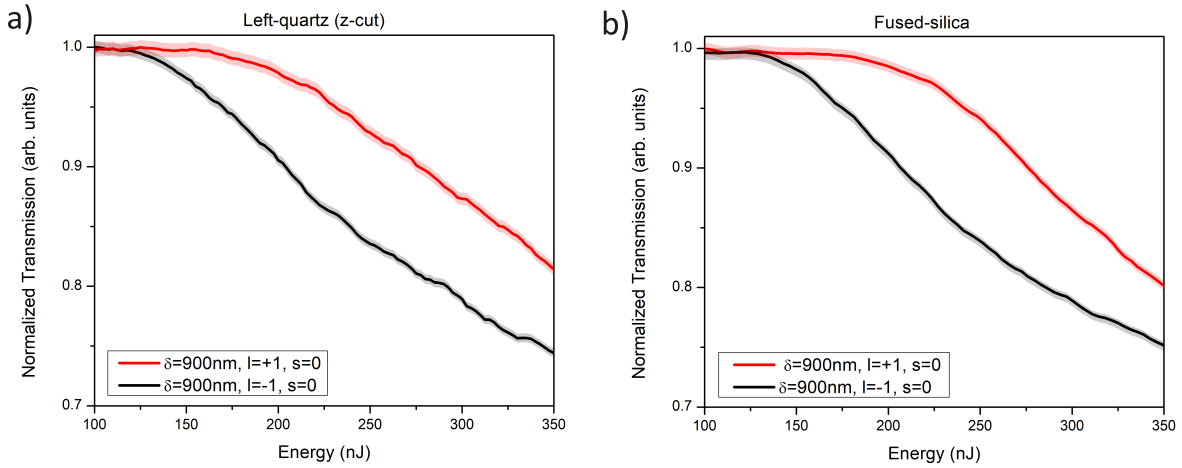


Figure 5.1: **Quartz and fused-silica transmission curves.** **a)** Experimental measurement for **a)** Left-handed quartz for asymmetric OAM beam ($l = +1, \delta = 900\text{nm}$) in red and ($l = -1, \delta = 900\text{nm}$) in black and **b)** fused-silica for asymmetric OAM beam ($l = +1, \delta = 900\text{nm}$) in red and ($l = -1, \delta = 900\text{nm}$) in black.

The similar transmission curves obtained for crystalline quartz and amorphous material, shown in figure 5.1, suggest that the effect of differential absorption is a beam property and is the major cause of this observed phenomenon. The combined efforts of the handedness of the helical phase with the asymmetry introduced by displacing the singularity results in a difference in the rate of change of the electric field, within the interaction region. Consequently, the nonlinear absorption threshold of the material is different between the left- and right-handed asymmetrical helical light. The measurements were performed by translating the sample for every laser shot. Therefore, the ability to observe this difference in a short-range disorder sample suggests that the electron transition is performed in a quasi-order environment or else the signal would fluctuate and average to zero over the interaction region.

Due to the small six-photon absorption cross-section of quartz and its similar transmission behaviour to fused silica, a pure multiphoton approach would not suffice to explain helical dichroism. Additionally, within the experimental intensity range, both multiphoton absorption and tunneling occur but are not the dominant processes. However, their combined efforts are the more prevalent process [63, 64]. Therefore, a different approach is needed to explain HD in both crystalline and amorphous solids.

In the case of solids, the overlap in energy levels of individual atoms results in the generalized energy bands

i.e. conduction and valence bands. The disordered structure of the amorphous material cannot be partially aligned by the incident field due to its solid-state nature. Any helical phase dependence of amorphous material must occur in a partially ordered environment to exhibit HD. Amorphous material does have some order, it is in the length scale of $\sim 20\text{\AA}$ [94–96]. The origin of helical dichroism in solids can be understood in terms of multiphoton absorption from the ground to a higher energy state and subsequent tunnel ionization, a process known as MPAT. During the tunneling process, the electron is ionized within a small spatial displacement which is within the short-range order of amorphous material.

5.2 MULTIPHOTON ASSISTED TUNNELING

In the case of strong-field-induced absorption or tunneling regime in solids, the time derivative of the associated current density. This current is fundamental to maintain energy conservation, as the energy needed to realize the interband excitation process must appear as a loss in the field energy density u through $\dot{u} = -\mathbf{J} \cdot \mathbf{E}$ [97]. In optical tunneling, energy conservation is fulfilled when this current reflects a spatial displacement of the electrons by $\mathbf{x}_0 = \mathbf{E}E_g/(q_e E^2)$, where E_g is the bandgap. For amorphous fused silica with band gap $\approx 9\text{eV}$, the electron displacement distance is between $6 - 18\text{\AA}$ within its short to medium range order $\sim 20\text{\AA}$.

The injection current ($\vec{J} = qn_0\vec{x}_0\Gamma$) associated with energy conservation of the promotion of valence electron to the conduction band is proportional to a spatial displacement of the electron (x_0) and the injection rate ($\dot{\rho}$) which is proportional to the rate of ionization (Γ) [97]. This rate can be obtained from the transition amplitude which is defined as a projecting of a non-interacting state to a fully evolved state at large times given by $M_{fi} = \lim_{t \rightarrow \infty} \langle \psi_f(t) | \Psi_i(t) \rangle$ where $\Psi_i(t)$ total wavefunction evolved from the bound states and is the solution to the time-dependent Schrodinger equation given by equation 3.60. For the time-dependent Hamiltonian and a relatively weak perturbation, the electron can access intermediate states. According to Quantum mechanics, any state wavefunction describing the perturbed system may be expanded in terms of a superposition of stationary states [6], $|\Psi(\tau)\rangle = \sum_m c_m^{(N)}(\tau) |\Psi_m(\tau)\rangle$ where

$$c_m^{(N)}(\tau) = \left(\frac{1}{i\hbar}\right)^N \sum_l \int_{t_0}^{\tau} dt' \langle m | V(t') | l \rangle c_l^{(N-1)}(t') e^{i\omega_{ml}t'} \quad (5.1)$$

is the time-dependent coefficient for spatial expansion of $\Psi(\tau)$ in terms of $\Psi_m(\tau)$ for an Nth order perturbation i.e. multiphoton probability amplitude for an atom in energy eigenstate l at time τ . To determine the first-order amplitude $c_m^{(1)}(\tau)$ we set $a_l^{(0)} = \delta_{lg}$ corresponding to an atom in the ground state [6]. Substituting equation 5.1 into equation 3.60 we get

$$|\Psi(t)\rangle = |\phi_g(t)\rangle - \left(\frac{1}{i\hbar}\right)^{N-1} \sum_m \sum_l \int_{t_0}^t \Theta(t-\tau) \hat{U}(t, \tau) V(\tau) |\psi_m(\tau)\rangle \int_{-\infty}^{\tau} \langle m|V(t')|l\rangle c_l^{(N-1)}(t') e^{i\omega_m t'} dt' d\tau \quad (5.2)$$

The formal expanded the wavefunction of a time-dependent Hamiltonian in terms of a perturbative expansion with subsequent time order events. The last event represents the jump from an excited bound state to a continuum for atoms and from deformed valence band/band-tail states to conduction band for solids.

Projecting the final state onto our time-evolved state we obtain the transition amplitude for MPAT.

$$M_{fi} = - \left(\frac{1}{i\hbar}\right)^{N-1} \sum_m \sum_l \int_{t_0}^t \langle \psi_f(t) | \hat{U}(t, \tau) V(\tau) | \psi_m(\tau) \rangle \int_{-\infty}^{\tau} \langle m|V(t')|l\rangle c_l^{(N-1)}(t') e^{i\omega_m t'} dt' d\tau \quad (5.3)$$

This amplitude is not only limited to a transition from the initial to the final state such as one photon absorption or pure tunneling. It has the flexibility to introduce an intermediate partition of the total Hamiltonian to introduce intermediate Hamiltonian, to represent tunneling form an excited state, $\psi_m(\tau)$, at time τ . Here $\psi_m(\tau)$ represents the excited state achieved after n-photon absorption from t' to τ . After each photon absorption, there is a changed wavefunction with higher energy and will extend to a larger distance. Thus, ionization by tunneling can occur readily from such extended and weakly bound states. In the semi-classical limit, this transition amplitude can be reduced to Keldysh's amplitude for tunneling when the laser field is strong enough to eliminate any excitation to intermediate states. Further details on this mechanism and experimental results of helical dichroism in solids are given in the article titled "Intrinsic dichroism in amorphous and crystalline solids with helical light".

5.3 INTRINSIC DICHROISM IN AMORPHOUS AND CRYSTALLINE SOLIDS WITH HELICAL LIGHT

Amorphous solids do not possess long-range order due to the disordered arrangement of atoms. As a result, their physical properties exhibit isotropy in which they remain the same in all directions. Lack of translational and rotational symmetry also means amorphous solids are not expected to exhibit differential absorption of polarized light, called dichroism.

Here we demonstrate, the existence of intrinsic dichroism in amorphous solids using helical light beams that carry OAM. Our approach is based on probing the nonlinear absorption of linearly polarized, asymmetric helical light beams propagating through the solid. We show that HD is a phase effect and model it by considering inter-band electron transitions via MPAT. The electron displacement during this process is within the short-to-medium range order in amorphous solids enabling to probe intrinsic dichroism. The sensitivity to the helicity of

light arises from the coupling of electric dipole and quadrupole term and can be precisely tuned and controlled.

We also demonstrate that dichroism exists in both achiral and chiral crystalline solids. In chiral crystals, the material handedness (non-superimposable mirror images) is often differentiated using circularly polarized Gaussian light beams as a chiral reagent in which the tip of the electric field traces a corkscrew pattern. However, the inherent birefringence and macroscopic anisotropies often mask the chiroptical signal as in solid-state circular dichroism. We demonstrate efficient chiral recognition in quartz using linearly polarized helical light beams, in which the handedness is defined by helical wavefront structure tracing a corkscrew pattern in space.

The major advances of our work are:

- (i) Introduction of a novel form of solid-state optical dichroism based on the nonlinear absorption of linearly polarized asymmetric helical light beams.
- (ii) Demonstration of HD that is intrinsic to both amorphous and crystalline materials. These results show that solid-state matter is responsive to the phase of the incident light.
- (iii) Challenging the conventional wisdom that dichroism does not exist in amorphous solids. The observation of dichroism in amorphous materials is attributed to the presence of short-medium range order. This new development shifts the paradigm of optical dichroism from using laser polarization to optical phase and will aid in understanding the mysterious nature of amorphous materials.
- (iv) Probing crystal chirality with enhanced efficiency using linearly polarized helical light. It extends our recent work on liquids and opens new, so far unexplored direction of research in next-generation chiroptical spectroscopy.
- (v) Control and precise tuning of HD by varying the superposition of OAM and Gaussian beams, and by displacing the singularity present in an OAM beam. This unique feature of our technique has no comparable equivalent to other existing solid state-based chiroptical techniques. It opens new opportunities in the development of enantioselective catalysis on surfaces, chiral sensors and molecular electronic devices.
- (vi) Unique instrumental advantage due to scaling of HD signal with orbital angular momentum value and continuous tunability by electrical detuning of q-plate used to produce OAM beams. A single higher-order q-plate is sufficient to reproduce the results of all lower-order q-plates by controlling its voltage.
- (vii) Bandgap dependence of HD that can be used, in principle, as an in-situ probe of locally induced structural/conformational changes on a micron scale inside a solid.

Authors contribution: My colleague Ashish Jain and I contributed equally to this work. The contributions spanned all aspects of the research, experimental measurements, and theoretical advancements including the conception and design of the study, data collection and analysis, manuscript preparation and revision. Therefore, both should be considered as co-first authors.

Intrinsic dichroism in amorphous and crystalline solids with helical light

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Amorphous solids do not exhibit long-range order due to the disordered arrangement of atoms. They lack translational and rotational symmetry on a macroscopic scale and are therefore isotropic. As a result, differential absorption of polarized light, called dichroism, is not known to exist in amorphous solids. Using helical light beams that carry orbital angular momentum as a probe, we demonstrate that dichroism is intrinsic to both amorphous and crystalline solids. We show that in the nonlinear regime, helical dichroism is responsive to the short-range order and its origin is explained in terms of interband multiphoton assisted tunneling. We also demonstrate that the helical dichroism signal is sensitive to chirality and its strength can be controlled and tuned using a superposition of OAM and Gaussian beams. Our research challenges the conventional knowledge that dichroism does not exist in amorphous solids and enables to manipulate the optical properties of solids.

Light as a tool to probe the structure and symmetry of solids is limited due to the fact that the wavelengths of photons (UV–visible–IR) are significantly longer than the interatomic distances. In spite of this limitation, some degree of information on symmetry and phonon modes can be obtained from light scattering techniques such as Raman spectroscopy^{1,2}. In crystalline solids (c-solids), periodic arrangement of atoms leads to long-range order that gives rise to anisotropy in which the physical properties depend on the crystal orientation. Such an anisotropy in absorption and emission of light via high harmonic generation has been exploited to map the crystal symmetry^{3,4}. In chiral c-solids, material handedness (non-superimposable mirror images), in principle, leads to differential absorption of right- and left-circularly polarized light, known as circular dichroism (CD). However, the chiroptical signal is often influenced by linear birefringence and inherent macroscopic anisotropies present in c-solids⁵. As a result, sophisticated techniques such as single-crystal X-ray diffraction⁶, scanning and transmission electron microscope-based methods⁷ are often utilized to differentiate chiral crystals but are limited by the need for large single crystal of high purity.

In contrast, amorphous solids (a-solids) do not have long-range order due to random arrangement of atoms and are isotropic. A

consequence of the lack of symmetry in a-solids is that they do not exhibit CD. However, a-solids are characterized by short- and medium-range order in which the spatial variation of parameters (such as interatomic distances and angles between neighboring atoms) provides average structural information and the degree to which the short and medium-range order is conserved^{8,9}. Studying short- and medium-range order of a-solids is an active field of research^{9,10} because it can lead to some phenomena that are typically observed in c-solids. With recent technological advances, it is now possible to directly observe the local atomic structure of disordered solids^{11,12}. The presence of short- and medium-range order in a-solids is in fact responsible for delocalized energy valence and conduction band states, whereas the long-range disorder causes the formation of bond tail energy states between energy bands¹³. In amorphous glass, the short to medium-range order extends up to 20 Å^{9,14–16}.

Most optical techniques to study solids, to date, relied on using polarized Gaussian beams (carrying spin angular momentum $0, \pm \hbar$) with the interaction described using the dipole dominant molecular transitions. Such transitions are generally independent of the phase associated with the wavefront of the incident beam. However, light can also carry orbital angular momentum (OAM), $\pm \ell \hbar$, associated with

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dynamical rotation of wavefront structure. The handedness of these beams is characterized by the twisting of the wavefront undergoing l intertwined rotations in one wavelength^{17–19}. The intensity profile of such light is characterized by a phase singularity (optical vortex) and hence a null intensity region at the center of the beam. These vortex beams are also referred as helical light beams^{19–21} where the helicity is associated with the helical wavefront structure which is chiral in nature. This is analogous to the chiral structure of the electric field associated with circular polarized light.

The theoretical unboundedness of OAM value generated significant interest in using helical light beams as a chiral probe to study light-matter interaction. Early studies on differential absorption of helical light beams focused mostly on the linear absorption involving coupling of electric-magnetic dipole (EIM1) term, which was known to be responsible for CD. These studies were not successful in demonstrating the efficacy of using OAM as a chiral reagent. Recently, Helical Dichroism (HD), defined as differential absorption of left- and right-handed helical light, was demonstrated in nanoparticle aggregates²², chiral metasurfaces²³, powdered molecular media²⁴, and achiral/chiral liquids in nonlinear regime²⁵. Theoretically, several recent studies proposed the phased-based dichroism effect originates from the higher-order transition moments, which were shown to be non-vanishing only in the medium with some degree of orientational order^{26,27}. Traditionally, the origin of such effects can be understood in terms of parity-time (PT) symmetry arguments. Electric dipole transition moment E1 has odd spatial parity, magnetic dipole moment M1 and electric quadrupole moment E2 have even parity. Hence, the EIM1 and EIE2 coupling terms represent a time-even space-odd pseudoscalars which changes sign on spatial inversion indicating a broken symmetry. However, symmetry arguments can only provide qualitative insight into the existence of dichroism in crystals and does not predict its presence in amorphous solids. Therefore, comprehensive models are required for quantitative understanding of the behavior of HD that takes into account the interband transition dynamics in matter and spatial structure of the helical light beams.

In this article, we first demonstrate existence of intrinsic HD in amorphous solids using asymmetrical helical light beams. Such an effect is typically not expected in amorphous materials due to the disorderly state of the medium. We define differential absorption of left- and right-helical light for the same material as HD (Type I). Therefore, it is a beam-dominated property and can also be observed in achiral and chiral crystalline solids. In case of amorphous and achiral solids, HD (Type I) is not considered as true chirality as it does not involve chiral light and chiral matter interaction. Second, our technique demonstrates higher efficiency in probing chiral solids compared to conventional solid-state-based optical techniques. This was achieved in terms of HD (Type II), defined as difference of absorption between the left- and right-handed chiral solid for a specific-handed helical light. It is a material-dominated property and its definition requires both the material and light to be chiral entities. Third, we show that helical dichroism is tunable and can be precisely controlled by (i) superposition of OAM and Gaussian beams (ii) varying the l -value, and (iii) displacement of phase singularity in the beam. These features combined with the bandgap dependence of HD set our technique apart from any other existing chiroptical methods. Finally, we model HD by considering electron transitions via multiphoton-assisted tunneling (MPAT). This process ensures that electron displacement remains within the short- to medium-range order in solids, allowing us to effectively probe intrinsic dichroism.

Results

We studied HD in both amorphous and crystalline solids by measuring the absorption of loosely focused femtosecond helical light pulses (Supplementary Section 1 for experimental setup). We produced helical light beams carrying OAM using a birefringent plate, called q -

plate, in which the incident Gaussian beam acquires an OAM that is two times the topological charge, $q^{21,28}$. To disentangle the effects of spin and orbital angular momentum on helical dichroism we used linearly polarized helical light beams. In addition, asymmetric helical light beams were produced by displacing the phase singularity in the OAM beam by translating the q -plate in a plane perpendicular to the incident beam. Additional experimental details are provided in “Methods” (“Differential absorption measurements”, “Generation of OAM beams”, and “Displacement of singularity”) and Supplementary (Sections 5–7).

Achiral crystalline solids

Helical dichroism, HD (Type I) $= A(+l, s) - A(-l, s)$, defined as differential absorption of linearly polarized ($s = 0$) left- and right-helical light ($l = \pm 3$) in the same material, is shown in Fig. 1a for a MgO achiral crystal as a function of the position of the singularity in the OAM beam. The inset shows normalized transmission of a single left- and right-handed helical light pulse as a function of peak laser fluence (Supplementary Section 4) when the singularity was displaced by 900 nm. Each curve in the inset is an average of three independent measurements, and the color band represents the statistical standard error. Differences in the transmission of the two helicities start to appear at a fluence of -0.8 J/cm^2 from the onset of nonlinear absorption and persist over a broad range of peak laser fluences. For each position of the singularity, HD (Type I) was obtained by averaging transmission (shown in the inset) over a fluence range from the onset of nonlinear absorption to 5 J/cm^2 .

Dichroism does not exist in achiral solids for a circularly polarized Gaussian beam and also for a linearly polarized symmetric OAM beam ($\delta = 0 \pm \Delta$ in Fig. 1a). However, when the singularity in the OAM beam is displaced from the center, the material exhibits helical dichroism. HD (Type I) signal increases with the displacement, reaches a maximum around $\pm 1500 \text{ nm}$ and displays a sinusoidal behavior with a change in sign as the singularity traverses the zero-position (Supplementary Section 7). This can be understood in terms of parity-time symmetry argument. HD (Type I) is odd under PT resulting in a change in sign with respect to the δ position. In the experiment, alignment of the singularity at the center of the OAM beam can only be defined before the objective, which translates to an uncertainty $\Delta \pm 100 \text{ nm}$ at the focus (see “Displacement of singularity” for calibration). HD (Type I) signal decreases at large displacement of singularity, as expected, since the intensity profile of asymmetric OAM beam starts to resemble a Gaussian beam.

Orientation-dependent nonlinear absorption of helical light pulses in MgO crystal is shown in Fig. 1b–d for three different displacements of the singularity as labeled in Fig. 1a. MgO (100) has a cubic unit cell with a fourfold rotational symmetry and therefore shows a modulation with a periodicity of $\pi/2$. For $\delta = 0$, there is no difference in absorption of left- and right-handed helical light and the curves overlap (Fig. 1b). When the singularity is shifted to either side from the center of the beam, the dominance of absorption switches between the two helicities of light (Fig. 1c, d). The orientation-dependent transmission is invariant of the position of the singularity. However, the magnitude of HD (Type I) signal remains unaffected with crystal orientation but depends on the position of the singularity. Similar results were obtained for ZnO (11–20) and α -quartz (z-cut) (Supplementary Section 2). Orientation dependence in crystals can also be obtained with non-OAM beams²⁹ (Supplementary Section 2) and via high harmonic generation^{3,4} in nonlinear regime. Extraction of crystal symmetry is due to the multiphoton nature of the interaction and direction dependence of the effective mass of the electron that acts as a local probe.²⁹

Amorphous solids

In a-solids, dichroism and modulation in nonlinear absorption are not expected due to the absence of long-range order. However, Fig. 2a

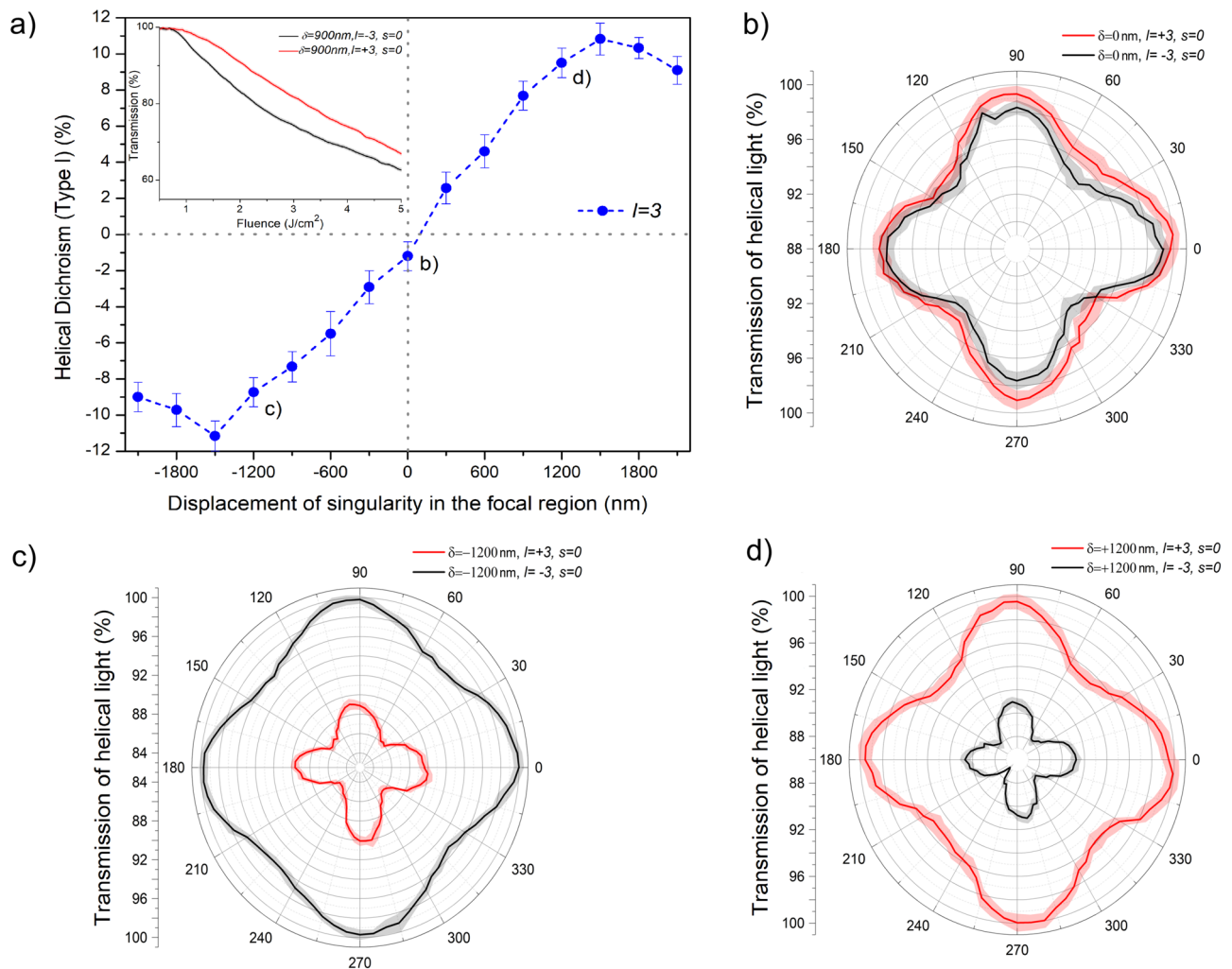


Fig. 1 | Helical dichroism and orientation dependent transmission of helical light in a crystal. **a** HD (Type I) = $A(+l, s) - A(-l, s)$ for crystalline MgO (100) as a function of the displacement of the singularity (δ) in linearly polarized ($\epsilon = 0.05$) asymmetrical OAM beam ($l = \pm 3$). Inset shows transmission of $l = \pm 3$ beam as a function of peak laser fluence for $\delta = 900 \text{ nm}$. **b–d** Orientation-dependent

transmission of $l = \pm 3$ in MgO at the position of displaced singularities marked in **(a)**. The error bars in **(a)** represent the standard error, of multiple measurements ($n = 3$), calculated for an average fluence range used to obtain HD (see text for details). The error bands in **(b–d)** represent the standard error at every position of the crystal for $n = 20$ points.

shows that dichroism exists even in a-solids. For asymmetric helical beams, HD (Type I) in fused silica and borosilicate glass, plotted as a function of the displacement of the singularity, shows similar behavior as in c-solids (Fig. 1a). Figure 2b shows orientation-dependent transmission of helical light in fused silica (for $\delta = -1200 \text{ nm}$), confirming the lack of symmetry since periodic modulation is absent at all positions of the singularity. However, nonlinear absorption of light with opposite helicities is different representing the HD (Type I) shown in Fig. 2a. The results of Figs. 1 and 2 suggest that helical dichroism is independent of the crystal orientation and is intrinsic to both materials. This is in contrast to conventional understanding that dichroism with circularly polarized light is absent in disordered solids (Supplementary Section 5).

Helical dichroism in liquids was recently shown to arise from coupling between the electric dipole and the electric quadrupole transition terms^{25,30}. In disordered solids, this coupling term is expected to vanish upon isotropic averaging while it can survive in gas and liquid phases due to laser-induced dipole force. The presence of HD (Type I) in a-solids and its resemblance to c-solids, while displaying no symmetry in the orientation-dependent transmission due to the absence of long-range order, suggests that HD (Type I) can be attributed to short- to medium-range order. The origin of HD in solids can be

understood in terms of electron transitions via Multiphoton-assisted tunneling (MPAT). The electron displacement during the MPAT serves as a local probe of the short- and medium-range order whereas the helicity dependence arises from higher-order multipoles.

In MPAT process, nonlinear absorption of the incident light is first initiated by multiphoton absorption which promotes an electron from the valence band to an intermediate excited state within the bandgap from which tunneling to conduction band takes place. In a-solids, such intermediate states are the so-called band tail states that extend into the bandgap. Long-range disorder leads to localized states near the bottom (top) of the conduction (valence) band and their density decreases exponentially away from the band edges. In addition, defects, impurities and dangling bonds give rise to localized states in the middle of the bandgap¹³.

MPAT occurs at moderate intensities where the nonlinear absorption is not dominated by either ground-state tunneling or multiphoton transition alone. These two regimes are typically identified by Keldysh parameter³¹ given by Eq. (3) (see “Electron displacement during interband transition” for details). Multiphoton (or tunneling) transition is dominant when the Keldysh parameter is larger than -2 (or smaller than 1)^{32–34}. In fused silica, the Keldysh parameter corresponding to our experimental intensities used to

obtain HD are in the range of -1.1–2.5 where MPAT process is pre-dominant resulting in strong-field induced interband excitation.

In ground-state tunneling, the electron that is promoted from valence to conduction band gains a spatial displacement (x_0) that is proportional to the bandgap E_g and can be approximated by Eq. (2) (“Electron displacement during interband transition”). In MPAT process, E_g has to be replaced by the energy difference between the band tail state and conduction band edge. This leads to a smaller x_0 compared to the upper limit set by tunneling from valence to conduction band, which is in the range of 6–18 Å for fused silica ($E_g \approx 9\text{ eV}^{34,35}$). In comparison, the short- to medium-range order in fused silica is <20 Å^{9,14–16}. The total electron displacement which is a sum of the displacements during tunneling from the intermediate state to the conduction band and multiphoton absorption from valence to intermediate state, is within this range.

Therefore, in a-solids photons are absorbed in a quasi-ordered environment over distances defined by the short- to medium-range order. This results in nonzero isotropic averaging of molecular response tensor. The three-dimensional network of SiO₂ could still consist of periodic clusters each oriented in a different direction. However, these clusters of ordered molecules will absorb the incident light at varying degrees depending on the overlap between the laser polarization and their absorption transition moments³⁶. Therefore, the total absorbed energy by these clusters give rise to a finite contribution towards interband transitions and a nonzero l -dependence (see “Origin of Helical dichroism in solids” for details). As a result, the behavior of HD (Type I) signal is the same in disordered and ordered solids. In c-solids, the ordered environment always ensures nonzero isotropic averaging where HD (Type I) arises from electric dipole electric quadrupole coupling term. Electron transitions via MPAT process can still play a role where the intermediate states could be due to degenerate exciton states, defects, impurities, and boundary effects^{37–39}.

Chiral crystalline solids

C-solids also exhibit chirality, typically studied using sophisticated diffraction and imaging techniques^{6,7}. Conventional CD using Gaussian light (Supplementary Section 5) is inefficient as it is convoluted by competing signals from optical and material properties⁵. Using helical light we show in Fig. 3 that the handedness of a chiral solid can be probed. Figure 3a shows HD (Type I) signal in crystalline (z-cut) left-

quartz (L) and right-quartz (R) for different positions of the singularity in OAM beam. The spatial variation of HD (Type I) is similar to other crystals and amorphous solids (Figs. 1a and 2a). A key difference is that with asymmetric OAM beam, the magnitude of helicity-dependent absorption in the two chiral structures is different. This difference suggests that chiral solids exhibit another type of dichroism, defined as HD (Type II: $\pm l; \pm s$) = $2 \frac{R(\pm l; \pm s) - L(\pm l; \pm s)}{R(\pm l; \pm s) + L(\pm l; \pm s)}$. HD (Type II) is the difference in absorption of a specific-handed helical light in the left- and right-handed chiral solid. It represents a chiral light–chiral matter interaction and is odd under PT symmetry.

HD (Type II) signal, shown in Fig. 3b, as a function of peak laser fluence changes sign with the helicity of the incident light enabling to efficient differentiation the handedness of crystal structure. This chiral signal, obtained at a specific position of the singularity marked by the rectangle in Fig. 3a, is more prominent with asymmetric OAM beam and is weakly influenced by the position of the singularity within the OAM beam. Chiral signal using circularly polarized Gaussian beam (with $l=0, s=\pm 1$) is also shown in Fig. 3b and demonstrates the signal fluctuations with lower average efficiency. The obtained chiral signal is an order of magnitude higher than the reported values from solid-state-based CD in complex chiral crystals^{40,41} and is comparable to recently demonstrated hard X-ray-based HD in powdered molecular media²⁴.

Another representation of HD (Type II) is the orientation-dependent transmission in different-handed quartz for specific helicity shown in Fig. 3c, obtained when the singularity is at the positions marked by a solid rectangle in Fig. 3a. A modulation of $\pi/3$ shows the sixfold rotational symmetry for quartz (Supplementary Section 2). This shows that transmission for specific helicity and position of singularity is different for both chiral solids. Therefore, crystal structure and chirality can be probed simultaneously.

Bandgap dependence of helical dichroism

Figure 4 demonstrates HD (Type I) in materials with different bandgaps. Figure 4a, shows spatial variation of HD (Type I) as a function of displacement of the singularity, for TeO₂ (red, bandgap of 3 eV)⁴², ZnO (cyan, 3.4 eV)⁴³, MgO (black, 7.7 eV)⁴⁴, fused silica (magenta, 9 eV)^{34,35}, and quartz (blue, 9.5 eV)⁴⁵. The different magnitudes of HD (Type I) suggest it is a material-dependent property and HD signal increases with the bandgap. This material dependence can also be observed in

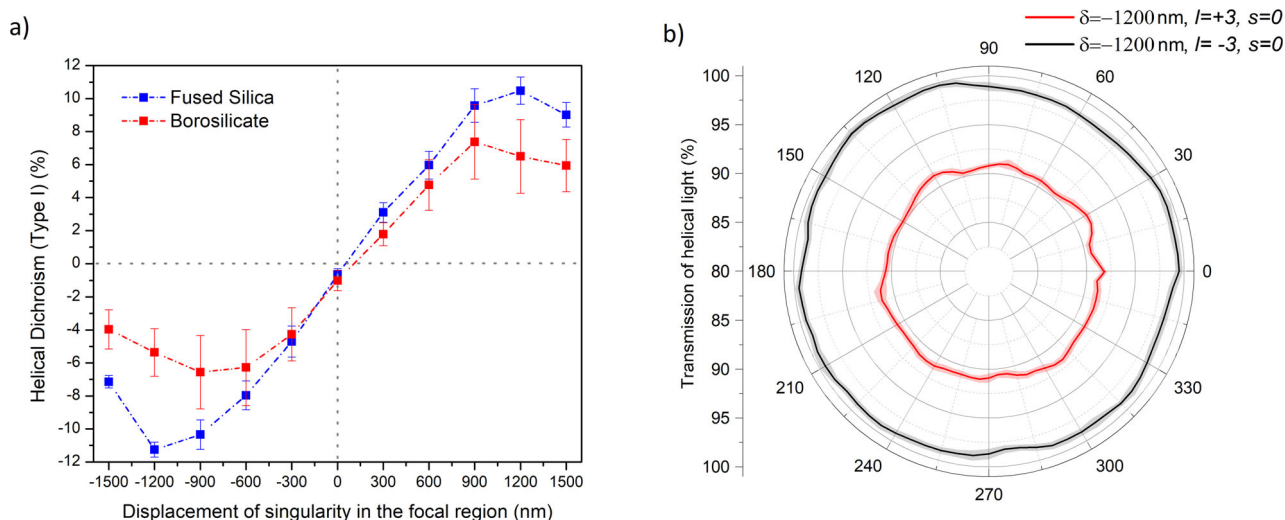


Fig. 2 | Helical dichroism in amorphous solids. **a** HD (Type I) for fused silica (blue) and borosilicate (red) as a function of displacement of the singularity with linearly polarized ($\epsilon = 0.05$) asymmetrical OAM beam ($l = \pm 3$). **b** Orientation-dependent transmission of $l = \pm 3$ in fused silica at $\delta = -1200\text{ nm}$. The error bars in **(a)** represent

the standard error, of multiple measurements ($n = 3$), calculated for an average fluence range used to obtain HD. The error bands in **(b)** represent the standard error at every position of the crystal for $n = 20$ points.

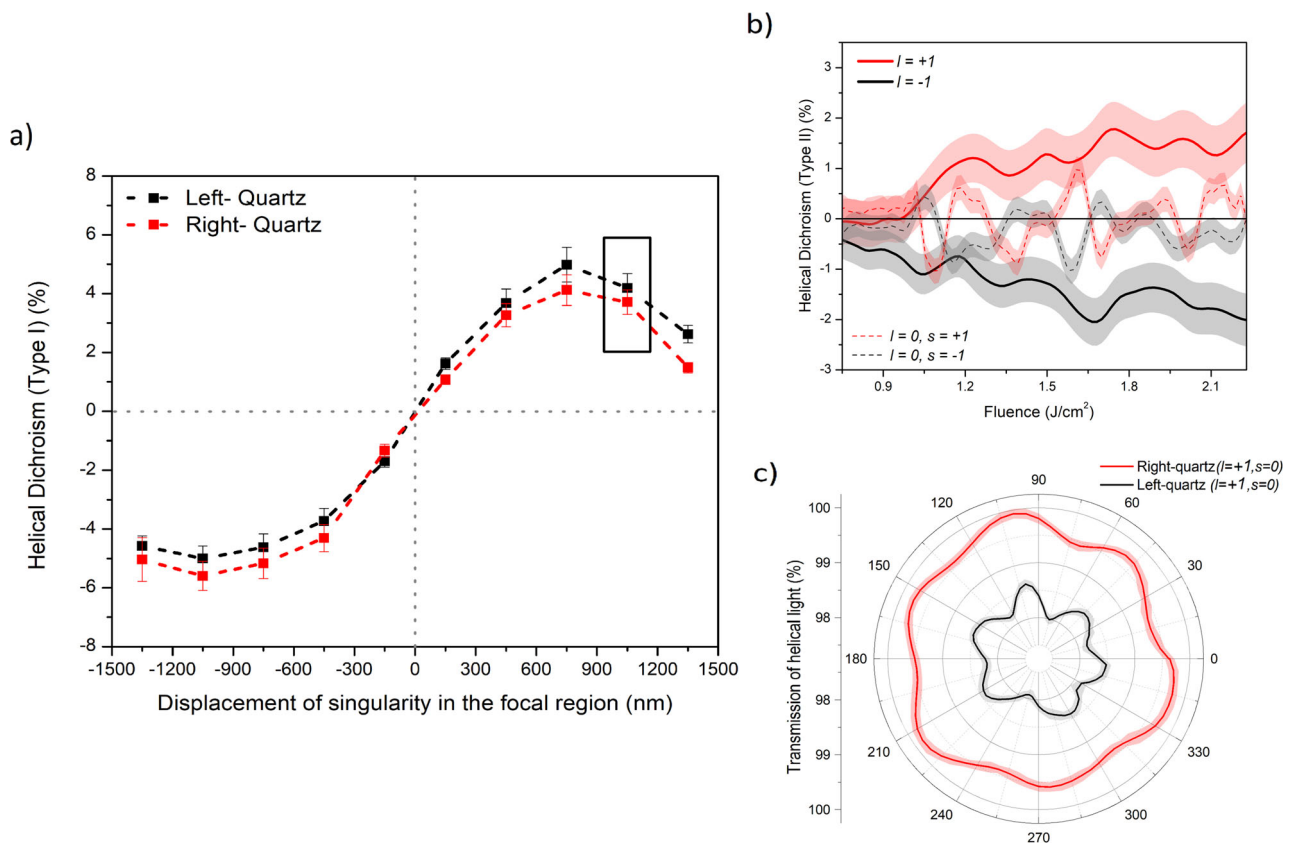


Fig. 3 | Probing chirality in quartz with linearly polarized ($\epsilon = 0.05$) asymmetrical OAM beams. a HD (Type I) for left- and right-handed quartz as a function of displacement of the singularity ($l = \pm 1$). **b** Chiral signal, HD (Type II; $\pm l; \pm s$) = $2 \frac{R(\pm l; \pm s) - L(\pm l; \pm s)}{R(\pm l; \pm s) + L(\pm l; \pm s)}$ as function of peak laser fluence for linearly polarized $l = \pm 1$ and circularly polarized $l = 0$ beams. **c** Orientation-dependent transmission of $l = +1$ in right- and left-handed in quartz. **b, c** were obtained when the singularity was at the

position marked by a solid rectangle in (a). The error bars in (a) represent the standard error, of multiple measurements ($n = 3$), calculated for an average fluence range used to obtain HD. The error bands in (b) represent the error propagation of the standard error of multiple transmission curves. The error bands in (c) represent the standard error at every position of the crystal ($n = 20$ points).

our qualitative model discussed in “Origin of Helical dichroism in solids”. Figure 4b, depicts an average HD (Type I) signal, for three δ positions (600, 900, and 1200 nm) of Fig. 4a, plotted as a function of bandgap.

Control and tunability of HD (Type I)

Figure 5 shows simulated and experimental curves obtained by (i) superimposing Gaussian and OAM beams, and (ii) varying the l -value. To model HD (Type I), we considered the total rate of interband transition ($W_{cv}^{\pm}$) evaluated using Eq. (20). It is a product of multiphoton transition probability amplitude from the ground to the intermediate state and tunnel ionization probability amplitude from the intermediate state to the conduction band. HD (Type I) is defined in terms of differential averaged energy absorbed $\Delta\Gamma$, normalized with respect to the incident laser energy (see “Origin of Helical dichroism in solids” for details).

$$\Delta\Gamma = \Gamma^{+} - \Gamma^{-} = \mathcal{D}(\Upsilon^{+} - \Upsilon^{-}) = \mathcal{D}\left(\text{Re}\left[\nabla_i E_j^{+} E_i^{+*}\right] - \text{Re}\left[\nabla_i E_j^{-} E_i^{-*}\right]\right) \quad (1)$$

where $\Upsilon^{\pm}$ is optical helicity which describes the handedness of helical light and E_{ij} is the electric field described by Eq. (23) (“Superposition of OAM and Gaussian” and Supplementary Section 7 for details). $\mathcal{D}$ represents a collection of physical quantities (given by Eqs. (18)–(20)) that are independent of helicity within our approach, and can be estimated to be 7.3×10^{-5} (“Origin of Helical dichroism in solids” and Supplementary Section 9). Therefore, HD (Type I) is a beam-dominated property and does not exist for symmetric LG beams

($\delta = 0$). For asymmetric LG beams ($\delta \neq 0$), the electric–magnetic dipole coupling term in Eq. (17) vanishes (because we take the difference between the left- and right-helical beams for the same polarization), and the electric dipole–quadrupole coupling term is nonzero resulting in HD (Type I). The electric dipole–quadrupole coupling term also contains the gradient of the electric field giving rise to l -dependence, as can be seen in Fig. 5c. The simulation curves shown in Fig. 5 are plotted by integrating HD (Type I) over the whole beam cross-section, $\text{HD (Type I)} = \int_{-w_0}^{w_0} \Delta\Gamma dx dy$.

For simplicity, we treated intermediate state tunneling within the dipole approximation and reduced the multiphoton absorption to a single-photon transition expanded to higher-order multipoles. We simulate HD (Type I) for different ratios of superposition of Gaussian and OAM beams (Fig. 5a) and l -values (Fig. 5c) using the above equation. For a specific l -value of an asymmetric OAM beam, the magnitude of HD (Type I) signal is maximum for a pure OAM beam and decreases as the amount of Gaussian beam in the superposition increases (Fig. 5a). In case of linearly polarized light, HD signal vanishes for a pure Gaussian beam. Experimental results shown in Fig. 5b for fused silica agrees with the simulations (Fig. 5a). Also, simulated and experimental HD signals scale with l -value as shown in Fig. 5c, d for two different l -values. Similar control and tunability of HD was also observed in c-solids such as MgO (Supplementary Section 3). The simulated HD values differ by few orders of magnitude compared to experimental values. This variation could be due the approximate values used for electric dipole and quadrupole moment, and material response.

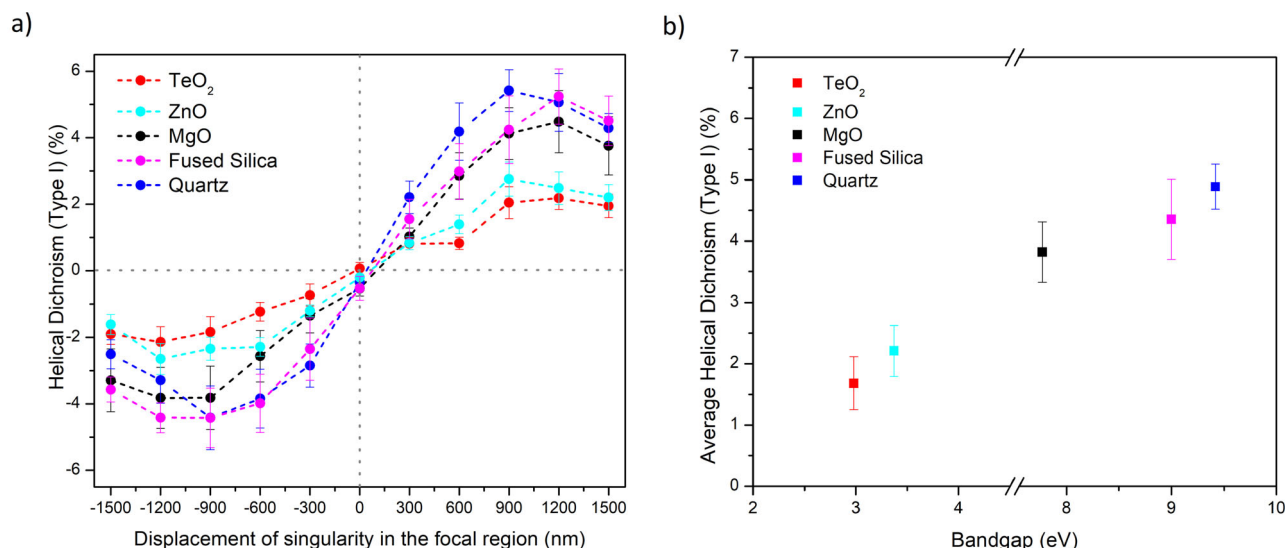


Fig. 4 | Bandgap dependence of helical dichroism. **a** HD (Type I) in different materials as a function of displacement of singularity in the OAM beam for $l = \pm 1$ in crystalline and amorphous solids. **b** Average magnitude of HD (Type I) as a function of bandgap for $l = \pm 1$. The error bars in (a) represent the standard error, of multiple

measurements ($n = 3$), calculated for an average energy range used to obtain HD. The error bars in (b) represent the average of three δ positions in (a) where the HD (Type I) signal is maximum. All curves are obtained under identical experimental conditions.

HD signal changes in discrete steps when l -value is varied but can be tuned almost continuously by changing the superposition of OAM and Gaussian beams. In addition, HD signal can also be varied by changing the ellipticity of laser polarization²⁵. These are the features of our technique that has no comparable equivalent in other existing solid-state-based chiroptical techniques. Continuous tunability of HD by superposition of OAM and Gaussian beams by electrical detuning of optical retardation offers instrumental advantage. A single higher-order q-plate is sufficient to reproduce the results of all lower-order q-plates by controlling the voltage on the q-plate.

Discussion

In conclusion, we demonstrate HD in both amorphous and crystalline solids including chiral systems. HD in the condensed phase provides valuable information on chirality. Conventional solid-state chiroptical techniques such as CD have poor efficiency because the chiral signal is weaker than the artifact signals from macroscopic anisotropies such as linear birefringence. The efficiency of HD enables to achieve chiral recognition on a solid surface and is of fundamental importance in various fields of surface and material sciences. In addition, the control and tunability of HD provides new opportunities in the development of enantioselective catalysis⁴⁶ and asymmetric synthesis of bioactive molecules⁴⁷, chiral sensors^{48,49}, and molecular electronic devices^{50,51}. In laser processing of transparent materials, localized changes induced in the bulk can result in structural changes on sub-micron dimensions confined to the laser focal volume^{52,53}. These changes modify the bandgap and are hard to study due to lack of in situ probes. Pump-probe spectroscopy involving Gaussian and OAM beams can shed light on such changes by monitoring the magnitude of HD signal due to its dependence on the bandgap.

The presence of intrinsic dichroism in amorphous materials is due to the existence of short- to medium-range order. Material response to the phase of light associated with OAM beams will aid the efforts to understand the mysterious nature of amorphous materials. Furthermore, HD can be extended to conjugated polymers that are used as active materials in devices for printed and flexible organic electronics⁵⁴. Transport properties in such polymers is widely believed to be due to long-range order, so research focused primarily on increasing the crystallinity of polymers. However, recent studies

showed that local aggregation over few chains is sufficient to ensure high mobility⁵⁵. In other words, the key to designing high-mobility polymers is not to increase their crystallinity but rather to improve their tolerance for disorder. Typically, information on short-range ordering in polymers is often achieved by means of radial distribution function derived from X-ray diffraction⁵⁶. HD can shed light on short-range order that influences electronic properties in polymers and semiconducting alloys.

Methods

Differential absorption measurements

Transmission measurements were performed using a Ti:Sapphire laser amplifier system, operating in an external trigger mode producing 45 fs, 800 nm pulses with a maximum pulse energy of 2.5 mJ. An aspheric objective lens (NA = 0.3) was used to focus the femtosecond pulses into solid samples with typical dimensions of $10 \times 10 \times 1$ mm. A second aspheric objective with the same or higher numerical aperture (NA = 0.5) collected and collimated the transmitted light onto a photodiode (PD2), positioned immediately after the objective (Supplementary Section 1 for a schematic of the experimental setup). For every laser shot, the transmitted light signal on PD2 was normalized with the incoming light signal on PD1, reflected off a glass plate positioned in the beam path at an angle of -20° to avoid Brewster's angle. The signals generated by PD1 and PD2 were stretched by an electronic pulse stretcher, discretized, and recorded by a data acquisition card. A combination of a half-wave plate and a polarizer was used to vary the pulse energy (Supplementary Section 1). The incident pulse energies were measured before the objective. During the measurement, for every laser shot, the pulse energy was increased by ~ 3 nJ and the sample was translated by $5 \mu\text{m}$ to irradiate a fresh sample. Multiple transmission curves similar to the inset of Fig. 1a were obtained for each sample to be averaged and smoothed. The difference in the normalized transmission of left- and right-helical light is proportional to the differential absorption. To ensure shortest pulses in the interaction region, a negative chirp was introduced and optimized by measuring the second harmonic generation in a BBO crystal placed at the location of the sample. A single-shot auto-correlator then continuously monitored the pulse duration. The pulse duration at the interaction region is about 100 fs. Prior to each experiment,

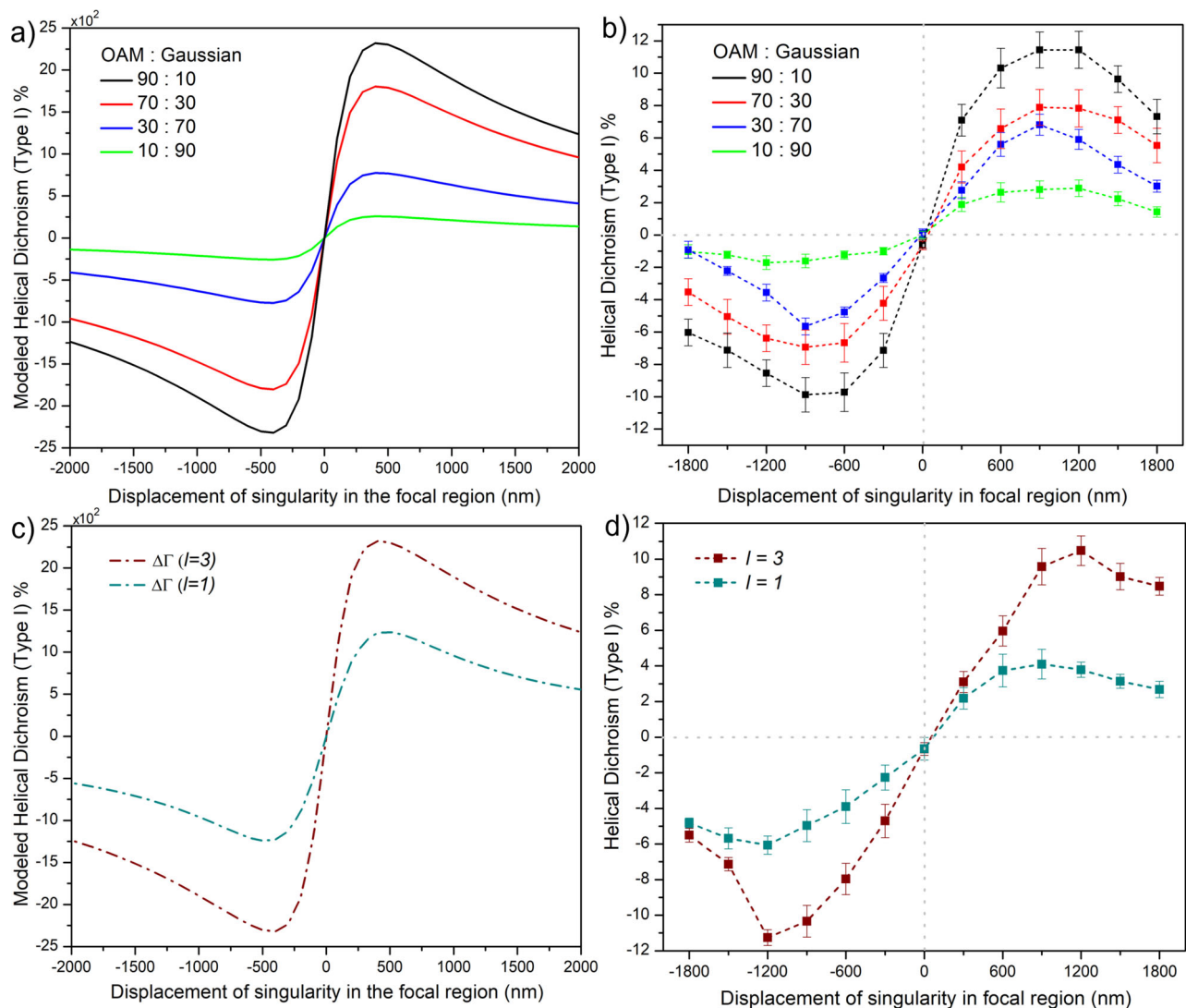


Fig. 5 | Tunability of Helical dichroism. Simulated and measured HD (Type I), in fused silica as a function of the displacement of singularity for **(a, b)** variable ratios of superposition of linearly polarized ($\epsilon = 0.05$) OAM ($l = \pm 3$) and Gaussian beams, and **c, d** linearly polarized ($\epsilon = 0.05$) helical light with $l = \pm 1, \pm 3$. In simulation, displacement of the singularity was considered perpendicular to the polarization following experimental conditions. The error bars in **(b, d)** represent the standard

error, of multiple measurements ($n = 3$), calculated for an average fluence range used to obtain HD. The HD (Type I) was modeled using the relation $\int_{-w_0}^{w_0} \Delta \Gamma dx, dy = \int_{-w_0}^{w_0} \mathcal{D}(\Upsilon^+ - \Upsilon^-) dx, dy$ where $\mathcal{D}$ represents a collection of physical quantities and $\Upsilon^\pm$ is optical helicity which describes the handedness of helical light (see text and “Methods” for details).

transmission measurements were always performed without a sample (in air) to determine and minimize background errors resulting from any discrepancies between the photodiodes (Supplementary Section 6). In addition, the measured single-shot beam profile, pulse spectrum, and OAM value remained unchanged after transmission through the samples²⁵. The crystal samples were procured from MTI Corp., MSE Supplies and chiral quartz from Knight Optical. Fused silica was bought from SPI Supplies.

Generation of OAM beams

Light beams carrying orbital and/or spin angular momentum were generated and controlled by OAM/SAM unit (Supplementary Fig. 1) consisting of a combination of half- and quarter-wave plates (HWP and QWP), linear polarizer (LP) and a birefringent liquid crystal based phase plate called q -plate^{21,28,57}. When an incident Gaussian beam propagates through the q -plate with a topological charge q , it acquires an OAM defined by $l = \pm 2q$ with a phase singularity and hence a null intensity region at the center of the beam - an optical vortex. The

wavefront structure of such beams undergo l intertwined rotations in one wavelength, the direction of rotation is determined by the sign of the input polarization. The conversion efficiency of the q -plates were $91 \pm 2\%$ for $l = 1, 3$. Linearly polarized OAM light $s = 0, l = \pm 1$ was generated using a combination of QWP, q -plate, QWP, and LP. The ellipticity of linearly polarized OAM light was $5 \pm 2\%$ reaching the sample.

Displacement of singularity

The singularity/null intensity region in the OAM beam was displaced by translating the q -plate, mounted on a x, y-stages with a step size of $250 \pm 10 \mu\text{m}$. When focused by the objective, this translated to a displacement step size of $300 \pm 20 \text{ nm}$ with respect to the center of the beam. The calibration was achieved by measuring the total translation required to displace the singularity to the periphery of the defocused beam and comparing it to the measured spot size of $2 \pm 0.2 \mu\text{m}$ obtained by knife-edge measurements. The helical vortex beams can be further classified into vector and scalar vortex beams. The superposition of vector vortex beams with linear Gaussian leads to the

shifting of singularity towards the periphery of the beam for $l=1$ and splitting of the singularity for higher-order l -value⁵⁸. The superposition of linear Gaussian with scalar vortex beam causes the null intensity region to fade and does not lead to the shifting of singularity, which was used in the experiments.

Electron displacement during interband transition

Classically, in atoms, tunneling results in spatial displacement of the electron given by $\mathbf{x}_0 = I_p / (eE)$, where I_p is the ionization potential^{31,59}. $\mathbf{x}_0$ is the distance traversed by the electron through the barrier to the tunnel exit. This concept can also be extended to solids. The energy absorbed from the incident laser fields is proportional to the associated injection current given by $\mathbf{J} = en_0 \mathbf{x}_0 \dot{\rho}$, where e is the electron charge, n_0 is electron density in the conduction band, $\dot{\rho}$ is the injection rate which is proportional to the transition rate W , $\mathbf{x}_0$ is the spatial displacement of the electrons after being promoted from the valence band to the conduction band. ($\mathbf{J}$) is fundamental to maintain energy conservation ($\dot{u} = -\mathbf{J} \cdot \mathbf{E}$). In optical tunneling, energy conservation is fulfilled when this current reflects a spatial displacement of the electrons given by⁶⁰

$$\mathbf{x}_0 = \mathbf{E} E_g / (eE^2) \quad (2)$$

where E_g is the bandgap and $\mathbf{E}$ is the electric field. We assume a parabolic conduction band to eliminate contributions from band anharmonicities and Bloch oscillations due to reflections at zone boundaries⁶⁰.

Injection current was recently used to explain the origin of strong-field-induced harmonic generation in fused silica⁶⁰. In amorphous fused silica ($E_g \approx 9 \text{ eV}$ ^{34,35}), $\mathbf{x}_0$ varies from 6 to 18 Å for the laser intensities used in our experiments. Transition of electron from valence to conduction band can occur via two mechanisms, multiphoton or tunneling, depending on the laser intensity. They are typically identified by the Keldysh parameter (γ)^{31,33}. For solids, it is defined as

$$\gamma = \frac{\omega}{e} \left[\frac{mc n \epsilon_0 E_g}{I} \right]^{1/2} \quad (3)$$

where ω is the laser frequency, I is the incident laser intensity (Supplementary Section 4), m and e are the reduced mass and charge of the electron, c is the velocity of light, n is the refractive index of the material, E_g is the bandgap of the material and ϵ_0 is the permittivity of free space. When $\gamma > 2$, interband excitations are dominated by multiphoton process and when $\gamma < 1$ it is dominated by tunneling.

For the laser intensities in the range of 2×10^{13} to $8 \times 10^{13} \text{ W/cm}^2$ that were used in the experiments, Keldysh parameter varied from ~2.5 to 1.1 for fused silica. In the intermediate regime when $1 \lesssim \gamma \lesssim 2$ the electron transitions are dominated by multiphoton-assisted tunneling (MPAT)^{33,61}. The MPAT process, developed for atoms, can be extended to solids and visualized as electron transition from valence band to an intermediate state by multiphoton absorption and subsequent tunneling from that state to the conduction band^{31,61}.

In MPAT process, there will be two contributions to electron displacement—one from multiphoton transition to the intermediate state and the other from subsequent tunneling to the conduction band ($\mathbf{x}_0$ is given by Eq. (2) where E_g needs to be replaced by the energy gap between intermediate and conduction band states). However, $\mathbf{x}_0$ in MPAT will be smaller compared to direct tunneling transitions from valence band to conduction band which sets the upper limit for electron displacement^{32,61}. $\mathbf{x}_0$ in MPAT is comparable to short-medium-range order in fused silica which is $< 20 \text{ Å}$ ^{9,14–16}. As a result, isotropic averaging is restricted to an ordered environment giving rise to finite contribution in a-solids. In c-solids, the ordered environment always ensures a nonzero HD signal upon isotropic averaging. Moreover, our transmission curves reproduce the crystal symmetry due to its

dependence upon the injection current, similar to the results that were obtained from the high harmonic yields⁶⁰.

Origin of Helical dichroism in solids

Helical Dichroism in solids can be understood in terms of molecular multipole moments during light-matter interaction. When the incident laser intensity is not sufficient for direct interband tunneling, electron transitions are facilitated by multiphoton excitation to intermediate states and subsequent tunneling to the conduction band. The transition amplitude for MPAT process involving a single-photon absorption (SPA) from the valence band (ψ_v) to an intermediate excited state (ψ_m) and subsequent tunneling to the conduction band (ψ_c) is given by (Supplementary Section 8 for further details)

$$M_{cv} = \sum_m \underbrace{\langle \psi_m | \hat{V}_i | \psi_v \rangle}_{M_{SPA}} \underbrace{\frac{i}{\hbar(\omega_{mv} - \omega)} \int_{t_0}^t d\tau \langle \psi_c(\tau) | \hat{V}_f(\tau) | \psi_m(\tau) e^{i(\omega_{mv} - \omega)\tau} }_{M_{TNL}} \quad (4)$$

where ω is the laser frequency, $\omega_{mv} = (E_m - E_v)/\hbar$, E_m , and E_v are the energies of the intermediate and valence band states, respectively. In addition, $\hat{V}_i$ and $\hat{V}_f$ are multiphoton and tunneling interaction Hamiltonians written in multipole expansion and dipole approximation, respectively. The MPAT transition amplitude is a product of two factors; a time-independent single-photon transition amplitude M_{SPA} and a time-dependent excited state tunneling amplitude M_{TNL} . The interaction Hamiltonian is given by $\hat{V}(t) = \frac{1}{2m} [2\mathbf{e} \cdot \mathbf{A}(R, t) + e^2 \mathbf{A}^2(R, t)]$, where the m is the electron mass, $\mathbf{p}$ is the momentum vector in the molecular frame ($\mathbf{r}$) and $\mathbf{A}(R, t)$ is the vector potential in the laboratory frame ($\mathbf{R}$).

In crystals, the eigenstates are written in terms of Bloch wavefunctions (plane wave modulated by the crystal periodicity function $u_{\mathbf{k}}(\mathbf{r})$). For a-solids, we can approximate the eigenstates as Bloch-like wavefunctions (as long as the electron displacement is within $\mathbf{x}_0$ ¹³) with effective wave vectors $\mathbf{k}'$, $\mathbf{k}''$ and $\mathbf{k}$ for valence band state, intermediate state and the conduction band state, respectively. The valence band and intermediate state wavefunctions are given by

$$|\psi_v(\mathbf{r}, t)\rangle = u_{\mathbf{k}'}^v(\mathbf{r}) e^{i\mathbf{k}' \cdot \mathbf{r}} e^{-i\frac{E_v}{\hbar} t} \quad (5)$$

$$|\psi_m(\mathbf{r}, t)\rangle = u_{\mathbf{k}''}^m(\mathbf{r}) e^{i\mathbf{k}'' \cdot \mathbf{r}} e^{-i\frac{E_m}{\hbar} t} \quad (6)$$

The conduction band state is approximated by a Volkov-type solution⁶²

$$|\psi_c(\mathbf{r}, t)\rangle = u_{\mathbf{k}}^c(\mathbf{r}) \exp \left[i \left(\mathbf{k} \cdot \mathbf{r} - \frac{1}{\hbar} \int_0^t E_c[\mathbf{k}(t'')] dt'' \right) \right] \quad (7)$$

$$E_c[\mathbf{k}(t'')] = E_g + \frac{1}{2m_1} (\hbar \mathbf{k} - e\mathbf{A}(t''))^2 \quad (8)$$

where $E_v = \frac{\hbar^2 k^2}{2m_0}$, m_0 and m_1 are the effective mass of the valence and the conduction bands, E_g is the bandgap, $\mathbf{r}$ is the spatial coordinate in molecular frame and $\mathbf{A}$ is the vector potential in laboratory frame given by $\mathbf{A}(t) = A_0(\alpha \cos \omega t \hat{x} + \beta \sin \omega t \hat{y})$ for elliptical polarization. In our intensity range, the above Volkov-like wavefunction can be limited to a linear dependency of the vector potential. Solving the time integral leads to

$$|\psi_c(\mathbf{r}, t)\rangle = \frac{u_{\mathbf{k}}^c(\mathbf{r})}{(2\pi)^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r} - i(E_g \tau + E_c \tau + \gamma_0 \hbar [k_x \alpha \sin(\omega \tau) - k_y \beta \cos(\omega \tau)])} \quad (9)$$

where $E_c = \frac{\hbar^2 k^2}{2m_1}$ is the kinetic energy of the conduction band and $\gamma_0 = \frac{eA_0}{m_1 \omega}$ is the quiver amplitude. Substituting all the above states (Eqs. (5)–(7)) in the transition amplitude (Eq. (4)) and taking the

evolution of states over $t_0 = -T/2$, $t = T/2$, with the limit $T \rightarrow \infty$ ^{62,63}, we obtain

$$M_{cv} = \frac{iA_0 e}{mh(2\pi)^{3/2}} \sum_m \frac{1}{h(\omega_{mv} - \omega)} \int_{-\infty}^{\infty} u_k^{m*}(\mathbf{r}) \hat{V}_i u_k^m(\mathbf{r}') e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d^3 r' \int_{-\infty}^{\infty} u_k^c(\mathbf{r}) u_k^m(\mathbf{r}) e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} d^3 r' \\ \times \lim_{T \rightarrow \infty} \int_{-T/2}^{T/2} e^{i(E_g + \epsilon - N\hbar\omega)\tau} (\alpha p_x \cos \omega\tau + \beta p_y \sin \omega\tau) e^{i\hbar\omega_0[k_x \sin(\omega\tau) - k_y \beta \cos(\omega\tau)]} d\tau \quad (10)$$

Solving the time integral using Jacobi–Anger expansion $\cos \omega t e^{i\alpha \sin \omega t} = \frac{1}{\alpha} \sum_{n=-\infty}^{\infty} J_n(\alpha) e^{in\omega t}$, we obtain

$$M_{cv} = \frac{iA_0 e}{mh(2\pi)^{3/2}} \frac{1}{\gamma_0} \sum_m p_{mv}^{SPA} \sum_{\eta, \zeta=-\infty}^{\infty} i^\zeta \int_{-\infty}^{\infty} u_k^c(\mathbf{r}) \left[\frac{p_x}{k_x} \eta + \frac{p_y}{k_y} \zeta \right] u_k^m(\mathbf{r}) e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d^3 r' \\ \times J_\eta(-\gamma_0 k_x \alpha) J_\zeta(\gamma_0 k_y \beta) \left[\lim_{T \rightarrow \infty} \frac{2\hbar \sin\left((E_g + \epsilon - N\hbar\omega)\frac{T}{2\hbar}\right)}{(E_g + \epsilon - N\hbar\omega)} \right] \quad (11)$$

where $\epsilon = \frac{\hbar^2 k^2}{2m^*}$ is the total kinetic energy, $m^{*-1} = m_1^{-1} - m_0^{-1}$ is the total effective electron mass, and $N\hbar\omega = (\eta + \zeta)\hbar\omega + \hbar\omega$ is the total number of photons absorbed during the MPAT process. Use of Jacobi–Anger expansion allowed us to discretize the tunneling contribution and, for analytical analysis, treated the transition from intermediate state to conduction band state non-perturbatively. p_{mv}^{SPA} represents the single-photon absorption probability amplitude given by

$$p_{mv}^{SPA} = \frac{1}{h(\omega_{mv} - \omega)} \int_{-\infty}^{\infty} u_k^{m*}(\mathbf{r}) \hat{V}_i u_k^m(\mathbf{r}') e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d^3 r' \quad (12)$$

We further define the tunneling probability amplitude as

$$p_{cm}^{TNL} = \frac{m_1}{mh(2\pi)^{3/2}} \sum_{\eta, \zeta=-\infty}^{\infty} i^\zeta J_\eta(-\gamma_0 k_x \alpha) J_\zeta(\gamma_0 k_y \beta) \int_{-\infty}^{\infty} u_k^c(\mathbf{r}) \left[\frac{p_x}{k_x} \eta + \frac{p_y}{k_y} \zeta \right] u_k^m(\mathbf{r}) e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d^3 r' \quad (13)$$

Using the property $\lim_{T \rightarrow \infty} T^2 \frac{\sin^2(x)}{x^2} = 2\pi\hbar T \delta(\epsilon + E_g - N\hbar\omega)$ where $x = (E_g + \epsilon - N\hbar\omega)\frac{T}{2\hbar}$ ⁶⁴, the transition rate from the valence to the conduction band, defined as $W_{cv} = \frac{d}{dt} |M_{cv}|^2$, can be expressed as

$$W_{cv}(\mathbf{k}) = 2\pi\hbar\omega^2 \sum_m |p_{cm}^{TNL}|^2 |p_{mv}^{SPA}|^2 \delta(\epsilon + E_g - N\hbar\omega) \quad (14)$$

where the delta function demonstrates the energy conservation for the full transition. The transition rate $W_{cv}(\mathbf{k})$ is proportional to a product of the single-photon absorption probability $|p_{mv}^{SPA}|^2$ (electron promoted from the valence band to intermediate state) and the tunneling probability $|p_{cm}^{TNL}|^2$ (electron tunneling from intermediate state to conduction band). Expanding $|p_{mv}^{SPA}|^2$ in Eq. (14) in terms of higher-order multipoles²⁵, the absorption rate for left- and right-helical light (with identical polarization) represented by $\pm$ sign, $W_{cv}^{(\pm)}$, can be written as

$$W_{cv}^{(\pm)}(\mathbf{k}) = 2\pi \sum_m \left[(|p_{cm}^{TNL}|^2 |\mu_i^{mv}|^2) |E_i^\pm|^2 + (|p_{cm}^{TNL}|^2 |m_i^{mv}|^2) |B_i^\pm|^2 + 2(|p_{cm}^{TNL}|^2 \mu_i^{mv} m_i^{vm})_p \right. \\ \left. \text{Im}[E_i^\pm B_i^\pm] + \frac{2}{3} (|p_{cm}^{TNL}|^2 \mu_i^{mv} \theta_{ij}^{vm})_p \text{Re}[\nabla_i E_j^\pm E_i^\pm] \right] \frac{\delta(\epsilon + E_g - N\hbar\omega)}{h(\omega_{mv} - \omega)^2} \quad (15)$$

where, E and B are incident electric and magnetic fields (Supplementary Section 7 for asymmetric Laguerre–Gaussian beam equation), μ_i represents the intrinsic electric dipole, m_i is the intrinsic magnetic dipole, θ_{ij} represents the intrinsic electric quadrupole. Since photons are absorbed in an ordered environment within the short-range distances in both c-solids and a-solids, we assume that the anisotropic averaging, $\langle \rangle_p$, results in a finite orientation-dependent weighing factor

$\Omega_{i=1,4}$. As a result of this simplification, the above expression reduces to

$$W_{cv}^{(\pm)}(\mathbf{k}) = 2\pi \sum_m |p_{cm}^{TNL}|^2 \left[\underbrace{\Omega_1 |\mu_i^{mv}|^2 |E_i^\pm|^2}_{\text{EIE1}} + \underbrace{\Omega_2 |m_i^{mv}|^2 |B_i^\pm|^2}_{\text{MIM1}} + \underbrace{\Omega_3 (2\mu_i^{mv} m_i^{vm}) \text{Im}[E_i^\pm B_i^\pm]}_{\text{EIM1}} \right. \\ \left. + \underbrace{\Omega_4 \left(\frac{2}{3} \mu_i^{mv} \theta_{ij}^{vm} \right) \text{Re}[\nabla_i E_j^\pm E_i^\pm]}_{\text{EIE2}} \right] \frac{\delta(\epsilon + E_g - N\hbar\omega)}{h(\omega_{mv} - \omega)^2} \quad (16)$$

where E1 and M1 are electric and magnetic dipoles, respectively, and E2 is the electric quadrupole. The coupling terms EIM1 and EIE2 are pseudoscalars and change signs under improper rotation. $W_{cv}^{(\pm)}(\mathbf{k})$ is a product of tunneling probability amplitude $|p_{cm}^{TNL}|^2$ and single-photon absorption probability amplitude $|p_{mv}^{SPA}|^2$. The above equation can be generalized to the multiphoton case and was also shown to be responsible for the origin of HD in chiral and achiral molecules²⁵.

HD (Type I) is proportional to the difference in the interband transition rates between left- and right-handed helical light with beam asymmetry parameter δ can be expressed as:

$$\Delta W_{cv} = W_{cv}^+ - W_{cv}^- = 2\pi \sum_m |p_{cm}^{TNL}|^2 \left[\Omega_3 (2\mu_i^{mv} m_i^{vm}) (\text{Im}[E_i^+ B_i^+] - \text{Im}[E_i^- B_i^-]) \right. \\ \left. + \Omega_4 \left(\frac{2}{3} \mu_i^{mv} \theta_{ij}^{vm} \right) (\text{Re}[\nabla_i E_j^+ E_i^+] - \text{Re}[\nabla_i E_j^- E_i^-]) \right] \frac{\delta(\epsilon + E_g - N\hbar\omega)}{h(\omega_{mv} - \omega)^2} \quad (17)$$

EIE1 and MIM1 terms do not contribute to HD (Type I) because the field intensities and profiles remain the same for both helicities. Evaluation of above equation shows that HD (Type I) is a beam-dominated property as the material tensors are identical for both the helicities. Moreover, within dipole approximation, the tunneling contribution $|p_{cm}^{TNL}|^2$ results in identical rates for both helicities.

The HD (Type I) is dependent on the beam asymmetry parameter δ where $\delta = 0$ represents symmetric beam and $\delta \neq 0$ asymmetric beam (Supplementary Section 7 for beam profiles). The EIM1 contribution for both symmetric and asymmetric beam vanishes because we take the difference between the left- and right-helical beams for the same polarization. Therefore, HD (Type I) arises due to EIE2 coupling term. The EIE2 term contains the gradient of the electric field giving rise to l -dependence. Therefore, for symmetric beams EIE2 contributions average out to zero and only exist for asymmetric beams. For left- and right-circularly polarized light, the EIM1 term is nonzero and gives rise to conventional chiral signal

The total transition rate, W_{cv} , can be obtained by integrating, $W_{cv}(\mathbf{k})$, over all momentum states. For numerical estimation, shown in Fig. 5, we assume the summation over all intermediate states in the above equation is dominated by a single state that is pre-determined by the incident photon. The total transition rate is enhanced when the intermediate state is in resonance with the incident photon energy. In addition, we use linearly polarized light to simplify $W_{cv}(\mathbf{k})$ and perform the integration using the properties of Bessel's functions and the weak-field limit for the non-perturbative discrete transition rate^{31,62,63} (Supplementary Section 9 for details) to obtain

$$\Delta W = W_{cv}^+ - W_{cv}^- = \frac{2\Omega_4 (\mu_i^{mv} \theta_{ij}^{vm})}{3\hbar^2 (\omega_{mv} - \omega)^2} \tilde{W} (\text{Re}[\nabla_i E_j^+ E_i^+] - \text{Re}[\nabla_i E_j^- E_i^-]) = D(\Upsilon^+ - \Upsilon^-) \quad (18)$$

where $\Upsilon^\pm = \text{Re}[\nabla_i E_j^\pm E_i^\pm]$ represent the optical helicity describing the handedness of the helical light, its association with the field gradient gives rise to l -dependence. This quantity is odd under parity with a change in the sign of the displacement of the singularity, δ , and time

reversal changes the handedness of helical light. Also,

$$\bar{W} = \frac{1}{(2\pi)^4 \hbar} \left(\frac{m_1 \omega p_{cm}}{m(\eta-1)!} \right)^2 \left(\frac{eA_0}{2m_1 \omega} \right)^{2\eta} \left(\frac{2m^*}{\hbar^2} \right)^{(2\eta+1)/2} \left(\frac{n\hbar\omega - E_g}{(2\eta-1)} \right)^{(2\eta-1)/2} \quad (19)$$

where $n = \eta + 1$ is the total photons absorbed for linearly polarized light. HD (Type I) can now be defined in terms of energy absorbed Γ normalized with respect to the incident laser energy, $\mathcal{E}_{inc}$ as:

$$\Delta\Gamma = \Gamma^+ - \Gamma^- = \frac{\hbar(W_{\delta}^+ - W_{\delta}^-)}{\mathcal{E}_{inc}} = \mathcal{D}(\Upsilon^+ - \Upsilon^-) \quad (20)$$

where $\mathcal{D} = \frac{\hbar\mathbf{D}}{\mathcal{E}_{inc}}$. HD (Type I) is obtained by integrating over the beam cross-section $\int_{-w_0}^{w_0} \Delta\Gamma dx dy$

For an order of magnitude estimation of $\mathcal{D}$, we used the following values; the intrinsic dipole as $\mu_i \approx 1.65 \times 10^{-30}$ Cm⁶⁵, the quadrupole for fused silica molecule as $\theta_{ij} \approx 9.3 \times 10^{-49}$ Cm²(glass)⁶⁶, $A_0 = E_0/\omega$ where $E_0 = 7.1 \times 10^9$ to 1.5×10^{10} V/m and $\omega = 2.35 \times 10^{15}$ Hz. $p_{cm}/m \approx E'_g/m^*E'_g$ is the bandgap between intermediate and conduction band (~ 7.4 eV), $m^* = m_0 = m_1 \approx 10^{-30}$ kg³⁴, and $E_g \approx 9$ eV is the full bandgap. We assumed (i) $\Omega_4 = 1$ (ordered environment for crystals and amorphous materials within the short-medium-range distances), (ii) single level dominates the total transition rate, (iii) The summation of the Bessel functions is evaluated by retaining in the sum over n only the term closest to resonance for the intermediate state tunneling contribution and (iv) one-photon transition is highly nonresonant so that $\omega_{mw} - \omega \approx \omega^{64}$ (v) dominant component of optical helicity (Υ) with respect to displacement of singularity. Due to discretization of transition from intermediate state to the conduction band during the tunneling process we assume $\eta = 5$ and $n = \eta + 1$ corresponding to bandgap energy. Thus, the value of $\mathcal{D}$ is 7.3×10^{-5} . The above numerical estimate was plotted in Fig. 5a, c as a function of displacement of singularity. The estimated HD values differ by few orders of magnitude compared to experimental values. This variation could be due the approximate values used for electric dipole and quadrupole moment and the material response.

For n -photon transitions, $|p_{mv}^{SPA}|^2$ should be substituted by the multiphoton contribution ($|p_{mv}^{MPA}|^2$) in the transition rate $W_{cv}(\mathbf{k})$ and will contain multitude of cross-correlation terms arising from the summation in the modulus square of the transition amplitude. However, optical helicity $\Upsilon^\pm$ will still be present giving rise to the observed HD (Type I)²⁵.

Helical dichroism obtained using MPAT is not only limited to the tunneling interaction Hamiltonian $\hat{V}_f$ written in the dipole approximation. Our experimental results can also be described as long as one or both of the interaction Hamiltonian either $\hat{V}_f$ ($\hat{V}_i$) used in the tunneling (multiphoton) probability amplitude includes the contribution of higher-order multipoles to obtain the EIE2 coupling term. For higher incident intensities, the interband excitations are dominated by ground-state tunneling transitions. In this regime, the HD can be explained as long as the interaction Hamiltonian contains the contribution of higher-order multipoles which gives rise to the l -dependence.

Superposition of OAM and Gaussian

The experimental optical setup consists of a combination of waveplates and a q -plate (Supplementary Section 1). When an incident circularly polarized Gaussian beam propagates through the q -plate, it acquires an OAM defined by $l = \pm 2q$. Experimentally, we can measure the efficiency of the conversion process. If the conversion efficiency is not 100%, as is often the case, the transmitted light will consist of a superposition of Gaussian and Laguerre–Gaussian beam. In other words, a portion of the incident Gaussian will transmit

unaffected and the remaining portion will be converted to OAM. In our setup, the incident light is vertically polarized.

$$\begin{aligned} |V\rangle &\rightarrow \text{QWP}(\pm 45) \xrightarrow{\text{LHC}} \\ &\text{RHCQ-plate} \xrightarrow{l+} \\ l\text{-QWP}(\mp 45) &\rightarrow \text{QWP}(\theta) \end{aligned} \quad (21)$$

Vertically polarized light incident onto the first quarter-wave plate (QWP) generates left-CPL (Right-CPL) if the angle of incidence is 45° (-45°) with respect to the horizontal axis. Experimentally, the transmitted light has an ellipticity between 90 and 95% therefore the major and minor axes are not identical. We must take this in account by introducing two variables α and β (such that $|\alpha|^2 + |\beta|^2 = 1$) which are used to vary the ellipticity of the transmitted light that is subsequently incident on the q -plate. Depending on the conversion efficiency of the q -plate, a portion of the light will remain unchanged and the other will acquire an l -value with opposite polarization due to the retardance of π radians. The ratio of Gaussian to Laguerre–Gaussian is determined by the retardation angle ξ . The second QWP was used to generate linearly polarized superimposed Gaussian and OAM beam. The third QWP could be used to produce the desired ellipticities. To determine the polarization state after each optics we will implement the Jones matrices convention for QWP(θ) and HWP(θ), where θ is the angle with respect to the horizontal axis^{68,69}. We can define the operation of the q -plate by means of a unitary operator M_Q ^{57,70}. The handedness of the helical light is determined by the incident circular polarization on the q -plate.

$$\begin{cases} M_Q |LHC\rangle = \cos\left(\frac{\xi}{2}\right) |LHC\rangle + i \sin\left(\frac{\xi}{2}\right) |RHC\rangle e^{i\phi} \\ M_Q |RHC\rangle = \cos\left(\frac{\xi}{2}\right) |RHC\rangle + i \sin\left(\frac{\xi}{2}\right) |LHC\rangle e^{-i\phi} \end{cases} \quad (22)$$

The portion of the light that acquires an l -value also gains a π phase shift between polarization components i.e., the q -plate acts like a HWP with respect to the incident polarization. The output unit vectors of the electromagnetic field can be determined via Jones matrix multiplication of the second and third QWP. Introducing the spatial components of the incident light we can express the electric field for both helicities as

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix}_{l\pm} = \frac{1}{\sqrt{2}} \left[\cos(\xi/2) \begin{pmatrix} \alpha \\ i\beta \end{pmatrix} e^{-i\frac{\pi}{2}} u_g(x, y, z) + \sin(\xi/2) \begin{pmatrix} \beta \\ -i\alpha \end{pmatrix} u_0^\pm(x, y, z) \right] \quad (23)$$

The magnetic field can be obtained via the relation $\mathbf{B}(x, y, z) = \hat{z} \times \mathbf{E}(x, y, z)$.

$$\begin{pmatrix} B_x \\ B_y \end{pmatrix}_{l\pm} = \frac{1}{\sqrt{2}} \left[\cos(\xi/2) \begin{pmatrix} \beta \\ i\alpha \end{pmatrix} e^{-i\pi} u_g(x, y, z) + \sin(\xi/2) \begin{pmatrix} i\alpha \\ \beta \end{pmatrix} u_0^\pm(x, y, z) \right] \quad (24)$$

These expressions were used for the simulations shown in Fig. 5a, c. The $u_0^\pm(x, y, z)$ and $u_g(x, y, z)$ are the Laguerre–Gaussian and Gaussian beam expressions given in Supplementary Section 7²⁵. The $\pm$ sign represents the handedness of the helical light.

Data availability

The minimum dataset necessary to interpret the results can be obtained from the corresponding authors upon request. The raw and processed data are not deposited in a repository because transmission measurements generate multiple sets of columns and without proper context the data could be hard to interpret.

Code availability

The simulation data were obtained by evaluating the equations using standard technical software. The code is available upon request to the corresponding authors.

References

- Weber, W. H. & Merlin, R. *Raman Scattering in Materials Science* (Springer, 2000).
- Zhao, Y. F. et al. Raman spectra of bulk and few-layer GeSe from first-principles calculations. *Front. Mater.* **8**, 736057 (2021).
- You, Y., Reis, D. & Ghimire, S. Anisotropic high-harmonic generation in bulk crystals. *Nat. Phys.* **13**, 345–349 (2017).
- Heinrich, T. et al. Chiral high-harmonic generation and spectroscopy on solid surfaces using polarization-tailored strong fields. *Nat. Commun.* **12**, 3723 (2021).
- Kuroda, R., Novoa, J. J. (Ed.), Braga, D. (Ed.), & Addadi L. (Ed.) Chirality in crystals. *Engineering of Crystalline Materials Properties*. 251 (Springer, 2008).
- Valentín-Pérez, Á., Rosa, P., Hillard, E. A. & Giorgi, M. Chirality determination in crystals. *Chirality* **34**, 163–181 (2021).
- Dong, Z. & Ma, Y. Atomic-level handedness determination of chiral crystals using aberration-corrected scanning transmission electron microscopy. *Nat. Commun.* **11**, 1588 (2020).
- Mavracic, J. et al. Similarity between amorphous and crystalline phases: the case of TiO₂. *J. Phys. Chem. Lett.* **9**, 2985–2990 (2018).
- Lan, S. et al. A medium-range structure motif linking amorphous and crystalline states. *Nat. Mater.* **20**, 1347–1352 (2021).
- Hufnagel, T. Finding order in disorder. *Nat. Mater.* **3**, 666–667 (2004).
- Hirata, A. et al. Direct observation of local atomic order in a metallic glass. *Nat. Mater.* **10**, 28–33 (2011).
- Hirata, A. & Chen, M. Angstrom-beam electron diffraction of amorphous materials. *J. Non-Cryst. Solids* **383**, 52–58 (2014).
- Singh, J. & Shimakawa, K. *Advances in Amorphous Semiconductors*, 1 edn. (CRC Press, 2003).
- Elliott, S. R. Medium-range structural order in covalent amorphous solids. *Nature* **354**, 445–452 (1991).
- Price, D. L. Intermediate-range order in glasses. *Curr. Opin. Solid State Mat. Sci.* **1**, 572–577 (1996).
- Salmon, P. et al. Topological versus chemical ordering in network glasses at intermediate and extended length scales. *Nature* **435**, 75–78 (2005).
- Allen, L. et al. Orbital angular momentum of light and the transformation of Laguerre-Gaussian laser modes. *Phys. Rev. A* **45**, 8185 (1992).
- Andrews, D. L., & Babiker, M. *The Angular Momentum of Light* (Cambridge University Press, 2013).
- Padgett, M., Courtial, J. & Allen, L. Light's orbital angular momentum. *Physics Today* **57**, 35–40 (2004).
- Andrews, D. L., Davila Romero, L. C. & Babiker, M. On optical vortex interactions with chiral matter. *Opt. Comm.* **237**, 133–139 (2004).
- Marrucci, L. et al. Optical Spin-to-orbital angular momentum conversion in inhomogeneous anisotropic media. *Phys. Rev. Lett.* **96**, 163905 (2006).
- Brullot, W. et al. Resolving enantiomers using the optical angular momentum of twisted light. *Sci. Adv.* **2**, 150134 (2016).
- Ni, J. et al. Giant helical dichroism of single chiral nanostructures with photonic orbital angular momentum. *ACS Nano* **15**, 2893–2900 (2021).
- Rouxel, J. R. et al. Hard X-ray helical dichroism of disordered molecular media. *Nat. Photon.* **16**, 570–574 (2022).
- Bégin, J. L. et al. Nonlinear helical dichroism in chiral and achiral molecules. *Nat. Photon.* **17**, 82–88 (2023).
- Forbes, K. A. & Andrews, D. L. Spin-orbit interactions and chiroptical effects engaging orbital angular momentum of twisted light in chiral and achiral media. *Phys. Rev. A* **99**, 023837 (2019).
- Forbes, K. A. & Andrews, D. L. Optical orbital angular momentum: twisted light and chirality. *Opt. Lett.* **43**, 435–438 (2018).
- Hugo, L. et al. Arbitrary optical wavefront shaping via spin-to-orbit coupling. *J. Opt.* **18**, 124002 (2016).
- Gertsch, M. et al. Orientation-dependent multiphoton ionization in wide band gap crystals. *Phys. Rev. Lett.* **101**, 243001 (2008).
- Jain, A., Bégin, J. L. & Bhardwaj, R. Helical dichroism in enantiomeric solutions. *J. Chem. Phys.* **7**, 014504 (2023).
- Keldysh, L. V. Ionization in the field of a strong electromagnetic wave. *Sov. Phys. JETP* **20**, 5 (1965).
- Klaiber, M. & Briggs, J. S. Crossover from tunneling to multiphoton ionization of atoms. *Phys. Rev. A* **94**, 053405 (2016).
- Schaffer, C. B. et al. Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses. *Meas. Sci. Technol.* **12**, 1784 (2002).
- Wu, A. Q. et al. Femtosecond laser absorption in fused silica: numerical and experimental investigation. *Phys. Rev. B* **72**, 085128 (2005).
- Sudrie, L. et al. Femtosecond laser-induced damage and filamentary propagation in fused silica. *Phys. Rev. Lett.* **89**, 186601 (2002).
- Vorobiev, A. K. ESR study of photoselection and photo-orientation. *J. Phys. Chem.* **98**, 11835 (1994).
- Lee, C. C. & Fan, H. Y. Two-photon absorption with exciton effect for degenerate valence bands. *Phys. Rev. B* **9**, 3502 (1974).
- Gnani, E. et al. Band-structure calculations of SiO₂ by means of Hartree-Fock and density-functional techniques. *IEEE Trans.* **47**, 10 (2000).
- Gnani, E., Reggiani, S. & Rudan, M. Density of states and group velocity of electrons in SiO₂ calculated from a full band structure. *Phys. Rev. B* **66**, 195205 (2002).
- Alagna, L. et al. X-ray natural circular dichroism. *Phys. Rev. Lett.* **80**, 21 (1998).
- Peacock, D. R. & Stewart, B. Natural circular dichroism in X-ray spectroscopy. *J. Phys. Chem. B* **105**, 351–360 (2001).
- Naseri, M. et al. Electronic and optical properties of paratellurite TeO₂ under pressure: a first-principles calculation. *Optik* **139**, 9–15 (2017).
- Davis, K. et al. Band gap engineered zinc oxide nanostructures via a sol-gel synthesis of solvent driven shape-controlled crystal growth. *RSC Adv.* **9**, 14638 (2019).
- Chang, K. J. & Cohen, M. L. High-pressure behavior of MgO: structural and electronic properties. *Phys. Rev. B* **30**, 8 (1984).
- Güler, E. et al. A theoretical study for the band gap energies of the most common silica polymorphs. *Chi. J. Phys.* **65**, 472 (2020).
- Nuggent, W. et al. Beyond nature's chiral pool: enantioselective catalysis in industry. *Science* **259**, 479–483 (1993).
- Rouf, A. & Taneja, S. C. Synthesis of single-enantiomer bioactive molecules: a brief overview. *Chirality* **26**, 63–78 (2014).
- Torsi, L. et al. A sensitivity-enhanced field-effect chiral sensor. *Nat. Mater.* **7**, 412–417 (2008).
- Lee, Y. Y. et al. Plasmonic metamaterials for chiral sensing applications. *Nanoscale* **12**, 58 (2020).
- Aiello, C. D. et al. A chirality-based quantum leap. *ACS Nano* **16**, 4989 (2022).
- Shang, Z. et al. Chiral-molecules-based spintronic devices. *Small* **18**, 2203015 (2022).
- Gross, S. et al. Femtosecond laser induced structural changes in fluorozirconate glass. *Opt. Mater. Express* **3**, 574 (2013).
- Juodkazis, S. et al. Structural changes in femtosecond laser modified regions inside fused silica. *J. Opt.* **12**, 12400 (2010).
- Facchetti, A. π Conjugated polymers for organic electronics and photovoltaic cell applications. *Chem. Mater.* **23**, 733 (2011).

55. Wang, S. et al. Experimental evidence that short-range inter-molecular aggregation is sufficient for efficient charge transport in conjugated polymers. *Proc. Natl. Acad. Sci. USA* **112**, 10599–10604 (2015).
56. Longman, G. W. et al. Investigation of short range ordering in polymers by means of radial distribution functions derived from X-ray diffraction. *J. of Mat. Sci.* **11**, 1339–1346 (1976).
57. Rubano, A. et al. Q-plate technology: a progress review. *J. Opt. Soc. Am. B* **36**, 5 (2019).
58. Rahimian, M. G. et al. Spatially controlled nano-structuring of silicon with femtosecond vortex pulses. *Sci. Rep.* **10**, 12643 (2020).
59. Geissler, M. et al. Light propagation in field-ionizing media: extreme nonlinear optics. *Phys. Rev. Lett.* **83**, 15 (1999).
60. Jürgens, P. et al. Origin of strong-field-induced low-order harmonic generation in amorphous quartz. *Nat. Phys.* **16**, 1035–1039 (2020).
61. Serebryannikov, E. E. & Zheltikov, A. M. Strong-field photoionization as excited-state tunneling. *Phys. Rev. Lett.* **116**, 123901 (2016).
62. Brandi, H. S. & de Araujo, C. B. Multiphoton absorption coefficients in solids: a universal curve. *J. Phys. C Solid State Phys.* **16**, 5929 (1983).
63. Brandi, H. S. et al. High-intensity approximations applied to multiphoton ionization. *Phys. Rev. A* **24**, 2044 (1981).
64. Boyd, R. W. *Nonlinear Optics*, 3rd edn. (Academic Press, 2020).
65. Golding, B. et al. Intrinsic electric dipole moment of tunneling systems in silica glasses. *Phys. Rev. Lett.* **43**, 1817 (1979).
66. Burin, A. L. et al. Low-temperature breakdown of coherent tunneling in amorphous solids induced by the nuclear quadrupole interaction. *Phys. Rev. B* **73**, 014205 (2006).
67. Vaidyanathan, A. et al. Two-photon absorption in several direct-gap crystals. *Phys. Rev. B* **21**, 743 (1980).
68. Pedrotti, F. & Pedrotti, L. *Introduction to Optics*, 2nd edn. (Prentice-Hall International, Inc., 1993).
69. Saleh, B. E. A. & Teich, M. C. *Fundamentals of Photonics*, 3rd edn. (John Wiley & Sons, Inc, 2019).
70. Delaney, S. et al. Arithmetic with q-plates. *App. Opt.* **56**, 596–600 (2007).

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Author contributions

A.J., J.-L.B., and R.B. conceived, designed, and planned the experiments. A.J. and J.-L.B. conducted the experiments and analyzed the results. A.J., J.-L.B., T.B., and R.B. worked on the theory and conducted numerical simulations. P.C., E.K., and R.B. supervised the project. A.J., J.-L.B., T.B., and R.B. prepared the first draft, and all authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Intrinsic dichroism in amorphous and crystalline solids with helical light

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Contents

1	Experimental setup	1
2	Crystal symmetry from transmission measurement	2
3	Tunability and scalability of HD(Type I) in crystals	4
4	Fluence Calculation	4
5	Differential absorption with circularly polarized Gaussian beam	5
6	Noise check: Transmission measurements in air in the absence of sample	5
7	Asymmetric Laguerre-Gaussian beams	6
8	Multiphoton assisted tunneling	7
9	Total MPAT transition rate for linear polarization	9
10	Supplementary References	10

1 Experimental setup

Transmission measurement were performed using a Ti: Sapphire laser amplifier system (45 fs, 800 nm pulses, pulse energy of 2.5 mJ). Figure S1 shows the schematic of our experimental setup. For each successive laser pulse, the energy was varied using a combination of half-wave plate (HWP) and polarizer. Light beams carrying orbital and/or spin angular momentum were generated and controlled by OAM/SAM unit consisting of a combination of quarter-wave plates (QWP), linear polarizer (LP) and a birefringent liquid crystal based phase plate called q -plate^{1,2}. When an incident Gaussian beam propagates through the q -plate with a topological charge q , it acquires an OAM defined by $l = \pm 2q$ with a phase singularity (optical vortex). The singularity/null intensity region in the OAM beam was displaced by translating the q -plate, mounted on a x-,y-stages. Moving the q -plate with a step size of $250 \pm 10 \mu\text{m}$ translates to a displacement of the singularity by $300 \pm 20 \text{nm}$ at the focus.

For every laser shot, the transmitted light signal on the photodiode (PD2) was normalized with the incoming light signal on PD1, reflected off a glass plate positioned in the beam path. An aspheric objective lens (NA=0.3) was used to focus the femtosecond pulses to a spot size $2 \pm 0.2 \mu\text{m}$ into solid samples mounted on a three-axis translation stage. A second aspheric objective with the same NA collected and collimated the transmitted light onto a photodiode (PD2), positioned immediately after the objective. For each experiment, laser was focussed in the middle of solid sample with typical dimensions $10 \times 10 \times 1 \text{ mm}$. This was achieved by accurately finding the surface of the sample using back-reflected light that was imaged by a CCD camera. The signals generated by PD1 and PD2 were stretched by an electronic pulse stretcher, discretized and recorded by a data acquisition card. The incident pulse energies were measured before the objective. During the measurement, for every laser shot, the sample was translated by $5 \mu\text{m}$ to irradiate fresh sample. A single-shot auto-correlator (not shown) continuously monitored the pulse duration. The pulse duration at the interaction region was about 100fs.

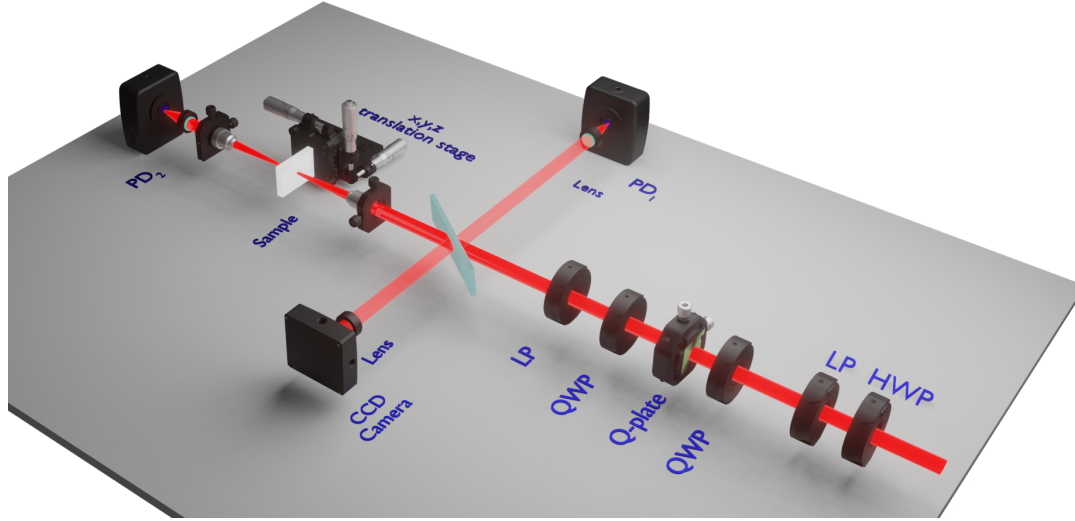


FIG. S 1. Schematic of the experimental setup. The power control consists of a combination of linear polarizer (LP) and half-wave plate (HWP). The OAM and SAM control consists of a combination of quarter-wave plates (QWPs), a birefringent liquid-crystal phase plate (q-plate) and LP (a third QWP can be used to generate elliptically polarized OAM light). Photodiode PD1 (PD2) monitors the incident (transmitted) light. The CCD camera was used to find the surface of the sample. A (x,y,z) translation stage was used to displace the sample. A combination of two aspheric lens (NA=0.3) was used to focus and collimate the incident and transmitted light.

2 Crystal symmetry from transmission measurement

Orientation dependent nonlinear absorption of helical light pulses in ZnO (11-20) and left-handed quartz (z-cut) crystal are shown in Fig. S2 for a specific displacements of the singularity. ZnO (11-20) has a cubic unit cell with 4-fold rotational symmetry and therefore shows a modulation with a periodicity of $\pi/2$. Quartz has a cubic unit cell with 6-fold rotational symmetry and therefore shows a modulation with a periodicity of $\pi/3$. Both crystals exhibit differential absorption between left- and right-handed asymmetrical helical light, defined as HD(Type I). The orientation dependence of transmission is independent of the position of the singularity. However, the magnitude of HD(Type I) signal remains invariant with crystal orientation. Similar results obtained for MgO (100) were presented in the main text.

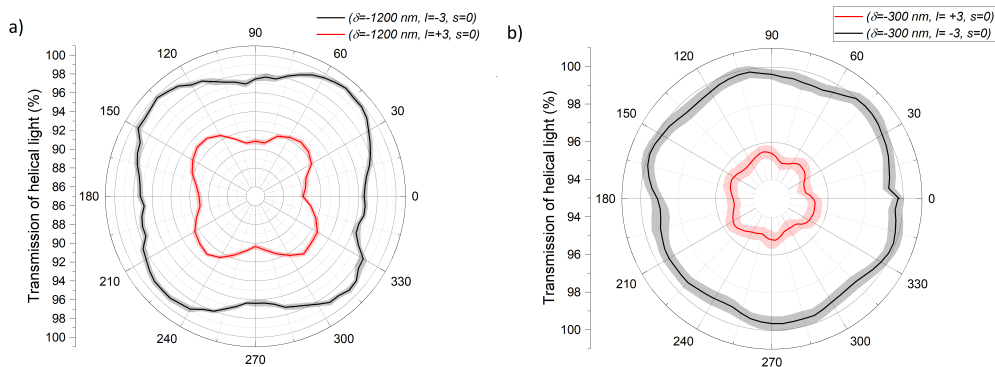


FIG. S 2. Orientational dependent transmission of helical light in crystal. For linearly polarized ($\varepsilon = 0.05$) asymmetrical OAM beam ($l = \pm 3$) in (a) ZnO (11-20) for a displaced singularity ($\delta = -1200$ nm) and (b) Left-handed α -quartz (z-cut) for a displaced singularity ($\delta = -300$ nm). The error bands represent the standard error at every position of the crystal for $n=20$.

The crystal structure can also be reproduced using linearly polarized Gaussian light pulses as shown in Fig. S3a for MgO (100) crystal, similar to the case of helical light (fig 1b-d). Therefore, the orientation dependent transmission is not limited to helical light. Fig. S3b shows the energy dependent transmission for a linearly polarized symmetric OAM beam ($l = +1$, $\delta = 0$) plotted as a function of crystal orientation. As the pulse energy is increased, the transmission of helical light decreased due to the increase in nonlinear absorption. For all three pulse energies above the onset for nonlinear absorption, the 4-fold symmetry is present.

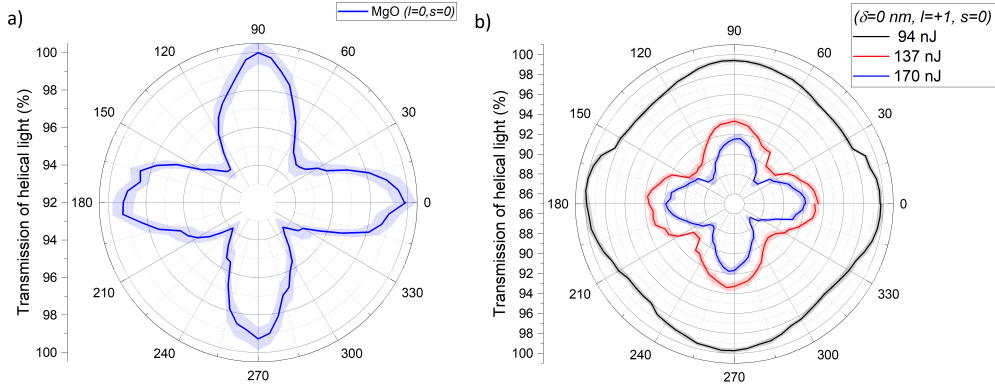


FIG. S 3. Angle dependent transmission of helical light in MgO (100). (a) For linearly polarized ($\varepsilon = 0.05$) Gaussian beam. (b) Energy dependent transmission as a function of crystal orientation for linearly polarized ($\varepsilon = 0.05$) symmetrical OAM beam ($l = \pm 3$). The error bands represent the standard error at every position of the crystal for $n=20$.

Fourier analysis of the orientation dependent transmission identifies the different modulation periodicities associated with the crystal symmetry. Figure S4 shows the Fourier power spectrum for the orientation dependent transmission curves of MgO (black) and quartz (blue). For MgO, single peak at 90° corresponds to a 4-fold symmetry. The quartz exhibits a dominant peak at 60 degrees and a smaller one at 120 degrees demonstrating the 6-fold symmetry. Stronger modulation depth in MgO than in quartz could be due to different crystal nonlinearities.

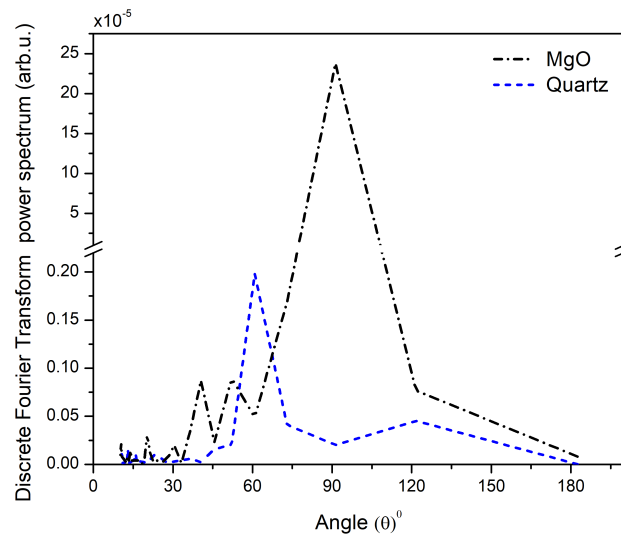


FIG. S 4. Discrete Fourier transform of the orientational dependent transmission in crystals. The black (blue) curve demonstrate the $\pi/2$ ($\pi/3$) periodicity in MgO (left-handed, z-cut, α -quartz).

3 Tunability and scalability of HD(Type I) in crystals

Figure S5 shows experimental results on control and tunability of HD(Type I) in MgO, obtained by (i) superimposing Gaussian and OAM beams, and (ii) varying the l -value. Similar to a-solids (Figure 5), the electric dipole-quadrupole coupling term is non-zero for asymmetric LG beams resulting in HD(Type I). Since this coupling term contains the gradient of the electric field it gives rise to l -dependence, both on its sign and value.

In c-solids, the MPAT process can still play a role, although ordered environment, both short and long range always ensures non-zero HD(Type I) signal upon isotropic averaging. In this case the intermediate states could be due to degenerate exciton states, defects, impurities, and boundary effects^{3,4}.

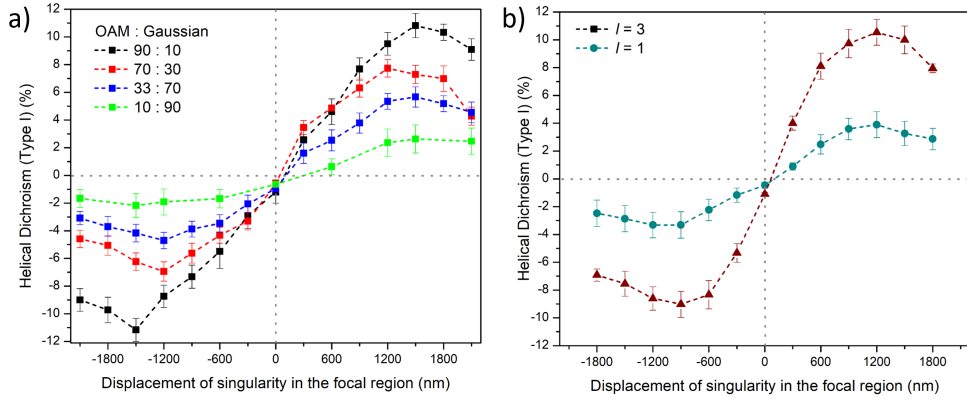


FIG. S 5. Tunability of Helical dichroism. Measured HD(Type I) in MgO as a function of the displacement of singularity for **a)** variable ratios of superposition of linearly polarized ($\epsilon = 0.05$) OAM ($l = \pm 3$) and Gaussian beams, and **b)** linearly polarized ($\epsilon = 0.05$) helical light with $l = \pm 1, \pm 3$. The error bars in **a)** and **b)** represent the standard error, of multiple measurements ($n=3$), calculated for an average peak fluence range used to obtain HD.

4 Fluence Calculation

In Laguerre-Gaussian beams with increasing l -value, the size of the null intensity region at the center increases. Consequently, for the same spot size higher pulse energies are required to reach the threshold for the onset of nonlinear absorption⁵. However, the peak fluence and intensity remains the same for all l -values as can be seen from the inset of Fig. 1a for $l=3$ and Fig.S6 for $l=0$.

From the threshold energies and peak power, the l -dependent peak fluence and the intensity was calculated based on the following equations⁶:

$$F_l \left[\frac{J}{cm^2} \right] = \frac{2^{(|l|+1)} r^{2|l|} e^{\frac{-2r^2}{w(z)^2}}}{|l|! \pi w(z)^{2(|l|+1)}} E_l [J] \quad I \left[\frac{W}{cm^2} \right] = \frac{2^{(|l|+1)} r^{2|l|} e^{\frac{-2r^2}{w(z)^2}}}{|l|! \pi w(z)^{2(|l|+1)}} P_l [W] \quad (1)$$

where $l = 0; \pm 1; \pm 2; \pm 3 \dots$ is the orbital angular momentum value, r is the radial direction, $w(z)$ is the radius of a beam evaluated at z and E_l is the threshold pulse energy, and P_l is the peak power for different l -values.

The peak fluence was obtained by evaluating the radial parameter r at the maxima of the intensity profile, which occurs when $r_l^2 = w_0^2 |l|/2$. So, for a Gaussian beam ($l = 0$) $r = 0$, and at for OAM beam with $l = 1$ $r_1 = \pm \frac{w_0}{\sqrt{2}}$ and so on. Substituting the above values for radial parameter, we obtain

$$\text{For } l = 0 \text{ beam : } F_0(r_0) = 2 \frac{E_0}{\pi w_0^2} \quad (2)$$

$$\text{For } l = 1 \text{ beam : } F_1(r_1) = 2e^{-1} \frac{E_1}{\pi w_0^2} \quad (3)$$

The l -dependent peak intensity was used to obtain the Keldysh parameter (eq - main text) and the spatial displacement x_0 . Similarly, peak laser fluences or intensities were obtained for higher order OAM beams. In our experiments with different

l -values (Fig-1,4), HD was obtained by taking an average of differential absorption between left- and right- handed helical light over a peak fluence range after the onset of nonlinear absorption. This insured that response regime we investigated remained the same.

5 Differential absorption with circularly polarized Gaussian beam

Circular dichroism (CD), defined as differential absorption of circularly polarized (CP) Gaussian beam, is not expected to be observed in amorphous solids. On the other hand, chiral solids such as quartz exhibit CD. However, solid-state CD signal is often overshadowed by signals arising from macroscopic anisotropies and linear birefringence⁷, as can be seen in the figure below.

To discern the role of polarization and phase of light, we performed transmission measurements with CP Gaussian beams ($l=0$) in crystalline and amorphous solids. Figure S6 shows normalized transmission of a left- and right-CP Gaussian beam propagating through left-handed quartz and fused silica. In the absence of phase, the two curves overlap in the linear regime exhibiting no differential absorption. In the nonlinear regime, any signal fluctuations are within noise for both types of solids. Similar results were obtained in the case of MgO and right- handed quartz (not shown).

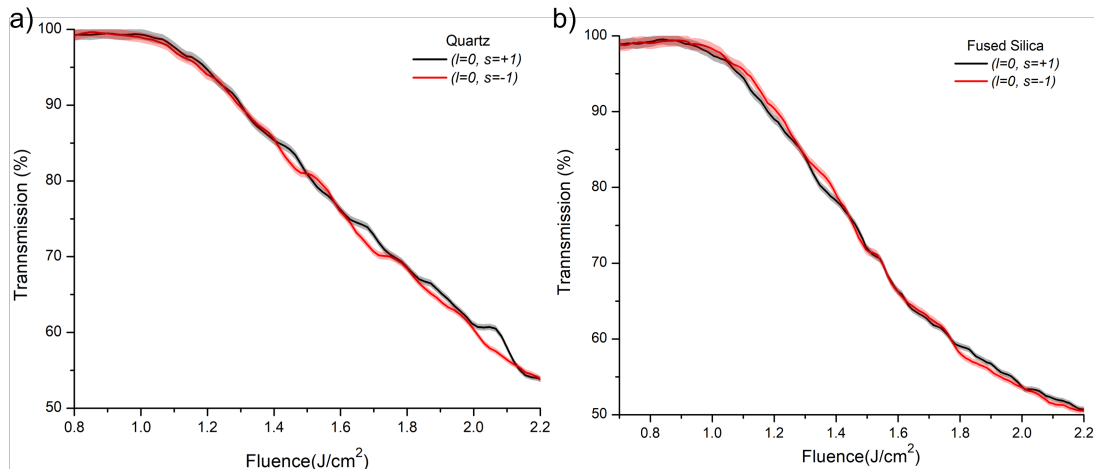


Fig S 6. Normalized transmission of Gaussian beams as a function of peak fluence in crystalline and amorphous solids. Transmission curves for left-circularly polarized ($s = +1$) and right-circularly polarized ($s = -1$) light in **a)** left-handed α -quartz and **b)** fused silica. The error bands represent the standard error for $n=3$ independent measurements.

6 Noise check: Transmission measurements in air in the absence of sample

In order to check the background noise in our experimental setup, we performed transmission measurements conducted in air (absence of a sample). Such measurements enable us to ensure that the photodiodes detect identical signals when changing the helicity of the incoming linearly polarized light from $+l$ to $-l$. Fig. S7 a) shows transmission curves (ratio of PD_2/PD_1) of left (black) and right (red) handed asymmetrical LG beams through air. The red and black curves overlaps (within 0.5%) over the entire fluence range. In addition, Fig. S7 b) shows the difference between the PD1 (PD2) signal for linearly polarized $+l$ and $-l$. Signals are centered about zero with a fluctuation of $\pm 0.05V$ and curves almost overlap over the entire energy range. Both these results demonstrates that there is no arbitrary signal/noise introduced by the experimental setup to the observed differential absorption in crystalline and amorphous solids. Transmission measurements in air were performed before every experimental run and for every position of the displaced singularity.

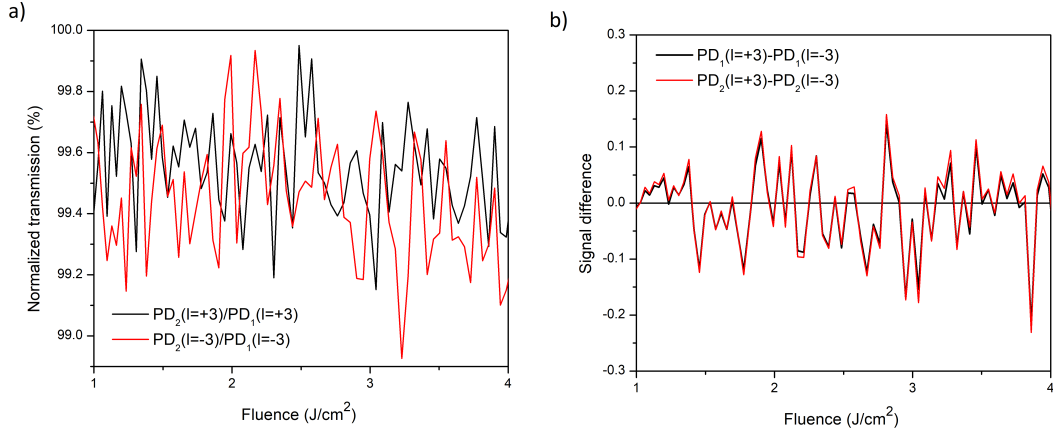


FIG. S 7. Transmission of linearly polarized ($\varepsilon = 0.05$) helical light in air for symmetrical OAM beam. a) Ratio of PD2 and PD1 signals for $l = +3$ (black) and $l = -3$ (red). **b)** The difference in photodiode signals for the two helicities, PD1 in black and PD2 in red. PD1 (PD2) monitors the incident (transmitted) light.

7 Asymmetric Laguerre-Gaussian beams

Asymmetric Laguerre-Gaussian beams denoted by an asymmetry parameter, δ , was used in our theoretical analysis. For arbitrary polarization in the paraxial regime, the field components can be written as⁵

$$u_o^\pm(x, y, z) = E_0 \exp[ikz] \left(\frac{\sqrt{2}((x \mp i\eta\delta) \pm i(y \mp i\zeta\delta))}{w_0} \right)^{|l|} \exp\left(-\frac{(x^2 + y^2)}{w_0^2}\right) L_{p-j}^{|l+j|} \left(\frac{2\rho^2}{w_0^2} \right) \quad (4)$$

$$\mathbf{E}^\pm(x, y, z) = \begin{cases} \alpha u_0^\pm(x, y, z) \\ \beta u_0^\pm(x, y, z) \\ if \left[(\alpha \pm i\beta) \frac{|l|w_0((x \mp i\eta\delta) \mp i(y \mp i\zeta\delta))}{(x \mp i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_0^\pm(x, y, z) - \frac{2}{w_0} (\alpha(x) + \beta(y)) u_0^\pm(x, y, z) \right] \end{cases} \quad (5)$$

$$\mathbf{B}^\pm(x, y, z) = \begin{cases} -\beta \frac{k}{\omega} u_0^\pm(x, y, z) \\ \alpha \frac{k}{\omega} u_0^\pm(x, y, z) \\ if \frac{k}{\omega} \left[(\alpha \pm i\beta) \frac{|l|w_0((y \mp i\zeta\delta) \pm i(x \mp i\eta\delta))}{(x \mp i\eta\delta)^2 + (y \mp i\zeta\delta)^2} u_0^\pm(x, y, z) - \frac{2}{w_0} (\alpha(y) - \beta(x)) u_0^\pm(x, y, z) \right] \end{cases} \quad (6)$$

where $f = \lambda/2\pi w_0$, ω is the laser frequency and $\rho = \sqrt{x^2 + y^2}$. The $\pm$ represents the rotational direction of l with no radial node, $p = 0$. The polarization factors α and β are normalized such that $|\alpha|^2 + |\beta|^2 = 1$. Displacement of singularity in the x-y plane was achieved by varying η and ζ . For generalization, we substituted $\eta = 3/2$ and $\zeta = 1/8$, considering the movement of singularity to be perpendicular to the polarization following experimental conditions.

E_0 is the normalization factor obtained by integrating the intensity over all space ($-\infty$ to $+\infty$), for ($l = 1$) it is given as :

$$E_0 = \sqrt{\frac{2k^2 w_0^2}{\pi(\alpha^2 + \beta^2)(2w_0^2 + k^2 w_0^4 + 2(\zeta^2 + \eta^2)\delta^2(1 + k^2 w_0^2))}} \quad (7)$$

Intensity profile of asymmetrical Laguerre-Gaussian beam with varying singularity position (δ) is shown in Fig. S8. As a correction to the paraxial regime (due to its finite l dependence) the longitudinal component of the field (E_z) can be considered^{8,9}. The contribution of the longitudinal component becomes significant when light is focused tightly using a higher NA objective and is recently demonstrated in differentiating nanoparticle aggregates using helical light¹⁰.

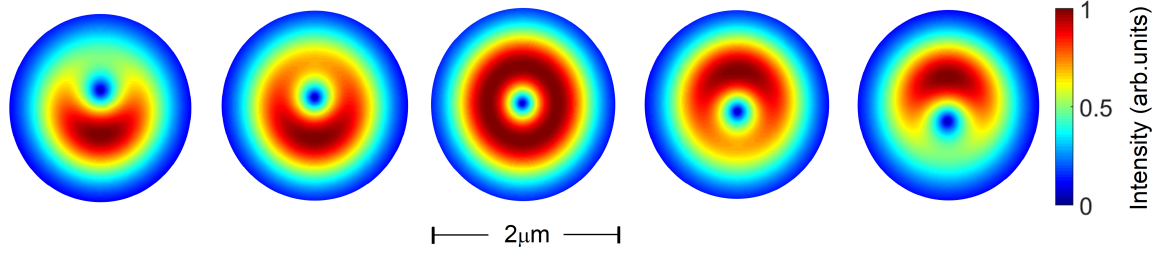


FIG. S 8. Asymmetrical Laguerre-Gaussian beam. Simulated intensity profiles of asymmetric OAM beams obtained by varying the δ parameter.

8 Multiphoton assisted tunneling

Absorption of electromagnetic field by any material results in electron transition from an unperturbed ground state to an excited state or continuum (conduction band in case of solids). The transition mechanism is primarily governed by the energy of the incident photon and energy difference between the ground and excited/continuum states. When photon energy is lower than the energy difference, absorption is dominated by nonlinear process either via multiphoton absorption when the incident field intensity is low or via tunneling when the field intensity is sufficiently large. The type of mechanism can be identified by Keldysh parameter, γ , for both solids and gases. When $\gamma \gtrsim 2$, transitions are dominated by multiphoton and when $\gamma < 1$ they are dominated by tunnelling^{11–13}. $1 < \gamma < 2$ is the intermediate regime in which combination of both multiphoton and tunneling contribute to electron transitions, known as Multiphoton Assisted Tunneling (MPAT).

In MPAT, electron transitions from the ground state (valence band in solids) to an intermediate state (band tail/defect states in solids) by absorption of a single or multiple photons followed by transition to the continuum (conduction band in solids) via tunneling. MPAT is therefore responsible for the smooth and continuous transition from the dominant multiphoton ionization to the pure tunneling regime characterized by the varying Keldysh parameter. The idea of MPAT is based on the fact that whenever an incident photon is absorbed it causes the wavefunction to extend to larger distances depending on the wavelength and intensity of the incident light. Ionization via tunneling can readily occur from such extended and weakly bound states¹¹.

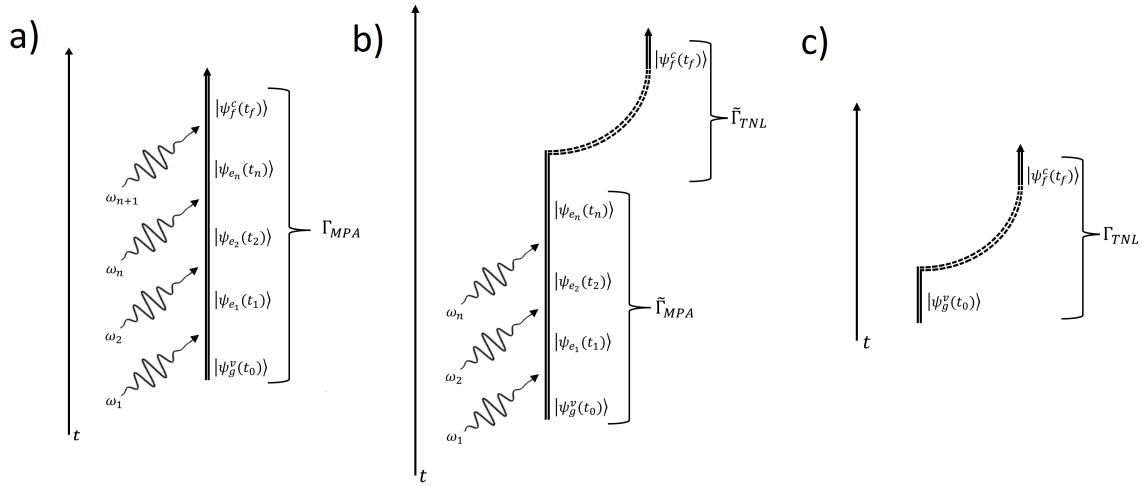


FIG. S 9. Feynman diagrams for a) multiphoton regime, it takes an absorption of $(n + 1)\hbar\omega$ to reach the conduction band. b) MPAT process, absorption of n -photon leading to an excited/tail state and subsequent tunneling to the conduction band. c) tunneling regime, the incident field is strong enough to force the electron to tunnel from the valence band (ψ_g^v) to the conduction band (ψ_f^c).

Ionization probability for MPAT process can be qualitatively understood by a unified approach where the total probability amplitude consists of a product of two separate amplitudes corresponding to single/multiphoton absorption and tunneling. It can also be visually understood using Feynman diagram shown in Fig. S9 for all three different regimes. In general, transition

amplitude is defined as a projection of non-interacting state to a fully evolved state at large times^{14–16} given by

$$M_{fi} = \lim_{t \rightarrow \infty} \langle \psi_f(t) | \Psi_i(t) \rangle \quad (8)$$

where $\Psi_i(t)$ is the total wave function of time-evolved ground state, ψ_g , when the laser field is turned on. $\Psi_i(t)$ is a solution of the time-dependent Schrodinger equation, $[i\hbar \frac{\partial}{\partial t} - \hat{H}(t)]\Psi_i(t) = 0$. In the presence of the laser field, the full Hamiltonian is given by $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ where $\hat{H}_0$ is the field-free Hamiltonian and $\hat{V}(t)$ represents the interaction Hamiltonian of the system at time t . The final state $\psi_f(t)$, and initial state are orthogonal, $\langle \psi_f | \psi_g \rangle = 0$. The total wavefunction is obtained by solving the the time-dependent Schrodinger equation using the Green function $\hat{G}(t, t')$. The Green function is closely related to the time evolution operators, $\hat{G}(t, t') = -i\Theta(t - t')\hat{U}(t, t')$ ^{14, 16} where $\Theta(t - t')$ is the Heaviside step function and $\hat{U}(t, t')$ is a unitary time operator. Therefore, the total wavefunction can be expressed as

$$|\Psi_i(t)\rangle = \hat{U}_0(t, t_0)|\psi_g\rangle - \frac{i}{\hbar} \int_{t_0}^t \Theta(t - t')\hat{U}(t, t')V(t')|\psi_g(t')\rangle dt' \quad (9)$$

The first term corresponds to unperturbed evolution, $\hat{U}_0(t, t_0)$, of the ground state and the second term corresponds to evolution of the ground state when the laser is turned on at time t_0 .

The transition amplitude is not limited to just initial and final states. We can partition the total Hamiltonian to introduce intermediate excited states, which can be obtained by expanding the time propagator $\hat{U}(t, t')$ in terms of the Dyson series^{14–17}. In the Dyson expansion, we consider up to the second order term which corresponds to first order MPAT process (a single photon absorption to the intermediate state and subsequent tunnelling from this intermediate state to the continuum/conduction band). By substituting the expanded time propagator into the total wavefunction (eq. 9) and afterwards inserting this expanded wavefunction into the transition amplitude (eq. 8) we obtain

$$M_{fg} = \frac{1}{i\hbar} \int_{t_0}^t \langle \psi_f(\tau_1) | \hat{V}_i(\tau_1) | \psi_g(\tau_1) \rangle d\tau_1 + \frac{1}{\hbar^2} \int_{t_0}^t \int_{t_0}^{\tau} \langle \psi_f(\tau) | \hat{V}_f(\tau) \hat{U}(\tau, \tau_1) \hat{V}_i(\tau_1) | \psi_g(\tau_1) \rangle d\tau_1 d\tau \quad (10)$$

where $\hat{V}_i$ and $\hat{V}_f$ are the interaction Hamiltonian at time τ_1 and τ , respectively. Also, we used the property of the Heaviside step function $\lim_{t \rightarrow \infty} \Theta(t - \tau) = 1$. The first term in the above equation represents standard ground state tunneling and the second term represents the first order MPAT process. When experimental intensities are not sufficient for ground state tunneling (intermediate regime, $1 \lesssim \gamma \lesssim 2$) the second term becomes dominant. Therefore, for a multitude of intermediate states, the MPAT transition amplitude is given by

$$M_{fg} = \frac{1}{\hbar^2} \sum_m \int_{t_0}^t \int_{t_0}^{\tau} \langle \psi_f(\tau) | \hat{V}_f(\tau) | \psi_m(\tau) \rangle \langle \psi_m(\tau) | \hat{U}(\tau, \tau_1) \hat{V}_i(\tau_1) | \psi_g(\tau_1) \rangle d\tau_1 d\tau \quad (11)$$

where we introduced the projection of the intermediate state $\mathbb{1} = \sum_m |\psi_m(\tau)\rangle \langle \psi_m(\tau)|$ ¹⁸. Using the property $\langle \psi_m(\tau) | \hat{U}(\tau, \tau_1) = \langle \psi_m(\tau_1) |$, and explicitly writing the time component we obtain

$$M_{fg} = \frac{1}{\hbar^2} \sum_m \int_{t_0}^t \langle \psi_f(\tau) | \hat{V}_f(\tau) | \psi_m(\tau) \rangle \int_{t_0}^{\tau} \langle \psi_m | \hat{V}_i(\tau_1) | \psi_g \rangle e^{i\omega_{mg}\tau_1} d\tau_1 d\tau \quad (12)$$

The multiphoton component of the interaction Hamiltonian, $\hat{V}_i$, can be written in a non-dipole form containing E1, M1 and E2 terms. For single photon absorption, we substitute $\hat{V}_i(t') = \hat{V}_i e^{-i\omega t'}$ in the above equation (where ω is the laser frequency) to get

$$M_{fg} = \underbrace{\sum_m \frac{\langle \psi_m | \hat{V}_i | \psi_g \rangle}{\hbar(\omega_{mg} - \omega)}}_{M_{SPA}} \underbrace{\frac{i}{\hbar} \int_{t_0}^t d\tau \langle \psi_f(\tau) | \hat{V}_f(\tau) | \psi_m(\tau) \rangle e^{i(\omega_{mv} - \omega)\tau}}_{M_{TNL}} \quad (13)$$

The transition amplitude M_{fg} is a product of time-independent transition amplitude, M_{SPA} , corresponding to a single photon absorption to an intermediate state and time-dependent amplitude, M_{TNL} , corresponding to tunneling from intermediate state to continuum/conduction band. $\hat{V}_i$ ($\hat{V}_f$) is the multiphoton (tunneling) interaction Hamiltonian.

For the n^{th} order MPAT process, the transition amplitude consists of a product of the n -photon absorption and subsequent tunneling.

$$M_{fg} = \left(\frac{1}{i\hbar} \right)^2 \sum_m \sum_l \int_{t_0}^t d\tau \langle \psi_f(\tau) | \hat{V}_f(\tau) | \psi_m(\tau) \rangle \int_{t_0}^{\tau} dt' \langle \psi_m | \hat{V}(t') | \psi_l \rangle c_l^{(n-1)}(t') e^{i\omega_{ml}t'} \quad (14)$$

where $c_l^{(n-1)}(\tau)$ is the probability amplitude of the $(n-1)^{\text{th}}$ order perturbation (multiphoton probability amplitude)¹⁹. The n^{th} order probability amplitude can be expressed as

$$c_m^{(n)}(\tau) = \left(\frac{1}{i\hbar} \right) \sum_l \int_{t_0}^{\tau} dt' \langle \psi_m | \hat{V}(t') | \psi_l \rangle c_l^{(n-1)}(t') e^{i\omega_{ml}t'} \quad (15)$$

Multiphoton transitions in MPAT will result in multitude of excited state cross-correlation terms and coupling terms arising from multipole expansion due to the tensor nature of the material response. However, the material cross terms (such as electric–magnetic dipole and electric dipole–quadrupole coupling) will have similar qualitative behaviour as that of a single photon case. Therefore, to keep the equations tractable, we consider the MPAT process using single photon absorption in the manuscript.

Equations 12 can also be obtained by writing the time evolved initial state $\psi_g(\tau)$ as a linear combination of eigenstates (bound-state) of the unperturbed Hamiltonian^{19,20}, as

$$|\psi_g^{(n)}(\mathbf{r}, \tau)\rangle = \sum_m c_m^{(n)}(\tau) e^{-i\frac{E_m}{\hbar}\tau} |\psi_m(\mathbf{r})\rangle = \sum_m c_m^{(n)}(\tau) |\psi_m(\mathbf{r}, \tau)\rangle \quad (16)$$

where E_m is the energy of the m^{th} eigenstate, $\psi_m(\mathbf{r})$, where $\omega_{ml} = (E_m - E_l)/\hbar$

9 Total MPAT transition rate for linear polarization

To obtain a numerical estimate of the total transition rate, for simplicity, we consider the incident field as linearly polarized. Therefore the probability amplitude from the main text (equation 11) becomes:

$$M_{cv} = \frac{iA_0 e}{m\hbar(2\pi)^{3/2}} \frac{1}{\gamma_0} \sum_m p_{mv}^{SPA} \frac{p_{cm}}{k_x} \sum_{\eta=-\infty}^{\infty} \eta J_{\eta}(-\gamma_0 k_x) \left[\lim_{T \rightarrow \infty} \frac{2\hbar \sin((E_g + \varepsilon - n\hbar\omega) \frac{T}{2\hbar})}{(E_g + \varepsilon - n\hbar\omega)} \right] \quad (17)$$

where $\varepsilon = \frac{\hbar^2 k^2}{2m^*}$ is the total kinetic energy, $m^{*-1} = m_1^{-1} - m_0^{-1}$ is the total effective electron mass and $n\hbar\omega = \eta\hbar\omega + \hbar\omega$, and assuming the intermediate and conduction band states have similar $\mathbf{k}$ ($\mathbf{k}'' \approx \mathbf{k}' \approx \mathbf{k}$) the material response $p_{cm} = \int_{-\infty}^{\infty} u_{\mathbf{k}}^{c*}(\mathbf{r}) p_x u_{\mathbf{k}''}^m(\mathbf{r}) d^3r$

Following the main text, we further define the tunneling transition contribution as

$$p_{cm}^{TNL} = \frac{m_1}{m\hbar(2\pi)^{3/2}} \frac{p_{cm}}{k_x} \sum_{\eta=-\infty}^{\infty} \eta J_{\eta}(-\gamma_0 k_x) \quad (18)$$

Using the property $\lim_{T \rightarrow \infty} T^2 \frac{\sin^2(x)}{x^2} = 2\pi\hbar T \delta(\varepsilon + E_g - n\hbar\omega)$ where $x = (E_g + \varepsilon - n\hbar\omega) \frac{T}{2\hbar}$ ¹⁹, the transition rate from valence to the conduction band, defined as $W_{cv} = \frac{d}{dt} |M_{cv}|^2$, can be expressed as

$$W_{cv}(\mathbf{k}) = 2\pi\hbar\omega^2 \sum_m |p_{cm}^{TNL}|^2 |p_{mv}^{SPA}|^2 \delta(\varepsilon + E_g - n\hbar\omega) \quad (19)$$

The total transition rate (per unit of volume) can be obtained by integrating over crystal momentum associated with the discrete transition:

$$W = \int \frac{d^3k}{(2\pi)^3} W_{cv}(\mathbf{k})$$

Using the properties of Bessel's functions, the weak-field limit for the non-perturbative discrete transition rate is given by^{21,22}

$$W = \frac{1}{(2\pi)^4 \hbar} \sum_m \left(\frac{m_1 \omega p_{cm}}{m(\eta-1)!} \right)^2 |p_{mv}^{SPA}|^2 \left(\frac{eA_0}{2m_1 \omega} \right)^{2\eta} \left(\frac{2m^*}{\hbar^2} \right)^{(2\eta+1)/2} \left(\frac{(n\hbar\omega - E_g)}{(2\eta-1)} \right)^{(2\eta-1)/2} \quad (20)$$

where

$$|p_{mv}^{SPA}|^2 = \frac{1}{\hbar^2 (\omega_{mv} - \omega)^2} \left[|\mu_i^{mv}|^2 |E_i^\pm|^2 + |m_i^{mv}|^2 |B_i^\pm|^2 + 2\langle \mu_i^{mv} m_i^{vm} \rangle_P \text{Im} [E_i^{\pm*} B_i^\pm] + \frac{2}{3} \langle \mu_i^{mv} \theta_{ij}^{vm} \rangle_P \text{Re} [\nabla_i E_j^\pm E_i^{\pm*}] \right] \quad (21)$$

Difference in the interband transition rates between left- and right-handed helical light with beam asymmetry parameter δ can be expressed as:

$$\Delta W = W_\delta^+ - W_\delta^- = \frac{1}{\hbar^2 (\omega_{mv} - \omega)^2} \tilde{W} \left[\Omega \left(\frac{2}{3} \mu_i^{mv} \theta_{ij}^{vm} \right) \left(\text{Re} [\nabla_i E_j^+ E_i^{+*}] - \text{Re} [\nabla_i E_j^- E_i^{-*}] \right) \right] = D (\Upsilon^+ - \Upsilon^-) \quad (22)$$

HD(Type I) can now be defined in terms of energy absorbed Γ normalized with respect to incident energy, $\mathcal{E}_{inc}$ as:

$$\Delta \Gamma = \underbrace{\Gamma^+ - \Gamma^-}_{\text{HD (Type I)}} = \frac{\hbar}{\mathcal{E}_{inc}} (W_\delta^+ - W_\delta^-) = \mathcal{D} (\Upsilon^+ - \Upsilon^-) \quad (23)$$

where $W = |p_{mv}^{SPA}|^2 \tilde{W}$ from eq-29, $\mathcal{D} = \frac{\hbar D}{\mathcal{E}_{inc}}$ and $\Upsilon^\pm = \text{Re} [\nabla_i E_j^\pm E_i^{\pm*}]$ represent the optical helicity term describing the handedness of helical light. Optical helicity can be expanded as²³, $\Upsilon^\pm = [(\nabla_\alpha E_\beta E_\alpha^* + E_\alpha (\nabla_\alpha E_\beta)^\dagger)] = \text{Re} [E_i^{\pm*} \nabla_i E_j^{\pm\dagger}]$. The above equation was plotted in Fig.5 as a function of displacement of singularity in the main text.

10 Supplementary References

1. Marrucci, L., Manzo, C., & Paparo, D., Optical Spin-to-Orbital Angular Momentum Conversion in Inhomogeneous Anisotropic Media. *Phys. Rev. Lett.*, **96**, 163905 (2006).
2. Hugo, L., et al. Arbitrary optical wavefront shaping via spin-to-orbit coupling. *J. Opt.* **18**, 124002 (2016).
3. Lee, C.C., & Fan, H.Y. Two-photon absorption with exciton effect for degenerate valence bands *Phys. Rev. B* **9**, 3502 (1974).
4. Gnani, E., et al. Band-structure calculations of SiO₂ by means of Hartree-Fock and Density-Functional Techniques *IEEE transactions on electron devices* **47**, no. 10 (2000)
5. Bégin, J.L., Jain, A., & Parks, A. et al. Nonlinear helical dichroism in chiral and achiral molecules. *Nat. Photon.* **17**, 82–88 (2023).
6. Hnatovsky, C., et al. Materials processing with a tightly focused femtosecond laser vortex pulse. *Opt. Lett.* **35** **20**, 3417 (2010).
7. Kuroda, R., Novoa, J.J., Chirality in crystals. Engineering of crystalline materials properties, *Springer*; New York. p. 251 (2008)
8. Cerjan, A., et al. Orbital angular momentum of Laguerre-Gaussian beams beyond the paraxial approximation. *J. Opt. Soc. Am. A* **28**, 2253-2260 (2011).
9. Forbes, K.A., et al. Relevance of longitudinal of paraxial optical vortices. *J. Opt.* **23**, 075401 (2021).
10. Brulot, W., et al. Resolving enantiomers using the optical angular momentum of twisted light. *Sci. Adv.* **2**, 150134 (2021).
11. Klaiber, M. & J.S. Briggs Crossover from tunneling to multiphoton ionization of atoms. *Phys. Rev. A* **94**, 053405 (2016)
12. Schaffer, C.B., et al. Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses *Meas. Sci. Technol.* **12**, 1784 (2002)
13. Wu, A.Q., et al. Femtosecond laser absorption in fused silica: Numerical and experimental investigation *Phys. Rev. B* **72**, 085128 (2005)
14. Long, Z.J. & Liu, W-K. Keldysh theory of strong-field ionization *Canadian journal of Physics* **88**, 4, (2010)

15. Becker, A. & Faisal F.H.M. Intense-field many-body S-matrix theory *J. Phys. B: At. Mol. Opt. Phys.* **38** (2005)
16. Reiss, H.R. Theoretical methods in quantum optics: S-matrix and Keldysh techniques for strong-field processes *Prog. Quant. Electr.* **16**, 1-71 (1992)
17. Becker, W. et al. Above-Threshold Ionization: From Classical Features to Quantum Effects. *Advances In Atomic, Molecular, and Optical Physics, Academic Press*, **48** (2002).
18. Sakurai, J., & Napolitano, J. *Modern Quantum Mechanics (2nd ed.)* Cambridge University Press (2017).
19. Boyd, R.W., *Nonlinear Optics (3rd ed.)* (Academic Press, 2020).
20. Serebryannikov, E.E., & Zheltikov, A.M., Strong-Field Photoionization as Excited-State Tunneling *Phys. Rev. Lett.* **116**, 123901, (2016)
21. Brandi, H.S. & de Araujo, C.B., Multiphoton absorption coefficients in solids: a universal curve. *J. Phys. C: Solid State Phys.* **16** 5929 (1983)
22. Brandi, H.S., Davidovich, L., & Zagury N., High-intensity approximations applied to multiphoton ionization. *Phys. Rev. A* **24**, 2044 (1981)
23. Bégin, J.L., Jain, A., & Parks, A. et al. Nonlinear helical dichroism in chiral and achiral molecules. *Nat. Photon.* **17**, 82–88 (2023).

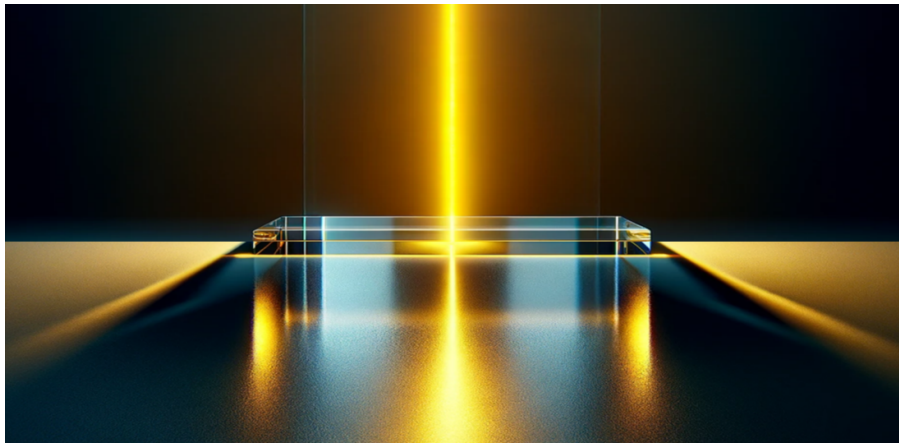


Figure 5.2: **Illustration** of a fused silica being irradiated by asymmetrical helical light.

GAS PHASE - HELICAL LIGHT INTERACTION

This chapter will focus on the experimental results obtained from a time-of-flight mass spectrometer where ions produced in the interaction region are detected. It will be divided into two gas phase techniques to study molecular and atomic systems in the strong-field regime. The first section will consist of the chiroptical technique, as detailed in our fourth article published in Scientific Reports. Here, we found that the chiral recollision yields of ions and fragments are influenced by the handedness of the elliptically polarized light. This variation in ionization results in an efficiency comparable to PECD and surpasses CD. A detailed section on recollision dynamics lays the foundations for the description of the mechanisms responsible for the chiroptical effects.

The second section focuses on orbital angular momentum-dependent strong-field ionization an article submitted to Nature Physics. In this approach the chiral optical probe is replaced from CPL to asymmetrical helical light, offering new degrees of control over the ionization of atoms and molecules. Our findings indicate that ionization of chiral and achiral molecules are strongly influenced by the handedness, l -value, and can be manipulated by shifting the phase singularity. This observed differential ionization is also shown for atomic systems such as argon. Lastly, by using asymmetrical helical light, the field strength and the field gradient around the optical vortex can be manipulated to increase the ponderomotive energy and force with l -value. A theory section on non-dipole tunnel ionization with asymmetrical LG beam is provided with additional supplementary

information.

6.1 RECOLLISION DYNAMICS

Recollision dynamics in strong field physics can be understood by expanding the transition amplitude in SFA to higher-order terms using the Dyson series (S-matrix method). Such higher interactions include non-sequential double ionization (NSDI), recollision-induced excitation and subsequent ionization (RESI), and Field-induced excitation and subsequent recollision ionization (FESI). These exhibit chiral dynamics when the polarization of the driving field is elliptical and when higher-order multipoles such as M1 are included.

There are three main steps in recollision dynamics: i) ionization of the atom or molecule, ii) the liberated electron propagates in the continuum and gains kinetic energy from the oscillating electromagnetic field. iii) recollision of the liberated electron with the parent ion. The collision can be elastic or inelastic. The elastic collision generates higher energetic photoelectrons or high-frequency photons. The inelastic recollision generates correlated double ionization of the parent ion.

In general, the transition amplitude is defined as a projection of a non-interacting state to a fully evolved state at large times [40, 65], given by equation 3.60 in chapter 3 section 3.2.5 and is often referred as Keldysh amplitude. The transition amplitude is not limited to initial and final states. We also partition the total Hamiltonian to introduce an intermediate excited state [77] to the conduction band. Thus, the transition amplitude for a certain excited state to the final state can be expressed using Dyson equations[76, 77].

The final-state partition of the total Hamiltonian is $H(t) = H_{0f}(t) + V_f(t)$ where $H_{0f}(t)$ is the final-state reference Hamiltonian and $V_f(t)$ is the final-state interaction. We can also introduce a third (intermediate) partition of the total Hamiltonian $H(t) = H_{0i}(t) + V_i(t)$ which corresponds to the intermediate reference Hamiltonian $H_{0i}(t)$, $V_i(t)$ is the intermediate interaction [65, 76, 77].

$$\hat{U}(t, \tau) = \hat{U}_f(t, \tau) + \int_{t_i}^{t_f} \hat{U}_f(t, \tau_1) \hat{V}_f(\tau_1) \hat{U}(\tau_1, \tau) d\tau_1 + \int_{t_i}^{t_f} \int_{t_i}^{t_f} \hat{U}_f(t, \tau_2) \hat{V}_f(\tau_2) \hat{U}(\tau_2, \tau_1) \hat{V}_i(\tau_1) \hat{U}(\tau_1, \tau) d\tau_1 d\tau_2 + \dots \quad (6.1)$$

Substituting the expanded time propagator into the full wavefunction.

$$\begin{aligned} |\Psi_i(t)\rangle &= \hat{U}_0(t, t_0) |\phi_g\rangle - i \int_{t_i}^{t_f} \Theta(t - \tau) \hat{U}_f(t, \tau) \hat{V}_0(\tau) |\psi_g(\tau)\rangle d\tau \\ &\quad - i \int_{t_i}^{t_f} \int_{t_i}^{t_f} \Theta(t - \tau_1) \hat{U}_f(t, \tau_1) \hat{V}_f(\tau_1) \hat{U}(\tau_1, \tau) \hat{V}_0(\tau) |\psi_g(\tau)\rangle d\tau d\tau_1 \\ &\quad - i \int_{t_i}^{t_f} \int_{t_i}^{t_f} \int_{t_i}^{t_f} \Theta(t - \tau_2) \hat{U}_f(t, \tau_2) \hat{V}_f(\tau_2) \hat{U}(\tau_2, \tau_1) \hat{V}_i(\tau_1) \hat{U}(\tau_1, \tau) \hat{V}_0(\tau) |\psi_g(\tau)\rangle d\tau d\tau_1 d\tau_2 + \dots \end{aligned} \quad (6.2)$$

The time propagator takes care of the time ordering, where t_f and t_i are replaced by physical times related to

their interaction time range. Projecting the non-interacting state onto the fully evolved state as $t \rightarrow \infty$ and using the Volkov wavefunction as continuum state $\langle \phi_f(t) | \hat{U}(t, t') \rightarrow \langle \phi_f^V(t') |$ gives us the higher order transitions amplitudes which describe the first, the second and third order interactions.

$$M_{fi} = \underbrace{\frac{1}{i\hbar} \int_{t_0}^t \langle \phi_f^V(\tau) | \hat{V}_0(\tau) | \psi_g(\tau) \rangle d\tau}_{\text{First order}} + \underbrace{\left(\frac{1}{i\hbar} \right)^2 \int_{t_0}^t \int_{t_0}^{\tau_1} \langle \phi_f^V(\tau_1) | \hat{V}_f(\tau_1) \hat{U}(\tau_1, \tau) \hat{V}_0(\tau) | \psi_g(\tau) \rangle d\tau d\tau_1}_{\text{Second order}} + \underbrace{\left(\frac{1}{i\hbar} \right)^3 \int_{t_0}^t \int_{t_0}^{\tau_2} \int_{t_0}^{\tau_1} \langle \phi_f^V(\tau_2) | \hat{V}_f(\tau_2) \hat{U}(\tau_2, \tau_1) \hat{V}_i(\tau_1) \hat{U}(\tau_1, \tau) \hat{V}_0(\tau) | \psi_g(\tau) \rangle d\tau d\tau_1 d\tau_2}_{\text{Third order}} \quad (6.3)$$

1. The first order interaction term typically represents the probability amplitude of the tunnel ionization of an electron from ground state to continuum where $\hat{V}_0(\tau) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$ is the external field multipole interaction Hamiltonian.
2. The second order can be used to describe the transition amplitude for NSDI [98, 99] depicted in figure 6.1 a). The first electron gets ionized by the external field multipole interaction Hamiltonian $\hat{V}_0(\tau) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$ and kicks off a second electron from the ion a half cycle later through an electron-electron interaction $\hat{V}_f(\tau_1) = V_{12} = \frac{1}{|\tau_1 - \tau_2|}$.
3. The third interaction probability amplitude describes the RESI [100, 101] depicted in figure 6.1 b). This occurs when the first electron is ionized by the external field multipole interaction Hamiltonian $\hat{V}_0(\tau) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$ and recollides with the ion with low kinetic energy resulting only in the excitation of the second electron via the electron-electron interaction $\hat{V}_i(\tau_1) = V_{12}$ and then gets ionized by the remnant external field $\hat{V}_f(\tau_2) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$ or the ion undergoes reconfiguration which leads to a second electron ionization.
4. The third interaction probability amplitude can also describe the FESI depicted in figure 6.1 c). When the first electron is ionized by the external field multipole interaction Hamiltonian $\hat{V}_0(\tau) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$ and propagates in the continuum, the parent ion interacts with the surrounding field and the second electron gets promoted to an excited state via the external electromagnetic field $\hat{V}_i(\tau_1) = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \dots$. The liberated electron recollides with the excited state electron in the parent ion with enough kinetic energy to ionize the second electron via electron-electron interaction $\hat{V}_f(\tau_2) = V_{12}$.

When dealing with the evolution of two-electron (for example NSDI, RESI, and FESI) the initial and final state can be assumed as a product state of the two interacting electrons [98–101], $|\psi_g^{(1)}(\tau), \psi_g^{(2)}(\tau)\rangle = |\psi_g^{(1)}(\tau)\rangle \otimes |\psi_g^{(2)}(\tau)\rangle$. Moreover, these transition amplitude can be elaborated in further detail by introducing projectors from the interaction onto the electron [98–101].

Using these recollision dynamics, we can explain the chiral discrimination of limonene observed in a gas phase chiroptical technique called Elliptical Dichroism by recollision-enhanced femtosecond laser mass spectrom-

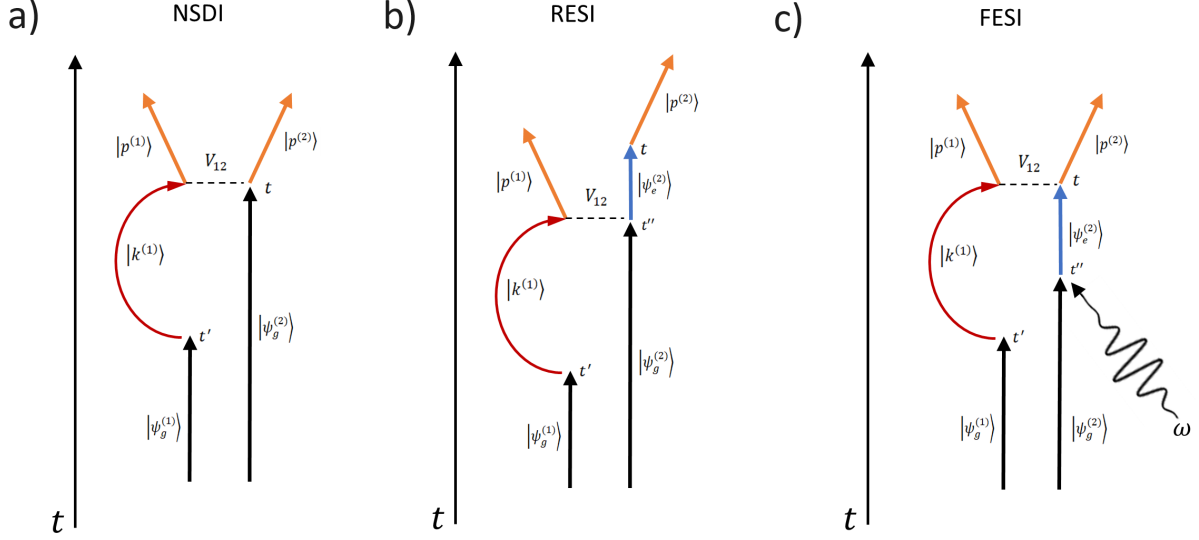


Figure 6.1: **Feynman diagrams** for **a)** non-sequential double ionization (NSDI), **b)** recollision induced excitation and subsequent ionization (RESI), and **c)** field induced excitation and subsequent recollision ionization (FESI).

etry (ED-REFLMS). There are three main mechanisms responsible for the chiral-sensitive double ionization of limonene:

1. Mechanism 1: Evolution of the parent ion during electron propagation in the continuum.
2. Mechanism 2: evolution of the parent ion after recollision
3. Mechanism 3: Evolution of the liberated electron in the laser field

Further details are shown after the article titled "Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry" to explain the observed mechanisms.

6.2 CHIRAL DISCRIMINATION BY RECOLLISION ENHANCED FEMTOSECOND LASER MASS SPECTROMETRY

Our paper introduces an extreme nonlinear chiroptical technique, ED-REFLMS, that combines strong field physics with mass spectrometry. We demonstrate an enhancement of one to two orders in the enantio-sensitivity of limonene due to the recollision dynamics of the ionized electron in an elliptically polarized laser field. The resultant chiral signal represented by Elliptical Dichroism (ED) is 5 times higher than the most efficient technique to date, the PECD [23–25]. The origin of enhanced enantio-sensitivity of ED-REFLMS can be attributed to two mechanisms that rely on the recollision dynamics in the combined electric and magnetic fields of the driving laser: (i) The excited ionic state dynamics mediated either by the laser field or by the recollision process, and (ii) non-dipole effects that alter the electron's trajectories.

Below we provide the main highlights of our work.

- (i) In an intense elliptically polarized laser field, the ionized electron propagating under the influence of electric and magnetic fields acquires a helical trajectory and recollides with the parent ion. The inelastic collision causes either double ionization or fragmentation of the chiral molecule. By monitoring the byproducts of the recollision process, we show that the resultant chiral signal in limonene is more than an order of magnitude higher than conventional circular dichroism mass spectrometry.
- (ii) We demonstrate the enantiomeric response of the doubly charged and the fragment ion yields to be asymmetric around linear polarization. The ion yield for the two enantiomers is maximum for an ellipticity of $\pm 15\%$ and is sufficient to efficiently discriminate them.
- (iii) We demonstrate the ED signal to oscillate between positive and negative values in the wavelength range of 1300-2400 nm where S-limonene produces more doubly charged ion yield relative to R-limonene and vice-versa. For some wavelengths, the positive and negative ED signals mirror each other. At certain other wavelengths, the chiral signal is non-existent.
- (iv) We discuss how recollision dynamics in a non-dipole regime leads to a sign-dependent response between the enantiomers. In the presence of a magnetic field, electron trajectories become helical making them behave like a chiral reagent. Electron helicity is defined by the handedness of light. This universal mechanism combined with excited ionic state dynamics mediated either by the laser field or by the recollision process results in (a) enhancement of the chiral signal in ED-REFLMS, and (b) wavelength dependence.
- (v) Over a range of wavelengths, the chiral signal from ED-REFLMS is comparable to or at least 5 times higher than PECD which relies on pure electric dipole transitions in a neutral molecule. In contrast, ED-REFLMS relies on both electric and magnetic dipole transitions in the cation that are amplified further by the helical electron trajectories.

ED-REFLMS is an efficient and general technique that can be extended to complex molecules since the chiral response can be obtained from recollision-induced doubly charged or fragment ions. In principle, it does not require any variation of ellipticity of the laser polarization. The wavelength response of the chiral signal can be obtained at a fixed ellipticity. This is analogous to absorption CD spectroscopy, albeit with better efficiency.

ED-REFLMS is a variation of the previously examined cHHG method. However, HHG's poor conversion efficiency makes it technically challenging. In contrast, ED-REFLMS is simpler as it only depends on the detection of ions and is not limited to pure molecular samples. It enables quantitative chemical analysis of chiral substances even in a mixture of substances without prior chemical separation.



OPEN

Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry

Jean-Luc Bégin, Maye Alsaawy & Ravi Bhardwaj✉

Chiral molecules and their interactions are critical in a variety of chemical and biological processes. Circular dichroism (CD) is the most widely used optical technique to study chirality, often performed in a solution phase. However, CD has low-efficiency on the order of 0.01–1%. Therefore, there is a growing need to develop high-efficiency chiroptical techniques, especially in gas-phase, to gain background-free in-depth insight into chiral interactions. By using mass spectrometry and strong-field ionization of limonene with elliptically polarized light, we demonstrate an efficient chiral discrimination method that produces a chiral signal of one to two orders of magnitude higher than the conventional CD. The chiral response exhibits a strong dependence on wavelength in the range of 1,300–2,400 nm, where the relative abundance of the ion yields alternates between the two enantiomers. The origin of enhanced enantio-sensitivity in intense laser fields is attributed to two mechanisms that rely on the recollision dynamics in a chiral system: (1) the excited ionic state dynamics mediated either by the laser field or by the recollision process, and (2) non-dipole effects that alter the electron's trajectories. Our results can serve as a benchmark for testing and developing theoretical tools involving non-dipole effects in strong-field ionization of molecules.

Chiral molecules lack S_n symmetry (improper rotation axis) due to the presence of a chiral center in which an atom is connected to four different groups of atoms¹. Consequently, there is a handedness to the molecule. The left- and right-handed molecules are non-superimposable mirror images of each other, called enantiomers. They have identical physical and chemical properties making it difficult to differentiate them. Chiral discrimination requires an interaction between two chiral systems—a chiral reagent with known handedness that can induce enantio-selectivity in the second chiral system.

In nature, bio-molecules such as amino acids that make up life on earth are homochiral, where one enantiomer exists predominantly over the other due to asymmetric interactions². Homochirality plays a pivotal role in our daily life by serving as a chiral reagent for enantio-selectivity. For example, olfactory receptors in our nose, responsible for the sense of smell, interact differently with the two enantiomers of a chiral system. For instance, the right-handed enantiomer of limonene has an orange odour while the left-handed enantiomer has a lemon odour³.

In practice, enantio-selectivity can be achieved using circularly polarized light (CPL) as a chiral reagent. CD is one of the most widely used chiroptical techniques. It arises due to the coupling of the electric and magnetic dipole transitions, thereby resulting in a differential absorption of left- and right-circularly polarized light^{4–8}. CD has low-efficiency on the order of 0.01–1% because magnetic dipole transitions are involved^{9–12}. Moreover, CD measurements are mostly conducted in solution phase, making it difficult to isolate the optical response of the chiral molecule from the influence of solvent-solute interactions^{13,14}. Complementary techniques, such as vibrational circular dichroism and Raman optical activity¹⁵, have been used to specifically target the molecules in liquid media by probing the fundamental vibrational bands. However, their use in gas-phase studies has been limited. So, there is a continued effort to develop new gas-phase techniques to enhance chiral sensitivity; cavity ring-down polarimetry is one such example¹⁶.

Most gas-phase CD experiments employ highly sensitive techniques based on multiphoton ionization of chiral molecules instead of conventional absorption of CPL. Electrons or ions resulting from the light-matter interaction are detected using either imaging techniques such as photoelectron angular distribution¹⁷, mass spectrometry^{18–21} or a combination of both²². CD measurement with laser ionization mass spectrometry often use Resonance Enhanced Multiphoton Ionization (REMPI)^{18,23–27}. They rely on resonant electronic absorption of one

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photon, which gives rise to the CD effect and is specific to the molecule, followed by ionization with additional photons of either the same or different colours. There have been very few studies on non-resonant laser ionization mass spectrometry^{21,28}. Since the underlying principle of CD in laser ionization mass spectrometry is similar to the conventional CD, the effect is still considerably small for most UV–Vis transitions in organic molecules.

Photoelectron circular dichroism (PECD)^{9,29,30} has recently emerged as an effective gas-phase chiroptical technique with an efficiency of one to two orders of magnitude larger than CD. In PECD, the interaction between CPL and a chiral molecule results in asymmetric photoelectron angular dispersion that is identical but opposite in sign for the two enantiomers. PECD arises due to pure electric dipole transitions, therefore, it is highly efficient compared to conventional CD.

Coulomb explosion imaging is another chiroptical technique in which the momentum of each fragment is recorded when the molecule undergoes fragmentation upon rapid ionization by an intense laser pulse^{31,32}. The momentum vectors of the fragments are enantio-sensitive as they are of equal magnitude but of opposite sign due to the non-symmetric behaviour of their coulomb potential. This technique is capable of imaging the absolute configuration of chiral molecules. However, it cannot be extended to complicated molecules because (1) the detection efficiency decreases exponentially for the increasing number of fragments and (2) reconstruction of the molecular structure may not be possible from the kinematic properties of the fragments.

Here we introduce a new extreme nonlinear chiroptical technique based on strong-field ionization of chiral molecules combined with mass spectrometry. Left- and right-handed elliptically polarized driving laser fields produce differential yields of doubly charged parent ion or fragment enabling chiral discrimination. The basic principle of elliptical dichroism relies on recollision physics explained by the semi-classical three-step model³³:

1. Ionization of a chiral molecule by strong IR field in the tunneling regime defined by the Keldysh parameter $\gamma < 1$ ³⁴. For randomly orientated molecules, the laser field will preferentially ionize a subset of molecules whose molecular axes are aligned with the field.
2. Laser-induced propagation and acceleration of the ionized electron whose trajectory is influenced by the electric and magnetic field of the light; the latter corresponds to the non-dipole regime. The maximum energy of the recolliding electron is $3.17U_p$ where U_p is the ponderomotive energy³⁵.
3. Inelastic recollision of the liberated electron with the parent ion leading to direct ionization or excitation of the parent ion, depending on the kinetic energy of the recolliding electron.

Using limonene, $C_{10}H_{16}$, as a test case, we demonstrate Elliptical dichroism based on recollision enhanced femtosecond laser mass spectrometry (ED-REFLMS). It is an extreme nonlinear chiroptical technique with high efficiency compared to conventional CD (by at least an order of magnitude) and to PECD (by a factor of 5 for certain wavelengths). ED-REFLMS also exhibits a strong dependence on wavelength. This method is a variation of the previously examined chiral-high harmonic generation (cHHG) method³⁶, where coherent radiation emitted as high order harmonics of the driving field was used to differentiate the enantiomers. However, poor conversion efficiency makes cHHG technically challenging.

Results

Limonene consists of a cyclohexene ring with a methyl group on one end and an isopropenyl group on the other end connected to a carbon atom that serves as a chiral centre. The highest occupied molecular orbital (HOMO) is the carbon double bond ($C=C$) in the cyclohexene ring. $2\pi^{-1}$ is the ground state cation of limonene with an ionization energy of 8.54 eV^{37,38}. The first excited cationic state is a $1\pi^{-1}$ molecular orbital having an ionization energy of 9.08 eV and belongs to $C=C$ double bond of isopropenyl group. The higher electronic excited cation states belong to the ionization of sigma bonds σ^{-1} ^{30,37,39–41}. When irradiated with intense light pulses, limonene undergoes ionization and fragmentation.

Femtosecond laser mass spectrum of limonene. Figure 1 shows the mass spectrum of S-limonene at 2,000 nm. The dominant peak at $m/z = 68$ corresponds to the fragment $C_5H_8^+$. However, unlike electron impact ionization, the next dominant peak corresponds to the parent ion $C_{10}H_{16}^+$, which exhibits a strong dependence on the wavelength. Doubly charged limonene $C_{10}H_{16}^{2+}$ overlaps with the fragment $C_5H_8^+$ and can be differentiated using the isotopomer of the parent ion $^{13}C^{12}C_9H_{16}^+$. The insets show the isotopomer of the parent ion at $m/z = 137$ and its doubly charged ion at $m/z = 68.5$. Total doubly charged limonene yield varied from 20 to 50% relative to the fragment ion signal at $m/z = 68$ as the wavelength increased from 1,300 to 2,400 nm, as shown in Fig. 2a. At longer wavelengths, ionization is purely in the tunneling regime ($\gamma < 1$) resulting in less fragmentation. Reduced doubly charged ion yields at 1,850 and 1,900 nm is mainly due to lower yield of the parent ion. The total double ionization yield includes a contribution from both sequential and non-sequential double ionization. The latter is due to electron recollision which depends on the ellipticity, ϵ , of the laser polarization and disappears for CPL. Therefore, the double ionization signal in Fig. 2a as ϵ approaches ± 1 is due to sequential double ionization.

Ellipticity variation of doubly charged ion yield. Chiral response to elliptically polarized light, which acts as a chiral reagent, is shown in Fig. 2b. Positive (negative) values of ϵ correspond to left (right) handed elliptically polarized light. The behaviour of doubly charged limonene yield, as a function of laser ellipticity, exhibits key features: (1) the yields of the two enantiomers are not maximum for linearly polarized light as expected for an atom or achiral molecule. (2) The enantiomeric response is asymmetric around the linear polarization. The double ionization signal is maximum for $\epsilon \approx \pm 0.15$. (3) R-limonene (S-limonene) yield, at 1,700 nm, is higher

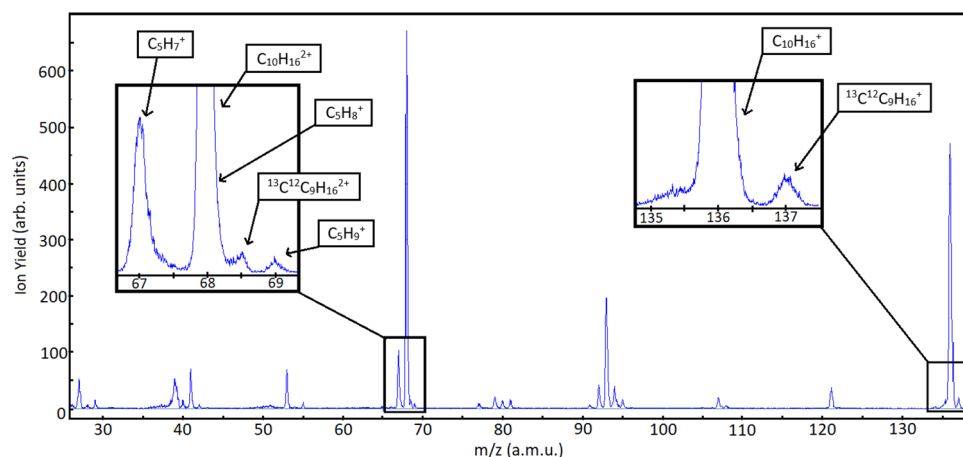


Figure 1. TOF mass spectrum of S-limonene at 2,000 nm and an intensity of 1.8×10^{14} W/cm². The right inset shows magnified region of the parent ion $C_{10}H_{16}^+$ and its isotopomer $^{13}C^{12}C_9H_{16}^+$. The left inset shows the magnified region consisting of the fragment $C_5H_8^+$ and doubly charged parent ion at $m/z = 68$ along with the doubly charged isotopomer $^{13}C^{12}C_9H_{16}^{2+}$ at $m/z = 68.5$.

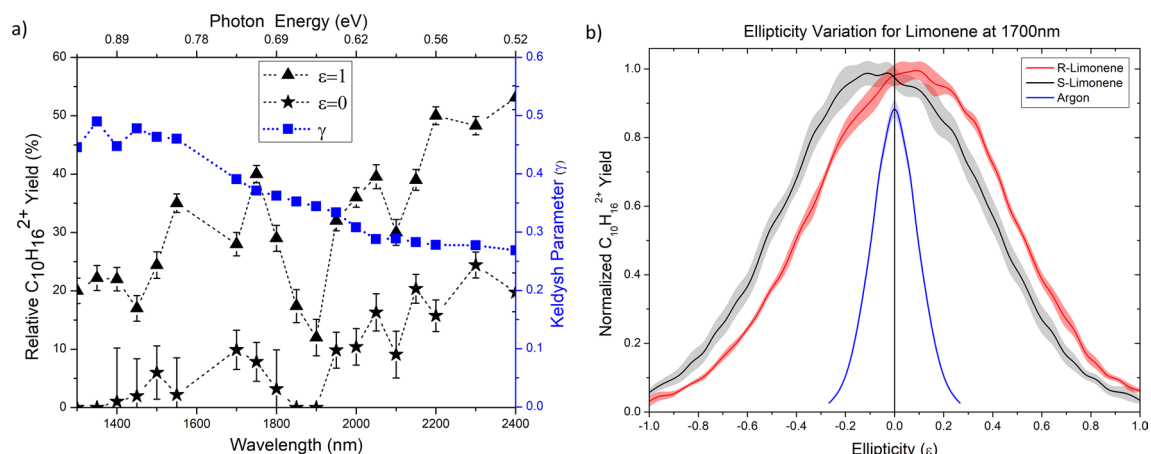


Figure 2. (a) Yield of doubly charged S-limonene relative to the fragment at $m/z = 68$ as a function of laser wavelength. The laser intensity was in the range of $9\text{--}10 \times 10^{13}$ W/cm². The solid triangle represents the total double ionization yield while the solid star symbol represents contribution from sequential double ionization process. The right ordinate shows the values of the Keldysh parameter used in the experiment (blue square). (b) Ellipticity dependence of doubly charged limonene enantiomers, S-limonene (black) and R-limonene (red), at 1,700 nm and an intensity of 9×10^{13} W/cm². The blue curve is the ellipticity variation for an achiral test case, argon. The shaded bands correspond to fluctuations in the ion yields.

for positive (negative) ellipticities. (4) Chiral discrimination is not possible with linearly polarized light since the doubly charged ion yields remain the same for R- and S-limonene. Small ellipticity values are sufficient to efficiently discriminate the enantiomers.

Wavelength effects in limonene. The colour maps of Fig. 3a,b depict the dependence of the signal intensity of doubly charged limonene as a function of ellipticities for a range of wavelengths (1,300–2,400 nm). No data could be collected at the degenerate wavelengths. The black dashed line corresponds to linear polarization and the white solid circles represent the ellipticities at which the double ionization signal intensities are maximum. The chiral response of S-limonene and R-limonene alternates about the linear polarization ($\epsilon = 0$) within an ellipticity range of $-0.15 < \epsilon < 0.15$. For some wavelengths, the enantio-sensitivity is strong while for others it does not exist.

The chiral response is commonly expressed in terms of circular dichroism value. Similarly, elliptical dichroism (ED) can be defined as the ratio of the difference of the double ionization yield to the average double ionization yield of the enantiomers at a set ellipticity ($\pm\epsilon$).

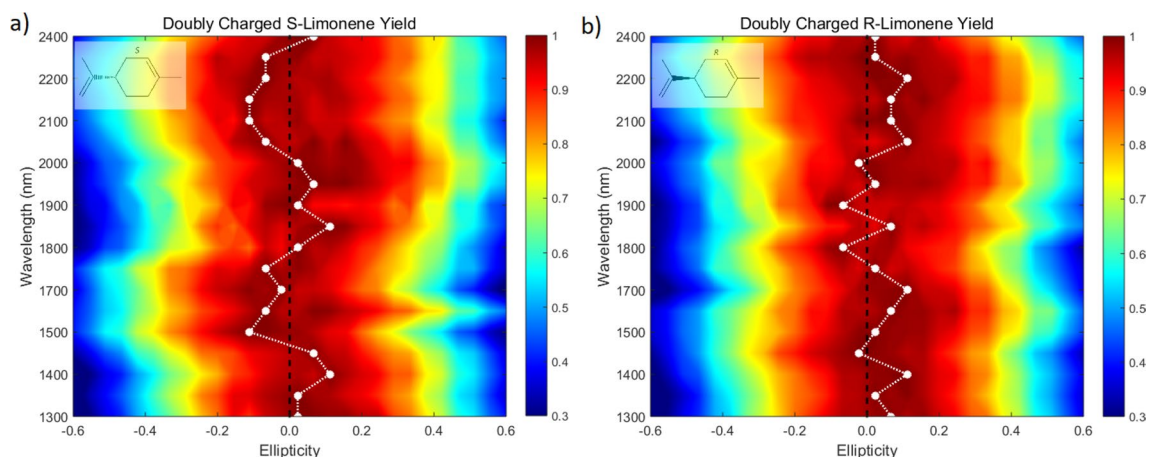


Figure 3. Ellipticity dependence of doubly charged S-limonene (left) and R-limonene (right) as a function of wavelength at an intensity of $9\text{--}10 \times 10^{13} \text{ W/cm}^2$. The black dashed line corresponds to linear polarization and the white solid circles represent the ellipticities at which the double ionization signal is maximum.

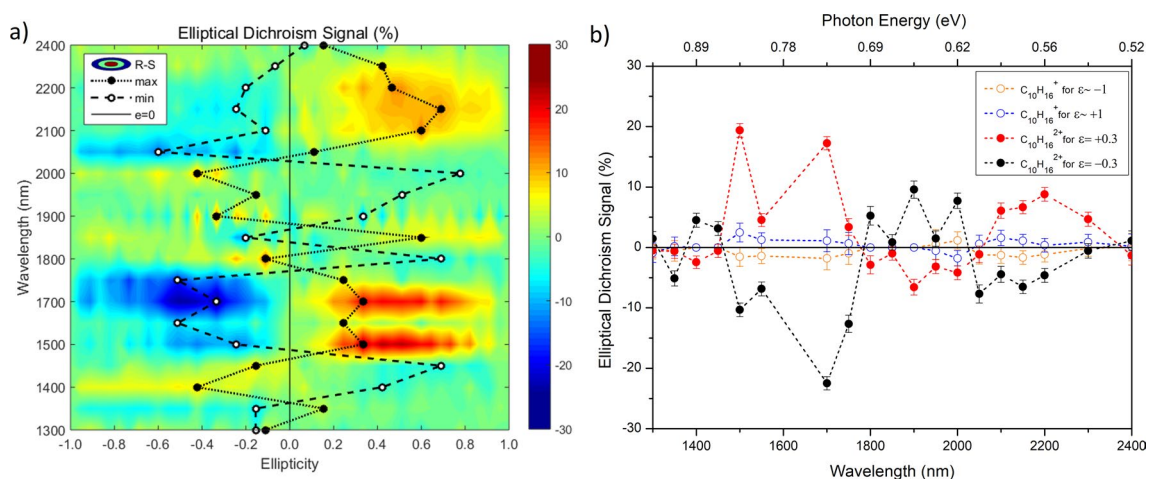


Figure 4. (a) Chiral signal represented by elliptical dichroism for $\text{C}_{10}\text{H}_{16}^{2+}$ as a function of ellipticity and at an intensity of $9\text{--}10 \times 10^{13} \text{ W/cm}^2$ over a range of wavelengths. Ellipticity values at which the ED signal is minimum (maximum) is represented by white circle (black circle) and the dashed lines are to guide the eye. (b) Wavelength dependent ED signal for $\text{C}_{10}\text{H}_{16}^{2+}$ at $\epsilon = +0.3$ (red solid circles) and for $\epsilon = -0.3$ (black solid circles). Also, shown is the CD signal for $\text{C}_{10}\text{H}_{16}^{+}$ at $\epsilon = +1$ (blue open circles) and for $\epsilon = -1$ (orange open circles). The error bars represent the fluctuations in the ion yields and the dotted lines are to guide the eye. The laser intensity was in the range of $9\text{--}10 \times 10^{13} \text{ W/cm}^2$.

$$ED(\pm\epsilon) = 2 \frac{R(\pm\epsilon) - S(\pm\epsilon)}{R(\pm\epsilon) + S(\pm\epsilon)} \quad (1)$$

Figure 4a shows the chiral signal expressed by ED for doubly charged limonene as a function of ellipticity for different wavelengths. Solid (open) circles represent the ellipticity values at which the ED signal is maximum (minimum) at a given wavelength. The chiral signal oscillating between positive and negative values indicates the double ionization yield of R-limonene being dominant for some wavelengths while S-limonene is dominant for the other wavelengths.

A full ellipticity scan is not essential to study wavelength-dependent chiral response. Instead, a wavelength scan at a fixed ellipticity should suffice, as shown in Fig. 4b for $\epsilon = 0.3$ or in Fig. 5a for $\epsilon = 0.2$. Figure 4b shows the wavelength dependence of the chiral signal for singly charged limonene for CPL ($\epsilon = \pm 1$) and doubly charged limonene for $\epsilon = \pm 0.3$. The following three key features are exhibited:

1. A typical laser mass spectrometer measures the CD signal using CPL. In limonene, a CD signal of 0.16%²⁵ was measured previously at a wavelength of 213 nm. In our measurements, in the wavelength regions of 1,500–1,750 nm and 1,950–2,300 nm, the CD signal is less than 2%. At other wavelengths, the singly charged ion yield was too low to measure the chiral signal. Similar results were obtained for elliptically polarized light.

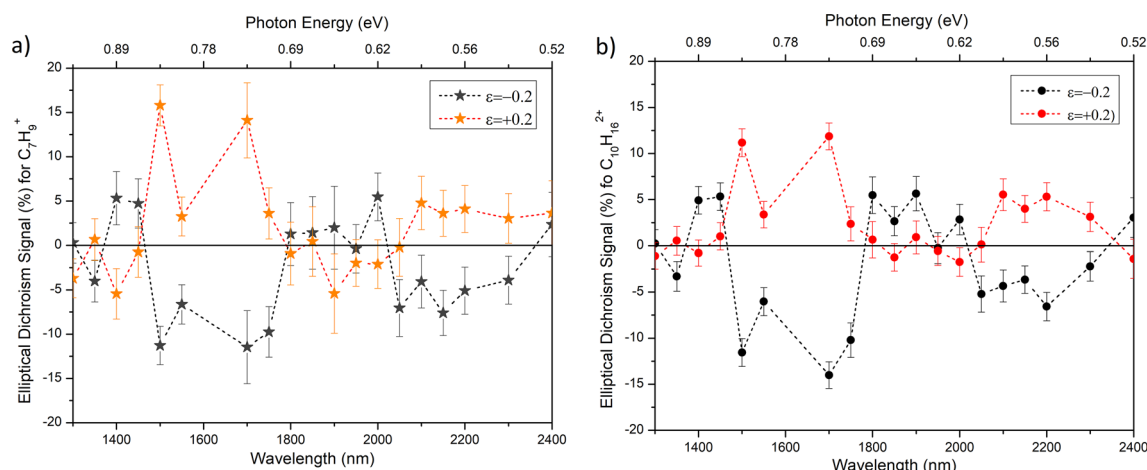


Figure 5. Wavelength dependence of ED signal (a) for singly charged limonene fragment $C_7H_9^+$, and (b) doubly charged limonene at $\epsilon = \pm 0.2$. The error bars represent fluctuations in the ion yields. The laser intensity was in the range of $9\text{--}10 \times 10^{13} \text{ W/cm}^2$.

- By monitoring the doubly charged limonene yield, which arises from recollision, the chiral signal represented by ED increased to $\sim 20\%$ at 1,700 nm with elliptically polarized light, an enhancement by up to a factor of 10. The enhancement factor peaks between $\epsilon = \pm 0.2$ and $\epsilon = \pm 0.4$ (Fig. 4a) and disappears for linear and circular polarization. As discussed later, such an enhancement of the chiral signal can arise from the recollision dynamics in the presence of the laser magnetic field. For comparison, the chiral signal measured by PECD using REMPI at 420 nm was at 4%³⁹.
- For some wavelengths, the positive and negative ED signals for doubly charged limonene mirror each other. At certain other wavelengths, the chiral signal is non-existent. In 1,500–1,750 nm and 2,050–2,300 nm wavelength regions, R-limonene produces more double ionization than S-limonene for positive ellipticities. Whereas, S-limonene produces higher doubly charged yield relative to R-limonene from 1,800–2,000 nm.

In molecules where it is not feasible to identify the doubly charged parent ion because it is either unstable or cannot be differentiated from a fragment, a chiral response can still be studied by monitoring recollision induced fragment. Figure 5a shows the wavelength dependence of ED signal for singly charged $C_7H_9^+$ fragment ion at an ellipticity of $\epsilon = \pm 0.2$. Chiral signal exhibits larger fluctuation due to lower yield of the fragment ion relative to the doubly charged yield. For comparison, the ED signal for doubly charged limonene at the same ellipticity value is shown in Fig. 5b. The ED signal and the wavelength dependence are nearly the same whether one monitors the fragment or doubly charged.

Discussion

Enantio-sensitivity always requires a sign dependent response between the enantiomers. In CD, the probability of measuring an enantio-sensitive transition is proportional to the matrix element involving the electric and magnetic dipole interference term or by the molecular rotatory strength which is sign variant under improper rotations^{4–6,42}. In PECD, the chiral response is described by the differential cross-section of a photoelectron defined in terms of the angular distribution function^{9,29,30}. The ionized electron exhibits a forward-backwards asymmetry in the angular distribution due to momentum conservation during the photoionization process.

Chiral discrimination by ED-REFLMS technique can be understood by considering recollision dynamics beyond the dipole approximation. Strong-field ionization is often formulated within the dipole approximation, which assumes the laser wavelength is longer than the electron trajectory or the electron velocity is much smaller than the speed of light. Therefore, the magnetic effects on the electron are ignored leading to trajectories that are always in the plane of the laser polarization. However, at higher intensities, the magnetic field begins to exert a significant force on the ionized electron and its trajectory exhibits a figure 8 motion with major axis along the direction of the electric field and the minor axis along the direction of propagation⁴³. The onset of the magnetic field effect occurs when the field-induced displacement along the propagation direction approaches an amplitude that is a significant fraction of an atomic unit^{43,44}. This happens at higher intensities for shorter wavelengths or at lower intensities for longer wavelengths. ED-REFLMS experiments are performed on limonene at an intensity of $9\text{--}10 \times 10^{13} \text{ W/cm}^2$ in the near IR region (1,300–2,400 nm) which falls in the non-dipole non-relativistic regime.

There are three possible mechanisms where the laser magnetic field plays a role in the recollision dynamics. All are described in terms of the time evolution of the chiral system at each step of the recollision process within the non-dipole approximation.

- Mechanism 1: Evolution of the parent ion during electron propagation in the continuum.

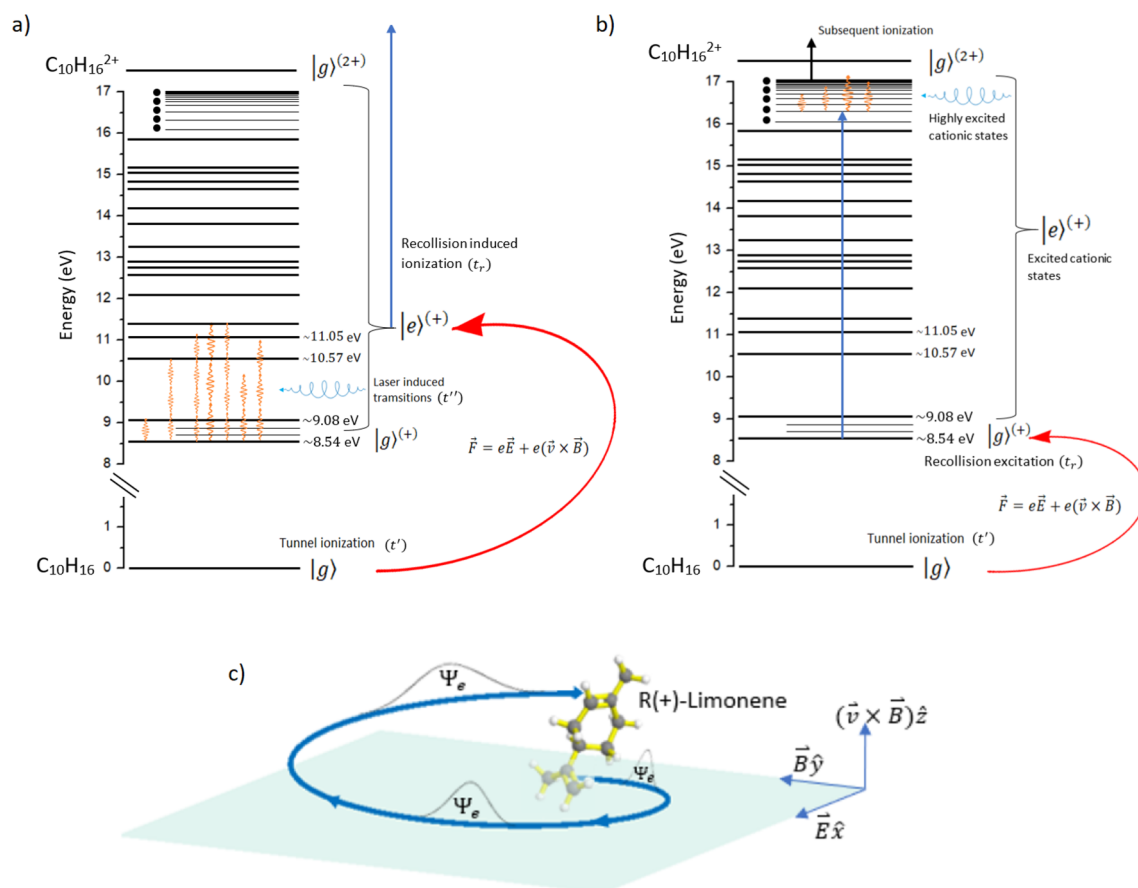


Figure 6. Energy level diagram illustrating chiral sensitive mechanisms 1 and 2 (a,b). The $|g\rangle$ and $|g\rangle^{(+)}$ represent the ground state of neutral and cationic states of $C_{10}H_{16}$. (a) Evolution of the parent ion from $|g\rangle^{(+)}$ $\rightarrow$ $|e\rangle^{(+)}$ cationic states induced by the elliptically polarized field (orange arrows) as the electron propagates in the continuum (red arrow). Recollision occurs on excited cationic state $|e\rangle^{(+)}$ of the molecule and the second electron is liberated to the continuum (blue arrow) resulting in non-sequential double ionization. (b) Evolution of the parent ion after recollision from the $|g\rangle^{(+)}$ to highly excited cationic states $|e\rangle^{(+)}$ (blue arrow). The elliptically polarized laser field induces electric and magnetic transitions (orange arrows) in these highly excited states that subsequently undergo field ionization. The energy levels were obtained from limonene photoelectron spectrum^{37,38}. (c) Schematic showing the electron trajectory in an elliptically polarized field along with asymmetric transverse momentum spread.

Between the ionization time (t') and the recollision time (t_r), the elliptical laser field can interact with a second electron in the ground state of the cation $C_{10}H_{16}^+$ and induce electric dipole (E1) and magnetic dipole (M1) transitions at time t'' . The interaction will be chiral sensitive when both the E1 (polar-vector) and M1 (pseudovector) transitions are involved. Recollision takes place on an excited state of the parent ion, as shown in Fig. 6a. For molecules containing C=C bond, a $\pi \rightarrow \pi^*$ transition is E1 allowed. However, the M1 transition is forbidden in an achiral system. For a chiral system, the M1 transition is nonzero due to the asymmetrical properties of the enantiomers and is sign variant when either the ellipticity of light or the enantiomer is switched^{45–47}.

In limonene, E1–M1 transitions can promote the singly charged ion from ground state $|g\rangle^{(+)}$ to an excited electronic cationic state $|e\rangle^{(+)}$ (orange arrows in Fig. 6a) as the ionized electron propagates in the laser field (red arrow). Recollision occurs on the excited cationic state $|e\rangle^{(+)}$ at time t_r . Due to chiral-sensitive transitions induced by the elliptical field, electron densities in the excited cationic states are enantiomer dependent. After recollision, the double ionization signal (blue arrow) is dominant for one enantiomer compared to the other for the same ellipticity. This mechanism is similar to the “type-II” mechanism of cHHG³⁶ and is also analogous to CD. However, E1–M1 transitions in CD occur in the ground state of the neutral molecule while in ED-REFLMS they occur in the parent ion.

2. Mechanism 2: Evolution of the parent ion after recollision.

In recollision, the maximum kinetic energy for the returning electron is $3.17U_p$ when it is released into the continuum near the peak of the laser field. Electrons can also be released into the continuum before or after the peak, resulting in long or short trajectories. Soft recollisions can occur for electrons with lower ponderomotive energies from either shorter trajectories, or from longer trajectories that return to the parent ion at a clipping angle. Depending on the electron impact cross-section for the parent ion, the inelastic collision

can promote the cation to a highly excited Rydberg-like state instead of removing the second electron (blue arrow Fig. 6b). The remnant laser field interacting with the highly excited cation can induce chiral sensitive transitions (orange arrows), and eventually lead to removal of the second electron.

3. Mechanism 3: Evolution of the liberated electron.

In an elliptically polarized laser field, an electron in the continuum acquires a helical trajectory due to the influence of the magnetic field (Fig. 6c). Since the helicity of the electron trajectory is defined by the handedness of the light, it behaves like a chiral reagent. A chiral response can arise when (a) for a given electron helicity the collisional cross-section is different between the two enantiomers, or (b) the recolliding electron interacts with different regions of an enantiomer for opposite ellipticities.

In addition, the tunneling electron acquires an asymmetry in its initial transverse momentum along the direction of propagation due to the Lorentz force. This asymmetry in the electron transverse momentum translates into an asymmetry in double ionization probability⁴⁸. In the dipole regime, with E-field along $\hat{x}$ -axis, the initial transverse momentum of the electron is symmetric in the $\hat{y}$ – $\hat{z}$ plane. The magnetic field together with recollision dynamics acts as a gate selecting only a subset of the initial tunneling-electron momenta that are opposite to the propagation direction of the laser field. Only this subset of electrons can lead to double ionization⁴⁸. The asymmetry is either in a positive or negative $\hat{z}$ -direction depending on the direction $\mathbf{B}\hat{y}$ -field (handedness of incident elliptical light).

For a chiral molecule in the presence of an elliptically polarized field, the asymmetric electron wavepacket behaves like the chiral reagent. Thus, the combined effect of breaking the symmetry of the electron momentum distribution and out of plane electron trajectories can lead to different double ionization yields of limonene enantiomers for a given ellipticity of light (Fig. 6c). This is a universal phenomenon and becomes prominent at longer wavelengths and higher intensities.

All three mechanisms can occur simultaneously in limonene. However, mechanisms 1 and 2 require magnetic dipole transitions in the cation that can still be relatively weak. Together with the universal mechanism 3, they can give rise to the observed enhancement. Any insight into such efficient extreme nonlinear chiroptical response requires new theoretical tools that take into account the non-dipole effects on strong-field ionization of molecules.

Wavelength dependence of chiral signal has been observed in chiroptical techniques such as absorption CD and PECD^{37,45}. In absorption CD, it is attributed to the Cotton effect^{49,50}, a change in the extinction coefficients of S- and R-limonene for right and left circularly polarized light^{5,49}. In single and multi-photon PECD of limonene, varying the photon energy led to (a) modulation of the chiral signal mirroring the principal vibrational features observed in the photoelectron spectrum, and (b) flipping of the forward–backwards asymmetry in the angular emission of electrons relative to the photon beam direction^{30,37,38}. The wavelength effects of the chiral signal are attributed to the excitation of vibronic states of the cation and/or intermediate electronic states of the neutral molecule.

Although CD and PECD involve excitation of intermediate states, since PECD arises from pure electric dipole interaction, the chiral signal is several orders of magnitude greater than the absorption CD. Currently, understanding the role of the intermediate resonances is subject of experimental and theoretical investigations. Recently it was demonstrated, by decoupling bound–bound and bound–continuum transitions, that the helicity of the light pulse that drives the bound–bound transitions has a negligible effect on the PECD^{51,52}. However, circularly and linearly polarized laser pulses still lead to different PECDs because of the angular dependence of the excitation process, which induces different anisotropies.

In ED-REFLMS, where the photon energy was varied from 0.51 to 0.95 eV, all three mechanisms that can contribute to the chiral signal are wavelength dependent. However, mechanism 3 alone cannot give rise to the flipping of the chiral signal with laser wavelength as it does not involve any intermediate states of the cation. In mechanism 1, when an electron is promoted into the continuum, the laser field is still intense enough to induce vibronic and multiphoton electronic excitation of the cation $\text{C}_{10}\text{H}_{16}^+$. Some of these bound–bound multiphoton transitions can exhibit varying responses in the two enantiomers for different wavelengths. Therefore, upon recollision, the excited state dynamics influence the double ionization rates.

For example, from 1,500 to 1,750 nm where R-limonene produced more double ionization signal than S-limonene, the HOMO-2 at 10.57 eV and HOMO-3 at 11.05 eV can be accessed by 3-photon and 4-photon excitation, respectively. Similarly, from 2,150 to 2,300 nm they can be accessed 4-photon and 5-photon excitation, respectively. In the wavelength range where S-limonene produced more double ionization signal than R-limonene, HOMO-3 can be accessed by 4-photon excitation over the entire range, whereas HOMO-2 can be accessed only from 1,750 to 1,830 nm by 3-photon excitation.

In mechanism 2, the parent ion is promoted to a highly excited Rydberg-like state. At recollision time, the field is minimum, decreasing the probability of multi-photon absorption. The induced transitions are, therefore, most likely from 1-photon absorption to a dense manifold of vibrational Rydberg-like cationic states. In either of the above mechanisms, laser-induced transitions access different excited higher electronic and vibronic cationic states. The change of wavelength can affect the allowed molecular orbital transitions within an enantiomer. Small variation in the orientation of the E1 and M1 dipole transitions alters the coupling term which favours certain transition channels over others directly influencing the chiral signal detected by ED-REFLMS.

The similarities between the elliptical dichroism signal for double ionization and fragmentation can be understood by considering the complex potential energy surfaces of limonene. Upon photoionization, the molecular ions can undergo fragmentation through a multitude of dissociation pathways via intermediary states where several rearrangement reactions occur prior to dissociation⁵³. The ionization energy of limonene is ~ 8.54 eV while the appearance energies of fragment ions such as $\text{C}_9\text{H}_{13}^+$, $\text{C}_8\text{H}_{12}^+$, C_7H_9^+ and C_5H_8^+ are in the range of 9–11.5

eV. The pathways to these fragment ions are direct elimination of the associated neutral fragment or sequential elimination of CH_3 and C_2H_4 . The same fragment ions can also arise from the dissociation of excited di-cationic states, in which case, two charged fragment ions are formed that have appearance energies close to the double ionization threshold.

In mechanism 1, recollision takes place on excited cationic states. Under normal circumstances, these excited cationic states evolve in time leading to more fragmentation. However, because the recollision dynamics occur on a short time scale of 2.5–5.5 fs (2/3 of an optical cycle for wavelengths in the range of 1,300–2,400 nm), much shorter than the dissociation time, the molecule undergoes a direct transition from excited cationic state to either ground di-cationic state (double ionization) or excited di-cationic state (fragmentation). In mechanism 2, soft recollision with the parent ion leads to excitation of Rydberg like cationic states. The remnant laser field interacting with highly excited cationic states can induce chiral sensitive transitions leading to the removal of second electron or fragmentation. Coincidence measurements can shed light on the relative influence of the two mechanisms and on the origin of the fragment ion from the dissociation of excited cationic or di-cationic states.

ED-REFLMS is a highly efficient technique where the chiral response can be obtained from either recollision-induced fragment or doubly charged ion (Fig. 5). The technique is ideal for molecules that produce stable doubly charged molecular ions which can be easily identified from fragment ions. In large molecules, the detailed molecular structure can affect ionization. So, when fragmentation overwhelms ionization, the technique can still be used to discriminate enantiomers provided the fragment ions produced by recollision are still dominant. The technique would be severely limited when contributions from sequential processes outweigh the non-sequential processes. This could be the case for some complex molecules.

In principle, ED-REFLMS does not require any ellipticity variation. The wavelength response of the chiral signal can be obtained at a fixed ellipticity (Figs. 4b, 5). This is analogous to CD spectroscopy where the differential absorption of CPL is measured for different wavelengths, albeit with better efficiency. Moreover, ED-REFLMS enables quantitative chemical analysis of chiral substances by performing mass selective spectroscopy even in a mixture of substances without prior chemical separation. In addition, extreme nonlinear chiroptical techniques like cHHG and ED-REFLMS serve as a benchmark for testing and development of theoretical tools that include non-dipole effects in strong-field ionization of molecules. Such tools enable interpretation of the fundamental relationship between chiroptical properties and detailed molecular structure.

Methods

Experiment. In the ED-REFLMS technique, near-infrared femtosecond laser pulses are focused onto a randomly orientated limonene molecule $\text{C}_{10}\text{H}_{16}$ in gas phase by a parabolic mirror in a differentially pumped vacuum chamber housing a time-of-flight mass spectrometer (TOFMS). The ions produced in the interaction region of TOFMS, operating in a Wiley–McLaren geometry, are accelerated and propagated through a field-free region of 30 cm where they are detected by a micro-channel plate. The ion signal is then amplified, discriminated and recorded by a time digitizer to generate a TOF mass spectra. Mass calibration was achieved using Xenon atoms and the spectrometer has a FWHM mass resolution of 550 at an $m/z = 132$.

Both enantiomers of limonene (from Sigma Aldrich) have sufficient vapour pressure at room temperature to be introduced into the vacuum chamber in gas phase through a precision leak valve. Limonene underwent a freeze and thaw cycle to minimize contamination of the interaction region. The pressure inside the vacuum chamber was maintained at $\sim 1.2 \times 10^{-7}$ Torr. To minimize number density fluctuations in the interaction region, limonene was maintained at 25 °C using a temperature bath and the gas line along with the leak valve were maintained at a positive temperature gradient. S-limonene and R-limonene have a purity of 96% and 97%, respectively.

Since limonene has low ionization potential, experiments were performed in the wavelength range of 1,300–2,400 nm to ensure adiabatic ionization. These wavelengths were obtained from an optical parametric amplifier (TOPAS-C) pumped by a Ti:sapphire laser system (Spitfire, Spectra-Physics) operating at 1 KHz repetition rate, producing ~ 40 fs pulses with a maximum pulse energy of ~ 2.5 mJ. The pulse duration was monitored on a shot-to-shot basis by a single-shot autocorrelator. A half-wave plate polarizer combination was used to control the pulse energy. A fast photodiode continuously monitored the laser pulse energy incident on a 3 mm thick quartz window on the vacuum chamber.

A quarter-wave plate (QWP) on a motorized rotation stage (with a $\pm 0.005^\circ$ resolution) controlled the ellipticity, ϵ , of the laser polarization. For each laser wavelength, the QWP was calibrated and $\epsilon = 0$, corresponding to linear polarization, was accurately determined from the ellipticity dependence of doubly charged argon. The maximum ellipticity obtained was $\epsilon = \pm 0.96$ corresponding to nearly circular polarization. The uncertainty in ellipticity was ± 0.02 .

Doubly charged limonene yields were recorded for each enantiomer by varying the ellipticity from $\epsilon = -1$ (RCP) to $\epsilon = 1$ (LCP) in at least two different quadrants of the rotating QWP. Fluctuations of the ion yields and error bars related to the elliptical dichroism signal were computed based on repeated measurements under similar conditions. The ellipticity was varied in steps of 0.04 around linear polarization and in steps of 0.08 beyond $\epsilon = 0.2$. ED-REFLMS measurements in limonene were performed at an intensity of $9\text{--}10 \times 10^{13}$ W/cm² over the wavelength range of 1,300–2,400 nm, below the measured saturation intensity of $\sim 12\text{--}13 \times 10^{13}$ W/cm². At each wavelength, the intensity was calibrated by measuring the saturation intensity of argon.

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References

- Wagnière, G. H. *On Chirality and the Universe Asymmetry* 247 (Wiley, Zurich, 2007).
- Blackmond, D. G. The origin of biological homochirality. *Philos. Trans. R. Soc. B* **366**, 2878–2884 (2011).
- Laska, M. Olfactory discrimination ability of human subjects for enantiomers with an isopropenyl group at the chiral center. *Chem. Sens.* **29**(2), 143–152 (2004).
- Rosenfeld, L. Quantum-mechanical theory of the natural optical activity of liquids and gases. *Z. Phys.* **52**, 161 (1928).
- Condon, E. U. Theories of optical rotatory power. *Rev. Mod. Phys.* **9**, 432 (1937).
- Caldwell, D. J. & Eyring, H. *The Theory of Optical Activity* 244 (University of Utah, Salt Lake City, 1971).
- Tinoco, I. Two-photon circular dichroism. *J. Chem. Phys.* **62**, 1006 (1975).
- Stephens, P. J. Theory of vibrational circular dichroism. *J. Phys. Chem.* **89**(5), 748–752 (1985).
- Janseen, M. H. M. & Powis, I. Detecting chirality in molecules by imaging photoelectron circular dichroism. *Phys. Chem. Chem. Phys.* **16**, 856 (2014).
- Lambrech, A., Pfeifer, M., Konz, W., Herbst, J. & Axtmann, F. Broadband spectroscopy with external cavity quantum cascade lasers beyond conventional absorption measurements. *Analyst* **139**, 2070 (2014).
- Fujiki, M., Kawagoe, Y., Nakano, Y. & Nakao, A. Mirror-symmetry-breaking in poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-biphenyl] (PF8P2) is susceptible to terpene chirality, achiral solvents, and mechanical stirring. *Molecules* **18**(6), 7035–7057 (2013).
- Kang, J. *et al.* C₅-symmetric chiral corannulenes: Desymmetrization of bowl inversion equilibrium via “intramolecular” hydrogen-bonding network. *JACS* **136**(30), 10640–10644 (2014).
- Gottarelli, G., Osipov, M. A. & Spada, G. P. A study of solvent effect on the optical rotation of chiral biaryls. *J. Phys. Chem.* **95**(9), 3879–3884 (1991).
- Langeveld-Voss, B. M. W., Christians, M. P. T., Janssen, R. A. J. & Meijer, E. W. Inversion of optical activity of chiral polythiophene aggregates by a change of solvent. *Macromolecules* **31**(19), 6702–6704 (1998).
- Nafie, L. A. Infrared and raman vibrational optical activity: Theoretical and experimental aspects. *Annu. Rev. Phys. Chem.* **48**, 357–86 (1997).
- Müller, T., Wiberg, K. B. & Vaccaro, P. H. Cavity ring-down polarimetry (CRDP): A new scheme for probing circular birefringence and circular dichroism in the gas phase. *J. Phys. Chem. A* **104**(25), 5959–5968 (2000).
- Lux, C. *et al.* Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses. *Angew. Chem. Int. Ed.* **51**, 5001–5005 (2012).
- Li, R., Sullivan, R., Al-Basheer, W., Pagni, R. M. & Compton, R. N. Linear and nonlinear circular dichroism of R-(+)-3-methylcyclopentanone. *J. Chem. Phys.* **125**, 144304 (2006).
- Logé, C. & Boesl, U. Laser mass spectrometry with circularly polarized light: Circular dichroism of molecular ions. *Chem. Phys. Chem.* **13**, 4218–4223 (2012).
- Boesl, U., Bornschlegl, A., Logé, C. & Titze, K. Resonance-enhanced multiphoton ionization with circularly polarized light: Chiral carbonyls. *Anal. Bioanal. Chem.* **405**(22), 6913–24 (2013).
- Horsch, P., Urbasch, G. & Weitzel, K.-M. Analysis of chirality by femtosecond laser ionization mass spectrometry. *Chirality* **24**, 684–690 (2012).
- Fanood, M. M. R., Ram, N. B., Lehmann, C. S., Powis, I. & Janssen, M. H. M. Enantiomer-specific analysis of multi-component mixtures by correlated electron imaging-ion mass spectrometry. *Nat. Commun.* **6**, 7511 (2015).
- Boesl, U. & Bornschlegl, A. Circular dichroism laser mass spectrometry: Differentiation of 3-Methylcyclopentanone enantiomers. *Chem. Phys. Chem.* **7**, 2085–2087 (2006).
- Bornschlegl, A., Logé, C. & Boesl, U. Investigation of CD effects in the multi photon ionisation of R-(+)-3-methylcyclopentanone. *Chem. Phys. Lett.* **447**(4–6), 187–191 (2007).
- Logé, C. & Boesl, U. Multiphoton ionization and circular dichroism: New experimental approach and application to natural products. *Chem. Phys. Chem.* **12**, 1940–1947 (2011).
- Logé, C., Bornschlegl, A. & Boesl, U. Progress in circular dichroism laser mass spectrometry. *Anal. Bioanal. Chem.* **395**(6), 1631–1639 (2009).
- Logé, C., Bornschlegl, A. & Boesl, U. Twin mass peak ion source for comparative mass spectrometry: Application to circular dichroism laser MS. *Int. J. Mass Spectrom.* **281**(3), 134–139 (2009).
- Horsch, P., Urbasch, G. & Weitzel, K.-M. Circular dichroism in ion yields in multiphoton ionization of (R)-propylene oxide employing femtosecond laser pulses. *Z. Phys. Chem.* **225**(5), 587–594 (2011).
- Powis, I. Photoelectron circular dichroism of the randomly oriented chiral molecules glyceraldehyde and lactic acid. *J. Chem. Phys.* **112**, 301 (2000).
- Beaulieu, S. *et al.* Universality of photoelectron circular dichroism in the photoionization of chiral molecules. *New J. Phys.* **18**, 102002 (2016).
- Pitzer, M. *et al.* Direct determination of absolute molecular stereochemistry in gas phase by coulomb explosion imaging. *Science* **341**(6150), 1096–100 (2013).
- Pitzer, M. How to determine the handedness of single molecules using coulomb explosion imaging. *J. Phys. B Atmos. Mol. Opt. Phys.* **50**(153001), 17 (2017).
- Lewenstein, M., Balcou, P., Ivanov, M. Y., L’Huillier, A. & Corkum, P. B. Theory of high-harmonic generation by low-frequency laser fields. *Phys. Rev. A* **49**(3), 2117 (1994).
- Keldysh, L. V. Ionization in the field of a strong electromagnetic wave. *Sov. Phys. JETP* **20**(5), 1307–1314 (1965).
- Corkum, P. B. Plasma perspective on strong-field multiphoton ionization. *Phys. Rev. Lett.* **71**(13), 1994–1997 (1993).
- Cireasa, R. *et al.* Probing molecular chirality on a sub-femtosecond timescale. *Nat. Phys.* **11**, 654–658 (2015).
- Fanood, M. M. R., Janssen, M. H. M. & Powis, I. Wavelength dependent photoelectron circular dichroism of limonene studied by femtosecond multiphoton laser ionization and electron-ion coincidence imaging. *J. Chem. Phys.* **145**, 124320 (2016).
- Fanood, M. M. R. *et al.* Intense vibronic modulation of the chiral photoelectron angular distribution generated by photoionization of limonene enantiomers with circularly polarized synchrotron radiation. *Chem. Phys. Chem.* **19**(8), 921–933 (2018).
- Fanood, M. M. R., Janssen, M. H. M. & Powis, I. Enantioselective femtosecond laser photoionization spectrometry of limonene using photoelectron circular dichroism. *Phys. Chem. Chem. Phys.* **17**(14), 8614–8617 (2015).
- Smialek, M. A. *et al.* Limonene: Electronic state spectroscopy by high-resolution vacuum ultraviolet photoabsorption, electron scattering, He(I) photoelectron spectroscopy and ab initio calculations. *Phys. Chem. Chem. Phys.* **14**(6), 2056–2064 (2012).
- XiaoPeng, W. *et al.* Photoelectron spectroscopy of terpenoids and prediction of their rate constants in atmospheric oxidation reactions. *Environ. Chem.* **55**(35), 4018–4025 (2010).
- Ordóñez, A. F. & Smirnova, O. Generalized perspective on chiral measurements without magnetic interactions. *Phys. Rev. A* **98**(6), 063428–20 (2018).
- Reiss, H. R. The tunneling model of laser-induced ionization and its failure at low frequencies. *J. Phys. B Atmos. Mol. Opt. Phys.* **47**(204006), 9 (2014).
- Reiss, H. R. Limits on tunneling theories of strong-field ionization. *Phys. Rev. Lett.* **101**(4), 043002–4 (2008).
- Brint, P., Meshulam, E. & Gedanken, A. Excited electronic states of limonene: A circular dichroism and photoelectron spectroscopy study of d-limonene. *Chem. Phys. Lett.* **109**(4), 383–387 (1984).

46. Drake, A. F. & Mason, S. F. The absorption and circular dichroism spectra of chiral olefins. *Tetrahedron* **33**(9), 937–949 (1977).
47. Gross, K. P. & Schnepp, O. Circular dichroism spectra of straight chain mono-olefins. Assignment of ethylene transitions. *Chem. Phys. Lett.* **36**(4), 531–535 (1975).
48. Emmanouilidou, A., Meltzer, T. & Corkum, P. B. Non-dipole recollision-gated double ionization and observable effects. *J. Phys. B Atmos. Mol. Opt. Phys.* **50**(225602), 9 (2017).
49. Cotton, A. Absorption and dispersion of light. *Chim. Phys.* **8**, 347 (1896).
50. Hargreaves, M. Optical rotatory dispersion: Its nature and origin. *Nature* **195**, 560–566 (1962).
51. Beaulieu, S. *et al.* Multiphoton photoelectron circular dichroism of limonene with independent polarization state control of the bound-bound and bound-continuum transitions. *J. Chem. Phys.* **149**, 134301 (2018).
52. Goetz, R. E., Isaev, T. A., Nikoobakht, B., Berger, R. & Koch, C. P. Theoretical description of circular dichroism in photoelectron angular distributions of randomly oriented chiral molecules after multi-photon photoionization. *J. Chem. Phys.* **146**, 024306 (2017).
53. Fang, W. *et al.* Photoionization and dissociation of the monoterpene limonene: Mass spectrometric and computational investigation. *J. Mass. Spectrom.* **46**, 1152–1159 (2011).

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Author contributions

All authors were involved in planning and designing the experiments. J.B. and M.A. performed the experiments. J.B. performed the analysis and together with R.B. prepared the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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6.2.1 CHIRAL-SENSITIVE RECOLLISION DYNAMICS

Mechanism 1: Evolution of the parent ion during electron propagation in the continuum. The time propagator $U_g^{(1,2)}(t', t_0)$ describes the time evolution of the two-electron system in the ground state, $|\psi_g^{(1)}, \psi_g^{(2)}\rangle$, before the laser field is turned on. The interaction between the EM field and the neutral molecule is described by the interaction Hamiltonian $\hat{V}_{F1}$ at time t' . At t' the first electron is ionized creating a parent ion with the second electron remaining in the ground state. The time evolution of the liberated electron is described by the Volkov time propagator $U_V^{(1)}(t'', t')$ and $U_V^{(1)}(t, t'')$, the electron propagates in the continuum between ionization time t' and the recollision time t . At t'' , the second electron in the parent ion interacts with the laser field described by the interaction Hamiltonian $\hat{V}_{F2}$ at time t'' and transitions to a higher cationic state. The propagator $U_e^{(2)}(t, t'')$ describes the evolution of a second electron in an excited cation state from time t'' to the recollision time t . At the time t , the liberated electron recollides with the excited cationic state and spontaneously liberates the second electron into the continuum through an inelastic electron-electron impact described by the interaction potential $\hat{V}_{12}$. Both electron are ionized and evolve according to $U_V^{(1,2)}(\infty, t)$.

The mechanism is chiro-sensitive due to the chiral-chiral interaction between the coupling of the chiral molecular multipoles (the electric and magnetic dipoles) of the ion with rotating electric and magnetic driving field expressed by the term $\langle \psi_V^{(1)} | \tilde{V}_{F1}(t') | \psi_g^{(1)} \rangle$ for the first electron and $\langle \psi_e^{(2)} | \tilde{V}_{F2}(t'') | \psi_g^{(2)} \rangle$ for the second electron. The correlation term $\hat{V}_{12}$ can also demonstrate chirality due to the direction of the propagating electron (see mechanism 3). Let the non-dipole Volkov time-propagator be $U_V^{ND} = U_V$ for simplicity. Below is the full transition amplitude for mechanism 1.

$$M_1(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, t, t', t'') = \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt'' \int_{-\infty}^{t''} dt' \langle \Phi_{ND}^V(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}; r_1, r_2; t) | U_V^{(1)}(\infty, t) \otimes U_V^{(2)}(\infty, t) \tilde{V}_{12} U_V^{(1)}(t, t'') \otimes U_e^{(2)}(t, t'') \tilde{V}_{F2}(t'') U_V^{(1)}(t'', t') \otimes U_g^{(2)}(t'', t') \tilde{V}_{F1} U_g^{(1)}(t', t_0) \otimes U_g^{(2)}(t', t_0) | \psi_g^{(1)}, \psi_g^{(2)} \rangle \quad (6.4)$$

Where Φ_{ND}^V is the non-dipole Gordon-Volkov wavefunction, π_{ND} is the non-dipole canonical momentum (see the section on non-dipole Gordon-Volkov wavefunction in Appendix A.2). For convenience, we consider only two electrons and approximate them as a product state. We can write the transition amplitude in a more useful form by introducing the projectors.

Where $\tilde{V}_{F1} = |\pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)}\rangle \langle \psi_g^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t')| V_{F1} |\psi_g^{(1)}, \psi_g^{(2)}\rangle \langle \psi_g^{(2)}, \psi_g^{(1)}|$,
 $\tilde{V}_{F2} = |\pi_{ND}^{(1)}(k^{(1)}, t''), \psi_e^{(2)}\rangle \langle \psi_e^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t'')| V_{F2} |\pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)}\rangle \langle \psi_g^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t')|$, and
 $\tilde{V}_{12} = |\pi_{ND}^{(1)}(p^{(1)}, t), \pi_{ND}^{(2)}(p^{(2)}, t)\rangle \langle \pi_{ND}^{(2)}(p^{(2)}, t), \pi_{ND}^{(1)}(p^{(1)}, t)| V_{12} |\pi_{ND}^{(1)}(k^{(1)}, t''), \psi_e^{(2)}\rangle \langle \psi_e^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t'')|$.
 Note, $|\psi_g^{(1)}, \psi_g^{(2)}\rangle \langle \psi_g^{(2)}, \psi_g^{(1)}|$ is a projector onto the two-electron field free ground state.

$|\pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)}\rangle \langle \psi_g^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t')|$ projects the first electron onto the continuum state while projects the second electron onto the field free ground state.

$\left| \pi_{ND}^{(1)}(k^{(1)}, t''), \psi_e^{(2)} \right\rangle \left\langle \psi_e^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t'') \right|$ projects the first electron onto the continuum state and projects the second electron onto an excited ionic state.

$\left| \pi_{ND}^{(1)}(p^{(1)}, t), \pi_{ND}^{(2)}(p^{(2)}, t) \right\rangle \left\langle \pi_{ND}^{(2)}(p^{(2)}, t), \pi_{ND}^{(1)}(p^{(1)}, t) \right|$ projects both electron onto the continuum state. The simplified transition amplitude for mechanism 1 becomes

$$M_1 \left(\pi_{ND}^{(1)}(p^{(1)}), \pi_{ND}^{(2)}(p^{(2)}), t, t' \right) = \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt'' \int_{-\infty}^{t''} dt' \left\langle \pi_{ND}^{(2)}(p^{(2)}, t), \pi_{ND}^{(1)}(p^{(1)}, t) \right| V_{12}(t) \left| \pi_{ND}^{(1)}(k^{(1)}, t') \psi_e^{(2)} \right\rangle \left\langle \psi_e^{(2)} \right| V_{F2}(t'') \left| \psi_g^{(2)} \right\rangle \left\langle \pi_{ND}^{(1)}(k^{(1)}, t') \right| V_{F1}(t') \left| \psi_g^{(1)} \right\rangle e^{-iS(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, k, t, t', t'')} \quad (6.5)$$

where the phase is represented by

$$S \left(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, k, t, t', t'' \right) = -\frac{1}{2} \int_t^{\infty} d\tau \left(\pi_{ND}^{(1)}(p^{(1)}, \tau) \right)^2 - \frac{1}{2} \int_t^{\infty} d\tau \left(\pi_{ND}^{(2)}(p^{(2)}, \tau) \right)^2 - \frac{1}{2} \int_{t'}^t d\tau \left(\pi_{ND}^{(1)}(k, \tau) \right)^2 + E_e^{(2)}(t - t'') + E_g^{(2)}t'' + E_g^{(1)}t' \quad (6.6)$$

where the energy $E_g^{(1)}$ denotes the first ionization potential, $E_g^{(2)}$ the ground-state energy of the parent cation and $E_e^{(2)}$ the energy of the state to which the second electron is excited. The intermediate momentum of the first electron is given by k and the final momenta of both electrons by $p^{(1,2)}$. The full transition amplitude for mechanism 1 of ED-REFLMS describes a physical process in which the first electron leaves the atom at a time t' , propagates in the continuum with momentum k from t' to t , and upon return, kicks off the electron in the excited state of the cation. The second electron was promoted from a ground cationic state with energy $E_g^{(2)}$ to an excited cationic state with energy $E_e^{(2)}$ at time t'' . Both electron reaches the detector with momentum $p^{(1)}$ and $p^{(2)}$.

Mechanism 2: Evolution of the parent ion after recollision. The interaction between the EM field and the neutral molecule is described by the interaction Hamiltonian $\hat{V}_{F1}$ at time t' . At t' the first electron is ionized creating a parent cation with the second electron remaining in the ground state. The time evolution of the liberated electron is described by the Volkov time propagator $U_V^{(1)}(t'', t')$, the electron propagates in the continuum between ionization time t' and the recollision time t'' . At t'' , the liberated electron recollides with the ground cationic state, through the interaction $\hat{V}_{12}$, and promotes the cation to a highly excited Rydberg-like state because the recolliding energy of the liberated electron is not sufficient to directly ionize the second electron. The remnant laser field interacting with the highly excited cation, $\hat{V}_{F2}(t)$, can induce chiral sensitive photon transitions which can eventually lead to the removal of a second electron at time t . The propagator $U_e^{(2)}(t, t'')$ describes the evolution of a second electron in an excited cation Rydberg-like state after recollision time t .

The mechanism is chiro-sensitive due to the i) chiral-chiral interaction between the coupling of the chiral molecular multipoles of the ion with rotating electric and magnetic driving field expressed by the term $\langle \pi_{ND}^{(2)}(p^{(2)}) | \tilde{V}_F(t'') | \psi_e^{(2)} \rangle$, the electric and magnetic dipoles coupling term and ii) the collision between the chiral electron and the ion, $\langle \pi_{ND}^{(1)}(p^{(1)}, t), \psi_e^{(2)} | V_{12} | \pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)} \rangle$. The transition amplitude for mechanism 2 becomes

$$M_2(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, t, t', t'') = \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt'' \int_{-\infty}^{t''} dt' \langle \Phi_{ND}^V(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}; r_1, r_2; t) | U_V^{(1)}(\infty, t) \otimes U_V^{(2)}(\infty, t) \tilde{V}_{F2}(t)(t) U_V^{(1)}(t, t'') \otimes U_e^{(2)}(t, t'') \tilde{V}_{12}(t'') U_V^{(1)}(t'', t') \otimes U_g^{(2)}(t'', t') \tilde{V}_{F1}(t') U_g^{(1)}(t', t_0) \otimes U_g^{(2)}(t', t_0) | \psi_g^{(1)}, \psi_g^{(2)} \rangle \quad (6.7)$$

For convenience, we consider only two electrons and approximate them as a product state. We can write the transition amplitude in a more useful form by introducing the projectors.

$$\begin{aligned} \text{Where } \tilde{V}_{F1} &= | \pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)} \rangle \langle \psi_g^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t') | V_{F1} | \psi_g^{(1)}, \psi_g^{(2)} \rangle \langle \psi_g^{(2)}, \psi_g^{(1)} |, \\ \tilde{V}_{12} &= | \pi_{ND}^{(1)}(p^{(1)}, t''), \psi_e^{(2)} \rangle \langle \psi_e^{(2)}, \pi_{ND}^{(1)}(p^{(1)}, t'') | V_{12} | \pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)} \rangle \langle \psi_g^{(2)}, \pi_{ND}^{(1)}(k^{(1)}, t') |, \text{ and} \\ \tilde{V}_{F2} &= | \pi_{ND}^{(1)}(p^{(1)}, t), \pi_{ND}^{(2)}(p^{(2)}, t) \rangle \langle \pi_{ND}^{(2)}(p^{(2)}, t), \pi_{ND}^{(1)}(p^{(1)}, t) | V_{F2} | \pi_{ND}^{(1)}(p^{(1)}, t''), \psi_e^{(2)} \rangle \langle \psi_e^{(2)}, \pi_{ND}^{(1)}(p^{(1)}, t'') |. \end{aligned}$$

where the projector is similar to mechanism 1. The simplified transition amplitude for mechanism 2 becomes

$$\begin{aligned} M_2(\pi_{ND}^{(1)}(p^{(1)}), \pi_{ND}^{(2)}(p^{(2)}), t'', t') &= \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt'' \int_{-\infty}^{t''} dt' \langle \pi_{ND}^{(2)}(p^{(2)}, t) | V_{F2}(t) | \psi_e^{(2)} \rangle \\ &\langle \pi_{ND}^{(1)}(p^{(1)}, t''), \psi_e^{(2)} | V_{12}(t'') | \pi_{ND}^{(1)}(k^{(1)}, t'), \psi_g^{(2)} \rangle \langle \pi_{ND}^{(1)}(k^{(1)}, t') | V_{F1}(t') | \psi_g^{(1)} \rangle e^{-iS(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, k, t, t', t'')} \end{aligned} \quad (6.8)$$

where the phase is given by

$$\begin{aligned} S(\pi_{ND}^{(1)}, \pi_{ND}^{(2)}, k, t, t', t'') &= -\frac{1}{2} \int_{t''}^{\infty} d\tau (\pi_{ND}^{(1)}(p^{(1)}, \tau))^2 - \frac{1}{2} \int_t^{\infty} d\tau (\pi_{ND}^{(2)}(p^{(2)}, \tau))^2 \\ &- \frac{1}{2} \int_{t'}^{t''} d\tau (\pi_{ND}^{(1)}(k, \tau))^2 + E_e^{(2)}(t - t'') + E_g^{(2)}t'' + E_g^{(1)}t' \end{aligned} \quad (6.9)$$

The full transition amplitude for mechanism 2 of ED-REFLMS describes a physical process in which the first electron leaves the atom at a time t' , propagates in the continuum with momentum k from t' to t'' , and upon return, gives part of the kinetic energy to the core ion so the second electron is promoted from a state with energy $E_g^{(2)}$ to an excited cationic state with energy $E_e^{(2)}$ at time t'' . The first electron reaches the detector with momentum $p^{(1)}$. At a subsequent time t , the second electron tunnels from the excited state, reaching the

detector with momentum $p^{(2)}$.

Mechanism 3: The evolution of the liberated electron in the laser field. This mechanism shows the chiral trajectory of the liberated electron, thus acting as a chiral reagent. Consider the force felt by an electron in an electromagnetic field for right-handed elliptically polarized light, $\alpha\hat{x} + i\beta\hat{y}$, where α and β determine the degree of ellipticity of the light such that $|\alpha| + |\beta| = 1$. The polarization of magnetic field is $\hat{b} = \hat{z} \times \hat{e}$

$$\mathbf{F}_{RHC} = e\mathbf{E} + \mathbf{v} \times \mathbf{B} = eE(\alpha\hat{x} + i\beta\hat{y}) + eB(v_x\hat{x} + v_y\hat{y} + v_z\hat{z}) \times (-i\beta\hat{x} + \alpha\hat{y}) \quad (6.10)$$

$$\mathbf{F}_{RHC} = eE(\alpha\hat{x} + i\beta\hat{y}) + eB(-\alpha v_z\hat{x} - i\beta v_z\hat{y} + (\alpha v_x + i\beta v_y)\hat{z}) \quad (6.11)$$

Let's apply the reflection operator $\hat{\sigma}_y$, which is a unitary operator, $\hat{\sigma}_y\hat{\sigma}_y^\dagger = 1$, acting only on the y-component. $\hat{\sigma}_y|RHC\rangle\hat{\sigma}_y^\dagger = \hat{\sigma}_y(\alpha\hat{x} + i\beta\hat{y})\hat{\sigma}_y^\dagger = \alpha\hat{x} - i\beta\hat{y} = |LHC\rangle$. Therefore, when the reflection operator acts on the right-handed elliptical light it transforms it to left-handed. A similar operation can be performed on the Force.

$$\hat{\sigma}_y\mathbf{F}_{RHC}\hat{\sigma}_y^\dagger = \hat{\sigma}_y[eE(\alpha\hat{x} + i\beta\hat{y}) + eB(-\alpha v_z\hat{x} - i\beta v_z\hat{y} + (\alpha v_x + i\beta v_y)\hat{z})]\hat{\sigma}_y^\dagger \quad (6.12)$$

$$\hat{\sigma}_y\mathbf{F}_{RHC}\hat{\sigma}_y^\dagger = eE(\alpha\hat{x} - i\beta\hat{y}) + eB(-\alpha v_z\hat{x} + i\beta v_z\hat{y} + (\alpha v_x - i\beta v_y)\hat{z}) \quad (6.13)$$

This is the force acting on the electron for a right-handed elliptical field under the reflection operator which is not identical to the force acting on the electron for a left-handed elliptical field given by

$$\mathbf{F}_{LHC} = eE(\alpha\hat{x} - i\beta\hat{y}) + eB(-\alpha v_z\hat{x} + i\beta v_z\hat{y} + (\alpha v_x - i\beta v_y)\hat{z}) \quad (6.14)$$

resulting in a difference in the recollision dynamics. Moreover, using the parity operator we can see that the force from the laser field, from a left- or right-handed elliptical field, felt by the electron is similar in magnitude, however, the clockwise nature of the propagating electron is opposite, $\mathbf{F}_{RHC} \neq \mathbf{F}_{LHC}$. Symmetry can elucidate the difference in the electron trajectories. Thus, in the non-dipole approximation the electron behaves as a chiral reagent during propagation (between time t' and t_r). Without the magnetic field, the force on the electron would be identical.

6.3 ORBITAL ANGULAR MOMENTUM CONTROL OF STRONG-FIELD PHYSICS IN GAS PHASE

Recent advancements in strong-field ionization and electron dynamics have been largely due to the effects of polarization and carrier-envelope phase. However, with the newly emerged asymmetrical OAM beam, an additional degree of control in the form of OAM value can be employed to influence the ionization and recollision dynamics.

In this article, submitted to *Nature Physics*, we demonstrate that the tunnel ionization of atoms and molecules is strongly influenced by the sign and value of the OAM. This can be further manipulated by displacing the phase-singularity in the vortex beam. We reveal that the field gradients and the helical handedness of an asymmetric OAM beam directly influence the degree of distortion of the atomic and molecular potential, leading to l -dependent tunnel ionization and helical dichroism in both atoms and molecules (chiral and achiral).

Our approach includes the contribution of multipole moments, specifically the electric-quadrupole and magnetic-dipole, during strong-field ionization with linearly polarized, asymmetric helical light beams. We validate our experimental findings by extending Keldysh theory of SFA beyond the dipole approximation and incorporating the spatial profile of Laguerre-Gaussian beams into the analysis.

Furthermore, we demonstrate that the peak ponderomotive energy and average ponderomotive force increase with the OAM value and can be controlled by adjusting the displacement of the singularity in the vortex beam. Therefore, with an asymmetric OAM beam, a threefold increase in ponderomotive energy for $l = 9$ is achieved compared to a Gaussian beam. This results in extending the cut-off harmonics by the same amount without the need for a laser operating at longer wavelengths.

We conclude that ionization effects and photoelectron dynamics can be manipulated by varying the degree of OAM and the asymmetry in the optical probe.

The key advantages of our work:

- (i) Demonstration of OAM-dependent ionization in atoms and molecules. These results show that both atoms with spherical symmetry and molecules with broken symmetry are responsive to the helical phase of the incident light.
- (ii) Challenging the conventional wisdom that tunnel ionization is purely a peak field phenomenon. The field gradient of an asymmetrical probe combined with its OAM value affects the probability of ionization and directly influences the plasma density.
- (iii) Control and precise tuning of differential ionization by the displacement of singularity present in an OAM beam. This unique feature of our technique can be implemented in other chiroptical techniques such as PECD to enhance their efficiency of detection.

- (iv) Extension to Keldysh ionization model. With the contribution of the higher-order multipole moments, the chiral probe is shown to affect the distortion of Coulombic potential.
- (v) Scaling of the peak ponderomotive energy with l -value. This directly influences the recollision dynamics and can have implications in the three-step model via the HHG and NSDI.
- (vi) The variation of average ponderomotive force as a function of the position of singularity and l -values. This enhancement can facilitate the acceleration of charged particles in plasma physics.

We show that asymmetrical helical light distorts the atomic and molecular potential resulting in l -dependent ionization. This distortion of Coulomb potential can have a profound influence on the photoelectron angular distribution. By implementing the chiral probe with previously established gas phase chiroptical techniques such as PECD it could significantly improve their efficiency of detection. Moreover, the OAM control of single ionization can be easily extended to the study of doubly and triply charged ions. An asymmetrical OAM beam is shown to affect the ponderomotive energy which should influence the well-known NSDI knee shape as well as the electron wave packet spreading which can be investigated with ellipticity variation.

Asymmetrical OAM beams provide additional parameters to control extreme nonlinear processes in attosecond physics, recollision physics, plasma physics, and gas phase chiroptical detection. We believe our work will have a large impact on the future development of strong-field physics and its spectroscopic applications. The research should be applicable and intriguing for a very broad audience and merits publication in the leading magazine addressed to such an audience.

6.3.1 ADVANCEMENT IN STRONG-FIELD PHYSICS

Irradiation of an atom or a molecule by an intense laser pulse can cause the valence electron to overcome the potential barrier and transition into the continuum, leading to ionization. This process occurs when the laser field strength is comparable to the Coulomb field of the atom or molecule. The non-resonant strong field ionization is significantly impacted by the peak of the laser field and can be manipulated by varying the carrier-envelope phase [102], pulse shaping [103–105], coherent control [106, 107], and utilization of bichromatic light fields [108].

The freed electron experiences a quiver motion in the presence of the oscillating electric field of the laser, acquiring ponderomotive energy that scales linearly with the laser intensity and quadratically with the wavelength. This energy is pivotal in HHG process and serves as a foundation for attosecond science. The recombination of the ionized electron with the parent ion produces energetic photons extending up to soft X-rays within the water window. Rescattering between the laser-driven photoelectron wave packet and the parent ion also provides access to the molecular structure via laser-induced electron diffraction [109–111] and nuclear dynamics [82, 112, 113]. The dynamics of the ionized electron can be controlled with attosecond precision by the polarization of

light and customized optical waveforms [114]. Moreover, spatial gradients in the amplitude of the oscillating electric field generate ponderomotive force, a time-averaged force acting on charged particles, propelling them towards regions of weaker field strength. Ponderomotive force is a fundamental concept in plasma physics, extensively utilized to manipulate and control the motion of charged particles. It is integral to various laser-driven electron acceleration mechanisms, including direct laser acceleration [115–117] and acceleration by laser-driven plasma [118–121].

The primary focus of advancements in strong field and plasma physics revolved around the interaction of matter with Gaussian light beams. These beams exhibit a spatially symmetric field profile with a planar wavefront at their beam waist. In such beams, the contribution of field gradients to ionization is often neglected due to spatial averaging over the entire interaction region. Consequently, most theoretical models describe strong-field dynamics using the dipole approximation. For Gaussian beams, the two key factors significantly influence the electron dynamics: the peak strength of the electric field dictated by the carrier-envelope phase and the Spin Angular Momentum (SAM) that determines the polarization state of light.

Light can also carry OAM denoted by $\pm\hbar$, associated with the dynamic rotation of the wavefront structure. In OAM beams, the wavefront deviates from being planar and exhibits a handedness determined by the twist of the wavefront as it undergoes l intertwined rotations within one wavelength. Due to this twisting, light waves cancel each other along the beam axis, resulting in an optical vortex—a null intensity region at the center. These optical vortex beams are also known as helical light beams. OAM manifests as an azimuthal phase dependence in the plane perpendicular to the beam direction, providing an additional degree of freedom to influence light-matter interactions. Transfer of optical OAM to internal degrees of freedom of an atom requires multipolar transitions [122] leading to new position-dependent selection rules for absorption of twisted light by bound electron [123–126]. Interestingly, OAM-dependent nonlinear absorption of twisted light has been recently demonstrated in chiral and achiral systems, a phenomenon attributed to quadrupolar transitions that are frequently overlooked [127–129].

Most studies in strong field physics have employed symmetric OAM beams where the phase singularity (and consequently, the null intensity region) is at the center of the beam. For instance: (i) twisted driving light fields have been harnessed to generate twisted extreme ultraviolet light through HHG [130–134]. (ii) The OAM of an intense vortex pulse was probed via strong field photoionization involving two colors, co-rotating intense circular fields [135]. (iii) The effects of twisted electrons [136–138] were investigated using HHG [139] and rescattering photoelectron spectroscopy [140, 141]. (iv) The impact of OAM on photoelectrons has been explored theoretically [140, 142–144] and experimentally [145, 146] through the formation of interference vortices. However, the impact of asymmetric OAM (helical light) beams on the ionization of atoms and molecules along with the electron dynamics remains elusive. In such beams, the displaced phase singularity generates uneven field gradients, resulting in higher peak field strengths compared to symmetrical OAM beams. These field gradients significantly affect ionization, rendering the dipole approximation inadequate. Consequently, strong-

field ionization with asymmetrical helical beams necessitates extending the analysis beyond the dipole regime.

In this section, we demonstrate that strong field ionization of atoms and molecules depends on the OAM (specifically, the sign and value of l) when the phase singularity in the vortex beam is shifted away from the center. Ion yields increase significantly for a specific handedness of helical light, exhibiting the opposite behaviour for the other handedness. This selective ionization leads to helical dichroism in both atoms and molecules. Additionally, we simulate the ionization behaviour of Argon atoms by extending the Strong-Field Approximation (SFA) beyond the dipole approximation. We include the contribution of multipole moments during tunnel ionization for an asymmetrical LG beam. The OAM dependence of tunnel ionization arises due to field gradients in an asymmetric beam, resulting in differences in the distortion of the atomic potential when the handedness of helical light changes. Finally, we demonstrate that the peak ponderomotive energy and average ponderomotive force increase with the OAM value and can be controlled by adjusting the displacement of the singularity in the vortex beam. The control and tunability of ionization and the electron energy, demonstrated in this article, by manipulating the phase of asymmetric OAM beam paves the way for new opportunities. In spectroscopy, it allows to probe conformational changes in molecules with enhanced spatial resolution. In attosecond science, it enables efficient generation of higher-order harmonics at shorter wavelengths. In plasma physics, it facilitates efficient production of higher-energy charged particles, and by modifying the plasma density, laser filamentation can be effectively employed for remote sensing applications.

6.3.2 EXPERIMENTAL METHODS

To probe OAM-dependent strong field ionization of atoms and molecules we measured the ion yields using a time-of-flight mass spectrometer. A q-plate was used to convert the incident Gaussian beam to an OAM beam via spin-orbit coupling. Translating q-plate with respect to the incident beam generated asymmetric OAM beams in which the phase singularity (and hence the null intensity region) is displaced within the focal spot.

6.3.2.1 IONIZATION MEASUREMENTS

Experiments were conducted by focusing near-infrared femtosecond laser pulses with a parabolic mirror in the interaction region of a TOFMS housed inside a differentially pumped vacuum chamber. A Ti:Sapphire laser system (Spitfire, Spectra-Physics) operating at $\lambda = 800\text{nm}$ and a repetition rate of 1 KHz produced ~ 40 fs pulses with a maximum pulse energy of ~ 2.5 mJ. A combination of a half-wave plate and a polarizer were used to control the pulse energy. The pulse duration was continuously monitored by a single-shot autocorrelator. A fast photodiode was used to continuously monitor the laser pulse energy incident on a 3 mm thick quartz window on the vacuum chamber. The ions produced in the interaction region of TOFMS, operated in Wiley-McLaren geometry, travel through a field-free region of 30 cm after acceleration and are detected by a microchannel plate. The signal is then amplified, discriminated, and recorded by a time digitizer to generate a TOF mass

spectrum. A precision leak valve was used to introduce atoms and molecules in the gas phase. The pressure inside the vacuum chamber was maintained at $\sim 1.3 \times 10^{-6}$ Torr. Organic compounds like limonene and acetone had sufficient vapour pressure, at room temperature, to be introduced in the gas phase. They were subjected to freeze-and-thaw cycles to minimize contamination of the interaction region. To minimize number density fluctuations, the chemicals in the glass vial were immersed in a temperature bath at 22°C and the gas line along with the leak valve were maintained at a positive temperature gradient. The S-limonene and R-limonene were sourced from Sigma Aldrich with a purity of 96% and 97%, respectively. Measurements in limonene and acetone were performed at an intensity of $8 - 9 \times 10^{13} \text{W/cm}^2$, below the measured saturation intensities of $\sim 12 - 13 \times 10^{13} \text{W/cm}^2$. Measurements in argon were performed at an intensity of $9 - 15 \times 10^{13} \text{W/cm}^2$. The differential ionization curves were obtained by displacing the position of singularity in the cross-section of the OAM beam. A pair of mass spectra, measured for 100,000 laser shots, were recorded for each handedness of the incident helical light. Fluctuations of the ion yields and error bars related to the differential ionization signal were computed based on repeated measurements under similar conditions.

6.3.2.2 CALIBRATION OF MASS SPECTROMETER, LASER INTENSITY AND ELLIPTICITY

Mass calibration was achieved using Xenon atoms. The mass resolution of the spectrometer (full width at half maximum) was 550 at an m/z (mass-to-charge ratio) of 132. Laser intensity was calibrated by measuring the saturation intensity of argon. This was achieved by plotting Ar^+ yields as a function of pulse energy. The intercept on the energy axis of the semi-log plot corresponds to the theoretical saturation intensity of $\sim 2.5 \times 10^{14} \text{W/cm}^2$. The extracted focal spot size in the interaction region was $3 \pm 0.2 \mu\text{m}$, in agreement with previous measurements. A third QWP was used to change the ellipticity, ϵ , of the polarized helical light beam. It was calibrated by measuring the ellipticity dependence of doubly charged argon. We obtained $\epsilon = 0.05$ for linear polarization and $\epsilon = \pm 0.96$ for circular polarization, with an uncertainty of ± 0.02 . The ellipticity was varied in steps of 0.04 around linear polarization and in steps of 0.08 beyond $\epsilon = 0.2$.

6.3.2.3 GENERATION OF OAM BEAMS AND DISPLACEMENT OF SINGULARITY

A QWP on a motorized rotation stage (with a $\pm 0.005^\circ$ resolution) was used to generate circularly polarization light incident on a liquid-crystal-based phase plate (q-plate). The incident circularly polarized Gaussian beam propagating through the q-plate with a topological charge q , acquires an OAM defined by $l = \pm 2q$, with a phase singularity and hence a null intensity region at the centre of the beam, known as an optical vortex. The handedness of the incident circular polarization determines the direction of rotation of the wavefront structure. A second QWP was used to generate linearly polarized OAM beams. The conversion efficiencies of the q-plates were $\sim 86 \pm 2\%$ for $l = 1$ and $\sim 88 \pm 2\%$ for $l = 3$. The singularity in the OAM beam was displaced by translating the q-plate mounted on an x-, y-, and z-translation stage. Micrometre screw gauge with a step size

of $500 \pm 10 \mu\text{m}$. When focused by the parabolic mirror this translated to a displacement step size of $330 \pm 60 \text{ nm}$ in the interaction region with respect to the centre of the beam. The calibration was achieved by measuring the total translation required to displace the singularity to the periphery of the defocused beam and comparing it to the measured spot size of $3 \pm 0.2 \mu\text{m}$.

6.3.3 OAM DEPENDENT IONIZATION OF ATOM AND MOLECULES

Figure 6.2a displays the mass spectrum of R(+)-limonene, a chiral molecule, obtained with a linearly polarized symmetric OAM beam for $l = \pm 1$. The peak at $m/z=136$ corresponds to the singly charged parent ion, $C_{10}H_{16}^+$, while the peak at $m/z = 68$ corresponds to both the fragment $C_5H_8^+$ and doubly charged parent ion $C_{10}H_{16}^{2+}$. The latter were differentiated using the isotopomer of the parent ion $^{13}C_{12}C_9H_{16}^+$ ($m/z=137$). The inset shows the OAM beam profile. The mass spectrum is nearly identical for $l = 1$ (red) and $l = -1$ (black) suggesting that ionization does not depend on the handedness of the helical light.

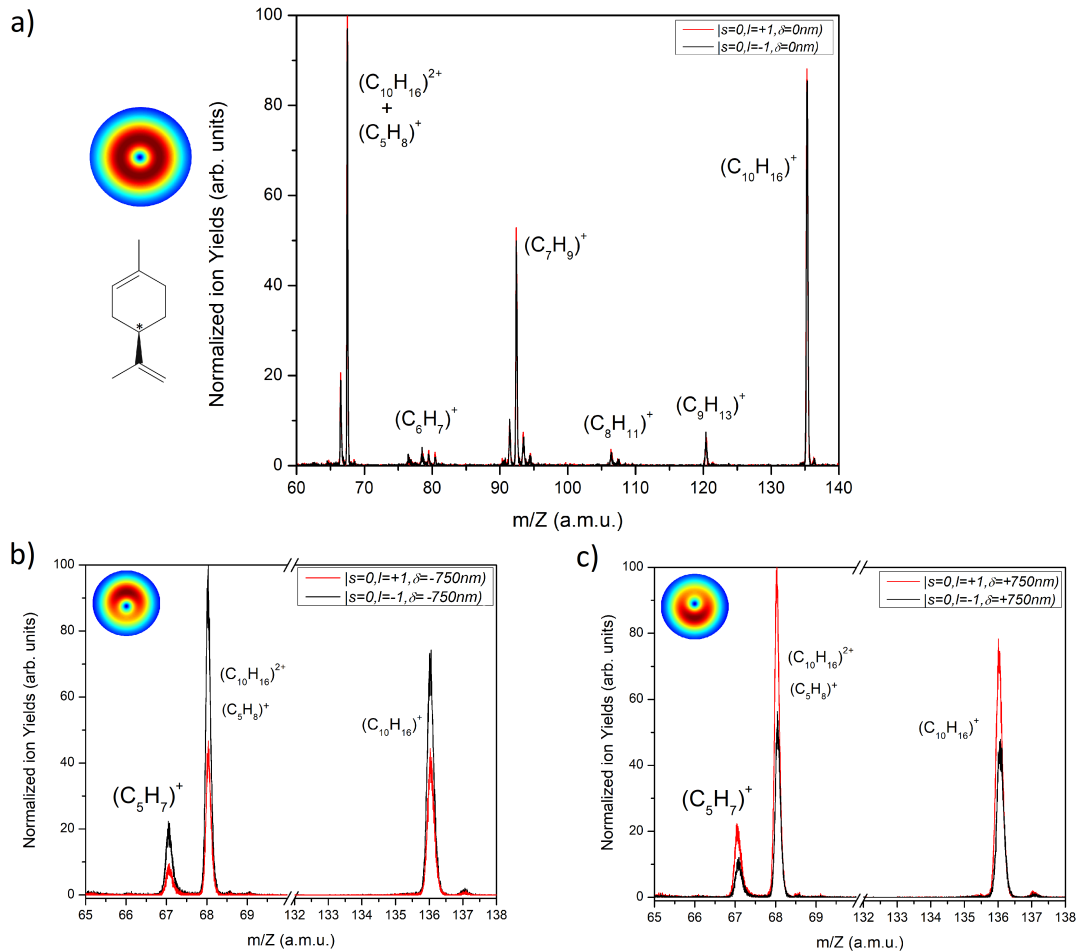


Figure 6.2: **Mass spectrum of R(+)-limonene for opposite helicities.** **a)** Symmetric OAM beam ($\delta = 0$) for $l = -1$ (black) and $l = +1$ (red). **b)** Asymmetric OAM beam ($\delta = -750 \text{ nm}$) for $l = -1$ (black) and $l = +1$ (red). **c)** same as (b) for $\delta = 750 \text{ nm}$. The laser polarization is linear ($s = 0$) and the wavelength and intensity were 800 nm and $8 \times 10^{13} \text{ W/cm}^2$, respectively. The insets show the intensity profile of LG beams.

Figure 6.2b,c shows the mass spectrum taken at two distinct positions of the singularity, $\delta = \pm 750\text{nm}$, away from the center. The insets show the beam profile at the corresponding δ -positions. When $\delta = -750\text{nm}$, the ionization yields are stronger for $l = -1$ compared to $l = +1$ (Fig.6.2b). When the singularity was moved from one side of the zero position to the opposite side, the behaviour of the ion yields changed with respect to the helicity of the light, and now the yields from $l = +1$ dominate over $l = -1$ (Fig.6.2c). Fig.6.2 suggests ionization yields are strongly influenced by the helicity of an asymmetric OAM beam and could be controlled by varying the position of the singularity.

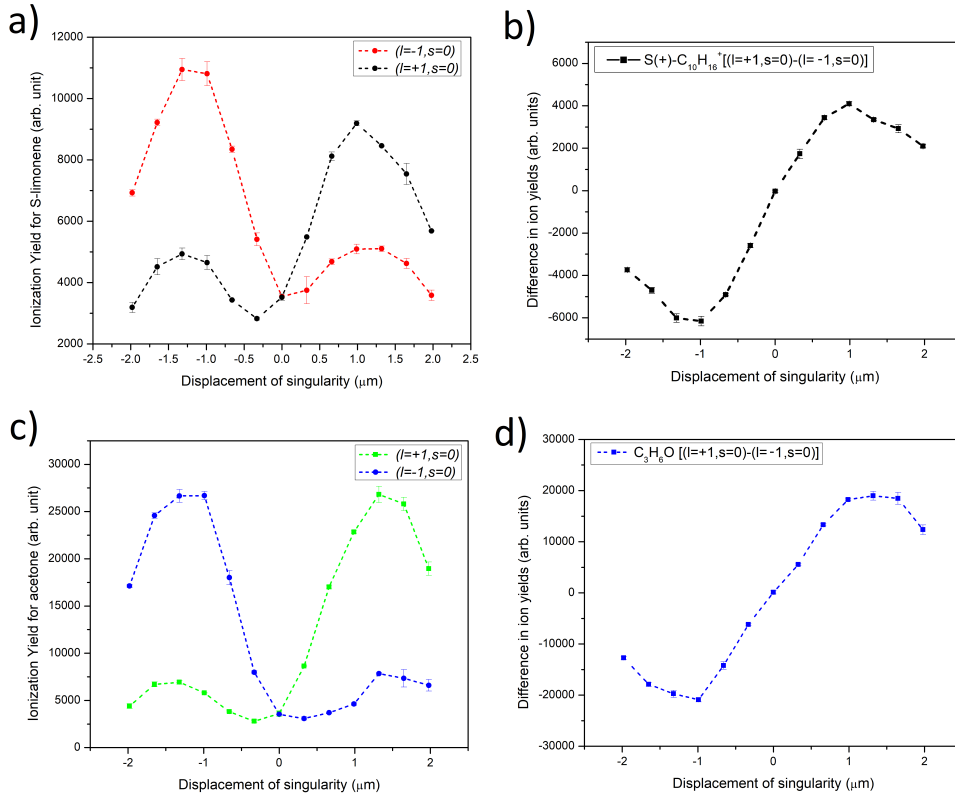


Figure 6.3: **OAM dependent ionization in molecules.** Single ionization yields for $l = +1$ (black) and $l = -1$ (red) as a function of displacement of the singularity in **a)** R(+)-limonene, **c)** acetone. **b), d)** shows the difference in the ionization yields between the left- and right-helical light for the respective molecules. The laser polarization was linear ($s = 0$) and the intensity was $8 \times 10^{13} \text{ W/cm}^2$ and $9 \times 10^{13} \text{ W/cm}^2$ for limonene and acetone, respectively.

Fig. 6.3a,c illustrate the variation of the singly charged ion yields for two specific molecules: R(+)-limonene and acetone (an achiral molecule). These measurements were taken as a function of the singularity position (δ) for $l = \pm 1$. The δ -dependence of ion yields for $-l$ mirrors that of the $+l$ around $\delta = 0$, where the ion yields are identical. For a specific handedness of helical light, both molecules exhibit an asymmetric double bump structure. The increase in the ion yields for an asymmetric OAM beam arises from the growing peak field strength and the change of the field gradient as the singularity is displaced (refer to insets in Fig.6.2). However, at large δ positions, the ion yields decrease because of the diminishing peak field as the beam profile starts resembling a Gaussian-like beam. At a specific δ -position, the difference in ionization between the left- and right-helical light persists up to saturation intensity (Fig. S6.10 in Supplementary).

Selective ionization with linearly polarized asymmetric helical light of opposite handedness leads to dichroism - a property typically observed in chiral molecules with broken symmetry. In our case, the interplay between the helicity of light and the broken symmetry, introduced by the δ -parameter, results in a differential response. Fig.6.3b,d illustrate the difference in ionization of R(+)-limonene (see Fig.S6.11 for the other enantiomer) and acetone, respectively, when subjected to linearly polarized helical light of opposite handedness. This difference denoted as $\Delta Y = Y(l = +1, s = 0) - Y(l = -1, s = 0)$, is known as Helical Dichroism (HD) and exhibits a characteristic sinusoidal shape. This phenomenon is akin to the recently observed nonlinear absorption of helical light in liquids and solids [127–129]. As δ increases, ΔY initially rises until around $\delta = 1\mu\text{m}$, after which it decreases as the position of the singularity approaches the periphery of the beam's cross-section. Similar results were obtained when the laser polarization was changed from linear to circular (see Fig. S6.13 in the Supplementary). For a specific δ position, the ion yields are predominant for one-handedness irrespective of the ellipticity of light (see Fig. S6.14, S6.15 in the Supplementary).

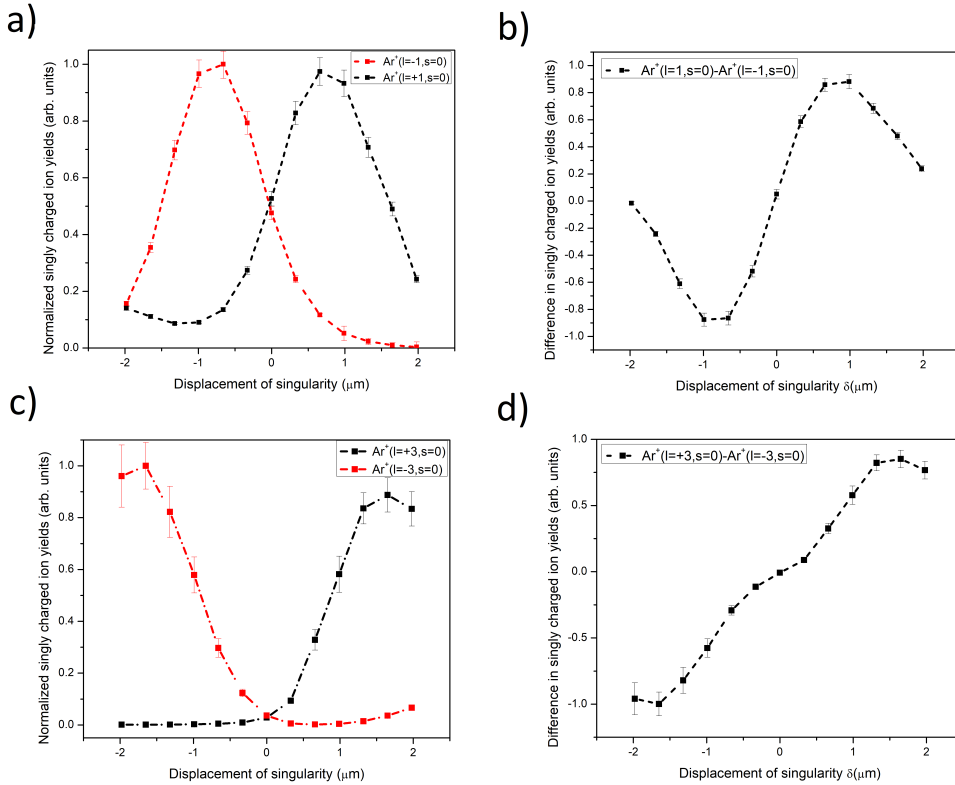


Figure 6.4: **OAM control of ionization of argon atom** **a)** Single ionization yields of argon for $l = +1$ (black) and $l = -1$ (red). **b)** Difference in ionization between left and right-handed helical light ($l = 1$). **c)** Single ionization yields of argon for $l = +3$ (black) and $l = -3$ (red). **d)** left and right-handed helical light ($l = 3$). The laser polarization was linear ($s = 0$) and the intensity for $l = 1$ was 10^{14} W/cm² and $l = 3$ was 1.5×10^{14} W/cm².

The phenomenon of OAM-dependent ionization is not limited to molecules; it also extends to atoms. Fig. 6.4a,c illustrate the variation of the normalized singly charged argon ion yields as a function singularity position. The black curves in a,c correspond to linearly polarized light $l = +1, +3$ while the red curve represents $l = -1, -3$. At higher l -values, the ratio of the maximum ion yields at $\delta \neq 0$ to the ion yields at $\delta = 0$ increases

for a specific handedness of the helical light. Similar to molecules, the δ -dependence of ion yields for $l = -1, -3$ mirrors that of the $l = +1, +3$ around $\delta = 0$. However, argon does not exhibit a double bump structure for a specific helicity of light. This is due to differences in their ionization potentials. In molecules, ionization occurs at lower peak fields leading to less suppression of ion yields relative to argon at $\delta = \pm 1 \mu m$. The differential ionization of argon in Figure 6.4b exhibits the signature sinusoidal behaviour as observed in chiral and achiral molecules. Notably, fig. 6.4d exhibits an intriguing feature around $\delta = 0$, resembling an inflection point. This behaviour is affected by the incident intensity and arises because the size of the singularity is greater for $l = 3$ relative to $l = 1$, necessitating a larger displacement to observe an appreciable increase in ion yield. Such an inflection point around $\delta = 0$ was also observed in limonene for $l = 3$ (See Fig.S6.12 in Supplementary).

6.3.4 SIMULATED OAM DEPENDENT IONIZATION OF ARGON

To understand the origin of OAM-dependent ionization we considered SFA of tunnel ionization and extended it to include contributions from multipole moments for an asymmetrical LG beam. In standard SFA model, the transition amplitude from the ground to the final state is given by [40, 65, 77]

$$M_{fg} = -i \int_{t_0}^t \langle \psi_V(t') | V(t') | \psi_g(t') \rangle dt' \quad (6.15)$$

where $\langle \psi_V(t') |$ is the Gordon-Volkov continuum wavefunction, which is a plane wave modulated by the laser field, $V(t')$ is the interaction Hamiltonian within dipole approximation and $|\psi_g(t')\rangle$ is the ground state wavefunction.

To introduce higher order multipoles in the interaction Hamiltonian, we Taylor expanded the vector potential to the second order about a point R in the velocity gauge and transformed it to length gauge to obtain $\hat{V}(t') = r_i E_i(R, t') + \frac{1}{2} r_i r_j \widehat{\partial_j E_i}(R, t') + \frac{1}{2} L_i B_i(R, t')$, where $E_i(R, t)$ and $B_i(R, t)$ are the incident electric and magnetic field of the asymmetrical LG laser beam, $r_{i,j}$ is the distance between positive and negative charge in the atom frame and R represent the coordinates of the laser beam profile. $\widehat{\partial_j E_i}$ represents the field gradient and L_i is the orbital angular momentum of the magnetic dipole transition moment (for full multipole expansion derivation see Appendix A.1).

The expanded Gordon-Volkov wavefunction that includes the higher order multipoles is therefore given by

$$\Psi_V(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i(p+A(R, t') - \int_{t'}^t \widehat{\partial_R A}(R, \tau)(p+A(R, \tau))d\tau) \cdot r} e^{-\frac{i}{2} \int_{t'}^t (p+A(R, t'') - \int_{t''}^t \widehat{\partial_R A}(R, \tau)(p+A(R, \tau))d\tau)^2 dt''} \quad (6.16)$$

where $A(R, t)$ is the vector potential of the laser field, p is the electron momentum and $\widehat{\partial_R A}(R, t)$ is the vector potential gradient (for full derivation see appendix a.2). Within dipole approximation, the field gradient tensor term does not exist in the Gordon-Volkov wave function.

The full transition amplitude used to describe tunnel ionization probability is given by

$$M_{fg} = -i \int_{-\infty}^t \left[\underbrace{\langle \pi(p, t, t') | r_i | \psi_g \rangle E_i(R, t')}_{\text{E1}} + \underbrace{\frac{1}{2} \langle \pi(p, t, t') | r_i r_j | \psi_g \rangle \widehat{\partial_j E_i}(R, t')}_{\text{E2}} + \underbrace{\frac{1}{2} \langle \pi(p, t, t') | L_i | \psi_g \rangle B_i(R, t')}_{\text{M1}} \right] \times \exp \left(\frac{i}{2} \int_{t'}^t (\pi^2(p, t, t'') + 2I_p) dt'' \right) dt' \quad (6.17)$$

where

$$\pi(p, t, t'') = p + A(R, t'') - \int_{t''}^t \widehat{\partial_R A}(R, \tau) (p + A(R, \tau)) d\tau \quad (6.18)$$

Equation (6.17) consists of three terms: M_{fg}^{E1} , M_{fg}^{E2} , and M_{fg}^{M1} which are the electric dipole, electric quadrupole, and magnetic dipole transitions, respectively. The probability of transition is given by

$$P_{fg} = |M_{fg}^{\text{E1}} + cM_{fg}^{\text{E2}} + M_{fg}^{\text{M1}}|^2. \quad (6.19)$$

For argon, the ionization probability for symmetric and asymmetric LG beam is depicted in figure 6.6b. We used the ground state 3p-orbital of argon and the electric field represented by asymmetric LG beam (see chapter section 2.1.4) and solved the electric dipole, magnetic dipole and electric quadrupole transition matrix elements in momentum space represented by canonical momentum $\pi(p, t, t')$. The resulting time component of the transition from ground to the continuum was evaluated using saddle point integration (see section 6.3.5).

To simulate the differential ionization results, we plotted the total transition probability integrated over the beam cross-section, given by

$$\bar{P}_{fg} = \int_{-w_0}^{w_0} |M_{fg}^{\text{E1}} + cM_{fg}^{\text{E2}} + M_{fg}^{\text{M1}}|^2 dR \quad (6.20)$$

and shown in figure 6.5. c is a constant introduced to adjust the relative strength of the electric quadrupole transitions. Both magnetic dipole and electric quadrupole transitions are typically $\sim 10^{-5}$ - 10^{-6} times weaker compared to dipole transitions, with their strength scaling inversely with the square of the fine structure constant. The only coupling term that contains l -dependence is the E1E2 term due to the presence of the field gradient. The mixed-coupling term E1M1 is responsible for circular dichroism and does not contribute to the differential signal for linearly polarized light.

Figure 6.5a depicts differential ionization probability between left- and right-helical light as a function of displacement of the singularity for $l = \pm 1$ and ± 3 . These probabilities, obtained at $c = 1$, mirror the experimental results shown in Fig. 6.3b,d and Fig 6.4b,d. For higher l -values, the null intensity region is larger, leading to stronger field gradients and higher peak field strengths. Consequently, differential ionization

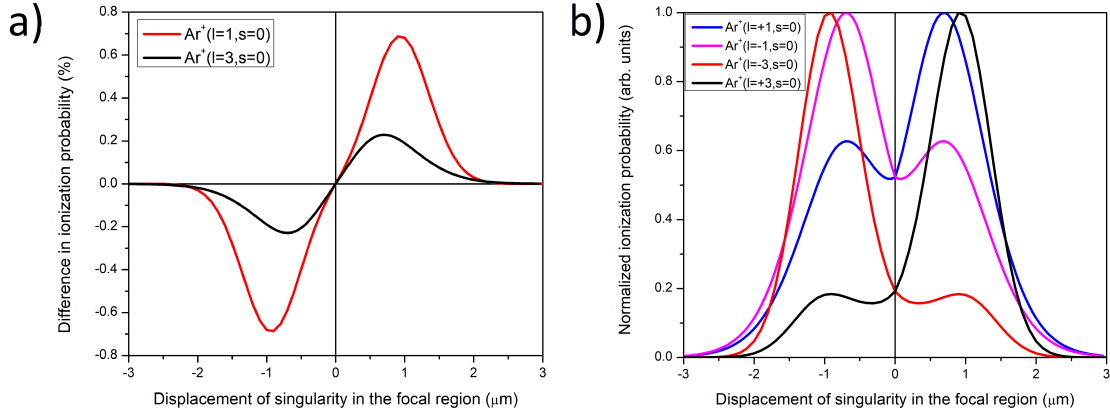


Figure 6.5: **Simulated differential ionization probability of argon.** **a)** Simulated difference in ionization probabilities of argon between left- and right-helical light for $l = 1$ in black and $l = 3$ in red, respectively. **b)** Single ionization probability of argon for $l = +1$ ($l = +3$) in black (blue) and $l = -1$ ($l = -3$) in red (magenta). They were obtained by solving Eq.6.20 for vertical polarization and intensity of 10^{14} W/cm^2 for $l = 1$ and $1.2 \times 10^{14} \text{ W/cm}^2$ for $l = 3$.

is enhanced but exhibits an inflection point around $\delta = 0$, accompanied by a change in the slope, as a larger displacement of the singularity are required to significantly alter the ion yield. This effect becomes more pronounced at higher laser intensities (see Supplementary Fig. S6.8a).

While the behaviour of differential ionization with asymmetry parameter δ is independent of the c -value, visualization and qualitative comparison of ionization probabilities with experimental ion yields from Fig. 6.3a,c necessitated amplifying quadrupole transitions. Fig. 6.5b illustrates the dependence of ionization probability on the displacement of the singularity for different l -values using $c = 200$. The electric quadrupole moments of atoms are known to be greatly enhanced, by a few orders, due to the hyperfine interaction of atomic electrons with the nucleus [147–150]. Since our theory excludes the Coulomb potential and thus ignores hyperfine interactions, higher c -values are required. Ionization as a function of δ -position exhibits an asymmetric double bump structure. This asymmetry increases with l -value, laser intensity and c -value (Fig. S6.8 Supplementary). It vanishes at low intensities and becomes prominent at higher intensities until the ground state is depleted. A quantitative comparison of the ionization probability with the experimental results of Fig. 6.4a,c could be obtained for $c = 200$ (see Supplementary Fig. S6.8b). The double bump structure remains unaffected by the angle through which the singularity is displaced across the center (Fig. S6.9 in Supplementary).

l -dependent ionization of an atom can be visualized by considering the distortion of an atomic potential, depicted in the schematic of Fig. 6.6a. For a Gaussian beam, the atomic potential is tipped by the applied electric field, allowing the electrons to tunnel through the barrier. The field gradients vanish for Gaussian beams when spatially averaged over the beam cross-section and therefore do not play a considerable role in ionization. In symmetric LG beams, beyond dipole approximation, the quadrupole term depends on the field gradient but vanishes upon spatial averaging. As a result, ionization is expected to be similar to a Gaussian beam. However, in asymmetric LG beams, the field gradient for both handedness at a specific position of the singularity (δ -position) are different ($\widehat{\nabla_j E_i}(+l, \pm\delta) \neq \widehat{\nabla_j E_i}(-l, \pm\delta)$) and survive spatial averaging. Within the

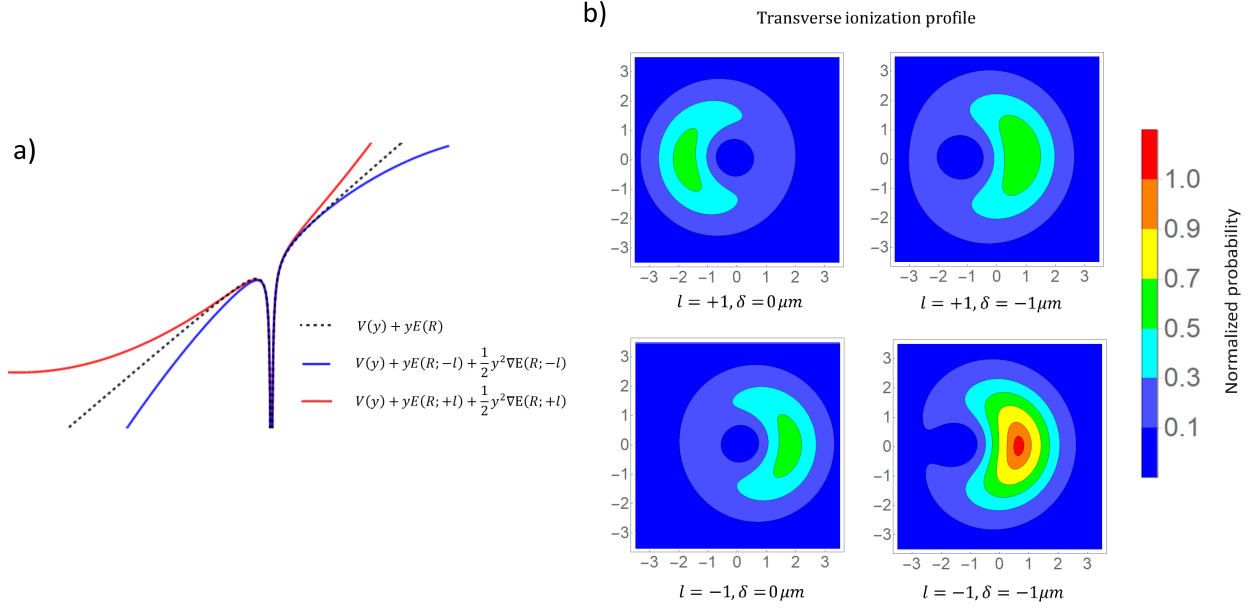


Figure 6.6: **OAM-dependent ionization in atoms.** **a)** Distortion of atomic potential at peak intensity for a vertically polarized Gaussian beam (black dashed line) and, for $l = -1$ (blue) and $l = +1$ (red) asymmetric LG beams. **b)** Normalized transverse profiles of ionization probability for symmetric ($\delta = 0 \mu\text{m}$) and asymmetric ($\delta = -1 \mu\text{m}$) LG beam at an intensity of 10^{14} W/cm^2 . The x and y-axis are given in microns. Figure a) was evaluated with the beam coordinates at $(1 \mu\text{m}, 0 \mu\text{m})$.

interaction region, the spatial rate of change of the electric field is different, thereby causing an l -dependent rate of ionization. Changing the helicity causes a reduction or enhancement of the distortion of the atomic potential (red and blue curves). This distortion is dependent on the location within the interaction region. The field gradient is much greater than the atom size, however, local hot-spots can enhance the signal. Therefore, the ionization can be manipulated by displacing the phase singularity, which directly affects the peak of the field, as well as the field gradient within the interaction region.

Figure 6.6b shows the transverse ionization probability profile for $l = \pm 1$ at $\delta = 0$ (left column) and $\delta = -1 \mu\text{m}$ (right column) calculated using equation (6.19). At $\delta = 0$, the average ionization probability is nearly identical for left- and right-helical light. However, a horizontal cut across the beam cross-section reveals a slight asymmetry in the distribution, with a slightly greater presence on the left (right) for $l = +1$ ($l = -1$). At $\delta = -1 \mu\text{m}$, the average ionization probability increases compared to $\delta = 0$ and is greater for $l = -1$ relative to $l = +1$. In addition, the asymmetry in ionization along a horizontal cut across the beam cross-section is enhanced for $l = -1$ compared to $l = +1$. For $\delta = +1 \mu\text{m}$, the trend reverses, with $l = +1$ producing higher ionization compared to $l = -1$, consistent with experimental results (Fig. 6.3, 6.4).

These subtle differences in the distortion of the atomic potential, induced by left- and right-handed OAM beams, give rise to intriguing phenomena in strong-field physics. They have the potential to imprint characteristic features on the angular distribution of the ionized electron with a preferred directionality by changing either the handedness of helical light or the sign of δ -position. When extended to chiral molecules, the asymmetry in the molecular potential could increase/decrease the photoelectron emission along a particular direction.

This can lead to efficient chiral discrimination, analogous to photoelectron circular dichroism, and be further enhanced through the utilization of higher l -values. Moreover, the directionality of the ejected electron can be controlled by angular rotation of the singularity in the transverse plane of the laser focus. This capability provides an additional control parameter to manipulate the molecular potential manifold and therefore the reaction dynamics. Additionally, the transverse spreading of the ionized electron wavepacket can be influenced, thereby affecting recollision dynamics (see Fig. S7.5 in the Supplementary).

The peak field strength varies across the beam profile when the singularity is displaced in an OAM beam. It rises with δ and eventually reaches a maximum. As δ increases further, approaching the edge of the beam cross-section, the peak field strength decreases as the beam profile starts resembling that of a Gaussian beam. This variation in peak field strength has a direct impact on the ponderomotive energy of the free electron, as depicted in Fig.6.7a. At higher l -values, the null intensity region expands, and the field gradient intensifies. Consequently, the ponderomotive energy increases with l -value and reaches a maximum at smaller δ values.

The tunability of ponderomotive energy with asymmetric OAM beams significantly impacts high harmonic generation, a critical process in attosecond science. Transitioning from a Gaussian beam to an asymmetric OAM beam, at an intensity of 10^{14} W/cm², results in a threefold increase in ponderomotive energy for $l=9$. This translates to extending the cut-off harmonics by the same amount without the need for a laser operating at longer wavelengths. Although, the phase matching condition and the ground state depletion may limit the extension of the cutoff. Moreover, the drift energy of the electron, which is proportional to the ponderomotive energy, can be regulated by displacing the singularity within the transverse plane of the laser focus.

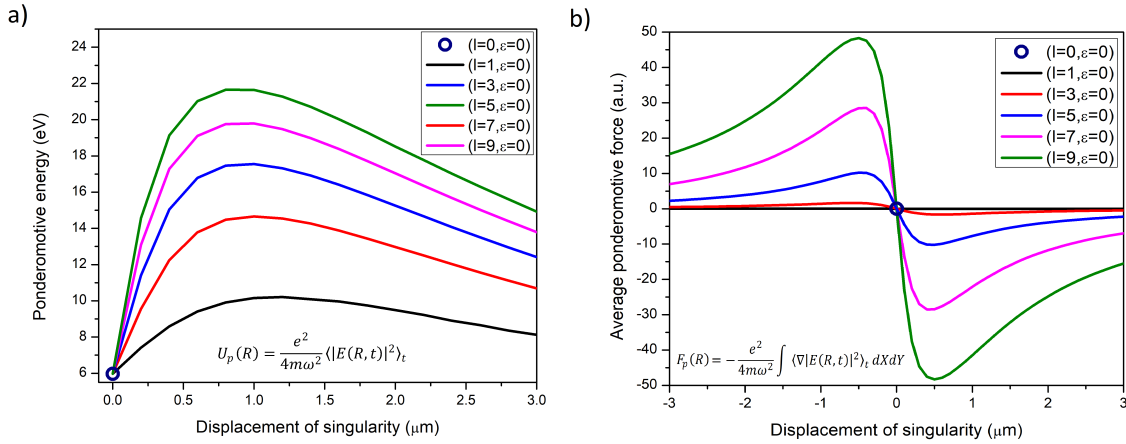


Figure 6.7: **Tuning the ponderomotive energy and force.** Simulation of **a)** peak ponderomotive energy, and **b)** average ponderomotive force, at an intensity of 10^{14} W/cm², for different positions of the singularity in a linearly polarized OAM beam and for different l -values. The open circles correspond to a Gaussian beam at the same laser intensity. The ponderomotive force was integrated over the beam cross-section at the laser focus.

The controlled generation of electron wavepackets with asymmetric OAM beams also facilitates to probe molecular dynamics by taking snapshots of conformational transformations. This is possible either by scattering of the electron wavepacket from its parent molecular ion (i) elastically leading to a diffraction pattern, or (ii) inelastically leading to multiple ionization and fragmentation from which changes to bond length and angles

could be extracted. The ability to increase the ponderomotive energy of the electron with OAM beams enhances the spatial resolution in such studies. However, the temporal electron dynamics in the laser field, *vis-à-vis* ionization and recollision times, remains the same for both Gaussian and OAM beams (see Supplementary 6.16).

Figure 6.7b illustrates variation of the average ponderomotive force at the focal plane as a function of the displacement of the singularity, δ , for different l -values. This force was obtained by integrating over the cross-section of the laser beam at the focus and depends on the gradient of the intensity. For a Gaussian beam, the average ponderomotive force is zero, represented by a circle. The behaviour is similar for symmetric OAM beams. However, when the singularity is displaced the ponderomotive force exhibits a local maxima and minima that increases with the l -value. The position of local maxima and minima in the ponderomotive force aligns with specific δ values where differential ionization exhibits maximum magnitude (Fig. 6.5b,d). In plasma physics, a factor of forty enhancement in ponderomotive force with asymmetric OAM beams facilitates the acceleration of charged particles to extremely high energies. This method serves as an alternative to the use of temporally asymmetric laser pulses to manipulate the characteristics of accelerated charged particles [121, 151–154]. In addition, l -dependent ionization of matter also enables to precisely control plasma density by an order of magnitude compared to a Gaussian beam. This could potentially be harnessed, for example, to manipulate laser filamentation and enhance its application in electromagnetic waveguiding and remote sensing of atmospheric molecules for accurate environmental monitoring.

In conclusion, we demonstrated l -dependent ionization of atoms and molecules that can be precisely controlled by manipulating the phase singularity within the OAM beam. Gas phase measurements were performed at higher intensity, compared to the liquid or solids counterparts, and relied on a pure tunneling process due to the absence of propagation effects. We extended strong-field tunnel ionization beyond the dipole approximation to simulate the ionization of atoms. Our study provides valuable insight into the intricate mechanisms underlying strong-field physics. OAM beams provide an additional tool to manipulate extreme nonlinear processes that drive a spectrum of research domains.

6.3.5 ARGON STRONG-FIELD NON-DIPOLE IONIZATION AMPLITUDE

Tunnel ionization of an atom is often described using strong-field approximation (SFA) where the laser field strength is comparable to the Coulomb field of an atom. It is predominant when the laser frequency is slower than the frequency of electron tunneling through the barrier. SFA assumes that only the ground state and the continuum are involved in the dynamics and that the intermediate states and ground state depletion are neglected.

Ionization probability can be obtained from the transition amplitude defined as a projection of the final state $\psi_f(t)$ to a fully evolved ground state at large times [40, 65, 77], given by $M_{fg} = \lim_{t \rightarrow \infty} \langle \psi_f(t) | \Psi(r, t) \rangle$, where $\Psi(r, t)$

is the total wave function of time-evolved ground state, ψ_g , when the laser field is turned on. $\Psi(r, t)$ is a solution of the time-dependent Schrodinger equation and is solved using the Green function $\hat{G}(t, t') = -i\Theta(t - t')\hat{U}(t, t')$ [40, 65] where $\Theta(t - t')$ is the Heaviside step function and $\hat{U}(t, t')$ is a unitary time operator. By using the orthogonality of the wavefunctions, the Born approximation where the perturbation acts only on the ground state, and approximating the final state as a Volkov wavefunction; $\langle\psi_f(t)|\hat{U}(t, t') \rightarrow \langle\psi_V(t')|$ we obtain the general SFA tunneling transition amplitude from the ground state to the continuum given by

$$M_{fg} = -i \int_{-\infty}^{\infty} dt' \langle\psi_V(t')|\hat{V}(t')|\psi_g(t')\rangle \quad (6.21)$$

In standard SFA, only the electric dipole moment is considered in the interaction Hamiltonian and the Volkov wavefunction. In principle, the transition amplitude can be expressed either in velocity or length gauges. Conversion from one gauge to the other can be achieved by using the generating function $\chi(r, R, t) = \int_0^1 \vec{r} \cdot \vec{A}(R + \lambda r, t) d\lambda$ and its resulting unitary operator $e^{-i\chi(r, R, t)}$ [17]. In the velocity gauge, the ground state wavefunction is given by $|\tilde{\psi}_g(t)\rangle = e^{-i\chi(r, R, t)}|\psi_g(t)\rangle$ and the Hamiltonian is given by $\hat{H}(t) = \frac{1}{2} \left(-i\vec{\nabla} + \vec{A}(r', t) \right)^2$ where $|\psi_g(t)\rangle$ is the ground state wavefunction in length gauge, $i\vec{\nabla}$ is the momentum operator and $\vec{A}(r', t)$ is the vector potential. We used the length gauge to derive the transition amplitude.

To introduce higher-order multipoles in the interaction Hamiltonian, we

1. (i) Taylor expanded the vector potential to the second order about a point R in the interaction Hamiltonian as, $\vec{A}(r', t) \approx \vec{A}(R, t) + \vec{r}^\top \widehat{\partial A}(R, t) \dots$, and in the generating function as, $A(R + \lambda r, t) = A(R, t) + \lambda \vec{r}^\top \widehat{\partial A}(R, t)$, where $\vec{r}^\top$ is the transpose of position vector.
2. (ii) Applied the unitary transformation operator $e^{-i\chi(r, R, t)}$ to explicitly express the existence of electric quadrupole and magnetic dipole in length gauge resulting in the non-dipole interaction Hamiltonian $\hat{V}(t') = r_i E_i(R, t') + \frac{1}{2} r_i r_j \widehat{\partial_j E_i}(R, t') + \frac{1}{2} L_i B_i(R, t')$, where $E_i(R, t)$ and $B_i(R, t)$ are the incident electric and magnetic fields, respectively, of the asymmetrical Laguerre-Gaussian laser beam, $r_{i,j}$ is the distance between positive and negative charge in the atomic frame and R represent the coordinates of the laser beam profile. $\widehat{\partial_j E_i}$ represents the field gradient and L_i is the orbital angular momentum of the magnetic dipole transition moment.

Lastly, we expanded the Volkov wavefunction to include the higher order multipoles to $O(\widehat{\partial A})$ and converted it from velocity to length gauge using the first order transformation, $e^{-i\chi(r, R, t)} \sim e^{-iA(R, t) \cdot r}$ to obtain equation 6.16 of the main text (see supplementary). The non-dipole free-electron wavefunction shown in equation 6.16 can be expressed in terms of time propagator, $\hat{U}_V(t, t')$, and a plane wave with a momentum $\pi(p, t, t')$

$$\Psi_V(r, t) = \frac{\hat{U}_V(t, t')}{(2\pi)^{3/2}} e^{i\pi(p, t, t') \cdot r} = \hat{U}_V(t, t') |\pi(p, t, t')\rangle \quad (6.22)$$

where

$$\pi(p, t, t') = \left(p + A(R, t') - \int_{t'}^t \widehat{\partial_R A}(R, \tau) [p + A(R, \tau)] d\tau \right); \quad \hat{U}_V(t, t') = e^{-\frac{i}{2} \int_{t'}^t (p + A(R, t'')) - \int_{t''}^t \widehat{\partial_R A}(R, \tau) [p + A(R, \tau)] d\tau)^2 dt''}$$

Therefore, the length gauge ground state tunneling transition amplitude up to $O(\widehat{\partial A})$ becomes

$$M_{fg} = -i \int_{-\infty}^t dt' \langle \pi(p, t, t') | \hat{U}_V(t, t') V(t') | \psi_g(t') \rangle = -i \int_{-\infty}^t dt' \langle \pi(p, t, t') | V(t') | \psi_g \rangle e^{iS(p, t, t')}$$

The full transition amplitude describing the tunnel ionization probability for an aLG beam, shown in equation 6.17 of the main text, can be obtained from

$$M_{fg} = -i \int_{-\infty}^t dt' \langle \pi(p, t, t') | r_i E_i(R, t') + \frac{1}{2} r_i r_j \widehat{\partial_j E_i}(R, t') + \frac{1}{2} L_i B_i(R, t') | \psi_g \rangle e^{iS(p, t, t')} \quad (6.23)$$

where

$$S(p, t, t') = \frac{1}{2} \int_{t'}^t \left[\left(p + A(t'') - \int_{t''}^t \widehat{\partial_R A}(p + A(\tau)) d\tau \right)^2 + 2I_p \right] dt'' \quad (6.24)$$

To calculate the electric dipole, magnetic dipole and electric quadrupole moment we consider the ground state wavefunction of argon to be a 3p-orbital given by $|\psi_g(r)\rangle = R_{nl}(r)Y_{lm}(\theta, \phi) = |nlm\rangle$, where n, l, m are principal, orbital and spin quantum numbers. These transition moments are expressed in the momentum space by applying the position operator on the momentum state to obtain

$$E1 = \langle \pi(p, t, t') | r_i | \psi_g(r, t') \rangle E_i^\pm(R, t') = i \partial_i | \psi_g(\boldsymbol{\pi}_P) \rangle E_i^\pm(R, t')$$

$$E2 = \frac{1}{2} \langle \pi(p, t, t') | r_i r_j | \psi_g(r, t') \rangle \widehat{\partial_j E_i^\pm}(R, t') = -\frac{1}{2} \partial_i \partial_j | \psi_g(\boldsymbol{\pi}_P) \rangle \widehat{\partial_j E_i^\pm}(R, t')$$

$$M1 = \frac{1}{2} \langle \pi(p, t, t') | L_i | \psi_g(r, t') \rangle B_i^\pm(R, t') = \frac{1}{4} \begin{pmatrix} \sqrt{l(l+1) - m(m+1)} | \psi_{g(m+1)}(\boldsymbol{\pi}_P) \rangle + \sqrt{l(l+1) - m(m-1)} | \psi_{g(m-1)}(\boldsymbol{\pi}_P) \rangle \\ -i \sqrt{l(l+1) - m(m+1)} | \psi_{g(m+1)}(\boldsymbol{\pi}_P) \rangle + i \sqrt{l(l+1) - m(m-1)} | \psi_{g(m-1)}(\boldsymbol{\pi}_P) \rangle \\ m | \psi_g(\boldsymbol{\pi}_P) \rangle \end{pmatrix} B_i^\pm(R, t') \quad (6.25)$$

where the momentum wavefunction is defined as $|\psi_g(\boldsymbol{\pi}_P)\rangle = \langle \pi(p, t, t') | \psi_g(r, t') \rangle$ and $|\psi_{g(m\pm 1)}(\boldsymbol{\pi}_P)\rangle = \langle \pi(p, t, t') | nl(m\pm 1) \rangle$ and where for convenience we drop the time component $\pi(p, t, t') = \boldsymbol{\pi}_P$. The angular momentum operator is expressed in terms of the raising and lowering operators ($L_x = \frac{1}{2}(L_+ + L_-)$, $L_y = \frac{1}{2i}(L_+ - L_-)$, L_z) and its definition on the spherical harmonics $L_\pm |nlm\rangle = \sqrt{l(l+1) - m(m\pm 1)} |nl(m\pm 1)\rangle$.

The momentum wavefunction was obtained by Fourier transforming the spatial radial wavefunction for hydrogen-like atoms [155, 156].

$$FT[R_{nl}(r)] = F_{nl}(p) = \left[\frac{2}{\pi} \frac{(n-l-1)!}{(n+1)!} \right]^{(1/2)} n^2 2^{2(l+1)} l! \frac{n^l p^l}{(n^2 p^2 + 1)^{l+2}} C_{n-l-1}^{l+1} \left(\frac{n^2 p^2 - 1}{n^2 p^2 + 1} \right) \quad (6.26)$$

where C_{n-l-1}^{l+1} is the Gegenbauer polynomial [155, 156].

Therefore, the ground state wavefunction for argon (3p orbital, $n=3$, $l=1$, $m = 0, \pm 1$) in momentum space is given by

$$|\psi_{g(m=\pm 1)}(\boldsymbol{\pi}_p)\rangle = \underbrace{\frac{500}{\sqrt{\pi}} \boldsymbol{\pi}_p \frac{(9\boldsymbol{\pi}_p^2 - 1)}{(9\boldsymbol{\pi}_p^2 + 1)^4}}_{F_{3,1}(\boldsymbol{\pi}_p)} \underbrace{\left[\mp \sqrt{\frac{3}{8\pi}} (\pi_{px} \pm i\pi_{py}) \frac{1}{\boldsymbol{\pi}_p} \right]}_{Y_{1,\pm 1}(\theta, \phi)} = \mp \frac{34}{81\pi} (\pi_{px} \pm i\pi_{py}) \frac{(\boldsymbol{\pi}_p^2 - 2I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^4}$$

$$|\psi_{g(m=0)}(\boldsymbol{\pi}_p)\rangle = \underbrace{\frac{500}{\sqrt{\pi}} \boldsymbol{\pi}_p \frac{(9\boldsymbol{\pi}_p^2 - 1)}{(9\boldsymbol{\pi}_p^2 + 1)^4}}_{F_{3,1}(\boldsymbol{\pi}_p)} \underbrace{\left[\sqrt{\frac{3}{4\pi}} \frac{\pi_{pz}}{\boldsymbol{\pi}_p} \right]}_{Y_{1,0}(\theta, \phi)} = \frac{3}{5\pi} (\pi_{pz}) \frac{(\boldsymbol{\pi}_p^2 - 2I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^4}$$

where $\sin\theta e^{(\pm i\phi)} = (\pi_{px} \pm i\pi_{py}) \frac{1}{\boldsymbol{\pi}_p}$, obtained by changing from spherical to Cartesian coordinates. The + and - symbols are associated to the magnetic quantum number (m) of the spherical harmonics and should not be confused with the superscript $\pm$ associated with the handedness of the electric and magnetic field of the asymmetric LG beams, $E_i^\pm(R)$ and $B_i^\pm(R)$ (see chapter 2 section 2.1.4).

The electric quadrupole was obtained by carrying out the differentiation.

$$-\frac{1}{2} \partial_{p_i} \partial_{p_j} |\psi_g(\boldsymbol{\pi}_p)\rangle = \pm \frac{17}{81\pi} \partial_{p_i} \left[-2(\pi_{px} \pm i\pi_{py}) \pi_{pj} \frac{(3\boldsymbol{\pi}_p^2 - 10I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^5} + \frac{(\boldsymbol{\pi}_p^2 - 2I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} (\delta_{pjpx} \pm i\delta_{pjpy}) \right] \quad (6.27)$$

$$= \pm \frac{17}{81\pi} \left[4(\pi_{px} \pm i\pi_{py}) \pi_{pj} \pi_{pi} \frac{(-108\boldsymbol{\pi}_p^2 I_p + 50I_p + 21\boldsymbol{\pi}_p^4)}{(\boldsymbol{\pi}_p^2 + 2I_p)^6} \right. \\ \left. - 2 \frac{(3\boldsymbol{\pi}_p^2 - 10I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^5} [(\delta_{pipx} \pm i\delta_{pi py}) \pi_{pj} + \delta_{pipj} (\pi_{px} \pm i\pi_{py}) + (\delta_{pjpx} \pm i\delta_{pjpy}) \pi_{pi}] \right]$$

Therefore, the electric dipole, electric quadrupole and magnetic dipole terms for argon atoms are given by the below two equations.

$$E1 = \langle \boldsymbol{\pi}(\mathbf{p}) | r_i | \psi_g(r) \rangle E_i^\pm(R) = \mp i \frac{34}{81\pi} \left[-2(\pi_{px} \pm i\pi_{py}) \pi_{pj} \frac{(3\boldsymbol{\pi}_p^2 - 10I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^5} + \frac{(\boldsymbol{\pi}_p^2 - 2I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} (\delta_{pjpx} \pm i\delta_{pjpy}) \right] E_i^\pm(R) \quad (6.28)$$

$$\begin{aligned}
 E2 = \frac{1}{2} \langle \boldsymbol{\pi}(\mathbf{p}) | r_i r_j | \psi_g \rangle \widehat{\partial_j E_i^\pm}(R) = & \pm \frac{17}{81\pi} \left[4(\boldsymbol{\pi}_{p_x} \pm i\boldsymbol{\pi}_{p_y}) \boldsymbol{\pi}_{p_j} \boldsymbol{\pi}_{p_i} \frac{(-108\boldsymbol{\pi}_p^2 I_p + 50I_p + 21\boldsymbol{\pi}_p^4)}{(\boldsymbol{\pi}_p^2 + 2I_p)^6} \right. \\
 & \left. - 2 \frac{(3\boldsymbol{\pi}_p^2 - 10I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^5} [(\delta_{p_i p_x} \pm i\delta_{p_i p_y}) \boldsymbol{\pi}_{p_j} + \delta_{p_i p_j} (\boldsymbol{\pi}_{p_x} \pm i\boldsymbol{\pi}_{p_y}) + (\delta_{p_j p_x} \pm i\delta_{p_j p_y}) \boldsymbol{\pi}_{p_i}] \right] \widehat{\partial_j E_i^\pm}(R) \quad (6.29)
 \end{aligned}$$

$$M1 = \frac{1}{2} \langle \boldsymbol{\pi}(\mathbf{p}) | L_i | \psi_g(r, t') \rangle B_i^\pm(R, t') = i \frac{34}{81\pi\sqrt{2}} \frac{(\boldsymbol{\pi}_p^2 - 2I_p)}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} [-\boldsymbol{\pi}_{p_y} B_x^\pm(R) + \boldsymbol{\pi}_{p_x} B_y^\pm(R)] \quad (6.30)$$

Using partial fraction expansion the above expressions for the electric dipole, electric quadrupole and magnetic dipole of argon can be rewritten as

$$\begin{aligned}
 E1 = \langle \boldsymbol{\pi}(\mathbf{p}) | r_i | \psi_g(r) \rangle E_i^\pm(R) = & \pm i \frac{68}{81\pi} (\boldsymbol{\pi}_{p_x} \pm i\boldsymbol{\pi}_{p_y}) \boldsymbol{\pi}_{p_j} \left(\frac{1}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} - \frac{16I_p}{3(\boldsymbol{\pi}_p^2 + 2I_p)^5} \right) E_i^\pm(R) \\
 & \mp i \frac{34}{81\pi} \left(\frac{1}{(\boldsymbol{\pi}_p^2 + 2I_p)^3} - \frac{4I_p}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} \right) (\delta_{p_j p_x} \pm i\delta_{p_j p_y}) E_i^\pm(R) \quad (6.31)
 \end{aligned}$$

$$\begin{aligned}
 E2 = \frac{1}{2} \langle \boldsymbol{\pi}(\mathbf{p}) | r_i r_j | \psi_g \rangle \widehat{\partial_j E_i^\pm}(R) = & \pm \frac{17}{81\pi} \left[4(\boldsymbol{\pi}_{p_x} \pm i\boldsymbol{\pi}_{p_y}) \boldsymbol{\pi}_{p_j} \boldsymbol{\pi}_{p_i} \left(\frac{(50(6I_p^2 + I_p))}{(\boldsymbol{\pi}_p^2 + 2I_p)^6} - \frac{192I_p}{(\boldsymbol{\pi}_p^2 + 2I_p)^5} + \frac{21}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} \right) \right. \\
 & \left. - 2 \left(\frac{1}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} - \frac{16I_p}{3(\boldsymbol{\pi}_p^2 + 2I_p)^5} \right) [(\delta_{p_i p_x} \pm i\delta_{p_i p_y}) \boldsymbol{\pi}_{p_j} + \delta_{p_i p_j} (\boldsymbol{\pi}_{p_x} \pm i\boldsymbol{\pi}_{p_y}) + (\delta_{p_j p_x} \pm i\delta_{p_j p_y}) \boldsymbol{\pi}_{p_i}] \right] \widehat{\partial_j E_i^\pm}(R) \quad (6.32)
 \end{aligned}$$

$$M1 = \frac{1}{2} \langle \boldsymbol{\pi}(\mathbf{p}) | L_i | \psi_g(r, t') \rangle B_i^\pm(R, t') = i \frac{34}{81\pi\sqrt{2}} \left(\frac{1}{(\boldsymbol{\pi}_p^2 + 2I_p)^3} - \frac{4I_p}{(\boldsymbol{\pi}_p^2 + 2I_p)^4} \right) [-\boldsymbol{\pi}_{p_y} B_x^\pm(R) + \boldsymbol{\pi}_{p_x} B_y^\pm(R)] \quad (6.33)$$

These two terms were substituted in transition amplitude (equation 6.17 of the main text) and the time integral was solved by saddle-point integration using the method of steepest descent (stationary phase method) [157–160]. The resultant transition amplitude has the form $M_{fg} = -i \int_C g(p, t, t') e^{iS(p, t, t')} dt'$ where $g(p, t, t') = \langle \pi(p, t, t') | \hat{V}(R, r, t') | \psi_g(t') \rangle$ represents the transition matrix element from the ground state to the continuum. It contains 11 terms; 4 for the electric dipole, 5 for the electric quadrupole, and 2 for the magnetic dipole, respectively, as shown in the above two equations. Each term has a generic form $\sim \frac{\zeta_i(p, t, t')}{(2I_p + \pi^2(p, t, t'))^n}$ where $n = 3, 4, 5$ for electric dipole and $n = 4, 5, 6$ for electric quadrupole. $\zeta_i(p, t, t')$ is the numerator specific to each term. $g(p, t, t')$ varies slowly compared to the fast oscillating function $e^{iS(p, t, t')}$, so the integral averages to zero unless there are regions where the phase of the oscillation, $S(p, t, t')$, stays nearly constant. In other words, areas around the point where the derivative of the function in the phase goes to zero, *i.e.* $\frac{\partial}{\partial t'} S(p, t, t') = 0 = S'(p, t, t')$. This occurs at a saddle point t_s where $S'(p, t, t') = 2I_p + \pi^2(p, t, t') = 0$. As a result, all the terms in electric dipole and electric quadrupole transitions contain a singularity at the saddle point t_s .

To solve the transition amplitude M_{fg} , we Taylor expand $S(p, t, t') \approx S(p, t, t_s) + \frac{1}{2} S''(p, t, t_s) (t' - t_s)^2$ around the saddle point and substitution gives the below generic expression for each of the 9 terms involved in electric dipole and

electric quadrupole transitions

$$M_{fg}(p, t) = -i\zeta_i(p, t, t_s) e^{iS(p, t, t_s)} e^{i\phi} \int_{C'} \frac{1}{S'(p, t, t')^n} e^{i\frac{1}{2}S''(p, t, t_s)\epsilon^2} d\epsilon \quad (6.34)$$

where the deformed contour C' is going through the saddle point as a straight line at an angle ϕ .

To handle the singularity in the denominator in the vicinity of the saddle point t_s we approximated the term to $S'(p, t, t_s) = S''(p, t, t_s)(t' - t_s)$ [157, 159], leading to

$$M_{fg}(p, t) = -i \frac{\zeta_i(p, t, t_s)}{S''(p, t, t_s)^n} e^{iS(p, t, t_s)} e^{i\phi} \int_{C'} \frac{1}{(t' - t_s)^n} e^{i\frac{1}{2}S''(p, t, t_s)(t' - t_s)^2} dt' \quad (6.35)$$

Substituting the definition of the Gamma function in the transition amplitude, $\frac{\Gamma(n)}{(t' - t_s)^n} = \int_0^\infty x^{n-1} e^{-x(t' - t_s)} dx$, leads to a double integral given by

$$M_{fg}(p, t) = -i \frac{\zeta_i(p, t, t_s)}{S''(p, t, t_s)^n} e^{iS(p, t, t_s)} e^{i\phi} \int_0^\infty \frac{x^{n-1}}{\Gamma(n)} \left[\int e^{i\frac{1}{2}S''(p, t, t_s)(t' - t_s)^2} e^{-x(t' - t_s)} dt' \right] dx \quad (6.36)$$

To solve this we applied a change of variable $\epsilon = (t' - t_s)$, to get

$$M_{fg}(p, t) = -i \frac{\zeta_i(p, t, t_s)}{S''(p, t, t_s)^n} e^{iS(p, t, t_s)} e^{i\phi} \int_0^\infty \frac{x^{n-1}}{\Gamma(n)} \left[\underbrace{\int e^{-(-i\frac{1}{2}S''(p, t, t_s)\epsilon^2 + x\epsilon)} d\epsilon}_I \right] dx \quad (6.37)$$

in which the time integral $I = \int e^{-(-i\frac{1}{2}S''(p, t, t_s)\epsilon^2 + x\epsilon + \lambda^2 - \lambda^2)} d\epsilon = e^{\lambda^2} \int e^{-(a\epsilon + \lambda)^2} d\epsilon = e^{\lambda^2} \frac{\sqrt{\pi}}{a}$

where $a = \sqrt{-i\frac{1}{2}S''(p, t, t_s)}$ and $\lambda = \frac{x}{2\sqrt{-i\frac{1}{2}S''(p, t, t_s)}} = \tilde{\lambda}x$.

Substituting the time integral I in equation 6.37, using $\int_0^\infty x^{n-1} e^{\tilde{\lambda}^2 x^2} dx = \frac{\Gamma(n/2)}{2} \left(-\frac{1}{\tilde{\lambda}^2}\right)^{n/2}$ and rearranging leads to

$$M_{fi}(p, t) = -i \frac{\Gamma(n/2)}{2\Gamma(n)} \zeta_i(p, t, t_s) \sqrt{\frac{2i\pi}{S''(p, t, t_s)}} \left(\frac{2i}{S''(p, t, t_s)} \right)^{n/2} e^{iS(p, t, t_s)} e^{i\phi} \quad (6.38)$$

We retain only the odd values of $(n = 2k + 1)$ since they result in a non-zero residue from series expansion over the contour integral of equation 6.35.

$$M_{fi}(p, t) = -i\sqrt{\pi} \frac{\Gamma((2k+1)/2)}{2\Gamma(2k+1)} \zeta_i(p, t, t_s) \left(\frac{2i}{S''(p, t, t_s)} \right)^{k+1} e^{iS(p, t, t_s)} e^{i\phi} \quad (6.39)$$

We replace $\zeta(p, t, t_s)$ for the electric dipole and electric quadrupole moments with their respective terms for $n = 3$ and $n = 5$ given in equation 6.31 and 6.32 to get

$$M_{fg}(p, t) = 2i\sqrt{\pi} \frac{\Gamma(3/2)}{\Gamma(3)} \left(\frac{\zeta_i(p, t, t_s)}{S''(p, t, t_s)^2} \right) e^{iS(p, t, t_s)} e^{i\phi}; \quad M_{fg}(p, t) = -4\sqrt{\pi} \frac{\Gamma(5/2)}{\Gamma(5)} \left(\frac{\zeta_i(p, t, t_s)}{S''(p, t, t_s)^3} \right) e^{iS(p, t, t_s)} e^{i\phi} \quad (6.40)$$

The full transition moment after integration is given by

$$M_{fg}^{E1}(p, t) = \pm \frac{68}{81\sqrt{\pi}} \left[4i \frac{\Gamma(5/2)}{\Gamma(5)} (\boldsymbol{\pi}_{px} \pm i\boldsymbol{\pi}_{py}) \boldsymbol{\pi}_{pi} \left(\frac{16I_p}{3S''(p, t, t_s)^3} \right) + \frac{\Gamma(3/2)}{\Gamma(3)} \left(\frac{1}{S''(p, t, t_s)^2} \right) (\delta_{pipx} \pm i\delta_{pi py}) \right] E_i^\pm(R) e^{iS(p, t, t_s)} e^{i\phi} \quad (6.41)$$

$$M_{fg}^{E2}(p, t) = \pm \frac{68}{81\sqrt{\pi}} \frac{\Gamma(5/2)}{\Gamma(5)} \left[4(\boldsymbol{\pi}_{px} \pm i\boldsymbol{\pi}_{py}) \boldsymbol{\pi}_{pj} \boldsymbol{\pi}_{pi} \left(\frac{192I_p}{S''(p, t, t_s)^3} \right) - 2 \left(\frac{16I_p}{3S''(p, t, t_s)^3} \right) [(\delta_{pipx} \pm i\delta_{pi py}) \boldsymbol{\pi}_{pj} + \delta_{pi pj} (\boldsymbol{\pi}_{px} \pm i\boldsymbol{\pi}_{py}) + (\delta_{pjpx} \pm i\delta_{pj py}) \boldsymbol{\pi}_{pi}] \right] \widehat{\partial_j E_i^\pm(R)} e^{iS(p, t, t_s)} e^{i\phi} \quad (6.42)$$

$$M_{fg}^{M1}(p, t) = \frac{68}{81\sqrt{2\pi}} \frac{\Gamma(3/2)}{\Gamma(3)} \left(\frac{1}{S''(p, t, t_s)^2} \right) (\boldsymbol{\pi}_{py} B_x^\pm(R) - \boldsymbol{\pi}_{px} B_y^\pm(R)) e^{iS(p, t, t_s)} e^{i\phi} \quad (6.43)$$

For linearly polarized light to $O(\widehat{\partial A})$, $S''(p, t, t_s)$ can be written as

$$S''(p, t, t_s) = \mp 2i\sqrt{2I_p} E_i(t_s) \left[1 + \int_{t_s}^t \partial_i A_i(\tau) d\tau \right] \quad (6.44)$$

At the saddle point $\frac{\partial}{\partial t'} S(p, t, t') = 0 \Rightarrow \left(p + A(t') - \int_{t'}^t \widehat{\partial_R A}(\tau) (p + A(\tau)) d\tau \right)^2 = -2I_p$, this expression describes tunneling. It shows that the electron kinetic energy at time t' is negative, its velocity is complex and hence the time $t' = t_s \pm i\eta$. The time t' can be identified with the moment when the electron enters the barrier. Its real part t_s will then correspond to the time when the electron exits the barrier. Substituting the complex time at the saddle point, regrouping real and imaginary terms in $S(p, t, t')$ and after variable transformation ($\tau' = t'' = t_s$; $d\tau' = dt''$ and taking $t_s \rightarrow 0$ and $t' \rightarrow \pm i\eta$) and neglecting $O(\widehat{\partial A}^2)$ terms we get

$$iS(p, t, t_s) = \frac{i}{2} \int_{t_s \pm i\eta}^t dt'' (\pi^2(p, t, t'') + 2I_p) = \frac{i}{2} \left[\int_{t_s}^t (\pi^2(p, t, t'') dt'' + 2I_p) - \int_0^{\pm i\eta} (\pi^2(p, t, \tau') + 2I_p) d\tau' \right] \quad (6.45)$$

$$iS(p, t, t_s) = -\frac{(2I_p)^{3/2}}{3E_i(t_s)} \left(1 + \frac{3}{4I_p} \sum_{j \neq i} \left[p_j + \frac{2I_p}{3E_i(t_s)} \partial_j A_i(t_s) - \int_{t_s}^t d\tau (A_i(\tau) - A_i(t_s)) \partial_j A_i(\tau) \right]^2 \right) \quad (6.46)$$

From the saddle point method, we can represent the momentum in terms of the ionization potential $\boldsymbol{\pi}_p = i\sqrt{2I_p}$. For elliptical light, the momentum components takes the form $\boldsymbol{\pi}_{px} = \alpha\boldsymbol{\pi}_p$ and $\boldsymbol{\pi}_{py} = \beta\boldsymbol{\pi}_p$ where α, β are the polarization factors. By considering only the normalized field amplitude for the dominant first order term in $iS(p, t, t_s)$ and $S''(p, t, t_s)$, the non-dipole total transition probability can be calculated using

$$\bar{P}_{fg} = \int_{-w_0}^{w_0} |M_{fg}^{E1} + M_{fg}^{E2} + M_{fg}^{M1}|^2 dR \quad (6.47)$$

to describe the ionization probability over the interaction region shown in Fig. 6.5b and the difference in the ionization

probability, analogous to HD, defined as $\Delta\bar{P}_{fg} = \bar{P}_{fg}(+l) - \bar{P}_{fg}(-l)$ shown in Fig. 6.5a.

6.3.6 SUPPLEMENTARY INFORMATION

This section includes an additional set of experimental and theoretical results and materials essential to support the main text and its content.

6.3.6.1 EFFECT OF INTENSITY AND E1E2 STRENGTH ON THE IONIZATION PROBABILITY

Figure S6.8a shows the influence of intensity on the ionization probability of argon as a function of displacement of the singularity for $l = -1$. At low intensity, the ionization is symmetric around $\delta = 0$. The ionization probabilities overlap for both handedness of the helical light (not shown). As the intensity is increased, ionization becomes asymmetric around $\delta = 0$, and a double bump shape appears. The difference in ionization between the positive and negative singularity positions becomes more prominent until the saturation intensity is reached.

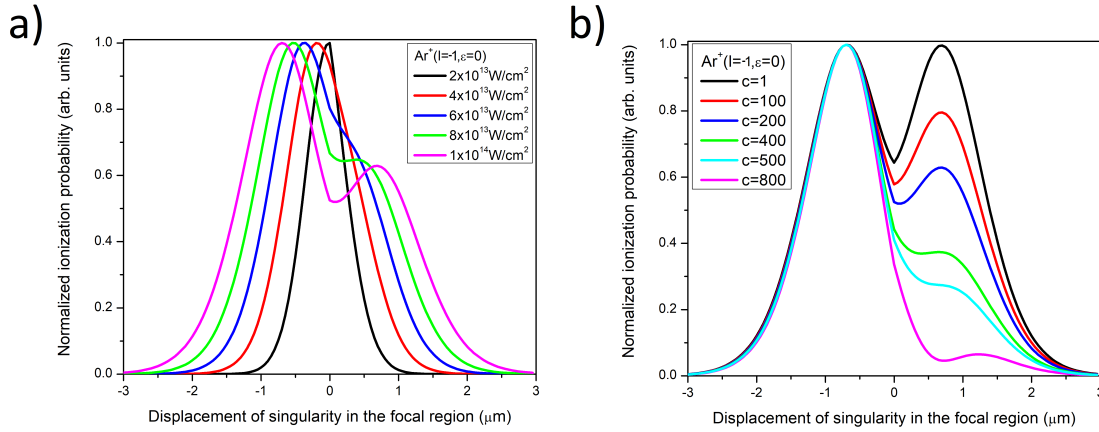


Fig S 6.8: **Influence of laser intensity and the E1E2 strength on the ionization probability.** a) Depiction of ionization probability at various intensities. b) ionization probability curves with various E1E2 strength. The behaviour flips for $l = +1$ (not shown).

Figure S6.8b shows the effect of the E1E2 strength on the ionization probability for an intensity of $1 \times 10^{14} \text{ W/cm}^2$. As the relative strength of E1E2 transitions increases, represented by the constant c , it suppresses the ionization for a positive δ -position and remains unchanged for the negative δ -position. This behaviour is mirrored for the opposite helicity ($l = +1$). For a higher suppression constant, the ionization curves exhibit more features similar to the experimental curve in Figure 6.3a. Atoms and molecules in an electric field can experience small shifts and splitting in the atomic, and molecular energy levels caused by the nuclear magnetic dipole moment interacting with the magnetic field generated by the electrons and the nuclear electric quadrupole moment in the electric field gradient due to the distribution of charge within the atom. Hyperfine structure is known to enhance the quadrupole transition for a p -orbital which would result in increasing the strength of the E1E2 transitions suppressing the ionization for one helicity over the other. The c -values used in the simulation of Fig. S6.8b are within the expected range of enhancement [147–149].

6.3.6.2 IONIZATION AS A FUNCTION OF SINGULARITY

This simulation, fig. S6.9, depicts the behaviour of ionization of argon as a function of the asymmetrical parameter in the interaction region. It maps the ionization probability for a $l = -1$ OAM beam polarized along the y -direction for different radial angles. A cut along the x -axis gives Fig. S6.8. The asymmetric double bump structure persists when the singularity is moved through the center at different angles. For all angles, the ionization probability is higher for negative δ -position compared to positive δ -positions. However, When the singularity is displaced along y -axis, the double bump structure is symmetric. The asymmetry in ionization with respect to the δ -position varies with angle and becomes maximum along the x -direction for linear polarization in the y -axis. This mapping behaviour is mirrored for the opposite handedness of light.

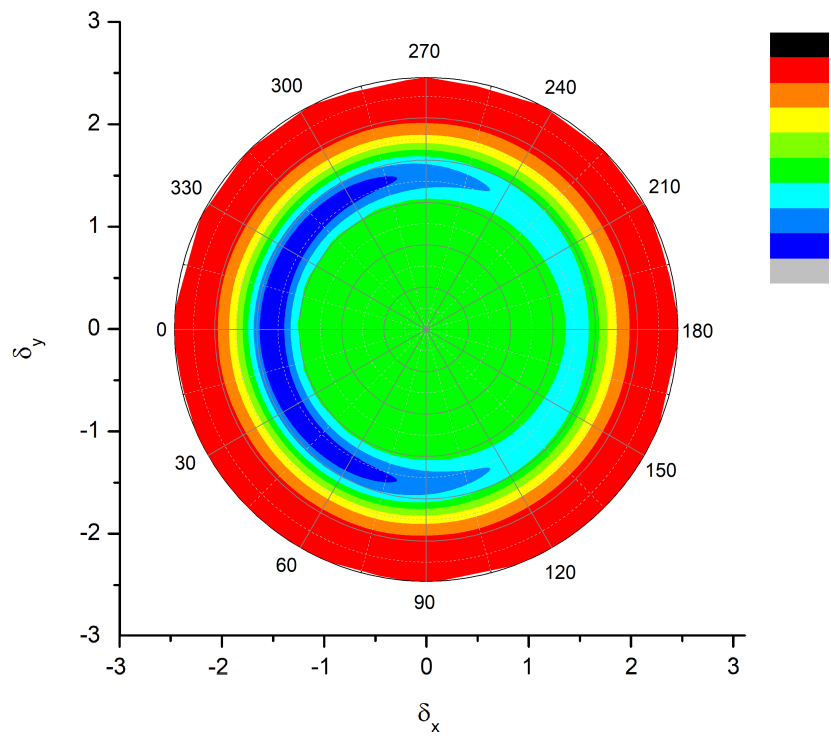


Fig S 6.9: **Ionization map for linearly polarized $l = -1$ beam.** Polar contour map of the ionization as a function of displacement of singularity in the x, y -plane within the interaction region.

6.3.6.3 CORRELATION BETWEEN INTENSITY VARIATION AND DIFFERENTIAL IONIZATION

Figure S6.10 shows differential ionization for S(-)-limonene, defined as the difference in ion yields between left- and right-handed helical light. For a specific position of the singularity, differential ionization persists over a range of laser intensities up to saturation as shown in the insets (for $\delta = \pm 1\mu\text{m}$ and $\delta = \pm 1.5\mu\text{m}$). When the singularity is at the center, the two ion yield curves overlap as a function of laser intensity (not shown).

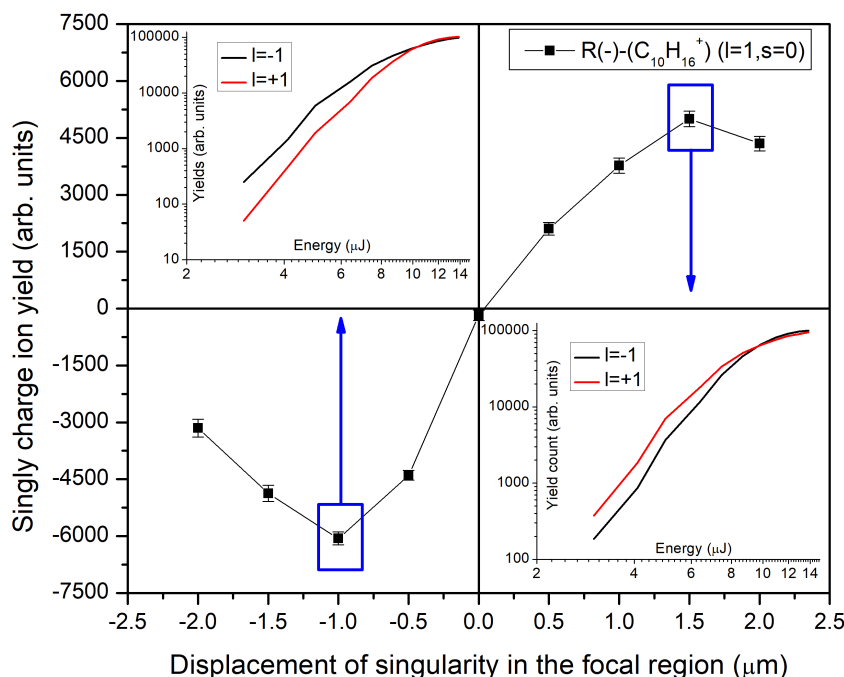


Fig S 6.10: **Differential ionization of singly charged R(+)-limonene** as a function of displacement of the singularity for linearly polarized $l = 1$. The insets show the intensity variation of R(+)-limonene for $l = +1$ ($l = -1$) in red (black) at the positions denoted by the blue rectangles.

6.3.6.4 DIFFERENTIAL IONIZATION OF S(-)- AND R(+)-LIMONENE

We observe a strong dependence of ion yields of S(-)- and R(+)-limonene for opposite OAM values which is uniquely observed for an asymmetrical OAM beam. For every δ -position, the difference in the ion yields for the opposite-handed helical light gives differential ionization, shown in Figure S6.11 for singly and doubly charged R(+)- and S(-)-limonene for linearly polarized OAM ($l = \pm 1$) beam. The blue and green curve represents the difference between $l = +1, s = 0$ and $l = -1, s = 0$ for the left- and right-handed parent ion, $(C_{10}H_{16})^+$, the peak $136m/z$ from the mass spectrum. Similarly, the black and red curves were obtained from the doubly charged ion, $(C_{10}H_{16})^{+2}$, and the fragment, $(C_5H_8)^+$, both located as the peak $68m/Z$ in the mass spectrum. The difference in ion yields is greater for the peak $68m/Z$ vs the parent ion $136m/Z$. There is no strong differential ionization between the handedness of the molecule.

For the intensities used in the experiment, the Keldysh parameter is less than unity, so tunnel ionization is predominant where the electron transitions semi-classically from the ground state to the continuum excluding the chiral-sensitive transition in the excited states. Therefore, the rate of ionization can be expected to be similar for both enantiomers, albeit in different directions. In TOF measurements, one can only measure the total yield during ionization and not the emission directions. However, in the case of doubly charged ions chiral sensitive transitions can occur during the recollision [28, 161] but are considerably suppressed at wavelengths used in the experiment.

Figure S6.12a) shows the variation of the singly charged S(-)-limonene ion yields as a function of the singularity displacement for $l = -3$ in red and $l = +3$ in black. The increase in the ion yields for an asymmetric OAM beam arises

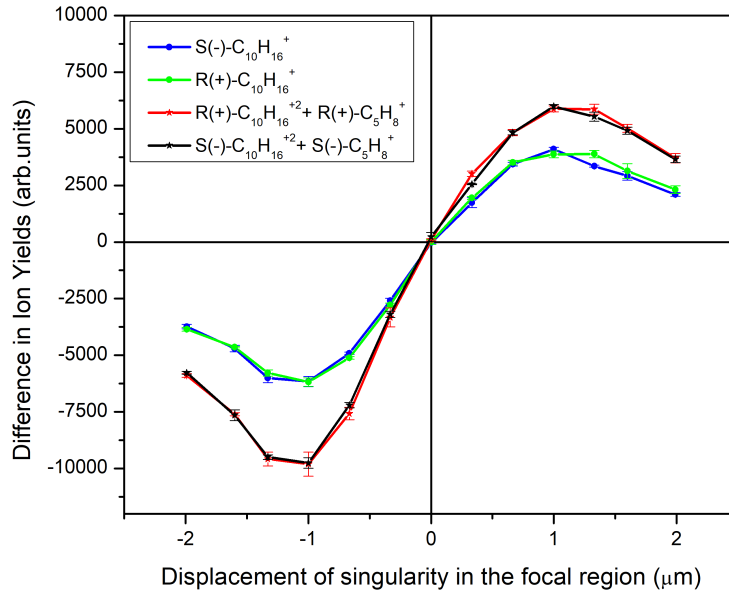


Fig S 6.11: **Differential ionization for single, double and fragment ions of limonene enantiomers** for linearly polarized $l = 1$. Parent ion yields ($m/z = 136$), for S(-)-limonene (R(+)-limonene) in blue (green), and doubly charged/fragments ($m/z = 68$), for S(-)-limonene (R(+)-limonene) in black (red). The laser intensity was $8 \times 10^{13} \text{ W/cm}^2$.

from the increasing peak field strength as the singularity is displaced. Results are similar to argon, in the main text. Therefore, at large δ positions, the ion yields should decrease because the peak field decreases and the beam profile resembles a Gaussian-like beam. However, experimental limitation resulted in a maximum displacement of $2 \mu\text{m}$ in the interaction region without affecting the quality of the beam.

Figure S6.12b) depicts the characteristic sinusoidal shape of differential ionization observed in atoms. It also features an inflection point around $\delta = 0$ similar to that observed in argon.

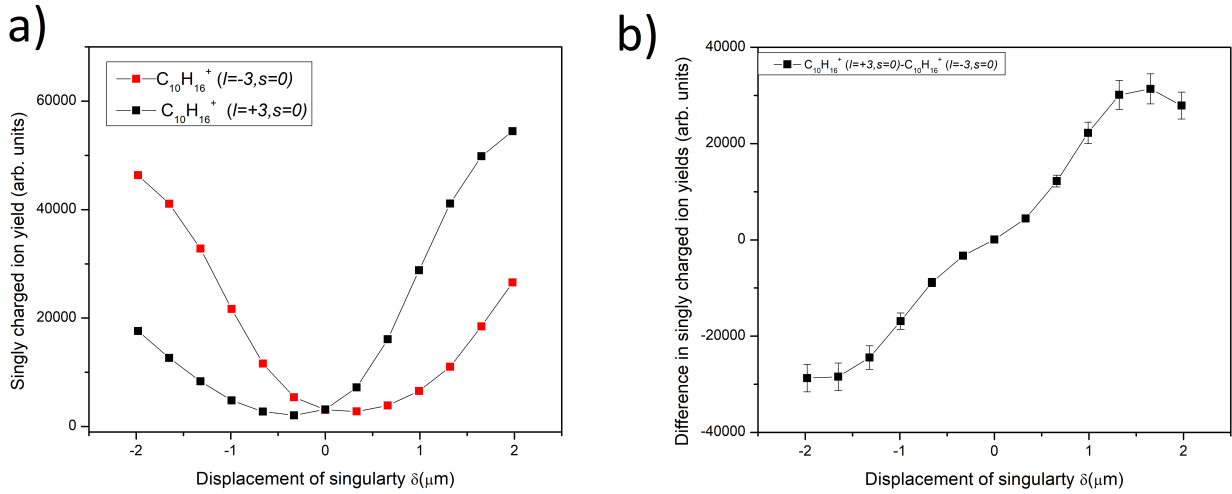


Fig S 6.12: **Single ionization control of limonene for $l = \pm 3$.** **a)** Single ionization yields of R(+)-limonene for $l = +3$ (black) and $l = -3$ (red). **b)** Difference between left and right-handed helical light ($l = 3$) for singly charged limonene ion yield. The laser intensity was $9 \times 10^{13} \text{ W/cm}^2$.

Figure S6.13 shows the normalized differential ionization of S(-)- and R(+)-limonene for circularly polarized OAM ($l = \pm 1$) as a function of displacement of the singularity. Blue and green curves represent the difference between right- and right-circular polarizations with a specific helicity ($l = \pm 1$) for the parent ion. The black and red curves represent the difference between the two helicities of light with a specific circular polarization for the parent ion. Error bars represent the standard deviation of 2 runs and the pulse energy was $\sim 5.5\mu J$.

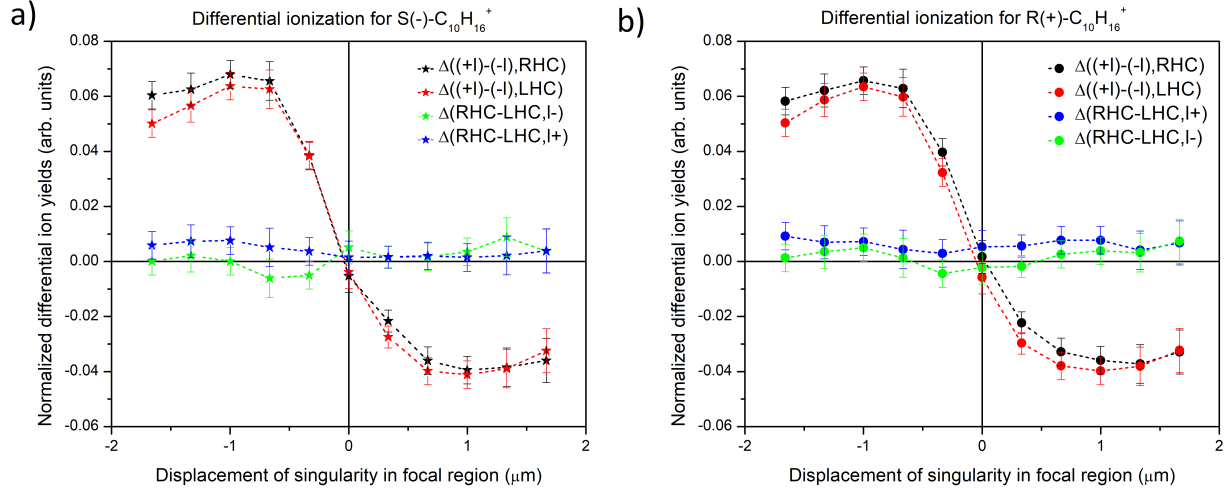


Fig S 6.13: **Ionization control of limonene for circularly polarized $l = \pm 3$ beam.** a),b) Differential ionization yields of S(-)-limonene and R(+)-Limonene between RHC and LHC for a specific helicity of light; $l = +1, s = \pm 1$ (blue) and $l = -1, s = \pm 1$ (green). Differential ion yields of S(-)-limonene and R(+)-limonene between helicity of light for a specific polarization for singly charged $l = \pm 1, s = -1$ (red), $l = \pm 1, s = +1$ (black). The laser intensity was $8 \times 10^{13} \text{ W/cm}^2$.

6.3.6.5 ELLIPTICITY DEPENDENCE OF IONIZATION

Correlation between ellipticity and differential ionization. The sinusoidal behaviour of differential ionization with respect to the δ position is independent of the laser polarization as shown in figure S6.14. However, its magnitude will change with the ellipticity of the laser polarization. Fig. S6.14a shows the differential ionization in S(-)-limonene for linearly polarized $l = 1$ OAM beam, where the two insets show ellipticity dependence of single ionization for left- and right- helical light at $\delta = \pm 1\mu\text{m}$, marked by the rectangles. For a symmetric OAM beam the ellipticity variation for left- and right-helical light overlap. At that specific position, as the ellipticity is increased, the magnitude of differential ionization should decrease if the peak field strength is not adjusted to maintain the same intensity in the interaction region. Figure S6.14 b),c) represent the simulated ellipticity variation in argon for a δ -position comparable to that identified in a). The simulated curves display the flipping behaviour of the ionization probability for the handedness of the helical light as you displace the singularity across the zero position.

Ellipticity and OAM effect on argon ions. Figure S6.15 shows the normalized singly charged argon yields as a function of ellipticity. Figure S6.15 a) shows ellipticity variation of single ionization of argon atoms, experimental ion yields (solid points with dashed lines) and simulated ionization probabilities (solid lines), for symmetric (black) and asymmetric OAM beam with positive (red) and negative (blue) displacement of the singularity, δ . The maximum ionization yield is obtained for linearly polarized light ($\epsilon = 0$) and decreases monotonically as the ellipticity increases

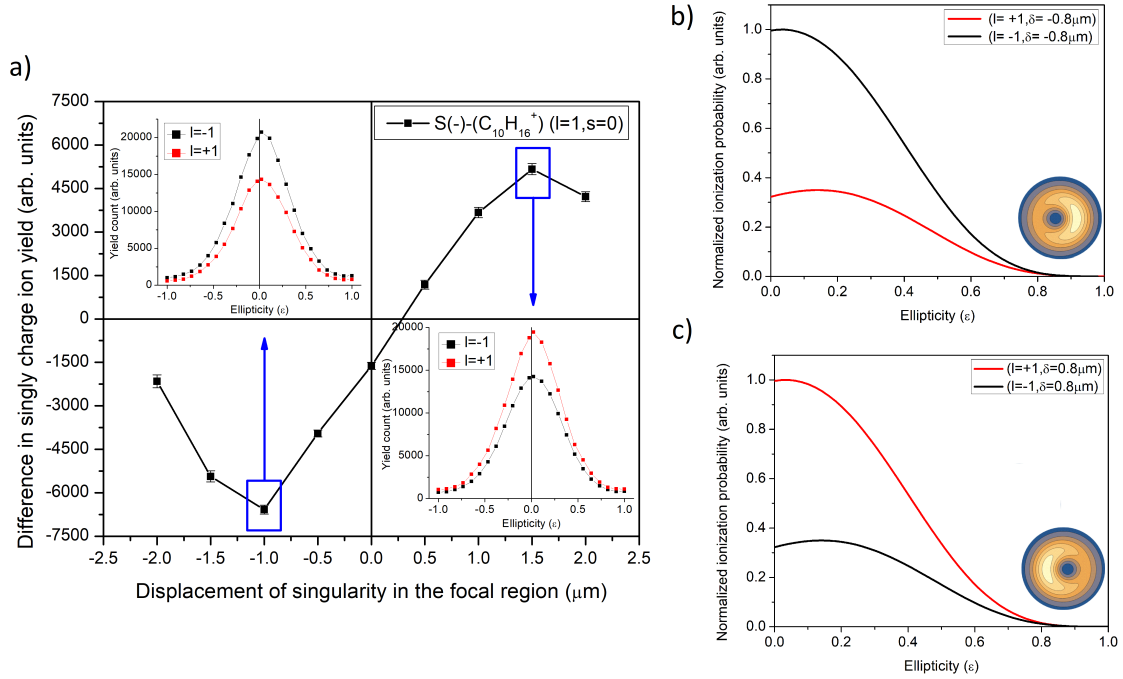


Fig S 6.14: **Ellipticity dependence of single ionization of limonene** . **a)** Difference in single ionization yields of S(-)-limonene for $l = 1$. The insets show the ellipticity variation for S(-)-limonene for $l = +1$ ($l = -1$) in red (black) at the positions denoted by the blue rectangles. The laser intensity was 8×10^{13} W/cm². **b), c)** Simulated ellipticity variation for asymmetrical parameters comparable to the insets in **a)**. The ionization probability for $l = +1$ ($l = -1$) is denoted by the red (black) curve. The laser intensity was 10^{14} W/cm².

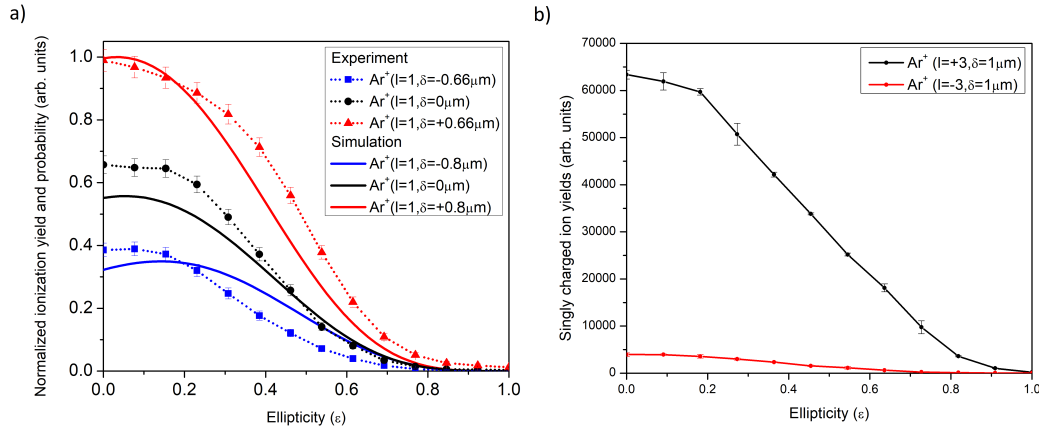


Fig S 6.15: **a) Normalized experimental and simulated ellipticity variation**. Single ionization yields of argon for $l = +1$ and $\delta = 0$ in black, $\delta = 1$ in red, and $\delta = -1$ in blue, as a function of laser ellipticity. The solid lines represent the simulated ionization probabilities. The laser intensity was 10^{14} W/cm² for both experiments and theory. **b)** Single ionization yields of argon for $l = +3$ (black) and $l = -3$ (red) for $\delta \sim 1 \mu\text{m}$. The laser intensity was 1.2×10^{14} W/cm². The error bars represent fluctuations in the ion yields over repeated measurements.

and reaches the minimum for circularly polarized light. All three curves exhibit a Gaussian-like behaviour. At higher intensities, circular polarization leads to appreciable ionization.

Figure S6.15 b) shows the ellipticity variation of argon for $l = \pm 3$ OAM beam at a displacement of $\sim 1 \mu\text{m}$. The difference between the handedness of helical light and ellipticity is more prominent than that of $l = \pm 1$ obtained in figure S6.15 a). This behaviour flips when the asymmetrical parameter δ is displaced in the negative axis (not shown). The potential barrier for $l = 3$ is strongly suppressed for one handedness over the other due to a strong peak field strength and

field gradient compared to $l = 1$. As the l -value is increased, the ionization yields for one-handedness would eventually be completely suppressed.

6.3.6.6 PEAK INTENSITY AND BEAM WAIST FOR INCREASING l -VALUE

In Laguerre-Gaussian beams with increasing l -value, the size of the null intensity region at the center increases. Consequently, for the same spot size higher pulse energies are required to reach the threshold for ionization.

From the threshold energies and peak power, the l -dependent peak intensity can be calculated based on the following equation [60]:

$$I \left[\frac{W}{cm^2} \right] = \frac{2^{(l+1)} r^{2|l|} e^{\frac{-2r^2}{w(z)^2}}}{|l|! \pi w(z)^{2(l+1)}} P_l [W] \quad (6.48)$$

For a symmetric LG beam, the maximum intensity is achieved when $r_{|l|}^2 = w_0^2 |l|/2$. The beam waist of the LG beams are expected to increase with the l -value, however, experimental OAM beams do not exhibit this behaviour. To take this into account a correction to the symmetric beam waist for higher order l -value must be considered, $\tilde{w}_0^2(l) = \frac{|l|!}{|l|!} w_0^2(l=0) e^{-|l|}$. This adjustment ensures the same beam waist and peak field strength for different l -values of a symmetric LG beam.

For asymmetric LG beams, the displacement of the singularity must also be adjusted to ensure it remains the same for beams with different l -values, such that $\Delta^2(l) = \frac{|l|!}{|l|!} \delta^2(l=0) e^{-|l|}$, where δ represent the displacement of singularity for the beam waist of $w_0(l=0)$ and Δ is the adjustment for higher l -value. Accordingly, the beam waist also needs to be adjusted for higher l -values given by $w_0(l) = \tilde{w}_0(l) + |\Delta w_0(l)|$, where $\Delta w_0(l) = (\Delta(l)/w_0(l=0))(w_0(l=0) - \tilde{w}_0(l))$. This ensures the ratio of displacement of singularity to the beam waist remains identical for different l -values and that at large δ -positions the beam waist would remain constant and behave like a Gaussian.

6.3.6.7 KINETIC ENERGY OF RECOLLISION FOR ASYMMETRICAL LAGUERRE-GAUSSIAN BEAM.

The ability to increase the ponderomotive energy by displacing the singularity directly correlates to an increase in the kinetic energy of the recolliding electron according to the equation of motion, see Fig S6.16. Although the magnitude is influenced by the asymmetry of the beam, the time component of the dynamics of ionization and recollision remains unchanged compared to a Gaussian. Controlling the kinetic energy of the electron with the singularity position and the l -value can significantly impact the high harmonic generation process because higher recollision energy can be achieved for a driving field with an asymmetrical beam profile compared to a Gaussian beam profile. The recolliding energy for an asymmetrical Laguerre-Gaussian beam with $l = 9$ at $800nm$ is comparable to a Gaussian beam with a wavelength of $1500nm$.

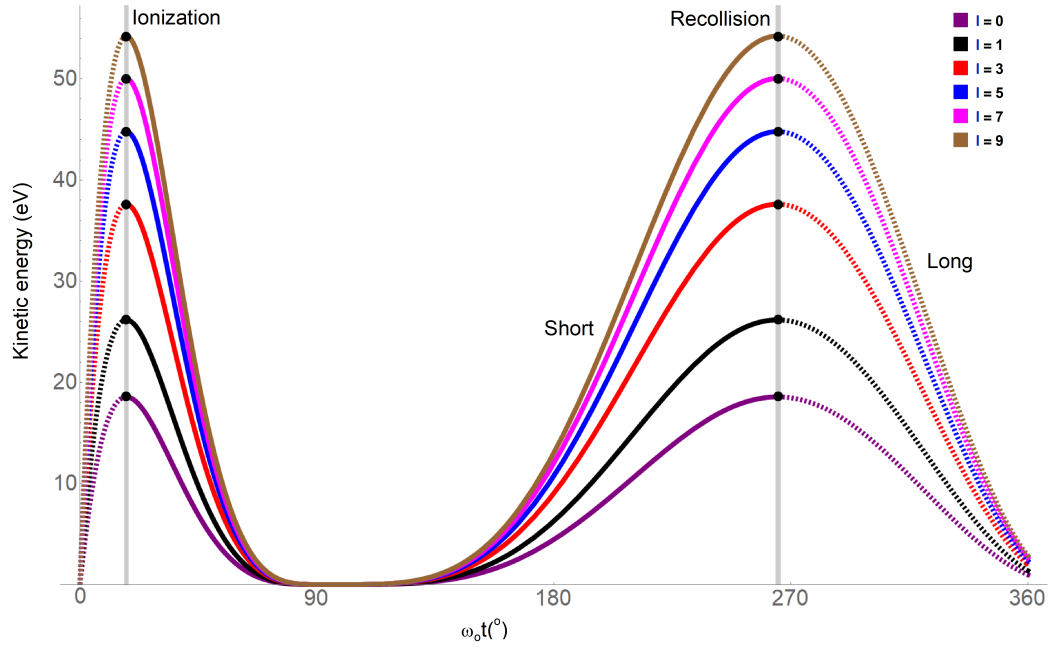


Fig S 6.16: **Electron recollision in argon for various l -value.** The dash (solid) lines represent the long (short) trajectories created when the electron is ionized before (after) the peak located at $\omega_0 t' = 0.05 \times 2\pi = 18^\circ$. The electron will return to the parent ion at $\omega_0 t = 0.7 \times 2\pi = 252^\circ$

CONCLUSION AND FUTURE IMPACT

The final chapter of this dissertation will contain the concluding remarks and the future scope of my research. This will include a discussion on the potential impact this research has on the scientific community, such as further advancement in strong-field physics, plasma physics, nonlinear optics, and attosecond dynamics. The findings from this research open many opportunities for future experiments such as HHG with asymmetric LG beam, PEHD, and OAM-dependent NSDI. These new ideas followed by their proof of principle are included. This research and future scope should encourage further investigation into the mysterious nature of helical light-matter interaction. The potential for new discoveries and advancements is immense, and the implications of such could be far-reaching.

7.1 CONCLUSION

The work conducted in this dissertation is original research that has contributed to the field of light-matter interaction. It shows the development of a new chiroptical technique using asymmetrical helical light to probe and control light-matter interaction in three phases of matter in the nonlinear and extreme nonlinear regimes. It exhibits high efficiency and control over the chiral signal and can induce differential signals in achiral molecules and atoms.

Chiral interactions were shown to depend on two major elements, the helical pitch and the field strength. By implementing this new form of chiral probe we can achieve a stronger interaction with matter by increasing the number of intertwined twists within the helical pitch and simultaneously varying the polarization. Moreover, the direction of

rotation of the helical phase was shown to significantly impact the observed signal. The different interaction regimes were achieved by varying the incident pulse energy and were further controlled by introducing asymmetrical parameter δ , which affects the field strength and the field gradient around the optical vortex for a fixed pulse intensity. Therefore, by using asymmetrical helical light as a chiral probe, we gain two extra degrees of freedom to study chiral interactions. This benefit is not limited to chiral matter it was shown to have a significant influence on achiral matter and atoms.

We have also shown significant advancement in the mechanism responsible for the observed helical effect. In the multiphoton absorption regime, we demonstrated the importance of the higher-order multipoles for the differential absorption in isotropic and anisotropic mediums. This resulted in two parameters: i) a polarization effect that is responsible for CD in linear and nonlinear regimes. ii) A conceptually new chiral parameter, the optical helicity, a phase effect and responsible for HD in the nonlinear regime. These were shown to be responsible for helical dichroism in enantiopure liquids, enantiomeric solutions, and achiral liquids. In the extreme nonlinear regime, we show the significance of the higher-order multipoles in MPAT and extend the standard SFA tunnel ionization transition amplitude to include non-dipole terms of a structured field. HD was shown to be sensitive to the short-range order and the superposition of OAM and Gaussian beams exhibit a control over the HD signal. Moreover, in the strong field regime, atoms with symmetric potential can experience a difference in the distortion of their atomic potential due to the presence of asymmetry in the probe combined with the handedness of the helical phase. This allows for the suppression of ionization and control of the kinetic energy as well as the force exerted on the liberated electron. The control over the null intensity allows for the manipulation of the peak intensity or "hot spot" demonstrated through the differential ionization of atoms and molecules and can be extended to photo-excitation of matter.

Overall, the research shown in this dissertation has potential implications for the development of new and surprising phenomena in light-matter interaction of strong-field physics. This optical probe holds promising applications across various disciplines such as physics, chemistry, and material science. Its adaptability allows it to be incorporated into existing CD spectrophotometers and expanded to plasmonic metasurfaces or transparent polymers. This research lays the foundation for progress in chiroptical spectroscopy, asymmetric catalysis, molecular electronic devices, chiral sensors, and electron dynamics in attosecond and plasma physics. The high efficiency of HD facilitates chiral recognition on solid surfaces, a key factor in surface and material sciences. Furthermore, it opens up new possibilities for the development of enantioselective catalysis and the asymmetric synthesis of bioactive molecules.

7.2 FUTURE IMPACT

We describe three new extensions of our work which show the promising future and impact of asymmetrical OAM beams in strong-field physics. i) Investigate the effect of asymmetrical beams on high harmonics generation and its control over the phase matching condition. ii) Explore the effect of asymmetrical helical light on the photoelectron angular distribution. Develop photoelectron helical dichroism (PEHD), a spectroscopic imaging technique, to improve the efficiency of chiral-sensitive detection and discover new pathways of ionization for atoms. iii) Explore the effect of OAM and its asymmetry on the recollision dynamics. Analyze the transverse spread of the electron wavepacket and the OAM-dependent non-sequential double ionization pathway through the "knee-shape".

7.2.1 HIGH HARMONICS AND PHASE MATCHING USING ASYMMETRICAL OAM BEAM

We aim to examine the phase-matching condition for high-order harmonic generation using linearly polarized aLG beams. We want to compare the conditions for efficient phase matching for aLG beams with those of LG and Gaussian beams. Recent studies have shown that the OAM of the incident LG beams influence the phase-matching conditions for the short and long trajectories that result from the saddle-point approximation of the dipole moment [162, 163]. This shows that the coherence length for the short trajectories decreases for LG beams near the focus compared to Gaussian beams. However, efficient phase matching can be achieved both before and after the focus. Moreover, it has been demonstrated that the coherence length for the long trajectory behind the focus plane can be manipulated by the OAM.

To generate HHG, dense atomic targets are used since the radiation emitted from a single atom is too weak. Therefore, to increase the efficiency of HHG one must analyze the single atom interaction and the ensemble response of the individual atoms. The interaction volume can consist of $> 10^{12}$ atoms, thus within this region the radiation emitted by these atoms are generally not in phase. An area where the radiation emission is in phase and adds constructively is considered phase-matched, the area where this condition is fulfilled is the coherence length. Up to date, phase-matching conditions have only been investigated for Gaussian and symmetric OAM beams. However, asymmetrical OAM beams allow for additional control over the ionization process (discussed thoroughly in Chapter 6 section 6.3) which is the first step of HHG and can influence the efficiency of HHG. A higher yield, as well as high recollision energy, can be achieved for an asymmetric OAM beam compared to a symmetric beam and Gaussian beam. By displacing the singularity the peak field increases, this combined with the field gradient of the left- and right-handed aLG beam directly affects the ionization yields. In Chapter 6 we show that the ponderomotive energy for an asymmetrical LG beam at 800nm can increase by displacing the singularity and by increasing the l -value (see figure 6.7). This will increase the high harmonic cutoff compared to a Gaussian with the same wavelength (see figure 6.16).

This section will investigate the effect of δ -position and its implication with the OAM value on phase matching of HHG for linear polarization. To confirm that the phase matching condition is fulfilled the phase of each harmonic emitted must be known. The focus will be on the i) dipole phase due to the response of a single atom to the incident intensity and ii) the intrinsic beam phase due to the focusing of the laser beam.

HHG is often described by the Lewenstein model. However, the use of asymmetrical OAM beams requires the contribution of the electric dipole and quadrupole. Therefore, we will extend the induced dipole moment to order $\widehat{\partial A}$. The response of the individual atom is proportional to the induced multipole moment $M(t) = \langle \Psi(t) | \hat{V}_L(t) | \Psi(t) \rangle$ where $\Psi(t)$ is the time-evolved wavefunction given by 7.1 and $\hat{V}_L(t)$ is the interaction Hamiltonian given by A.18. Within the SFA the wavefunction takes the form

$$|\Psi(t)\rangle = \hat{U}_0(t, t_0)|\phi_g\rangle - i \int_{t_0}^t \hat{U}_V(t, t') V(t') \hat{U}_0(t', t_0)|\phi_g\rangle dt' \quad (7.1)$$

The first term describes ionization, and the second term describes the evolution of the non-ionized part of the electron wavefunction. Where $\hat{U}_V(t, t')$ is the non-dipole Volkov time-propagator and its plane wave forms a complete basis $1 = \int |\boldsymbol{\pi}(\mathbf{p}, t, t')\rangle \langle \boldsymbol{\pi}(\mathbf{p}, t, t')| d\mathbf{p}$ where $\boldsymbol{\pi}(\mathbf{p}, t, t')$ is the non-dipole kinetic momentum.

$$\boldsymbol{\pi}(\mathbf{p}, t, t') = \left(\mathbf{p} + \mathbf{A}(R, t') - \int_{t'}^t \widehat{\partial_R \mathbf{A}}(R, \tau) [\mathbf{p} + \mathbf{A}(R, \tau)] d\tau \right); \quad \hat{U}_V(t, t') = e^{-\frac{i}{2} \int_{t'}^t (\mathbf{p} + \mathbf{A}(R, t'')) \cdot \widehat{\partial_R \mathbf{A}}(R, \tau) [\mathbf{p} + \mathbf{A}(R, \tau)] d\tau} dt''$$

Assuming no permanent dipole in the ground state and neglecting the continuum-continuum transitions we can express the induced multipole as a transition from bound to continuum state.

$$\mathbf{M}(t) = -i \int_{t_0}^t dt' \mathbf{p} \left(\mathbf{m}^* [\boldsymbol{\pi}(\mathbf{p}, t, t')] \mathbf{E}(R, t') \mathbf{m} [\boldsymbol{\pi}(\mathbf{p}, t, t')] e^{-iS(\mathbf{p}, t, t')} + c.c. \right) \quad (7.2)$$

where the phase is $S(\mathbf{p}, t, t') = \frac{1}{2} \int_{t'}^t \left[(\mathbf{p} + \mathbf{A}(R, t'')) - \int_{t''}^t \partial_R \widehat{\mathbf{A}}(R, \tau) (\mathbf{p} + \mathbf{A}(R, \tau)) d\tau \right]^2 + 2I_p dt''$, the multipole transition moment is represented by $\mathbf{m}[\boldsymbol{\pi}(\mathbf{p}, t, t')] = \langle \boldsymbol{\pi}(\mathbf{p}, t, t') | \hat{V}_L(t) | \phi_g \rangle$, and the linearly polarized electric field is $\mathbf{E}(t') = E_0(R) \cos(\omega t) \hat{x}$ ($E_0(R)$ is the transverse beam profile of the asymmetric LG beam given by 2.26). For any hydrogen-like state, the induced multipole can be solved similarly using saddle-point integration as performed in Chapter 6 section 6.3.5 which was performed for argon.

Although the higher multipole was shown to affect the ionization step when irradiated with asymmetric Laguerre-Gaussian beams and could result in interesting behaviours in HHG it is normally accepted to describe the harmonics generation through the dominant multipole, the electric dipole. For phase matching we can limit ourselves to the dipole approximation, the high order multipole are ignored and the interaction Hamiltonian reduces to $V_L(t') = \mathbf{d} \cdot \mathbf{E}(t')$ and the field gradient tensor $\partial_R \widehat{\mathbf{A}}(R, \tau) \rightarrow 0$ no longer exist in the phase $S(\mathbf{p}, t, t') = \frac{1}{2} \int_{t'}^t \left[(\mathbf{p} + \mathbf{A}(R, t''))^2 + 2I_p \right] dt''$ and kinetic momentum $\boldsymbol{\pi}(\mathbf{p}, t') = \mathbf{p} + \mathbf{A}(R, t')$. the induced multipole moment reduces to the standard SFA dipole moment.

$$\mathbf{D}(t) = -i \int_{t_0}^t dt' \mathbf{p} \left(\mathbf{d}^* [\boldsymbol{\pi}(\mathbf{p}, t)] \mathbf{E}(R, t') \mathbf{d} [\boldsymbol{\pi}(\mathbf{p}, t')] e^{-iS(\mathbf{p}, t, t')} + c.c. \right) \quad (7.3)$$

and after saddle-point approximation, the harmonic dipole can be expressed as a summation over the saddle-points $S(\mathbf{p}, t, t')$

$$\mathbf{D}(q\omega) = -i \sum_s \frac{2\pi}{\sqrt{\det(S''(\mathbf{p}, t, t'))}} \left(\frac{2\pi}{t_s - t'_s} \right)^{3/2} \mathbf{d}^* [\boldsymbol{\pi}(\mathbf{p}_s, t_s)] \mathbf{E}(R, t'_s) \mathbf{d} [\boldsymbol{\pi}(\mathbf{p}_s, t'_s)] e^{-iS(\mathbf{p}_s, t_s, t'_s) + iq\omega t_s} \quad (7.4)$$

where $S''(\mathbf{p}, t, t')$ is the Hessian matrix of the action $S(\mathbf{p}, t, t')$ with respect to t and t' evaluated at the stationary points $s = (\mathbf{p}_s, t_s, t'_s)$ [160, 162, 164]. The saddle-point approximation is closely related to classical trajectories of a free electron.

The phase $S(\mathbf{p}, t, t')$ accumulated by the electron during its propagation in the continuum and its recombination under the emission of the q th harmonic is called the dipole phase. The dipole phases of the short and long trajectories are different due to their difference in times for recollision. However, the closer to the harmonic cutoff $3.17U_p + I_p = q\omega$ the closer the dipole phase of the two trajectories. For relatively low intensity and gas pressure, the phase matching condition only includes the intrinsic phase of the driving laser field as well as the single-atom response. Other contributions such as the plasma defocusing and the neutral atom dispersion are excluded in this analysis. Although we expected plasma defocusing to play an important role in phase matching due to our ability to manipulate the plasma density by displacing the phase singularity. The phase matching is satisfied when

$$\mathbf{k}_q = qk_0 \hat{z} - q \nabla \phi_l(R, z) + \nabla \phi_{\text{dipole}}(R, z) \quad (7.5)$$

where $\phi_l(R, z) = \arg[\mathbf{E}_{0,l}(R, z)]$ and $\phi_{\text{dipole}}(R, z) = q\omega - S(\mathbf{p}, t, t')$. For both short and long trajectories, we can

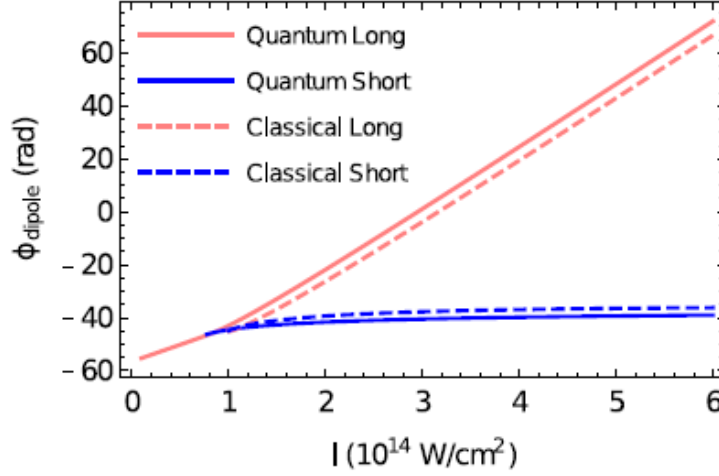


Fig 7.1: **Dipole phase** for an atom as a function of intensity for short (blue) and long (red) trajectories calculated by classical trajectories (dashed) and quantum orbits (solid) that contribute to the 21st harmonic. For the harmonic plateau, the dipole phase increases linearly with intensity. The slope of the dipole phase of the short trajectories is approximately $\alpha_s = 1.5 \times 10^{14} \text{ W/cm}^2$, whereas the slope of the dipole phase for the long trajectories is $\alpha_L = 22 \times 10^{14} \text{ W/cm}^2$ [162]

write a linear dependence of the dipole phase on intensity as both trajectories increase with intensity, $\phi_{\text{dipole}}(R, z) = \alpha_{i=L,S}^q |\mathbf{E}_{0,l}(R, z)|^2$, where $\alpha_{i=L,S}^q$ is dependent on the long and short trajectories as shown in figure 7.1 [162].

$$\mathbf{k}_q = qk_0 \hat{z} - q \nabla \arg [\mathbf{E}_{0,l}(R, z)] + \alpha_{i=L,S}^q \nabla |\mathbf{E}_{0,l}(R, z)|^2 \quad (7.6)$$

The phase matching condition can be determined over the entire interaction region. For the basic principle, consider only the phase matching on maximum (one-dimensional case) where the harmonics are emitted at the peak intensity.

For a **Gaussian** beam ($l = 0$), the maximum coincides with the beam axis ($R_{l,max}(z) = 0$) [60, 163]. Then, the phase-matching condition is given by

$$\mathbf{k}_q = qk_0 \hat{z} - q \nabla \arctan \left(\frac{z}{z_r} \right) + \alpha_{i=L,S}^q \nabla |\mathbf{E}_{0,l=0}(0, z)|^2 \quad (7.7)$$

For a **symmetrical LG** beam ($l \neq 0, \delta = 0$), the peak of the field is located at $R_{l,max}(z) = \sqrt{\frac{|l|}{2}} w(z) = \sqrt{\frac{|l|}{2}} w_0 \sqrt{1 + \frac{z^2}{z_r^2}}$ [60, 163]. Then the phase-matching condition is

$$\mathbf{k}_q = qk_0 \hat{z} - q(|l|+1) \nabla \arctan \left(\frac{z}{z_r} \right) - qk_0 \frac{R_{l,max}^2(z)}{2R_R(z)} + \alpha_{i=L,S}^q \nabla |\mathbf{E}_{0,l}(R_{l,max}(z), z)|^2 \quad (7.8)$$

For an **asymmetrical LG** beam ($l \neq 0, \delta \neq 0$), the phase and the intensity profile is given by

$$\arg [\mathbf{E}_{0,l}(R, z)] = \arctan \left[\tan \left(-k \left(\frac{R^2}{2R_R(z)} \right) - (|l|+1) \arctan \left(\frac{z}{z_r} \right) \pm |l| \arctan \left[\frac{(Y + \eta\delta)}{(X + \zeta\delta)} \right] \right) \right] \quad (7.9)$$

and

$$|\mathbf{E}_{0,l}(R, z)|^2 = |E_0|^2 \left(\frac{w_0}{w(z)} \right)^2 \left(\frac{\sqrt{2}}{w(z)} \right)^{2|l|} \exp \left[-\frac{2r^2}{w^2(z)} \right] ((X + \zeta\delta)^2 + (Y + \eta\delta)^2)^{|l|} \quad (7.10)$$

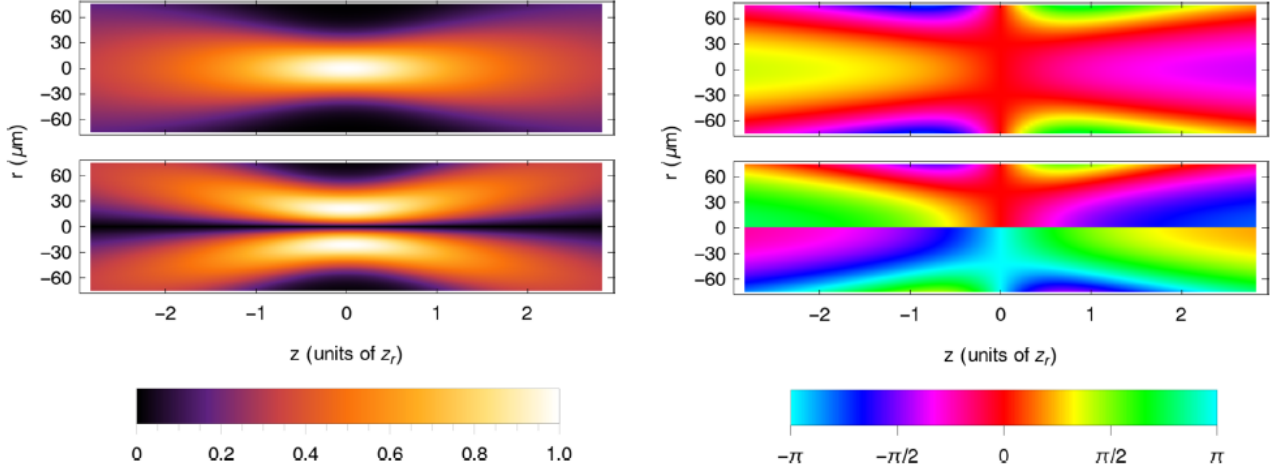


Fig 7.2: **Longitudinal cross-section** of the intensity and phase profile of Gaussian (upper row) and a symmetric LG beam (lower row). The Gaussian has a transverse intensity maximum at the beam axis and for the LG beam, it is off-axis located at $R_{l,max}$. The phase profile of the Gaussian beam shows the phase shift from $\pi/2$ to $-\pi/2$ due to the Gouy phase. The focal phase modifies the phase off-axis. The phase profile of the LG beam has a phase singularity on the propagation axis due to the term $il\phi$. In addition the phase shift caused by the Gouy phase is increased, from π to $-\pi$ [162]

Where the intensity is evaluated at the maximum field strength determined by $R_{l,max}(z)$. Due to the complexity of the aLG beam, it is difficult to find an analytical formula for the maximum for all l -value and δ -positions. However, it is easily determined numerically. Therefore, the phase-matching condition is

$$\mathbf{k}_q = qk_0\hat{z} - q\nabla\arctan\left[\tan\left(-k\left(\frac{R_{l,max}(z)^2}{2R_R(z)}\right) - (|l|+1)\arctan\left(\frac{z}{z_r}\right) \pm |l|\arctan\left[\frac{(Y_{max} + \eta\delta)}{(X_{max} + \zeta\delta)}\right]\right)\right] \pm \alpha_{i=L,S}^q \nabla|\mathbf{E}_{0,l}^{|\delta|}(R_{l,max}(z), z)|^2 \quad (7.11)$$

The gradient of the phase from the laser field, $\nabla\arg[\mathbf{E}_{0,l}(R, z)]$, is dependent on the l -value, the handedness of helical phase, and the magnitude and sign of asymmetric parameter δ . The dipole phase, $\alpha_{i=L,S}^q \nabla|\mathbf{E}_{0,l}^{|\delta|}(R_{l,max}(z), z)|^2$, is independent of the handedness of the helical phase but dependent on the l -value and the magnitude and sign of the asymmetrical parameter δ . The dipole phase changes sign for a negative and positive δ displacement over the entire interaction region or at the peak of the electric field as depicted by figure 6.7. Therefore, with this additional degree of control, it seems possible to improve the phase matching condition for asymmetrical LG beam.

Figure 7.3 depicts the phase profile of a Gaussian, symmetric and asymmetric LG beam. The Gaussian and symmetric phase profile in figure 7.3 agrees with the figure 7.2 published in [162]. The phase profile of the Gaussian beam shows the phase shift from $\pi/2$ to $-\pi/2$ due to the Gouy phase modifying the phase off-axis. The phase profile of the symmetric and asymmetric LG beam has a phase singularity on the propagation axis due to the term $il\phi$. In addition, the phase shift caused by the Gouy phase is increased, from π to $-\pi$. For an asymmetric LG beam, the shift in the null intensity results in an off-axis phase singularity. At the beam focus, there seems to be a smooth transition in the phase for $\delta = -1\mu m$ (figure 7.3 c) and a more drastic change for $\delta = +1\mu m$ (figure 7.3 d) at the focus. This behaviour flips for the opposite handedness of the helical phase (not shown). This drastic change in phase combined with the plasma defocusing will suppress the ionization and can affect the phase-matching for the generation of high harmonics. Therefore, phase-matching for asymmetrical LG beams can be manipulated simply by displacing the singularity position, this seems to

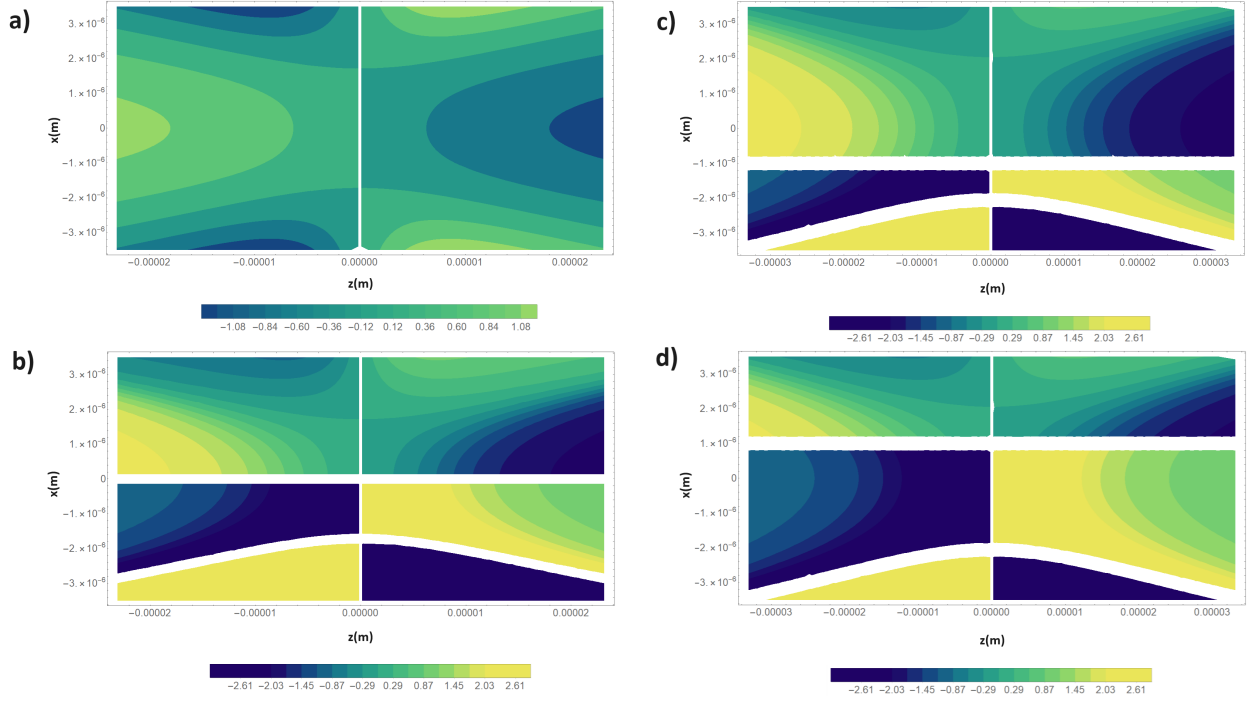


Fig 7.3: **Longitudinal phase profile** of Gaussian (a), a symmetric LG beam (b), and asymmetrical LG beam for $\delta = \pm 1$ (c and d). The y-axis represents the the beam waist $w(z)$ in the x-direction and the x-axis represents the Rayleigh range z_R . The white lines are merely a relic of the computation.

be analogous to increasing the efficiency of second-harmonic by angular rotation of a nonlinear crystal.

This phase matching control combined with the ability to tune the ponderomotive energy arises by simply displacing the phase singularity influencing the overall yields of HHG. It seems plausible that asymmetric LG beams can increase the efficiency of HHG compared to a symmetric OAM beam or even potentially to a Gaussian beam.

7.2.2 PHOTOELECTRON HELICAL DICHROISM

Time-resolved photoelectron spectroscopy is a technique employed to measure photoelectron kinetic energy and angular distribution. The photoelectron velocity vectors v_z and v_x/v_y are measured using a TOF method and position-sensitive detectors. VMI is used to map the initial velocity vector of an electron to a specific point on the detector. Photoelectrons that originate from the interaction region expand in spherical shells, referred to as Newton spheres. The radius of these spheres grows at a rate that is proportional to the electron's kinetic energy as shown in figure 7.4.

These 3D Newton spheres are detected by a MCP as a 2D projection. The electron's kinetic energy is encoded in the radial coordinate, and the angular distribution is encoded in the angular coordinate of the 2D projection. By using cylindrical symmetry about an axis parallel to a detector, the 3D distribution can be reconstructed from the 2D projection using Abel inversion, which is related to the Fourier and Hankel transform with certain axial symmetry. The power of VMI lies in its ability to measure the angular distributions of photoelectrons, providing detailed insights into photoionization dynamics.

By implementing the VMI detection scheme with an asymmetrical OAM beam, as the source of ionization, we can expand on the OAM-dependent ionization result of Chapter 6 section 6.3 to elucidate the effect of OAM and asymmetrical

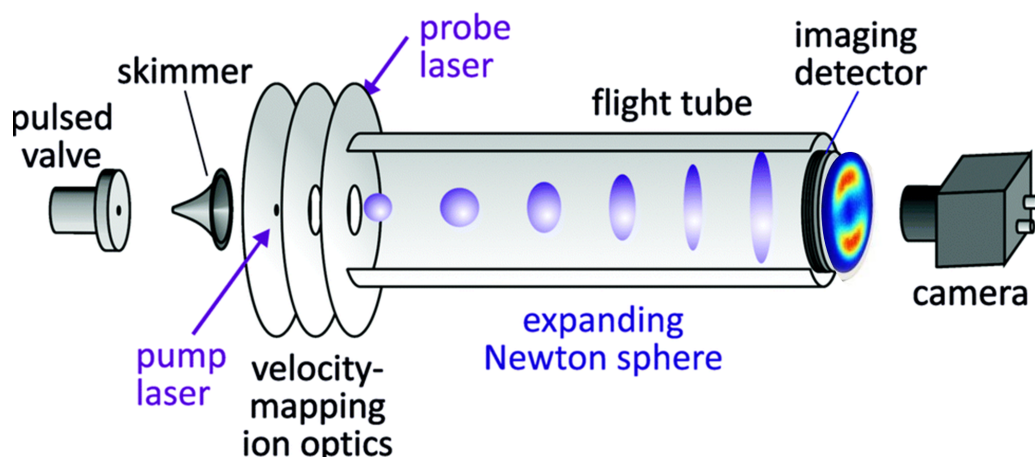


Fig 7.4: **Velocity map imaging** of the photoelectron angular distribution by ionization of chiral molecules using asymmetrical helical light. The purpose is to enhance the chiral signal by generating larger dichroic contrast and higher-order sidebands compared to PECD. These measurements can also be performed for achiral molecules and atoms. This is an extension of the TOF-MS OAM-dependent ionization, in chapter 6. Analyze the ionization dynamics by imaging the asymmetrical PAD instead of the charged ions and fragments [165].

parameter δ on the photoelectron emission. By measuring the electrons instead of the ions more information on the photoionization dynamics can be achieved. In principle, this will be an extension of PECD, described in Chapter 1 section 1.2.2, where the chiral probe is no longer a circular polarized Gaussian beam but symmetric and asymmetric LG beams. This will utilise the benefits of high energy resolution of VMI detection with the additional elements of control helical light provides such as the handedness of the helical phase, the polarization, the unbound l -value and the asymmetrical parameter δ . PEHD will not be limited to chiral molecules but could also be employed with atoms and achiral molecules. The forward and backward asymmetrical emission of the PAD could be studied and controlled. This will elucidate the effect of OAM and asymmetric parameter δ on photoionization dynamics and reaction pathways.

The absorption of photons carrying a total angular momentum $j = l + s$ in the propagation direction over the transverse beam profile will consist of spin-orbit coupling during the absorption or ionization process. According to the conservation laws, the total angular momentum, $J = \sum_i j_i = \sum_i (l_i + s_i)$, must be conserved during the interaction. This alters the selection rules allowing for new pathways not accessible with the conventional circularly polarized Gaussian. For typical PECD, the irradiating field consists only of spin angular momentum $s = \pm 1$ and $l = 0$, thus j is restricted to 0,1,2. However, when $l \neq 0$ j is no longer required between 0...2. Therefore, the coefficients b_j^p of PECD defined by the Clebsch-Gordon coefficient will no longer be limited to 2, see equation 1.52. For PECD, enantio-sensitivity and the asymmetry in the PAD is mainly due to the first order term ($b_1^{+1} = -b_1^{-1}$) and is only present for circularly polarized light. For linear polarization, no asymmetry is expected for chiral and achiral molecules. However, with the introduction of OAM, such Clebsch-Gordon coefficients are not restricted to such conditions. Potentially, allowing the presence of asymmetry PAD for linear polarized LG beams and new coefficients that could alter the rate or symmetry of the photoelectron.

7.2.2.1 PROOF OF PRINCIPLE

Different ionization pathways and photoelectron emission rates can be achieved due to the presence of OAM in the interaction region and the asymmetry introduced by the irradiating field. By expressing the transition matrix in the

spherical basis new selection rules can be extracted from the photoionization with OAM beams [123]. Consider a single photon interaction of atoms with an OAM beam, the quantum states can be expressed as a radial and spherical basis $\psi(\vec{r}) = R_{nl}(r)Y_{lm}(\hat{r})$. Taking the first interaction Hamiltonian, $\hat{V} = -\frac{q}{2m}(\mathbf{p} \cdot \mathbf{A}(\rho, t) + \mathbf{A}(\rho, t) \cdot \mathbf{p})$, the matrix element takes the form

$$\frac{d\sigma}{d\Omega} = \frac{\alpha a_0^2}{2\pi} k E_{\hbar\omega} |\langle \psi_f(\vec{r}) | \mathbf{r} \cdot \mathbf{A}(\rho) | \psi_i(\vec{r}) \rangle|^2 \quad (7.12)$$

In chapter 1 section 1.2.2.1 we showed the relation between the transition rate and the differential cross-section for an electron to transition from ground to continuum given by equation 1.54. where $\mathbf{A}(\rho) = A_0 \left(\frac{\sqrt{2}\rho}{w_0} \right)^{|l|} e^{i(\mp|l|\phi)}$ is either the symmetrical LG beam and $\rho = \sqrt{x^2 + y^2}$. For convenience, the vector potential is written in the dipolar and transverse spatial approximation (a Gaussian beam can be considered as a plane wave) [123]. Taking the quantization axis in the beam propagation direction, the position vector can thus be written as $\mathbf{r} = (x, y, z) = r\{\sin(\theta)\cos(\phi), \sin(\theta)\sin(\phi), \cos(\theta)\}$ and expressing the vector potential in spherical basis using $\rho = r\sin\theta$ [123]. For the show of principle consider the symmetrical LG beam

$$\begin{aligned} \langle R_{n'l'}(kr)Y_{l'm'}(\hat{r}) | \mathbf{r} \cdot \mathbf{A}(\rho) | R_{nl}(r)Y_{lm}(\hat{r}) \rangle &\propto \langle R_{n'l'}(kr)Y_{l'm'}(\hat{r}) | r \left[\alpha (\sin\theta)^{|l|+1} \cos(\phi), \beta (\sin\theta)^{|l|+1} \sin(\phi) \right] \\ &A_0 \left(\frac{\sqrt{2}r}{w_0} \right)^{|l|} e^{i(\mp|l|\phi)} | R_{nl}(r)Y_{lm}(\hat{r}) \rangle \quad (7.13) \end{aligned}$$

$$\begin{aligned} \langle R_{n'l'}(kr)Y_{l'm'}(\hat{r}) | \mathbf{r} \cdot \mathbf{A}(\rho) | R_{nl}(r)Y_{lm}(\hat{r}) \rangle &\propto A_0 \int_0^\infty dr R_{n'l'}(kr) r^3 \left(\frac{\sqrt{2}r}{w_0} \right)^{|l|} R_{nl}(r) \times \\ &\int d\Omega Y_{l'm'}^*(\hat{r}) \left[\begin{aligned} \alpha (\sin\theta)^{|l|+1} \cos\phi &= \frac{\alpha}{2} \left((\sin\theta)^{|l|+1} e^{i(\mp|l|+1)\phi} + (\sin\theta)^{|l|+1} e^{i(\mp|l|-1)\phi} \right) \\ \beta (\sin\theta)^{|l|+1} \sin\phi &= \frac{\beta}{2i} \left((\sin\theta)^{|l|+1} e^{i(\mp|l|+1)\phi} - (\sin\theta)^{|l|+1} e^{i(\mp|l|-1)\phi} \right) \end{aligned} \right] Y_{lm}(\hat{r}) \quad (7.14) \end{aligned}$$

where the angular contribution can be expanded in terms of spherical harmonics $Y_l^l = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sin^l \theta e^{il\phi}$ [123]. OAM beams introduce new spherical harmonics in the interaction where their product results in new Clebsch-Gordon coefficients resulting in different selection rules. Thus, the differential cross-section for PEHD will have different coefficients in terms of b_j^p in the angular distribution $I(\theta)$ compared to PECD, shown in chapter 1 section 1.2.2. By altering with the beam transverse profile we can expect a larger exchange of angular momentum transfer by increasing the OAM and SAM.

A similar approach can be performed using an asymmetrical beam as well as including the higher order multipoles to the differential cross-section.

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}^{\text{E1E1}} + \frac{d\sigma}{d\Omega}^{\text{E1M1}} + \frac{d\sigma}{d\Omega}^{\text{E1E2}} + O(\alpha^3 a_0^2) \quad (7.15)$$

The first term is given by equation 7.12 and the higher order coupling differential cross-section is by [27]

$$\frac{d\sigma}{d\Omega}^{\text{E1M1}} = \frac{(\alpha a_0)^2}{2\pi} k E_{\hbar\omega} \text{Im} \left[\langle \psi_f(\vec{r}) | \mathbf{r} \cdot \mathbf{A}(\rho) | \psi_i(\vec{r}) \rangle^* \langle \psi_f(\vec{r}) | \mathbf{L} \cdot i \left(\hat{\mathbf{k}} \times \mathbf{A}(\rho) \right) | \psi_i(\vec{r}) \rangle \right] \quad (7.16)$$

$$\frac{d\sigma^{\text{E1E2}}}{d\Omega} = -\frac{(\alpha a_0)^2}{2\pi} k E_{\hbar\omega} \text{Im} \left[\langle \psi_f(\vec{r}) | \mathbf{r} \cdot \mathbf{A}(\rho) | \psi_i(\vec{r}) \rangle^* \langle \psi_f(\vec{r}) | (\mathbf{r} \cdot \mathbf{A}(\rho)) \left(\hat{\mathbf{k}} \cdot \mathbf{r} \right) | \psi_i(\vec{r}) \rangle \right] \quad (7.17)$$

The full solution to all three expressions is quite extensive and requires further investigation, however, the E1E1 and E1E2 terms are expected to be responsible for any form of asymmetry in the PAD with linear polarized light and the E1M1 will become significant for highly elliptical light. An increase of coefficients would be expected and include the transverse asymmetry of the beam, δ -parameter, resulting in asymmetric photoelectron emission for either the handedness of helical light or the δ -position. That is, the additional asymmetry and OAM carried by the irradiating field will alter the photoelectron emission symmetry of chiral and achiral molecules as you displace the δ -position.

The ionization profile shown in figure 6.6 (chapter 6 section 6.3) depicts ionization hot spots within the beam cross-section. Although this is a local effect in the interaction region, some asymmetry is expected to translate to the 3D Newton rings and be detected by the 2D projection due to the difference in kinetic energy of the photoelectron after ionization. Some differences are expected to occur due to the resolution from the electron spread when accelerated after the ionization process. The electron momentum direction could alter the shape however the yield count of the electron should be different between the two-handedness of the helical phase for a specific δ -position and this behaviour should flip as the singularity traverses the origin. It would be interesting to know if the cross-sectional beam profile and OAM can be imprinted onto the PAD and detected using a VMI system. Furthermore, these measurements could be performed with a photoelectron-photoion coincidence spectroscopy (PEPICO) to determine if any additional information between the electron and ions can be extracted during the ionization process.

7.2.3 OAM DEPENDENT NON-SEQUENTIAL DOUBLE IONIZATION

Non-sequential double ionization is a strong-field process characterized by the correlation emission of two-electron ionization. The process follows the three-step model as depicted in Chapter 3 section 3.2.6 in figure 3.8: i) the first electron is removed from the outermost electron via tunnel ionization to the continuum at the peak of the field. Leaving the second electron unaffected by the field due to the decreasing amplitude of the field which is proportional to the time elapse. Although in some cases, where the molecular I_p is low or at higher field strengths, this remnant field can excite the cation to higher states. ii) The field drives the continuum electron away from the parent ion where it gains kinetic energy and broadens in the transverse plane. Upon reversal of the laser field, the electron is driven back to the parent ion and undergoes a laser-driven recollision with the parent ion. Depending on the laser polarization, the recolliding electron can return with a transverse displacement decreasing the probability of recollision. The recollision probability is greater for linear polarization and decreases as the ellipticity is increased. For circular polarization, the electron misses the parent ion and the measured double ionization is mostly due to sequential double ionization. iii) Upon recollision the energy imparted allows for two pathways, the second electron is directly ionized by the electron impact (NDSI) or the second electron is subsequently ionized by the field after impact (RESI).

The proposed experiment is to study the influence of asymmetrical OAM beams on the electron recollision process. Can the helical phase combined with polarization alter the electron recollision, either increase or decrease the probability of recollision and can this be further controlled by displacing the singularity. We have demonstrated that the ionization step of argon, limonene and acetone are strongly influenced and controlled by the handedness of the helical light and

the asymmetric parameter δ , see figure 6.3 and 6.4. Since the first step exhibits differential yields, similar features are expected to persist if not enhanced by the electron-electron correlation for NSDI or RESI.

NSDI could be investigated by measuring the momentum distribution of the ions and electrons generated. Complete measurements of the double ionization dynamics obtained by the coincident detection of the two electrons and the doubly charged ion will allow for the direct observation of the correlated electron momenta in the presence of SAM and OAM and potentially controlled using the asymmetric parameter δ of the LG beam. This must consist of sophisticated setups such as COLTRIMS or a PEPICO setup.

However, some information can still be extracted by measuring the ions with the current TOFMS setup. Two simple measurements can help to elucidate the recollision dynamics: measure the doubly charged ion yields as a function of i) ellipticity or ii) pulse intensity.

i) By measuring the doubly charged yields of an atom as a function of laser polarization, the yields during the recollision process decrease as the ellipticity is increased exhibiting a Gaussian-like distribution. The transverse displacement of the electron can be extracted from the width of the yield vs ellipticity curve. Figure 7.5 shows preliminary results of argon for Gaussian ($l = 0$), symmetric OAM beam ($l = 1, \delta = 0\mu m$), and asymmetrical OAM beam ($l = 1, \delta = 1\mu m$). All the measurements were made at the same laser intensity. As a result, the single ion yields for Gaussian and symmetric OAM beams are nearly identical at all ellipticities. However, for asymmetrical OAM beams, the single ion yields are higher owing to a larger distortion of the atomic potential. Due to recollision, the doubly charged argon ion yields decrease rapidly with ellipticity compared to the singly charged ions. From the ellipticity dependence, the transverse displacement and spreading of the electron wavepacket after tunnel ionization could be extracted. The observed small differences suggest OAM and δ -position can affect the transverse momentum of the electron. However, these subtle differences require further investigation, to improve the signal these measurements could be performed by using atoms with lower ionization potential such as Xenon, with higher pulse energies to reduce the errors in the ion yields, and at longer wavelengths to increase any visible difference owing to the larger propagation time of the liberated electron.

Additionally, the smaller the hole for tunneling the greater the transverse momenta of the ionized electron and vice versa. Asymmetric OAM beam can strongly influence the suppression of the atomic potential affecting the initial momentum spread of the first ionized electron and directly influencing the rescattering process.

ii) By measuring the doubly charged yields of an atom as a function of pulse intensity, the ion yields increase as the intensity is increased. In these measurements, NSDI manifests itself as a knee shape in the intensity-dependent double-ionization curve, see figure 7.6. The rate of doubly charged ion yields is reduced due to the electron-electron correlation. This knee shape is not expected for a sequential double ionization process because the first and second ionization are independent from each other. In the intensity region below the knee structure, a strong correlation in the electron momenta is observed while above the knee is a structureless distribution. This correlated character in the electron emission in NSDI is a consequence of the rescattering process, in which a first electron, liberated via tunnel ionization, is strongly accelerated by the laser field and driven back to the parent core where an inelastic collision triggers the ionization of a second electron. It is expected that the scattering process will be influenced by the field distribution of an asymmetrical OAM beam. By using the scattering theory for recollision dynamics, as in Chapter 6 section 6.1 and 6.2, the difference in the probability of recollision can be investigated.

The knee shape is influenced by the ellipticity and the wavelength of the incident laser field. The higher the ellipticity

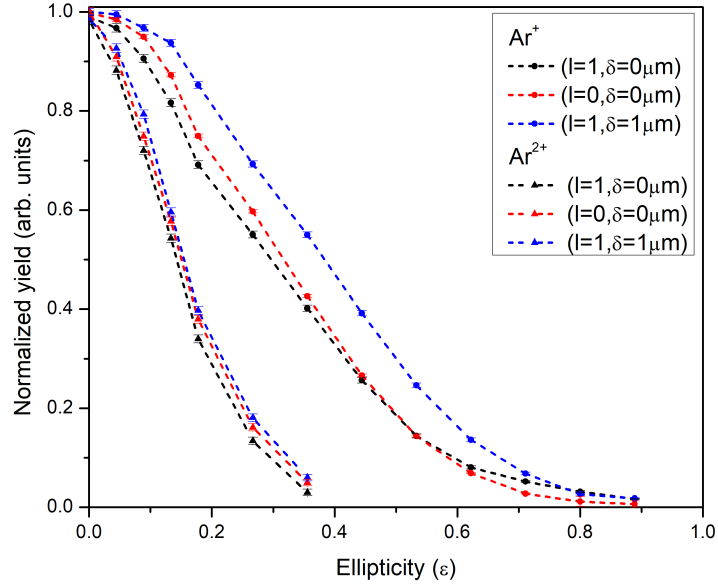


Fig 7.5: **Ellipticity variation of singly (circles) and doubly (triangles) charged argon** as a function of laser ellipticity for $l = 0, \delta = 0 \mu\text{m}$ in red, $l = 1, \delta = 0 \mu\text{m}$ in black, and $l = 1, \delta \sim +1 \mu\text{m}$ in blue. The laser intensity was $1.1 \times 10^{14} \text{ W/cm}^2$ and dashed lines are for visual guidance.

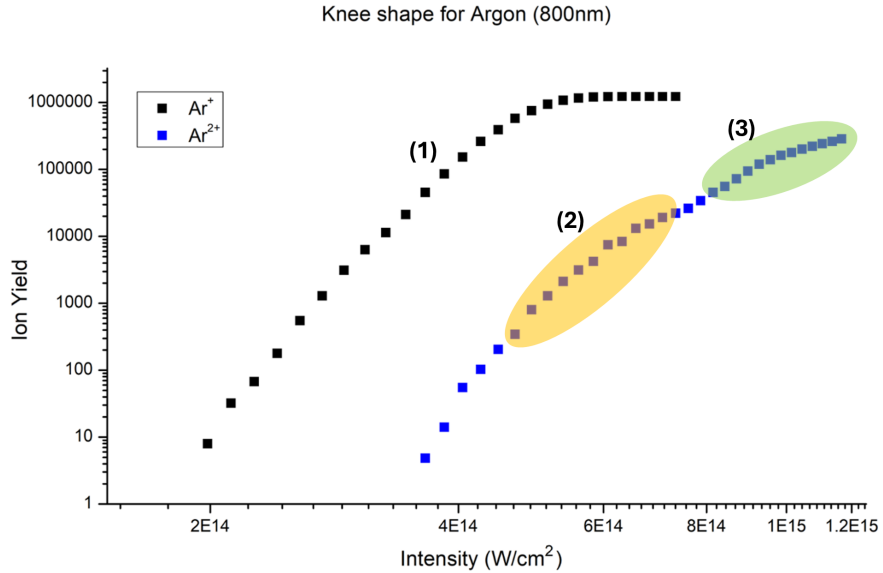


Fig 7.6: **Argon Ion yields as a function of pulse intensity.** (1) Single ionization, $\text{Ar} \rightarrow \text{Ar}^+ + e^-$. (2) Dominance of the non-sequential double ionization, $\text{Ar} \rightarrow \text{Ar}^{2+} + 2e^-$, the momentum distribution will show a distinct double peak. (3) the double ionization rate is described by the sequential process, $\text{Ar} \rightarrow \text{Ar}^+ + e^- \rightarrow \text{Ar}^{2+} + 2e^-$, the momentum distribution shows a single peak as for the single ionization. All curves can be simulated by SFA with the Coulomb correction or ADK/PPT.

and the longer the wavelength the more pronounced the knee shape. This is commonly attributed to the rescattering process and the ponderomotive energy of the liberated electron. The ponderomotive energy scales linearly with the laser intensity and quadratically with the wavelength. The electron trajectory, in the continuum, is influenced by the ellipticity, the maximum y-displacement is $y_{max} \propto \varepsilon x_{max}$ where ε is the ellipticity. Therefore, since ponderomotive energy can be further increased with asymmetrical LG beams by using a higher l -value or by displacing the singularity, the knee shape is expected to exhibit different features. By comparing the knee shape of Gaussian, symmetric and asymmetric OAM beams we could expect a variation in the knee shape onset, its rate (slope) and prominence over a certain intensity range.

APPENDICES

A

APPENDIX

A.1 MULTIPOLE EXPANSION OF THE INTERACTING HAMILTONIAN

This section will derive and define the electric-dipole (E1), the electric-quadrupole (E2) and the magnetic-dipole (M1) by converting the common velocity gauge Hamiltonian, $\hat{V}(t) = \frac{1}{2} [\vec{p} + \vec{A}(r', t)]^2$, for a single electron in an electromagnetic field to the length gauge. This is useful as ground state of hydrogen-like atoms are only valid in length-gauge. This will allow us to express the transition amplitudes in such a gauge.

The ground state wavefunction, in velocity gauge, is expressed with a unitary operator $\hat{W} = e^{-i\chi(r, t)}$ to maintain the Schrodinger Equation (SE) invariance. The ground state wavefunction is

$$|\tilde{\phi}_g(t)\rangle = e^{-i\chi(r, t)} |\phi_g(t)\rangle \quad (\text{A.1})$$

where $\chi(r, t)$ is the generating function. The velocity gauge Schrodinger equation becomes

$$i \frac{\partial}{\partial t} \left(e^{-i\chi(r', t)} |\phi_g(t)\rangle \right) = \frac{1}{2} (-i\nabla + A(r', t))^2 e^{-i\chi(r', t)} |\phi_g(t)\rangle \quad (\text{A.2})$$

To introduce higher-order multipoles in the interaction Hamiltonian, Taylor expanded the vector potential to the second order about a point R in the velocity gauge and transformed it into the length gauge. Taylor expansions of vector fields

are most easily seen through directional derivatives.

$$f(r') = f(R) + ([r' - R] \cdot \nabla') f(r')|_{r'=R} + \frac{1}{2!} ([r' - R] \cdot \nabla')^2 f(r')|_{r'=R} \quad (\text{A.3})$$

Following this definition and using $r = r' - R$ we expand the vector potential to the second term.

$$\vec{A}(r', t) = \vec{A}(R, t) + (\vec{r} \cdot \vec{\nabla}) \vec{A}(R, t) + \dots = \begin{bmatrix} A_x(R, t) + (\vec{r} \cdot \vec{\nabla}) A_x(R, t) \\ A_y(R, t) + (\vec{r} \cdot \vec{\nabla}) A_y(R, t) \\ A_z(R, t) + (\vec{r} \cdot \vec{\nabla}) A_z(R, t) \end{bmatrix} = \vec{A}(R, t) + \vec{r}^\top \widehat{\partial A}(R, t) + \dots \quad (\text{A.4})$$

It can be shown that $(\vec{r} \cdot \vec{\nabla}) \vec{A}(R, t)$ is equal to $\vec{r}^\top \widehat{\partial A}(R, t)$ where $\vec{r}^\top$ represents the transpose of the vector position and $\widehat{\partial A}(R, t)$ is a second rank tensor defined as

$$\widehat{\partial A} = \begin{bmatrix} \partial_x A_x & \partial_x A_y & \partial_x A_z \\ \partial_y A_x & \partial_y A_y & \partial_y A_z \\ \partial_z A_x & \partial_z A_y & \partial_z A_z \end{bmatrix} \quad (\text{A.5})$$

Thus, the expanded vector potential is $\vec{A}(r', t) \approx \vec{A}(R, t) + \vec{r}^\top \widehat{\partial A}(R, t)$. Substituting this vector potential into the velocity gauge SE, by rearranging and simplifying we get

$$i \frac{\partial}{\partial t} \left(e^{-i\chi(r, R, t)} |\phi_g(t)\rangle \right) = \left[\frac{1}{2} (-i\nabla + A(R, t))^2 + \vec{r}^\top \widehat{\partial A}(R, t) (-i\nabla + A(R, t)) \right] e^{-i\chi(r, R, t)} |\phi_g(t)\rangle \quad (\text{A.6})$$

Applying the unitary operator $\hat{W}$ to both sides in order of expression of the Schrodinger equation in length gauge.

$$\frac{\partial \chi(r, R, t)}{\partial t} |\phi_g(t)\rangle + i \frac{\partial |\phi_g(t)\rangle}{\partial t} = \left[\frac{1}{2} (-i\nabla + A(R, t) - \nabla \chi(r, R, t))^2 + \vec{r}^\top \widehat{\partial A}(R, t) (-i\nabla + A(R, t) - \nabla \chi(r, R, t)) \right] |\phi_g(t)\rangle \quad (\text{A.7})$$

Omitting the higher-order terms for the vector field and the generating function in $(A(R, t) - \nabla \chi(r, R, t))^2$, we get

$$i \frac{\partial |\phi_g(t)\rangle}{\partial t} = \left[-\frac{\partial \chi(r, R, t)}{\partial t} - \frac{\nabla^2}{2} - i(A(R, t) - \nabla \chi(r, R, t)) \nabla + \vec{r}^\top \widehat{\partial A}(R, t) (-i\nabla + A(R, t) - \nabla \chi(r, R, t)) \right] |\phi_g(t)\rangle \quad (\text{A.8})$$

Using the fact of the field-free Hamiltonian acting on a state is $H_0|\phi\rangle = -\frac{\nabla^2}{2}|\phi\rangle$, we obtain

$$\left(i \frac{\partial}{\partial t} - H_0 \right) |\phi_g(t)\rangle = \left[-\frac{\partial \chi(r, R, t)}{\partial t} - i(A(R, t) - \nabla \chi(r, R, t)) \nabla + \vec{r}^\top \widehat{\partial A}(R, t) (-i\nabla + A(R, t) - \nabla \chi(r, R, t)) \right] |\phi_g(t)\rangle \quad (\text{A.9})$$

From the Schrodinger equation with the total Hamiltonian, $i \frac{\partial}{\partial t} |\phi_g(t)\rangle = [H_0 + V_L(t)] |\phi_g(t)\rangle$, we can define the length the interacting Hamiltonian $V_L(t)$ as

$$V_L(t) = -\frac{\partial \chi(r, R, t)}{\partial t} - i(A(R, t) - \nabla \chi(r, R, t)) \nabla + \vec{r}^\top \widehat{\partial A}(R, t) (-i\nabla + A(R, t) - \nabla \chi(r, R, t)) \quad (\text{A.10})$$

A complete multipole expansion is obtained by choosing a generating function, in the canonical transformation. It is convenient to use the following integral representation for the generating function, $\chi(r, R, t) = \int_0^1 r \cdot A(R + \lambda r, t) d\lambda$. The Taylor expanded generating function is obtained by expanding the vector potential as $A(R + \lambda r, t) = A(R, t) + (\lambda r \cdot \nabla)A(R, t)$

$$\chi(r, R, t) = \int_0^1 r \cdot A(R, t) d\lambda + \int_0^1 \lambda r^\top \widehat{\partial A}(R, t) r d\lambda = r \cdot A(R, t) + \frac{1}{2} r^\top \widehat{\partial A}(R, t) r \quad (\text{A.11})$$

Therefore, from the coulomb gauge, we can convert the vector potential to an electric field and extract the electric dipole and quadrupole moment.

$$\frac{\partial}{\partial t} \chi(r, R, t) = - \underbrace{r \cdot E(R, t)}_{\text{E1}} - \underbrace{\frac{1}{2} r^\top \widehat{\partial E}(R, t) r}_{\text{E2}} \quad (\text{A.12})$$

For the magnetic dipole, more arithmetic is needed. Consider the second term of A.10 with the vector potential and the gradient of $\chi(r, R, t)$.

$$A(R, t) - \nabla \chi(r, R, t) = -\frac{1}{2} \nabla \left(r^\top \widehat{\partial A}(R, t) r \right) = -\frac{1}{2} \nabla_k r_i r_j \widehat{\partial_j A_i}(R, t) \quad (\text{A.13})$$

$$A(R, t) - \nabla \chi(r, R, t) = -\frac{1}{2} \left(\delta_{ki} r_j \widehat{\partial_j A_i}(R, t) + r_i \delta_{kj} \widehat{\partial_j A_i}(R, t) \right) \quad (\text{A.14})$$

$$A(R, t) - \nabla \chi(r, R, t) = -\frac{1}{2} \left(r_j \widehat{\partial_j A_k}(R, t) + r_i \widehat{\partial_k A_i}(R, t) \right) = -\frac{1}{2} r^\top \left(\widehat{\partial A}(R, t) + \widehat{\partial A}(R, t)^\top \right) \quad (\text{A.15})$$

Keeping only $O(\widehat{\partial A})$, therefore ignore $A(R, t) - \nabla \chi(r, R, t)$ in the last term on the right-hand side of A.10 as it will generate higher order terms. Now substitute A.12 and A.15 into the interaction Hamiltonian A.10 to obtain

$$V_L(t) = r \cdot E(R, t) + \frac{1}{2} r^\top \widehat{\partial E}(R, t) r + i \left(\frac{1}{2} r^\top \left(\widehat{\partial A}(R, t) + \widehat{\partial A}(R, t)^\top \right) \right) \nabla - i r^\top \widehat{\partial A}(R, t) \nabla \quad (\text{A.16})$$

$$V_L(t) = r \cdot E(R, t) + \frac{1}{2} r^\top \widehat{\partial E}(R, t) r - i \left(\frac{1}{2} r^\top \left(\widehat{\partial A}(R, t) - \widehat{\partial A}(R, t)^\top \right) \right) \nabla \quad (\text{A.17})$$

Here the last term is the magnetic dipole $-i \left(\frac{1}{2} r^\top \left(\widehat{\partial A}(R, t) - \widehat{\partial A}(R, t)^\top \right) \right) \vec{\nabla} = \frac{1}{2} \vec{r} \hat{B} (-i \vec{\nabla}) = \frac{1}{2} \vec{L} \cdot \vec{B}$ recall the magnetic dipole $\vec{L} = \vec{r} \times (-i \vec{\nabla})$. Therefore, the interaction Hamiltonian in the length gauge and atomic units can be written as

$$V_L(t) = r_i E_i(R, t) + \frac{1}{2} r_i r_j \widehat{\partial_j E_i}(R, t) + \frac{1}{2} L_i B_i(R, t) \quad (\text{A.18})$$

In standard units this results in the standard multipole expansion of the interacting Hamiltonian.

$$\hat{V}_L(R, r, t) = \underbrace{\mu_i E_i(R, t)}_{\text{E1}} + \underbrace{Q_{ij} \widehat{\nabla_j E_i}(R, t)}_{\text{E2}} + \underbrace{m_i B_i(R, t)}_{\text{M1}} \quad (\text{A.19})$$

Where we can explicitly define the E1, M1, and E2 terms for an ensemble of charges in a system as

$$\boldsymbol{\mu} = \sum_n q_n \mathbf{r}_n \quad (\text{A.20})$$

$$\mathbf{m} = \sum_n \frac{q_n}{2m_n} \mathbf{r}_n \times \mathbf{p}_n \quad (\text{A.21})$$

$$\mathbf{Q} = \sum_n \frac{q_n}{2} \mathbf{r}_n \mathbf{r}_n \quad (\text{A.22})$$

A.2 NON-DIPOLE CONTINUUM WAVEFUNCTION

The Gordon-Volkov wavefunction is a laser field modulated plane wave solution to the Hamiltonian of a liberated photoelectron when neglecting the influence of the atomic potential $U(r)$. The non-dipole free-electron wavefunction was obtained from the velocity gauge Schrodinger equation.

$$i \frac{d}{dt} \Psi(r, t) = \frac{1}{2} (-i \vec{\nabla} + \vec{A}(r, t))^2 \Psi(r, t) \quad (\text{A.23})$$

We can express the higher order multipoles in the Hamiltonian by Taylor expanding the vector potential to the second order about a point R in the velocity gauge.

$$i \frac{d}{dt} \Psi(r, t) = \left[\frac{1}{2} [-i \vec{\nabla} + \vec{A}(R, t)]^2 + \vec{r} \cdot \widehat{\partial_R A}(R, t) [-i \vec{\nabla} + \vec{A}(R, t)] \right] \Psi(r, t) \quad (\text{A.24})$$

The Hamiltonian commutes with the momentum operator $\hat{p} = -i \vec{\nabla}$ and since the momentum state $|k\rangle = e^{ik \cdot r}$ is an eigenfunction of p with an eigenvalue k we seek a solution having the following behaviour $\Psi(r, t) = \frac{1}{(2\pi)^{3/2}} e^{ik \cdot r} f_k(t)$, where $f_k(t)$ is the time modulation of the plane wave in the presence of the laser field. The Schrodinger equation can be rewritten as

$$\frac{df_k(t)}{dt} = -i \left[\frac{1}{2} [k + A(t)]^2 + i \nabla_k^\top \widehat{\partial_R A} [k + A(t)] \right] f_k(t) \quad (\text{A.25})$$

We use the following transformation, to order $O(\widehat{\partial_R A})$, to simplify the solution to the differential equation by eliminating the second term on the right-hand side.

$$k = p - \int_{-\infty}^t \widehat{\partial_R A}(t') [p + \vec{A}(R, t')] dt'; \quad p = k - \int_{-\infty}^t \widehat{\partial_R A}(t') [k + \vec{A}(R, t')] dt' \quad (\text{A.26})$$

Using the total derivative chain rule to rewrite the time derivative on the left-hand side of equation A.25.

$$\frac{d}{dt} = \frac{\partial f}{\partial p} \cdot \frac{dp}{dt} + \frac{\partial f}{\partial t} \cdot \frac{dt}{dt} = \nabla_p^\top \frac{d}{dt} \left(k - \int_{-\infty}^t \widehat{\partial_R A}(R, t') [k + \vec{A}(R, t')] dt' \right) + \frac{\partial f}{\partial t} \quad (\text{A.27})$$

$$\frac{d}{dt} = \nabla_p^\top \widehat{\partial_R A}(R, t) (k + \vec{A}(R, t)) + \frac{\partial}{\partial t} \quad (\text{A.28})$$

In the non-resonant process ($t \rightarrow \infty$) we can consider only the first order term of the transformation and substitute $\nabla_p \rightarrow \nabla_k$.

$$\left(\nabla_k^\top \widehat{\partial_R A}(R, t) (k + \vec{A}(R, t)) + \frac{\partial}{\partial t} \right) f_k(t) = -i \left[\frac{1}{2} (k + \vec{A}(R, t))^2 + i \nabla_k^\top \widehat{\partial_R A}(R, t) (k + \vec{A}(R, t)) \right] f_k(t) \quad (\text{A.29})$$

$$\frac{\partial}{\partial t} f_k(t) = -i \left[\frac{1}{2} (k + \vec{A}(R, t))^2 \right] f_k(t) \Rightarrow f_k(t) = e^{-\frac{i}{2} \int (k + \vec{A}(R, \tau))^2 d\tau} \quad (\text{A.30})$$

The total wavefunction is obtained from the above solution for $f_k(t)$ combined with the plane wave solution.

$$\Psi(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k} \cdot \vec{r}} e^{-\frac{i}{2} \int (k + \vec{A}(R, \tau))^2 d\tau} \quad (\text{A.31})$$

Using the other transformation from A.26, we can express the total wavefunction in terms of p .

$$\Psi_V(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i(\vec{p} - \int_{t'}^t \widehat{\partial A}(R, \tau)(\vec{p} + \vec{A}(R, \tau)) d\tau) \cdot \vec{r}} e^{-\frac{i}{2} \int_{t'}^t (\vec{p} + \vec{A}(R, t'') - \int_{t''}^t \widehat{\partial A}(R, \tau)(\vec{p} + \vec{A}(R, \tau)) d\tau) dt''} \quad (\text{A.32})$$

This is the non-dipole Gordon-Volkov wavefunction to order $O(\widehat{\partial A})$ in the velocity gauge. By considering the velocity to length gauge transformation to first order, $e^{-i\chi(r, R, t)} \sim e^{-i\vec{A}(R, t) \cdot \vec{r}}$, we can express the free-electron wavefunction in length gauge as

$$\Psi_L(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i(\vec{p} + \vec{A}(R, t') - \int_{t'}^t \widehat{\partial A}_R(R, \tau)(\vec{p} + \vec{A}(R, \tau)) d\tau) \cdot \vec{r}} e^{-\frac{i}{2} \int_{t'}^t (\vec{p} + \vec{A}(R, t'') - \int_{t''}^t \widehat{\partial A}_R(R, \tau)(\vec{p} + \vec{A}(R, \tau)) d\tau) dt''} \quad (\text{A.33})$$

where the non-dipole momentum is defined as

$$\pi(p, t, t') = \left(\vec{p} + \vec{A}(R, t') - \int_{t'}^t \widehat{\partial A}_R(R, \tau) [\vec{p} + \vec{A}(R, \tau)] d\tau \right) \quad (\text{A.34})$$

The non-dipole Volkov wavefunction can be reduced to the dipole approximation, $\exp(-i\vec{k} \cdot \vec{r}) \approx 1$, by setting the field gradient tensor to zero and reducing the vector potential to include only the time component, $A(t) = A_0 \sin(\omega t)$, to get

$$\Psi_L(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i(\vec{p} + \vec{A}(t')) \cdot \vec{r}} e^{-\frac{i}{2} \int_{t'}^t (\vec{p} + \vec{A}(t''))^2 dt''}. \quad (\text{A.35})$$

REFERENCES

1. Wagnière, G. On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image. *John Wiley and Sons*. **1** (2007).
2. Im, S. W. *et al.* Chiral surface and geometry of metal nanocrystals. *Advanced materials* **32**, 1905758 (41 2020).
3. Eyring, H., Liu, H. & Caldwell, D. Optical rotatory dispersion and circular dichroism. *Chemical reviews* **68**, 525 (5 1968).
4. Kvittingen, L., Sjørnes, B. J. & Schmid, R. Limonene in citrus: A string of unchecked literature citings? *Journal of chemical education* **98**, 3600 (11 2021).
5. Foot, C. J. & Shotton, M. D. Double well potentials and quantum gates. *American journal of physics* **79**, 762 (7 2011).
6. Boyd, R. Nonlinear optics. *Academic Press* (3 2020).
7. Ordóñez, A. F. & Smirnova, O. Generalized perspective on chiral measurements without magnetic interactions. *Phys. Rev. A* **98**, 063428 (2018).
8. Ayuso, D., Ordóñez, A. & Smirnova, O. Ultrafast chirality: the road to efficient chiral measurements. *Phys. Chem. Chem. Phys.* **24**, 26962 (2022).
9. Chau, K. Investigation of the chiral origins of electromagnetic activity. *Opt. Lett.* **35**, 1187–1189 (2010).
10. Sato, H. A new horizon for vibrational circular dichroism spectroscopy: a challenge for supramolecular chirality. *Phys. Chem. Chem. Phys.* **22**, 7671 (2020).
11. Peacock, R. D. & Stewart, B. Natural circular dichroism in x-ray spectroscopy. *J. Phys. Chem* **105**, 351 (2001).
12. Andrews, S. Using rotational averaging to calculate the bulk response of isotropic and anisotropic samples from molecular parameters. *J. Chem. Educ.* **81**, 877 (6 2004).
13. Caldwell, D. J. & Eyring, H. The theory of optical activity. *Wiley-Interscience*, 244 (1971).
14. Tang, Y. & Cohen, A. Optical Chirality and Its Interaction with Matter. *Phys. Rev. Lett.* **104**, 163901 (2010).
15. Tang, Y. & Cohen, A. Enhanced enantioselectivity in excitation of chiral molecules by superchiral light. *Science* **332**, 33 (2011).
16. Yang, N. & Cohen, A. Local Geometry of Electromagnetic Fields and Its Role in Molecular Multipole Transitions. *Journal of Physical Chemistry B* **115**, 5304 (18 2011).
17. Frutak, J. The multipole expansion in quantum theory. *Can. J. Phys.* **41**, 12 (1963).
18. Papasimakis, N. *et al.* Electromagnetic toroidal excitations in matter and free space. *Nature mater* **15**, 263 (2016).
19. Tan, H. B. T., Xiao, D. & Derevianko, A. Parity-mixed coupled-cluster formalism for computing parity-violating amplitudes. *Phys. Rev. A* **105**, 022803 (2022).
20. Barron, L. Molecular Light Scattering and Optical Activity. *Cambridge University Press* (2004).
21. Buckingham, A. Permanent and induced molecular moments and long-range intermolecular forces. *Advances in chemical physics: intermolecular forces* **12** (1967).
22. Buckingham, A. & Dunn, M. Optical Activity of Oriented Molecules. *J. Chem. Soc. (A)*, 1988 (1971).
23. Powis, I. Photoelectron Circular Dichroism of the Randomly oriented Chiral Molecules Glyceraldehyde and Lactic acid. *J. Chem. Phys.* **112**, 301 (2000).
24. Janseen, M. & Powis, I. Detecting chirality in molecules by imaging photoelectron circular dichroism. *Phys. Chem. Chem. Phys.* **16**, 856 (2014).
25. Beaulieu, S. *et al.* Universality of photoelectron circular dichroism in the photoionization of chiral molecules. *New J. Phys.* **18**, 102002 (2016).
26. Svoboda, V. *et al.* Femtosecond photoelectron circular dichroism of chemical reactions. *Sci. Adv.* **8** (28 2022).
27. Ritchie, B. Theory of the angular distribution for ejection of photoelectrons from optically active molecules and molecular negative ions. II. *Phys. Rev. A* **14**, 359 (1976).
28. Cireasa, R. *et al.* Probing molecular chirality on a sub-femtosecond timescale. *Nature Phys.* **11**, 654 (2015).
29. Corkum, P. B. Plasma perspective on strong-field multiphoton ionization. *Phys. Rev. Lett.* **71**, 1994 (13 1993).
30. Lewenstein, M. *et al.* Theory of high-harmonic generation by low-frequency laser fields. *Phys. Rev. A* **49**, 2117 (3 1994).
31. Keldysh, L. Ionization in the field of a strong electromagnetic wave. *Sov. Phys. JETP*. **20** (5 1965).
32. Chang, Z. Fundamentals of attosecond optics. *CRC Press. Taylor and Francis group*, 519 (2011).
33. Pitzer, M. *et al.* Direct Determination of Absolute Molecular Stereochemistry in Gas Phase by Coulomb Explosion Imaging. *Science* **341**, 1096 (2013).
34. Pitzer, M. How to determine the handedness of single molecules using Coulomb explosion imaging. *J. Phys B: At, Mol. Opt. Phys.* **50**, 153001 (2017).

35. Andrews, L. & Phillips, R. Laser Beam Propagation through Random Media. *SPIE optical Engineering Press* **PM152**, 808 (2 2005).
36. Saleh, B. & Teich, M. Fundamentals of photonics. *Wiley and Sons Inc.*, 1177 (2 2007).
37. Cerjan, A. & Cerjan, C. Orbital angular momentum of Laguerre-Gaussian beams beyond the paraxial approximation. *J. Opt. Soc. Am. A Opt. Image Sci. Vis.* **28**, 2253–2260 (Nov. 2011).
38. Basistiy, I., Soskin, M. & Vasnetsov, M. Optical wavefront dislocations and their properties. *Optics Communications* **119**, 604 (5 1995).
39. Bovino, F. A. Quantum like representation of a Spiral Phase Plate. *arXiv:1104.2201* (2011).
40. Long, T., Zhou, C., *et al.* Generation of relativistic vortex laser beams by spiral shaped plasma. *Phys. Rev. Research* **2**, 033145 (2020).
41. Marrucci, L. *et al.* Optical Spin-to-Orbital Angular Momentum Conversion in Inhomogeneous Anisotropic Media. *Phys. Rev. Lett.* **96**, 163905 (2006).
42. Hugo, L. *et al.* Arbitrary optical wavefront shaping via spin-to-orbit coupling. *J. Opt* **18**, 124002 (2016).
43. Rubano, A. *et al.* Q-plate technology: a progress review. *Journal of the optical society of america B* **36**, 124002 (5 2019).
44. Piccirillo, B. *et al.* Photon spin-to-orbital angular momentum conversion via an electrically tunable q-plate. *Appl. Phys. Lett.* **97**, 241104 (2010).
45. Slussarenko, S. *et al.* Tunable liquid crystal q-plates with arbitrary topological charge. *Opt. Express* **19**, 40854090 (2011).
46. Slussarenko, S. *et al.* Liquid crystal spatial-mode converters for the orbital angular momentum of light. *J. Opt.* **15**, 025406 (2013).
47. Delaney, S. *et al.* Arithmetic with q-plates. *App. Opt.* **56** (2007).
48. Pedrotti, F., Delaney, L. P., *et al.* Introduction to optics. *Prentice-Hall International, Inc.* (2 1993).
49. Moulton, P. F. Spectroscopic and laser characteristics of Ti:Al₂O₃. *Journal of The Optical Society of America B-optical Physics* **3**, 125–133 (1986).
50. Strickland, D. & Mourou, G. Compression of amplified chirped optical pulses. *Optics Communications* **56**, 219 (3 1985).
51. Weiner, A. *Ultrafast Optics* (Wiley-Blackwell, Feb. 2008).
52. Wiley, W. C. & McLaren, I. TIME-OF-FLIGHT MASS SPECTROMETER WITH IMPROVED RESOLUTION. *Review of Scientific Instruments* **26**, 1150–1157 (1955).
53. Mitra, M. *et al.* Spatially controlled nano-structuring of silicon with femtosecond vortex pulses. *Sci. Rep.* **10**, 12643 (2020).
54. De Araújo, M. A. C., Silva, R., de Lima, E., Pereira, D. P. & de Oliveira, P. C. Measurement of Gaussian laser beam radius using the knife-edge technique: improvement on data analysis. *Appl. Opt.* **48**, 393–396 (Jan. 2009).
55. Li, C. Nonlinear optics: Principles and applications. *Springer Singapore*, 386 (1 2017).
56. Sheik-Bahae, M. & Hasselbeck, M. Third order optical nonlinearities. *OSA Handbook of optics, chapter 17* **4** (2000).
57. Naskrecki, R. & *et al.* Three-photon absorption cross-section of simple molecular liquids. *Optics communications* **153**, 32 (1-3 1998).
58. Sutherland, R. Handbook of nonlinear optics. *Marcel Dekker, Inc.*, 993 (2 2005).
59. M. Sheik-Bahaei, P. M. & Kwok, H. Two-photon and three-photon absorption coefficients of InSb. *J. Opt. Soc. Am. B* **3**, 379 (3 1985).
60. Hnatovsky, C. *et al.* Materials processing with a tightly focused femtosecond laser vortex pulse. *Opt. Lett.* **35**, 3417 (20 2010).
61. Nathan, V., Guenther, A. & Mitra, S. Review of multiphoton absorption in crystalline solids. *J. Opt. Soc. Am. B* **2**, 294 (2 1985).
62. Drobizhev, M., Karotki, A., Rebane, A & Spangler, C. W. Dendrimer molecules with record large two-photon absorption cross section. *Opt. Lett.* **26**, 1081–1083 (July 2001).
63. Klaiber, M. & Briggs, J. Briggs Crossover from tunneling to multiphoton ionization of atoms. *Physical Review A* **94** (2016).
64. Serebryannikov, E. E. & Zheltikov, A. M. Strong-field photoionization as excited-state tunneling. *Phys. Rev. Lett.* **116**, 123901 (Mar. 2016).
65. Reiss, H. Theoretical methods in quantum optics: S-matrix and Keldysh techniques for strong-field processes. *Prog. Quant. Electr.* **16**, 1 (1992).
66. Landau, L. & Lifshitz, E. Quantum mechanics: non-relativistic theory. *Pergamon Press* **3**, 632 (2 2011).
67. Perelomov, A., Povov, V. & Terentev, M. Ionization of atoms in an alternating electrical field I. *Soviet Physics - JETP* **23**, 924 (1966).
68. Perelomov, A., Povov, V. & Terentev, M. Ionization of atoms in an alternating electrical field II. *Soviet Physics - JETP* **24**, 207 (1967).
69. Perelomov, A. & Povov, V. Ionization of atoms in an alternating electrical field III. *Soviet Physics - JETP* **25**, 336 (1967).
70. Ammosov, M., Delone, N. & Krainov, V. Tunnel ionization of complex atoms and of atomic ions in an alternating electromagnetic field. *Soviet Physics - JETP* **64**, 1191 (6 1986).
71. Delone, N. & Krainov, V. Energy and angular electron spectra for the tunnel ionization of atoms by strong low-frequency radiation. *J. Opt. Soc. Am. B* **8**, 1207 (6 1991).

72. Bisgaard, C. & Madsen, L. Tunneling ionization of atoms. *American Journal of Physics* **72**, 249 (2 2004).
73. Tong, X., Zhao, Z. & Lin, C. Theory of molecular tunneling ionization. *Phys. Rev. A* **66**, 033402 (2002).
74. Ivanov, M. Ionization in strong low-frequency fields. Attosecond and XUV Physics: Ultrafast Dynamics and Spectroscopy, chapter 6. *Wiley-VCH Verlag GmbH Co*, 177–200 (2014).
75. Long, Z. & Liu, W.-K. Keldysh theory of strong-field ionization. *Can. J. Phys.* **88**, 227–245 (2010).
76. Becker, A. *et al.* Above-Threshold Ionization: From Classical Features to Quantum Effects. *Advances In Atomic, Molecular, and Optical Physics* **48** (2002).
77. Becker, A. & Faisal, F. Intense-field many-body S-matrix theory. *J. Phys. B: At. Mol. Opt. Phys.* **38** (2005).
78. Hickstein, D. D. *et al.* Direct visualization of laser-driven electron multiple scattering and tunneling distance in strong-field ionization. *Phys. Rev. Lett.* **109**, 073004 (Aug. 2012).
79. Paulus, G. G., Nicklich, W., Xu, H., Lambropoulos, P. & Walther, H. Plateau in above threshold ionization spectra. *Phys. Rev. Lett.* **72**, 2851–2854 (May 1994).
80. Krause, J. L., Schafer, K. J. & Kulander, K. C. High-order harmonic generation from atoms and ions in the high intensity regime. *Phys. Rev. Lett.* **68**, 3535–3538 (June 1992).
81. Xu, J. *et al.* Diffraction using laser-driven broadband electron wave packets. *Nat. Commun.* **5**, 4635 (Aug. 2014).
82. Blaga, C. I. *et al.* Imaging ultrafast molecular dynamics with laser-induced electron diffraction. *Nature* **483**, 194–197 (Mar. 2012).
83. Brewczyk, M., Rzaewski, K. & Clark, C. W. Appearance intensities for multiply charged ions in a strong laser field. *Phys. Rev. A* **52**, 1468–1473 (Aug. 1995).
84. Augst, S., Strickland, D., Meyerhofer, D. D., Chin, S. L. & Eberly, J. H. Tunneling ionization of noble gases in a high-intensity laser field. *Phys. Rev. Lett.* **63**, 2212–2215 (Nov. 1989).
85. Araoka, F., Verbiest, T., Clays, K. & Persoons, A. P. Interactions of twisted light with chiral molecules: An experimental investigation. *Physical Review A* **71**, 055401 (2005).
86. Brulot, W., Vanbel, M. K., Swusten, T. & Verbiest, T. Resolving enantiomers using the optical angular momentum of twisted light. *Sci. Adv.* **2**, e1501349 (Mar. 2016).
87. Ni, J. *et al.* Giant helical dichroism of single chiral nanostructures with photonic orbital angular momentum. *ACS Nano* **15**, 2893–2900 (Feb. 2021).
88. Andrews, D. *et al.* On optical vortex interactions with chiral matter. *Optics Communications* **237**, 133–139 (2004).
89. K. Das, H. B. & Sanyal, K. Amino acid chirality: Stereospecific conversion and physiological implications. *ACS Omega* **9**, 5084 (2024).
90. Ando, T. & Tamura, K. Mechanism of Chiral-Selective Aminoacylation of an RNA Minihelix Explored by QM/MM Free-Energy Simulations. *Life* **13**, 722 (3 2023).
91. Blackmond, D. The Origin of Biological Homochirality. *Cold Spring Harb Perspect Biol* **11**, a032540 (2019).
92. Wu, A. Q., Chowdhury, I. H. & Xu, X. Femtosecond laser absorption in fused silica: Numerical and experimental investigation. *Phys. Rev. B Condens. Matter Mater. Phys.* **72** (Aug. 2005).
93. Güler, E., Uğur, G., Uğur, Ş. & Güler, M. A theoretical study for the band gap energies of the most common silica polymorphs. *Chin. J. Phys.* **65**, 472–480 (June 2020).
94. Lan, S. *et al.* A medium-range structure motif linking amorphous and crystalline states. *Nat. Mater.* **20**, 1347–1352 (Oct. 2021).
95. Elliott, S. R. Medium-range structural order in covalent amorphous solids. *Nature* **354**, 445–452 (1991).
96. Price, D. L. Intermediate-range order in glasses. *Current Opinion in Solid State and Materials Science* **1**, 572–577 (1996).
97. Jürgens, P. *et al.* Origin of strong-field-induced low-order harmonic generation in amorphous quartz. *Nat. Phys.* **16**, 1035–1039 (Oct. 2020).
98. De Morisson Faria, C. F. & Becker, W. Quantum-Orbit Analysis of Nonsequential Double Ionization. *Laser Physics* **13**, 1196–1204 (2003).
99. De Morisson Faria, C. F., Liu, X. & Becker, W. S -Matrix Theory of Nonsequential Double Ionization (2007).
100. Shaaran, T., Nygren, M. T. & Figueira de Morisson Faria, C. Laser-induced nonsequential double ionization at and above the recollision-excitation-tunneling threshold. *Phys. Rev. A* **81** (June 2010).
101. Shaaran, T. & Figueira de Morisson Faria, C. Laser-induced nonsequential double ionization: kinematic constraints for the recollision-excitation-tunneling mechanism. *J. Mod. Opt.* **57**, 984–991 (June 2010).
102. Kubel, M. Strong-field control of the dissociative ionization of N₂O with near-single-cycle pulses. *New J. Phys* **16** (2014).
103. Huang, S.-W. *et al.* High-energy pulse synthesis with sub-cycle waveform control for strong-field physics. *en. Nat. Photonics* **5**, 475–479 (Aug. 2011).
104. Spanner, M. *et al.* Strong-field ionization and high-order-harmonic generation during polyatomic molecular dynamics of N₂O₄. *Phys. Rev. A* **85** (2012).
105. Li, S. *et al.* Pulse shaping in strong-field ionization: Theory and experiments. *Phys. Rev. A (Coll. Park.)* **105** (May 2022).
106. M., S. *et al.* Selective strong-field enhancement and suppression of ionization with short laser pulses. *Phys. Rev. A* **93** (2016).

107. Kaufman, B., Rozgonyi, T., Marquetand, P. & Weinacht, T. Coherent control of internal conversion in strong-field molecular ionization. *Phys. Rev. Lett.* **125**, 053202 (July 2020).
108. Chaloupka, J. L. & Hickstein, D. D. Coherent Control of Internal Conversion in Strong-Field Molecular Ionization. *Phys. Rev. Lett.* **116** (2016).
109. Pullen, M. G. *et al.* Imaging an aligned polyatomic molecule with laser-induced electron diffraction. *Nat. Commun.* **6**, 7262 (June 2015).
110. Meckel, M *et al.* Laser-induced electron tunneling and diffraction. *Science* **320**, 1478–1482 (June 2008).
111. Meckel, M *et al.* Signatures of the continuum electron phase in molecular strong-field photoelectron holography. *Nat. Phys.* **10**, 594–600 (Aug. 2014).
112. Walt, S. G. *et al.* Dynamics of valence-shell electrons and nuclei probed by strong-field holography and rescattering. *Nat. Commun.* **8**, 15651 (June 2017).
113. Haertelt, M., Bian, X.-B., Spanner, M., Staudte, A. & Corkum, P. B. Probing molecular dynamics by laser-induced backscattering holography. *Phys. Rev. Lett.* **116**, 133001 (Apr. 2016).
114. Yang, Y. *et al.* Strong-field coherent control of isolated attosecond pulse generation (May 2021).
115. Pukhov, A. *et al.* Strong field interaction of laser radiation. *Rep. Prog. Phys.* **66** (2003).
116. Gahn, C *et al.* Multi-MeV electron beam generation by direct laser acceleration in high-density plasma channels. *Phys. Rev. Lett.* **83**, 4772–4775 (Dec. 1999).
117. Singh, K. P. Electron acceleration by a circularly polarized laser pulse in a plasma. *Physics of Plasmas* **11**, 3992–3996 (Aug. 2004).
118. Modena, A. *et al.* Electron acceleration from the breaking of relativistic plasma waves. *Nature* **377**, 606–608 (Oct. 1995).
119. Wagner, R, Chen, S.-Y., Maksimchuk, A & Umstadter, D. Electron acceleration by a laser Wakefield in a relativistically self-guided channel. *Phys. Rev. Lett.* **78**, 3125–3128 (Apr. 1997).
120. Connor, J. W. *et al.* A review of internal transport barrier physics for steady-state operation of tokamaks. *Nucl. Fusion* **44**, R1–R49 (Apr. 2004).
121. Leemans, W. P. *et al.* Electron-yield enhancement in a laser-wakefield accelerator driven by asymmetric laser pulses. *Phys. Rev. Lett.* **89**, 174802 (Oct. 2002).
122. Babiker, M, Bennett, C. R., Andrews, D. L. & Dávila Romero, L. C. Orbital angular momentum exchange in the interaction of twisted light with molecules. *Phys. Rev. Lett.* **89**, 143601 (Sept. 2002).
123. Picon, A. *et al.* Photoionization with orbital angular momentum beams. *Opt. Exp.* **18** (2010).
124. Schmiegelow, C. T. *et al.* Transfer of optical orbital angular momentum to a bound electron. *Nat. Commun.* **7**, 12998 (Oct. 2016).
125. Afanasev, A. *et al.* Experimental verification of position-dependent angular-momentum selection rules for absorption of twisted light by a bound electron. *New J. Phys.* **20**, 023032 (Feb. 2018).
126. Stopp, F. *et al.* Coherent transfer of the transverse momentum of an optical vortex beam to the motion of a single trapped ion (June 2022).
127. Bégin, J.-L. *et al.* Nonlinear helical dichroism in chiral and achiral molecules. *Nat. Photonics* **17**, 82–88 (Jan. 2023).
128. Jain, A., Bégin, J.-L. & Bhardwaj, R. Helical dichroism in enantiomeric solutions. *J. Chem. Phys.* **159** (July 2023).
129. Jain, A., Bégin, J.-L., *et al.* Intrinsic dichroism in amorphous and crystalline solids with helical light. *Nat. Commun.* **15**, 1350 (Feb. 2024).
130. Gariépy, G. *et al.* Creating high-harmonic beams with controlled orbital angular momentum. *Phys. Rev. Lett.* **113**, 153901 (Oct. 2014).
131. Généaux, R *et al.* Synthesis and characterization of attosecond light vortices in the extreme ultraviolet. *Nat. Commun.* **7**, 12583 (Aug. 2016).
132. Kong, F. *et al.* Controlling the orbital angular momentum of high harmonic vortices. *Nat. Commun.* **8**, 14970 (Apr. 2017).
133. Rego, L. *et al.* Generation of extreme-ultraviolet beams with time-varying orbital angular momentum. *Science* **364**, eaaw9486 (June 2019).
134. Hernández-García, C. *et al.* Attosecond Extreme Ultraviolet Vortices from High-Order Harmonic Generation. *Phys. Rev. Lett.* **111**, 083602 (2013).
135. Fang, Y. *et al.* Probing the orbital angular momentum of intense vortex pulses with strong-field ionization. *Light Sci. Appl.* **11**, 34 (Feb. 2022).
136. Uchida, M. & Tonomura, A. Generation of electron beams carrying orbital angular momentum. *Nature* **464**, 737–739 (Apr. 2010).
137. Verbeeck, J, Tian, H & Schattschneider, P. Production and application of electron vortex beams. *Nature* **467**, 301–304 (Sept. 2010).
138. McMorran, B. J. *et al.* Electron vortex beams with high quanta of orbital angular momentum. *Science* **331**, 192–195 (Jan. 2011).
139. Gmsheim, S. & Rost, J.-M. High-order harmonic generation with twisted electrons. *Phys. Rev. A (Coll. Park.)* **100** (Oct. 2019).
140. Tolstikhin, O. I. & Morishita, T. Strong-field ionization, rescattering, and target structure imaging with vortex electrons. *Phys. Rev. A (Coll. Park.)* **99** (June 2019).

141. Cajiaoovélez, F, Kaminski, J. Z. & Krajewska, K. Generation of propagating electron vortex states in photodetachment of H^- . *Physical Review A* **101** (2020).
142. Yuan, K.-J., Chelkowski, S. & Bandrauk, A. D. Photoelectron momentum distributions of molecules in bichromatic circularly polarized attosecond UV laser fields. *Phys. Rev. A (Coll. Park.)* **93** (May 2016).
143. Ngoko Djiokap, J. M. Dynamical electron vortices in attosecond double photoionization of H_2 . *Physical Review A* **98** (2018).
144. Maxwell, A. S. *et al.* Manipulating twisted electrons in strong-field ionization. *Faraday Discuss.* **228**, 394–412 (May 2021).
145. Pengel, D *et al.* Electron vortices in femtosecond multiphoton ionization. *Phys. Rev. Lett.* **118**, 053003 (Feb. 2017).
146. Bayer, T, Philipp, C., Eickhoff, K & Wollenhaupt, M. Atomic photoionization dynamics in ultrashort cycloidal laser fields. *Phys. Rev. A (Coll. Park.)* **102** (July 2020).
147. Derevianko, A. Hyperfine-induced quadrupole moments of alkali-metal-atom ground states and their implications for atomic clocks. *Phys. Rev. A* **93**, 012503 (2016).
148. Kozhedub, Y. & Shabaev, V. Relativistic Theory of the Electric Quadrupole Moment of a Hydrogen-Like Atom in the $s_{1/2}$ and $p_{1/2}$ States. *Opt. Spectrosc.* **100** **959** (2006).
149. Amusia, M., Kuchiev, M. & Yakhontov, V. Quadrupole moment of atoms with the ground-state term $P_{1/2}$. *J. Phys. B: Atom. Mol. Phys.* **19**, L541 (1986).
150. Moss, R. & Sadler, I. The electric quadrupole moments of one-electron atoms. *J. Phys. B: Atom. Mol. Phys.* **19**, L503 (1986).
151. Sedaghat, M, Amouye Foumani, A & Niknam, A. R. Controlling the characteristics of injected and accelerated electron bunch in corrugated plasma channel by temporally asymmetric laser pulses. *Sci. Rep.* **12**, 8115 (May 2022).
152. Rezaei-Pandari, M, Akhyani, M, Jahangiri, F, Niknam, A. R. & Massudi, R. Effect of temporal asymmetry of the laser pulse on electron acceleration in vacuum. *Opt. Commun.* **429**, 46–52 (Dec. 2018).
153. Gopal, K & Gupta, D. N. Optimization and control of electron beams from laser wakefield accelerations using asymmetric laser pulses. *Phys. Plasmas* **24**, 103101 (Oct. 2017).
154. Huijts, J. *et al.* Waveform control of relativistic electron dynamics in laser-plasma acceleration. *Phys. Rev. X.* **12** (Feb. 2022).
155. Bethe, H. A. & Salpeter, E. E. *Quantum mechanics of one- and two electron atoms* (Springer• Verlag Berlin Heidelberg, New York, 1957).
156. Whittaker, E. T. & Watson, G. N. *A Course of Modern Analysis* (Cambridge University Press, 1927).
157. Gribakin, G. F. & Kuchiev, M. Y. Multiphoton detachment of electrons from negative ions. *Phys. Rev. A* **55**, 3760–3771 (May 1997).
158. Vanne, Y. V. & Saenz, A. Exact Keldysh theory of strong-field ionization: Residue method versus saddle-point approximation. *Physical Review A* **75** (2007).
159. Kjeldsen, T. K. & Madsen, L. B. Strong-field ionization of atoms and molecules: The two-term saddle-point method. *Phys. Rev. A* **74** (Aug. 2006).
160. Smirnova, O. & Ivanov, M. Multielectron high harmonic generation: Simple man on a complex plane, 201–256 (Mar. 2014).
161. Bégin, J.-L., Alsaawy, M. & Bhardwaj, R. Chiral discrimination by recollision enhanced femtosecond laser mass spectrometry. *Sci. Rep.* **10**, 14074 (Aug. 2020).
162. Paufler, W., Boning, B. & Fritzsche, S. Coherence control in high-order harmonic generation with Laguerre-Gaussian beams. *Physical Review A* **100** (2019).
163. Jin, C. & *et al.* Phase-matching analysis in high-order harmonic generation with nonzero orbital angular momentum Laguerre-Gaussian beams. *Physical Review A* **102** (2020).
164. Le, A.-T. & *et al.* Strong-field approximation and its extension for high-order harmonic generation with mid-infrared lasers. *J. Phys. B: At. Mol. Opt. Phys* **49** (2016).
165. Vallance, C. Multi-mass velocity-map imaging studies of photoinduced and electron-induced chemistry. *Chem. Commun. (Camb.)* **55**, 6336–6352 (May 2019).