

Homodyne High-Harmonic Spectroscopy: Coherent Imaging of a Unimolecular Chemical Reaction

by

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'Plus grand est l'obstacle, et plus grande est la gloire de le surmonter.'
The greater the obstacle, the more the glory in overcoming it.

-Molière



Figure 1: Water fountain on the hill of *Villa Borghese*, in front of the 'Académie Française' looking onto *Città del Vaticano* in the horizon. The image of objects illuminated by sunlight is obtained via reflection on the water surface. In a similar fashion, illuminating the molecular scene with a strong laser field allows to image electronic structure via a laser-matter interaction known as high harmonic generation. In this thesis, we develop attosecond techniques that exploit the coherence imposed by the strong laser field to fully characterize the high-harmonic XUV light emitted from molecules undergoing dynamics. This work paves the way for time-resolved tomographic imaging of single-molecule chemical reactions.

List of Publications

1. H. J. Wörner, Hiromichi Niikura, **J. B. Bertrand**, P. B. Corkum and D. M. Villeneuve
Observation of Electronic Structure Minima in High-Harmonic Generation
Physical Review Letters 102, 103901 (10 March 2009).
2. J. -P. Brichta, M. C. H. Wong, **J. B. Bertrand**, H.-C. Bandulet, D. M. Rayner and V. R. Bhardwaj
Comparison and real-time monitoring of high-order harmonic generation in different sources
Physical Review A 79, 033404 (11 March 2009).
3. H. Akagi, L. Arissian, **J. B. Bertrand**, P. B. Corkum, M. Gertssov, D. Pavicic, D. M. Rayner, C. Smeenk, A. Staudte, D. M. Villeneuve and H. J. Wörner
An STM for Molecules and Wide-Bandgap Crystals
Laser Physics 19, pp. 1697-1704 (1 August 2009).
4. H. J. Wörner, **J. B. Bertrand**, P. B. Corkum and D. M. Villeneuve
Controlling the Interference of Multiple Molecular Orbitals in High-Harmonic Generation
Physical Review Letters 104, 233904 (11 June 2010).
5. H. J. Wörner, **J. B. Bertrand**, D.V. Kartashov, P. B. Corkum and D. M. Villeneuve
Following a chemical reaction using high-harmonic interferometry
Nature (London) 466, pp. 604-607 (29 July 2010).
6. H. J. Wörner, **J. B. Bertrand**, P. B. Corkum and D. M. Villeneuve
High-Harmonic Homodyne Detection of the Ultrafast Dissociation of Br₂ Molecules
Physical Review Letters 105, 103002 (1 September 2010).
7. **J. B. Bertrand**, H. J. Wörner, H.-C. Bandulet, É. Bisson, M. Spanner, J.-C. Kieffer, D. M. Villeneuve and P. B. Corkum
Ultrahigh-Order Wave Mixing in Noncollinear High Harmonic Generation
Physical Review Letters 106, 023001 (11 January 2011).

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8. C. Jin, H. J. Wörner, V. Tosa, A.-T. Le, **J. B. Bertrand**, R. R. Lucchese, P. B. Corkum, D. M. Villeneuve and C. D. Lin
Separation of target structure and medium propagation effects in high-harmonic generation
Journal of Physics B: Atomic, Molecular and Optical Physics 44, 095601 (20 April 2011).
 9. H. J. Wörner, **J. B. Bertrand**, B. Fabre, J. Higuët, H. Ruf, A. Dubrouil, S. Patchkovskii, M. Spanner, Y. Mairesse, V. Blanchet, E. Mével, E. Constant, P. B. Corkum and D. M. Villeneuve
Conical Intersection Dynamics in NO₂ Probed by Homodyne High-Harmonic Spectroscopy
Science 334, pp. 208-212 (14 October 2011).
 10. C. Jin, **J. B. Bertrand**, R. R. Lucchese, H. J. Wörner, P. B. Corkum, D. M. Villeneuve, A.-T. Le and C. D. Lin
Intensity dependence of multiple orbital contributions and shape resonance in high-order harmonic generation of aligned N₂ molecules
Physical Review A 85, 013405 (9 January 2012).
 11. A. Rupenyan, **J. B. Bertrand**, P. B. Corkum, D. M. Villeneuve and H. J. Wörner
All-Optical Measurement of High-Harmonic Amplitudes and Phases in Aligned Molecules
Physical Review Letters 108, 033903 (20 January 2012).
 12. P. M. Kraus, Y. Arasaki, **J. B. Bertrand**, S. Patchkovskii, P. B. Corkum, D. M. Villeneuve, K. Takatsuka and H. J. Wörner
Time-resolved high-harmonic spectroscopy of non-adiabatic dynamics in NO₂
Physical Review A 85, 043409 (12 April 2012).
 13. E. Frumker, C. T. Hebeisen, N. Kajumba, **J. B. Bertrand**, H. J. Wörner, M. Spanner, D. M. Villeneuve, A. Naumov and P. B. Corkum
Oriented rotational wave packet dynamics studied via high harmonic generation
Accepted in Physical Review Letters (March 2012).
 14. **J. B. Bertrand**, H. J. Wörner, P. Salières, D. M. Villeneuve and P. B. Corkum
All-Optical Retrieval of Attosecond Spectral Phase for Molecular Imaging
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15. **J. B. Bertrand**, H. J. Wörner, P. Hockett, D. M. Villeneuve and P. B. Corkum
Revealing the Cooper Minimum of N₂ by Molecular Frame High-Harmonic Spectroscopy
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 16. E. Frumker, N. Kajumba, **J. B. Bertrand**, H. J. Wörner, C. T. Hebeisen, P. Hockett, M. Spanner, S. Patchkovskii, G. G. Paulus, D. M. Villeneuve, A. Naumov and P. B. Corkum
Probing Polar Molecules with High Harmonic Spectroscopy
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17. **J. B. Bertrand**, H. J. Wörner, D. M. Villeneuve and P. B. Corkum
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In preparation (2012).
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20. **J. B. Bertrand**, H. J. Wörner, P. Hockett, J. Lévesque, H. Pépin, J. -C. Kieffer, D. M. Villeneuve and P. B. Corkum
Probing the Highest Occupied Orbitals of Benzene by Laser Alignment and High Harmonic Generation
In preparation (2012).
21. **J. B. Bertrand**, H. J. Wörner, D. M. Villeneuve and P. B. Corkum
Observation of Avalanche-Like Ionization in Doped Nanodroplets by XUV Fluorescence
In preparation (2012).

Abstract

At the heart of high harmonic generation lies a combination of optical and collision physics entwined by a strong laser field. An electron, initially tunnel-ionized by the field, driven away then back in the continuum, finally recombines back to rest in its initial ground state via a radiative transition. The emitted attosecond (atto= 10^{-18}) XUV light pulse carries all the information (polarization, amplitude and phase) about the photorecombination continuum-to-ground transition dipolar field. Photorecombination is related to the time-reversed photoionization process. In this perspective, high-harmonic spectroscopy extends well-established photoelectron spectroscopy, based on charged particle detection, to a fully coherent one, based on light characterization.

The main achievement presented in this thesis is to use high harmonic generation to probe femtosecond (femto= 10^{-15}) chemical dynamics for the first time. Thanks to the coherence imposed by the strong driving laser field, homodyne detection of attosecond pulses from excited molecules undergoing dynamics is achieved, the signal from unexcited molecules acting as the reference *local oscillator*. First, applying time-resolved high-harmonic spectroscopy to the photodissociation of a diatomic molecule, $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$, allows us to follow the break of a chemical bond occurring in a few hundreds of femtoseconds. Second, extending it to a triatomic (NO_2) lets us observe both the previously unseen (but predicted) early femtosecond conical intersection dynamics followed by the late picosecond statistical photodissociation taking place in the reaction $\text{NO}_2 \rightarrow \text{NO} + \text{O}$.

Another important realization of this thesis is the development of a complementary technique to time-resolved high-harmonic spectroscopy called LAPIN, for Linked Attosecond Phase INterferometry. When combined together, time-resolved high-harmonic spectroscopy and LAPIN give access to the complex photorecombination dipole of aligned excited molecules. These achievements lay the basis for electron recollision tomographic imaging of a chemical reaction with unprecedented angström (1 angström= 0.1 nanometer) spatial resolution. Other contributions dedicated to the development of attosecond science and the generalization of high-harmonic spectroscopy as a novel, fully coherent molecular spectroscopy will also be presented in this thesis.

Sommaire

La physique optique et celle des collisions sont reliées au coeur du processus de la génération d'harmoniques d'ordres élevés par un champ laser intense. Un électron, d'abord ionisé par effet tunnel dans ce champ, est éloigné puis à nouveau accéléré dans le continuum avant de revisiter son milieu d'origine, menant finalement à la recombinaison dans son état fondamental par transition radiative. Le pulse attoseconde ($\text{atto}=10^{-18}$) émis contient toute l'information (polarization, amplitude et phase) sur le champ dipolaire de photorecombinaison induit lors de la transition continuum-à-fondamental. La photorecombinaison est reliée au processus inverse de photoionization. Dans cette optique, la spectroscopie à harmoniques d'ordres élevés, basée sur la cohérence et la caractérisation de lumière, vient compléter la spectroscopie photoélectronique déjà bien établie, basée sur la détection de particules chargées.

La principale réalisation présentée dans cette thèse est celle d'utiliser, pour la première fois, la génération d'harmoniques d'ordres élevées afin de sonder de la dynamique chimique femtoseconde ($\text{femto}=10^{-15}$). Grâce à la cohérence imposée par le champ fort, la détection homodyne de pulses attosecondes provenant de molécules excitées en cours de dynamique est accomplie, le signal provenant des molécules non-excitées agit à titre de référence ou *oscillateur local*. D'abord, appliquer la génération d'harmoniques d'ordres élevés résolue en temps à la photodissociation d'une molécule diatomique, $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$, nous permet de suivre la brisure d'un lien chimique en quelques centaines de femtosecondes. Ensuite, utiliser notre technique dans le cas d'une molécule triatomique, NO_2 , nous donne accès autant à la dynamique hâtive (femtoseconde), associée à l'intersection conique, qu'à celle tardive (picoseconde), qui a lieu lors de la photodissociation statistique $\text{NO}_2 \rightarrow \text{NO} + \text{O}$.

Une autre réalisation importante de cette thèse est le développement d'une technique complémentaire, à celle de la génération d'harmoniques d'ordres élevés résolue en temps, appelée LAPIN pour 'Linked Attosecond Phase INterferometry'. Combinées, ces deux techniques donnent accès au champ dipolaire de photorecombinaison provenant de molécules alignées et excitées. Ces accomplissements établissent la base pour l'imagerie

tomographique d'une réaction chimique avec une résolution spatiale sans précédent de l'ordre de 1 angström= 0.1 nm. D'autres contributions reliées au développement de la science attoseconde et celui de la génération d'harmoniques d'ordres élevés, afin d'établir celle-ci comme nouvelle spectroscopie moléculaire, seront aussi présentées dans cette thèse.

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Chapter 1

Introduction

The atomic constituents of a molecule are held together by chemical bonds [1]. The essence of chemistry is to understand how these bonds are formed and/or broken during chemical reactions. It is the electromagnetic forces between the nuclei and their valence electrons that will determine the nature of the bond [2] and govern molecular dynamics. The arrival of the laser in the 1960s [3, 4] allowed high resolution spectroscopy to unravel the rotational, vibrational and electronic energy structure of molecules [5, 6, 7, 8] with unprecedented spectral precision. Today, even more precise spectral information is at hand with the use of state-of-the-art laser techniques: for example, optical frequency combs [9, 10] hold the promise to beat the current atomic clocks accuracy, of about 1 part in 10^{16} , by several orders of magnitude [11].

In the last few decades, while lasers dramatically improved the resolution of measurements performed in the spectral domain, they also triggered an important, complementary class of atomic and molecular studies: time-resolved spectroscopy. In this thesis, we contribute to the development of time-resolved high-harmonic spectroscopy (TRHHS), a novel atomic and molecular spectroscopy allowing, ultimately, chemical imaging with unprecedented angström (10^{-10} m.) -attosecond (10^{-18} s.) spatiotemporal resolution.

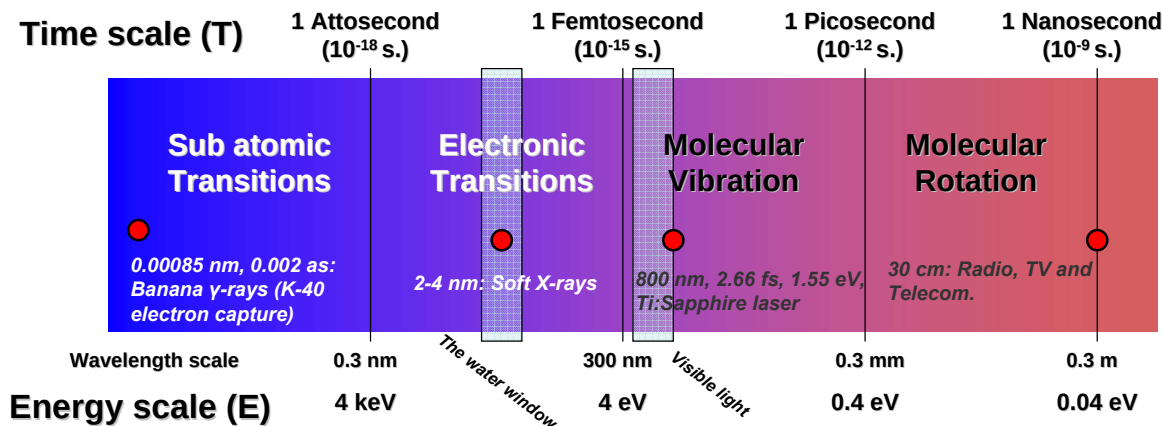


Figure 1.1: The relation between a quantum of energy E and the associated photon period T using the Planck-Einstein equation: $E = h\nu = h/T$, where ν is the frequency and h is the Planck constant [12]. This relationship allows us to relate the energy E and time T scales associated to dynamics in atoms and molecules. Of particular interest for the new field of attosecond science is the ‘water window’ located around $E \sim 300\text{--}500$ eV ($\sim 2\text{--}4$ nm in wavelength): in that spectral range, water is transparent to radiation, an ideal scheme for X-ray microscopy of organic molecules in aqueous solutions.

1.1 Ultrafast Chemical Imaging

Ultrafast pulsed lasers spectroscopies have revealed important information about molecular dynamics down to the femtosecond (10^{-15} s.) time scale. To honour these latest pioneering developments, the 1999 Nobel Prize in Chemistry was awarded to Ahmed Zewail for “his studies of the transition states of chemical reactions using femtosecond spectroscopy” [13]. The relevant timescales in time-resolved chemical imaging may well, however, extend beyond the femtosecond resolution [14, 15]. As shown in Fig. 1.1, bound molecules typically (1) rotate in few picoseconds, (2) vibrate in few femtoseconds and, finally, (3) undergo electronic oscillations on the attosecond time scale. During chemical reactions, not only do atoms move (1 and 2) but, the valence electrons have to redistribute (3) to form new bonds and molecular structures. Do electronic rearrangements happen on a faster time scale than nuclei move (femtoseconds)? How valid is the Born-Oppenheimer approximation [16], which decouples the nuclear and electronic degrees of

freedom, when a chemical bond breaks? Up to now, those are important fundamental questions to which only partial answers were given due to the limited temporal precision offered by femtosecond spectroscopies: we refer the reader to a topical review by Zewail in ref. [17]. A new approach at answering these questions, the most direct one, is to improve the temporal resolution of electronically-sensitive probing techniques down to the natural time scale of electron motion: attoseconds.

From Femtosecond to Attosecond Science

In the last few years, important developments in generating short attosecond XUV light pulses (~ 80 attoseconds (as) in duration [18]) made attosecond science or spectroscopy a new reality [19]. It allowed, for example, to measure the attosecond temporal profile of electrons liberated by tunnel ionization from core levels in atoms [20, 21, 22] and solids [23]. Yet, measurements performed with attosecond temporal resolution in the context of a chemical reaction have not been conducted. A serious drawback naturally arises when using attosecond pulses: they are composed of a broad light spectrum centered on photon energies (~ 50 eV [18]) well above the valence electron ionization potential (typically, in molecules $I_p \sim 10\text{-}15$ eV). As a result, attosecond pulses will preferentially ionize deeper-lying (core) electrons, obscuring the real-time observation of the valence ones. A recent related approach, based on spectrally resolved absorption of attosecond pulses [24], may be more suited for time-resolving valence electron attosecond dynamics in chemical reactions.

In this thesis, we contribute to the development of a novel spectroscopy that lies in between femtosecond and attosecond spectroscopies in terms of temporal resolution. It is called: high-harmonic spectroscopy [25, 26]. It uses as a probe the process of high harmonic generation (HHG) [19]. We will describe it in details in the following sections 1.2-1.3. Essentially, it is a nonperturbative upconversion process whereby a femtosecond laser pulse of fundamental frequency ω_0 yields a broad XUV spectrum, in the energy range of tens to hundreds of electronvolts (eV), made of high harmonics at frequency $\Omega = q\omega_0$, where q is an integer. The resulting XUV light comes in attosecond pulses that contain signatures (in their spectral polarization, amplitude and phase) from the atomic or molecular valence electronic structure involved in the process. The femtosecond

aspect of high-harmonic spectroscopy comes from the pulse duration of the HHG driving laser field, typically between 5 and 30 femtoseconds. The attosecond aspect, however, arises because the coherent XUV light is generated on a sub-laser-cycle time scale [19], the optical cycle of commonly used laser pulses centered on 800 nm being ~ 2.7 femtoseconds. In a multi-cycle laser pulse, this leads to the production of a train of attosecond pulses that will interfere with each other: spectral interferometry of attosecond pulses is a central theme to this thesis.

For imaging chemical reactions, time-resolved high-harmonic spectroscopy (TRHHS) is very much analogous to well-established time-resolved photoelectron spectroscopy (TRPES) [27, 28, 29]. Both time-resolved high-harmonic and photoelectron spectroscopies allow temporally, spectrally and angularly (molecular frame)-resolved photoionization measurements of valence electrons. In high-harmonic spectroscopy, photoionization is measured via the related time-reversed photorecombination process. We will give more details on this aspect in the upcoming sections 1.2-1.3. However, high-harmonic spectroscopy does extend photoelectron spectroscopy, based on charged particle detection, to a fully coherent and broadband one, based on light characterization, see ref. [30] for a comparative review between TRPES and TRHHS. As a result, high-harmonic spectroscopy has unique capabilities by bringing together aspects of femtosecond and attosecond spectroscopies via coherent light detection.

In particular, we highlight that high-harmonic spectroscopy, by allowing full characterization (spectral polarization, amplitude and phase) of broadband attosecond XUV light pulses, provides all the necessary information for spatial imaging of atomic [31] or molecular [32, 33, 34, 35] valence electronic orbitals with unprecedented angström resolution. We will discuss high-harmonic imaging in further detail in see section 1.4. In addition, even when using femtosecond probing laser pulses, attosecond electron hole dynamics can be inferred from high-harmonic spectroscopy of molecules where multiple high-lying electronic states (orbitals) coherently contribute [25, 33]. In this thesis, we concentrate on applying time-resolved high-harmonic spectroscopy to a chemical reaction to, ultimately, retrieve time-resolved, angström-resolution images of its valence electrons.

We shall next describe the workhorse of attosecond science and high-harmonic spectroscopy: the high harmonic generation process. In sections 1.2 and 1.3, we respectively

introduce both the pictorial and more rigorous theoretical background, while, in section 1.4, we elaborate on high-harmonic molecular imaging. Finally, in light of all the aspects treated in the introduction, we formulate the main goal of this thesis in section 1.5. In order to facilitate reading this thesis, throughout the introduction sections 1.2-1.5, we shall refer to the following chapters 2-6 and the articles (see List of Publications on page ii) therein.

1.2 High Harmonic Generation (HHG)

The high harmonic generation (HHG) process results from a laser-matter interaction whereby harmonics of the fundamental laser field are produced. HHG was first observed in the 1970s in plasmas [36] and in gaseous media in the late 1980s [37, 38]. HHG differs from perturbative nonlinear harmonic generation [39]: the observed light spectra extend to high multiphoton frequencies in a nonperturbative fashion. As shown in Fig. 1.2, a typical HHG spectrum extends to high frequencies (right side) with a relatively flat profile, known as the ‘plateau’, and then falls abruptly at the highest frequencies, known as the ‘cutoff’ [40]. Only odd harmonic frequencies of the fundamental laser field are observed due to the centrosymmetry of the process, as similarly known from perturbative nonlinear optics. In section 1.3.4, we will elaborate on symmetry breaking mechanisms making the observation of even harmonics possible, after having introduced, next, the nonperturbative framework of HHG.

A Mix of Optical and Collision Physics

High harmonic generation can be understood by combining optical and collision physics [42]. The process is well-understood using a semi-classical three-step mechanism [43, 44]: (1) an electron first tunnel-ionized by the strong laser field undergoes (2) a laser-driven trajectory away then back towards its parent ion before (3) photorecombining back to rest through a radiative dipolar transition. This yields high-harmonic photons of energy

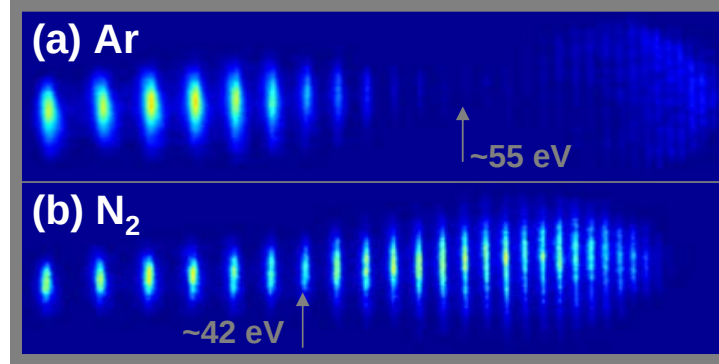


Figure 1.2: High-harmonic spectra generated in (a) argon (Ar) and (b) unaligned dinitrogen (N₂) using a 40 fs pulse centered on 1360 nm focused to a peak intensity of 1.2×10^{14} W/cm², the photon frequency Ω increases towards the right side. Spectral features such as Cooper minima, known from photoionization [41], are measured by high harmonic generation. In (a) argon, the minimum is around ~ 55 eV, see publications 1 and 8, and (b) N₂, it is around ~ 42 eV, more details on this latter minimum are given in publication 15, section 3.2.

Ω given by the following dispersion relation [45]:

$$\Omega = k^2/2 + I_p, \quad (1.1)$$

where k is the magnitude of the electron's wavevector $\mathbf{k}$ (or magnitude p for the momentum vector $\mathbf{p} = \hbar\mathbf{k}$) at the moment of recollision and I_p is the ionization potential of the target atom or molecule. We always use atomic units ($m_{electron} = \hbar = e = 1$) unless stated otherwise. As will be explained next, it is the spectrally broad recolliding wave packet, created every half laser cycle, that gives rise to the broad nonperturbative shape of the high-harmonic spectrum, as shown in Fig. 1.2. The three-step model (3SM) factorizes the electron recollision process in three chronological steps, see Fig. 1.3(a): (1) ionization (I) (2) propagation (P) and (3) recombination (R). We will respectively use the letter in parenthesis to refer to each step throughout this thesis. The simple man's semi-classical model [43], based on solving the classical equation of motion of an electron in an oscillating laser field, gives an intuitive picture describing the prominent features of a high harmonic spectrum and is still, up to now, a valid description for HHG.

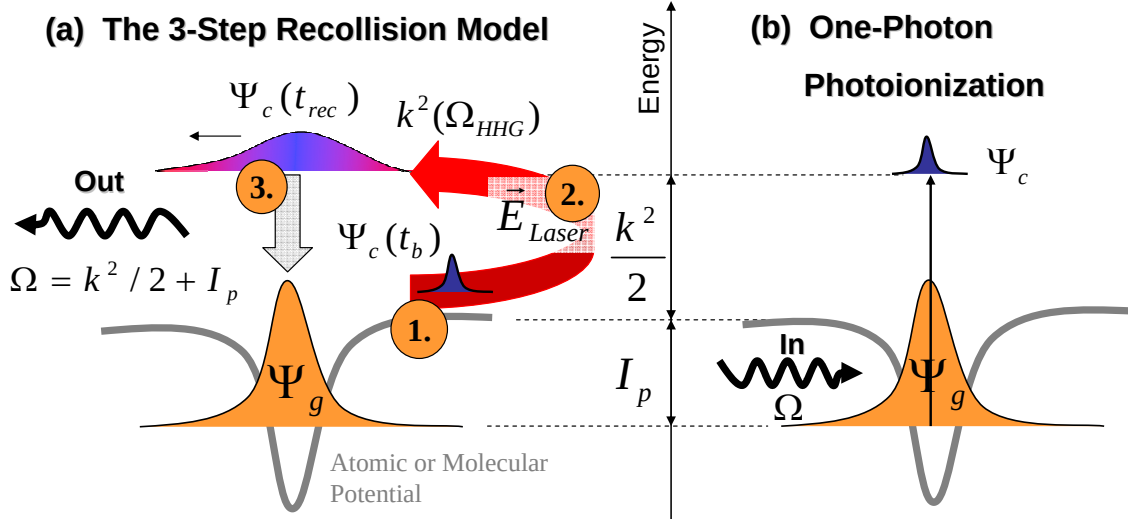


Figure 1.3: (a) The three-step model (3SM) for high harmonic generation: (1) ionization, (2) propagation and (3) recombination. An electron is (1) partially ionized from its ground state (Ψ_g) by the strong laser field at the moment of birth t_b . (2) The part that is ionized (Ψ_c) appears free (from the binding potential) in the continuum and then undergoes acceleration under the force exerted by the driving laser field (represented by the red arrow). (3) At the moment of recollision t_{rec} , the recolliding electron ($\Psi_c(t_{rec})$) recombines back to rest in its ground state Ψ_g via a dipolar transition, releasing a photon of energy $\Omega = k^2/2 + I_p$, where $k^2/2$ is the kinetic energy of the free electron at the moment of recollision and I_p is the ionization potential of the target atom or molecule. (b) Recombination (step 3) is related to the time-reversed process of single-photon photoionization, where a photon of energy Ω incident on a target will release an electron with kinetic energy $k^2/2 = \Omega - I_p$. See text for details.

The electron is favorably tunnel-ionized close to the peak of the laser electric field and will subsequently follow a trajectory under the force exerted by strong laser field, see Fig. 1.4, also see book chapter ref. [46]. At this point, we must emphasize that the probability of ionization depends inverse exponentially on the ionization potential I_p . We give an analytical expression for it in section 1.3, see eqs.(1.19)-(1.23). Therefore, in high harmonic generation, the ionization step (step 1) acts as a natural filter to favorably select (or interact with) valence electrons only. The Lorentz force (magnetic field) can be neglected below laser intensities of 10^{16} W/cm² [47], typical to all experiments

presented in this thesis. Following the simple man's model [43], after the electron is ionized (step 1) from its ground state (represented by the wave function Ψ_g), it appears free, with no initial velocity, in the continuum (represented by the wave function Ψ_c). Then, it undergoes spectral dispersion and spatial spreading during propagation (step 2) before it photorecombines (step 3): it recollides on itself (the parent ion), as shown in Fig. 1.4 (b). Each photorecombination kinetic energy ($E_{Kin} = k^2/2$) can be mapped to a given classical trajectory $x(t)$ by solving Newton's second law in a cosine field shown in Fig. 1.4 (c):

$$\ddot{x}(t) = -E_0 \cos(\omega_0 t) \quad (1.2)$$

$$\dot{x}(t) = -\frac{E_0}{\omega_0} (\sin(\omega_0 t) - \sin(\omega_0 t_b)) \quad (1.3)$$

$$x(t) = \frac{E_0}{\omega_0^2} (\cos(\omega_0 t) - \cos(\omega_0 t_b)) + \frac{E_0}{\omega_0} \sin(\omega_0 t_b) (t - t_b) \quad (1.4)$$

This yields a transcendental equation linking every time of birth (t_b), defined as the moment when the electron becomes ionized, i.e. free from its binding Coulomb potential (see upcoming section 1.3 for more details), to a specific time of recollision (t_{rec}), defined as the moment when the recolliding electron revisits its original neighborhood, that is, $x(t_{rec}) = 0$:

$$\omega_0(t_{rec} - t_b) \sin(\omega_0 t_b) = \cos(\omega_0 t_b) - \cos(\omega_0 t_{rec}) \quad (1.5)$$

Only the electrons tunnel-ionized (step 1) after the peak of the laser field will recollide. In Fig. 1.4 (d), we show how each time of birth is mapped to a specific recollision time t_{rec} and recolliding kinetic energy E_{kin} . Here we express the energy in terms of the ponderomotive energy $U_p = E_0^2/(4\omega_0^2)$, which corresponds to the averaged kinetic energy of the electron in the oscillating laser field of peak amplitude E_0 and fundamental frequency $\omega_0 = 2\pi/\lambda_0$. Two families of trajectories, known as the short and long trajectories, will yield high-harmonic photons at the same frequency Ω , however, corresponding to rather

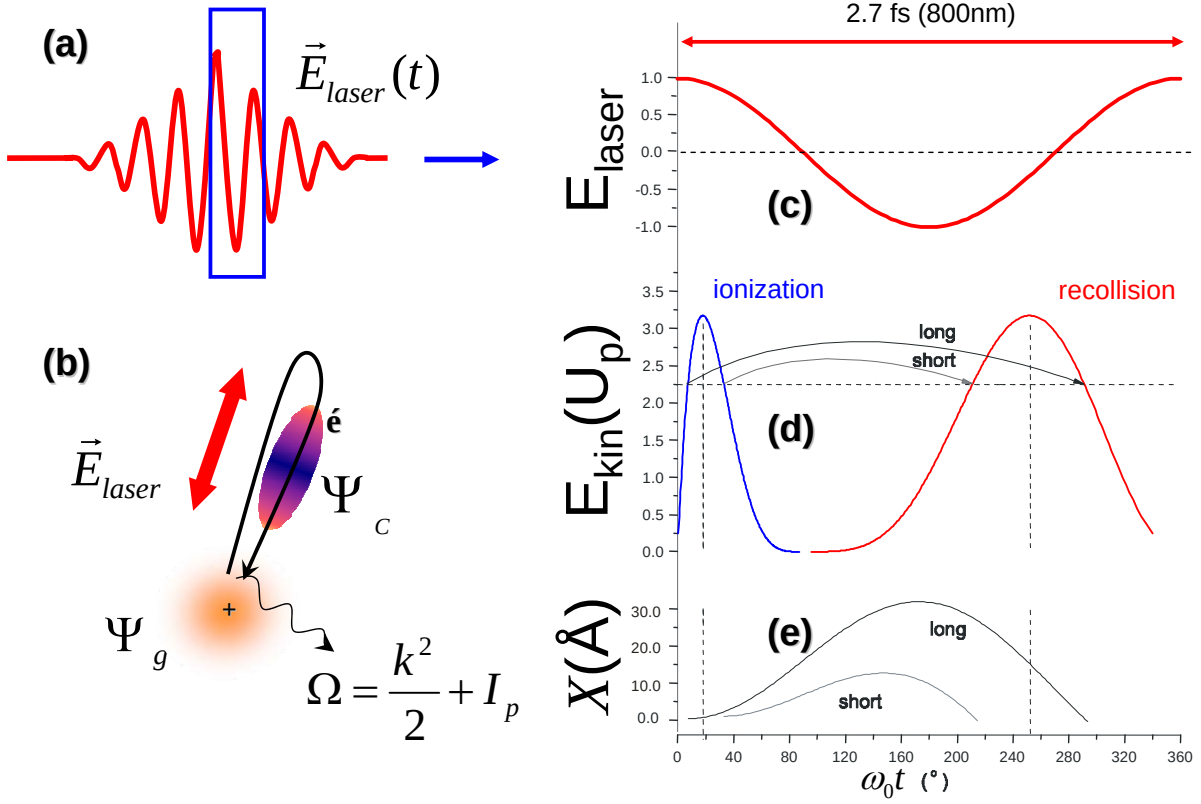


Figure 1.4: (a) In high harmonic generation, an electron is tunnel-ionized close to the peak of the laser electric field before it follows a given trajectory under the force exerted by this field. (b) We reproduce a simplified version of Fig. 1.3(a): following the simple man's model [43], when the electron is ionized (step 1) from its ground state (represented by the wave function Ψ_g), it appears free in the continuum (represented by the wave function Ψ_c) and undergoes spectral dispersion and spatial spreading during propagation (step 2) before it photorecombines (step 3) by recolliding with the part of itself left behind at ionization (step 1). Each observed photon energy Ω can be mapped to a given classical trajectory using Newton's second law. (c) In a cosine field, (d) each time of birth (t_b) is mapped to a specific recollision time (t_{rec}) by the transcendental equation 1.5. (e) Two families of trajectories $x(t)$, known as the short and long trajectories, will yield high-harmonic photons of the same energy Ω , but, corresponding to rather different excursion paths in the continuum. These trajectories are for a given laser intensity and wavelength, we refer to reader to book chapter ref. [46] for more details.

different excursion paths in the continuum as shown in Fig. 1.4 (d) and (e).

Experimentally, unless specified differently, we always select the short trajectories by positioning the nonlinear medium (gas jet) slightly after the laser focus to favor collimated emission of the short trajectories only [48]. The long trajectories are significantly more divergent and can, then, be spatially separated on the way to the light detector, see appendix A for a description of the experimental setup. We must emphasize that equations (1.2-1.5) are general and therefore scalable to any driving field wavelength λ_0 (via ω_0) and/or peak intensity I_0 (via $I_0 = E_0^2$). Small corrections to these trajectories are found when solving for both the times of birth and recollision using the full quantum mechanical Strong Field Approximation (SFA) approach [49], which we will discuss in sect. 1.3, also refer to Fig. 1.5 in ref. [50] for more details. We use the classical trajectories given by eqs. (1.2)-(1.5) throughout this thesis' work.

As we just described, high harmonic generation therefore combines optical and collisions physics in a rather exquisite fashion. Provided that the laser field ionizes an electron, a spectrally broad continuum electronic wave packet (Ψ_c), extending up to $3.2U_p$ in kinetic energy at the time of recollision, see Fig. 1.4 (d), will coherently probe what was left of itself in the ground state (Ψ_g) when recolliding. A more precise definition of the bound wave function that the recolliding electron sees at the moment of recollision is the Dyson orbital: it represents the overlap between the initial N -electron wave function Ψ_g and the $N-1$ electron wave function of the ionized system. The Dyson orbitals are usually very similar to the Hartree-Fock single-electron orbitals Ψ_g for the molecules studied in this thesis [51, 52]. Therefore, throughout this thesis, we will use the unperturbed laser-free single-electron wave function Ψ_g as the partially-ionized ground state.

Since experiments are performed on a macroscopic ensemble of molecules, only the XUV light that constructively adds, as the driving field propagates in the generating medium, will emerge and be observed. This is called: phase matching [53]. As a result, the phase matched high-harmonic radiation will propagate mostly along the propagation vector of the driving laser field. Also, although the medium is significantly ionized by the driving field, only the XUV light associated with recombination in the neutral species (atoms or molecules) will phase match. There are many radiative recombination channels. These radiate isotropically and are overwhelmed by the phase matched emission. It is

difficult to produce harmonics from the ions because they are more difficult to ionize due to their higher ionization potential (I_p), the ionization probability decreases exponentially with I_p [54, 55]. Still, efficient HHG from ions has been reported before but under particular experimental conditions: for example, in a capillary discharge [56]. In this thesis, phase matching enforces HHG from neutral species only to be measured.

The experiments presented in this thesis are typically performed at a laser intensity of $I_0 = 1.5 \times 10^{14}$ W/cm², which corresponds to $U_p \sim 10$ eV at $\lambda_0 = 800$ nm. Note that U_p scales quadratically with wavelength and linearly with laser peak intensity I_0 , see above. Therefore, one benefits enormously in high-harmonic cutoff by increasing the driving field wavelength and/or intensity. However, quantum dispersion (or diffusion) of the electron wavepacket Ψ_c during propagation (step 2) strongly diminishes the efficiency of HHG with increasing the driving field wavelength (the electron spends more time in the continuum), as shown in a recent detailed study [57]. This suggests a potential upper limit on the wavelength.

We highlight that the recollision picture for high harmonic generation physically corresponds to a few-nanometer-sized electron accelerator. As shown in Fig. 1.4 (e), the typical maximum excursion distance $x(t)$ of the electron approaches few tens of angströms. When combined with the alignment techniques in the laboratory frame, tomographic images of Ψ_g can be taken [32]. We will elaborate more on this important application in section 1.4. While the factorization in three steps is intuitively introduced in the simple man's semi-classical description of electron recollision [43], it becomes rigorously transparent when treating HHG using the quantum mechanical Strong Field Approximation (SFA) formalism [49, 58]. We shall now introduce this theoretical description of HHG and comment on each of the 3 steps. The SFA formalism together with the 3-step factorization will be used throughout this thesis.

1.3 Theory for HHG

In perturbative nonlinear optics [39, 59, 60], the optical response of a given system to a time-dependent electric field strength $E(t)$ is given via the nonlinear polarization

$P_{NL}(t)$, which is the dipole moment $d(t)$ per unit volume. If $P_{NL}(t)$ oscillates in time, then it radiates an electromagnetic field described by Maxwell's equations [61]. $P_{NL}(t)$ is written as a power series of the applied electric field and the nonlinear susceptibility tensor χ^q of the system. Here, for simplicity, we consider only a single component of the possibly multi-dimensional vectors of polarization $\mathbf{P}_{NL}(t)$ and electric field $\mathbf{E}(t)$, and the susceptibility tensor χ^q . Following perturbation theory:

$$P_{NL}(t) = \chi^{(1)}E(t) + \chi^{(2)}E(t)^2 + \chi^{(3)}E(t)^3 + \dots \quad (1.6)$$

In this approach, the optical response is then obtained by solving Maxwell's wave equation where $P_{NL}(t)$ enters the equation as a source term [39]. As a result, the generated harmonic signal (energy) of nonlinear order q , $S_{NL}^{(q)}$, which corresponds to the combination of q photons, will depend nonlinearly on the time-integrated intensity $\langle I(t) \rangle_t = \langle |E(t)|^2 \rangle_t$ proportional to the energy contained in the applied electric field $E(t)$, where $\langle \rangle_t$ represents time integration. In the case of a long pulse, where the nonlinearity occurs over multiple cycles of $E(t)$, we drop the time integration and use only the peak intensity $I_0 = E_0^2$, this gives the important relationship governing perturbative multiphoton processes:

$$S_{NL}^{(q)} \propto I_0^q \quad (1.7)$$

In perturbative nonlinear optics, higher order q -processes are significantly less probable than lower ones, the probability usually falls off exponentially with q -order [39]. In high harmonic generation, however, light spectra extend nonperturbatively to high multiple q -order frequencies, as seen earlier in Fig. 1.2. The formalism required to describe HHG is rather different, it is based on the semi-classical 3-step model exposed earlier, see sect. 1.2. Although these two perspectives –perturbative and nonperturbative nonlinear optics– seem orthogonal, we show in chapter 2, section 2.1, an experiment bridging the conceptual gap between them. For now, we shall again start from the time-dependent dipole $d(t)$ as above for perturbative nonlinear optics, but, from a fully quantum mechanical perspective, and recover the semi-classical nonperturbative picture.

1.3.1 The Strong Field Approximation (SFA)

In the strong field approximation (SFA) approach [49], the time-dependent dipole field vector $\mathbf{d}(t)$ created by the presence of a strong laser field is, at the single-emitter level:

$$\mathbf{d}(t) = \langle \Psi(t) | \mathbf{r} | \Psi(t) \rangle \quad (1.8)$$

where the system is represented by the time-dependent wave function $|\Psi(t)\rangle$ which can be solved for using the Schrödinger equation. Here, we have dropped the spatial ($\mathbf{r}$) dependence in $|\Psi(\mathbf{r}, t)\rangle$ to lighten the notation. The origin $\mathbf{r} = 0$ can be arbitrarily defined, but is typically chosen as the highest symmetry point in the electronic wavefunction $\Psi(\mathbf{r})$ of the single-emitter. In SFA, three main approximations are made:

1. Only the ground electronic state $|\Psi_g(t)\rangle$ is considered, all other bound states are neglected. Only recently, the contribution of multiple bound states has been introduced [25, 62, 63, 64] to the attosecond science community. We will further develop on this issue in chapter 3, section 3.1, where we consider the coherent participation of multiple high-lying orbitals to the HHG process in aligned molecules.

2. In the continuum, the ionized part of the ground state electron, $|\Psi_c(t)\rangle$, the Volkov wave function, is treated as free from the binding Coulomb potential.

3. The depletion of the ground state (must be) is small. This is particularly important since the time-dependent dipolar oscillation giving rise to high harmonics comes from the interference of the recolliding electron $|\Psi_c(t)\rangle$ with the part of itself left behind (unionized) in the ground state $|\Psi_g(t)\rangle$ [43].

As a preliminary result of these approximations, we can therefore write the total time-dependent wave function with the following ansatz [43]:

$$|\Psi(t)\rangle = |\Psi_g(t)\rangle + |\Psi_c(t)\rangle. \quad (1.9)$$

In SFA, only the transitions back to the ground state are considered, the other terms are typically neglected [49]. The time-dependent dipole becomes:

$$\mathbf{d}(t) = \langle \Psi_g(t) | \mathbf{r} | \Psi_c(t) \rangle + c.c., \quad (1.10)$$

where c.c. means the complex conjugate, enforcing the emitted dipolar field to be real, as it should be for any physical observable [65]. Here, $|\Psi_g(t)\rangle$ is written as the spatial, laser field-free stationary state $|\Psi_g\rangle$ multiplied by the time-evolution phase factor $e^{-iI_p t}$. The SFA expression for the time-dependent dipole becomes:

$$\mathbf{d}(t) = i \int_0^t dt' \int d\mathbf{p} \mathbf{d}^*(\mathbf{p} - \mathbf{A}(t)) e^{iS(\mathbf{p}, t', t)} E(t') \mathbf{d}(\mathbf{p} - \mathbf{A}(t')) + c.c., \quad (1.11)$$

with

$$S(\mathbf{p}, t', t) = - \int_{t'}^t \left[\frac{(\mathbf{p} - \mathbf{A}(t''))^2}{2} + I_p \right] dt'', \quad (1.12)$$

where we have introduced the canonical momentum $\mathbf{p} = \mathbf{v} + \mathbf{A}(t)$, $\mathbf{v}$ corresponding to the kinetic momentum of the electron and $\mathbf{A}(t)$ is the vector potential of the laser field ($\mathbf{E}(t) = -\frac{\partial \mathbf{A}(t)}{\partial t}$). $\mathbf{d}(\mathbf{p} - \mathbf{A}(t'))$ denotes the atomic or molecular dipole matrix element for the photoionization bound-to-continuum (Ψ_g -to- $\mathbf{v}(t')$) transition dipole, in the length gauge:

$$\mathbf{d}(\mathbf{p} - \mathbf{A}(t')) = \langle \mathbf{v}(t') | \mathbf{r} | \Psi_g \rangle. \quad (1.13)$$

In a similar way, $\mathbf{d}^*(\mathbf{p} - \mathbf{A}(t))$ denotes the atomic or molecular dipole matrix element for the photorecombination continuum-to-bound ($\mathbf{v}(t)$ -to- Ψ_g) transition dipole, in the length gauge:

$$\mathbf{d}^*(\mathbf{p} - \mathbf{A}(t)) = \langle \Psi_g | \mathbf{r} | \mathbf{v}(t) \rangle. \quad (1.14)$$

We recognize in eq. (1.11) the 3-step process semi-classical description introduced earlier in sect. 1.2. An electron is ionized at the time of birth $t_b = t'$ via a dipolar transition of probability amplitude $E(t') \mathbf{d}(\mathbf{p} - \mathbf{A}(t'))$. Once in the continuum, this electron propagates and accumulates a complex phase, also called the Volkov phase, given by the quasiclassical action $S(\mathbf{p}, t', t)$ in eq. (1.12). Finally, it later recombines back to the ground state, at the moment of recollision $t_{rec} = t$, via another dipolar transition $\mathbf{d}^*(\mathbf{p} - \mathbf{A}(t))$.

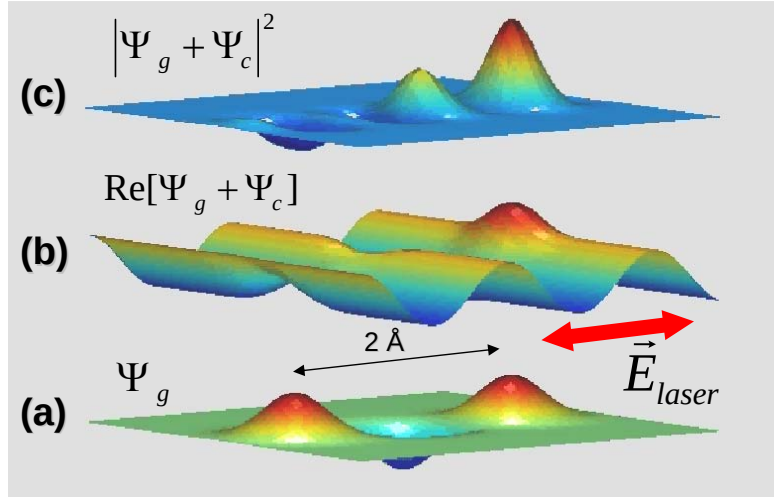


Figure 1.5: (a) The ground state wave function Ψ_g of N_2 (HOMO: highest occupied molecular orbital) is a σ_g orbital. (b) The spatial overlap between the ground and continuum Ψ_c states at an arbitrary moment t , we take the real part (Re) of their sum. Here, we choose Ψ_c to be a plane wave of de Broglie wavelength $\lambda_{\text{electron}}(E_{\text{Kin}} = k^2/2 = 60\text{eV}) \sim 1.6$ angströms. Ψ_c moving along the laser field polarization (red arrow), which is parallel to the internuclear bond. Taking Ψ_c as plane waves is an approximation [32], see section 1.3.2 for details. The bond length of N_2 is ~ 1.1 angströms, about half the distance between the two amplitude extrema of Ψ_g , as shown in (a) with the black arrow. (c) The passage of the recolliding electron Ψ_c in the vicinity of the ground state Ψ_g causes the electronic density to oscillate: this leads to a non-zero time-dependent dipole that will radiate.

The dipolar oscillation due to recollision is illustrated in Fig. 1.5. For example, we use the highest occupied molecular orbital (HOMO) of N_2 as the ground state Ψ_g , shown in (a). The spatial overlap between the ground Ψ_g and continuum Ψ_c states at an arbitrary moment t is shown in (b). Here, we choose Ψ_c to be a plane wave of de Broglie wavelength $\lambda_{\text{electron}}(E_{\text{Kin}} = k^2/2 = 60\text{eV}) \sim 1.6$ angströms. Ψ_c moving along the laser field polarization (red arrow), which is parallel to the internuclear bond. Taking Ψ_c as a set of plane waves is an approximation [32], see section 1.3.2 for more details. The bond length of N_2 is ~ 1.1 angströms, about half the distance between the two amplitude extrema of Ψ_g , as shown in (a) with the black arrow. In (c), we show that the passage of the recolliding electron Ψ_c in the vicinity of the ground state Ψ_g causes the electronic

density to oscillate: this leads to a non-zero time-dependent dipole that will radiate. The dipole oscillation (spectral polarization, amplitude and phase) will vary significantly with the electron de Broglie wavelength (which corresponds to a particular recolliding kinetic energy $E_{Kin} = k^2/2$ that maps to a given frequency Ω in the high-harmonic spectrum via eq. 1.1) but, also, with the spatial shape and orientation of the ground state Ψ_g wave function. This is the basis of tomographic high-harmonic imaging which will be explained in further details in section 1.4.

The evaluation of eq. (1.11) is not straightforward due to the fast oscillating Volkov phase $S(\mathbf{p}, t', t)$, see eq. (1.12). The stationary phase method is used to evaluate eq. (1.11). We shall summarize the main three findings resulting from this procedure [49]:

1. The transcendental equation (1.5) linking each time of birth t_b to a given time of recollision t_{rec} is recovered.
2. Energy conservation is obtained, as expected, and naturally yields the dispersion relation $\Omega = k^2/2 + I_p$ presented earlier, see eq. (1.1).
3. The sum of the kinetic energy of the electron at the time of birth t_b and the ionization potential must be zero ($v(t_b)^2/2 + I_p = 0$). This is not possible classically, but, is allowed if the time of ionization is complex (commonly associated to tunnel-ionization, see ref. [66] and references therein for more discussion on the 'tunneling time'). The real part of the time of birth (t_b) and recollision (t_{rec}) are close to the ones predicted by classical trajectories [43], see e.g. ref. [50] for more details. We will use classical times throughout this thesis' work.

For this thesis, the most important result coming from the strong field approximation is the separation/factorization of the dipole into three amplitude contributions related respectively, to the chronological three steps of the semi-classical three-step model (sect. 1.2) in the time-domain [58]. Next, we shall introduce analytical expressions for each of these amplitudes in the perspective of performing actual calculations of the time-dependent dipole $\mathbf{d}(t)$. For simplicity, here, we will consider only the component of the time-dependent dipole that is parallel to the linearly polarized driving laser field. This is equivalent to generating harmonics in an atomic gas using a linearly polarized electric field where the resultant macroscopic emission is only parallel to the driving field by

symmetry and phase matching arguments. The time-dependent dipole is as follows [67]:

$$d(t) = \Re \left[e^{-i\pi/4} \sum_{\text{trajectories}} a_I(t) a_P(t) a_R(t) \right] \quad (1.15)$$

with,

$$a_I(t) = \left(\frac{dn(t_b)}{dt} \right)^{1/2} \quad (1.16)$$

$$a_P(t) = \left(\frac{2\pi}{t - t_b} \right)^{3/2} \frac{(2I_p)^{1/4}}{|E(t_b)|} e^{-i(t-t_b)I_p - iS(t)} \quad (1.17)$$

$$a_R(t) = \sqrt{1 - n(t_{rec})} \frac{A(t_b) - A(t)}{[2I_p + \{A(t_b) - A(t)\}^2]^3} \quad (1.18)$$

where the accumulated action integral in this notation is $S(t) = \frac{1}{2} \int_{t_b}^t [A(t') - A(t_b)]^2 dt'$, $n(t_b) = 1 - e^{-\int_{-\infty}^{t_b} \Gamma(t') dt'}$ is the probability of having ionized a neutral atom by the moment t_b with $\Gamma(t)$ the instantaneous ionization rate and finally, $A(t) = -\int_{-\infty}^t E(t') dt'$.

We numerically implement this particular formalism to calculate high-harmonic emission in publication 7, see chapter 2: calculations successfully reproduce our experimental observations. Note that, in the approach above [67], the photon energy dependence of the photorecombination transition dipole (if known) is not included but can be readily incorporated in the spectral domain [68].

The ionization rate $\Gamma(t)$, can be calculated numerically following various approaches: these include Perelemov-Popov-Terent'ev (PPT) [69], Ammosov-Delone-Krainov (ADK) [54] and Yudin-Ivanov [55]. We implement the latter, which is a generalized formula based on the seminal work by Keldysh [70], followed by modifications from PPT and ADK, and adapted to the instantaneous field strength by Yudin and Ivanov in ref. [55]. The instantaneous ionization rate is then given by the following:

$$\Gamma(t) \sim \exp \left(\frac{E_0^2 f^2(t)}{\omega_0^3} \Phi(\gamma(t), \theta(t)) \right), \quad (1.19)$$

with,

$$\Phi(\gamma(t), \theta(t)) = (\gamma(t)^2 + \sin^2 \theta(t) + \frac{1}{2}) \ln c - \frac{3\sqrt{b-a}}{2\sqrt{2}} \sin |\theta(t)| - \frac{\sqrt{b+a}}{2\sqrt{2}} \gamma(t), \quad (1.20)$$

and,

$$a = 1 + \gamma^2(t) - \sin^2 \theta(t) \quad (1.21)$$

$$b = \sqrt{a^2 + 4\gamma^2(t) \sin^2 \theta(t)} \quad (1.22)$$

$$c = \sqrt{\left(\sqrt{\frac{b+a}{2}} + \gamma(t)\right)^2 + \left(\sqrt{\frac{b-a}{2}} + \sin |\theta(t)|\right)^2} \quad (1.23)$$

where the dynamical Keldysh parameter $\gamma(t) = \gamma/f(t)$, with $\gamma = \sqrt{I_p/2U_p}$, $f(t)$ is the laser pulse envelope and $\theta(t)$ is the carrier phase. We emphasize the approximately inverse exponential dependence of the ionization rate $\Gamma(t)$ on the ionization potential I_p : this provides a natural filter for preferentially interacting with the highest-lying electrons. Prefactors to eq. (1.19) are available in ref. [55].

The Keldysh parameter γ is used to characterize ionization dynamics: (1) when $\gamma \ll 1$, it is considered as the tunnel ionization regime, and (2) when $\gamma \gg 1$, it is considered as the multiphoton regime. This classification originates from a time-domain perspective: the Keldysh parameter represents a measure of (proportional to) the ratio between the time τ_t it takes for the electron to cross the potential barrier lowered by the field and the period of the driving laser $T_0 = 2\pi/\omega_0$ [70]. That is:

$$\gamma \propto \tau_t/T_0. \quad (1.24)$$

As a result, the Keldysh parameter is referred to as a measure of adiabaticity in ionization: in case (1), tunneling occurs on a faster time scale than the laser oscillation, thereby corresponding to the adiabatic regime, while case (2) refers to the nonadiabatic

case. In the experiments presented in this thesis (typically, $I_0 = 1.5 \times 10^{14}$ W/cm² and $\lambda_0=800$ nm), we work in an intermediate regime where $\gamma \sim 0.5$. The nonadiabatic regime is likely to engender collective or multi-electron dynamics, e.g. we refer the reader to the “bathtub” model for polyatomic molecules [71]. It is therefore not surprising to see the single active electron (SAE) approximation (see earlier approximation 1 in SFA [49]) failing in the interpretation of high-harmonic experiments. Nonetheless, the inverse exponential dependence of the ionization rate on the ionization potential I_p acts as a natural filter forcing mostly the removal of valence electrons in step 1 of the high harmonic generation process. The participation of deeper-lying electrons than the ones from the highest occupied (molecular) orbitals (HOMO) will be treated in this thesis. Prefactors complementing eq. (1.19) are available in ref. [55].

The high-harmonic spectrum as a function of photon frequency (or energy) Ω is the Fourier transform of the dipole acceleration [72]:

$$S_{HHG}(\Omega) = \left| \int_{-\infty}^{\infty} dt \ddot{\mathbf{d}}(t) e^{i\Omega t} \right|^2 = \Omega^4 \left| \int_{-\infty}^{\infty} dt \mathbf{d}(t) e^{i\Omega t} \right|^2 \quad (1.25)$$

and the spectral phase is

$$\Phi(\Omega) = \arg \left[\int_{-\infty}^{\infty} dt \ddot{\mathbf{d}}(t) e^{i\Omega t} \right]. \quad (1.26)$$

Here, we re-introduce bold fonts in $\mathbf{d}(t)$ to emphasize that the dipole can have multiple polarization components and, hence, multiple corresponding spectral phases written as $\Phi(\Omega)$.

Since the complex dipole is experimentally accessible only via spectral measurements, see eqs. (1.25) and (1.26), it is also practical to factorize it in the spectral domain. We now use capital letters to specify quantities in the spectral (Fourier) domain:

$$\mathbf{D}(\Omega) = A_I(\Omega) A_P(\Omega) \mathbf{A}_R(\Omega) \quad (1.27)$$

To our knowledge, the factorization in each steps (I -ionization, P -propagation and R -recombination) in the spectral domain has been initially introduced in ref. [32] and, more recently, generalized in the framework of “quantitative rescattering theory” (QRS)

in ref. [73]. In this formulation, we conveniently assume that the recombination step ($\mathbf{A}_R(\Omega)$) dictates the polarization state of the dipole. Modifications to this formulation may be required if, for example, there is ellipticity in the driving laser field (ellipticity from the laser field could be transferred to the high-harmonic radiation in addition to the one coming from the recombination step alone). The factorization is particularly useful to fully characterize the polarization, amplitude and phase of the photorecombination dipole matrix elements $\mathbf{A}_R(\Omega) = \mathbf{d}^*(\Omega) = \langle \Psi_g | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle$, see eqs. (1.11) and (1.14), where the modulus of the momentum vector $\mathbf{k}(\Omega)$ is given by the dispersion relation eq. (1.1). For a detailed proof that the factorized formula for high harmonic generation involves the exact photorecombination cross section, $\mathbf{A}_R(\Omega)$, please refer to ref. [74].

A_I and A_P in eq. (1.27) carry contributions to the amplitude and phase due, respectively, to the ionization and propagation steps. $A_I(\Omega)$ will shape the amplitude spectrum via the time-dependent sub-cycle instantaneous ionization rate, discussed earlier in eq. (1.16), and could possibly carry a spectral phase which has not been addressed so far in atoms but is a subject of debate in molecules where multiple orbitals can contribute to high harmonic generation [25, 75]. $A_P(\Omega)$ will shape the amplitude spectrum mostly due to the spreading of the wave packet, see eq. (1.17), which depends on the harmonic frequency Ω via the associated transit time $\tau_\Omega = (t_{rec,\Omega} - t_{b,\Omega})$ that the electron spends in the continuum, see eq. (1.5). $A_P(\Omega)$ will also contribute a large phase (typically, multiple tens of radians) associated to the quasiclassical action integral eq. (1.12).

The factorization is now widely used for understanding molecular dynamics probed by high harmonic generation; whether it is for treating HHG in aligned molecules [25, 64, 73] and rotational dynamics [76, 77]; vibrational dynamics [62, 78]; or chemical dynamics, see publications 5, 6, and 9 in chapter 4. For example, the simultaneous measurements of the ionization probability as well as the high-harmonic yield can help isolate the contributions from the recombination step, as first done in ref. [77] in aligned molecules.

In aligned molecules, we define θ as the angle between the laser field polarization (always linear, unless specified otherwise) axis and the molecule's most polarizable axis, usually the internuclear axis in the case of linear or symmetric top molecules [79]. Each polarization component of the complex dipole is characterized by a spectral amplitude $|D(\Omega, \theta)|$ and phase $\Phi(\Omega, \theta)$ that contains the contributions from the three steps as

just described in eq. (1.27). For simplicity, we consider one polarization component of the complex dipole and use a common notation for the 3-step factorization in aligned molecules [73]:

$$D(\Omega, \theta) = |D(\Omega, \theta)|e^{i\Phi(\Omega, \theta)} = \sqrt{I(\Omega, \theta)}P(\Omega, \theta)R(\Omega, \theta) \quad (1.28)$$

with

$$\Phi(\Omega, \theta) = \Phi_I(\Omega, \theta) + \Phi_P(\Omega, \theta) + \Phi_R(\Omega, \theta). \quad (1.29)$$

$I(\Omega, \theta)$ is the ionization probability (hence $\sqrt{I(\Omega, \theta)}$ is the amplitude) and $P(\Omega, \theta)$ is the complex amplitude contribution from the propagation step. As above for atoms in eq. (1.27), the polarization state of the dipolar field is given by the full (all polarization components included) photorecombination dipole matrix elements:

$$\mathbf{R}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle. \quad (1.30)$$

We now use the notation $\Psi_g(\mathbf{r}; \theta)$ to specify that the molecule, represented by the stationary state $\Psi_g(\mathbf{r})$, is aligned at an angle θ with respect to the polarization of the laser field given by the wave vector $\mathbf{k}$ of the recolliding electron. The polarization of $\mathbf{R}(\Omega, \theta)$ is typically decomposed in terms of the laboratory frame parallel and perpendicular –to the laser polarization $\mathbf{k}$ – components, see section 1.3.3. The molecular frame components, defined with respect to the molecular axis, are required for tomographic imaging of $\Psi_g(\mathbf{r})$: they can be obtained by the appropriate rotation of the laboratory frame components, as later described in section 1.4.2.

1.3.2 The SFA-Plane Wave Approximation

Eq. (1.28) can be simplified considerably if we first regroup the spectral contributions of the ionization (I) and propagation (P) steps together into the spectral amplitude $a(k(\Omega))$ of the recolliding electron wavepacket Ψ_c , where the magnitude $k(\Omega)$ is given by eq. (1.1). Second, if we suppose that the angular dependence of the propagation step is negligible,

we can write the expected signal from eq. (1.25):

$$S_{Mol}(\Omega, \theta) = \Omega^4 I(\theta) |a(k) \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | \mathbf{k} \rangle|^2. \quad (1.31)$$

We have expanded the continuum state $|\Psi_c(\mathbf{k})\rangle$ into a set of normalized $|\mathbf{k}\rangle$ states with the wavevectors $\mathbf{k}$ propagating along the laser polarization. The spatial profile of these continuum states can be obtained via various techniques: these include the eikonal-Volkov approximation (EVA) which incorporates the effect of the Coulomb potential in the framework of SFA [80] and, more recently, ePolyScat [81, 82] which calculates the exact single-photon photoionization differential cross section using the molecular orbitals as an input to solving the quantum scattering problem. Photoionization and photorecombination cross sections are proportional based on detailed balancing [65, 73, 74]: we take the complex conjugate of photoionization matrix elements for photorecombination as done in ref. [73]. The exact continuum electron scattering states $|\mathbf{k}\rangle$ can also be solved for using other numerical methods where analytical expressions for the atomic or molecular potential are available. For example, these types of calculations can agree well with experiments, as is the case for predicting the Cooper minimum in argon (Ar), see publication 1.

Eq. (1.31) can be further simplified if we assume the continuum $|\mathbf{k}\rangle$ states to be plane waves. This is called the plane wave approximation (PWA). It results in:

$$S_{Mol,PWA}(\Omega, \theta) = \Omega^4 I(\theta) |a(k) \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | e^{i\mathbf{k}\cdot\mathbf{r}} \rangle|^2 \quad (1.32)$$

In eq. (1.32), we recognize that the predicted signal $S_{Mol,PWA}(\Omega, \theta)$ contains the spatial Fourier transform of the ground state wave function which we shall now write as the PWA photorecombination dipole:

$$\mathbf{R}_{PWA}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | e^{i\mathbf{k}\cdot\mathbf{r}} \rangle \quad (1.33)$$

Despite the generally poor agreement between calculations based on the plane wave approximation and experiments [83, 84], the practical form of $\mathbf{R}_{PWA}(\Omega, \theta)$ allows the ground state wave function $\Psi_g(\mathbf{r})$ to be fully (amplitude and phase) reconstructed by

inverse Fourier transform as first shown in ref. [32]. More details on high-harmonic imaging are given in section 1.4. Molecular imaging is a key application of HHG and it is related to the main goal of this thesis (section 1.5).

1.3.3 Alignment Averaging in HHG from Aligned Molecules

Field-free laser alignment of molecules in the laboratory allows one to observe physical processes in the molecular frame [79]. Alignment of the molecules with respect to the driving laser field polarization (linear) axis is required to, for example, image molecular orbitals using high harmonic generation and the observation of laser-induced electron diffraction, see section 1.4. We achieve field-free alignment using nonadiabatic alignment: under the influence of a strong, non-resonant and non-ionizing laser pulse, molecules tend to align their most polarizable axis along the polarization of the field. An anisotropic well of depth $H = -\Delta\alpha E_0^2/4$ is thus created, where E_0 is the maximum electric field strength and $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, the difference in the polarizability components of the molecule [79]. Typically, $H \approx 1.25$ eV for $I_0 = 5 \times 10^{13}$ W/cm² and $\Delta\alpha = 10$ Å³.

If the pulse duration is considerably shorter than the rotational period of the molecule, a nonadiabatic interaction takes place: rotational states of the molecule are being coherently populated by a Raman excitation from the aligning pulse, thus creating a rotational wave packet. The degree of alignment obtained will depend on the strength of the interaction, as given by H , but also on the rotational temperature T_{rot} of the gas. The quantity commonly used to evaluate the degree of alignment is the expectation value of $\cos^2 \theta'$ on the alignment distribution $A(\theta', \phi')$, which represents the molecular ensemble:

$$\langle \cos^2 \theta' \rangle = \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \cos^2 \theta' A(\theta', \phi') \sin \theta' d\phi' d\theta', \quad (1.34)$$

where θ' and ϕ' defined as the zenithal and azimuthal angles between the alignment distribution axis (z' , see Fig. 1.6(a)) and the molecule's internuclear axis (any point on $A(\theta', \phi')$). For an isotropic distribution, $\langle \cos^2 \theta' \rangle = 1/3$. In nonadiabatic alignment, $\langle \cos^2 \theta' \rangle$ will first peak shortly after the interaction with the aligning pulse, this is the prompt alignment. It will subsequently modulate strongly at fractional revival times

[85, 86], therefore offering field-free aligned molecules.

Measurements performed on aligned molecules suffer the blurring effect coming from the imperfect alignment distribution achieved in the laboratory frame. The alignment distribution can be measured directly [86] or inferred from the time-dependent profile of rotational wave packets in ionization or HHG experiments [87]. The alignment angle dependence HHG measurements are performed on the molecular ensemble when the degree of alignment is the highest, that is when molecules form a prolate (cigar shape) alignment distribution $A(\theta', \phi')$, as shown in Fig. 1.6(a), around the full rotational revival time. The angle α between the alignment distribution main axis (z' , see Fig. 1.6(a)) and the probing field (also linearly polarized) is varied by rotating the polarization angle of the alignment pulse. The angular dependence (θ) of the molecular frame signal of interest is therefore not readily accessible. Please note that α and θ are interchanged in the supplementary information part of publication 14 in chapter 5.

The high-harmonic signal measured in the laboratory frame, $S(\Omega, \alpha)$, is a coherent angular convolution of the molecular frame dipole field $\mathbf{D}(\Omega, \theta(\theta', \phi', \alpha))$ with the prolate alignment distribution $A(\theta', \phi')$, where θ is the molecular frame angle between the laser field polarization axis (linear) and the molecule's internuclear axis, and Ω is the harmonic frequency:

$$S(\Omega, \alpha) = \left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \mathbf{D}(\Omega, \theta(\theta', \phi', \alpha)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right|^2. \quad (1.35)$$

The angle θ is given by the laboratory to molecular frame coordinates transformation via the alignment distribution [88], as shown in Fig. 1.6 (b):

$$\cos \theta = \cos \alpha \cos \theta' - \sin \alpha \sin \theta' \sin \phi'. \quad (1.36)$$

In our typical experimental conditions (pulsed valve backing pressure $P_{back}=2$ atm., gas rotational temperature in the supersonic expansion $T_{rot}=30-40$ K and alignment peak intensity $I_{align} = 5 \times 10^{13}$ W/cm²), we estimate $\langle \cos^2 \theta' \rangle = 0.60 \pm 0.05$ [89]. Our estimate is supported by recent supersonic gas expansion studies in similar conditions [90]. The corresponding alignment distribution $A(\theta', \phi')$ can be approximated analytically and the

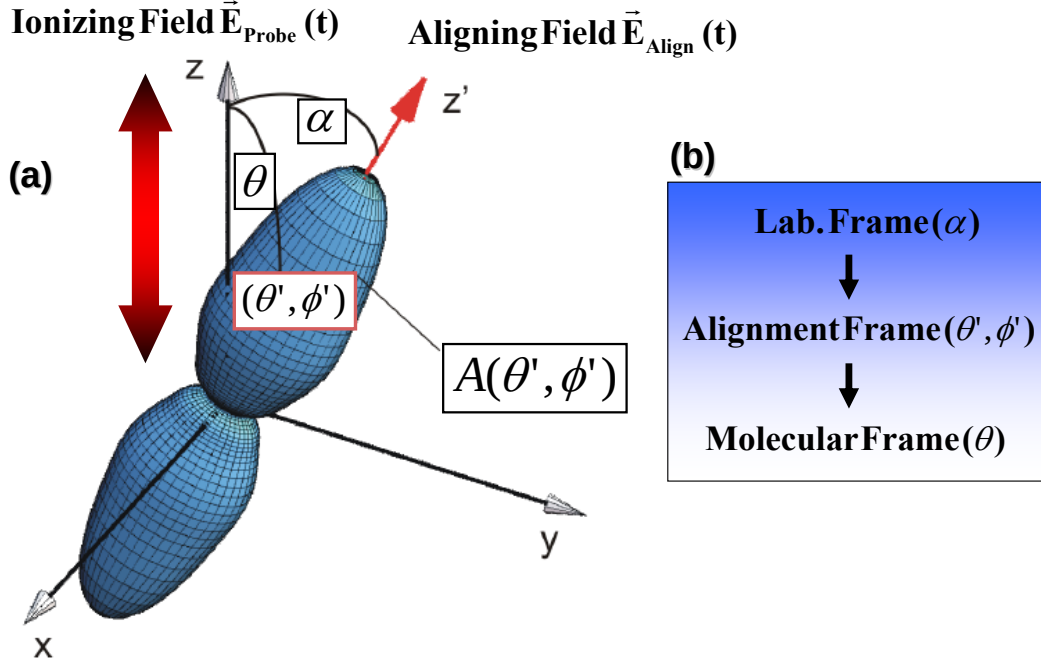


Figure 1.6: (a) Experiments performed on aligned molecules involve the alignment distribution $A(\theta', \phi')$: the distance from the common origin to the colored (blue) prolate surface represents the probability amplitude of alignment in any given direction. (b) There is a relation between the laboratory frame (α) and molecular frame (θ) alignment angles via the alignment distribution $A(\theta', \phi')$, see eq. (1.36).

dependence on ϕ' is lost by cylindrical symmetry. We use the following alignment distribution as inspired from ref. [88]:

$$A(\theta') = \left(-1 + \frac{a}{\sqrt{\cos(\theta')^2 + \epsilon^2 \sin(\theta')^2}} \right) \quad (1.37)$$

with the parameters $a = 3.5, \epsilon = 3.123$ for $\langle \cos^2 \theta' \rangle = 0.60$.

A full characterization of the single-molecule molecular frame high-harmonic XUV field $\mathbf{D}(\Omega, \theta)$ requires to solve, first, for the polarization state of the light as well as, second, both the amplitude and phase of each polarization component from laboratory frame measurements. Following previous works [91, 92], we decompose the polarization

state of the electric field $\mathbf{E}(\Omega, \alpha)$ detected in the laboratory frame in terms of parallel ($\parallel$) and perpendicular ($\perp$) components with respect to the driving laser field polarization axis (linear):

$$\mathbf{E}(\Omega, \alpha) = \Re \begin{bmatrix} |E_{\parallel}(\Omega, \alpha)| e^{i\Phi_{\parallel}(\Omega, \alpha)} \\ |E_{\perp}(\Omega, \alpha)| e^{i\Phi_{\perp}(\Omega, \alpha)} \end{bmatrix}. \quad (1.38)$$

We use a thin ($100 - 250 \mu\text{m}$ orifice, thin when compared to the HHG probing pulse Rayleigh range of $\sim 20 \text{ mm}$) gas jet in our experiment, see section A.3.2 for more experimental details. This allows us to assume perfect phase matching conditions: that is, we assume there is a direct correspondence, besides angular averaging, between the measured macroscopic high-harmonic electric field $\mathbf{E}$ and the single-emitter (atom or molecule) dipolar field $\mathbf{D}$ [93]. As a result, in aligned molecules, the electric field amplitude and phase of each component measured in the lab are, respectively, directly related to the single-molecule molecular frame dipole $\mathbf{D}(\Omega, \theta)$ via an angular convolution integral as follows:

$$\begin{aligned} |E_{\parallel, \perp}(\Omega, \alpha)| &= \\ \sqrt{S_{\parallel, \perp}(\Omega, \alpha)} &= \left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{\parallel, \perp}(\Omega, \theta(\theta', \phi', \alpha)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right|, \end{aligned} \quad (1.39)$$

$$\Phi_{\parallel, \perp}(\Omega, \alpha) = \arg \left[\int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{\parallel, \perp}(\Omega, \theta(\theta', \phi', \alpha)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right]. \quad (1.40)$$

We refer here to $D_{\parallel, \perp}(\Omega, \theta)$ as the polarization components of $\mathbf{D}(\Omega, \theta)$, also defined with respect to the driving laser field polarization axis. From perfect phase matching, the measured signal (energy) $S_{\parallel, \perp}(\Omega, \alpha)$ is proportional to the single-molecule response power spectrum (energy) $|E_{\parallel, \perp}(\Omega, \alpha)|^2$. Since we are mostly interested in the relative change of the signal with θ or Ω , we dropped the proportionality and directly use the equality sign in eqs. (1.39) and (1.40).

By polarimetry measurements, the values of eqs. (1.39) and (1.40) can be measured [91, 92]. These equations must be simultaneously solved for in order to retrieve

each components of the molecular frame dipolar field, introduced earlier in eq.(1.28):

$$\mathbf{D}(\Omega, \theta) = \Re \begin{bmatrix} |D_{\parallel}(\Omega, \theta)| e^{i\Phi_{\parallel}(\Omega, \theta)} \\ |D_{\perp}(\Omega, \theta)| e^{i\Phi_{\perp}(\Omega, \theta)} \end{bmatrix}. \quad (1.41)$$

Another approach to measure the values of eqs. (1.39) and (1.40) would be, instead, to combine two amplitude and two phase measurements in the presence of an XUV polarizer placed between the generation medium and the light detector, refer to the experimental setup in Fig. A.4. One can select either the parallel or perpendicularly polarized emission by setting the driving field parallel or perpendicular to the polarizer transmission axis and only rotate the molecules. The amplitude is then obtained directly from the signal (energy) measurements $S_{\parallel, \perp}(\Omega, \alpha)$ while the phases, $\Phi_{\parallel, \perp}(\Omega, \alpha)$ could be obtained by two-source harmonic phase interferometry, see refs. [25, 94] and publication 14, using the same experimental configuration (with XUV polarizer). We have considered this approach but it is not presented in this thesis.

In chapter 3, sect. 3.2, we explore the possibility of retrieving the molecular frame dipole amplitude $|\mathbf{D}(\Omega, \theta)| = \sqrt{|D_{\parallel}(\Omega, \theta)|^2 + |D_{\perp}(\Omega, \theta)|^2}$ following certain justified assumptions which include treating eqs. (1.39) and (1.40) as incoherent sums. In particular, this approach allows us to improve the limited angular resolution of two-dimensional laboratory frame (Ω, α) high-harmonic profiles. By removing alignment averaging, we access the molecular frame (Ω, θ) response. As an example, our procedure uncovers the Cooper-like minimum [41] centered on $\theta = 0$ and $\Omega = 45 \pm 5$ eV in aligned N_2 molecules, see publication 15 in chapter 3.

1.3.4 Breaking the Centrosymmetry of the HHG Process

The spatial centrosymmetry of the HHG process can be broken either by, first, the use of an asymmetric driving laser field or, second, an asymmetric generation medium. As a result, other photon frequencies than the odd high-order harmonics of the fundamental driving field will be observed. This introductory section is important for understanding the work presented in publication 16 of chapter 2, where we report the first observation of even harmonics from oriented heteronuclear (CO) molecules.

In the first case, photons at frequencies $\Omega = \sum_{i=1}^x n_i \omega_i$, where $\sum_{i=1}^x n_i = 2k-1$ with n_i and k integers [95, 96], will be produced by the combination of x laser fields at frequencies ω_i , provided their combination is intense enough to support HHG. We present additional evidence for this comprehensive *frequency-domain* multiphotonic description of HHG by multicolor laser fields in chapter 2, publication 7, where we non-collinearly combine laser fields to produce harmonics in a gas jet. Another approach for understanding the generation of other –sideband– frequencies than the usual odd high harmonics comes by examining the HHG process from the *time-domain* semi-classical picture, provided by the three-step model introduced earlier in sections 1.2 and 1.3. Adding another laser field to the intense fundamental driving laser field will act as a sub-cycle temporal ‘gate’ on the HHG process. The first evidences of this gate came from studies where changing the relative phase (timing) between the fundamental driving laser field and its second harmonic revealed sub laser-cycle control on the generation of even-order harmonics [97, 98, 99]. To understand this temporal gate, we shall next describe HHG from a multi-cycle driving laser field by considering the cycle-averaged high-harmonic emission.

In Fig. 1.7 (a), we illustrate HHG during the full cycle of a multi-cycle fundamental driving laser field. At each half cycle of the driving laser field $\vec{E}(t)$, an attosecond pulse is emitted. In the spectral domain (Ω), we write the total time-averaged generated high-harmonic electric field $E_{Tot}(\Omega)$ as the contributions from two consecutive recollisions. For simplicity, here, we consider only a single polarization component of the emission:

$$E_{Tot}(\Omega) = E_{up}(\Omega) + E_{down}(\Omega) \propto 1 - A_0(\Omega)e^{i\Delta\Phi(\Omega)}e^{iT_0\Omega/2} \quad (1.42)$$

with $T_0 = 2\pi/\omega_0$, where ω_0 is the fundamental driving field frequency, $\Omega = q\omega_0$ and q is the high-harmonic order. We introduce the relative spectral amplitude $A_0(\Omega)$ and phase $\Delta\Phi(\Omega)$ between the two consecutive pulses, $E_{up}(\Omega)$ and $E_{down}(\Omega)$, and the minus comes from the vectorial inversion (through the origin in space) of the dipolar charge oscillation between each half cycle of the fundamental field, refer to Fig. 1.5 (c) for an illustrative explanation of the vectorial inversion. We write the resulting high-harmonic

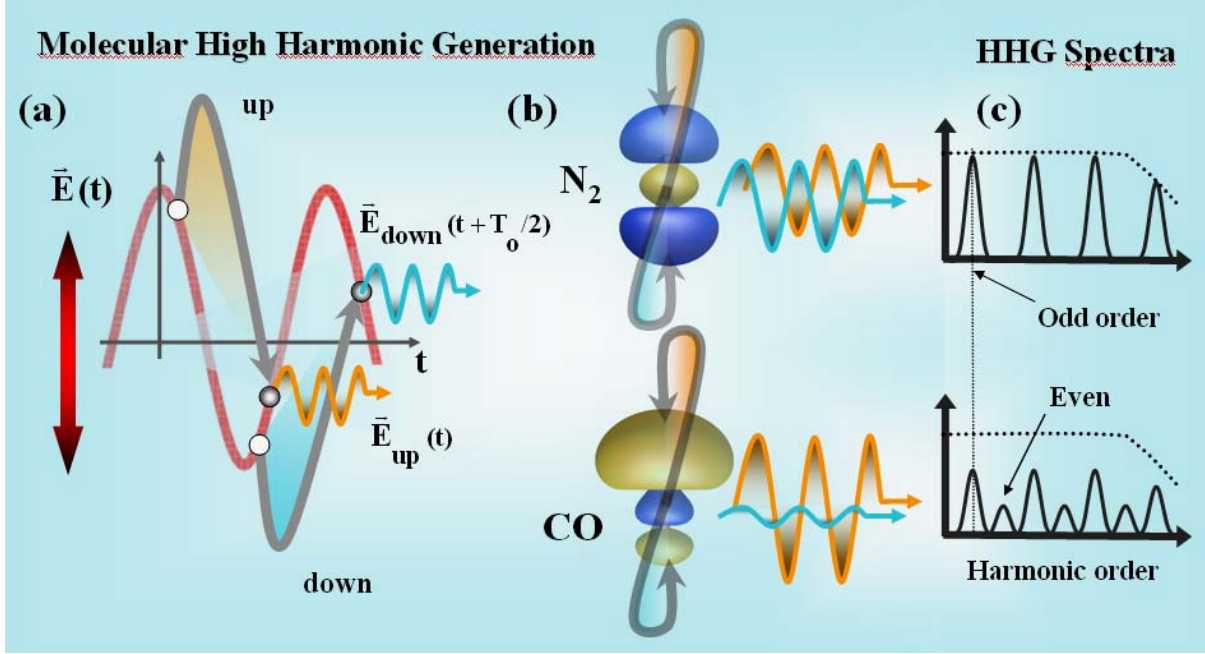


Figure 1.7: Breaking the centrosymmetry of the HHG process. (a) Attosecond pulses are generated every half cycle of an up-down symmetric fundamental driving laser field $\vec{E}(t)$. The spectral interference of two consecutive attosecond pulses can be used to estimate the cycle-averaged high-harmonic spectrum generated by a multi-cycle laser field. (b) In a centrosymmetric (non-centrosymmetric) medium, such as aligned (oriented) N_2 (CO) molecules, as shown in the upper (lower) panels, (c) only odd (both odd and even, see publication 16) high harmonics light spectra are observed.

power spectrum $S_{Tot}(q = \Omega/\omega_0) = |E_{Tot,q}|^2$:

$$S_{Tot}(q) \propto \left| 1 - (-1)^q A_0(q) e^{i\Delta\Phi(q)} \right|^2. \quad (1.43)$$

Straightforwardly, from eq. (1.43), for HHG in a centrosymmetric generation medium, where $A_0(q)=1$ and $\Delta\Phi(q)=0$, we obtain a spectrum of odd harmonics only, as is the case in perturbative harmonic generation [39]. We recall that the spectral amplitude and phase of attosecond pulses contain the contribution from all three steps of the three-step model (ionization (I), propagation (P) and recombination (R)): these are not only defined by the generation medium, but, also by the driving laser field, see earlier sec-

tion 1.3. Therefore, it is possible to break the symmetry in the spectral amplitude or phase between successive attosecond pulses generated from a centrosymmetric medium by tailoring accordingly the laser field $\vec{E}(t)$.

For example, superposing a weak ($\sim 10^{-3}$ in intensity, with respect to the strong driving field $\vec{E}(t)$) second harmonic field on top of the fundamental field creates a small asymmetry in the total field sufficient to strongly control the production of even and odd harmonics [98]. In this case, it is an up-down asymmetry occurring mainly in the Volkov phase (Φ_P), associated with the propagation step (step 2), that provides control on the production of even or odd harmonics. Since Φ_P extends over multiple tens of radians [48], only a weak perturbation (the second harmonic field) can coherently switch the production of odd into even harmonics ($\Delta\Phi(\Omega) = n\pi$, n is an integer) by changing the relative phase between the fundamental and the weak second harmonic fields [98]. Along those lines (fundamental + second harmonic), an up-down amplitude asymmetry $A_0(\Omega) \neq 1$ can also be created. In the limit where the second harmonic intensity becomes comparable to the fundamental, attosecond pulse emission will occur only every cycle of the fundamental pulse because ionization only happens once per cycle ($A_0=0$): in that case, both odd and even harmonics are equally observed [97], refer to eq. 1.43 above.

We can consider the case where an asymmetric medium and a symmetric laser field are used: this also leads to the production of even harmonics. It can then be used as a measurement of the up-down asymmetry in the spectral amplitude $A_0(\Omega)$ or phase $\Delta\Phi(\Omega)$ of consecutive attosecond pulses. For example, following eq. (1.43), HHG from a surface will typically produce equal amounts of even and odd harmonics since the emission will occur only every full laser cycle ($A_0=0$). Unequal amounts of even and odd harmonics will be obtained if there is a degree of orientation in the surface with respect to the driving laser field, one could for example imagine HHG from an inclined surface with molecules loosely attached to it [100].

We can generalize the production of even harmonics as a measurement of the degree of up-down asymmetry in the amplitude $A_0(q)$ and phase $\Delta\Phi(q)$. In the limit where we assume a slow variation of the amplitude and phase asymmetries with harmonic order q , i.e. $A_0(q+1) \approx A_0(q)$ and $\Delta\Phi(q+1) \approx \Delta\Phi(q)$, the signal ratio $\frac{S_{Tot}(q+1)}{S_{Tot}(q)}$ between

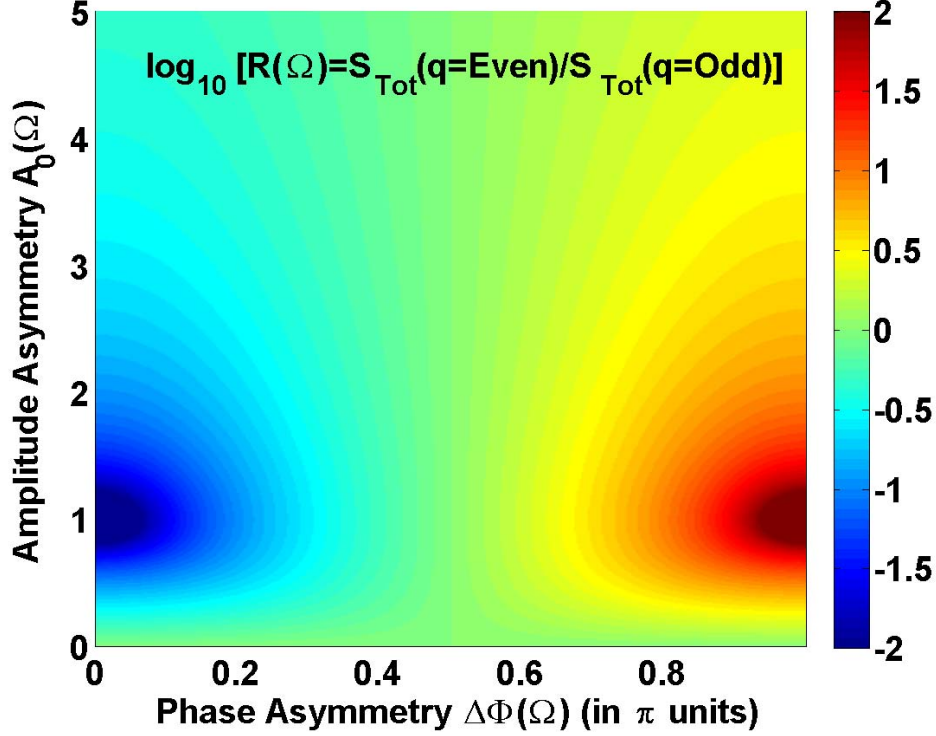


Figure 1.8: $R(\Omega) = \frac{S_{Tot}(q=Even)}{S_{Tot}(q=Odd)}$, the signal of even harmonics relative to adjacent odd harmonics (see eq. 1.44) as a function of up-down (see Fig. 1.7) asymmetry in the spectral amplitude A_0 (vertical axis) and phase $\Delta\Phi$ (horizontal axis) between two successive attosecond pulses in a multi-cycle laser field. We use a $\log_{10}$ color scale. Here, we consider a general case: asymmetry in both the generation medium and the driving laser field are combined in $A_0(\Omega)$ and $\Delta\Phi(\Omega)$.

adjacent even $(q + 1)$ and odd (q) harmonics becomes:

$$R(\Omega = q\omega_0) \approx \frac{|1 - A_0(\Omega)e^{i\Delta\Phi(\Omega)}|^2}{|1 + A_0(\Omega)e^{i\Delta\Phi(\Omega)}|^2}. \quad (1.44)$$

In Fig. 1.8, we summarize eq. (1.44). This simple model generalizes the few examples of symmetry breaking (either in the driving laser field or in the generation medium) mentioned above. For example, the cases where there is no amplitude asymmetry, $A_0(\Omega)=1$,

are correctly predicted: only the odd (even) harmonics are observed for $\Delta\Phi(\Omega) = 0$ ($\Delta\Phi(\Omega) = \pi$) [98]. This simple model is useful for giving an estimate of the expected amount of even harmonics for intermediate symmetry breaking cases. For example, for an amplitude asymmetry of $A_0(\Omega)=2$ and a phase asymmetry of $\Delta\Phi(\Omega) = \pi/3$, the relative signal of even to odd harmonics will be on the order of $R(\Omega)=10^{-0.5} \approx 0.3$, see Fig. 1.8. As is always the case in coherent detection, the visibility of the asymmetry depends more strongly on the relative phase $\Delta\Phi(\Omega)$ (horizontal axis) than the relative amplitude $A_0(\Omega)$ (vertical axis).

In chapter 2, section 2.2 (publication 16), we apply this simple ‘two consecutive recollisions’ model to HHG from oriented CO molecules. In that experiment, we observe $R(\Omega)$ up to a maximum value of ~ 0.1 ($= 10^{-1}$). After applying an equation similar to eq. (1.44) (the equation is modified to account for the fraction of oriented molecules which approaches $r \approx 15\%$) and assuming the amplitude asymmetry $A_0(\Omega)$, we retrieve a phase asymmetry approaching $|\Delta\Phi(\Omega)| = \pi$. As will be shown in publication 16, the background-free observation of even harmonics provides a direct molecular-scale measurement of asymmetry, in spectral amplitude and/or phase, between two consecutive attosecond pulses. This offers a new benchmark for testing the accuracy of theoretical models predicting the spectral amplitude and phase of high-harmonic radiation, a previously inaccessible perspective from HHG in centrosymmetric systems.

1.4 Molecular Imaging

In the last decade, the field of ultrafast optics has witnessed important developments in molecular imaging based on high-harmonic spectroscopy. We refer the reader to a topical review on the subject in ref. [35]. Here, we shall first situate high-harmonic imaging with respect to other state-of-the-art imaging techniques in terms of spatial and temporal resolutions in section 1.4.1. Then, we explain high-harmonic molecular imaging, a tomographic technique based on electron recollision, in section 1.4.2. Before we move on, we should highlight the unique in-situ character of this technique.

High-harmonic tomographic imaging is an in-situ technique whereby a tabletop light-matter interaction probes/images valence electronic structures from the emission of broad

XUV (few tens to few hundreds of eV photons) light spectra of high-harmonic radiation. As will be shown in the upcoming sections, to reconstruct actual images, the emitted XUV light needs to be fully characterized: the light polarization, amplitude and phase, each spectrally and angularly (molecular alignment)-resolved, must be measured. In parts, (1) spectrally-resolved light detection as well as (2) the natural applicability of various coherent detection schemes and (3) compatibility of HHG with field-free molecular alignment techniques make in-situ high-harmonic molecular imaging readily accessible to tabletop instrumentation.

Other important emerging imaging techniques, also based on HHG, are ex-situ: they require to first generate high-harmonic radiation that will be then be further used for probing/imaging by diffraction. So far, while available photon energies have reached the water window (~ 300 - 500 eV)[101], the photon flux remains rather too low in that high-energy range to perform diffraction experiments. We will discuss possible improvements on that aspect further below. Another similar type of ex-situ high-harmonic imaging technique is based on spectrally-resolved absorption of attosecond pulses [24]. We will not discuss this technique here because, although it may allow angular imaging of orbitals, it does not (yet) compare with actual techniques that spatially image objects with angström-size spatial resolution, such as in-situ high-harmonic imaging.

Of relevance to compare with in and ex-situ high-harmonic imaging techniques are: X-ray and electron diffractions. We consider both of them as ex-situ techniques since they require, other than the generation of intense femtosecond laser pulses, to first generate the probing radiation. X-ray and electron beams are typically produced in large synchrotron and/or free-electron laser (XFEL) facilities. Nowadays, electron pulses can also be produced via tabletop photoactivated (laser) guns and electron bunches compression techniques [102]. Next, we shall compare all techniques mentioned above, based on the spatial and temporal resolutions they offer.

1.4.1 Ultrafast-Angström Molecular Imaging: State-of-the-Art

Spatial Resolution

In imaging based on scattering or diffraction, the spatial resolution is generally given by the shortest wavelength of the incident probing radiation [103]. As shown in Fig. 1.9, for the same quantum of energy E carried by the incident radiation, electrons have a much shorter (de Broglie) wavelength: the 1 angström wavelength is achievable by 150 eV electrons while it is a lot more expensive for photons which require $E \sim 12$ keV. For this economic reason, using the wave properties of electrons for imaging matter is very attractive. In-situ high-harmonic imaging [35] and laser-driven electron diffraction [104], because they are based on electron recollision [43], both benefit from this significant advantage.

Recent developments in the field of electron diffraction have shown its capability to time-resolve changes of internuclear distances which accompany phase transitions in crystalline structures. For example, “melting at the atomic level” in a metal, using tabletop femtosecond electron diffraction ($\lambda_{electron}(E = 30 \text{ keV}) \sim 0.1$ angström), has been observed with much less than 1 angström precision [105] on the internuclear distances. In electron diffraction, the diffracted signal is usually much stronger (by few orders of magnitude) than in the case of X-ray diffraction due to differences in the respective scattering cross sections. These differences arise in part because electrons diffract strongly from interacting with the positively charged nuclei and all electrons, while the diffracted X-ray photons will rather weakly interact with the diffuse electron cloud [106, 107, 108]. In this view, X-ray diffraction is therefore more suited to study chemical dynamics, where one seeks sensitivity to valence electrons –the protagonists of chemistry– as emphasized earlier on in section 1.1. However, few keVs X-rays will rather interact preferentially with inner-shell or core electrons. X-ray diffraction experiments done in at XFEL facilities such as LCLS [109] and FLASH [110] typically operate in the energy range of few keVs or more ($\lambda_{photon}(E = 2 \text{ keV}) \sim 6.0$ angströms).

Experimentally, to cope with the weak X-ray diffraction signal, the radiation intensity must be increased to very high levels where destruction of the target is inevitable. However, the combination of bright and short (≤ 10 femtoseconds) X-ray pulses would

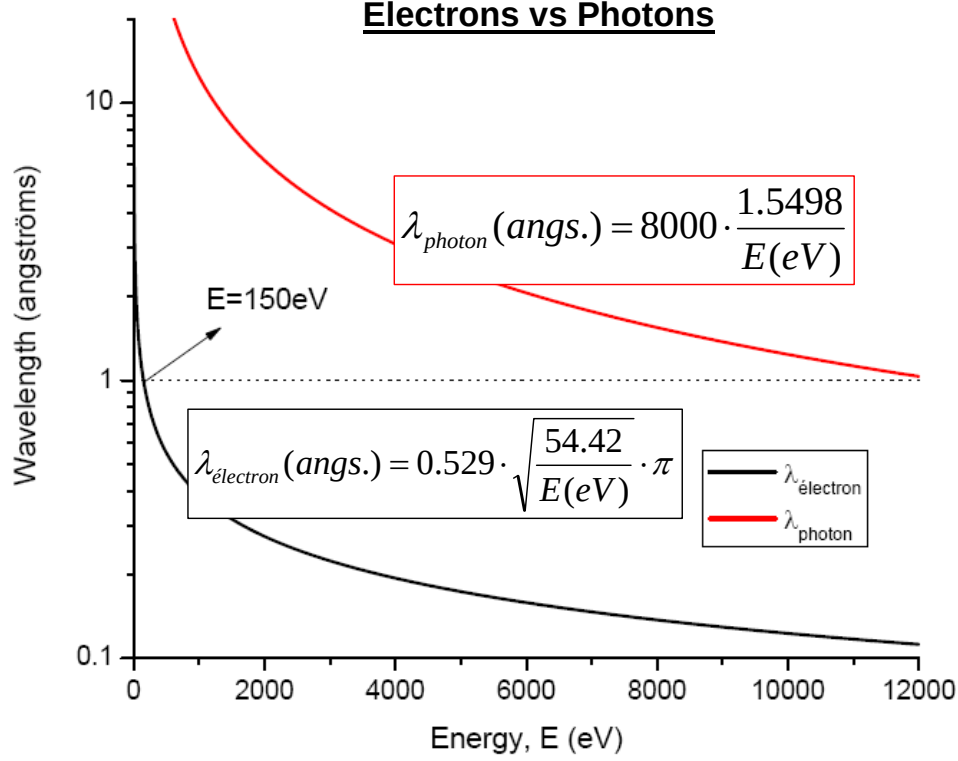


Figure 1.9: The photon (red) and electron de Broglie (black) wavelengths as a function of the photon or the electron's kinetic energy E . For the same quantum of energy E carried by the incident radiation, electrons have a much shorter (de Broglie) wavelength: the 1 angström wavelength is achievable by $E = 150$ eV electrons while it is a lot more expensive with photons which require $E \sim 12$ keV. For this economic reason, using the wave properties of electrons for imaging is very attractive. In-situ high-harmonic imaging [35] and laser-driven electron diffraction [104], because they are based on electron recollision [43], both benefit from this significant advantage. λ_{photon} is derived directly from the Planck-Einstein equation: $E = h\nu = hc/\lambda_{\text{photon}}$, where ν is the frequency, c is the speed of light and h is the Planck constant [12]. The recolliding electron de Broglie wavelength $\lambda_{\text{electron}}$ is obtained from considering a non-relativistic electron of kinetic energy $E = k^2/2$, with $k = 2\pi/\lambda_{\text{electron}}$.

make this apparent difficulty surmountable [111, 112]. Recently, images of nanocrystalline structures containing proteins [113] as well as a noncrystalline biological sample

(mimivirus) [114] were successfully reconstructed from few femtosecond 2 keV X-ray pulses diffraction data. In in-situ high-harmonic imaging, because of the low efficiency ($\sim 10^{-6} - 10^{-4}$, see publication 2) of the HHG process, the use of short and intense driving pulses is similarly required. However, macroscopic phase-matching will usually insure measuring the response from only the neutral molecules of interest in HHG experiments.

In typical high-harmonic spectra extending to cutoff photon energies around 100 eV, the shortest deBroglie electron wavelength observed ($\lambda_{electron}$) is in the range of 1 to 1.5 angströms, refer to Fig. 1.9. This is roughly the spatial resolution of atomic [31] and molecular [32, 33, 34, 35] orbitals reconstructed so far by in-situ high-harmonic imaging.

Finally, we mention that ex-situ high-harmonic imaging, via diffraction of soft-X-ray light ($E < 100$ eV), has allowed to image micrometer-size objects with a spatial resolution of few tens of nanometers [115, 116]. This technique may be scalable to the higher photon energy with the important recent developments of infrared laser sources intended to increase the high-harmonic cutoff [101, 117]. Also, ex-situ high-harmonic imaging may well benefit from intracavity [10] high-harmonic generation where the repetition rate is considerably increased, from the Hz and kHz up to the tens of MHz regime. Other important applications, such as frequency comb precision metrology in the XUV, see refs. [10, 118] and references therein, will vastly benefit from these latest developments. Ultimately, the development of brighter sources of attosecond pulses could replace current X-ray sources (like XFELs and synchrotrons) for diffraction experiments, towards unprecedented ultrafast spatiotemporal angström-attosecond structural imaging of matter.

Temporal Resolution

The temporal resolution of ex-situ techniques relies directly on the ability of making the shortest pulses of probing radiation. In electron diffraction, the lowest durations possible approach few hundreds of femtoseconds and will not easily go below that limit due to the fundamental limits imposed by charge repulsion [119]. One approach to overcome this limit is to diminish the number of electrons in each bunch down to a single one [120]. This approach would apparently allow sub-100-fs electron pulses: this is the temporal

precision needed for resolving vibrational chemical dynamics, as discussed in section 1.1.

In X-ray diffraction, the shortest pulse duration approaches the sub-10 fs range and could become much shorter with the development of seeding techniques for XFELs. Ultimately, XFELs could amplify attosecond X-ray pulses when seeded by high-harmonic light pulses, see e.g. refs. [121, 122] for recent developments in that area. In ex-situ high-harmonic imaging, the temporal resolution can go below 100 attoseconds [18]. Experiments where attosecond pulses are used both as pump and probe pulses, however, have not yet been conducted because of the insufficient brightness of current (Hz-kHz repetition rate) light sources.

The temporal resolution of in-situ high-harmonic imaging is limited by the pulse duration of the driving laser pulse. Recent developments in the control of the carrier envelope phase (CEP) can limit the HHG process to essentially a single recollision per driving laser pulse [123]. In brief, the best temporal resolution achievable by in-situ high-harmonic imaging is inevitably given by the duration of a single cycle of the driving laser field, i.e. few femtoseconds, depending on the central wavelength.

To summarize, in-situ high-harmonic imaging emerges as a tabletop, prospective combination of the various techniques discussed above. It benefits from the economic aspect of using electrons for spatial imaging via their shorter de Broglie wavelength, when compared to photons of the same energy. In terms of temporal resolution, it remains limited to about a single (optical to infrared) cycle. Unlike all other techniques presented above, however, in-situ high-harmonic imaging is uniquely sensitive to both nuclei and valence electrons. For these reasons, it is particularly well-suited to accomplish the main goal of this thesis (section 1.5): imaging valence electrons during a chemical reaction. We should mention that, like diffraction-based techniques, in-situ high-harmonic imaging relies on theoretical modeling and approximations. Here, the plane wave approximation [32], see section 1.3.2, which is key to the reconstruction of actual images, is undoubtedly subject to further improvement [51, 52, 84, 124].

As we demonstrated earlier in section 1.3, the high-harmonic light (polarization, amplitude and phase) contains all the information about the photorecombination transition dipole $\mathbf{R}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle$ from eq. 1.30. We now show how this information can be used to reconstruct the spatial profile of a single-molecule electronic valence

orbital $\Psi_g(\mathbf{r})$.

1.4.2 In-Situ High-Harmonic Tomographic Imaging

The spectral (Ω) polarization, amplitude and phase of high-harmonic emission from aligned (θ) molecules can be fully characterized experimentally [125]. As shown earlier in section 1.3, this corresponds to a measurement of the complex photorecombination (R) transition dipole from eq. (1.30): $\mathbf{R}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle$. When the plane wave approximation (see section 1.3.2) is applied, the dipole becomes the spatial Fourier transform eq. (1.33): $\mathbf{R}_{PWA}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | e^{i\mathbf{k}\cdot\mathbf{r}} \rangle$. This formulation is compatible with computerized tomographic (CT) imaging that is used in multiple areas of science including medicine. A. M. Cormak and G. N. Hounsfield received the 1979 Nobel Prize in Medicine "for the development of computer assisted tomography".

Tomographic imaging of an object, denoted as the spatial function $f(x, y)$, is based on the Fourier slice theorem [103]. It consists on rotating the object to an angle θ , project it into a new reference frame, denoted here as the (u, v) coordinates as shown in Fig. 1.10 (a), along a first dimension –say v – and take its Fourier transform along the remaining dimension –say u –. The coordinates are related via the frame transformation (clockwise rotation):

$$\begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}. \quad (1.45)$$

This type of operation occurs frequently in various imaging techniques where scattering is involved and the incident, probing radiation on aligned targets is treated as plane waves. It also occurs in high-harmonic generation from aligned molecules if we approximate the recolliding electron as a set of plane waves (the plane wave approximation, sect. 1.3.2).

At a given alignment angle θ , we define the object $f(x, y)$ in the (u, v) coordinates as $f_\theta(u, v)$. Respectively, the projection of $f_\theta(u, v)$ along v and its Fourier transform along

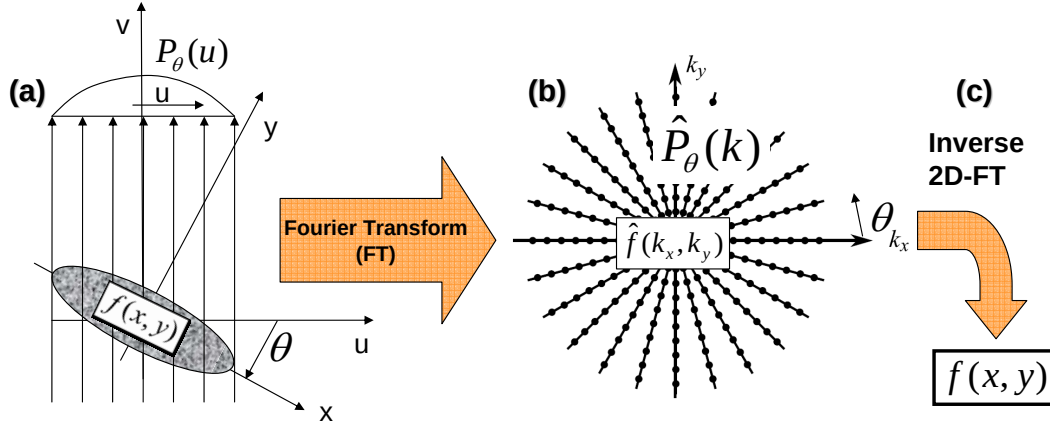


Figure 1.10: (a) In a static reference frame (u, v) , the Fourier slice theorem stipulates that the spatial Fourier transform ($F_{u \rightarrow k}$) of the rotated (at an angle θ) and projected (along v) object $f(x, y)$, corresponds to a line $\hat{P}_\theta(k) = \hat{f}(k_x, k_y)$ in (b) the reciprocal space (k_x, k_y) , where $(k_x, k_y) = (k \cos \theta, k \sin \theta)$. See details in the text. (c) The inverse two-dimensional Fourier transform of $\hat{f}(k_x, k_y)$ allows to spatially reconstruct the object $f(x, y)$ that was projected in the first place. This formalism applies to high-harmonic generation in aligned samples where the recolliding electron wave packet $\Psi_c(\mathbf{k})$, refer to Fig. 1.4 (b), is approximated by a set of plane waves associated to wave vectors $\mathbf{k}$.

the remaining dimension u are:

$$P_\theta(u) = \int_{-\infty}^{+\infty} dv f_\theta(u, v) \quad (1.46)$$

$$\hat{P}_\theta(k) = \int_{-\infty}^{+\infty} dv P_\theta(u) e^{-iku} = F_{u \rightarrow k}[P_\theta(u)] \quad (1.47)$$

The Fourier slice theorem stipulates that:

$$\hat{P}_\theta(k) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx dy f(x, y) e^{-ik(x \cos \theta + y \sin \theta)}. \quad (1.48)$$

This last equation can be obtained by performing the change of variables using the coordinates transformation given in eq. (1.45) [103]. Eq. (1.48) corresponds to a two-

dimensional Fourier transform of the object $f(x, y)$, $\hat{P}_\theta(k) = \hat{f}(k_x, k_y)$, performed at the reciprocal frequencies $(k_x, k_y) = (k \cos \theta, k \sin \theta)$. Hence, at an alignment angle θ of the object, $\hat{f}(k_x, k_y)$ becomes determined over a set of points forming a line (or slice) at an angle θ with respect to the k_x horizontal axis in the cartesian reciprocal space (k_x, k_y) . It can be practical to represent the reciprocal space in polar coordinates (r, θ) with the radius r representing the angular-independent spatial frequency $k = \sqrt{k_x^2 + k_y^2}$ and the angle $\theta = \tan^{-1}(k_y/k_x)$. Taking multiple projections $\hat{f}(k_x, k_y)$ over all alignment angles θ , allows to measure the full two-dimensional Fourier transform of the object, as shown in Fig. 1.10 (b). The object $f(x, y)$ can then be reconstructed by inverse two-dimensional Fourier transform.

In high harmonic generation from aligned (θ) molecules, the same formalism applies. The spatial frequencies k covered in the experiment are given by the measured high-harmonic frequencies Ω via eq. (1.1) and the object $f(x, y)$ measured in the reciprocal space $\mathbf{k} = (k_x, k_y)$ is contained in the photorecombination dipole $\mathbf{R}_{PWA}(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | e^{i\mathbf{k} \cdot \mathbf{r}} \rangle$, see eq. (1.33). By analogy with eq. (1.48), we recognize that the object to be imaged via the Fourier slice theorem is $\Psi_g^*(\mathbf{r}; \theta) \cdot \mathbf{r}$, where $\mathbf{r} = \mathbf{x} + \mathbf{y}$. The $\mathbf{x}$ and $\mathbf{y}$ are vectors, respectively, of length x and y , and directions pointing parallel and perpendicular to the molecule's symmetry axis. It does not necessarily have to be aligned parallel to the x -axis, we choose this for convenience.

Two molecular frame polarization components, along the $\mathbf{x}$ and $\mathbf{y}$ axis, will therefore, respectively, contribute to the tomographic reconstruction of the objects $f_x(x, y)$ and $f_y(x, y)$. The polarization state of the high-harmonic emission from aligned molecules is usually defined in terms of the laboratory frame parallel $R_\parallel(\Omega, \theta)$ and perpendicular $R_\perp(\Omega, \theta)$ components with respect to the laser field polarization (linear), see section 1.3.3. Here, the laser field polarization is along the u -axis, see Fig. 1.10 (a). The molecular frame polarization components (along $\mathbf{x}$ and $\mathbf{y}$) are obtained by a clockwise rotation (of θ), see eq. 1.45, of the laboratory frame components. We therefore write the two reconstructed objects as follows [32]:

$$f_x(x, y) = \sum_{\Omega} \sum_{\theta} [R_\parallel(\Omega, \theta) \cos \theta + R_\perp(\Omega, \theta) \sin \theta] e^{ik(\Omega)(x \cos \theta + y \sin \theta)} \quad (1.49)$$

$$f_y(x, y) = \sum_{\Omega} \sum_{\theta} [-R_{\parallel}(\Omega, \theta) \sin \theta + R_{\perp}(\Omega, \theta) \cos \theta] e^{ik(\Omega)(x \cos \theta + y \sin \theta)} \quad (1.50)$$

A reconstructed image of the single-molecule real-valued ground state wave function $\Psi_g(\mathbf{r})$ involved in the process of high harmonic generation is then obtained by removing the contribution of the dipolar operator ($\mathbf{r} = \mathbf{x} + \mathbf{y}$) from the reconstructed object $f(x, y)$:

$$\Psi_g(x, y) = \Re(f_x/x + f_y/y) \quad (1.51)$$

We notice that a projection, along the z axis, which denotes the direction of propagation of the driving laser field, has been performed. In order to image the third (z) dimension of the wave function, we would require both tridimensional molecular alignment [79] and polarization measurements, which is, although feasible, currently beyond the state-of-the-art in in-situ high-harmonic imaging. Also, we must note that alignment averaging, discussed in section 1.3.3, was neglected here. In this section, we have assumed perfect alignment: that is, the laboratory frame and molecular frame polarization components are linked only by a rotation matrix, see eq. 1.45. In section 1.3.3, however, we show how to ultimately access the true molecular frame response: it requires to simultaneously solve the angular convolution integrals in eqs. (1.39) and (1.40). Another simpler approach towards accessing the true molecular frame response is to increase the degree of alignment in the experiment.

To date, tomographic imaging of orbitals has been applied to argon atoms [31] and, N_2 [32, 33] and CO_2 [34] molecules. The current limitations and potential improvements of this technique are well exposed in a recent review article ref. [35]. In chapter 3, section 3.1, we show how changing the driving laser field wavelength can help disentangling the participation of multiple valence molecular orbitals and, therefore, better assign the actual reconstructed object $\Psi_g(x, y)$. Also, we demonstrate how the angular (molecular alignment angle) resolution of the high-harmonic spectra used for imaging can be improved by removing the blurring effect of alignment averaging, other than by full polarimetry measurements as explained in section 1.3.3, in section 3.2. Finally, in chapter 5, we present a novel technique for measuring, for the first time, the full two-dimensional phase of the photorecombination dipole $\mathbf{R}(\Omega, \theta)$, a most needed quantity for

in-situ high-harmonic molecular imaging [35]. These improvements are part of the path to our ultimate goal: time-resolved tomographic imaging of a chemical reaction.

1.5 Goal of this thesis

The main goal of this thesis is to extend in-situ high-harmonic molecular imaging to chemical reactions: make an angström-femtosecond resolution movie of the valence electrons wave function $\Psi_e(\mathbf{r}, \Delta t)$ involved in the break or formation of a chemical bond. We use the subscript e to refer to excited molecules undergoing dynamics, as opposed to g for unexcited (static) ground state molecules, as used earlier. To this purpose, we need to develop tools for the full characterization (angular and spectral polarization, amplitude and phase) of the corresponding time-resolved (Δt) high-harmonic photorecombination dipole moment $\mathbf{R}_e(\Omega, \theta, \Delta t) = \langle \Psi_e(\mathbf{r}; \theta, \Delta t) | \mathbf{r} | \Psi_g(\mathbf{k}(\Omega)) \rangle$, refer to eq. (1.30) in section 1.4. We refer to Δt as the elapsed time between the start and the moment of observation of a chemical reaction.

Along the path to this ultimate goal, we should also attempt to improve different aspects of high-harmonic molecular imaging, as well as to contribute to the emerging field of attosecond science. The entire work is divided in the next four chapters 2-5 which are globally summarized in the conclusion chapter 6. We will finish by giving an update on our current progress towards time-resolved tomographic imaging of valence electrons, represented by the wave function $\Psi_e(\mathbf{r}, \Delta t)$, involved in the prototypical bond breaking $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$ photodissociation chemical reaction.

Chapter 2

Extending Perturbative Nonlinear Optics to High Harmonic Generation

2.1 Ultrahigh-Order Wave Mixing in Noncollinear High Harmonic Generation (publication [7](#))

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Ultrahigh-Order Wave Mixing in Noncollinear High Harmonic Generation
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2.1.1 Author Contributions

J.B.B. and H.J.W performed the experiment at CNRC in Ottawa. The noncollinear geometry was first (accidentally) encountered when preparing the transient grating Br₂ photodissociation experiment (publication [5](#)). H.-C.B. and E.B. performed similar measurements by mixing lasers of incommensurate frequencies at the Advanced Laser Light

Source in Varennes, Qc (unpublished results). H.J.W proposed the multiphoton picture and the associated conservation laws. D.M.V. and J.B.B. did the modeling. J.B.B. conducted the CNRC data analysis and wrote the first draft. All authors contributed to the final manuscript.

Ultrahigh-Order Wave Mixing in Noncollinear High Harmonic Generation

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We show that noncollinear high harmonic generation (HHG) can be fully understood in terms of nonlinear optical wave mixing. We demonstrate this by superposing on the fundamental ω_1 field its second harmonic ω_2 of variable intensity in a noncollinear geometry. It allows us to identify, by momentum conservation, each field's contribution (n_1, n_2) to the extreme ultraviolet emission at frequency $\Omega = n_1\omega_1 + n_2\omega_2$. We observe that the photon (Ω) yield follows an n_2 power law on the ω_2 intensity, before saturation. It demonstrates that, although HHG is a highly nonperturbative process, a perturbation theory can still be developed around it.

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Perturbative nonlinear optics [1], introduced in the 1960s [2], arises from the interaction of light with materials where the response is described by perturbation theory. That is, only a few photons are involved and higher order processes are less important than lower ones, providing the lower one is allowed. Perturbative nonlinear optics is critical for short pulse science and technology. For example, the nonlinear response of materials is exploited in all pump-probe spectroscopy. Major technologies rely on nonlinear optics, optical communications being only one [3].

Nonperturbative nonlinear optics, introduced in the 1990s [4,5] for high harmonic generation (HHG), treats light interaction with materials nonperturbatively. Often the interaction is approximated with classical physics—photons are not even needed to qualitatively understand the phenomena. Nonperturbative nonlinear optics has led to attosecond pulse formation [6] and new methods of imaging matter [7–9]. These two major trends—perturbative and nonperturbative nonlinear optics—seem conceptually very different.

Our experiment and analysis show that a perturbative nonlinearity can be fabricated on a highly nonperturbative nonlinear process. This opens a route to transfer the powerful techniques of perturbative nonlinear optics to high intensity, highly nonlinear phenomena such as a broad range of novel noncollinear HHG experiments.

To demonstrate this, we perform an experiment in which an intense fundamental laser pulse of frequency ω_1 and a weak second harmonic field ω_2 are noncollinearly crossed in a gas jet target. We show that the positions of discrete harmonics in the HHG spectrum can be described simply in terms of conservation of energy, momentum, and parity, based on the net number of photons (n_1, n_2) absorbed from each field. That is, $\Omega = n_1\omega_1 + n_2\omega_2$ and $\vec{k}_\Omega(n_1, n_2) = n_1\vec{k}_1 + n_2\vec{k}_2$. By studying the intensity dependence of the harmonic yield for a particular combination (n_1, n_2), we

find that, at low intensity I_2 of the weak field, the harmonic signal scales as $I_2^{n_2}$ and that each higher order in n_2 is less important than the lower one—just as we expect from perturbation theory. Therefore, HHG is nonperturbative regarding the high intensity fundamental beam and it is perturbative for the much weaker second harmonic beam.

Our work builds on a long history of experiments on using multiple color fields to produce high harmonics [10–18]. Early experiments confirmed that energy, momentum, and parity are preserved when high harmonics are generated in two-color fields [10]. This introduced the potential to control the high-harmonic process [11–13], leading to the generation of attosecond pulse trains with individual pulses separated by the laser period [14] and new approaches to isolating a single attosecond pulse [15–17] and generating tunable extreme ultraviolet (XUV) radiation [18]. Recently, it has been shown that weak-field control of high harmonic generation allows attosecond pulses to be measured as they are being produced in the medium [19]. Tacitly, *in situ* measurement suggests an ability to construct a perturbative nonlinear optics theory upon the physics of high harmonic generation.

Noncollinear techniques were also used previously mainly to separate high-harmonic radiation from the fundamental beam [20–22]. An important recent application is in extreme ultraviolet frequency comb metrology where a noncollinear control pulse switches high-harmonic radiation from a buildup cavity [23].

The experimental setup is composed of a Ti:sapphire multipass laser system (35 fs, 800 nm, 50 Hz, 10 mJ per pulse), an optical setup to both split and recombine laser pulses, and a high-harmonic chamber composed of a source chamber (pulsed valve, 250 μ m orifice), an XUV grating, a microchannel plate detector, and a camera readout. The laser output is divided using a 50/50 beam splitter.

In one arm of the Mach-Zehnder interferometer, second harmonic of the fundamental laser field is generated in a type-I BBO crystal of 100 μm thickness and the remaining fundamental light is removed by two reflections on 400 nm-only reflective mirrors. In both arms, the intensity is adjusted with neutral absorption-type density filters. The fundamental ω_1 and its second harmonic ω_2 are then recombined using a dichroic mirror, where ω_2 is reflected and the beams are spaced vertically by 7 mm. Finally, both beams are focused ($f = 50$ cm) ~ 2 mm before and ~ 1 mm downstream of the gas jet (N_2) in the source chamber [Fig. 1(a)].

Figure 1(b) shows the XUV emission resulting from the superposition of a weak second harmonic field ω_2 (400 nm, $I_2 = 1.5 \times 10^{13}$ W/cm 2) crossing a strong fundamental field ω_1 (800 nm, $I_1 = 1.5 \times 10^{14}$ W/cm 2) at an angle $\phi \approx 14$ mrad [see schematic in Fig. 1(a)]. The fundamental alone generates a high-harmonic spectrum along the $\theta = 0$ axis shown by the dashed line. The addition of the weak field gives rise to off-axis radiation at various discrete angles in the vertical direction. We use conservation of energy and momentum to determine the contribution of each field $\omega_{1,2}$ to the resulting XUV emission. For example, the photon centered at $\Omega = 13\omega_1$ in the direction $\theta = 8.4$ mrad has a unique solution given by

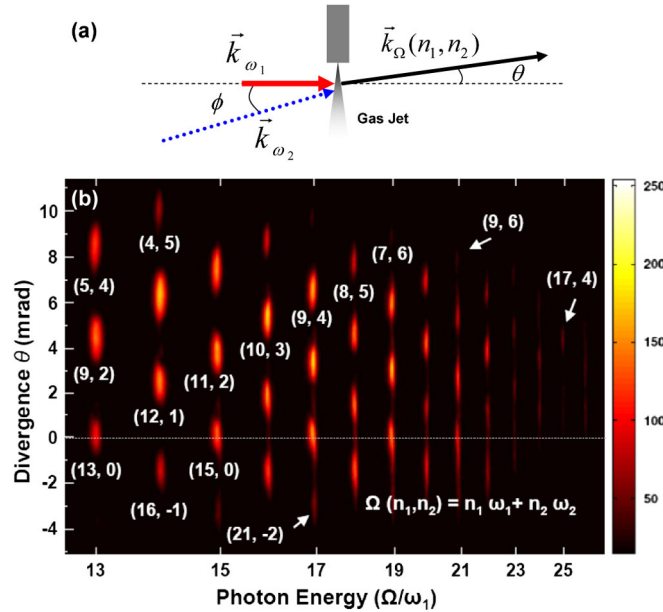


FIG. 1 (color online). Noncollinear harmonic generation from the superposition of an intense fundamental ω_1 (800 nm, $I_1 = 1.5 \times 10^{14}$ W/cm 2) and weaker ω_2 (400 nm, $I_2 = 1.5 \times 10^{13}$ W/cm 2) fields in randomly aligned N_2 gas. (a) Schematic representation: The ω_1 beam is in the horizontal plane and the ω_2 beam points upwards at an angle $\phi \approx 14$ mrad such that they form a plane parallel to the entrance slit of the XUV spectrometer. (b) XUV emission as seen on the spectrometer detector. Each field's contribution is labeled as (n_1, n_2) at frequency $\Omega = n_1\omega_1 + n_2\omega_2$.

$(n_1, n_2) = (5, 4)$. As the intensity of the weak field increases, the off-axis emission increases away from $\theta = 0^\circ$, but the positions of the harmonic peaks $(\Omega/\omega_1, \theta)$ do not change.

High-harmonic radiation comes from the recombination of an electron back to its ground state [4]. Since a single XUV photon is emitted through this dipolar transition, parity conservation requires that the wave function of the continuum electron and the ion together be in a state of different parity (+ or -) than the original ground state (- or +) [10,24]. Consequently, only the net absorption of an odd total number of photons $n = n_1 + n_2$ can lead to emission. From this approach, it is possible to produce the same frequency but with various (n_1, n_2) combinations. For example, see Fig. 2(a), $\Omega = 8\omega_1$ can be obtained from the net sum $(n_1, n_2) = (6, 1)$ but also the net difference $(10, -1)$ frequency-mixing pathways. The noncollinear scheme offers the advantage of distinguishing them spatially as required by momentum conservation; see Fig. 2(b). We now understand the alternate appearance of even and odd harmonics as a function of θ in Fig. 1: an n_2 odd (even) number of photons involved from the weak field results in the observation of even (odd) harmonic orders.

Next, keeping the intensity of the strong ω_1 beam fixed (1.5×10^{14} W/cm 2), we measure spectra for various peak intensities of the weak ω_2 $[(0.1-7) \times 10^{13}$ W/cm 2]. In Fig. 3(a), we plot, on a log-log scale, the spatially (θ) and spectrally (Ω/ω_1) integrated signal for different values of n_2 from 0 to 6. This scaling allows us to determine the order of nonlinearity connecting the noncollinear XUV yield with the weak-field intensity.

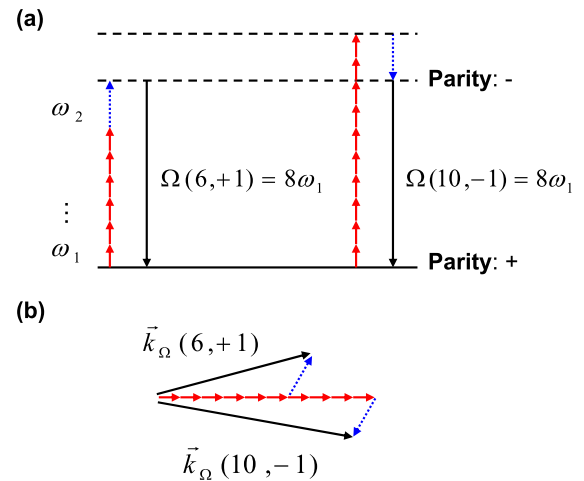


FIG. 2 (color online). Frequency-domain perspective on two-color noncollinear HHG. (a) Sum and difference frequency emission $\Omega = n_1\omega_1 + n_2\omega_2$: only the odd net totals $n = n_1 + n_2$ are dipole-allowed transitions; see text. Illustrated is the production of $\Omega = 8\omega_1$ with $n_2 = \pm 1$. (b) Momentum conservation yields phase-matched XUV radiation in the direction of $\vec{k}_\Omega(n_1, n_2) = n_1\vec{k}_1 + n_2\vec{k}_2$.

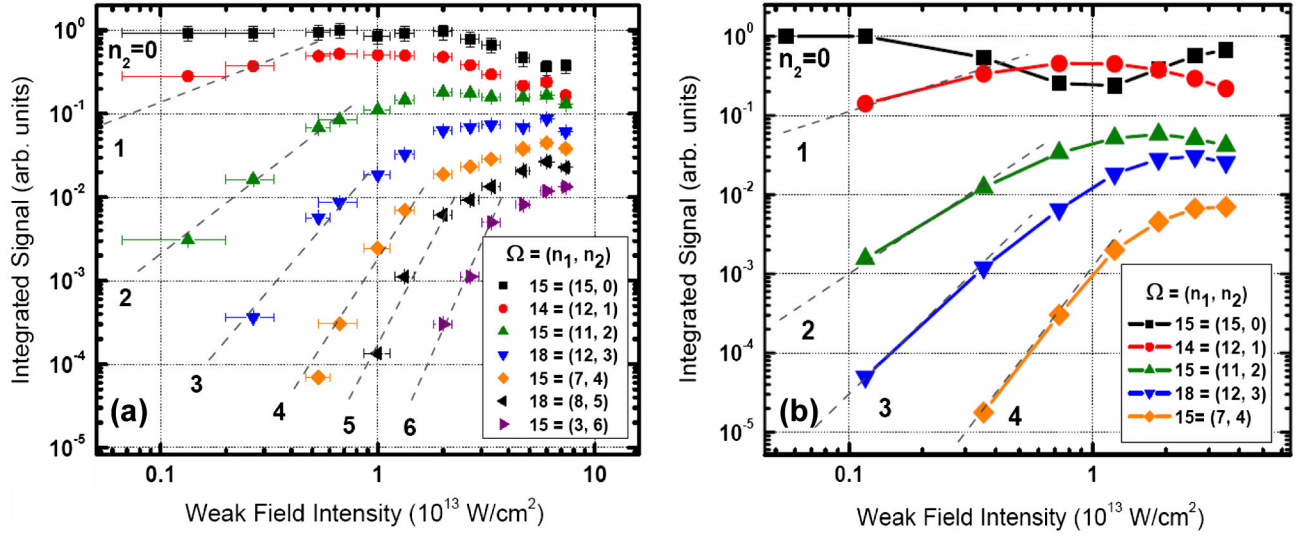


FIG. 3 (color online). (a) Experiment: Power scaling of the noncollinear harmonic emission as a function of the weak-field (400 nm) peak intensity (I_2) for different numbers (n_2 from 0 to 6) of weak ω_2 field photons absorbed. The intensity of the fundamental ω_1 field is kept constant ($I_1 = 1.5 \times 10^{14}$ W/cm²). The measured curves are labeled by n_2 and, respectively, multiplied vertically by a factor (1, 1/2, 1/8, 1/10, 1/40, 1/60, 1/150) for clarity. Slopes of n_2 from 0 to 6 are also displayed (dashed line). (b) Theory: Calculated power scaling. Noncollinear XUV spectra are obtained by solving for two-color HHG in the laser focus on a 2D grid (plane formed by $\vec{k}_1 + \vec{k}_2$, see text) and adding coherently the radiation in the far field. Each curve is scaled vertically by the same factors as in Fig. 3(a) and theoretical slopes of n_2 from 0 to 4 are displayed (dashed line).

We observe that for each value of n_2 , the yield increases then saturates, the processes with lower n_2 saturating earlier. The values of Ω are chosen arbitrarily [see legend of Fig. 3(a)], emphasizing that the main shape of the curves for any (n_1, n_2) is mainly dictated by n_2 . We have also performed the same scaling with the ω_2 field polarized perpendicular (not shown) to ω_1 and observed a similar scaling. The main difference being that the off-axis emission is less ($\approx 1/10$ for $\Omega(12, 1) = 14$) at the same intensity of ω_2 .

We deduce from the linear part of each curve that the photon yield follows a perturbative power law of the form $I_2^{n_2}$. This behavior is seen in optical wave mixing in media in which a time-dependent nonlinear polarization is induced [1]. The formalism behind it, perturbation theory, is not intuitively applicable to a highly nonperturbative process such as HHG. Cascaded wave mixing has been proposed [25] to explain the new frequency components, where the initial odd harmonics undergo four-wave mixing with the remaining $\omega_{1,2}$ fields. Next, we find instead that the perturbative power-law scaling of the form $I_2^{n_2}$ finds its origin directly in the single-atom HHG process.

We perform a two-dimensional calculation incorporating both the single-emitter response and the macroscopic noncollinear overlap of $\omega_{1,2}$ beams as in the experiment. At each point on a 2D grid (plane formed by $\vec{k}_1 + \vec{k}_2$), we solve for the time-dependent XUV fields produced by the two noncollinear beams. We use the strong field approximation formalism as described in [26]. The grid size was 400 (diameter) by 800 (axial) points, creating a source size

of $100 \times 200 \mu\text{m}$. We coherently sum the emission from each grid point on the detector in the far field at a distance $L = 80$ cm and generate the power spectrum. The calculated noncollinear HHG spectra are very similar to what is measured experimentally [see Fig. 1(b)]; i.e., the positions of the various harmonic orders were correctly predicted in both frequency and angle.

In Fig. 3(b), we vary the intensity I_2 of the weak field and evaluate the integrated XUV emission of various $\Omega(n_1, n_2)$ points as in the experiment. In the low intensity range, we reproduce the perturbative $I_2^{n_2}$ nonlinear dependence observed experimentally [see Fig. 3(a)]. At higher intensity we also observe a saturation effect. Our simple model for noncollinear HHG predicts the perturbative $I_2^{n_2}$ scaling of the noncollinear $\Omega(n_1, n_2)$ emission. It shows that the yield of noncollinear harmonic emission due to an additional weak (ω_2) field can be understood essentially from the strong field approximation single-emitter perspective with macroscopic phase matching, and amounts to building a perturbation theory on HHG initially driven by a strong (ω_1) field alone.

A feature common to both theory and experiment is that the emission is always weaker for $n_2 < 0$ than for $n_2 > 0$, e.g., by more than 1 order of magnitude between the +1 and -1 orders in this experiment [see Fig. 1(b)]. Our calculated noncollinear XUV pattern also shows this up-down asymmetry, but not as strongly. We observe that it depends weakly on the length of the medium used in the calculation. Further modifications, including the implementation of propagation effects [13], are needed to further

investigate this aspect. Asymmetry between sum and difference frequency-mixing processes in HHG have been reported before in collinear experiments using incommensurate two-color $\omega_{1,2}$ fields [17,27,28]. They could originate from an interplay between the single-emitter response and propagation effects [13,29].

In conclusion, we have confirmed that the framework of perturbative optical wave mixing applies to describe HHG modified by a weak laser field. First, we demonstrated that the laws of momentum, energy, and parity can predict the direction of the allowed emission. This view will be important in future experiments as four-wave-mixing-like noncollinear schemes, such as transient grating spectroscopy [9,30,31], are migrating to attosecond science. Furthermore, noncollinear two-color HHG can act as an all-optical XUV beam splitter which could be implemented for XUV (pump)-XUV (probe) interferometry experiments. Second, our observation revealed an important property of the HHG process, which is that, although it is a highly nonperturbative process, a perturbative formalism can still be developed around it, up to ultrahigh orders of nonlinearity.

Our experiment bridges the conceptual gap between perturbative nonlinear optics and HHG. It opens new avenues for exploiting the powerful concepts of wave mixing: these include background-free detection of molecular dynamics and the probing of electronic coherence by HHG [9].

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2.2 Probing Polar Molecules with High Harmonic Spectroscopy

(publication [16](#))

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Probing Polar Molecules with High Harmonic Spectroscopy

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2.2.1 Author Contributions

P.B.C. proposed the experiment and E.F. led the project. E.F., N.K. and C.T.H. performed the CO molecular alignment experiments. J.B.B. and H.J.W. first observed even harmonics in the oriented molecules. M.S. and S.P. performed calculations that contributed to the theoretical model; P.H. and H.J.W. performed the ePolyScat [\[81, 82\]](#) photoionization dipole calculations. J.B.B. proposed and performed the phase reconstruction (-C- vs. -O- sides) with preliminary measurements. E.F. led the data analysis. All authors interpreted the data and contributed to writing the article.

Probing Polar Molecules with High Harmonic Spectroscopy.

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We bring the methodology of orienting polar molecules together with the phase sensitivity of high harmonic spectroscopy to experimentally compare the phase difference of attosecond bursts of radiation emitted upon electron recollision from different ends of a polar molecule. This phase difference has an impact on harmonics from aligned polar molecules, suppressing emission from the molecules parallel to the driving laser field while favoring the perpendicular ones. For oriented molecules, we measure the amplitude ratio of even to odd harmonics produced when intense light irradiates CO molecules and determine the degree of orientation and the phase difference of attosecond bursts using molecular frame ionization and recombination amplitudes. The sensitivity of the high harmonic spectrum to subtle phase differences in the emitted radiation makes it a detailed probe of polar molecules and will drive major advances in the theory of high harmonic generation

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High harmonic generation is a sub-optical-cycle process. During successive half-periods, an electron wave packet recollides with its parent ion from alternate directions producing successive attosecond bursts of XUV radiation [1]. If a symmetric molecule is the nonlinear medium, then this periodicity produces odd harmonics because successive bursts are identical except for a π phase difference.

A polar molecule, on the other hand, looks different depending on the direction in which it is viewed. When high harmonics are generated from polar molecules, alternate attosecond bursts have different amplitude and phase. Thus, molecular asymmetry is embedded in the single molecule response and in the phase-matched spectrum that we measure (as illustrated in Fig. 1). Asymmetry is imposed at each step of the harmonic generation process [1] - when the electron wave packet is detached from the target molecule; when the liberated electron gains energy and phase in the continuum as it accelerates away from the parent ion and then is driven back to recollide; and when the electron recombines with the parent ion.

We study high harmonics from CO molecules. We use both the techniques of laser-alignment [2] (up-down symmetric with respect to the aligning laser field [3]) and two-color laser-orientation [4] (broken up/down symmetry) of molecules to make HHG measurements in the aligned as well as the oriented molecular frame. We confirm that an oriented rotational wave packet is produced in CO by probing with Coulomb explosion imaging [5]. These measurements are repeated on aligned N₂ which serves as an isoelectronic non-polar reference for comparison. Their orbital structure, their angular dependent ionization probability and their transition moments are all shown in Fig 2. Our experiment shows how informa-

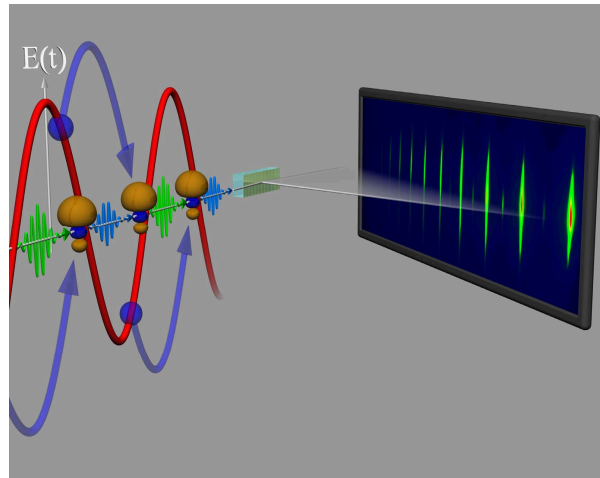


FIG. 1: Spectral interference lies at the heart of high harmonic generation from oriented molecules. Every 1/2 period of the fundamental intense infrared laser pulse (shown in red), an electron wave packet is detached from an oriented molecule, oscillates in the time-dependent electric field and recombines to create an attosecond burst of XUV light. An example of four such bursts of a train is shown in the Figure. In our experiment, this attosecond pulse train is diffracted and imaged by the grating. The spectral interference of such a train results in the formation of even and odd harmonics. An experimental spectrum is shown in the Figure.

tion on the polar molecule is encoded in both the odd harmonic spectrum of aligned molecules and in the even harmonics of oriented molecules.

We implement the two-color method of laser-induced orientation [6, 7] for the high density gas [8]. Early studies on two-color orientation considered only the hyper-

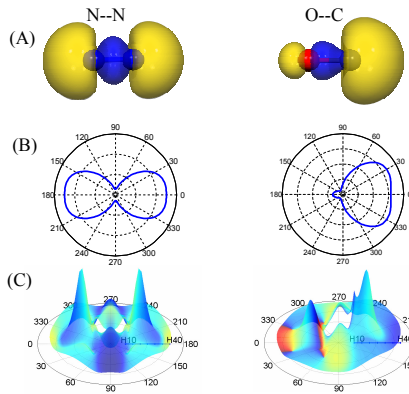


FIG. 2: (a) The Dyson orbital for the most weakly bound valence electron of the isoelectronic pair, N₂ and CO. The color code represents a π phase difference. The orientation is preserved in (b) and (c). (b) The total ionization yield as a function of the angle between the molecular axis and the electrical field calculated for a 1/2 cycle of 800nm with intensity 1.5×10^{14} W/cm². (c) The amplitude (vertical axis) and phase (color code) of the transition moment as a function of angle and harmonic order (radial axis) for XUV light polarized along the molecular axis.

polarizability mechanism [7] of laser-generated orientation. As discussed in full elsewhere [8, 9], we believe an ionization depletion mechanism is active in our experiment. Briefly, the molecular ionization probability of polar molecules is sensitive to the orientation between the molecular frame and the ionizing laser polarization [10, 11]. Therefore, in a maximally asymmetric electric field produced by adding a pulse with frequency ω to a second-harmonic pulse at 2ω , ionization will partially deplete the neutral population of an initially randomly oriented sample at certain orientations, while leaving molecules in their neutral state at other orientations. The orientation-dependent ionization creates an oriented molecular distribution in both the neutral molecule and in the ion and the same laser pulse launches the rotational molecular wavepacket. In the unionized (ground-state) the molecular ensemble is transiently aligned and oriented during the rotational wavepacket revivals.

Either N₂ or CO (ionization potential (IP) = 15.6 eV and 14.0 eV respectively, and dipole moment (D_{CO}) = 0.112 Debye) [12] was separately injected into a vacuum system using a supersonic jet. Experiments have shown that they have similar ionization probabilities when averaged over all orientations [13, 14]. We achieve alignment and orientation using a pulse of 800nm light and its second harmonic ($\omega + 2\omega$). After a variable delay, we probe the rotational wave packet by generating high harmonics with an intense 800nm pulse incident at an angle to the

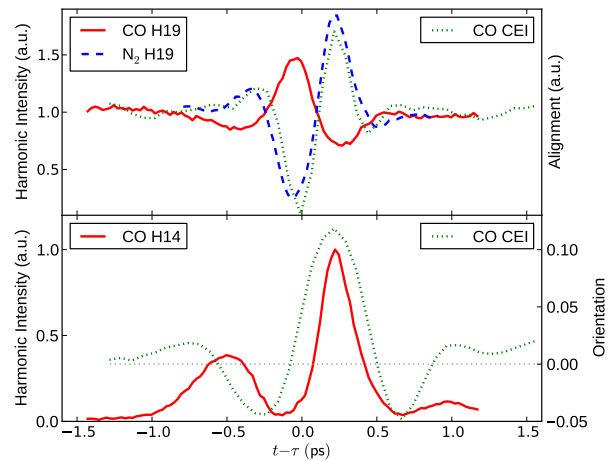


FIG. 3: : Upper plot: Dotted green curve shows alignment of CO determined from a Coulomb explosion imaging measurement. The time-resolved high harmonic yields (19th harmonic), corresponding to the same rotational wavepacket, are shown for CO (solid red curve) and N₂ (dashed blue curve) near the time of their first full revival (set at $t=0$). Lower plot: An orientational wave packet in CO excited by the superposition of 800 nm and 400 nm light. Dotted green curve shows the orientation of CO measured by Coulomb explosion imaging. The red curve shows the time dependent signal for the 14th harmonic. Note that the even harmonic signal is maximum when the orientation is greatest.

probe beam so that any harmonics created by the pump are spatially separated from those created by the pump beam. By delaying the probe, we observe the neutral rotational wave packets at different stages of alignment and orientation. The full optical setup is described elsewhere [8].

Figure 3 (upper panel) shows the time evolution of a typical odd harmonic (H19; $h\nu = 29$ eV) for N₂ (dashed blue line) and CO (solid red line). The origin of the time axis for both molecules is taken as the time of the first full rotational revival ($\tau = \pi/B$ where B is the rotational constant). For comparison, the dotted green curve in Fig. 3 (upper panel) shows a non-oriented rotational wave packet of CO as measured by Coulomb explosion imaging [5]. CO is parallel to the laser field at the time of the H19 minimum. In contrast, the harmonic signal maximizes when N₂ is parallel [15]. This contrasting behavior between N₂ and CO persists for all harmonics that we have studied except for the very lowest (H11 and H13).

There are two possible reasons for this contrasting behavior. First, the orbital structure of CO and N₂ allows the HOMO-1 orbital to contribute when the molecule is perpendicular. This enhances the high harmonic yield for perpendicular molecules [16].

Second, when the laser polarization is along the direc-

tion of asymmetry, successive attosecond bursts are quite different. The complex spectral amplitude of the emitted radiation within a single period of the fundamental field is given by $\tilde{E}(\nu) = \tilde{E}_1(\nu) - \tilde{E}_2(\nu)e^{-i\pi\nu T}$, where $\tilde{E}_1(\nu)$ and $\tilde{E}_2(\nu)$ are spectral complex amplitudes of the attosecond bursts emitted from opposite sides of the polar molecule, ν is the frequency of the emitted radiation and T is the period of the driving laser field. The phase factor $e^{-i\pi\nu T}$ accounts for the fact that the second burst - $E_2(t)$ is shifted in time by half period $T/2$ relatively to the first one - $E_1(t)$.

When the driving laser field is composed of multiple cycles the even and odd harmonics are formed with the respective complex spectral amplitudes given by $\tilde{E}_{\text{even}}(2n/T) = \tilde{E}_1(2n/T) - \tilde{E}_2(2n/T)$, and $\tilde{E}_{\text{odd}}((2n-1)/T) = \tilde{E}_1((2n-1)/T) + \tilde{E}_2((2n-1)/T)$ with $n = 1, 2, \dots$. The phase and/or amplitude differences (beyond the normal π phase difference for symmetric systems) between subsequent attosecond bursts lead to even harmonic formation at the single molecule level, but it also reduce the odd harmonic response [17] since maximal constructive interference of the odd harmonics does not, in general, occur. As already discussed (Fig. 1), this cycle-to-cycle spectral interference is at the heart of harmonic generation with polar molecules and the reason for its inherent sensitivity to molecular asymmetries.

The emission of odd harmonic signal is independent of the degree of orientation [17], thus the reduction of the odd harmonic signal persists, even when the sample as a whole is symmetric. In other words, the angle dependence of the odd harmonic signal carries information on a polar molecule. Assuming HOMO orbitals only, in Supplemental Material we present a simulation of parallel and perpendicular odd harmonics for N_2 and CO . We will return to this issue later in the paper.

The time-dependent orientation of CO , as determined by Coulomb explosion imaging, is plotted in the lower panel of Figure 3 (dashed green curve). Orientation is measured by the cosine of the angle between an axis parallel to the electric field of the two-colour laser pulse and the momentum (or inverse momentum) of the C^{++} (or O^{++}) fragments. The time dependence of a typical even harmonic (H14; $h\nu = 22\text{eV}$; solid red line) maximizes when the orientation maximizes. The even harmonics appear on zero background, allowing a signal-to-noise of better than 500:1.

Figure 4 shows the harmonics spectrum taken at a pump-probe time delay of 8.85ps – the time of maximum orientation. Even harmonics are visible between the stronger odd harmonics. To ensure the greatest possible linearity of the detector and to facilitate extended dynamic range data acquisition, the MCP detector was operated at a low voltage (1700 V across the MCP chevron pair), and the same image was acquired by the cooled CCD multiple times with different integration times. We

determined the linear range of the camera with respect to the integrated intensity and masked out saturated and non-linear regions of each image. The remaining parts of the images were integrated and calibrated according to the total acquisition time of each pixel. This method provides substantial noise reduction and an extended dynamic range over single acquisitions.

In Figure 4, the upper curve is the integrated signal of the experimental image. The ratio of intensities of each even harmonic to the average of the adjacent odd harmonic orders is plotted as the upper of the two bar graphs. The ratio increases up to $h\nu = 28\text{eV}$ (H18). It has a clear minimum around a photon energy of 37eV (H24) and then grows monotonically to the cut-off. In the lower panel of the same figure we plot the ratio, $R = (S_{aa} - S_a)/S_b$ is plotted for the odd harmonics from a rotational wave packet. Here, S_{aa} , S_a and S_b represent the harmonic signal for aligned (a), anti-aligned (aa) and baseline (b) molecular axis distributions. We measure S_b after the revival has dephased. The similarity of the two bar graphs, measuring seemingly different quantities – alignment dynamics and even to odd harmonic ratios – is striking.

Along with the phase asymmetry, the measurement of the ratio of even to the average of the adjacent odd harmonics allow us to estimate the degree of orientation in our experiments as described in Section B of Supplemental Material. We find the degree of orientation to be $\alpha_0 = 0.24$ consistent with the estimate of 0.2 in Ref. [8].

To progress further we follow each step of the three-step model of high harmonic generation [1]. *Tunnelling:* On adjacent crests of the electric field, an electron wave packet is launched with a different amplitude and phase. The calculated molecular frame ionization probability is shown in Fig. 2(b, right column). Amplitude ratios $r_t = A_t^O/A_t^C$ of the electron wave packets created by tunnelling have been measured for a few polar diatomic molecules [13, 14]. Here O represents the oxygen side of the molecule and C the carbon side. As discussed earlier, it is this significant difference in tunnelling probability shown in Figure 2(b) which facilitates the creation of an oriented sample via depletion [8, 9].

Wave packet propagation: Once the electron wave packet is launched into the continuum by tunnelling, phase accumulates rapidly relative to the Stark-shifting ion ground state. Asymmetry primarily arises because of the different Stark shift the molecule experiences when the field is parallel or antiparallel to the dipole moment of the molecule and molecular ion [18]. While propagation will have little impact on the amplitude asymmetry of the attosecond burst, phase difference, $\delta\phi_p$, will strongly depend on the harmonic order.

Recombination: The final step describes the electron wave packet recombining to its initial bound state. Quantum chemistry codes are well developed for calculating field-free dipole transition moments [19, 20], shown in

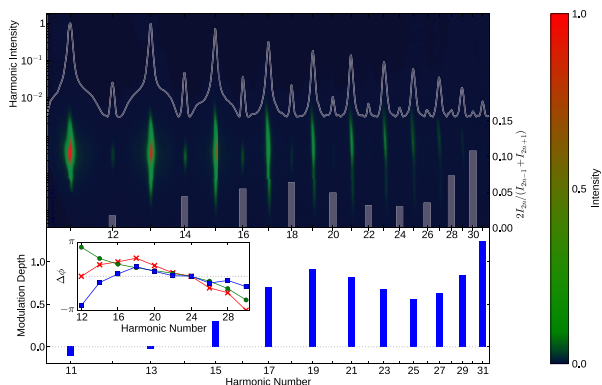


FIG. 4: The high harmonic spectrum is shown at 8.85fs, the time of maximum orientation. The intensity of all harmonics is presented in the top panel of the figure, showing in graphical form what is measured in the image below. The ratio of even to the average of the adjacent odd harmonics is shown in the upper bar graph. The lower bar graph plots the normalized difference - $R = (S_{aa} - S_a)/S_b$. The figure inset shows the phase difference (in green, circle marks) for an electron departing from the -C- side and the -O- side of the molecule as determined by e-polyscat simulations. The red (cross marks) curve is the measured spectral phase asymmetry of successive attosecond XUV (recollision electron) pulses (relative to the normally expected asymmetry). The blue (square marks) curve is the recolliding electron wave-packet spectral phase asymmetry.

Fig. 2(c) for CO. Both amplitude (plotted in the third dimension) and phase (represented by color) depend on the photoelectron's direction relative to the molecule leading to an amplitude ratio r_r and a phase difference $\delta\phi_p$. The field-free transition moment amplitudes have been used to successfully describe high harmonic generation from atoms and small molecules [21, 22].

Using the amplitude ratios shown in Figure 2 (b and c) and the experimentally estimated degree-of-orientation [23] we can estimate the electric field amplitude asymmetry of the attosecond bursts. With this ratio known, the measured spectrum allows determination of the phase difference between successive attosecond XUV pulses as shown in the Supplemental Material. The reconstructed phase difference of the attosecond pulses, $\delta\phi_A$ is plotted in the inset in Figure 4 as the red curve (the π -phase difference that arises from the oppositely directed re-collision on each half cycle has been subtracted for clarity).

We are now in a position to return to the normalized difference for the odd harmonics (lower panel of Figure 4). We have just seen that the phase difference of successive XUV pulses is π near $h\nu = 37\text{eV}$ (H25). Therefore, the successive attosecond pulses contribute optimally to the odd harmonics of the aligned molecule near H25 just as they do for all frequencies for anti-aligned molecules.

While other aspects could contribute, we should not be surprised to see a minimum in the modulation depth $R = (S_{aa} - S_a)/S_b$ (Fig. 4 bottom panel). In other words, the minimum in the normalized difference and even/odd harmonic ratio probably shares a common origin because $\delta\phi_A = 0$ at H25 (37eV).

The high harmonic spectra from oriented polar molecules pose challenges for theoretical models since, unlike the case for high harmonic generation from homogeneous samples, the calculation of the emitted spectra demands that the subtle phase asymmetries present in each step be determined accurately. Sub-cycle measurements will make this and other phase differences experimentally accessible parameters. The three-step model requires that $\delta\phi_A = \delta\phi_t + \delta\phi_p + \delta\phi_r + \pi$ where the three terms represent the phase difference the electron acquires on tunnelling, propagation and recombination. To show the potential impact of measurements on polar molecules, we use the recombination phase from quantum chemistry codes to evaluate $\delta\phi_r$ (shown in Figure 2 (c, right column) and replotted as the green curve in the inset in Figure 4). With the recombination phase removed, the sum $\delta\phi_t + \delta\phi_p + \pi$ is the phase asymmetry of the attosecond electron wave packet at the moment of recollision. This phase of the re-collision electron wave packet will be experimentally accessible in above threshold ionization experiments [24]. We could estimate the propagation phase $\delta\phi_p$, determining the unknown tunnelling phase, but meaning of this parameter would require a special discussion. Future theory and experiments will allow us to zero in on a well-defined tunneling phase.

In conclusion, by orienting high density samples of molecules, we have shown how the coherence of high harmonic spectroscopy provides a new, powerful tool for probing asymmetries of polar molecules. In carefully designed experiments, sub-cycle physics [25] will give us access to all parameters. The phase differences that will become accessible arise, in part, from subtle differences in the local fields and from the quantum exchange interaction that the electron experiences when it is born and when it recombines. Thus, polar molecules will drive major advances in the theory of high harmonic generation while high harmonic spectroscopy will yield unprecedented insight into polar molecules and into multi-electron physics.

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Supplemental Material

A. Calculation of numerical high harmonic spectra

We calculate the high harmonic spectrum using the computational method outlined in Ref.[1]. The calculation requires a grid large enough to allow the continuum wavepacket to propagate away from the core some distance before returning to the core for recollision.

We use a grid extending from ± 17.5 a.u. in directions perpendicular to the laser polarization axis and ± 42.5 a.u. along the laser polarization axis. The space step size was 0.213 a.u. and the time step size was again 0.002666 a.u. The absorbing boundaries were used with a width of 8.2 a.u. in all directions. In order to calculate the harmonic spectrum, we use the Fourier transform of the dipole expectation value

$$S_{HHG}(\omega) = \omega^4 \left| \int dt d(t) e^{i\omega t} \right|^2 \quad (1)$$

where

$$d(t) = \langle \Psi(t) | \vec{r} \cdot \vec{e}_L | \Psi(t) \rangle \quad (2)$$

and $\vec{e}_L$ is the laser polarization direction. In the notation of Ref.[1] the dipole becomes

$$d(t) = \sqrt{n} \left[a_m^*(t) \langle \tilde{\phi}_m^S | \vec{r}_n | \chi_m(t) \rangle + \mathcal{N}_{\tilde{N}} b^*(t) \langle \vec{\phi}_m^C | \chi_m(t) \rangle \right] \cdot \vec{e}_L + c.c. \quad (3)$$

where *c.c.* means complex conjugate (see Ref.[1] for specific definition of all symbols in this equation). The dipole $d(t)$ was calculated for a simulation running 2.5 cycles of monochromatic (no envelope was used) 800 nm light. The Fourier transform used to calculate $S_{HHG}(\omega)$ included only the final 2 cycles of $d(t)$, thus minimizing assymetries due to the initial turn on of the field. In addition, we used a Welch window when implementing the numerical Digital Fourier Transform to avoid discontinuities of $d(t)$ at the edges of the time window. Figure 1 shows the numerically simulated high harmonic spectra for the HOMO channels of N₂ and CO at a peak intensity of 2.8×10^{14} W/cm². Two configurations are shown; the parallel case where the molecular axis is along the polarization direction of the laser and the perpendicular case where the molecular axis is orthogonal to the laser polarization. (For CO, harmonics in the parallel case are calculated by coherently adding the contributions from '0°' and '180°' configurations.) For N₂, the perpendicular case is roughly 2 orders of magnitude below the parallel case indicating no inversion of the harmonic alignment revivals.

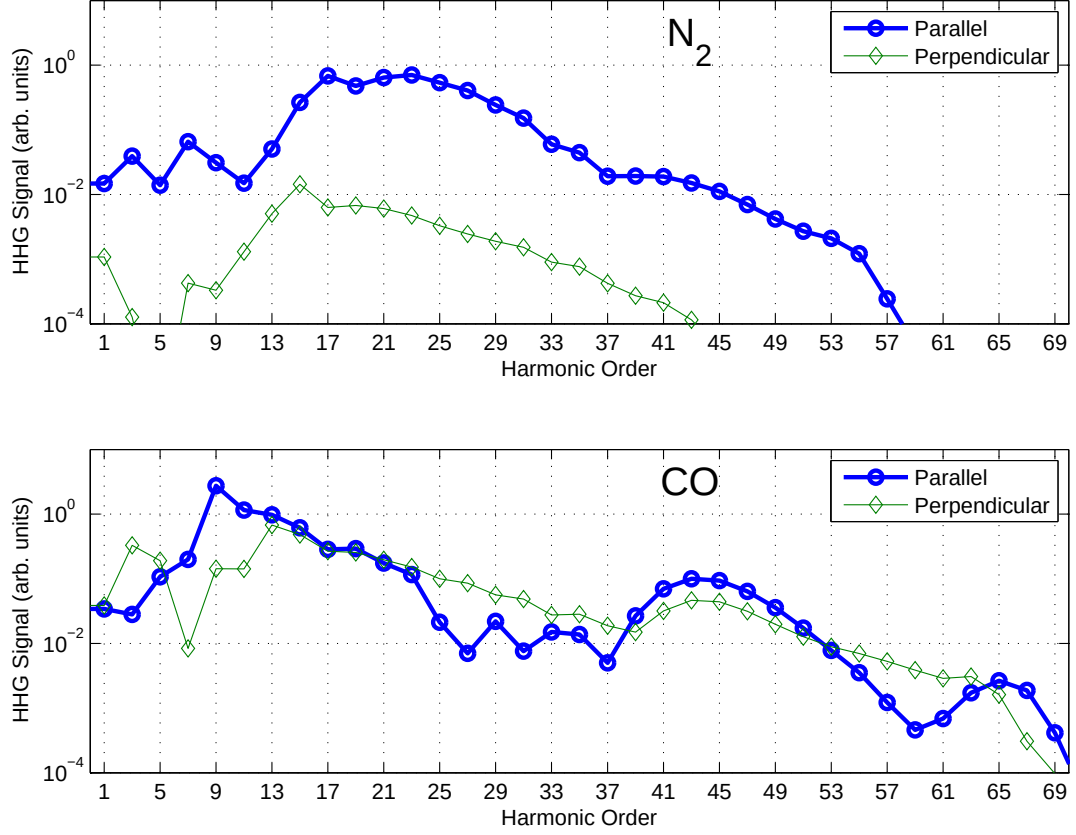


FIG. 1: Numerical high harmonic spectra of the HOMO channel of N_2 (top) and CO (bottom) at $2.8 \times 10^{14} \text{ W/cm}^2$.

However, for CO the harmonics in the perpendicular geometry are not only on the same order as the parallel harmonics across the spectrum, but they even dominate for a larger region indicating inversion of the harmonic alignment revivals.

B. Phase reconstruction

Knowledge of amplitude asymmetry, together with estimation of the degree-of-orientation, allows us to determine the phase asymmetry of successive attosecond XUV pulses in the train from the measured even/odd harmonic amplitude ratio - $r(\nu_{2n})$ (shown in Fig. 4 in the body of the paper). To exemplify our approach, we assume a model in which molecules are perfectly aligned and only partially oriented (with $n_{\uparrow}$ molecules

pointing up and $n_{\downarrow}$ pointing down). In this case the degree-of-orientation is defined as $\alpha_o \equiv (n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$. For a single polar molecule, emitting attosecond bursts with the spectral amplitudes $E_C(\nu) = |E_C(\nu)| \exp(i\varphi_C(\nu))$ and $E_O(\nu) = |E_O(\nu)| \exp(i\varphi_O(\nu))$, the intensity of emitted even harmonics is proportional to $|E_C(\nu) - E_O(\nu)|^2$, while intensity of the odd harmonics is proportional to $|E_C(\nu) + E_O(\nu)|^2$. Within this model the spectral phase asymmetry ($\Delta\varphi = \varphi_C - \varphi_O$) can be approximated as

$$\Delta\varphi(\nu_{2n}) \simeq \pm \arccos \left[\frac{1 + \eta(\nu_{2n})}{2\sqrt{\eta(\nu_{2n})}} \cdot \left(1 - \frac{2r(\nu_{2n})}{r(\nu_{2n}) + \alpha_o^2} \right) \right] \quad (4)$$

where $\eta(\nu_{2n})$ - is the spectral intensity ratio of $-C-$ vs. $-O-$ attosecond bursts, which we calculate based on asymmetry in ionization rate [1] and in amplitude of recombination dipole [2, 3].

The HHG is a coherent process, therefore the measured signal is proportional to the square of the number of emitters. This implies that the ratio of even to the average of the adjacent odd harmonics $r(\nu_{2n})$ would be proportional to the square of the degree-of-orientation. Assuming that the spectral phase between attosecond bursts changes significantly across the spectrum, we may estimate the degree-of-orientation as an average value of $r(\nu_{2n})$, shown in the upper bar graph in Figure 4 (main text). This average value is around $\sim .05$, which implies a degree-of-orientation $\alpha_o \simeq 0.22$.

To further improve the estimation of α_o , we plot $\Delta\varphi(\nu_{2n})$ for a range of α_o in Fig. 2. In fact, the choice of possible values for the degree-of-orientation is restricted within a range of $0.13 - 0.24$, because $\Delta\varphi(\nu_{2n})$ becomes imaginary outside of this range - α_o within this range is consistent with our initial estimates. For all α_o , the phase asymmetry increases to a maximum value near H18 ($h\nu \sim 27\text{eV}$) and then decreases once again, exhibiting local minimum at H24. This local minimum is a robust feature, independent of the actual degree-of-orientation assumed.

For $\alpha_o \simeq 0.24$, the reconstructed phase touches the zero at H24. Both the positive (red line) and negative (dashed black line) values of the phase would produce the same interference signature in the even/odd harmonic ratio. Local minima are common in many branches of physics and physical chemistry. They are often a signature of the monotonic phase changes. Our estimates of the phase asymmetry acquired during propagation (using the strong field approximation) and recombination show monotonic behavior with no local

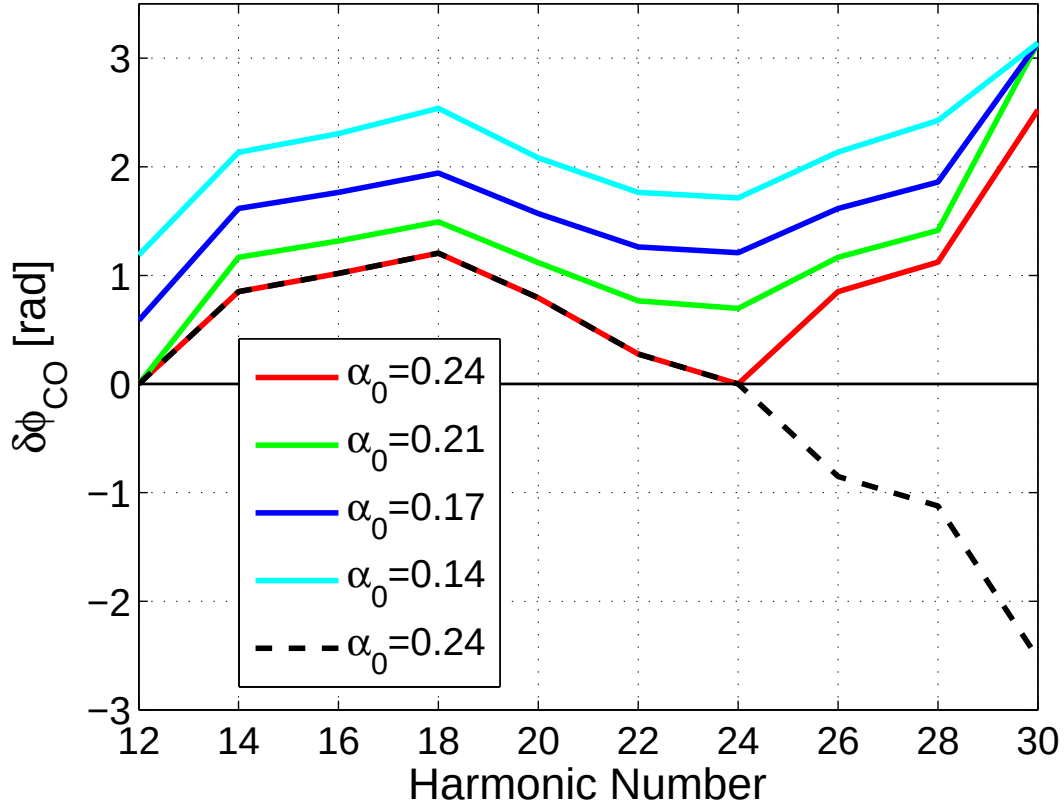


FIG. 2: Phase reconstruction.

minimum. This suggests that the total phase may be a monotonic function as well. For this reason we assume that the negative branch corresponds to physical reality.

In the laboratory frame the molecules are not perfectly aligned or oriented. We developed a more sophisticated model that takes into account averaging over alignment distributions. The results qualitatively are very similar to the simple model presented above - the overall shape of the curve, maximum (at H18) and minimum (at H24) positions are well reproduced.

Essentially the overall shape of the reconstructed phase, $\delta\phi_{CO}$ (black curve), is similar to the calculated phase asymmetry acquired during propagation and recombination, $\delta\phi_p + \delta\phi_r$, with both showing significant decrease towards the cut-off. The difference between the two would correspond to a residual phase which we define as a tunneling phase, $\delta\phi_t =$

$\delta\phi_{CO} - \delta\phi_p - \delta\phi_r$, as discussed in the body of the paper.

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Chapter 3

Contributing to High-Harmonic Spectroscopy of Aligned Molecules

3.1 Controlling the Interference of Multiple Molecular Orbitals in High-Harmonic Generation (publication [4](#))

H. J. Wörner, **J. B. Bertrand**, P. B. Corkum and D. M. Villeneuve

Controlling the Interference of Multiple Molecular Orbitals in High-Harmonic Generation
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3.1.1 Author Contributions

J.B.B. and H.J.W performed the experiment. Installing the optical setup and operating the operational parametric amplifier (OPA) was J.B.B.'s summer 2009 project. D.M.V., H.J.W and P.H. performed the ePolyScat [[81](#), [82](#)] photoionization dipole calculations. H.J.W. and J.B.B. conducted the data analysis. H.J.W. wrote the first draft. All authors contributed to the final manuscript.

Controlling the Interference of Multiple Molecular Orbitals in High-Harmonic Generation

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We demonstrate a new method to investigate the origin of spectral structures in high-harmonic generation. We report detailed measurements of high-harmonic spectra in aligned nitrogen and carbon dioxide molecules. Varying the wavelength and intensity of the generating laser field, we show that the minimum in aligned N_2 molecules is nearly unaffected, whereas the minimum in aligned CO_2 molecules shifts over more than 15 eV. Our quantitative analysis shows that both the interference of multiple orbitals and their structural characteristics affect the position of the minimum. Our method provides a simple approach to the investigation of the high-harmonic generation process in more complex molecules.

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High-harmonic generation (HHG) has become a tool to investigate the electronic and geometric structure of molecules on an ultrafast time scale [1–4]. HHG occurs when an electron is removed from the parent molecule under the action of an intense laser field and is forced to recollide with the parent less than one period of the field oscillations later [5]. The emission of radiation results from the recombination of an electron and a molecular ion and thus constitutes an inverse photoionization process [6–8]. Consequently, it is highly sensitive to the electronic structure of the target with the advantage that a broad range of photoelectron energies are probed simultaneously. Since the technique can be combined with nonadiabatic alignment, measurements can be performed in the molecular frame, revealing the detailed electronic structure of molecules [9]. An important example of structural information contained in high-harmonic spectra is the interference of the returning electron wave with two atomic centers [10]. This effect has been predicted and observed in H_2 [11] but whether it is applicable to larger molecules remains an object of debate. A spectral minimum observed in CO_2 molecules aligned parallel to the generating laser field was found at 39 eV in Ref. [2], at 54 eV in Ref. [12], and in a range of intermediate positions, depending on the intensity, in Ref. [4]. Recent theoretical work suggests ionization from multiple orbitals to be responsible for the intensity dependence of the minimum position [4], while other work suggests that the effect of the strong laser field on a single orbital can explain the intensity dependence [13].

We propose and demonstrate a new method to identify and control spectral structures observed in HHG from aligned molecules. We perform detailed measurements of the high-harmonic spectra of aligned N_2 and CO_2 molecules at two different wavelengths and a range of intensities. We report that the minimum in N_2 is largely independent of both the fundamental wavelength and the intensity which indicates that this minimum is associated with the electronic structure of the molecule. In contrast, we show that the minimum in CO_2 strongly depends on

both the intensity and the wavelength and is always located in the vicinity of the cutoff. This clearly demonstrates its origin as interference between channels originating in different orbitals. Varying the wavelength of the fundamental field allows us to vary the relative phase of the high-harmonic emission channels, thereby controlling the photon energy at which the destructive interference occurs. Our results show that in addition to the interference of multiple orbitals, the structure of the highest occupied molecular orbital (HOMO) affects the position of the minimum. Indeed, the interference of the recombining electron with the 2-center HOMO results in a strong phase variation of the recombination matrix element with photon energy.

The experimental setup consists of a chirped-pulse-amplified titanium-sapphire laser system, a high-energy optical parametric amplifier (HE-TOPAS, Light Conversion), and a vacuum chamber for generation and characterization of high-harmonic radiation. The laser system provides pulses at 800 nm, 12 mJ, 32 ± 2 fs, 50 Hz. The TOPAS is pumped using 8 mJ and provides 1200 nm pulses of 40 ± 5 fs duration. The remaining energy is split into two beams of adjustable intensity. The molecules are impulsively aligned using a stretched 800 nm pulse (duration ~ 80 fs) with a peak intensity of 5×10^{13} W/cm². The high-harmonic spectra are recorded at a time delay corresponding to the maximal alignment at the rotational half-revival (~ 4.1 ps in N_2 and ~ 21.2 ps in CO_2). The degree of alignment is estimated to be $\langle \cos^2 \theta \rangle = 0.6$ – 0.65 . A rotatable wave plate is used to adjust the relative polarization between the alignment and HHG pulses. The pulses are focused ~ 1 mm below and slightly before the orifice of a pulsed nozzle generating a supersonic expansion. This setup minimizes the effects of phase mismatch and reabsorption of the high-harmonic radiation and leads to the observation of the single-atom response [14]. The high-order harmonics are recorded using an extreme-ultraviolet spectrometer, a microchannel plate detector, and a charge-coupled device camera [9]. When converting the pixel

scale of the camera to the energy scale, we correct the spectral intensity to preserve the integral under the spectrum.

Figure 1 shows high-harmonic spectra of nitrogen molecules aligned parallel to the polarization of the generating field (blue line) or unaligned (green line) for different fundamental wavelengths and intensities. The spectrum shown in Fig. 1(a), recorded using a fundamental wavelength of 800 nm, reveals a weak minimum at H25 (39 ± 2 eV) as observed previously [1,9,15]. Turning to 1200 nm, Fig. 1(b) shows a clear minimum for a photon energy of 38 ± 2 eV for both aligned and unaligned molecules. In Fig. 1(c) the minimum is shifted to 41 ± 2 eV for both aligned and unaligned molecules.

We find that the minimum in N_2 is almost independent of wavelength and intensity, similar to the minimum in argon [16,17]. This shows that the minimum is associated with the electronic structure of the molecule, rather than with electronic dynamics induced by the laser field. A weak dependence on the intensity could be attributed to the effect of the strong laser field on the wave function of the recombining electron or that of the molecular cation, owing to the energetic proximity of the cationic ground (X) and first excited (A) states ($E_A - E_X \approx 1.3$ eV [18]). Moreover, the minimum is most pronounced at the lowest intensity we have used [Fig. 1(b)], suggesting that it is associated with the structure of the HOMO. Also, the overall variation of the harmonic intensity, increasing

monotonically from perpendicular to parallel alignment (not shown), is consistent with HOMO [9].

Figure 2(a) shows spectra of CO_2 molecules aligned parallel to the generating field (blue line) or unaligned (green line). At 800 nm and $\sim 2.1 \times 10^{14}$ W/cm² [Fig. 2(a)], we find a strong minimum at H27 or 42 ± 2 eV. Figures 2(b) and 2(c) both show clear minima in the high-harmonic spectra of molecules aligned parallel to the generating field. The minimum in Fig. 2(b) is at 51 ± 2 eV and the minimum in Fig. 2(c) is at 57 ± 2 eV. Unlike the minimum in N_2 , the minimum in CO_2 moves to higher photon energies with an increasing angle between the molecular axis and the direction of the generating field (not shown). This behavior is observed at 1200 nm and at 800 nm and is consistent with the pattern expected for 2-center interference [19]. However, the dependence of its position on intensity and wavelength clearly shows that the minimum cannot originate from the molecular structure alone.

The minimum observed in CO_2 molecules aligned parallel to the driving field has been attributed to the electronic structure of the HOMO [2,12,19] or to the interference of the channels associated with HOMO and HOMO-2 [4]. Here we show that both structural effects of the HOMO and the interference between HOMO and HOMO-2 are required to explain our observations. The three valence orbitals of CO_2 in order of increasing binding energy are of π_g , π_u , and σ_u symmetry and have ionization potentials of

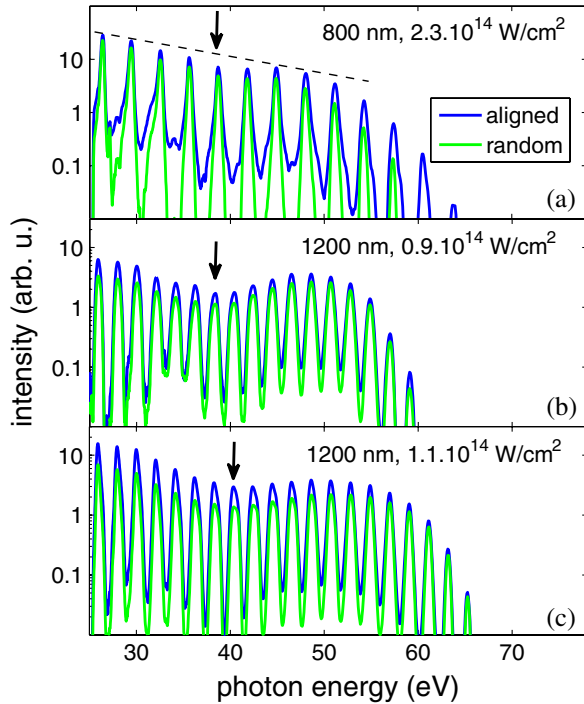


FIG. 1 (color online). High-harmonic spectra of N_2 molecules aligned parallel (blue curves) or randomly aligned (green curves) to the polarization of the generating laser field. The wavelength and intensities of the generating pulse are indicated in each figure. The arrows mark the position of the minima.

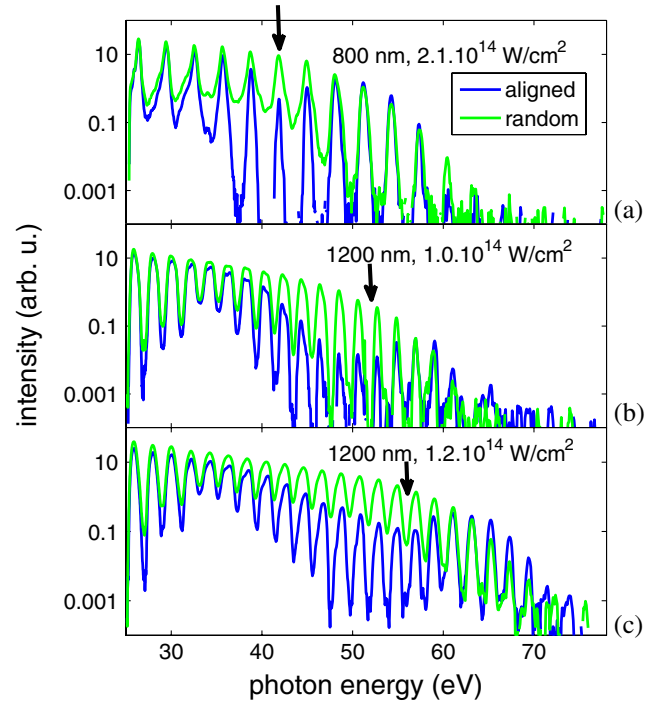


FIG. 2 (color online). High-harmonic spectra of CO_2 molecules aligned parallel (blue curves) or randomly aligned (green curves) to the polarization of the generating laser field. The wavelength and intensities of the generating pulse are indicated in each figure. The arrows mark the position of the minima.

13.8, 17.3, and 18.1 eV, respectively [18]. The angular variation of ionization rates and recombination dipoles are such that high-harmonic emission for molecules aligned at 0° is dominated by HOMO and HOMO-2, while it is dominated by HOMO and HOMO-1 at 90° [4,20,21].

In order to rationalize the above observations, we have developed a simple multichannel model of high-harmonic generation [4,20]. Clear recent evidence for strong-field ionization from lower orbitals has demonstrated the importance of including multiple orbitals in the description of HHG [4,22,23]. When laser-induced transitions in the molecular ion can be neglected, the high-harmonic signal is a coherent sum of the signals generated by ionizing from and recombining to the same molecular orbital. In the spirit of the three-step model, we write the complex high-harmonic amplitude as the product of three complex quantities [8,24]:

$$d(q, \theta) = \sum_i a_{\text{ion},i}(q, \theta) a_{\text{prop},i}(q) a_{\text{rec},i}(q, \theta), \quad (1)$$

where the sum i runs over all molecular orbitals that undergo significant ionization in the laser field, q is the harmonic order, and θ is the alignment angle. $a_{\text{ion},i}(q, \theta)$ describes tunnel ionization, $a_{\text{prop},i}(q)$ the propagation, and $a_{\text{rec},i}(q, \theta)$ is the complex photorecombination matrix element in the molecular frame which characterizes the electronic structure of the molecule. We assume that the phase of $a_{\text{ion},i}(q, \theta)$ is the same for both channels; i.e., there is no channel-specific ionization phase. This assumption will be supported by the agreement between theory and experiment. We calculate $a_{\text{prop},i}(q)$ using the semiclassical model [25] and $a_{\text{rec},i}(q, \theta)$ using the program EPOLYSCAT [26,27].

The results of the multichannel model are illustrated in Fig. 3. Two channels are included: HOMO (π_g) and HOMO-2 (σ_u), since Ref. [4] shows that HOMO-1 (π_u) does not contribute at 0° . The complex molecular-frame recombination matrix element from EPOLYSCAT is averaged over a molecular alignment distribution of $\cos^4\theta$ centered on the laser polarization axis. The angle dependence of the ionization probability is taken from [4]. The relative ionization probability is estimated from the ADK rates to be 0.04. The phase of the angle-averaged recombination matrix elements is shown in Fig. 3(a). The phase of $a_{\text{rec,HOMO-2}}$ is almost independent of the photon energy, whereas $a_{\text{rec,HOMO}}$ increases by ~ 2 rad around 40 eV where the recombination amplitude goes through a minimum [7].

Classical trajectory calculations [5,25] are used to evaluate the transit time of the electron in the continuum. As in photoionization, the high-harmonic photon energy Ω is related to the asymptotic momentum k of the photoelectron by $\Omega = k^2/2 + I_p$ (in atomic units). We have calibrated the intensities in the experiment by measuring high-harmonic emission from argon atoms and using the cutoff law $3.17U_p + I_p$ [5]. The phase difference of the electron propagation step, $\Delta I_p \tau$, is shown in Fig. 3(b) for the three

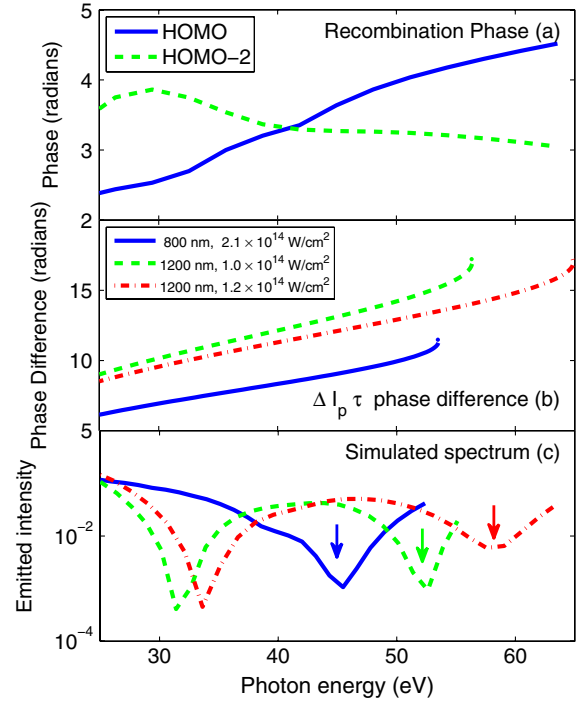


FIG. 3 (color online). Model of multichannel HHG from CO_2 molecules aligned at 0° to the laser field. (a) Phase of the angle-averaged recombination matrix elements of the two orbitals as calculated by EPOLYSCAT. (b) Phase difference acquired by the two channels during the electron excursion calculated from classical trajectories. (c) Simulated spectra from the coherent sum of the two channels. The three sets of laser parameters correspond to the experimental conditions from Fig. 2.

experimental laser conditions in Fig. 2, where I_p is the binding energy of the involved orbitals and τ is the transit time of the electron in the continuum [28].

Figure 3(c) shows the square of the coherent sum of the electric fields from each channel up to the cutoff of HOMO. The simulated electric fields include the $\Delta I_p \tau$ phase and the angle-averaged complex recombination dipole moments. For each laser condition, an interference minimum is seen in the higher energy part of the spectrum (arrows). For 800 nm, this minimum approximately corresponds to a propagation phase difference of 3π radians because the recombination phases are almost identical. For 1200 nm the minima do not correspond to 5π rad but to $\sim 4.5\pi$ rad (red dash-dotted curve) because of the difference in the recombination phases. The prediction of the 1200 nm spectra shows a 3π radian minimum at lower energy; these minima are not visible in the experimental spectra because of the intensity averaging that occurs for the lower order harmonics as they are being generated over a broad range of intensities. The interference minima located close to the cutoff survive intensity averaging because the corresponding harmonic orders are only generated at the peak of the laser field. The calculated minima at 45, 52, and 58 eV closely match the experimental minima seen in Fig. 2 at 42, 51, and 57 eV.

The coherent sum of the multiple channels can thus reveal both structural minima due to $a_{\text{rec},i}(q, \theta)$, or dynamical minima that occur from destructive interferences between channels. If the minimum is structural as in argon, its position is largely independent of the laser parameters including wavelength and intensity [6,7,16,17]. We have shown that the minimum in N_2 falls in this category. If the minimum is dynamical, the interference of the orbitals can be controlled directly by intensity and wavelength through the propagation factor $a_{\text{prop},i}(q)$. In addition to the relative phase of the two channels, the structure of the orbitals can lead to a significant phase variation of the recombination matrix element that also affects the observed minimum position.

The role of ionization phase $a_{\text{ion},i}(q, \theta)$ is not yet well understood. It is possible that there is an ionization phase that depends on the geometry and parity of the orbital involved. The ionization phase will determine the initial shape of the hole wave packet [4]. The agreement between our experiment and our model suggests that the difference in the ionization phase between the two channels in CO_2 aligned parallel to the laser field is small.

In this Letter, we have shown how the variation of the fundamental wavelength allows an unambiguous identification of structural and dynamical minima. In the case of nitrogen, we have discovered that the minimum at 39 eV primarily results from the electronic structure of the molecule. In CO_2 , the observed minimum results from the interference of the HOMO and HOMO-2 channels. The deviation of the minimum position from odd multiples of π in the relative phase of the channels is attributed to a photon-energy dependent difference in the recombination phase, thereby revealing a new route to trace both structural and dynamical minima in high-harmonic spectra. When the minimum is dynamical, the position of its associated phase jump can be controlled, which is equivalent to a tunable phase mask, permitting the shaping of attosecond pulses [19,29]. Generally, the wavelength scaling of spectral structures in HHG spectra of aligned molecules will improve our understanding of high-harmonic generation processes in more complex molecules. In the future, a systematic variation of the wavelength could be used to investigate the role of nonadiabatic electronic dynamics [30] in high-harmonic generation. Using different wavelengths will also greatly facilitate the understanding of pump-probe spectroscopy of photochemical reactions using HHG as the probe step. The homodyne interference of the emission from the ground and the excited states [31] is controllable via the wavelength, as shown in this Letter, which will help disentangle structural and dynamical information obtained in time-resolved experiments.

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3.2 Revealing the Cooper Minimum of N_2 by Molecular Frame High-Harmonic Spectroscopy (publication [15](#))

J. B. Bertrand, H. J. Wörner, P. Hockett, D. M. Villeneuve and P. B. Corkum

Revealing the Cooper Minimum of N_2 by Molecular Frame High-Harmonic Spectroscopy
To be resubmitted to Physical Review Letters (2012).

3.2.1 Author Contributions

J.B.B. and H.J.W performed the experiment. Installing the optical setup and operating the operational parametric amplifier (OPA) was J.B.B.'s summer 2009 project. H.J.W and P.H. performed the ePolyScat [[81](#), [82](#)] photoionization dipole calculations. J.B.B. conducted the data analysis and wrote the first draft. All authors contributed to the final manuscript.

Revealing the Cooper Minimum of N₂ by Molecular Frame High-Harmonic Spectroscopy

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Molecular frame high-harmonic spectra of aligned N₂ molecules reveal a Cooper-like minimum. By deconvolving the laboratory frame alignment distribution, what was previously thought to be a maximum of emission along the molecular axis is found to be maxima at 35 degrees off axis, with a spectral minimum on axis. Both of these features are supported by photoionization calculations that underline the relationship between high-harmonic spectroscopy and photoionization measurements. The calculations reveal that the on-axis spectral minimum is a Cooper-like minimum that arises from the destructive interference of the *p* and *f* partial wave contributions to high-harmonic photorecombination. Features such as Cooper minima and shape resonances are ubiquitous in molecular photoionization/recombination.

The photoionization transition moment is an observable that contains important information about the electronic structure of molecules [1]. When measured in the molecular frame and over a wide spectral range, the transition moment allows us to image valence electronic structure [2–4] and to follow electronic [5] or chemical dynamics [6, 7]. For decades, the photoionization transition moment could be measured using XUV radiation produced by a synchrotron [8]. However, retrieving the molecular frame XUV photoionization signal from valence molecular orbitals is challenging because the long pulse duration of the ionizing radiation [9] (~ 100 ps) prevents the use of field-free molecular alignment techniques [10] (~ 100 fs).

An alternative approach, high-harmonic spectroscopy, can measure the photorecombination transition moment over a wide range of photon energies simultaneously [11–13]. The short duration of the high-harmonic process (few tens of fs) allows the use of field-free molecular alignment. In high-harmonic spectroscopy, an intense femtosecond laser pulse removes a valence electron from the molecule. The laser field subsequently drives the electron back to the parent ion where it can radiatively recombine, resulting in the emission of an XUV photon in a phase matched process [14, 15]. The recombination process is essentially the time-reversal of photoionization, and can be treated as a measure of the same transition matrix elements [11, 12].

Here we measure the high-harmonic spectrum of molecular nitrogen (N₂) in the photon range of 20–80 eV. We apply recently developed deconvolution methods to access the molecular frame response [16, 17], revealing previously unseen features. We show that there is a minimum in the transition moment along the molecular axis at about 45 eV. We relate this to a Cooper-like minimum in which the transition moment goes through a minimum due to destructive interference between dominant partial wave components. The deconvolution shows that

there are maxima at around 35 degrees off-axis which have not previously been observed in laboratory frame measurements. The measured transition moments are in good agreement with photoionization calculations. By performing the experiment at two different laser wavelengths (800 nm and 1200 nm), we verify that we measure the electronic structure and not dynamic interference between orbitals [18].

For the experiment, we impulsively align N₂ molecules [10] with a stretched, non-ionizing pump pulse (70 ± 5 fs, 800 nm, $I_{align} = 5 \times 10^{13}$ W/cm²) and probe the aligned molecules with an intense ionizing pulse (800 nm: 32 ± 2 fs or 1200 nm: 40 ± 5 fs, both with peak intensity $I_{probe} = 1.5 \times 10^{14}$ W/cm² determined from the high-harmonic cutoffs). The 800 nm pulses are generated by a Ti:Sapphire multi-pass laser system (32 fs, 800 nm, 50 Hz, 12 mJ per pulse) and the 1200 nm pulses (~ 1 mJ) are generated by a high-energy optical parametric amplifier (HE-TOPAS) pumped with 800 nm light. The high-harmonic experimental chamber consists of a source chamber, a pulsed valve (250 μ m orifice), an XUV grating, a microchannel plate detector backed by a phosphor screen, and a camera readout.

High-harmonic spectra are recorded at maximal alignment, around the first rotational half-revival (4.12 ps). In the laboratory frame, we vary the angle α between the alignment distribution axis and the probing field by rotating the alignment (pump) beam polarization (both beams are linearly polarized). In Fig. 1, we show laboratory frame high-harmonic spectra taken with (a) 800 nm and (b) 1200 nm light. For both wavelengths, the experimentally observed high-harmonic yields peak along $\alpha = 0^\circ$, as also previously reported at 1300 nm in ref. [19]. A spectral minimum is located in the vicinity of ~ 42 eV and $\alpha = 0^\circ$. The minimum is evident with 1200 nm laser wavelength, but is not seen with 800 nm in the present experiment due to a lower cutoff. The minimum was pre-

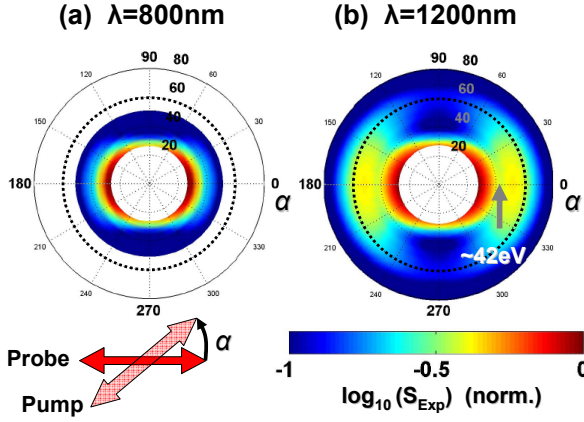


Figure 1: Experimentally recorded high-harmonic signal from aligned N_2 as a function of alignment angle α for two probe-pulse central wavelengths (800 or 1200 nm) at $I_{probe} = 1.5 \times 10^{14}$ W/cm². The radius of the polar plots corresponds to photon energies in the range of 0-80 eV, while the angle corresponds to the angle α between the probe polarization and the molecular alignment. The black dotted line marks 60 eV. The color scale is logarithmic.

viously observed around 40 eV at 800 nm but with higher laser intensity [2, 20].

The high-harmonic signal measured in the laboratory frame, $S(\Omega, \alpha)$, is a coherent convolution of the molecular frame dipole field $\vec{D}(\Omega, \theta)$ with the prolate alignment distribution $A(\theta', \phi')$, where θ is the angle between the laser field polarization and the molecule's internuclear axis, θ' and ϕ' are the zenithal and azimuthal angle with respect to the alignment distribution axis, and Ω is the harmonic frequency. The angle θ is given by the laboratory to molecular frame coordinate transformation: $\cos \theta = \cos \alpha \cos \theta' - \sin \alpha \sin \theta' \sin \phi'$ [16]. In the molecular frame, the emitted high-harmonic complex dipole field $\vec{D}(\Omega, \theta)$ can be considered in the 3-step model and therefore contains contributions from ionization, propagation and recombination processes [14]. To extract the molecular frame high-harmonic dipole from amplitude (XUV signal)-only measurements, we make the approximation that the dipole phase varies slowly ($\ll \pi$) within the alignment distribution ($\sim 25^\circ$ FWHM). It allows us to add the contribution from all angles incoherently as done previously [17]. This assumption will likely fail in the occurrence of a rapid variation of the angular phase caused, for example, by the presence of nodal planes in the highest occupied molecular orbital (HOMO) and/or the interplay of multiple orbitals [5].

In the experiment, we do not distinguish parallel and perpendicular polarization components, with respect to the driving laser (linear) polarization axis, of $\vec{D}(\Omega, \theta)$. Therefore, we group them directly as the total molecular frame dipole amplitude $|\vec{D}(\Omega, \theta)| =$

$\sqrt{|D_{\parallel}(\Omega, \theta)|^2 + |D_{\perp}(\Omega, \theta)|^2}$. Based on this approach, the integral form for the measured laboratory frame high-harmonic signal $S(\Omega, \alpha)$ becomes [21]:

$$\sqrt{S(\Omega, \alpha)} \approx \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \Omega^2 |\vec{D}(\Omega, \theta(\theta', \phi', \alpha))| \times A(\theta', \phi') \sin \theta' d\phi' d\theta' \quad (1)$$

For each signal $S(\Omega, \alpha)$, we solve eq. (1) using a nonlinear least-squares fit and by parametrization of the molecular frame solution, $|\vec{D}_{Exp}(\Omega, \theta)|$, using normalized even (0-6, determined by converging fits) Legendre polynomials ($P_{2i}(\theta)$): $|\vec{D}_{Exp}(\Omega, \theta)| = |\sum_{i=0}^3 a_{2i} P_{2i}(\theta)|$. An *a priori* knowledge of the alignment distribution $A(\theta', \phi')$ is required. In our experimental conditions ($P_{back}=2$ atm, $T_{rot}=30-40$ K, $I_{align} = 5 \times 10^{13}$ W/cm²), we estimate achieving a degree of alignment $\langle \cos^2 \theta' \rangle = 0.60 \pm 0.05$. Our estimate is supported by recent supersonic gas expansion studies in similar conditions [17]. The corresponding alignment distribution $A(\theta')$ is parametrized analytically [16]. We proceed with a distribution function A that corresponds to $\langle \cos^2 \theta' \rangle = 0.60$.

The molecular frame solution to eq. (1), $\Omega^2 |\vec{D}_{Exp}(\Omega, \theta)|$, is shown in Fig. 2 at both (a) 800 nm and (b) 1200 nm. We find that, while the lower-order harmonics peak at $\theta=0^\circ$, higher-order harmonics peak closer to $\theta \sim 35^\circ$ at both laser wavelengths. The retrieved molecular frame profiles depend somewhat on the degree of alignment but the on-axis minimum remains similar in the range $0.55 < \langle \cos^2 \theta' \rangle < 0.65$. At 1200 nm, the extended cutoff allows us to observe that the spectral minimum is an island near 45 eV and $\theta=0^\circ$ that is confined in energy and angle. To our knowledge, such features have never before been observed for the HOMO $3\sigma_g$ state of N_2 . The $2\sigma_g$ of N_2 photoionization cross-sections measured in synchrotron experiments show similar features [8]. Although it is not evident in Fig. 2(a), the island is also present at 800 nm. By normalizing the color scale the island becomes visible; see Fig. S1 in the supplementary online material.

Next, we compare our experimental findings to calculations, both in the molecular and laboratory frames. Photoionization transition moments from the $3\sigma_g$ HOMO orbital of N_2 are calculated in the molecular frame using ePolyScat [22, 23]. In Fig. 3(a), the calculated dipole amplitude $\Omega^2 |\vec{D}_{Calc}(\Omega, \theta)|$ contains the contributions from both the molecular frame ionization rate (I_{Calc}) and recombination amplitude (R_{Calc}),

$$|\vec{D}_{Calc}(\Omega, \theta)| = \sqrt{I_{Calc}(\theta)} \times \sqrt{|\vec{R}_{Calc,\parallel}(\Omega, \theta)|^2 + |\vec{R}_{Calc,\perp}(\Omega, \theta)|^2}. \quad (2)$$

Eq. (2) assumes that the propagation step is not angle de-

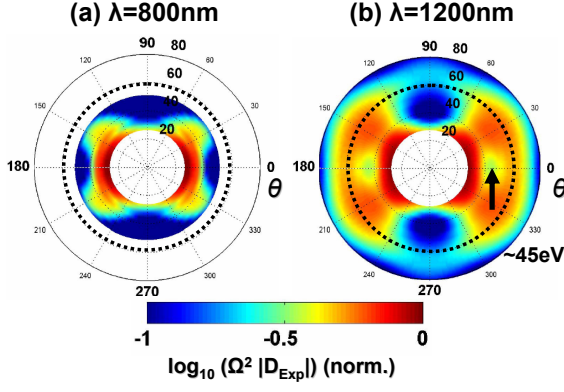


Figure 2: Experimental molecular frame transition moments in aligned N_2 , derived from the results in Fig. 1. We display the extracted amplitude $\Omega^2 |D_{Exp}(\Omega, \theta)|$ by deconvolving the molecular alignment distribution using eq.(1). While the laboratory frame signal peaks at $\alpha = 0^\circ$ (see Fig. 1) across the spectrum, in the molecular frame the amplitude instead peaks at a significant angle ($\theta \sim 35^\circ$) between the molecular axis and the laser polarization above 40 eV at 800 nm and at 45 ± 5 eV at 1200 nm.

pendent. We have used an energy independent recollision amplitude for the electron. This is valid for the plateau harmonics if they are generated with an infrared fundamental beam [13]. At 800 nm, the energy dependence of the recollision amplitude can be removed experimentally using the spectrum of an atomic reference [24].

The molecular frame ionization probability $I_{Calc}(\theta)$, sketched as the solid lines in the middle of the polar plots, is obtained using MO-ADK [25]. $\vec{R}_{Calc}(\theta)$ is obtained by taking the complex conjugate [26] of the calculated molecular frame photoionization dipoles for the N_2 HOMO only [27]. In good agreement with the experimental result shown in Fig. 2(b), the calculated amplitude in Fig. 3(a) also displays the angular bifurcation starting at ~ 50 eV and the associated spectral minimum along $\theta=0^\circ$, centered here at ~ 58 eV. The strong maximum centered at $\theta=0^\circ$ and ~ 35 eV, also partially observed experimentally, is a shape resonance [21].

Although high harmonics are generated primarily from the HOMO due to the exponential sensitivity of tunnel ionization to ionization potential, nevertheless inner valence orbitals can also contribute to the emission [3, 5, 28]. In N_2 , the HOMO-1 is of π_u symmetry, and hence only contributes in the vicinity of 90° [29]. The minimum that is seen in Figs. 2 and 3 is therefore not affected by the HOMO-1. The spectral position of this minimum has been reported to shift to higher photon energy (by ~ 5 eV, starting from 40 eV) when increasing the driving laser field peak intensity in the range of $I_{probe} = 1.4 - 2.0 \times 10^{14}$ W/cm 2 at 800 nm [20]. Calculations rule out the participation of lower-lying states (HOMO-1 and HOMO-2) to explain this effect [20, 29]. Here, working at $I_{probe} = 1.5 \times 10^{14}$ W/cm 2 insures

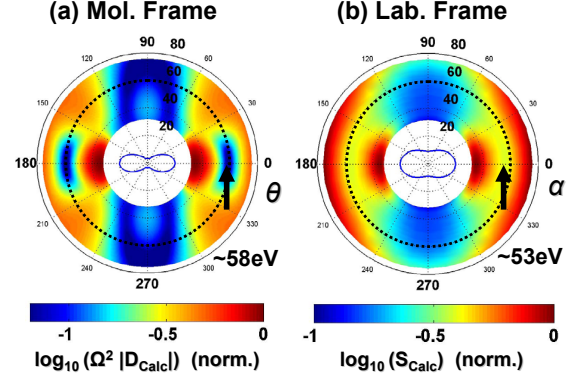


Figure 3: Theory: (a) molecular frame high harmonic amplitude $\Omega^2 |D_{Calc}(\Omega, \theta)|$ using calculated differential photoionization dipole matrix elements and analytical angular ionization probabilities. (b) Expected laboratory frame XUV signal $S_{Calc}(\Omega, \theta)$ using eqs. (1) and (2) to convolve the calculated molecular frame values from (a) with the experimental alignment distribution. The solid line in the middle is the normalized ionization rate in the respective frames calculated using MO-ADK. The alignment averaging shifts the spectral minimum at $\theta=0^\circ$ towards lower photon energy and reduces its depth, as seen experimentally.

we are essentially looking at HHG signal coming from HOMO at $\theta=\alpha=0^\circ$. The HOMO-1 will contribute to the experimental signal around 90° in Fig. 2(b), but not in the calculation in Fig. 3(a) which only considers the HOMO. Elsewhere [21] we are able to reproduce the experimental high-harmonic spectrum at $\alpha=90^\circ$ by considering the contribution from HOMO-1 [20, 28].

In Fig. 3(b), we compute the expected laboratory frame signal $S_{Calc}(\Omega, \alpha)$ using eqs. (1) and (2). We performed this summation in a coherent fashion (not shown), treating each polarization component separately before summing their square modulus to obtain $S_{Calc}(\Omega, \alpha) = S_{\parallel}(\Omega, \alpha) + S_{\perp}(\Omega, \alpha)$, where:

$$S_{\parallel, \perp}(\Omega, \alpha) =$$

$$\left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \Omega^2 D_{\parallel, \perp}(\Omega, \theta) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right|^2, \quad (3)$$

and $D_{\parallel, \perp}(\Omega, \theta) = \sqrt{I_{Calc}(\theta)} \times R_{\parallel, \perp}(\Omega, \theta)$, as similarly defined above in eq. (2). We observe no significant differences between a coherent and an incoherent sum. In both cases, the Cooper minimum around $\alpha=0^\circ$ remains quantitatively unchanged, see Fig. S2 in the supplementary information. In the coherent convolution, however, the signal is weaker in the vicinity of $\alpha=90^\circ$ as a result of destructive interference due to the rapid modulation of the angular phase over the angular width ($\sim 25^\circ$ FWHM) of the alignment distribution, see eq. (3). We refer the reader to ref. [27] for the calculated molecular frame dipole phase. Fig. 3(b) shows a shallow spectral minimum along $\alpha=0^\circ$ which now appears at ~ 53 eV,

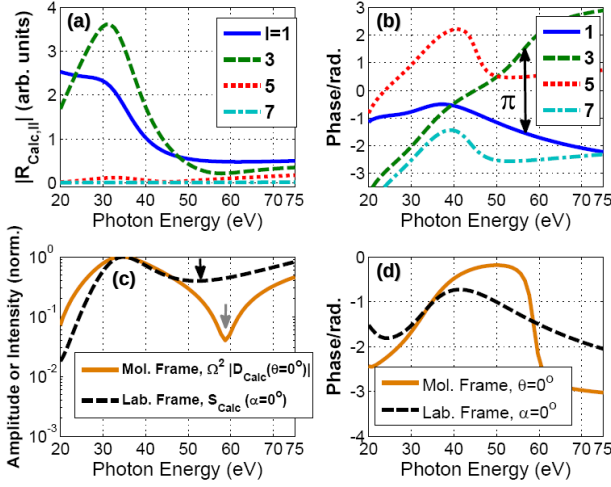


Figure 4: Decomposing the calculated photorecombination dipole $R_{Calc,\parallel}(\theta = 0^\circ)$ into contributions from the different partial spherical waves (l) describing the continuum Σ_u state in aligned ($\theta=0^\circ$) N_2 : (a) their relative amplitudes and (b) phases. A π phase difference between the dominant $l=1$ and 3 (p and f waves) components explains the strong spectral minimum at ~ 58 eV. This molecular electronic structural minimum is analogous to the Cooper minimum probed in argon [26] by high harmonic generation. (c-d) The calculated amplitude (c) and phase (d) in the molecular frame (solid line) and in the laboratory frame (dashed).

shifted to lower photon energy than found (~ 58 eV) in the molecular frame in Fig. 3(a). The shift depends on the degree of alignment. Experimentally, we observed a similar effect: from ~ 45 (Fig. 2(b)) to ~ 42 eV (Fig. 1(b)).

Our calculation also reproduces the measured high-harmonic signal at other angles: at intermediate angles ($\alpha \sim 45^\circ$) the spectral minimum almost disappears then reappears at $\alpha=90^\circ$. (At all angles, the signal in the cut-off region is stronger than observed experimentally, due to our assumption of a flat recollision amplitude spectrum as a function of energy Ω in eq. (2)). Concentrating on $\theta=\alpha=0^\circ$, our calculations agree well with experiment, the main difference being that the calculated spectral minimum is higher by ~ 8 eV. Next, we focus on the origin of this spectral minimum.

By symmetry arguments, at $\theta=\alpha=0^\circ$, only the parallel (to the laser polarization axis) component of the molecular frame recombination dipole $\vec{R}_{Calc}(\theta)$ is non-zero:

$$R_{Calc,\parallel}(\theta = 0^\circ) \propto \sum_{i=0}^{\infty} \left\langle \Psi_g^N | r | \hat{A} \Psi_g^{N-1} \Psi_{c,l=2i+1} \right\rangle, \quad (4)$$

where Ψ_g^N is the HOMO of N_2 from a Hartree-Fock calculation using a correlation-consistent valence-triple-zeta (cc-pVTZ) basis set using GAMESS [30], Ψ_g^{N-1} is the correlated $N-1$ electron ion core wave function, $\Psi_{c,l}$ are the one-electron continuum scattering states with Σ_u symmetry, and $\hat{A}$ is the appropriate antisymmetrization

operator [11]. Eq. (4) is expanded in terms of spherical harmonics $Y_l^{m=0}$ and the corresponding radial parts are solved numerically by ePolyScat [22, 23].

In Fig. 4, we decompose $R_{Calc,\parallel}(\theta = 0^\circ)$ into its partial waves (l) contributions. The two dominant components, the $l=1$ and 3 partial waves (p and f waves), are out of phase at ~ 58 eV, see Fig. 4(b), while their amplitudes are similar, see Fig. 4(a). The interference gives rise to a strong spectral minimum in the molecular amplitude, shown as the solid line in Fig. 4(c), and a less deep minimum in the expected laboratory frame spectral intensity, see dashed line in Fig. 4(c). This electronic structural minimum is analogous to the Cooper minimum [31] seen in argon [26]. In molecular photoionization, this type of interference is also referred to as a Cohen-Fano interference [32, 33]. In the molecular frame, this spectral feature correlates to a $\sim \pi$ radian phase jump, while in the laboratory frame, after coherent averaging along the lines of eqs.(1) and (2), it is only about $\pi/3$ radians, see Fig. 4(d). This is in good agreement with recent phase measurements which observe a smaller than π phase jump around the spectral minimum at $\alpha=0^\circ$ [3, 34].

Recent transient grating measurements allowed the angular amplitude and phase of aligned N_2 molecules to be retrieved [27]. They show the shape resonance around (~ 35 eV), however, due to the use of an 800 nm laser source, the Cooper minimum could not be resolved. To summarize, in aligned N_2 ($\theta=\alpha=0^\circ$), our calculations predict the co-existence of adjacent but spectrally separated features in the molecular frame: (i) the shape resonance [21] represented by the local amplitude maximum at low photon energy (~ 35 eV) followed by (ii) a local phase maximum (~ 50 eV) then (iii) the Cooper-like minimum at higher energy (~ 58 eV) accompanied with a rapid π phase change.

Our results show that we are able to extract molecular frame recombination transition moments from high harmonic measurements of aligned N_2 molecules. By deconvolving the axis alignment distribution, we are able to identify a minimum in the transition moment at 45 eV. Molecular frame photoionization calculations show qualitative agreement with the experiment, exhibiting a deep minimum at 58 eV. We provide an interpretation for this structural Cooper-like minimum which can be disentangled from a dynamical minimum underlying multi-electron hole dynamics [3, 5, 35]: the latter minimum shifts spectrally both with driving laser intensity and wavelength [5, 18]. The good agreement between experiment and theory further evidences that high-harmonic spectroscopy is a measure of field-free photorecombination dipole matrix elements [11, 12, 26]. The procedure that we have introduced will be particularly important for dynamic imaging of photo-induced chemical reactions [6, 7, 36] for which little *a priori* knowledge of the high-harmonic dipole is available. For example, it will be helpful for photo-excitation where we know the angular dis-

tribution of excited molecules exactly.

Our results are also important for the tomographic reconstruction of molecular orbitals [2]. In ref. [2], the authors assumed a π phase jump in the transition moment at 40 eV, on the basis of the observed minimum in the harmonic spectrum. In the present work, we show that the deconvolution procedure moves this minimum to 45 eV. The ePolyScat results confirm that it is indeed a π phase jump in the molecular frame. Incorporating the more accurate measurements into the tomographic procedure would reduce the observed internuclear spacing by 5%, demonstrating the accuracy of the technique.

Looking forward, it is experimentally feasible to simultaneously measure the ionization probability and the harmonic spectrum as a function of alignment angle [37, 38]. This dual procedure would further refine high-harmonic molecular frame photorecombination measurements by removing the contribution from the ionization step. We believe that high-harmonic spectroscopy will provide unparalleled resolution of the molecular frame photoionization/recombination cross section of high-lying orbitals for many molecules that can be laser-aligned.

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Supplementary Information for
Revealing the Cooper Minimum of N₂ by Molecular Frame
High-Harmonic Spectroscopy

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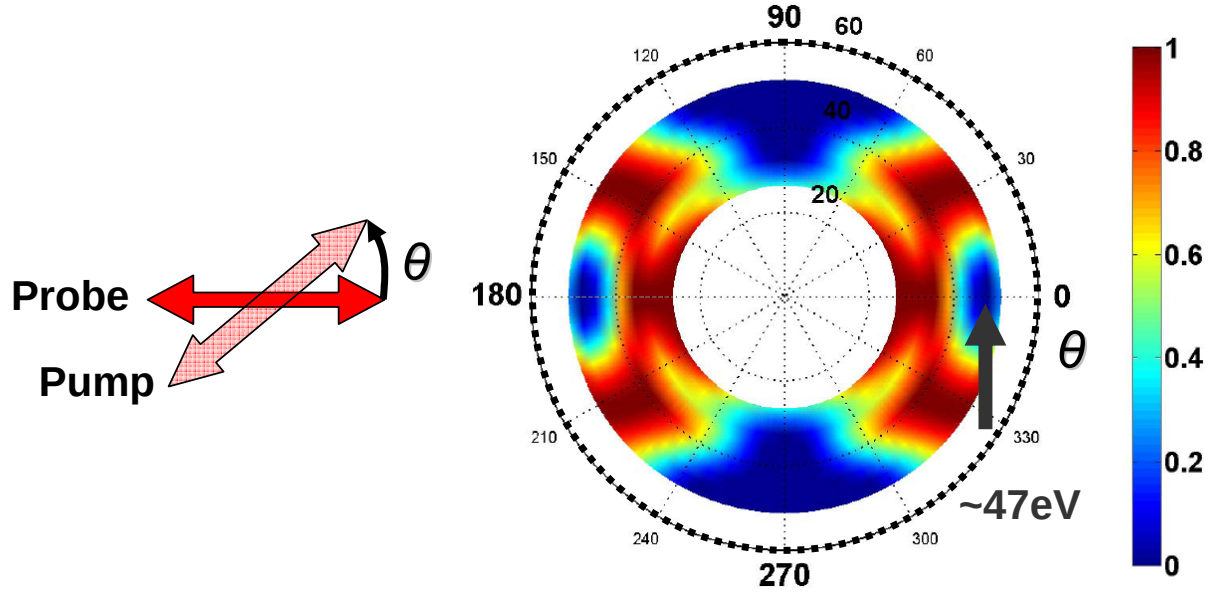


Figure S1: Normalized extracted molecular frame high-harmonic amplitude $\Omega^2 |D_{Exp}(\Omega, \theta)|$ in aligned N_2 at 800nm probe wavelength and $I_{probe} = 1.5 \times 10^{14} \text{ W/cm}^2$. The data here is the same as in Fig. 2(a) of the main paper but normalized to maximum angular yield at each photon energy. The Cooper-like minimum centered on $\theta = 0^\circ$ and $\sim 47 \text{ eV}$ at 800nm, also observed at 1200 nm driving wavelength in Fig. 2 (b) of the main paper, becomes visible here in the normalized profile. In Fig. 2 (a) of the main paper, the minimum is obscured by the low cutoff and the rapid fall off of the high-harmonic spectra with photon energy at 800 nm and $I_{probe} = 1.5 \times 10^{14} \text{ W/cm}^2$.

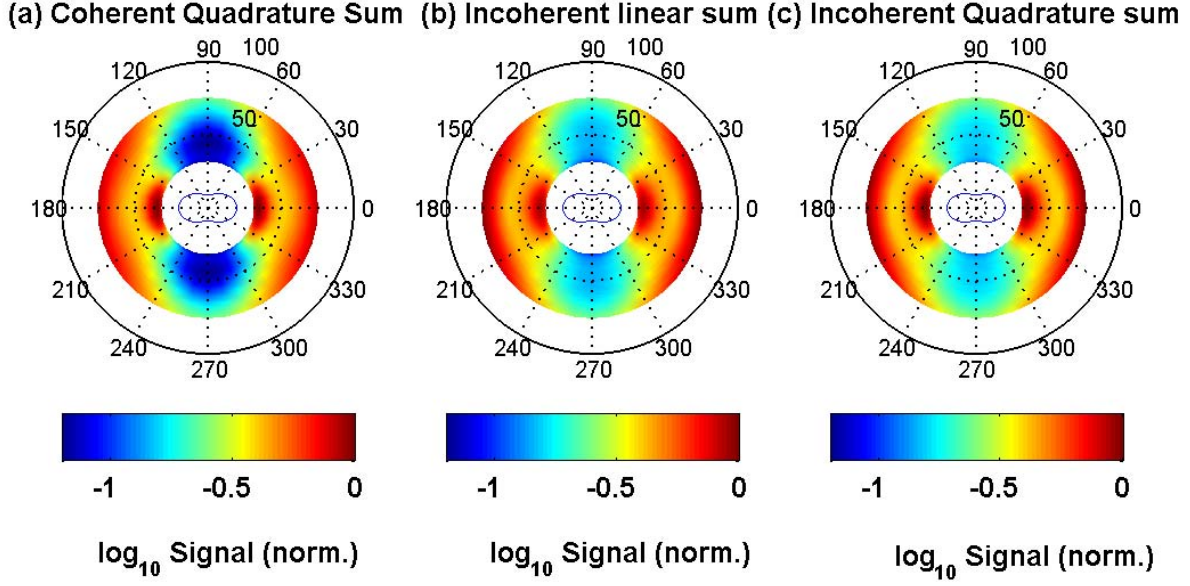


Figure S2: Calculated laboratory frame XUV Signal $S_{Calc}(\Omega, \alpha)$ using (a) coherent sums $S_{Calc}(\Omega, \alpha) = S_{\parallel}(\Omega, \alpha) + S_{\perp}(\Omega, \alpha)$ with $S_{\parallel, \perp}(\Omega, \alpha) = \left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \Omega^2 D_{\parallel, \perp}(\Omega, \theta(\theta', \phi', \alpha)) A(\theta', \phi') \times \sin \theta' d\phi' d\theta' \right|^2$ and $D_{\parallel, \perp}(\Omega, \theta) = \sqrt{I_{Calc}(\theta)} \times R_{\parallel, \perp}(\Omega, \theta)$ as defined in the paper, (b) an incoherent linear sum $S_{Calc}(\Omega, \alpha) = [\int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \Omega^2 (|D_{\parallel}| + |D_{\perp}|)(\Omega, \theta(\theta', \phi', \alpha)) A(\theta', \phi') \times \sin \theta' d\phi' d\theta']^2$, and (c) an incoherent sum of both quadratures $S_{Calc}(\Omega, \alpha) = [\int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} \Omega^2 \sqrt{|D_{\parallel}(\Omega, \theta(\theta', \phi', \alpha))|^2 + |D_{\perp}(\Omega, \theta(\theta', \phi', \alpha))|^2} A(\theta', \phi') \times \sin \theta' d\phi' d\theta']^2$ as done in eq.(1) of the main paper to retrieve the molecular frame amplitude from the experimental data. Signals are normalized to the maximum value of the parallel component in (a).

**Additional (unpublished) Supplementary Information for
Revealing the Cooper Minimum of N₂ by Molecular Frame
High-Harmonic Spectroscopy**

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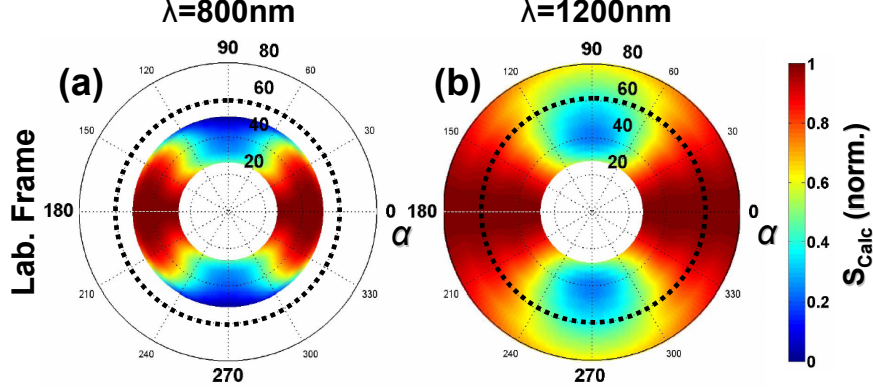


Figure 1: Normalized (per photon energy) high-harmonic yield ((a) or (b)) as a function of alignment angle α for two probe-pulse central wavelengths (800 or 1200 nm) at $I_{probe} = 1.5 \times 10^{14}$ W/cm² in aligned N₂. The high-harmonic spectra are shown on the 0-80 eV (radial) photon energy scale and, for clarity, the black dotted line always indicates the 60 eV photon energy.

I. 800 nm VS 1200 nm HIGH-HARMONIC YIELD MEASUREMENTS

In Fig. 1 (a)-(b), we show the normalized (per photon energy) laboratory frame high-harmonic spectra taken with (a) 800 nm and (b) 1200 nm light. For both wavelengths, the high-harmonic yields peak along $\alpha = 0^\circ$. At $I_{probe} = 1.5 \times 10^{14}$ W/cm², we observe no local maximum of high-harmonic yield at $\alpha = 90^\circ$ as seen for cutoff harmonics at higher laser intensity [1]. However, measuring the high-harmonic yield at two different driving field wavelengths allows us to observe that the strongest angular modulation (parallel-to-perpendicular) occurs at ~ 40 eV at 1200 nm (5-to-1) and rather always in the cutoff, here at ~ 50 eV, at 800 nm (>10 -to-1) in our experimental conditions. This laser wavelength dependence suggests that, although the measurements are made at the same low laser intensity and molecular alignment conditions, dynamical effects such as the interplay of HOMO-1 [2] may start to take place in the mid-plateau to cutoff regions (≥ 50 eV) at $\alpha = 90^\circ$. Further investigation is presented in [3].

At 1200 nm, in the retrieved molecular frame profile, the extended cutoff allows us to observe the spectral minimum in an island near 45 eV and $\theta=0^\circ$ which is confined in energy and angle, see Fig. 2(b) of the main paper. Although it is not evident in Fig. 2(a) of the main paper that the island is present at 800 nm, by normalizing the color (linear) scale the island becomes visible in Fig. 2.

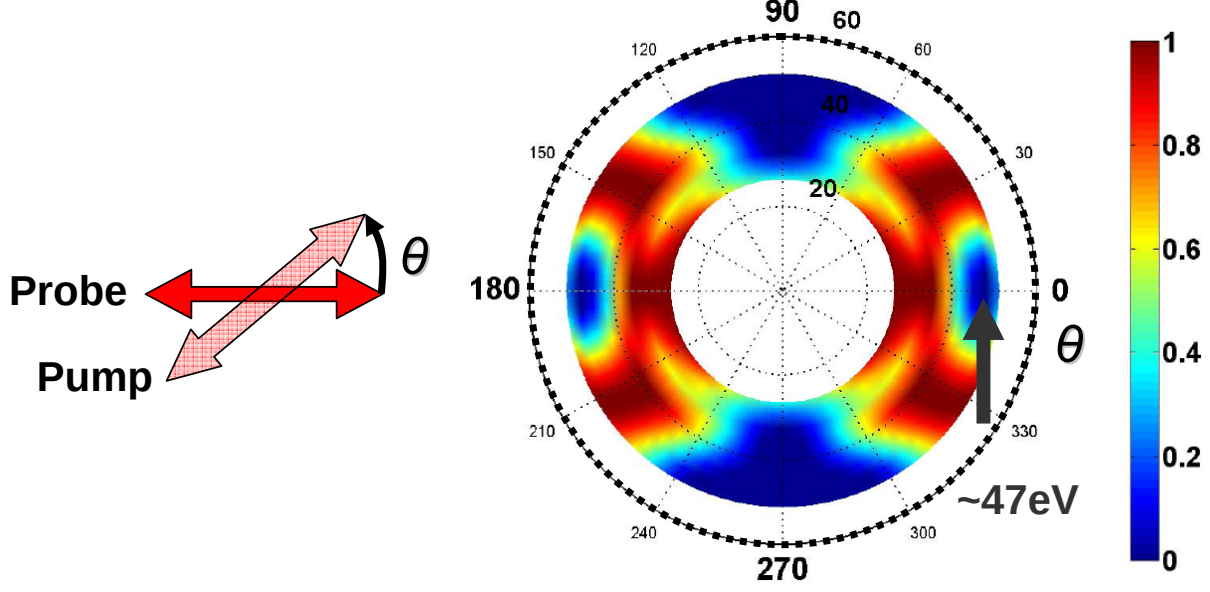


Figure 2: Normalized extracted molecular frame high-harmonic amplitude $\Omega^2 |D_{Exp}(\Omega, \theta)|$ in aligned N_2 at 800nm probe wavelength and $I_{probe} = 1.5 \times 10^{14}$ W/cm². Same as Fig. 2(a) of the main paper but normalized (per photon energy). The Cooper-like minimum centered on $\theta = 0^\circ$ and ~ 47 eV at 800nm, also observed at 1200 nm driving wavelength in Fig. 2 (b) of the main paper, becomes visible here in the normalized profile. In Fig. 2 (a) of the main paper, the minimum is obscured by the low cutoff and the rapid fall off of the high-harmonic spectra with photon energy at 800 nm and $I_{probe} = 1.5 \times 10^{14}$ W/cm².

II. COMPUTING THE RECOMBINATION DIPOLE AT $\theta=0^\circ$

We use the dispersion relation $\Omega=k^2/2+I_p$, where Ω is the high-harmonic photon frequency, k is the electron momentum defined at asymptotic distance from the core where the ionic potential is negligible and $I_p=15.7$ eV for the N_2 HOMO (σ_g). The molecular frame recombination dipole $\vec{R}_{Calc}(\Omega, \theta)$ is obtained in the following way:

$$\vec{R}_{Calc}(\Omega, \theta) = \begin{bmatrix} R_{Calc,\parallel} \\ R_{Calc,\perp} \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} d_{\parallel} \\ d_{\perp} \end{bmatrix} \quad (1)$$

where θ defines the angle between the laser polarization (linear) and the molecular axis. Initially, ePolyScat [4–6] provides a calculation of the parallel ($d_{\parallel}$) and perpendicular ($d_{\perp}$) transition dipoles defined with respect to the molecular axis. These latter quantities can be

expressed in terms of the contributions from different partial waves:

$$\begin{bmatrix} d_{\parallel} \\ d_{\perp} \end{bmatrix} \propto \begin{bmatrix} \sum_{i=0}^{\infty} \left\langle \Psi_g^N | r | \hat{A} \Psi_g^{N-1} \Psi_{c,l=2i+1} \right\rangle \\ \sum_{i=0}^{\infty} \left\langle \Psi_g^N | r | \hat{A} \Psi_g^{N-1} \Psi_{c,l=2i+1} \right\rangle \end{bmatrix} \quad (2)$$

where the scattering states $\Psi_{c,l}$ have respectively Σ_u and Π_u symmetries for the parallel and perpendicular components, Ψ_g^N is the HOMO of N_2 from a Hartree-Fock calculation using a correlation-consistent valence-triple-zeta (cc-pVTZ) basis set using GAMESS [7], Ψ_g^{N-1} is the correlated $N - 1$ electron ion core wave function, $\Psi_{c,l}$ are the one-electron continuum scattering states with Σ_u symmetry, and $\hat{A}$ is the appropriate antisymmetrization operator [8]. Eq. (2) is expanded in terms of spherical harmonics $Y_l^{m=0}$ and the corresponding radial parts are solved numerically by ePolyScat [4, 5]. Straightforwardly, in the case of molecular alignment $\theta=0^\circ$, only the parallel (to the laser field) component of the photorecombination dipole contributes to high harmonic generation:

$$R_{Calc,\parallel}(\theta = 0^\circ) = d_{\parallel} \propto \sum_{i=0}^{\infty} \left\langle \Psi_g^N | r | \hat{A} \Psi_g^{N-1} \Psi_{c,l=2i+1} \right\rangle. \quad (3)$$

See Fig. 4 (a)-(b) of the main paper for the evaluation of eq. (3).

III. THE TOTAL SCATTERING STATE AS A FUNCTION OF PHOTON ENERGY

In order to gain more physical insight into the molecular frame shape resonance at photon energy $\Omega \sim 32$ eV and the deep spectral minimum at $\Omega \sim 58$ eV, we look at the molecular frame spatial profile of the total scattering state modulus as a function of electron recolliding kinetic energy $k^2/2$: $|\sum_{i=0}^{\infty} \Psi_{c,l=2i+1}(r, \vartheta)|$, where the continuum scattering states $\Psi_{c,l=2i+1}$ have Σ_u symmetry, (r, ϑ) define the molecular frame polar coordinates in the two-dimensional plots presented in Figures 3 to 6, $\vartheta=0^\circ$ is along the horizontal x-axis (perpendicular to the internuclear axis).

In Fig. 2, we show that the shape resonance predicted in the molecular frame dipole amplitude around $\Omega \sim 30$ eV, see Fig. 3 (a) of the main paper, coincides with a rapid change in the shape of the total scattering state around $k^2/2=14$ eV ($\Omega=k^2/2+I_p$, where $I_p=15.7$ eV). Indeed, the dominant presence of the $l=3$ component (Fig. 4 (a) of the main paper), characterized by strong angular lobes at every $\vartheta=\pi/3$, is clearly observed around $k^2/2=14$ eV.

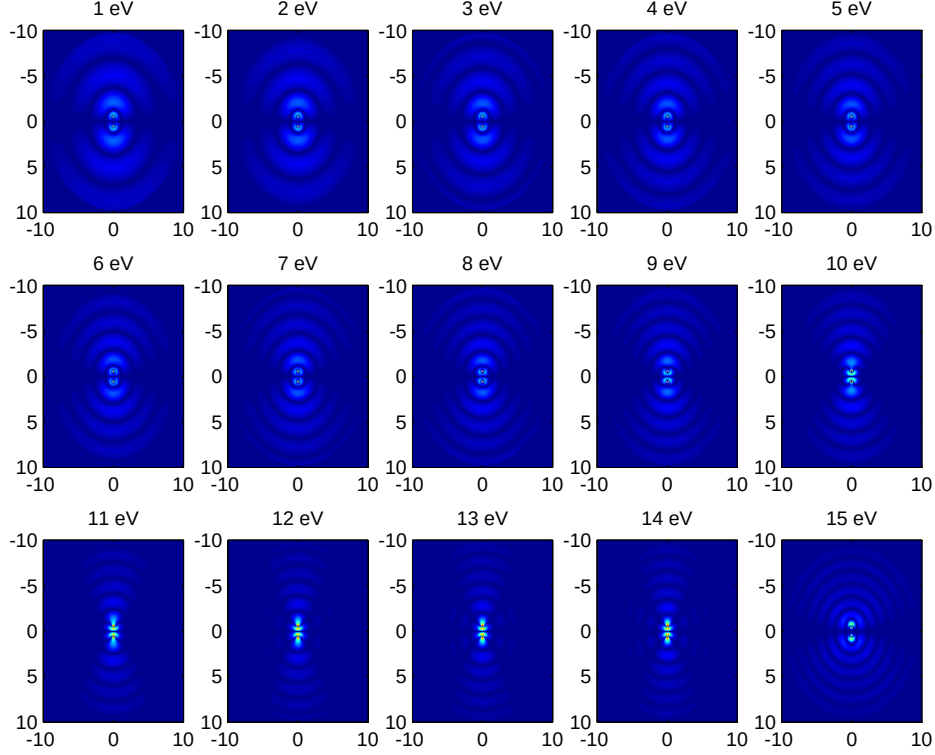


Figure 3: The modulus of the spatial profile $|\sum_{i=0}^{\infty} \Psi_{c,l=2i+1}(r, \vartheta)|$ of the only scattering state involved in photorecombination at $\theta=0^\circ$ (along the vertical axis) as a function of recolliding energy $k^2/2$. (r, ϑ) are the polar coordinates in the plots above, where $\vartheta=0^\circ$ is along the horizontal x-axis. The photon energy is given by $\Omega=k^2/2+I_p$, $I_p=15.7$ eV for the N_2 HOMO (σ_g orbital). Here, we show the range $k^2/2=1-15$ eV. The linear scale color map is renormalized at every $k^2/2$, where red represents maximum and dark blue is zero. The N_2 molecule is aligned along the vertical y-axis and each atom sits at $(x,y)=(0,\pm \sim 1.04)$ atomic units.

Increasing the recolliding kinetic energy $k^2/2$ further, no significant change is observed in the total scattering state (see Fig. 3) until $k^2/2=35$ eV ($\Omega \sim 50$ eV), see Fig. 4. This spectral location also corresponds to the onset of the deep minimum centered on $\Omega \sim 58$ eV at $\theta=0^\circ$ shown in Fig. 3 (b) of the main paper. Above $k^2/2=35$ eV, both $l=1$ and 3 are clearly visible, however, the position where the minimum is centered ($\Omega \sim 58$ eV, $k^2/2=43$ eV) can hardly be inferred solely from the spatial profile of the total scattering state.

To summarize, we have shown that both the predicted shape resonance ($\Omega \sim 30$ eV) and Cooper minimum ($\Omega \sim 58$ eV) in aligned ($\theta=0^\circ$) N_2 correlate with rapid changes in the

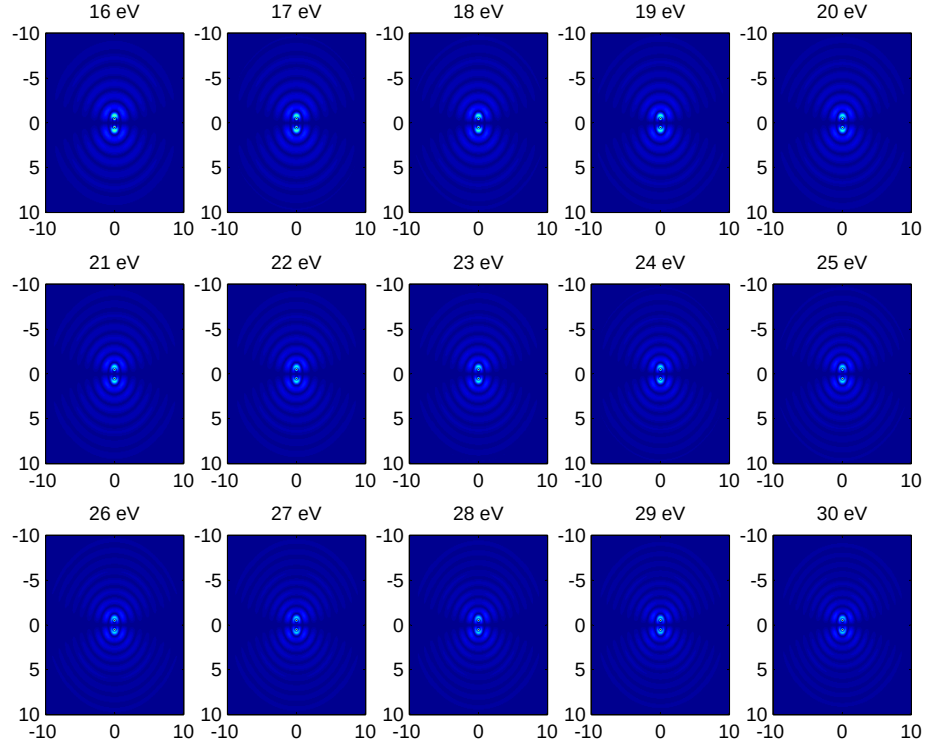


Figure 4: $k^2/2=16-30$ eV. Refer to Fig. 2 caption for all details.

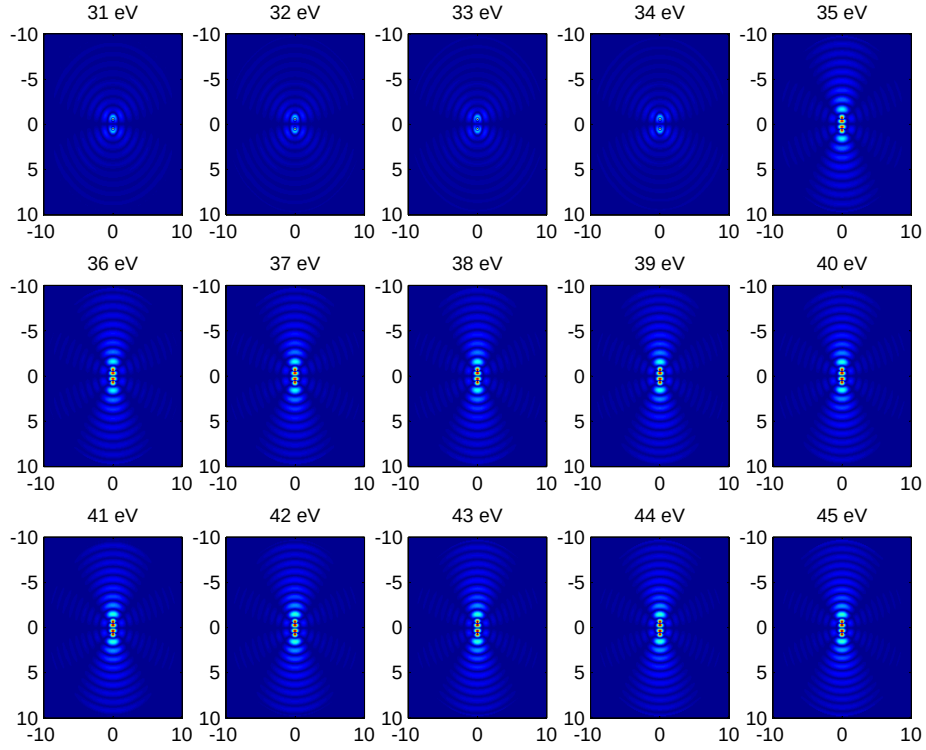


Figure 5: $k^2/2=31-45$ eV. Refer to Fig. 2 caption for all details.

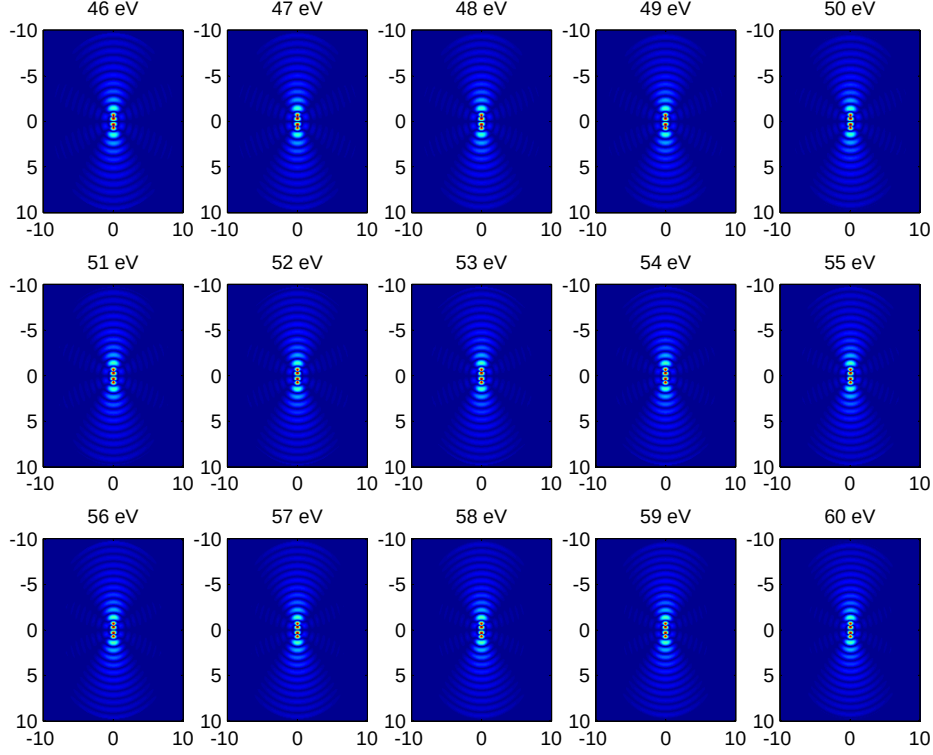


Figure 6: $k^2/2=46-60$ eV. Refer to Fig. 2 caption for all details.

spatial profile of the photorecombination one-electron continuum state $|\sum_{i=0}^{\infty} \Psi_{c,l=2i+1}(r, \vartheta)|$.

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Chapter 4

Homodyne High-Harmonic Spectroscopy of Chemical Reactions

4.1 High-Harmonic Homodyne Detection of the Ultrafast Dissociation of Br₂ Molecules (publication [6](#))

H. J. Wörner, **J. B. Bertrand**, P. B. Corkum and D. M. Villeneuve
High-Harmonic Homodyne Detection of the Ultrafast Dissociation of Br₂ Molecules
PHYSICAL REVIEW LETTERS 105, 103002 (1 September 2010).

4.1.1 Author Contributions

D.M.V. proposed the experiment. J.B.B. and D.V. Kartashov performed a series of preliminary experiments. J.B.B. adapted the experimental setup to study corrosive molecules in the gas phase, see [A.3.3](#). H. J. W. proposed the theoretical model and did the calculations. The published data was taken by H.J.W and J.B.B. and the first draft written by H.J.W. All authors interpreted the data and edited the Letter.

High-Harmonic Homodyne Detection of the Ultrafast Dissociation of Br₂ Molecules

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We report the time-resolved observation of the photodissociation of Br₂ using high-harmonic generation (HHG) as a probe. The simultaneous measurement of the high-harmonic and ion yields shows that high harmonics generated by the electronically excited state interfere with harmonics generated by the ground state. The resulting homodyne effect provides a high sensitivity to the excited state dynamics. We present a simple theoretical model that accounts for the main observations. Our experiment paves the way towards the dynamic imaging of molecules using HHG.

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PACS numbers: 33.20.Xx, 42.65.Ky, 82.53.Eb, 82.53.Kp

Simultaneous imaging of the geometric and electronic structure of a molecule as it undergoes a chemical reaction is one of the main goals of modern ultrafast science. Techniques based on diffraction [1,2] measure the position of the atoms within the molecule with high accuracy but are much less sensitive to the electronic structure of the molecule, particularly the valence shell in which the chemical transformations originate. A new complementary approach exploits the rescattering of an electron removed from the molecule by a strong laser field to measure the structure of the molecule [3]. The associated recollision also leads to high-harmonic generation (HHG) that encodes the structure of the orbital to which the electron recombines [4,5]. So far, these methods have been applied only to the electronic ground state of molecules [6–9]. Ultrafast dynamics in molecules occur predominantly in excited electronic states which can only be prepared in small fractions when multiphoton processes need to be avoided.

We extend high-harmonic spectroscopy from probing static molecular structure to probing photochemical dynamics. Using the impulsive photodissociation of molecular bromine, we show that the electromagnetic interference between high harmonics generated from the molecular ground state and the excited state occurs on the attosecond time scale. The coherent addition of the emitted radiation results in high visibility of the excited state dynamics despite the low excited state fraction.

The photorecombination step in high-harmonic generation is essentially a time reversal of photoionization. Before describing the experiment, it is useful to compare and contrast the two approaches. In femtosecond photoelectron spectroscopy, single-photon absorption creates a photoelectron which encodes information of the molecule's electronic structure in its spectrum [10,11]. In femtosecond high-harmonic spectroscopy, similar detailed information [12,13] is carried in the emitted photon. In photoelectron spectroscopy, different initial (neutral) and final (ionic) electronic states are distinguished through the

photoelectron energy. In high-harmonic spectroscopy, the broadband recolliding electron wave can only recombine to vacant states, which are selectively created by the tunnel ionization step. Tunnel ionization is exponentially sensitive to the binding energy of each ionization channel. The simultaneous measurement of a broad photon spectrum and the selection of the probed state by tunneling both point to greater simplicity for high-harmonic spectroscopy. However, the emitted photons originating from different initial electronic states overlap spectrally, adding an undesirable complexity to the interpretation of high-harmonic spectroscopy. We show that this apparent complexity becomes an advantage as the unexcited molecules can serve as a local oscillator against which we measure the excited state dynamics. Just as in a radio receiver, the local oscillator makes a weak signal that would be otherwise difficult to observe, readily visible. Moreover, the coherent detection provides a high sensitivity to the phase of the radiation, which reflects the evolution of the ionization potential along the dissociation coordinate.

The experimental setup consists of a chirped-pulse amplified titanium-sapphire femtosecond laser system, a high-harmonic source chamber equipped with a pulsed valve, and an xuv spectrometer. The laser system provides 800 nm pulses of 32 fs duration (FWHM). The laser beam is split into two parts of variable intensities using a half-wave plate and a polarizer. The minor part of the energy is sent through a 2:1 telescope and used to generate 400 nm radiation in a type I BBO of 60 μ m thickness. The major part is sent through a computer-controlled delay stage and is recombined with the 400 nm radiation using a dichroic beam splitter. The combined beams are focused into the chamber using a $f = 50$ cm spherical mirror.

High-order harmonics are generated in a supersonic expansion of Br₂ seeded in 2 bars of helium. The helium carrier gas is sent through liquid Br₂ kept at room temperature. Bromine molecules are excited by single-photon absorption at 400 nm to the repulsive $C^1\Pi_{1u}$ state (see Fig. 1) and high harmonics are generated in the strong

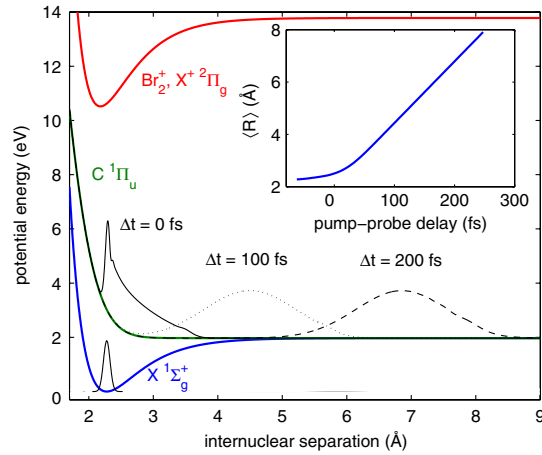


FIG. 1 (color online). Potential energy curves of Br_2 ($X^1\Sigma_g^+$ ground state and $C^1\Pi_{1u}$ excited state) and Br_2^+ ($X^+2\Pi_g$ ground state). The shape of the nuclear wave packet in the excited state after selected delays Δt is also shown. The wave packets were obtained by numerical propagation assuming a 40 fs excitation pulse centered at 400 nm. The inset shows the expectation value of the internuclear separation as a function of the pump-probe delay.

800 nm field. The focus of both beams is placed ~ 1 mm before the pulsed molecular jet expanding through a nozzle of 250 μm diameter. This setup minimizes the effect of phase mismatch and reabsorption of the high-harmonic radiation and leads to the observation of the single-molecule response [14]. The typical pulse energies of 1.5 mJ (800 nm) and 5 μJ (400 nm) result in intensities of 1.5×10^{14} W/cm² (800 nm) and 5×10^{11} W/cm². The total number of produced ions is measured by a wire mesh located 10 cm below the nozzle orifice. We have verified that the response of the ion detector was linear. The high harmonics are spectrally resolved using an aberration-corrected xuv grating and imaged by a microchannel plate detector backed with a phosphor screen using a charge-coupled device camera. The harmonic intensities are extracted by integrating the images spatially and spectrally.

Figure 1 shows the relevant potential energy curves of Br_2 and Br_2^+ . Single-photon excitation at 400 nm from the $X^1\Sigma_g^+$ ground state leads almost exclusively to the repulsive $C^1\Pi_{1u}$ state which dissociates into two bromine atoms in their ground spin-orbit state ($^2P_{3/2}$, $m_J = 1/2$) [15]. The figure also shows the shape of the vibrational wave function in the ground state and the calculated nuclear wave packet on the excited state surface at selected delays Δt after excitation by a 40 fs pump pulse centered at 400 nm. The $^2\Pi_{3/2g}$ ground state curve of Br_2^+ is also shown to illustrate the variation of the ionization potential with the internuclear distance.

Figure 2 shows the observed harmonic and ion signals in a pump-probe experiment with perpendicular polarizations. The power of H19 decreases during the excitation, reaches a minimum after the peak of the 400 nm pulse, and then recovers to its initial power level. In contrast, the ion yield increases, reaching its maximum after the peak of the

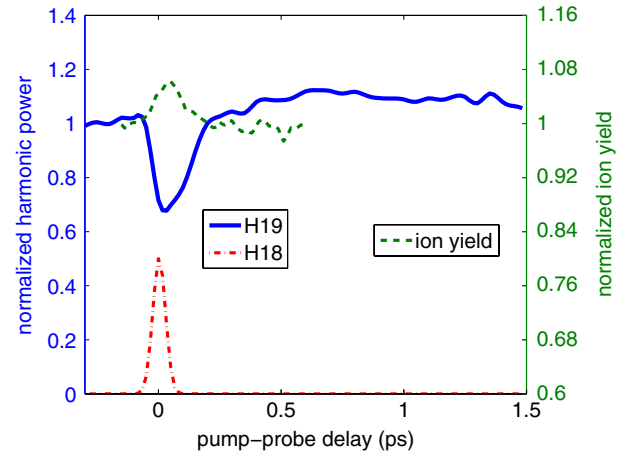


FIG. 2 (color online). Power of harmonics 19 (full line) and 18 (dash-dotted line) as a function of the delay between a 400 nm pump pulse and a perpendicularly polarized 800 nm pulse generating high harmonics (left-hand axis). The temporal overlap of 400 and 800 nm pulses leads to the emission of even-order harmonics, like H18. The total ion yield (dashed line, right-hand axis) was measured under identical conditions but with higher statistics.

400 nm pulse and subsequently decreases to its initial level. The maximum increase in ion yield amounts to 7%, whereas the harmonic signal is depleted by up to 30%. The signal of H19 and the ion yield have been normalized to unity at negative delays. This signal level corresponds to all molecules being in the ground electronic state. Temporal overlap of the 800 and 400 nm pulses leads to the appearance of even-order harmonics [16] which provide the time origin and a high-order cross correlation (~ 50 –60 fs).

When Br_2 is excited to the $C^1\Pi_{1u}$ state, the ionization potential for the removal of the most weakly bound electron is reduced from 10.5 to 7.5 eV, explaining the observed increase in the ion yield. The rising part of the ion yield curve reflects the buildup of the excited state population during the excitation pulse. As Br_2 dissociates along the repulsive $C^1\Pi_{1u}$ state, the ionization potential increases from 7.5 to 11.8 eV, resulting in a decreasing ionization rate of the excited state. Since the ionization rate increases at early delays, one might expect that the harmonic yield would also increase. However, the opposite is observed. Moreover, the variation of the harmonic signal is much larger than that of the ion signal and exceeds the excitation fraction by a factor of 2. These results clearly demonstrate a destructive interference between harmonics emitted by the excited molecules and those emitted by the ground state molecules. Destructive interference is the origin of the opposite behavior of ion and harmonic yield. To better understand the origin of the interference, we now compare the temporal evolution of different harmonic orders.

Figure 3 shows the evolution of the power of a range of odd harmonics (H13–23, $\lambda = 61$ –35 nm) with the pump-probe delay in an experiment using parallel polarizations.

The low-order odd harmonics (H13-19) approximately recover the power they had prior to excitation within a time scale of 300 fs whereas the high-order harmonics (H21-23) remain at a lower power level. The observed behavior in parallel and perpendicular (not shown) polarizations is qualitatively similar, although the time scales differ slightly.

The variation of the observed modulation with harmonic order demonstrates that the interference is tied to the nature of the trajectory of the continuum electron. The temporal extension of the short electron trajectories spans a range of 0–1.7 fs [17]. The electron transit time of harmonics emitted by species of different ionization potentials thus differs by hundreds of attoseconds [18], which is the time scale on which the interference occurs. In what follows, we develop a theoretical model to calculate the phase of the high-harmonic radiation emitted by the dynamically evolving excited state molecules.

We treat the problem within the Born-Oppenheimer approximation and write the molecular wave function at a delay Δt after excitation as

$$\Psi(\vec{r}, R, \Delta t) = c_g \Phi_g(\vec{r}) \chi_g(R) + c_e \Phi_e(\vec{r}, R) \chi_e(R), \quad (1)$$

where $\vec{r}$ is a set of electronic coordinates and R is the internuclear separation. $\Phi_g(\vec{r})$ and $\Phi_e(\vec{r}, R)$ are the electronic wave functions of the ground and excited states and χ_g and χ_e are the corresponding normalized nuclear wave functions. The radiated electric field corresponding to the photon energy Ω can be written as [19]

$$E(\Omega) \propto |c_g|^2 \langle \chi_g | \chi_g \rangle E_g(\Omega) + |c_e|^2 \langle \chi_e | \chi_e \rangle E_e(\Omega) + c_e^* c_g \langle \chi_e | \chi_g \rangle E_{eg}(\Omega) + c_g^* c_e \langle \chi_g | \chi_e \rangle E_{ge}(\Omega), \quad (2)$$

where $E_{i(j)}$ are complex spectral components. The first term in Eq. (2), proportional to $|c_g|^2$, corresponds to harmonic emission from the ground state of the molecule

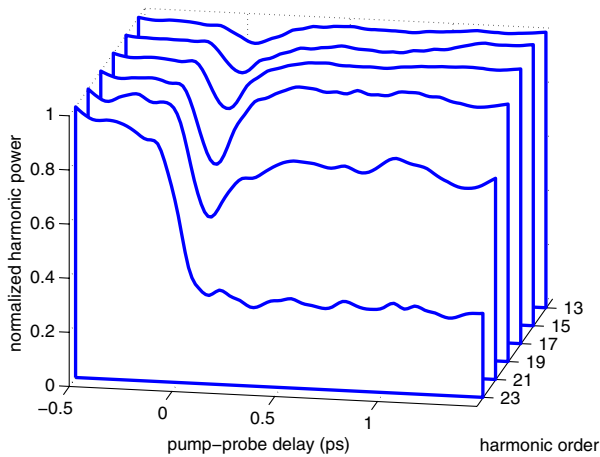


FIG. 3 (color online). Observed variation of the power of harmonics 13 to 23 as a function of the time delay between a 400 nm pump pulse and a parallel polarized 800 nm pulse generating high harmonics. The intensities have been normalized to their respective values at negative time delays.

alone, the second, proportional to $|c_e|^2$, represents emission from the excited state. Radiation can also be emitted by ionization of either of the two electronic states and recombination to the other one [20]. These cross terms are proportional to the overlap of the nuclear wave functions $\langle \chi_e | \chi_g \rangle$, which in our case decays to zero within 40 fs of the excitation. Therefore, we will only consider the first two terms. The total radiated field at photon energy $\Omega = q\omega$ can thus be represented as $E_q = (1 - r)d_g e^{i\phi_g} + r d_e e^{i\phi_e}$, where d_g and d_e are the real q th harmonic amplitudes and ϕ_g and ϕ_e are the q th harmonic phases of the ground and excited states, respectively, and $r = |c_e|^2$ is the excited state fraction.

Within the strong-field approximation, the phase of harmonic q is given by [21]

$$\phi(q, t_i, t_r) = \frac{1}{2} \int_{t_i}^{t_r} (\vec{A}(t_i) - \vec{A}(t))^2 dt + I_p(t_r - t_i) - q\omega t_r, \quad (3)$$

where t_i and t_r are the moments of ionization and recombination, respectively, $\vec{A}(t)$ is the vector potential of the laser field, and I_p is the ionization potential of the molecule. We use classical simulations of the short electron trajectories to calculate the total phase [17]. The first term in Eq. (3) is obtained by numerical integration over these trajectories. Additional contributions to the high-harmonic phase originate from the ionization and recombination steps but are neglected within the strong-field approximation.

The dissociation of Br_2 in the $C^1\Pi_{1u}$ state is simulated by propagating a wave packet on the repulsive surface using the split operator technique [22]. The potential energy curves of the $X^1\Sigma_g^+$ ground state, the $C^1\Pi_{1u}$ state, and the $X^+2\Pi_g$ ground state of the cation are shown in Fig. 1. We calculate the total harmonic power as a coherent sum of the emission from the ground and excited electronic states

$$P \propto |(1 - r)d_g e^{i\phi_g} + r \int dR |\chi_e(R)|^2 d_e(R) e^{i\phi_e(R)}|^2. \quad (4)$$

In the calculation, the excited state fraction is $r = 0.14$, matching the experimental conditions. We use an R -independent photorecombination amplitude but account for the increase in the number of emitters as one molecule dissociates into two atoms by modeling $d_e(R) = (\text{erf}(R/\text{\AA} - 4) + 1)/2 + 1$, i.e., a smoothed step function increasing from 1 to 2. ϕ_e depends on R through the coordinate dependence of the ionization potential and is calculated according to Eq. (3).

The comparison of Figs. 3 and 4 shows that the model provides a qualitative explanation of the experimental results. The power of all harmonics decreases during the excitation pulse and reaches a minimum after the peak of the excitation pulse. The power of the low harmonics (H13-H19) is found to partially recover, in agreement with the experiment. The power of the high harmonics remains low when the dissociation dynamics is over. This is the consequence of a destructive interference

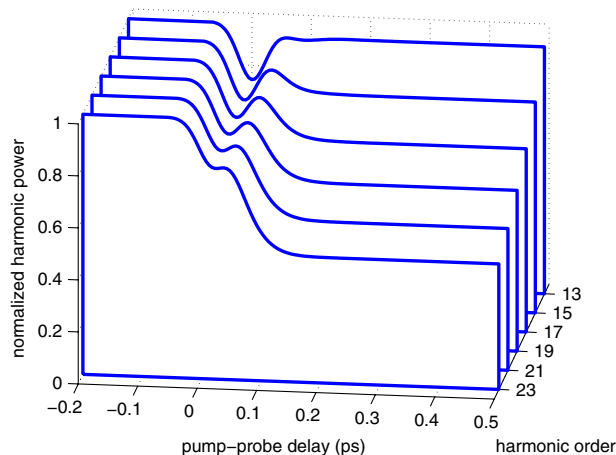


FIG. 4 (color online). Calculated variation of the power of harmonics 13 to 23 using Eq. (4). The calculations rely on a wave packet obtained by numerical propagation on the repulsive C state as shown in Fig. 1 and detailed in the text.

between the harmonics emitted by Br_2 molecules and Br atoms. The amplitude at long time delays relative to the amplitude at negative delays decreases with increasing harmonic order. This feature is observed in the experiment and is also reproduced in the calculations. The calculated phase difference of the harmonic emission between Br_2 molecules and Br atoms indeed increases from 1.6 rad for H13 to 2.5 rad for H23 under our conditions, explaining the increasingly destructive interference. The overall agreement between theory and experiment at early and late times indicates that the proposed interference model properly describes the physical phenomenon.

A noticeable difference between the experiment and the simulation is the time scale on which the high-harmonic signal reaches its asymptotic level. In the simulation, the time scale is close to 100 fs which corresponds to the time it takes to double the internuclear separation. In the experiment, the signal takes about 300 fs to recover. This time scale is surprisingly long and indicates that the transition between the molecular and atomic character of HHG takes significantly longer than what might be expected. The comparison between theory and experiment thus allows us to anticipate that the photorecombination amplitude varies with internuclear separation and that it only reaches the atomic value at very large internuclear separations ($> 9 \text{ \AA}$). More subtle differences between the experiment and the model calculations may also arise from contributions of the photorecombination phase to the harmonic phase and from the contribution of multiple orbitals to HHG. The full characterization of high-harmonic emission from dynamically evolving systems will thus require a simultaneous measurement of amplitude and phase of the high harmonics [23].

In conclusion, we have demonstrated that interference occurs on the attosecond time scale between high harmonics

emitted by the excited state of a dissociating molecule and those emitted by the ground state. This interference occurs in a single molecule but it is electromagnetic in nature. We have shown that the intrinsic homodyne nature of the method permits a very sensitive detection of chemical changes occurring on the femtosecond time scale and allows us to follow the breaking of a chemical bond. This opens up the possibility of tomographic imaging of molecular dynamics [4]. The method will allow us to follow the evolution of valence orbitals during a chemical reaction. Moreover high-harmonic generation offers the potential of attosecond temporal resolution. This advantage may be applied to study the electronic dynamics launched in the molecular cation by tunnel ionization and their dependence on the reaction coordinate.

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4.2 Following a chemical reaction using high-harmonic interferometry (publication [5](#))

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4.2.1 Author Contributions

D.M.V. proposed the experiment. H.J.W. and J.B.B. performed the experiments. J.B.B. assembled the transient grating setup. H.J.W. and J.B.B. proposed and H.J.W. conducted the data analysis. J.B.B. and D.V.K. performed a preliminary experiment. D.M.V. and H.J.W. did the theoretical calculations. H.J.W., J.B.B, P.B.C. and D.M.V. interpreted the data and wrote the Letter.

LETTERS

Following a chemical reaction using high-harmonic interferometry

H. J. Wörner¹, J. B. Bertrand¹, D. V. Kartashov^{1,2}, P. B. Corkum¹ & D. M. Villeneuve¹

The study of chemical reactions on the molecular (femtosecond) timescale typically uses pump laser pulses to excite molecules and subsequent probe pulses to interrogate them. The ultrashort pump pulse can excite only a small fraction of molecules, and the probe wavelength must be carefully chosen to discriminate between excited and unexcited molecules. The past decade has seen the emergence of new methods that are also aimed at imaging chemical reactions as they occur, based on X-ray diffraction¹, electron diffraction² or laser-induced recollision^{3,4}—with spectral selection not available for any of these new methods. Here we show that in the case of high-harmonic spectroscopy based on recollision, this apparent limitation becomes a major advantage owing to the coherent nature of the attosecond high-harmonic pulse generation. The coherence allows the unexcited molecules to act as local oscillators against which the dynamics are observed, so a transient grating technique^{5,6} can be used to reconstruct the amplitude and phase of emission from the excited molecules. We then extract structural information from the amplitude, which encodes the internuclear separation, by quantum interference at short times and by scattering of the recollision electron at longer times. The phase records the attosecond dynamics of the electrons, giving access to the evolving ionization potentials and the electronic structure of the transient molecule. In our experiment, we are able to document a temporal shift of the high-harmonic field of less than an attosecond ($1\text{ as} = 10^{-18}\text{ s}$) between the stretched and compressed geometry of weakly vibrationally excited Br_2 in the electronic ground state. The ability to probe structural and electronic features, combined with high time resolution, make high-harmonic spectroscopy ideally suited to measuring coupled electronic and nuclear dynamics occurring in photochemical reactions and to characterizing the electronic structure of transition states.

To image a molecule with an intense femtosecond laser field ($\sim 10^{14}\text{ W cm}^{-2}$), we extract an electron wave packet from one of the valence orbitals and drive it back to interfere with the remaining bound electronic state. If the electron recombines, it emits extreme-ultraviolet (XUV) radiation in a train of attosecond pulses, a process known as high-harmonic generation (HHG). All molecules in the sample radiate coherently in a phase-matched process. HHG can image a molecular orbital³ and probe rotational^{7,8} and vibrational dynamics^{9,10} in the electronic ground state. We demonstrate how HHG can also be applied to observe a chemical reaction in real time¹¹.

Molecular bromine (Br_2) serves as our exemplary molecule. Excitation at 400 nm transfers population from the $X^1\Sigma_g^+$ ground state to the repulsive $C^1\Pi_{1u}$ state in which it dissociates (Fig. 1a). Dissociation is essentially adiabatic, resulting in two bromine atoms in the $^2P_{3/2}$, $|m_j| = 1/2$ state¹². High-harmonic generation from a coherent superposition of two electronic states can proceed by ionizing from and recombining to the same or the other electronic state

(Supplementary Information section 1). All emitted fields are phase-locked to the generating field and interfere with each other, as illustrated in Fig. 1b. Once the overlap of the excited and ground-state

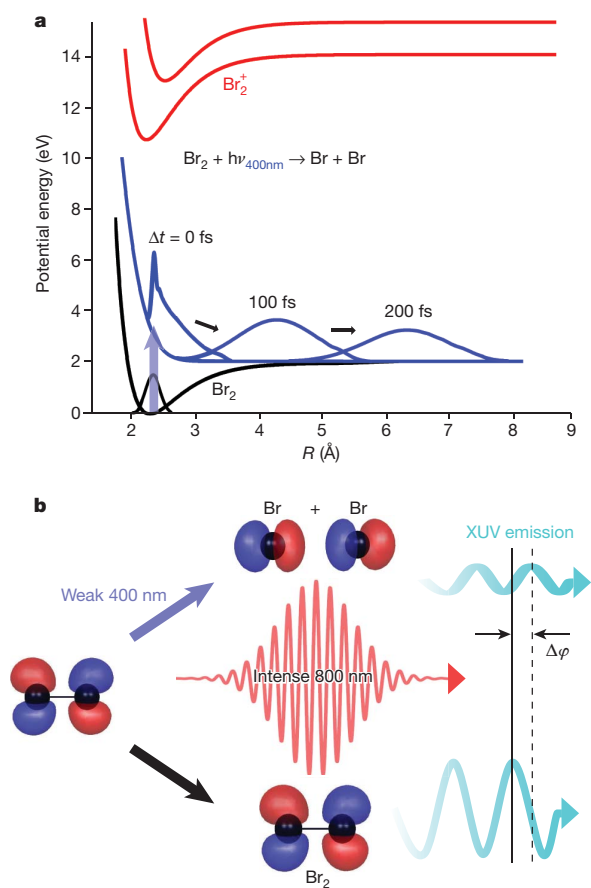


Figure 1 | High-harmonic interferometry of dissociating Br_2 . **a**, Potential energy curves of the ground and excited ($C^1\Pi_{1u}$) state of Br_2 (black and blue lines, respectively) and the lowest electronic states of Br_2^+ (red lines) as a function of the internuclear separation, R . Also shown (thicker lines) are the ground-state nuclear wavefunction (black) and the calculated excited-state wave packet (blue) at selected delays Δt following a 40-fs excitation pulse centred at 400 nm. **b**, Starting from the electronic ground state of Br_2 , a small fraction of the sample is excited and undergoes dissociation. An intense 30-fs 800-nm pulse (red) probes the dissociation dynamics at variable delays after excitation. The two electronic states, represented by their most weakly bound orbital, emit high harmonics (turquoise) that differ in amplitude and in phase ($\Delta\phi$).

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vibrational wave packets is lost, however, the coherent superposition can no longer be distinguished from a mixed sample of distinct ground-state and excited-state molecules. Only harmonics created by ionizing and recombining to the same state are possible.

We form a sinusoidal grating of excited molecules using two pump beams that cross in the medium, as shown in Fig. 2a. Horizontal planes of excited molecules alternate with planes of unexcited molecules. We generate high harmonics from this grating with a delayed 800-nm laser pulse (probe). The experiment is described in Methods. Figure 2b and c shows the yields of harmonics 13 to 21 in both the zero-order (Fig. 2b) and the first-order diffraction (Fig. 2c). The intensity of the zero-order diffraction decreases in all harmonic orders following excitation and subsequently increases to a level that depends on the harmonic order. By contrast, the first-order diffraction signal (not present at negative times) increases, reaching its asymptotic value about 300 fs after the excitation pulse. The zero time-delay and a cross-correlation time of 50 fs is monitored through the appearance of even-order harmonics (Supplementary Information section 6).

From zero- and first-order diffraction, we uniquely extract the harmonic amplitude d_e/d_g and phase $|\varphi_e - \varphi_g|$ of the excited state

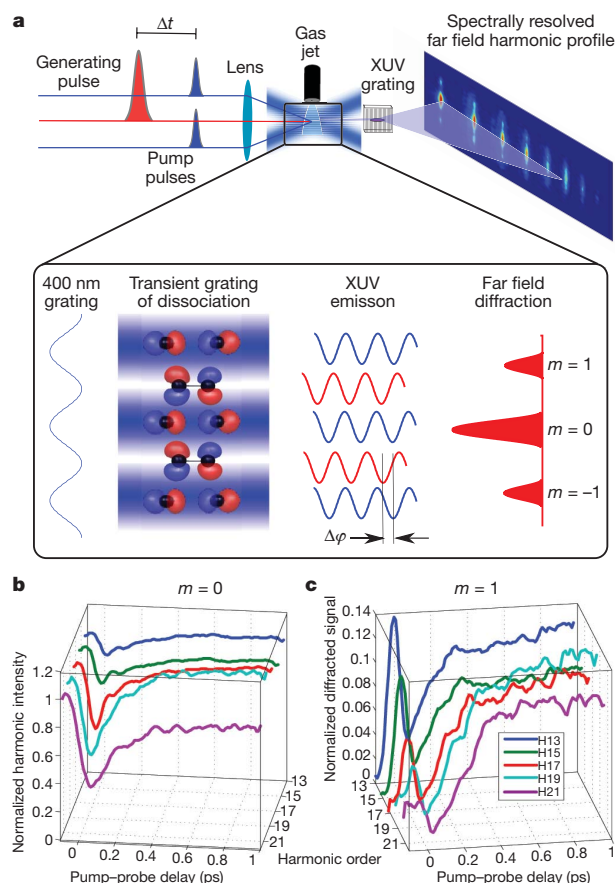


Figure 2 | High-harmonic transient grating spectroscopy. **a**, Two synchronized excitation pulses (400 nm) set up a transient grating of excitation in the molecular beam. A delayed 800-nm pulse generates high harmonics from the excited sample. The periodic modulation of the high-harmonic amplitude and phase in the near field (in the laser focus) results, in the far field (at the detector), in additional first-order diffraction ($m = 1$) signal. **b**, **c**, Evolution of the normalized intensities of harmonics 13 to 21 for parallel pump and probe polarizations in the zeroth order (**b**) and the first-order diffraction side band (**c**) with pump-probe delay. All signals have been normalized to the signal in the zeroth order at negative time delays, corresponding to molecules in the ground electronic state only.

relative to the ground state. (Here $d_{e,g}$ and $\varphi_{e,g}$ are respectively the harmonic amplitudes and phases of the ground (g) and excited (e) states, see Supplementary Information section 2). We show the experimentally determined values in Fig. 3, for pump and probe polarizations parallel (Fig. 3a) or perpendicular (Fig. 3b).

The different time evolution of the amplitude and the phase is striking. Whereas the phase reaches its asymptotic value after ~ 150 fs, the amplitude takes more than 300 fs. It is also notable that the temporal variation of the amplitude changes with the relative polarization of the excitation and harmonic generation pulses (Fig. 3a and b). In contrast, although the time-dependent phase is different for the different polarizations, it reaches the same asymptotic value at the same time delay. We will first concentrate on the phase, then discuss the amplitude.

There are two main contributions to the phase of high-harmonic radiation (Supplementary Information, section 3). First, the electron and the ion accumulate a relative phase between the time of ionization and the time of recombination. The phase shift between the same harmonic order q being emitted by two electronic states differing in ionization potential by ΔI_p can be expressed as $\Delta\varphi_q \approx \Delta I_p \bar{\tau}_q$ (ref 13), where $\bar{\tau}_q$ is the average transit time of the electron in the continuum.

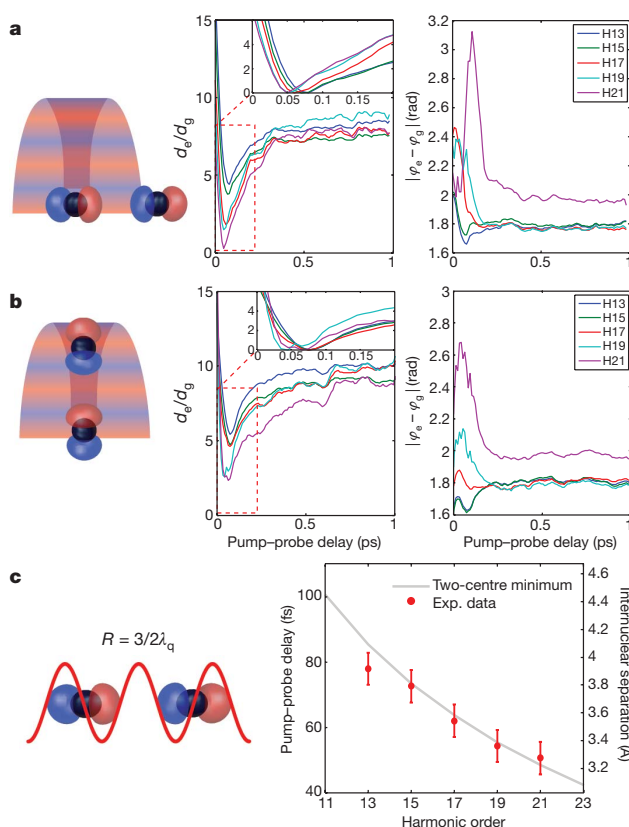


Figure 3 | Reconstruction of high-harmonic phases and amplitudes.

a, **b**, Reconstructed amplitudes (middle) and phases (right) of the excited state relative to the ground state for parallel (**a**) and perpendicular (**b**) polarizations of the 400-nm excitation pulse relative to the 800-nm generating pulse. As the $C \leftarrow X$ transition in Br_2 is perpendicular, the tunnel-ionized electron wave packet will follow a recolliding trajectory mostly perpendicular to the disk of excited molecules in **a** and parallel to it in **b**, as shown in the left column. In the insets of **a** and **b** (middle), the curves have been shifted vertically to show that the minimum occurs at different delays for different harmonic orders. **c**, Measured internuclear separation (R) as determined by the two-centre interference condition (illustrated on the left) of the dissociating molecule for each harmonic order q (error bars, s.d.). λ_q represents the de Broglie wavelength of the electron.

Second, when the electron recombines, the dipolar transition matrix element imposes an amplitude and a phase on the radiation^{14,15}. The first contribution depends on the electron trajectory (determined by the laser parameters) and the ionization potential. The second contribution characterizes the electronic structure of the molecule. It depends on the emitted photon energy and the angle of recombination in the molecular frame³.

The time evolution of the reconstructed phase in Fig. 3 can be split into two regions: the first 150 fs, where the phase varies rapidly, and the subsequent flat region where the phase is independent of the relative polarizations. The rapidly varying phase reflects the fast variation of the ionization potentials with delay. The strong dependence of the phase on the relative polarizations (Fig. 3a versus Fig. 3b) shows that the phase also traces the evolution of the electronic structure of the molecule as it dissociates. This variation occurs because the electronic structure of the bound state to which the electron recombines changes significantly. At asymptotic delays we measure Br atoms relative to ground state molecules. The phase shift is independent of the direction of recombination, because Br₂ dissociates into atoms in the $|m_l| = 1/2$ magnetic sub-level¹². The phase shift is 1.8 rad for the thirteenth harmonic (H13). Using the relation $\Delta\phi_q \approx \Delta I_p \bar{\tau}_q$, with $\bar{\tau}_q$ from a classical trajectory calculation¹⁶, we obtain $\Delta I_p = 1.3$ eV, in good agreement with the known ionization potentials of Br₂ and Br.

We now turn to the temporal evolution of the amplitudes. All harmonics go through a deep minimum at an early time (Fig. 3a and b, insets). The minimum, occurring between 51 ± 5 fs (H21) and 78 ± 5 fs (H13), measures the stretching of the orbital as the molecule dissociates. We obtain almost identical results in both polarizations because at early delays the ionization step selects molecules lying parallel to the laser field. When the electron recombines to the initial state, its de Broglie wavelength λ_q can destructively interfere with the initial state wavefunction (Fig. 3c). When the molecular orbital is an in-phase combination of two atomic orbitals, destructive interference occurs for internuclear separations $R = [(2n + 1)/2]\lambda_q$ (where n is an integer; ref. 17). Using $n = 1$ and the relation $\Omega = k^2/2$ between the photon energy Ω and the electron momentum k , we translate the minimum of H21 to a bond length of 3.3 Å and that in H13 to 3.9 Å (Fig. 3c)—in good agreement with wave-packet calculations (Supplementary Information section 4). Thus, we trace the bond length as a function of time using quantum interference.

As the molecule dissociates, one might expect additional minima corresponding to destructive interference with $n > 1$. Instead, we observe a slow rise of the amplitudes. At delays larger than 150 fs, the four valence molecular orbitals of Br₂ formed from the 4p atomic orbitals of Br become nearly degenerate, masking quantum interference in ionization or recombination. Consequently, it is only the propagation of the electron in the laser field that is affected by the second atom. For perpendicularly polarized pump and probe beams, the interaction of the ionized electron with the neighbouring atom is maximized, because the electron trajectory between tunnelling and recollision lies in the plane of the disk of dissociating atoms. As we show in Supplementary Fig. 5, the slower recovery of the amplitude in Fig. 3b reflects this fact. This property of high-harmonic spectroscopy is analogous to XAFS (extended X-ray absorption fine structure), and may be useful to probe the chemical environment of a low- I_p species (for example, a molecule in a helium droplet).

Time-resolved photoelectron measurements of the dissociation of Br₂ have demonstrated how the binding energies shift as the atoms move apart. In refs 18, 19 and 20, the time delay for the appearance of an atomic-like photoelectron spectrum is in the range 40–85 fs. In high-harmonic spectroscopy, recollision is sensitive to the electronic structure of the molecule rather than to the binding energy of individual orbitals. The minima between 50 and 80 fs show that the electron recombines with a two-centre molecular wavefunction. The absence of such minima between 100 and 150 fs suggests that at longer delays the recombination occurs to a single centre. An

analogous transition between two- and one-centre signatures has recently been observed in core-shell photoionization of a static molecule²¹. However, the recovery of the amplitudes in Fig. 3a shows that the atomic character of the electronic wavefunction is only fully established after 300 fs, significantly later than the photoelectron measurements suggest.

Before concluding, we show that spectral interferometry with high harmonics is a general technique. In every photochemistry experiment creating atomic fragments, there is a second static reference naturally present at long time delays. In our case, for time delays greater than ~ 300 fs, the medium consists of alternating planes of ground-state molecules and atomic fragments. Increasing the pump intensity to the level where the ground state depletion becomes significant, a vibrational wave-packet motion is clearly seen in the phase (Fig. 4)—but not in the amplitude (not shown)—of the highest harmonics (H19 and H21). The minimal observed modulation depth of the relative phase amounts to 0.02 rad for H19. Using the equation $\Delta\phi_q \approx \Delta I_p \bar{\tau}_q$, we measure ΔI_p as varying by 0.01 eV between the inner and outer turning points of the vibrational motion. We note that the measured phase shift corresponds to a temporal shift of the harmonic field of 450 zeptoseconds ($1 \text{ zs} = 10^{-21} \text{ s}$). The sinusoidal variation of the phase with time indicates an essentially linear variation of ΔI_p with R , which shows that the potential curves of the neutral and the ion are shifted with respect to each other²².

Clearly, there is a close connection between high-harmonic and photoelectron spectroscopy. Photoelectron spectroscopy identifies excited-state dynamics by changes in the photoelectron energy^{18,20} or angular distribution^{23,24}, whereas high-harmonic spectroscopy makes the identification through the interference of the emitted radiation. This interference gives high-harmonic spectroscopy access to both the amplitude and the phase of the recombination dipole. The phase of an outgoing photoelectron wave packet, in contrast, is very difficult to measure^{25,26}. Measuring high-harmonic phase will allow us to investigate attosecond dynamics induced by the laser field, electronic wave packets launched through ionization¹⁵, and non-adiabatic electronic dynamics^{27,28}.

Looking forward, measuring the amplitude and phase of the transition moment relative to a fully characterized ground-state reference³ will allow dynamic imaging of orbitals in a chemical reaction. Other applications in femtochemistry are possible, ranging from simple dissociation dynamics, to proton transfer, to non-adiabatic reaction

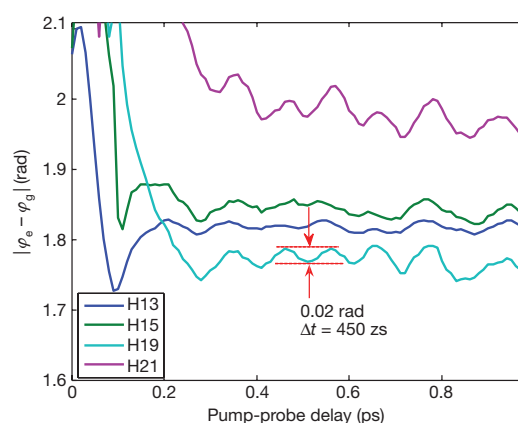


Figure 4 | Vibration-induced modulation of the high-harmonic phase. Reconstructed relative phases of harmonics 13 to 21 in an experiment similar to that shown in Fig. 3a but at higher intensity of the 400-nm excitation pulses. The fast transient in the first 200 fs measures the dissociation of the excited state. The subsequent modulation with a period of 100 fs measures the variation of the phase of the vibrating ground-state molecules relative to that of the atoms generated in the photo-dissociation process.

dynamics, to complex photochemical processes. For example, the change in electronic structure associated with the crossing of a conical intersection^{29,30} will be mapped into the harmonic radiation. In all these cases, the sensitivity of high-harmonic spectroscopy to electronic structure will provide new insight.

METHODS SUMMARY

The experiment uses a chirped-pulse amplified titanium-sapphire femtosecond laser, a high-harmonic source chamber equipped with a pulsed valve and a XUV spectrometer. The laser beam, comprising 8-mJ pulses of 32-fs duration (full-width at half-maximum, FWHM) at 800 nm, is split into two parts of variable intensities using a half-wave plate and a polarizer. The major part is sent through a computer-controlled delay stage towards the high-harmonic chamber, while the minor part is sent through a type I BBO crystal of 100- μm thickness to generate 400-nm pulses. A 50:50 beamsplitter generates two equally intense 400-nm beams that are recombined on a dichroic mirror with the 800-nm beam. The two 400-nm beams and the 800-nm beam are all parallel to each other with a vertical offset of ± 0.75 cm, and focused into the chamber using an $f = 50$ cm spherical mirror. The focus of the 800-nm beam is placed 1 mm before the molecular jet to favour the short trajectories. Typical pulse energies amount to 1 mJ (800 nm) and 3 μJ (400 nm), resulting in respective intensities of $10^{14} \text{ W cm}^{-2}$ (800 nm) and $10^{12} \text{ W cm}^{-2}$ in the bright zones of the grating. High-order harmonics are generated in a supersonic expansion of Br_2 seeded in 2 bar of helium. The high harmonics generated by the 800-nm field are spectrally resolved using an aberration-corrected XUV grating and imaged by a micro-channel plate detector backed with a phosphorescent screen using a charge-coupled device camera. The images are transferred to a computer for analysis. The harmonic intensities are extracted by integrating the images spatially and spectrally. We have verified that the reconstructed phases and amplitudes shown in Fig. 3a and b are insensitive to the chirp of the 800-nm laser pulse.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions D.M.V. proposed the experiment. H.J.W. and J.B.B. performed the experiments. J.B.B. assembled the transient grating set-up. H.J.W. proposed and conducted the data analysis. J.B.B. and D.V.K. performed a preliminary experiment. D.M.V. and H.J.W. did the theoretical calculations. H.J.W., J.B.B., P.B.C. and D.M.V. interpreted the data and wrote the Letter.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of this article at www.nature.com/nature. Correspondence and requests for materials should be addressed to D.M.V. (david.villeneuve@nrc.ca).

SUPPLEMENTARY INFORMATION

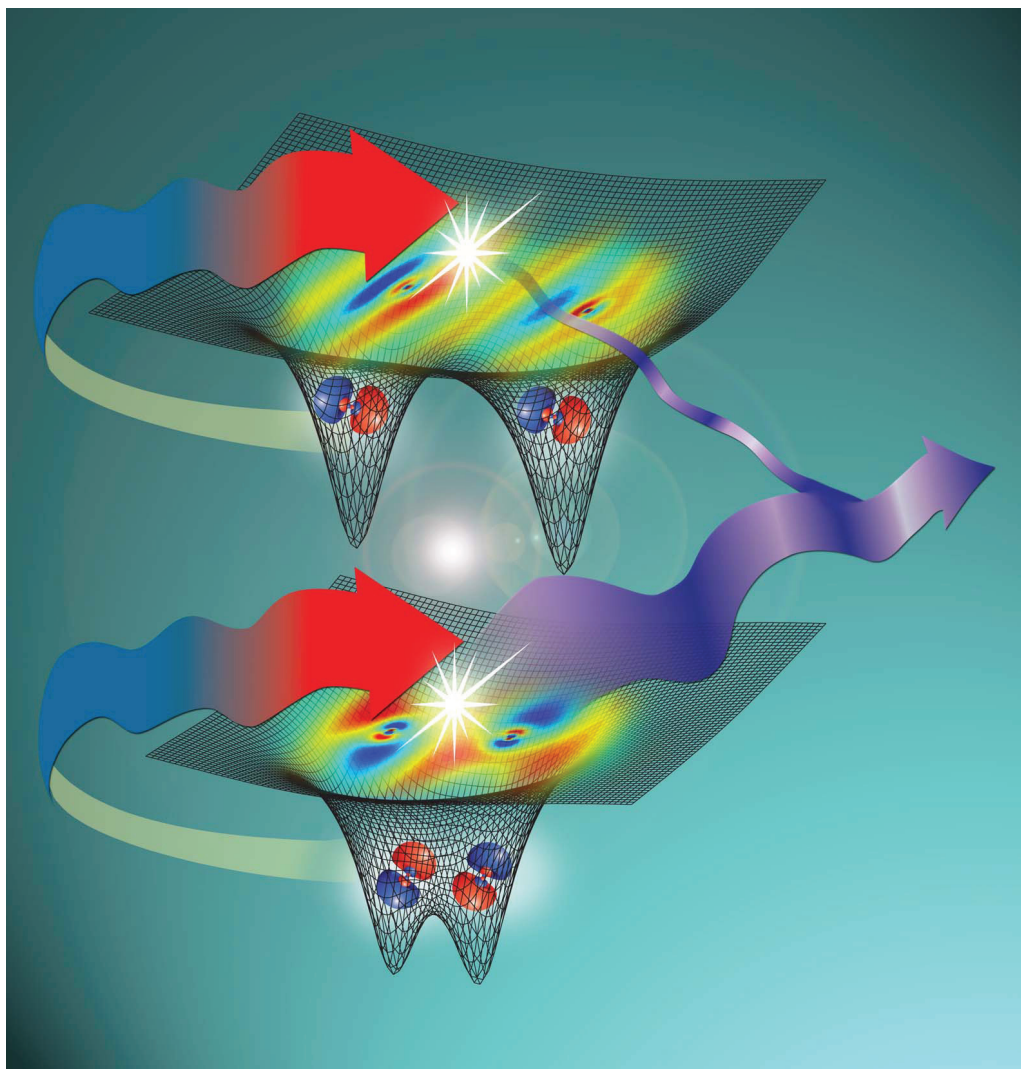


Fig. S1: High-Harmonic Interferometry of a Chemical Reaction — A weak femtosecond laser pulse excites a molecule from its ground state (on the bottom) to its excited state (on top) in which it dissociates. A strong femtosecond laser pulse removes an electron wave packet from the molecule through tunneling and accelerates it back to recollide with the parent molecule (red-blue arrows). The recollision results in emission of coherent soft-X-ray radiation (purple arrows). The figure illustrates schematically the molecular electrostatic potential and the orbital wave functions of the ground state (lower potential) and excited state (upper). We apply this method to repeatedly measure the structure of the molecule as it breaks in its excited electronic state. We exploit the static emission from the molecules in their ground state to measure, through coherent detection, both phase and amplitude of the light coming from a small number of excited molecules.

1 High-harmonic generation from a coherent superposition state

After photoexcitation, the molecule is in a coherent superposition of the ground state and an excited electronic state

$$\Psi(\vec{r}, R) = c_g \Phi_g(\vec{r}, R) \chi_g(R) + c_e \Phi_e(\vec{r}, R) \chi_e(R), \quad (1)$$

where Φ_g and Φ_e are the electronic wave functions of the ground and excited electronic states, χ_g and χ_e are the vibrational wave functions in the two states and c_g and c_e are the wave function coefficients. The electronic wave functions depend on the electronic coordinates $\vec{r}$ and depend parametrically on the internuclear separation R . The vibrational wave functions depend only on the internuclear separation R .

Using the strong-field approximation¹, the high-harmonic emission from this coherent superposition can be expressed as²

$$d_{\text{HHG}}(t) = -i \int_0^t dt' \int d\vec{k} E(t') e^{-i/2 \int_{t'}^t dt'' [\vec{k} + \vec{A}(t'')]^2} \quad (2a)$$

$$\times \left(|c_g|^2 \langle \chi_g | \chi_g \rangle d_g^*(\vec{k}, t) d_g(\vec{k}, t') e^{-iI_{p_g}(t-t')} \right. \quad (2b)$$

$$+ |c_e|^2 \langle \chi_e | \chi_e \rangle d_e^*(\vec{k}, t) d_e(\vec{k}, t') e^{-iI_{p_e}(t-t')} \quad (2c)$$

$$+ c_e^* c_g \langle \chi_e | \chi_g \rangle d_e^*(\vec{k}, t) d_g(\vec{k}, t') e^{-i(I_{p_e}t - I_{p_g}t')} \quad (2d)$$

$$+ c_g^* c_e \langle \chi_g | \chi_e \rangle d_g^*(\vec{k}, t) d_e(\vec{k}, t') e^{-i(I_{p_g}t - I_{p_e}t')} \Big),$$

where

$$d_i(\vec{k}, t) = \langle \vec{k}, t | \hat{r}_x | \Phi_i \rangle \quad (3)$$

and

$$\langle \vec{r} | \vec{k}, t \rangle = (2\pi)^{-3/2} e^{i[\vec{k} + \vec{A}(t)] \cdot \vec{r}}, \quad (4)$$

where $\vec{k}$ is the momentum of the electron and $\vec{A}$ is the vector potential of the laser field.

Four terms contribute to high-harmonic generation from a coherent superposition of two electronic states (see Eqs. (2)). Term (2a) represents high-harmonic emission by ionisation from and recombination to the ground electronic state and term (2b) represents the analogous process for the excited electronic state. Terms (2c) and (2d) represent events where ionisation takes place in the ground (excited) state and recombination leads to the excited (ground) state. The latter two terms are multiplied by the overlap of the nuclear wave packets in the two electronic states. The term $\langle \chi_e | \chi_g \rangle$ falls off very quickly for a dissociating molecule. When this term can be neglected, HHG emission is the same as for an incoherent mixture of molecules in Φ_g or Φ_e : only the first two terms in Eq. (2) play a role.

The high-harmonic generation pathways corresponding to ionization from one state and recombination to the other state are spectrally shifted from the odd harmonics. This has been shown in Refs.^{3,4}. For our case, where the two states differ in electronic parity, the emitted photon energy Ω is equal to

$$\Omega = \Omega_{ge} + 2n\omega, \quad (5)$$

where Ω_{ge} is the energetic separation of the two electronic states at the moment of excitation. In the case of Br_2 , this means that the coherent pathway is accompanied by the emission of even-order harmonics. In the experiment, even-order harmonics are also generated by the overlap of the 400 and 800 nm laser field (see Fig. S3), which shows no evidence of the coherent pathways.

2 High-harmonic emission from two electronic states and the transient grating

Assuming that the fraction of excited molecules is r (i.e. $|c_e|^2 = r$ and $|c_g|^2 = 1 - r$), that the amplitude and phase of harmonic emission are d_g and ϕ_g for the ground state and d_e and ϕ_e for the excited state, respectively, we introduce the relative amplitude $d_r = \frac{d_e}{d_g}$ and the relative phase $\Delta\phi = \phi_e - \phi_g$. The observed harmonic intensity for collinear excitation and high-harmonic generation pulses is:

$$\begin{aligned} I_{\text{total}}(r) &= |(1-r)d_g e^{i\phi_g} + r d_e e^{i\phi_e}|^2 \\ &= (1-r)^2 d_g^2 + r^2 d_e^2 + 2r(1-r)d_g d_e \cos(\Delta\phi) \\ &= d_g^2 (1 + 2r(d_r \cos(\Delta\phi) - 1) + r^2(d_r^2 - 2d_r \cos(\Delta\phi) + 1)). \end{aligned} \quad (6)$$

Normalization to the intensity from the unexcited sample (equal to d_g^2) provides

$$\frac{I(r)}{I(r=0)} = 1 + 2r(d_r \cos(\Delta\phi) - 1) + r^2(d_r^2 - 2d_r \cos(\Delta\phi) + 1). \quad (7)$$

In the transient grating geometry, the excited state amplitude is periodically modulated between 0 and $2r$ across the sample in the transverse direction with the spatial frequency k . The electric field of high harmonic emission from the ground state across a 1D-grating is

$$E_g(x) = d_g e^{i\phi_g} (1 - r(\cos(kx) + 1)) \quad (8)$$

and from the excited state

$$E_e(x) = d_e e^{i\phi_e} r(\cos(kx) + 1). \quad (9)$$

The signal in the far-field is the Fourier transform of this with the spatial frequency ξ

$$FT(E_g + E_e) = (d_g e^{i\phi_g} (1 - r) + d_e e^{i\phi_e} r) \delta(\xi) + \frac{r}{2} (d_e e^{i\phi_e} - d_g e^{i\phi_g}) \left(\delta\left(\xi - \frac{k}{2\pi}\right) + \delta\left(\xi + \frac{k}{2\pi}\right) \right). \quad (10)$$

The observed intensity distribution in the far-field is the power spectrum of Eq. (10) which means that the zeroth order has the intensity

$$\begin{aligned} I_{m=0} &= |d_g e^{i\phi_g} (1-r) + r d_e e^{i\phi_e}|^2 \\ &= d_g^2 |(1-r) + r d_r e^{i\Delta\phi}|^2 \\ &= d_g^2 (1 + 2r (d_r \cos(\Delta\phi) - 1) + r^2 (d_r^2 - 2d_r \cos(\Delta\phi) + 1)) \end{aligned} \quad (11)$$

Normalizing to the zeroth order before excitation provides

$$I_{m=0,n} = \frac{I_{m=0}}{I_{m=0}(r=0)} = (1 + 2r (d_r \cos(\Delta\phi) - 1) + r^2 (d_r^2 - 2d_r \cos(\Delta\phi) + 1)) \quad (12)$$

A single first order diffraction peak has the intensity

$$\begin{aligned} I_{m=1} &= \left| \frac{r}{2} (d_e e^{i\phi_e} - d_g e^{i\phi_g}) \right|^2 \\ &= d_g^2 \frac{r^2}{4} (d_r^2 - 2d_r \cos(\Delta\phi) + 1), \end{aligned} \quad (13)$$

and the normalized signal

$$I_{m=1,n} = \frac{I_{m=1}}{I_{m=0}(r=0)} = \frac{r^2}{4} (d_r^2 - 2d_r \cos(\Delta\phi) + 1). \quad (14)$$

Therefore, using r from the calculations described in Section 4, one can extract

$$d_r \cos(\Delta\phi) = \frac{I_{m=0,n} - 4I_{m=1,n} - 1}{2r} + 1 \quad (15)$$

and

$$d_r^2 = \frac{4}{r^2} I_{m=1,n} + 2d_r \cos(\Delta\phi) - 1, \quad (16)$$

and because $d_r \cos(\Delta\phi)$ was determined above, one gets d_r and thus $|\Delta\phi|$.

The excited state fraction r varies from 0 to r_{max} during the excitation pulse. To reconstruct d_e/d_g and $|\phi_e - \phi_g|$ from the experimental data we use the error function $\text{erf}(x)$ representing the integral of the Gaussian pulse envelope $G(t) = I_0 \exp(-t^2/2\sigma^2)$

$$r(\Delta t) = r_{max} \frac{1 + \text{erf}(\frac{\Delta t}{\sigma\sqrt{2}})}{2}, \quad (17)$$

where r_{max} is calculated by solving the time-dependent Schrödinger equation of a two state problem using the experimentally determined potential energy curves and transition dipole moments from Ref.⁷.

3 Phase of high-harmonic radiation

In the strong-field approximation, the phase of a given harmonic q has three contributions: the classical action of the laser field on the electron along its trajectory (Volkov phase), the phase accumulated by the ion relative to the neutral while the electron is in the continuum (I_p phase) and the phase resulting from the emission time of the harmonic (emission phase). Mathematically, this can be expressed as:

$$\phi_q(t, t', \vec{p}) = \int_{t'}^t dt'' \left[\frac{(\vec{p} - \vec{A}(t''))^2}{2} + I_p \right] - \Omega t, \quad (18)$$

where $\Omega = q\omega$, q is the harmonic order, ω the fundamental frequency, t' the time of ionisation and t the time of emission.

Now, if two electronic states with I_{p1} and I_{p2} emit in the same laser field, their harmonic phase can be calculated according to Eq. (18). We restrict our analysis to the short electron trajectories. If $\Delta I_p = I_{p2} - I_{p1}$ is small compared to the emitted photon energy and because the total phase must be stationary, the difference in Volkov and emission phases cancels to first order in the transit time $\tau = t - t'$. Therefore the relative harmonic phase of the two electronic states is approximately given by^{5,6}

$$\Delta\phi_q \approx \Delta I_p \bar{\tau}(q), \quad (19)$$

where $\bar{\tau}(q)$ is the average transit time for electrons originating from the two electronic states.

In the presence of a non-zero-range potential, an additional phase contribution comes from the ionisation and the recombination that will depend on the electronic state and the angle θ of the fundamental laser field with respect to the molecular axis. Thus, the total phase difference between the harmonics emitted by the two electronic states can be expressed as

$$\Delta\phi_q \approx \Delta I_p \bar{\tau}(q) + \Delta\phi_i(q, \theta) + \Delta\phi_r(q, \theta). \quad (20)$$

$\phi_i(q, \theta)$ is the phase of ionisation that will depend on the harmonic order and the angle θ , and $\phi_r(q, \theta)$ is the phase of the recombination dipole. The latter quantity carries information about the electronic structure of the molecule.

4 Wavepacket calculation of dissociation

We calculate the temporal evolution of the photodissociating nuclear wave packet on the repulsive $C^1\Pi_{1u}$ state of Br_2 by solving the time-dependent Schrödinger equation using the split-operator technique. The excited state potential curve is taken from Ref.⁷. The squared modulus of the calculated vibrational wave packet using an excitation pulse of 50 fs FWHM is shown in Fig. 1 of the main paper for delay times of 0, 100 and 200 fs. In addition, Fig. S2 shows the expectation value of the internuclear separation of the dissociating molecule.

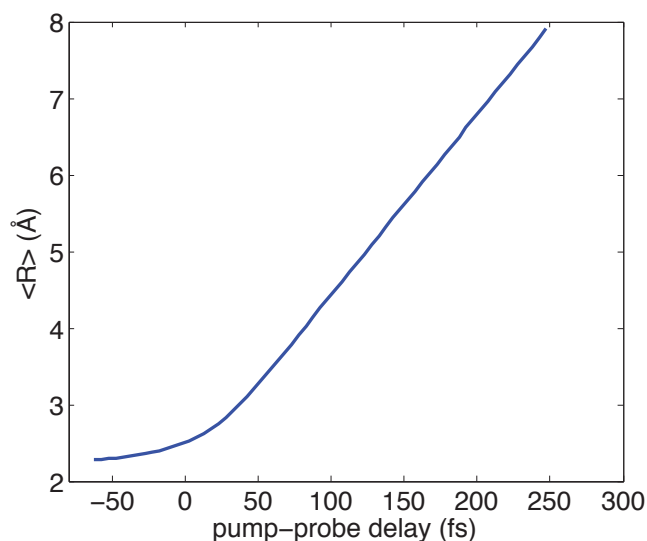


Fig. S2: Expectation value of the internuclear separation of Br_2 dissociating on the $\text{C } ^1\Pi_{1u}$ state following photoexcitation by a 50 fs (FWHM) pulse centered at 400 nm.

5 Modeling of ground state vibrational wave packet

We theoretically model the ground state vibrations in Br_2 by solving the time-dependent Schrödinger equation of a two state model subject to a 400 nm pump pulse using the potential energy curves and transition dipoles given in Ref.⁷. Using a 400 nm pump pulse matching the experimental conditions of Fig. 4 of the main article, we find that the expectation value of the internuclear separation modulates with a period of 100 fs and an amplitude of ± 0.006 Å. We estimate the high-harmonic phase difference between the vibrating ground state molecule and the atomic fragments by calculating the expectation value of the phase given in Eq. (19) over the vibrational wave packet:

$$\phi_e - \phi_g = \arg \left(\int_0^\infty |\Psi_{vib}(R)|^2 \exp(i(I_p(\text{Br}) - I_p(\text{Br}_2, g)(R))\tau) dR \right). \quad (21)$$

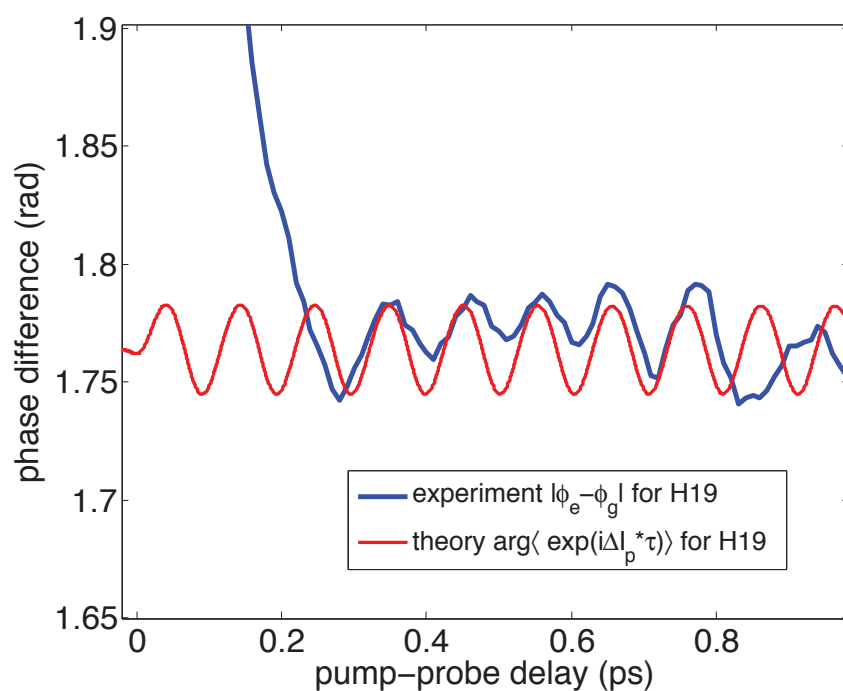


Fig. S3: Comparison of the reconstructed relative phase of H19 shown in Fig. 4 of the main article (blue line) with the theoretical value calculated as described in the above text (shifted vertically).

6 Additional experimental data

Fig. S4 illustrates the temporal resolution provided by our experiment. It shows the variation of the intensity of the zeroth order of H19 together with the variation of H20. The data is taken from the same experimental data set as Fig. 2 of the main article. The even harmonics are generated when the 800 nm and the 400 nm fields overlap because of the lost inversion symmetry of the electric fields. The appearance of even harmonics indicates the zero time delay and their width provides a high-order cross-correlation time of the two laser pulses. In Fig. S4 the FWHM of H20 amounts to 50 fs.

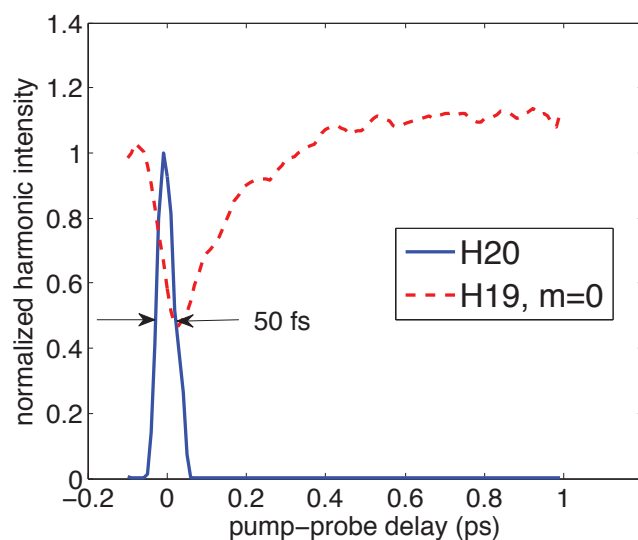


Fig. S4: Normalized intensities of the zeroth order of H19 (dashed red line) and the first order of H20 (full blue line) taken from the data set that was used to produce Fig.2 in the main article. The full-width-half-maximum of H20 amounts to 50 fs.

7 Analysis of high-harmonic amplitude dynamics

To quantify the time-evolution of the high-harmonic amplitudes shown in Fig. 3 of the main article, we have determined the delay at which the amplitude has recovered to half the asymptotic value and plot the result in Fig. S5. This delay is nearly independent of the harmonic order in the case of Fig. 3 (a) amounting to 170 ± 10 fs, whereas in case of Fig. 3 (b) it increases linearly from 150 ± 10 fs (H13) to 300 ± 10 fs (H21) corresponding to internuclear separations increasing from $5.6 \text{ \AA}$ to $9.1 \text{ \AA}$. The classical excursion amplitudes of the electron in the continuum increase from $2.6 \text{ \AA}$ to $6.6 \text{ \AA}$ over the same range of harmonics, as represented by the red line in Fig. S5, highlighting the direct relation between the extension of the electron trajectory and the internuclear separation.

We have thus shown that the high harmonic amplitude is highly sensitive to the presence of a neighboring atom up to very large distances.

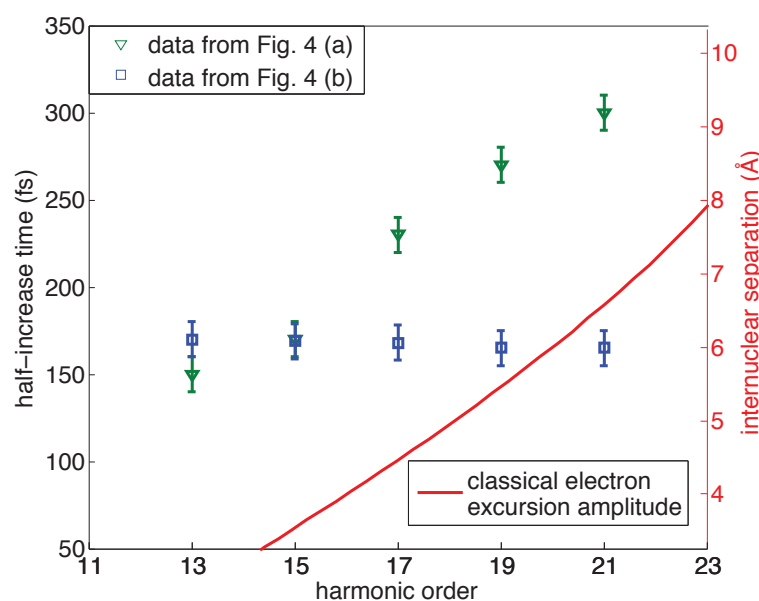


Fig. S5: Delays taken from Fig. 3 of the main article at which the amplitude d_e/d_g has recovered to half its asymptotic value. The right vertical axis represents the internuclear separation corresponding to the delay times indicated on the left vertical axis. The red line represents the extension of the classical electron trajectory corresponding to the emission of a given harmonic order.

It is interesting to note that there have been several single-electron, fixed-nuclei simulations suggesting that shorter wavelength high harmonics could be produced if dissociating molecules were used^{8–11}. This experiment tests that hypothesis on a realistic molecular system for the first time. Our results suggest that the conditions to achieve an extended plateau using molecular dissociation will be hard to meet. As pointed out in Ref.¹¹, electron correlation suppresses these "transfer harmonics" in symmetrically dissociating homonuclear diatomic molecules.

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4.3 Conical Intersection Dynamics in NO₂ Probed by Homodyne High-Harmonic Spectroscopy (publication 9)

H. J. Wörner, **J. B. Bertrand**, B. Fabre, J. Higuët, H. Ruf, A. Dubrouil, S. Patchkovskii, M. Spanner, Y. Mairesse, V. Blanchet, E. Mével, E. Constant, P. B. Corkum and D. M. Villeneuve

Conical Intersection Dynamics in NO₂ Probed by Homodyne High-Harmonic Spectroscopy Science 334, pp. 208-212 (14 October 2011).

4.3.1 Author Contributions

D.M.V. proposed the experiment and H.J.W. led the project. H.J.W., J.B.B., B.F., J.H., H.R., A.D. and E.C. performed the experiments (at CNRC in Ottawa). J.B.B. assembled the transient grating setup. H.J.W., S.P., M.S. and D.M.V. performed the calculations and elaborated the theoretical model. The first draft was written by H.J.W. All authors interpreted the data and contributed to writing the Report.

above examine relatively simple binary systems, where only a single type of DNA sticky end duplex is created. However, because of the polyvalent nature of the DNA-NPs and the base sequence programmability of DNA, one is not necessarily restricted to a single type of favorable particle interaction in a given lattice. By cofunctionalizing a nanoparticle with different linkers that contain different base sequences, multiple sequence-specific DNA duplex interactions are possible (Fig. 4A). This is an inherent distinction and potential advantage of using a sequence-programmable linker such as DNA, as opposed to entropy- or charge-dominated assembly processes.

This rule was tested by cofunctionalizing a nanoparticle with two different linkers: one that bore a self-complementary sticky end, and one that bore a sticky end sequence complementary to the sticky ends of a second particle. In this system, the cofunctionalized particle (blue particle, Fig. 4A) exhibited an attractive force with respect to all particles encountered in the system, whereas the second particle (red particle, Fig. 4A) was only attracted to the first particle type. When the hydrodynamic radius size ratio of the two NPs was ~ 0.3 to 0.4 , the sticky ends were presented at the correct distances from the particle surface to form a NaCl lattice (Fig. 4B); that is, the self-complementary and non-self-complementary linkers were both at a position to form duplexes in this crystallographic arrangement. Furthermore, when the inorganic core sizes were the same on both DNA-NPs, the particles formed a simple cubic lattice, as defined by the positions of the inorganic cores (Fig. 4C). Although NaCl and simple cubic structures are presented as the first examples of this multivalent strategy, one can envision even more sophisticated and complex systems (such as lattices with three or more nanoparticle components) using multiple DNA-programmed NP interactions.

We have presented a set of basic design rules for synthesizing a diverse array of nanoparticle superlattices using DNA as a synthetically programmable linker. These rules provide access to an easily tailorable, multifaceted design space in which one can independently dictate the crystallographic symmetry, lattice parameters, and particle sizes within a lattice. This in turn enables the synthesis of many different nanoparticle superlattices that cannot be achieved through other methodologies. Indeed, superlattices that do not follow the well-known hard-sphere packing parameter rules defined by Schiffrin and co-workers (6) and Murray and co-workers (8, 24) can easily be assembled as thermodynamically stable structures over a range of nanoparticle sizes and lattice parameters. The understanding gained from the use of these rules will both inform and enable future assembly efforts, allowing for the construction of new crystallographic arrangements that have emergent properties for use in the fields of plasmonics (14, 25, 26), photonics (27), catalysis (28, 29), and potentially many others.

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Supporting Online Material

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Tables S1 and S2
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Conical Intersection Dynamics in NO₂ Probed by Homodyne High-Harmonic Spectroscopy

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Conical intersections play a crucial role in the chemistry of most polyatomic molecules, ranging from the simplest bimolecular reactions to the photostability of DNA. The real-time study of the associated electronic dynamics poses a major challenge to the latest techniques of ultrafast measurement. We show that high-harmonic spectroscopy reveals oscillations in the electronic character that occur in nitrogen dioxide when a photoexcited wave packet crosses a conical intersection. At longer delays, we observe the onset of statistical dissociation dynamics. The present results demonstrate that high-harmonic spectroscopy could become a powerful tool to highlight electronic dynamics occurring along nonadiabatic chemical reaction pathways.

The outcome of chemical reactions is determined by the valence electronic structure of molecules. Therefore, the elucidation of elementary reaction mechanisms requires an understanding of the valence electron dynamics. Recently developed techniques that are efficient

in probing valence electron dynamics include attosecond transient absorption (1), extreme ultraviolet photoelectron spectroscopy (XUV-PES) (2), high-order harmonic spectroscopy (HHS) (3–5) and strong-field ionization (6). Both time-resolved PES (7) and time-resolved HHS are

sensitive to valence electron dynamics through the molecular photoionization matrix elements.

Electronic dynamics in molecules are particularly challenging to observe when they are strongly coupled to nuclear dynamics. Such situations often arise in polyatomic molecules where conical intersections between the potential energy surfaces induce very rapid radiationless transitions at particular nuclear configurations (see inset of Fig. 1) (8, 9). These features channel electronic excitation into atomic motion in such diverse contexts as the primary steps of vision (10) and the dynamics underlying electron transfer and the photostability of DNA bases (11).

Here, we show that high-harmonic spectroscopy reveals the variations in electronic character during the conical intersection dynamics and the subsequent dissociation of nitrogen dioxide (NO_2). We chose NO_2 , a radical, because of its model status for theories of unimolecular dissociation (12–14) and conical intersection dynamics (15–19). Our results translate the previously recognized sensitivity of HHS to electronic structure into a tool for elucidating chemical reaction dynamics.

High-harmonic spectroscopy can be factored into three steps: removal of an electron by an intense femtosecond laser field, acceleration of the electron in the laser field, and photorecombination (20, 21). Each step contributes an amplitude and a phase to the emitted XUV radiation (22–24, 20, 25). The measurement relies on a coherent detection scheme in a transient grating geometry, using unexcited molecules as a local oscillator (4, 5). It is thus sensitive to both amplitude and phase of the photorecombination matrix elements, a quantity that has recently attracted a lot of interest (26, 27). Time-resolved HHS is thus related to time-resolved PES but differs in its sensitivity to the continua associated with different ionic states. PES projects the molecular wave packet onto a set of ionic states, influenced by resonances, Franck-Condon factors, and dissociative ionization. HHS involves recombination from an energetic continuum electron with one or a few of the lowest ionic states that were selected by tunneling ionization.

A schematic representation of the potential energy surfaces of NO_2 is shown in Fig. 1. In the $\tilde{X}^2A_1$ electronic ground state, NO_2 possesses a bent equilibrium geometry and the dominant electronic configuration in the two highest occupied orbitals is $(b_2)^2(a_1)^1$. Single-photon absorption at 400 nm excites the molecule to the $\tilde{A}^2B_2$

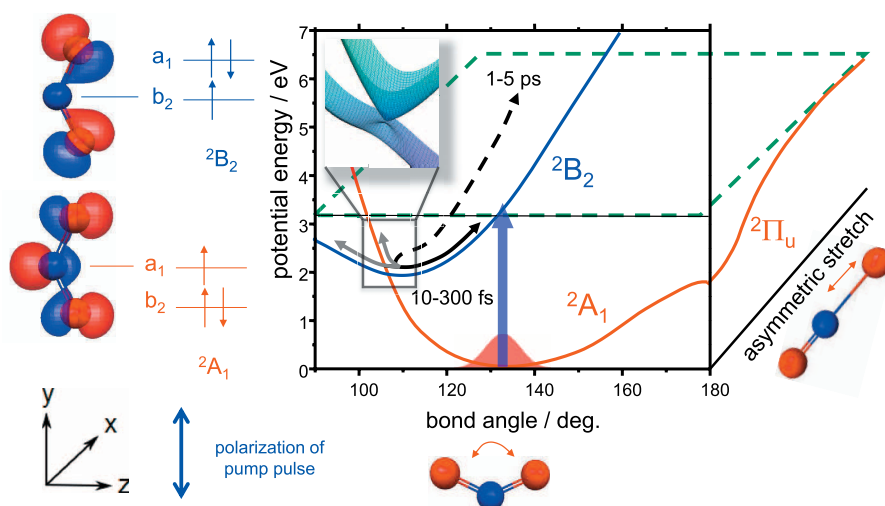


Fig. 1. Schematic representation of the potential energy surfaces of the ground $\tilde{X}^2A_1$ and excited $\tilde{A}^2B_2$ electronic states of NO_2 . The dominant electronic configuration in the two highest-lying molecular orbitals is shown for each state on the left. The orbitals are represented by isoamplitude surfaces of the wave function with color-coding of the sign. After excitation by a 400-nm pump pulse (blue arrow), the wave packet initially moves along the bending coordinate, crosses the conical intersection (shown in the top left inset) several times during the first 100 fs, and spreads along the asymmetric-stretch coordinate. Wave-packet population that has returned to the ground electronic state and possesses an energy above 3.1155 eV (green dashed line) dissociates on the picosecond time scale (dashed arrow).

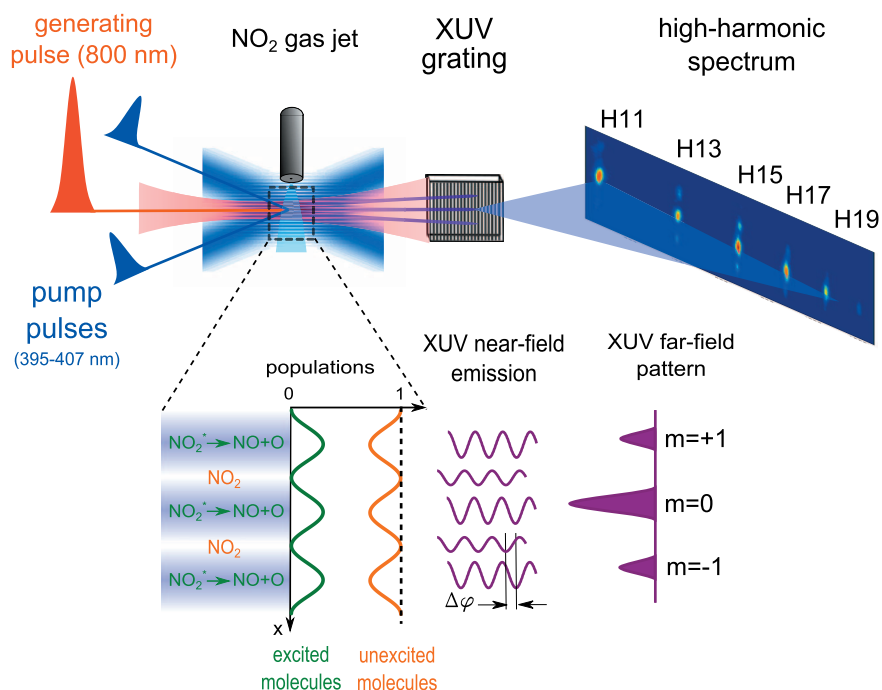


Fig. 2. Experimental setup for high-harmonic transient grating spectroscopy as first described in (4). The transient grating creates a spatially modulated population of excited molecules accompanied by a depletion of the unexcited molecules. The periodic structure results in a modulation of amplitude and phase of the XUV emission in the near field that leads to first-order diffraction in the far field. An XUV grating disperses the radiation in one dimension while the beam freely diverges in the other dimension. With $r(\cos(kx) + 1)$ being the spatially modulated excitation fraction, the signal in $m = 0$ is given by $I_{m=0} = |(1-r)d_g e^{i\phi_g} + r d_e e^{i\phi_e}|^2$ and that in $m = \pm 1$ by $I_{m=\pm 1} = \frac{r^2}{4} |d_e e^{i\phi_e} - d_g e^{i\phi_g}|^2$, where the symbols are defined in the text relating to Eq. 1.

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state of dominant configuration $(b_2)^1(a_1)^2$. The $\tilde{A}^2B_2$ excited state forms a conical intersection with the ground state (see inset of Fig. 1). Wave-packet calculations have shown that within the first femtoseconds after excitation, the nuclear wave packet moves along the bending coordinate toward the conical intersection, where it can either cross the intersection and remain on the same diabatic surface or else stay in the upper cone of the intersection and thus change the diabatic surface (gray arrows in Fig. 1) (15–18). After a few hundred femtoseconds, the nuclear wave packet returns to the electronic ground state through internal conversion. If the energy of the absorbed photon lies above the first dissociation limit at 3.1155 eV (397.95 nm) (all quoted wavelengths are vacuum values), the molecule dissociates into NO ($X^2\Pi_{\Omega}$) and O (3P_J) on the picosecond time scale (dotted arrow in Fig. 1). Previous studies using laser-induced fluorescence have characterized the picosecond dissociation in detail (14, 28). However, the femtosecond conical intersection dynamics has been largely obscured by competing multiphoton processes (19), requiring elaborate coincidence detection methods (29).

The experimental setup is illustrated in Fig. 2. We excite NO₂ in a transient grating formed from two synchronized 400-nm laser pulses and probe its dynamics by high-harmonic generation from an 800-nm, 32-fs laser pulse (4, 30). The excitation pulses are generated either in a 2-mm-thick β -barium borate (BBO) crystal, providing 160-fs pulses of 1-nm spectral width tunable from 395 to 407 nm or in a 100- μ m-thick BBO crystal, giving 40-fs pulses of 5-nm spectral width. The combination of the transient grating with an XUV monochromator allows us to spectrally resolve the high harmonics (H11 to H21 in this experiment) and to measure both the undiffracted ($m=0$) and diffracted ($m=\pm 1$) components of each harmonic order. The signal observed in $m=0$ is equivalent to a measurement done in a collinear pump-probe geometry, whereas the diffracted signal results from an interference between equal populations of excited and unexcited molecules (4).

We first discuss the picosecond photodissociation dynamics, which show that our measurement is dominated by single-photon absorption. The measurements were done with the 160-fs pulses, but we have obtained fully consistent results with the 40-fs pulses. The dynamics observed after excitation by pump pulses centered at 407 or 397.2 nm are shown in Fig. 3, A and C, respectively. Figure 3A shows a step-like decrease of the undiffracted XUV radiation and a corresponding increase of the diffracted intensity. The total ion yield, measured simultaneously and shown in Fig. 3B, increases, whereas the high-order harmonic signal decreases; this indicates a destructive interference between harmonics emitted by the ground state and those emitted by the excited state (4, 5). In this scan, performed with a 200-fs delay step, there is no

signature of any regular dynamics. Figure 3, C and D, however, show exponential growth or decay on the picosecond time scale, following the step-like variations.

The combined information from Fig. 3 shows that the step-like response to excitation below threshold characterizes electronic excitation without dissociation (Fig. 3, A and B), whereas the exponential variation of the signal in Fig. 3, C and D shows the unimolecular decomposition of NO₂. To quantify these observations, we introduce a simple model. When excitation takes

place below threshold, the radiated XUV field can be described as in Eq. 1

$$E_{\text{XUV}}(\Omega) = (1-r)d_g e^{i\phi_g} + r d_e e^{i\phi_e} \quad (1)$$

where r is the spatially modulated fraction of excited molecules, and d_g , d_e and ϕ_g , ϕ_e are the high-harmonic amplitudes and phases of the ground or excited molecular states, respectively. When the excitation frequency exceeds threshold, the excited molecules can undergo dissociation into NO($^2\Pi$)+O(3P) that, together, emit harmonics

Table 1. Molecular parameters for strong-field ionization and high-harmonic generation, determined by fitting Eqs. 1 and 2 to the experimental data shown in Fig. 3, A to D. The excitation fraction r has been determined from the experimental parameters as described in the text.

Species	r	i/l_i	H13		H15		H17	
			d/d_g	$ \phi - \phi_g (\text{rad})$	d/d_g	$ \phi - \phi_g (\text{rad})$	d/d_g	$ \phi - \phi_g (\text{rad})$
NO ₂ [*] (407 nm)	0.15	4.5	3.0	2.03	2.3	2.02	1.2	2.24
NO ₂ [*] (397 nm)	0.15	4.5	3.2	1.94	2.1	1.92	1.1	4.22
NO + O (397 nm)	0.15	2.3	6.1	2.09	4.1	2.00	1.4	1.87

$\tau = 2.71 \pm 0.15$ ps

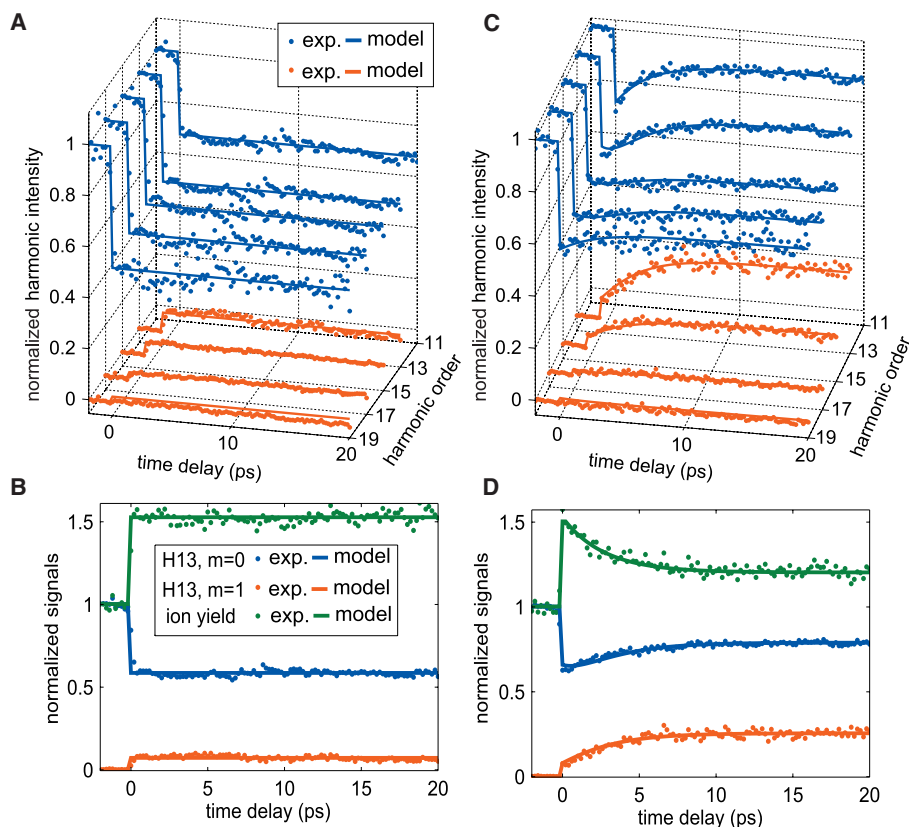


Fig. 3. High-harmonic and ion yields as a function of delay between two synchronized near-UV pump pulses setting up a transient grating and an 800-nm probe pulse generating high harmonics in the excited sample. (A) The yield of diffracted (red dots) and undiffracted (blue dots) high-harmonic signals, normalized to the undiffracted signal at negative pump-probe delays, for excitation by 407-nm pump pulses. The full lines represent the results of the theoretical model described in the text. (B) H13, $m=0$, and $m=1$ from (A) together with the total ion yield measured in parallel to the experiment (green dots) and the theoretical model (green line). (C and D) The same observables as (A and B), but for a pump pulse centered at 397.2 nm. Polarization of pump and probe are parallel. The typical pump energy is 10 μ J to minimize multiphoton processes.

with a resultant amplitude d_f and phase ϕ_f . The radiated XUV field is then given by Eq. 2

$$E_{\text{XUV}}(\Omega, t) = (1 - r)d_g e^{i\phi_g} + r e^{-t/\tau} d_e e^{i\phi_e} + r(1 - e^{-t/\tau}) d_f e^{i\phi_f} \quad (2)$$

where t is the time elapsed since excitation and τ is the time constant of the unimolecular dissociation.

To extract the relevant parameters from the measurement, both the diffracted and undiffracted high-harmonic signals are normalized by the signal measured in the absence of excitation (namely, $|d_g|^2$). We calculate the excited state fraction from the measured pulse energy, focal spot size, and the known absorption cross section of NO₂ and determine the unknown parameters in a global nonlinear least-squares fit. The determined parameters are given in Table 1, and the corresponding fit is shown as full lines in Fig. 3, A to D. The total ion yield is represented by equations similar to Eqs. 1 and 2 but with phases set to zero.

The global fit to all high-harmonic orders and ion signals in Fig. 3, B and D, provides a

time constant $\tau = 2.71 \pm 0.15$ ps, in agreement with the 2.78 ps measured previously at room temperature (14). The deep modulation of the signals demonstrates that the probed dynamics are dominated by one-photon absorption, which is in general difficult to achieve in femtosecond time-resolved measurements on molecules because of multiphoton processes (19). The strong-field ionization probability of vibrationally excited NO₂ molecules in the electronic ground state is larger than that of unexcited molecules [vertical ionization potential (I_p) =

11.2 eV] by a factor of $\left(\frac{I_p}{I_g}\right) \approx 4.5$. The ionization

rate of NO + O (dominated by NO because the vertical I_p values are 9.2 and 13.8 eV, respectively) exceeds that of the unexcited molecules by a factor of ≈ 2.3 . The relative high-harmonic amplitudes are larger for the excited molecules than for the unexcited molecules, especially for low harmonic orders, and the phase shift is substantial, as expected from the observed destructive interference. The relative amplitudes for the NO + O pair decrease particularly fast

with increasing harmonic order, as expected from the lower cutoff of the harmonic emission from NO. We thus conclude that the observed high-harmonic signal is dominated by single-photon excitation, in contrast to previous femtosecond time-resolved measurements that reported oscillatory components of periods in the range of 500 to 850 fs (31–33). The latter were indeed attributed to multiphoton excitations to higher-lying electronic states that would not emit high harmonics owing to their low binding energies.

In the following, we exploit this property to investigate the hitherto unobserved femtosecond dynamics of NO₂ in the $\tilde{A}^2B_2$ state. These measurements were done with 40-fs excitation pulses centered at 401 nm. The experimental results measured with cross-polarized laser pulses are shown in Fig. 4, A and B. Fig. 4A shows the undiffracted and diffracted signals measured in harmonics 11 through 17 (blue and red dots, respectively), and Fig. 4B shows the same quantities for H15 and H16 (green line). The latter allows an accurate determination of the zero time delay and the cross-correlation function (34). Whereas the $m = 0$ order decreases smoothly over the duration of the cross correlation, the diffracted order ($m = 1$) increases and reaches a maximum at a pump-probe delay of 35 fs. The diffracted signal subsequently decreases and reaches a minimum around 70 fs, followed by another maximum at 130 fs. Further modulations with decreasing contrast are observed at longer pump-probe delays. As we show and discuss in fig. S2 and the accompanying text, no modulations are observed in parallel polarization.

These oscillations, observed in the diffracted XUV radiation, are a fingerprint of the electronic dynamics of the molecule taking place around the conical intersection, as illustrated schematically in Fig. 4D. In the bright zones of the transient grating, the electronic character of the excited molecules oscillates between $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$. When the molecule is in the $\tilde{X}^2A_1$ state, the near-field variation of the high-harmonic emission is much smaller for most molecular geometries than when it is in the $\tilde{A}^2B_2$ state, which we detect as a variation of the intensity of diffracted radiation [see section VI of the supporting online material (SOM)].

To rationalize these observations, we introduce a simple model based on diabatic electronic states and coordinate-independent transition moments (more detailed calculations are given in the SOM). The total radiated XUV field is the coherent sum of contributions from the unexcited molecules (subscript g) and excited molecules in the two diabatic $\tilde{A}^2B_2$ and $\tilde{X}^2A_1$ states (Eq. 3)

$$E_{\text{XUV}}(\Omega, t) = [1 - r(t)]d_g e^{i\phi_g} + r_{\tilde{A}}(t)d_{\tilde{A}} e^{i\phi_{\tilde{A}}} + r_{\tilde{X}}(t)d_{\tilde{X}} e^{i\phi_{\tilde{X}}} \quad (3)$$

where $r(t) = r_{\tilde{A}}(t) + r_{\tilde{X}}(t)$ is the total fraction of excited molecules before dissociation takes

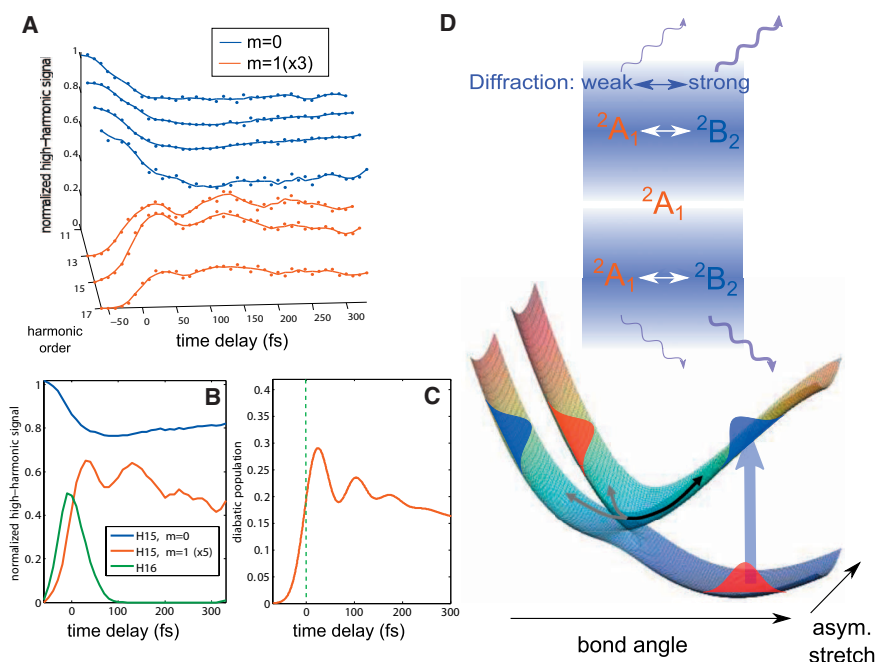


Fig. 4. (A) The high-harmonic yields after excitation by a pair of 10-μJ, 401-nm laser pulses in the undiffracted (blue) and diffracted orders (red) of the odd harmonics (H11 to H17). Experimental data points appear as dots and a three-point-smoothed version as lines. (B) The undiffracted (blue) and diffracted orders of H15 (red) and H16 (green line). (C) The diabatic excited state population from (17) convoluted with a 50-fs Gaussian cross-correlation function. (D) Illustration of how high-harmonic transient-grating spectroscopy probes the electronic character of the molecule during the conical intersection dynamics. The top illustrates the spatial intensity structure of the transient grating. The bottom shows schematically the lowest two potential energy surfaces of NO₂. When the molecule is in the excited diabatic state (represented as a blue wave packet), the high-harmonic emission differs significantly from the unexcited ($\tilde{A}^2B_2$) molecules, leading to a large variation of high-harmonic amplitude and phase across the transient grating and thus to strong diffraction. When population is transferred into the ground diabatic state (red wave packet), the modulation depth of high-harmonic amplitude and phase across the transient grating, and therefore the diffracted intensity, decreases.

place. The intensity of the diffracted light is thus given by Eq. 4 (4)

$$I_{m=1}(\Omega, t) = \frac{1}{4} |r_{\tilde{A}}(t)(d_{\tilde{A}}e^{i\phi_{\tilde{A}}} - d_g e^{i\phi_g}) + r_{\tilde{X}}(t)(d_{\tilde{X}}e^{i\phi_{\tilde{X}}} - d_g e^{i\phi_g})|^2 \quad (4)$$

The high-harmonic amplitude is determined by the probabilities of ionization and recombination. The phase is determined by the phase accumulated by the bound state ($I_p \tau$), and the recombination phase (24), where τ stands for the transit time of the electron in the continuum (~1 to 1.7 fs). To the first order, ionization from either $\tilde{A}^2B_2$ or $\tilde{X}^2A_1$ involves the removal and recombination of an a_1 electron in the cross-polarized case (Fig. 1). The main difference is due to the $I_p \tau$ phase. The ground-state channel $^1A_1 \leftarrow ^2A_1$ has an I_p of 11.2 eV, whereas the main excited-state ionization channel $^3B_2 \leftarrow ^2B_2$ has an I_p that varies between 9.8 eV and 13.2 eV as a function of the bending coordinate. The relative phase difference $\Delta\phi \tau$ stays close to zero for the $\tilde{X}^2A_1$ state, whereas it is significantly larger (between 1 and 3 radians) for most geometries of the $\tilde{A}^2B_2$ state. Hence, in Eq. 4, $|d_{\tilde{A}}e^{i\phi_{\tilde{A}}} - d_g e^{i\phi_g}| \gg |d_{\tilde{X}}e^{i\phi_{\tilde{X}}} - d_g e^{i\phi_g}|$ and the time dependence of the diffracted signal will be dominated by HHG emission from the $\tilde{A}^2B_2$ state. It is thus sensitive to the temporal variation of the population in the $\tilde{A}^2B_2$ state, as illustrated in Fig. 4D. This conclusion is also supported by the detailed calculations described in the SOM.

The observed polarization dependence of the oscillations is a consequence of the electronic symmetries. Photoexcited molecules have their y axis (O-O axis) parallel to the polarization of the exciting field (Fig. 1). In the cross-polarized experiment, the emission from excited molecules is thus dominated by those probed along their z axis (C_2 axis). The same orientation also dominates the emission from the unexcited molecules, resulting in a sensitivity to the diabatic electronic state of the excited molecule (2B_2 versus 2A_1). In the case of parallel polarizations, the photoexcited molecules are being probed along their y axis, whereas the unexcited molecules are probed along their z axis. Therefore, the emission from excited molecules in both diabatic states differs significantly from that of the unexcited molecules, and the amount of diffracted light is sensitive only to the total population of excited molecules.

Because the electronic dynamics between $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ have not been observed experimentally before, we compare the measurements to recent quantum dynamical calculations on NO_2 (17, 18). These three-dimensional wave packet calculations have predicted characteristic oscillations in the diabatic populations over the first few hundred femtoseconds. The diabatic $\tilde{A}^2B_2$ population $r_{\tilde{A}}(t)$, convoluted with a 50-fs Gaussian cross-correlation function, is shown in Fig. 4C. Both the overall behavior and the distinct features observed in the diffracted high-harmonic signal are present in the calculated

diabatic state population. The first maximum occurs at a delay of 26 fs, the first minimum at 68 fs, and the second maximum at 106 fs. The modulations in the diffracted signal thus reflect the diabatic state population dynamics. Considering the complexity of the problem and the simplicity of our model, the agreement is remarkable. To exclude the possibility that the observed modulations result from a change of the strong-field-ionization rate of the molecule as a function of the nuclear coordinates, we have also measured the total ion yield in parallel to the high-harmonic yield and have not observed any modulation on top of the smooth increase (see fig. S3 and accompanying text).

Comparing the experimental and theoretical results, we can draw a qualitative picture of the evolution of the electronic structure of the molecule as it crosses the conical intersection. Photoexcitation prepares the wave packet on the upper diabatic state as shown in Fig. 4D. When it first approaches the conical intersection, it has little expansion along the asymmetric stretch coordinate (the b_2 mode responsible for vibronic coupling), and thus most of the amplitude traverses the intersection and remains on the same diabatic state [80% according to the wave packet calculation (17)]. This fraction, the diabatic wave packet, returns to the conical intersection with a significant spread along the bond-stretching coordinate, resulting in a strong transfer to the ground diabatic state. This leads to the first minimum in the diabatic state population around 60 fs. After two or three periods of motion along the bending coordinate, wave packet components from diabatic and adiabatic traversals interfere with each other and extend so significantly along the symmetric and asymmetric stretch coordinates that no appreciable motion of the wave packet average position can be defined for times longer than 200 fs (15, 17).

High-harmonic spectroscopy is a powerful probe of electronic dynamics in nonadiabatic processes. The homodyne interference of species in different electronic states has enabled us to distinguish multiple photochemical pathways—electronic excitation to bound states versus excitation followed by dissociation. The coherence of the high-harmonic emission also enabled us to extract amplitudes and phases of the various species occurring in the photochemical transformation and to learn how to interpret them. Temporal variations in the dominant electronic configuration of the photoexcited wave packet are manifested in a polarization dependence of the pump-probe signal, which is expected to be a powerful property in future studies of electronic dynamics.

We have thus demonstrated how to use high-harmonic spectroscopy to elucidate a complex photochemical process from the first femtoseconds that are governed by a conical intersection to the picosecond time scale where dissociation proceeds statistically. Our results on the femtosecond dynamics may be used in the future to check high-level quantum dynam-

ical calculations. We anticipate that this property will be of great value to femtochemistry and ultrafast imaging.

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Supporting Online Material

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Materials and Methods

Figs. S1 to S5

Tables S1 to S6

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Correction: On pages 16 and 17, references 25, 28, and 32 have been corrected.

1 Materials and Methods

The experimental setup consists of a chirped-pulse amplified titanium-sapphire laser system (800 nm, 8 mJ, 32 fs, 50 Hz), an optical setup for generation and synchronization of multiple fundamental and second harmonic laser beams and a vacuum chamber for generation and spectral characterization of high-harmonic extreme-ultraviolet radiation.

The output of the laser system is split into two beams of variable intensities using a half-wave plate and a thin-film polarizer. The probe beam is sent through a computer-controlled delay stage. The pump beam is reduced in diameter by a 2:1 reflective telescope and frequency doubled in a BBO crystal of 0.1 or 2 mm thickness. Angle-tuning of the thick BBO crystal enables a limited tuning of the center wavelength of the second harmonic. The 400 nm beam is subsequently divided using a 50:50 beamsplitter and the two resulting beams are recombined with the 800 nm (probe) beam using a dichroic mirror. The 400 nm (pump) beams are vertically separated from the 800 nm (probe) beam by ± 0.75 cm and the three beams propagate parallel to each other onto a $f=50$ cm concave aluminum mirror that focuses them into a vacuum chamber equipped with a pulsed gas nozzle.

The nozzle is positioned ~ 2 mm after the focus of the 800 nm pulse to select high harmonics generated from the short electron trajectories. The two 400 nm beams are aligned such that they cross the 800 nm beam at the position where the high harmonics are generated. This is achieved by optimizing the wave-mixing signal described in Ref. (34). We use a supersonic expansion of neat NO_2 , using a backing pressure of ~ 1 atm and heating the nozzle to 100 °C to suppress the formation of N_2O_4 . The generated high-harmonic radiation propagates into a second vacuum chamber where it is spectrally dispersed by a spherical grating and the spectrum is imaged onto a microchannel plate detector backed with a phosphor screen. Spectral images are recorded using a charge-coupled device camera. The ions generated in the interaction region of the laser and gas pulses are collected by means of a copper mesh located 10 cm downstream of the nozzle orifice and the resulting current is detected (5).

2 Data analysis

The two pump beams set up a transient grating of intensity as shown in Fig. 2 of the main article:

$$I(x) = I_{\text{av}} (\cos(kx) + 1), \quad (1)$$

where $k = 2\pi/\Lambda$, $\Lambda = 13.3\mu\text{m}$ is the period of the grating and I_{av} is the average of the pump intensity over the dimension x . One-photon excitation transfers a fraction of the molecules from the ground state (g) into the excited state (e). Consequently, the excitation fraction is also modulated spatially according to

$$r(x) = r (\cos(kx) + 1), \quad (2)$$

where r is the excitation fraction averaged over x .

For a given photon energy Ω of the high-harmonic spectrum, the emission of the ground state can be written in terms of its amplitude and phase as $E_g(\Omega) = d_g e^{i\phi_g}$ and the emission of the excited state as $E_e(\Omega) = d_e e^{i\phi_e}$. The high-harmonic emission across the transient grating is thus given by

$$\begin{aligned} E(\Omega, x) &= E_g(\Omega, x) + E_e(\Omega, x) \\ &= (1 - r(x))d_g e^{i\phi_g} + r(x)d_e e^{i\phi_e} \\ &= (1 - r)d_g e^{i\phi_g} + r d_e e^{i\phi_e} + r \cos(kx) (d_e e^{i\phi_e} - d_g e^{i\phi_g}). \end{aligned} \quad (3)$$

The high-harmonic emission $E(\Omega, x)$ thus consists of a term that is independent of x and one that is proportional to $\cos(kx)$. The spectrally resolved far-field harmonic profile is given by the Fourier transform of $E(\Omega, x)$ which is (4)

$$FT(E(x)) = \left((1-r)d_g e^{i\phi_g} + r d_e e^{i\phi_e} \right) \delta(\xi) + \frac{r}{2} \left(d_e e^{i\phi_e} - d_g e^{i\phi_g} \right) \left(\delta\left(\xi - \frac{k}{2\pi}\right) + \delta\left(\xi + \frac{k}{2\pi}\right) \right). \quad (4)$$

The observed signal can thus be determined from Eq. (4) to consist of a non-diffracted part of intensity

$$I_{m=0} = \left| (1-r)d_g e^{i\phi_g} + r d_e e^{i\phi_e} \right|^2 \quad (5)$$

and first order diffraction ($m = \pm 1$) of intensity

$$I_{m=\pm 1} = \frac{r^2}{4} \left| d_e e^{i\phi_e} - d_g e^{i\phi_g} \right|^2. \quad (6)$$

The non-diffracted signal thus results from the interference of emissions from the two states, weighted by their populations, whereas the diffracted signal results from interference of the emissions with equal weights. The signal in $m = 0$ is thus equivalent to what is observed in a collinear pump-probe experiment (5), whereas the diffracted signal enhances the contribution of the excited state.

The spectral images observed for three different delay times between the two synchronized 400 nm (transient grating) pulses and the 800 nm generating pulse are displayed in Fig. S1. Image a) was taken at a negative time delay (800 nm pulse preceding the 400 nm pulse) and only shows the odd harmonics from H11 to H21. Image b) corresponds to temporal overlap of all three pulses and shows, in addition to the odd harmonics, several other frequency components arising from non-linear wave mixing of the three pulses, as described in Ref. (34). Image c) was taken at a positive time delay and shows diffracted high-harmonic radiation above and below each of the odd harmonic orders.

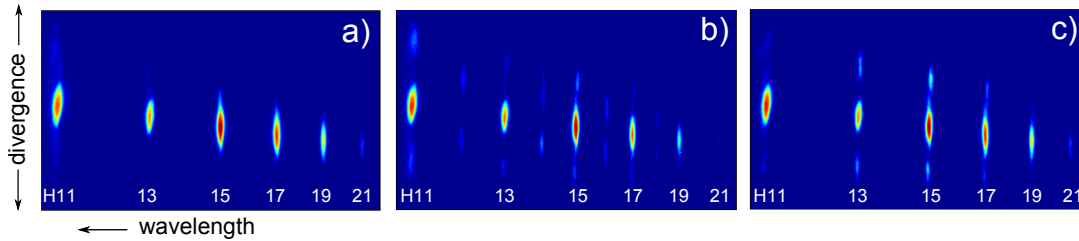


Fig. S1: Frequency-resolved far-field high-harmonic profiles observed from a transient grating experiment in NO_2 . Panels a, b and c correspond to negative, zero and positive delays between the 400 nm transient grating excitation (pump) pulses and the 800 nm pulse generating the high-harmonic radiation.

3 Polarization dependence of pump-probe signals

In experiments using perpendicularly polarized pump and probe pulses, a clear modulation was observed in the diffracted signal, as shown in Fig. 4 of the main article. Figure S2 shows the diffracted and undiffracted high-harmonic signals as a function of the delay between the parallel polarized pump (400 nm) and probe (800 nm) pulses under experimental conditions otherwise similar to those of Fig. 4. The absence of clear modulations from Fig. S2 thus reveals a strong polarization dependence of the modulations in the diffracted high-harmonic signal.

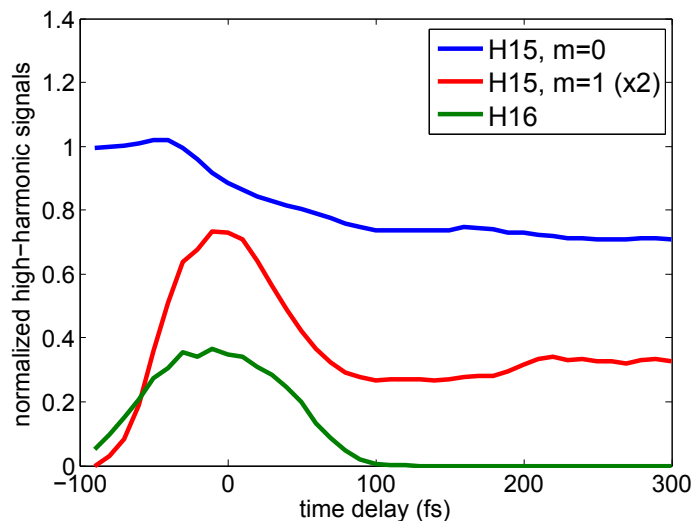


Fig. S2: High-harmonic yields as a function of the delay between a 401 nm pump pulse and an 800 nm probe pulse generating high-harmonics in the excited sample. The figure shows the yield of diffracted (red line) and undiffracted (blue line) high-harmonic signals, normalized to the undiffracted signal at negative pump-probe delays. The polarizations of pump and probe pulses were parallel. The pulse energy of the exciting pulses was 10 μ J.

4 Excluding contributions from N_2O_4

The absence of a clear modulation in the case of parallel polarized pulses shown in Fig. S2 has an additional importance. A molecular expansion of NO_2 unavoidably contains traces of N_2O_4 , although we have heated the nozzle to 100 $^\circ\text{C}$ to suppress the dimer formation. The vibrational period of the most strongly Raman active mode of N_2O_4 is 130 fs, which is close to the modulation observed here (3). However, vibrational wave packet motion has been observed by HHG in N_2O_4 and found to be much more pronounced in the case of parallel polarized pulses than in the cross-polarized case. The comparison of the results of the two polarization geometries thus enables us to exclude the contribution of dimer vibrations to the observed signal.

5 Excluding contributions from the ionization step

The modulations observed in the diffracted high-harmonic signal in Fig. 4 of the main article might be caused by a variation of the strong-field-ionization rate of the molecule as a function of the nuclear coordinates. To rule out this possibility we have measured the total ion yield in parallel to the high-harmonic yield and have not observed any modulation on top of the smooth increase as shown in Fig. S3. A comparison of the signal-to-noise ratios of the diffracted high-harmonic and ion yield measurement allows us to exclude a variation in the ionization rate as the origin of the observed modulations.

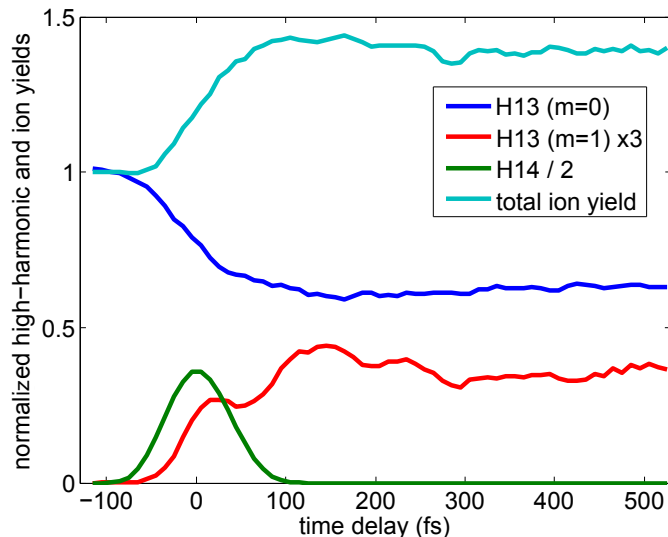


Fig. S3: High-harmonic and ion yields as a function of the delay between a 401 nm pump pulse and an 800 nm probe pulse generating high harmonics in the excited sample. The figure shows the yield of diffracted (red line), undiffracted (dark blue line) high-harmonic signals and total ion yields (light blue line), normalized to the undiffracted signals at negative pump-probe delays. The polarizations of pump and probe pulses were perpendicular.

6 Quantum chemistry calculations

We performed quantum chemical calculations of NO_2 at three geometries: (1) 134° angle corresponding to the ground state equilibrium geometry and to the outer turning point of the wave packet on the diabatic $\tilde{A}^2B_2$ state; (2) 102° angle corresponding to the saddle point of the diabatic $\tilde{A}^2B_2$ state; and (3) 85° angle corresponding to the inner turning point of the wave packet on the diabatic $\tilde{A}^2B_2$ state. At each geometry, we calculate (1) strong-field-ionization yield and its angular variation; (2) Dyson orbital corresponding to each ionization channel; (3) recombination transition dipole moment between the cation and the neutral states.

All electronic structure calculations were performed in GAMESS-US (35), using Complete Active Space (CAS) wavefunctions, with 17 electrons in 12 active orbitals. A spherical Gaussian valence triple-zeta quality basis set, augmented with diffuse basis functions (aug-cc-pVTZ (36, 37)) was used on all atoms. Strong-field ionization calculations were performed at the optimized pure-state CAS geometry of the $\tilde{X}^2A_1$ state ($r_{N-O} = 1.204 \text{ \AA}$; $\alpha_{O-N-O} = 133.9^\circ$), at the $\tilde{A}^2B_2$ saddle point ($r_{N-O} = 1.269 \text{ \AA}$; $\alpha_{O-N-O} = 101.7^\circ$) of the $\tilde{A}^2A'$ excited state, and at the approximate inner turning point on the $\tilde{A}^2B_2$, ($\alpha_{O-N-O} = 85^\circ$). The geometries are defined in Table S1.

Dyson orbitals and ionic Hartree potentials were evaluated (38) from the pure-state CAS(17,12) wavefunctions for the neutral NO_2 and equally-weighted, mixed-spin 3-state-averaged CAS(16,12) cation wavefunctions. Calculated relative energies of the low-lying electronic states of NO_2 and NO_2^+ at the three geometries are summarized in Table S2. Note that only the lowest state in each of the four irreducible representations was determined for the neutral species. The present CAS calculations do not include dynamical correlations and consistently underestimate the ionization potential of NO_2 ($^1A_1 \leftarrow ^2A_1$

vertical ionization potential is 11.23 eV experimentally (39)). However, the relative ionization potentials of the different channels are expected to be well reproduced.

Strong-field ionization rates were calculated within an uncoupled single-channel approach (40). The ionizing field was a half-cycle $\sin^2$ pulse with the peak intensity of 10^{14} W/cm² ($E_{max} = 0.05345$ a.u.), with the second time derivative of E at the field maximum chosen to match the shape of the 800-nm field maximum. The simulation was continued for 12 atomic units of time (au[t]) after the field turn-off, for the total of 90 au[t] (2.18 fs), to let ionized electrons reach the absorbing boundaries. The time step in leap-frog propagation of the wavefunction was 0.003 au[t]. The cubic simulation box extended to ± 18 Bohr in each direction. The Cartesian grid spacing was 0.15 Bohr. A reflection-free complex absorbing potential (41) extended 9.4 Bohr from the grid boundary. Angular dependence of the total photoelectron yield on the laser field polarization was calculated on the 38-point 9th-order Lebedev grid (42), then interpolated with spherical harmonics with angular momentum $L \leq 5$.

Calculated square norms of the Dyson orbitals, corresponding to the low-lying ionization channels at the three representative geometries are summarized in Table S3. Dyson orbital norms close to one indicate that an ionization channel is allowed as a single-electron transition (Koopmans' correlation-allowed channel). Values close to zero indicate that electronic rearrangement within the ion core must accompany an electron removal. For ionization channels where strong field ionization yields were calculated, total photoelectron yield for a randomly oriented sample is also given in Table S3. The shapes of the Dyson orbitals and the polarization dependence of the total photoelectron yield are illustrated in Fig. S5.

In the experiment, population on the $\tilde{A}^2B_2$ was produced by a laser pulse centered in the vicinity of 400 nm. At the equilibrium geometry of the $\tilde{X}^2A_1$ ground state of the NO₂ radical, the strongest single-photon dipole-allowed electronic excitation is to the $\tilde{A}^2A'$ ($\tilde{A}^2B_2$ at the C_{2v} geometry) state. The transition moment lies along the O-O direction, so that the pump pulse creates a partially aligned population of the $\tilde{A}^2A'$ state. Simultaneously, the population of NO₂ in the $\tilde{X}^2A_1$ is weakly depleted for molecules with the O-O axis along the pump field.

Figure S4 shows the potential energies for the important states as a function of the bend angle, derived from Ref. (18). We consider high-harmonic generation from the three geometries described above. The most probable transitions are labeled as channels #1-#7.

The Dyson orbitals and the angular variation of the strong-field photoionization probability are shown in Fig. S5. Only the Dyson orbitals corresponding to removal of a b_2 electron (channels #2, 4 and 6) are significantly different from the Dyson orbital of the unexcited molecules (channel 1).

Dipole matrix elements for the bound-continuum transitions were calculated in the eikonal single active-electron approximation (43). Eikonal scattering states were calculated in the Coulomb (nuclear attraction and Hartree repulsion) potential of the appropriate ion core, and are normalized to unit electron density. The target recombination channel is represented by the corresponding Dyson orbital. Orthogonalization and exchange effects involving the ion core are treated as described in Ref. (38). The calculation was performed on a uniformly-spaced Cartesian grid (grid spacing of 0.15 Bohr) extending to ± 18 Bohr from the coordinate origin. The transition dipoles are shown in Table S4. They are evaluated for an electron kinetic energy of 20 eV, about the maximum of each curve; this corresponds to a photon energy of about 30 eV close to harmonic order 19.

We now estimate the emitted signal from each channel. Table S4 summarizes the calculations for the three geometries. Tables S5 and S6 summarize the predictions of the emission for each channel for perpendicular and parallel laser polarizations. The column labeled Product is the relative amplitude of the emission, and is the product of the previous columns as indicated in the caption. For channels with non-zero signal, the radiated dipole shows both the amplitude and phase of the emitted electric field. The phase is determined by both the recombination dipole phase and the propagation phase ($\phi = \Delta I_p \tau$)

due to the difference ΔI_p in ionization potentials and the transit time of the electron in the continuum $\tau \approx 1.7$ fs (70 atomic units) for the highest harmonics.

The intensity of the high-harmonic emission that is diffracted into the first order of the transient grating is defined in the main text in eq. 4, which we repeat here.

$$I_{m=1}(\Omega, t) = \frac{1}{4} \left| r_{\tilde{A}}(t)(d_{\tilde{A}}e^{i\phi_{\tilde{A}}} - d_g e^{i\phi_g}) + r_{\tilde{X}}(t)(d_{\tilde{X}}e^{i\phi_{\tilde{X}}} - d_g e^{i\phi_g}) \right|^2. \quad (7)$$

We first study the sensitivity of the diffracted signal to the populations of the two diabatic states at the three characteristic geometries and then show that even in the case of a complete delocalization of the wave packet (as is essentially the case for a 40 fs excitation pulse), the diffraction is still sensitive to the population in the diabatic states. The following table summarizes the results for single geometries:

$$I_{m=1}(134^\circ, \text{perpendicular}) = \frac{1}{4} \left| r_A(95e^{-i3.3} - 52) + r_X(52 - 52) \right|^2 = 5371r_A^2 \quad (8)$$

$$I_{m=1}(134^\circ, \text{parallel}) = \frac{1}{4} \left| r_A(0 - 52) + r_X(5.2e^{i7.6} - 52) \right|^2 = 676r_A^2 + 1012r_X^2 + 1318r_A r_X \quad (9)$$

$$I_{m=1}(102^\circ, \text{perpendicular}) = \frac{1}{4} \left| r_A(69e^{i2.36} - 52) + r_X(0 - 52) \right|^2 = 3140r_A^2 + 676r_X^2 + 2940r_A r_X \quad (10)$$

$$I_{m=1}(102^\circ, \text{parallel}) = \frac{1}{4} \left| r_A(0 - 52) + r_X(10e^{i3.08} - 52) \right|^2 = 676r_A^2 + 961r_X^2 + 1611r_A r_X \quad (11)$$

$$I_{m=1}(85^\circ, \text{perpendicular}) = \frac{1}{4} \left| r_A(46e^{i5.35} - 52) + r_X(0 - 52) \right|^2 = 493r_A^2 + 676r_X^2 + 640r_A r_X \quad (12)$$

$$I_{m=1}(85^\circ, \text{parallel}) = \frac{1}{4} \left| r_A(8.5e^{-i0.67} - 52) + r_X(0 - 52) \right|^2 = 520r_A^2 + 676r_X^2 + 1179r_A r_X \quad (13)$$

First, let us examine the case of perpendicular laser polarizations. It can be seen that the model predicts that the diffracted high-harmonic signal at the outer turning point (134°) is determined by the population in the $\tilde{A}^2B_2$ state alone. In the 102° geometry (near the conical intersection), it can be seen that there is also a contribution from the $\tilde{X}^2A_1$ population, but the $\tilde{A}^2B_2$ still dominates. Bent geometries lower than 95° are not visited by the $\tilde{X}^2A_1$ wave packet at 3 eV of total excitation energy. Consequently, at the inner turning point of the $\tilde{A}^2B_2$ (85°) both the $\tilde{A}^2B_2$ and the unexcited $\tilde{X}^2A_1$ contribute equally. For the case of parallel polarizations, both states contribute about equally at all geometries.

Using the radiated dipoles in Tables S5 and S6, we now turn to estimate $I_{m=1}$ for perpendicular and parallel laser polarizations for a delocalized wave packet. We are evaluating how the wavepacket population in the $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ states contribute to the diffracted HHG signal. We estimate the emission from each surface by taking the average of the dipole at each of the three geometries in Tables S5 and S6. The two polarization cases are shown in eqs. (14)-(15).

We can estimate the sensitivity of the diffracted signal to r_A and r_X by taking differentials, shown in eqs. (16)-(17); we assume that $r_A = r_X = 0.1$ for the purpose of this estimate.

This shows that the diffracted signal is about 2.6 times more sensitive to population in $\tilde{A}^2B_2$ than in $\tilde{X}^2A_1$ when the laser polarizations are perpendicular. When the laser polarizations are parallel, the contributions to the diffracted signal are equal from both states. This agrees with the experimental observation that modulation of the $I_{m=1}$ signal is only seen for perpendicular polarizations. Therefore our model supports the conclusion that the high-harmonic-spectroscopy experiment is measuring the population in the diabatic $\tilde{A}^2B_2$ state. This simple model justifies this conclusion, but the strongest

$$\begin{aligned}
I_{m=1}(\text{perpendicular}) &= \frac{1}{4} \left| r_A \left(\frac{1}{3} (95e^{-i3.3} + 69e^{i2.36} + 46e^{i5.35}) - 52 \right) + r_X \left(\frac{1}{3} (52 + 0 + 0) - 52 \right) \right|^2 \\
&= 2066r_A^2 + 300r_X^2 + 1568r_Ar_X \tag{14}
\end{aligned}$$

$$\begin{aligned}
I_{m=1}(\text{parallel}) &= \frac{1}{4} \left| r_A \left(\frac{1}{3} (0 + 0 + 8.5e^{-i0.67}) - 52 \right) + r_X \left(\frac{1}{3} (5.2e^{i7.6} + 10e^{i3.08} + 0) - 52 \right) \right|^2 \\
&= 620r_A^2 + 754r_X^2 + 1365r_Ar_X \tag{15}
\end{aligned}$$

$$dI_{m=1}(\text{perpendicular}) = 569dr_A + 216dr_X \tag{16}$$

$$dI_{m=1}(\text{parallel}) = 260dr_A + 287dr_X \tag{17}$$

evidence is the good agreement between the experiment and the detailed calculations of Arasaki et al. (18).

Finally, let us see if our simple model agrees with the magnitude of the modulation of the diffracted signal, shown in Fig. 4B of the main article. We start with the calculated $\tilde{A}^2B_2$ population of Arasaki et al. (18), shown in Fig. 4C. We assume that our total excited state population fraction is 0.15, as shown in Table 1 in the main text, and so $r_A + r_X = 0.15$. Scaling Fig. 4C to this value, we associate the first peak with $r_A = 0.09$ and $r_X = 0.06$. The subsequent valley will have $r_A = 0.06$ and $r_X = 0.09$. We then substitute these values into eqs. (14)-(15), and scale the results vertically to match Fig. 4B. For perpendicular polarization, our model predicts that the first peak on Fig. 4B should be 0.64 and the first valley should be 0.45; this is a somewhat greater modulation than what was actually observed, but is quite close. For parallel polarizations, this simple model predicts a signal of 0.36 at the first peak and 0.37 at the first valley, i.e. it predicts that there is no modulation of the signal, as was observed experimentally.

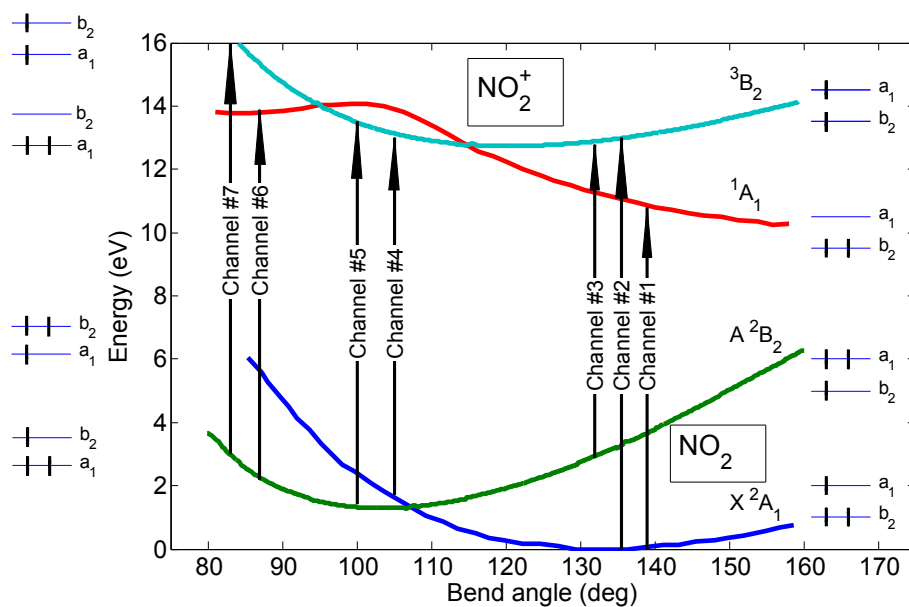


Fig. S4: Potential energy diagram of the relevant states of NO_2 and NO_2^+ , derived from Ref. (18). The primary strong-field ionization channels that lead to HHG are shown as arrows. Each channel is referred to in the text as channel #1-#7. Note that the energetic ordering of the a_1 and b_2 orbitals changes as a function of the bending angle.

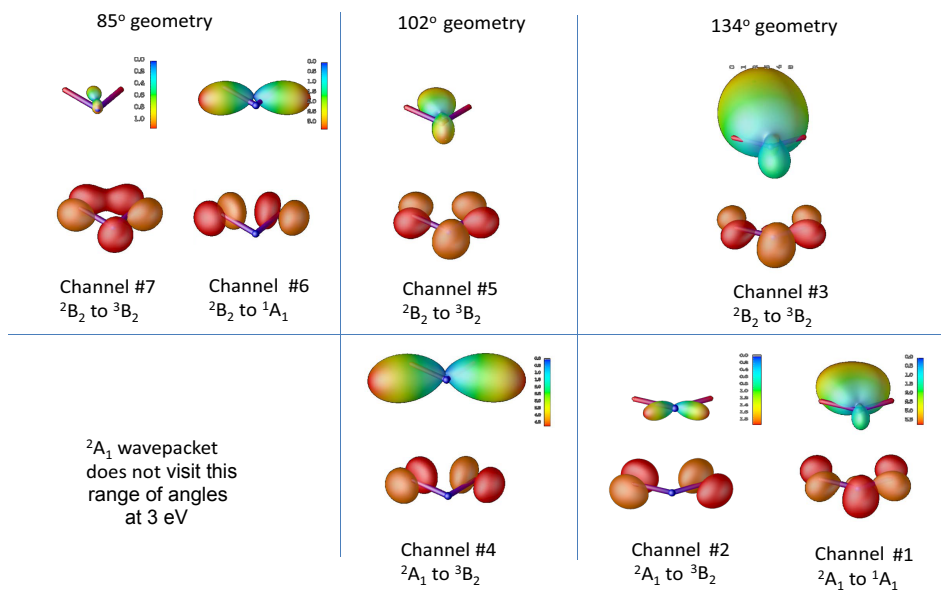


Fig. S5: Dyson orbitals and angular variation of strong-field ionization probabilities for each of the seven primary HHG channels. The Dyson orbitals are at the bottom of each panel, whereas the photoionization probability distributions are at the top of each panel. The channel labels are defined in Fig. S4. For the integrated ionization probability for each channel, see Table S1.

Table S1: Coordinates of the nuclei used for strong-field ionization simulations. Cartesian coordinates are given in Angstroms.

Atom Z_{nuc}	Coordinates (Å)		
	X	Y	Z
134° 2A_1 geometry			
7.00	0.00000	0.00000	-0.11398
8.00	0.00000	-1.10809	0.35699
8.00	0.00000	1.10809	0.35699
102° 2B_2 geometry			
7.00	0.00000	0.00000	-0.33393
8.00	0.00000	-0.98428	0.46696
8.00	0.00000	0.98428	0.46696
85° 2B_2 geometry			
7.00	0.00000	0.00000	-0.45098
8.00	0.00000	-0.88809	0.51820
8.00	0.00000	0.88809	0.51820

Table S2: Energies of the low-lying electronic states of NO_2 and NO_2^+ , in electron-Volts, relative to the energy of 1^2A_1 state at its optimized geometry, at the CASSCF(17,12)//aug-ccpVTZ level of theory. The energies of all ionic states need to be increased by 1.68 eV to match the experimental vertical ionization energy.

Geometry	R (Å)	Angle (°)	State	E (eV)
1^2A_1 134°	1.2040 neutral	133.9	2A_1	0.000
			2B_1	2.907
			2B_2	3.234
			2A_2	3.381
cation			1A_1	9.548
			3B_2	11.500
			3A_2	12.065
1^2B_2 102°	1.2690 neutral	101.7	2B_2	1.160
			2A_1	1.880
			2A_2	2.091
			2B_1	4.803
cation			3B_2	11.812
			1A_1	12.322
			3B_1	13.042
1^2B_2 85°	1.3146 neutral	85.0	2B_2	1.925
			2A_2	3.848
			2B_1	3.891
			2A_1	4.669
cation			1A_1	12.257
			3B_1	13.064
			3B_2	13.585

Table S3: Square of the Dyson orbital norms and strong-field-ionization yields for the three geometries considered. Total yield for a half cycle of 800 nm linearly polarized laser field at the peak intensity of 10^{14} W/cm².

Geometry	Neutral State	Cation State	Dyson norm ²	Ionization Yield (10^{-4})	Channel Label
$\tilde{X}^2A_1$ 134°	2A_1	1A_1	0.861	15.8	#1
		3B_2	0.878	7.74	#2
		3A_2	0.858		
	2B_2	1A_1	0.019	1.61	
		3B_2	0.842	37.2	#3
		3A_2	0.020		
$\tilde{A}^2B_2$ 102°	2B_2	3B_2	0.867	15.2	#5
		1A_1	0.506	3.01	
		3B_1	0.836		
	2A_1	3B_2	0.834	21.6	#4
		1A_1	0.326	2.73	
		3B_1	0.030		
85°	2B_2	1A_1	0.801	10	#6
		3B_2	0.856	6.1	#7
		3B_1	0.837	5	

Table S4: Summary of calculated results for the three geometries considered. For each geometry, the most significant channel for ionization from the ground and excited electronic states is shown. The directions for the ionization (P_{ion}) and recombination dipole moment (d) are: Z is parallel to the C_2 symmetry axis, and Y is parallel to the O-O axis as shown in Fig. 1 of the main article. The transition moment of the pump step is parallel to Y. When pump and probe pulses are cross-polarized, ionization and recombination take place along Z. In the case of parallel polarizations, ionization and recombination occur along Y.

Channel	Transition	P_{ion}	Dyson ²	d ampl	d phase (rad)	I_p (eV)
#1	$^1A_1 \leftarrow ^2A_1$	16 Z	0.86	14 Z	0	11.15
#2	$^3B_2 \leftarrow ^2A_1$	7.7 Y	0.88	2 Y	2.9	13.0
#3	$^3B_2 \leftarrow ^2B_2$	37 Z	0.84	17 Z	0.2	9.78
#4	$^3B_2 \leftarrow ^2A_1$	22 Y	0.83	2.5 Y	2.8	11.26
#5	$^3B_2 \leftarrow ^2B_2$	15 Z	0.87	19 Z	0.1	12.03
#6	$^1A_1 \leftarrow ^2B_2$	10 Y	0.80	3 Y	-0.9	11.20
#7	$^3B_2 \leftarrow ^2B_2$	6.1 Z	0.86	20 Z	0.1	13.19

Table S5: Summary of calculated results for the three geometries considered. The polarizations of pump and probe laser pulses are **perpendicular** to each other. For each channel, molecules that have their O-O axes aligned either parallel or perpendicular to the pump laser polarization are shown. The Excitation column indicates whether the pump laser excites the molecule for that orientation. The next columns contain numbers from Table S4. The column labeled "Product" is the product of the columns to the left: Product = Excitation $P_{ion}^{1/2}$ Dyson Dipole. $\Delta I_p \tau = (I_p - I_p(ref))70(at.un.)$ is the phase shift of the high-harmonic radiation relative to the unexcited ground state due to the differing ionization potentials.

Channel	Orientation	Excitation	P_{ion}	Dyson ²	Dipole	Product	$\Delta I_p \tau$ (rad)	Radiated Dipole
134° geometry								
#1		1	16	0.86	14	52	0	$d_g = 52$
	⊥	0	0	0.86	0	0	0	$d_X = 52$
#2		1	0	0.88	0	0	4.7	$d_X = 0$
	⊥	0	7.7	0.84	$2e^{i2.9}$	0	4.7	
#3		1	37	0.84	$17e^{i0.2}$	$95e^{i0.2}$	-3.5	$d_A = 95e^{-i3.3}$
	⊥	0	0	0.84	0	0	-3.5	
102° geometry								
#4		1	0	0.83	0	0	0.28	$d_X = 0$
	⊥	0	22	0.83	$2.5e^{i2.8}$	0	0.28	
#5		1	15	0.87	$19e^{i0.1}$	$69e^{i0.1}$	2.26	$d_A = 69e^{i2.36}$
	⊥	0	0	0.87	0	0	2.26	
85° geometry								
#6		1	0	0.80	0	0	0.13	$d_X = 0$
	⊥	0	10	0.80	$3e^{-i0.9}$	0	0.13	$d_A = 0$
#7		1	6.1	0.86	$20e^{i0.1}$	$46e^{i0.1}$	5.25	$d_A = 46e^{i5.35}$
	⊥	0	0	0.86	0	0	5.25	

Table S6: Summary of calculated results for the three geometries considered. The polarizations of pump and probe laser pulses are **parallel** to each other. For each channel, molecules that have their O-O axes are oriented either parallel or perpendicular to the pump laser polarization are shown. The Excitation column indicates whether the pump laser excites the molecule for that orientation. The next columns contain numbers from Table S4. The column labeled Product is the product of the columns to the left: Product = Excitation $P_{ion}^{1/2}$ Dyson Dipole. $\Delta I_p \tau = (I_p - I_p(ref))70(at.un.)$ is the phase shift of the high-harmonic radiation relative to the unexcited ground state due to the differing ionization potentials.

Channel	Orientation	Excitation	P_{ion}	Dyson ²	Dipole	Product	$\Delta I_p \tau$ (rad)	Radiated Dipole
134° geometry								
#1		1	0	0.86	0	0	0	$d_g = 52$
	⊥	0	16	0.86	14	0	0	$d_X = 0$
#2		1	7.7	0.88	$2e^{i2.9}$	$5.2e^{i2.9}$	4.7	$d_X = 5.2e^{i7.6}$
	⊥	0	0	0.84	0	0	4.7	
#3		1	0	0.84	0	0	-3.5	
	⊥	0	37	0.84	$17e^{i0.2}$	0	-3.5	$d_A = 0$
102° geometry								
#4		1	22	0.83	$2.5e^{i2.8}$	$10e^{i2.8}$	0.28	$d_X = 10e^{i3.08}$
	⊥	0	0	0.83	0	0	0.28	
#5		1	0	0.87	0	0	2.26	$d_A = 0$
	⊥	0	15	0.87	$19e^{i0.1}$	0	2.26	
85° geometry								
#6		1	10	0.80	$3e^{-i0.9}$	$8.5e^{-i0.9}$	0.13	$d_X = 0$ $d_A = 8.5e^{-i0.67}$
	⊥	0	0	0.86	0	0	0.13	
#7		1	0	0.86	0	0	5.25	$d_A = 0$
	⊥	0	6.1	0.86	$20e^{i0.1}$	0	5.25	

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Chapter 5

LAPIN: Linked Attosecond Phase Interferometry

5.1 Linked Attosecond Phase Interferometry for Molecular Frame Measurements (publication [14](#))

J. B. Bertrand, H. J. Wörner, P. Salières, D. M. Villeneuve and P. B. Corkum
Linked Attosecond Phase Interferometry for Molecular Frame Measurements
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5.1.1 Author Contributions

J.B.B. performed the experiments. H.J.W. and D.M.V. performed the ePolyScat [\[81, 82\]](#) photoionization dipole calculations that enter the multiple orbitals theory part. J.B.B. and H.J.W. conducted the data analysis. J.B.B. elaborated the LAPIN procedure and the theoretical modeling with D.M.V. J.B.B. and D.M.V. wrote the first draft. All authors contributed to the final manuscript.

Linked Attosecond Phase Interferometry for Molecular Frame Measurements

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(Dated: June 14, 2012)

Abstract

High-harmonic spectroscopy utilizes attosecond techniques to measure single-atom or molecule photorecombination cross sections [1–4]. While the amplitude of the extreme ultraviolet (XUV) light can be easily measured, the phase is much more challenging to access, yet it contains information about the attosecond synchronization of electron recollision dynamics [5], the instantaneous ionization potential [6], the photorecombination dipole moment [7], and the role of a possible ionization phase [8, 9]. In particular, knowledge of the recombination phase is necessary for tomographic imaging of the molecular orbital wave function with attosecond-Ångström resolution [10–13]. Present techniques [14, 15] cannot simultaneously measure the phase as a function of molecular angle and photon frequency, which is necessary for a full reconstruction of the wave function. We overcome this limitation with a new all-optical method. We apply it to record the full phase map of aligned bromine molecules relative to reference xenon atoms. It allows us to resolve, both spectrally and angularly, the participation of multiple molecular orbitals, and infer a phase of ionization.

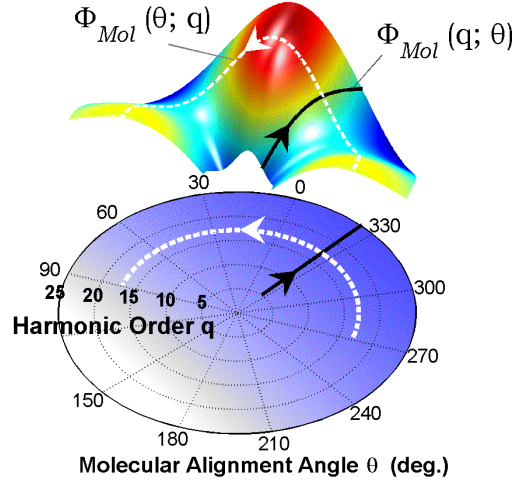


Figure 1: In aligned molecules, the high-harmonic spectral phase $\Phi_{Mol}(q, \theta)$ is a function of both harmonic order q and molecular alignment angle θ with respect to the driving laser field polarization axis (linear). Existing techniques can only measure one-dimensional cuts, either the harmonic phase $\Phi_{Mol}(q; \theta)$ (black line), or the angular phase $\Phi_{Mol}(\theta; q)$ (white dashed line). Here, we measure the two-dimensional phase $\Phi_{Mol}(q, \theta)$ relative to that of a reference atom $\Phi_{Ref}(q)$.

The high harmonic generation (HHG) process is composed of three steps: ionization, propagation, and photorecombination [16]. Each step contributes an amplitude and a phase to the emitted field $E_{Mol}(q, \theta) = |D_{Mol}(q, \theta)| e^{i\Phi_{Mol}(q, \theta)}$. As illustrated in Fig. 1, in molecules, the phase $\Phi_{Mol}(q, \theta)$ is a function of harmonic order q and molecular alignment angle θ . The phase is currently measured by methods developed in attosecond physics – RABBIT [14] and FROG-CRAB [15] – by using a synchronized infrared laser field to couple adjacent harmonics in the photoelectron spectrum. These techniques measure the derivative of the spectral phase, and cannot compare the phase between different targets or as a function of molecular angle. A self-referencing spectral interferometry approach [12], where the HHG signal from an imperfectly aligned ensemble of molecules is exploited, determines the angular variation of the phase but leaves the harmonic order-dependence undetermined.

In keeping with the traditions in the field of optical measurement, we call our method by an acronym which is also the name of a small animal. LAPIN (French for rabbit) Linked Attosecond Phase INterferometry is a two-step procedure. (1) A two-source interferometer measures the phase versus molecular angle, $\Phi_{Mol}(\theta; q)$, and (2) the HHG spectrum of the

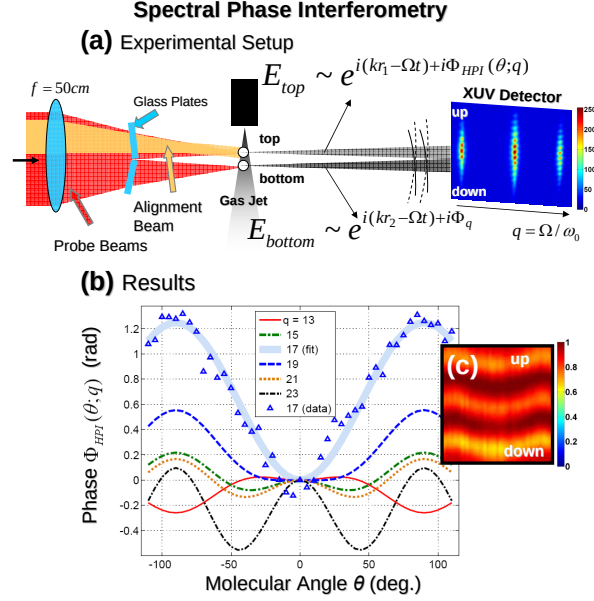


Figure 2: Spectral harmonic phase interferometry (HPI) of aligned Br_2 molecules. (a) Two XUV sources created in a supersonic gas jet interfere in the far field. We laser-align the molecules in the top source and observe the movement of the interference fringes as a function of alignment angle θ , providing a measurement of the high-harmonic spectral phase $\Phi_{HPI}(\theta; q)$. (b) $\Phi_{HPI}(\theta; q)$ for harmonic orders $q=13$ to 23 (cutoff). (c) The measured vertical motion of fringes for $q=17$ as the molecule is rotated from -90° to 90° . The distance between two bright fringes (dark red) corresponds to 2π in phase; see section I.B of the supplementary information for details.

aligned target molecule mixed with a reference atom is recorded. Each of these steps has been previously demonstrated [8, 17–19]. The difficulty until now was the lack of coupling between the two coordinates q and θ of the two-dimensional phase $\Phi_{Mol}(q, \theta)$. We show that by combining these two measurements, we can unequivocally determine the two-dimensional molecular phase $\Phi_{Mol}(q, \theta)$ relative to that of a reference atom $\Phi_{Ref}(q)$. We apply LAPIN to aligned Br_2 molecules and use xenon as reference atoms.

In the first step, we perform two-source harmonic phase interferometry [8]. As illustrated in Fig. 2(a), we obtain two identical XUV sources by spatially splitting the incoming laser beam using refractive elements placed between the focusing mirror and the gas jet [17] (refer to the Supplementary Information (SI) section I for experimental details). Using a thin gas jet allows us to minimize propagation effects and, therefore, to measure the single-molecule

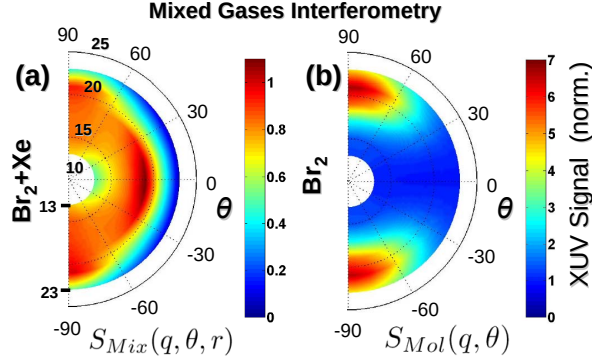


Figure 3: (a) Measured high harmonic generation signal $S_{Mix}(q, \theta)$ from a gas mixture of aligned Br_2 molecules and reference Xe atoms (ratio $r \approx 1:0.2$), and (b) $S_{Mol}(q, \theta)$ from aligned Br_2 molecules only. All measured signals are normalized choosing $S_{Mol}(q, \theta = 0^\circ) = 1$. The polarization of the high-harmonic generation (probe) driving laser field is fixed (linear along $\theta = 0^\circ$) and the molecular alignment angle θ is varied by rotating the polarization (also linear) of the prompt laser-alignment pump beam.

response at the XUV detector [4]. The peak intensity of the fundamental pulse in each source is estimated to be $1.5 \times 10^{14} \text{ W/cm}^2$, and the two sources are separated vertically by approximately $150 \mu\text{m}$ in the gas jet. We impulsively laser-align [20] the molecules in the top source only using a non-ionizing and stretched (130 fs, $3 \times 10^{13} \text{ W/cm}^2$) laser pulse which arrives 0.5 ps earlier to provide prompt molecular alignment. The molecular alignment angle is varied by rotating the alignment pulse with respect to the 2-source probe, all polarizations are linear.

The electromagnetic interference between the emitted fields from the top source with aligned (E_{top}) and bottom source with randomly aligned (E_{bottom}) molecules creates fringes in the far field at the XUV detector, shown in Fig. 2(a). Varying the molecular angle, in the top source only, causes the fringes to move up or down. The variation of the fringe position with molecular angle determines the angular phase for each harmonic, $\Phi_{HPI}(\theta; q)$. See SI sect. I.B for the definition of the sign convention. For $q=17$, the fringe displacement and the corresponding phase variation are shown respectively in Fig. 2(c) and (b). The distance between two bright fringes (dark red) is 2π in phase. We arbitrarily choose $\Phi_{HPI}(\theta=0^\circ; q)=0$ since no connection is made between adjacent harmonics in this measurement.

In the second step, we generate XUV radiation in a mixture of Br₂ molecules and xenon reference atoms. We use the latter as a local oscillator to connect the phase of the Br₂ emission between adjacent harmonics, $\Phi_{Mol}(q; \theta)$. We prepare a gas mixture with molar ratio $r \approx 0.2:1$ of Xe atoms to Br₂ molecules. In Fig. 3(a), we show the measured XUV signal $S_{Mix}(q, \theta, r)$ from this gas mixture, and in Fig. 3(b) the signal $S_{Mol}(q, \theta)$ from Br₂ alone, the density of Br₂ molecules being the same in both cases (see SI sect. I for details). All measured signals are normalized according to $S_{Mol}(q, \theta = 0^\circ) = 1$. Because the signal intensity with the mixed gases is ~ 7 times weaker than for pure Br₂ alone, we infer strong destructive interference between the emission of the two species. This even leads to a reversal of the signal angular modulation as seen for harmonic order $q=19$.

The bromine molecules are entrained in a helium carrier gas in the pulsed valve gas expansion. Due to helium's high ionization potential of 24.6 eV, the helium gas by itself generates no HHG signal. We can add $\sim 4\%$ by pressure of xenon to the helium, without affecting the gas expansion. However, we cannot directly measure the HHG spectrum from the reference atom alone $S_{Ref}(q)$, as in other experiments [18, 19], because the pulsed valve operation and thereby the gas expansion are different without Br₂ vapors. Instead, we separately record the HHG spectra of the bromine molecules alone ($S_{Mol}(q, \theta)$) and of the gas mixture ($S_{Mix}(q, \theta)$). This removes the difficulty in matching gas expansion conditions with and without Br₂ molecules, and relieves the necessity to know the precise ratio of gas pressures r : our fitting procedure uniquely determines the reference atom contribution. We express the mixed gas emission as the coherent sum of the emission from each species [19]:

$$S_{Mix}(q, \theta, r) = S_{Mol}(q, \theta) + r^2 S_{Ref}(q) + 2r \sqrt{S_{Ref}(q)} \sqrt{S_{Mol}(q, \theta)} \cos \Delta\Phi_{Mix}(q, \theta). \quad (1)$$

Here, we define $\Delta\Phi_{Mix}(q, \theta) = \Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)$ as the phase difference between the electromagnetic emission from the aligned molecules $E_{Mol}(q, \theta)$ and the reference atom $E_{Ref}(q)$. We know all quantities except for $r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$. For each harmonic order q , we have 21 measurements corresponding to different molecular angles θ . Therefore there is sufficient information to determine both $r^2 S_{Ref}(q)$ and $|\Delta\Phi_{Mix}(q, \theta)|$, provided that we parameterize the phase.

In mixed gases interferometry, an ambiguity on the phase arises because $\cos \Delta\Phi_{Mix}(q, \theta)$ is symmetric around $\Delta\Phi_{Mix}(q, \theta) = 0$. Two solutions, $\pm \Delta\Phi_{Mix}(q, \theta)$, can satisfy eq. (1), thereby

LAPIN Results

(a) Relative amplitude $r\sqrt{S_{Ref}(q)}$:

Harmonic order q	13	15	17	19	21	23
$r\sqrt{S_{Ref}(q)}$	0.66	0.48	0.72	1.55	1.64	1.37

(b) Relative phase $\Delta\Phi_{Mix}(q, \theta)$:

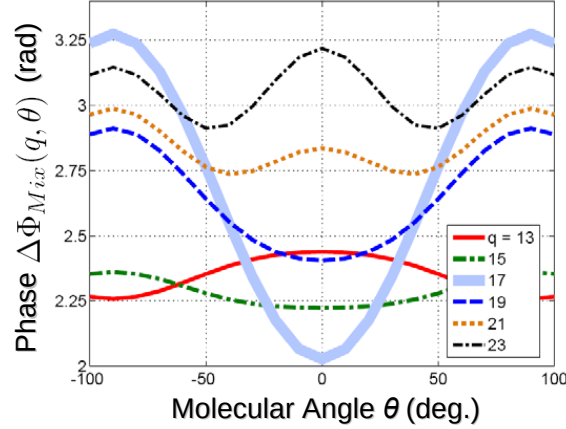


Figure 4: Parameters determined by LAPIN procedure. (a) Emission amplitude $r\sqrt{S_{Ref}(q)}$ of reference atom. (b) Phase $\Delta\Phi_{Mix}(q, \theta)$ between the molecule and reference atom. The mixed gases (see Fig. 3) and harmonic phase interferometry (see Fig. 2) measurements were combined in the LAPIN procedure.

accessing only $|\Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)|$. McFarland et al. [18] assumed a direction of the phase difference $\Delta\Phi_{Mix}(q, \theta)$ in order to extract it. We can use the redundant information provided by the spectral phase interferometry measurement (Fig. 2) to lift the sign ambiguity of the phase. For this purpose, we combine both experimental measurements into a global fitting procedure described in the SI sect. II.B.

The signal amplitude from the reference atom $r\sqrt{S_{Ref}(q)}$ and the phase $\Delta\Phi_{Mix}(q, \theta)$, determined by the LAPIN fitting procedure, are respectively shown in Fig. 4(a) and (b). For all harmonic orders q , the variation of $\Delta\Phi_{Mix}(q, \theta)$ with molecular angle resembles closely the phase measured by harmonic phase interferometry $\Phi_{HPI}(\theta; q)$ in Fig. 2(b). In both cases, the low harmonics ($q=13, 15$) modulate less, the strongest modulation occurs at $q=17$ and the cutoff harmonics ($q=21, 23$) show a double modulation.

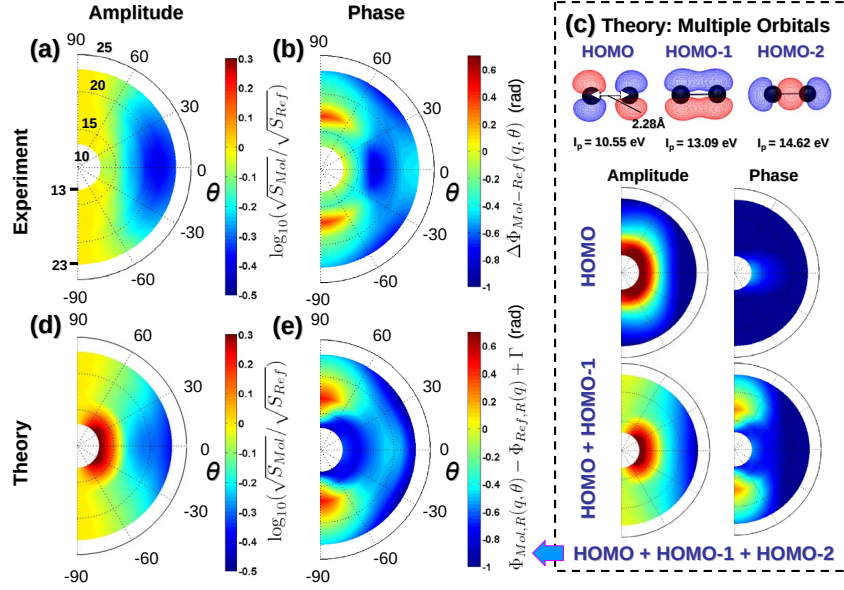


Figure 5: (a) Experimentally retrieved relative amplitude $\sqrt{S_{Mol}(q, \theta)/S_{Ref}(q)}$ and (b) phase $\Delta\Phi_{Mol-Ref}(q, \theta)$ between the emission from Br₂ molecules and reference atoms (Xe). (c) Theory: the amplitude and phase contribution from each Br₂ orbitals: HOMO, HOMO-1 and HOMO-2. We progressively add their weighted contributions coherently and show the calculated relative (d) amplitude and (e) photorecombination (*R*) phase difference. The theoretical calculations are relative to the same calculations for xenon atoms, and hence can be directly compared with the experiment. For clarity, all amplitudes (experiment and theory) are normalized to the values at $\theta=90^\circ$ ((a) and (d)) for each harmonic order, refer to SI sect. III for unnormalized plots, and all amplitudes and phases are, respectively, displayed using common color scales.

We have now demonstrated the LAPIN method, and its ability to measure the full two-dimensional spectral phase $\Delta\Phi_{Mix}(q, \theta)$. This novel XUV photonics method is important for molecular imaging [13] as it extracts contributions to HHG that are target-specific only, such as the photorecombination dipole. We now proceed to interpret the measurement and to compare it with single-molecule quantum chemistry and scattering predictions. We will extract the phase of the dipole moment, based on the measured relative electromagnetic phase $\Delta\Phi_{Mix}(q, \theta)$.

We recall that all three HHG steps contribute to the phase: ionization (*I*), propagation (*P*) and photorecombination (*R*). Since the same laser field is used to simultane-

ously generate harmonics in Br₂ and Xe in mixed gases interferometry, the phase difference ($\Delta\Phi_P(q)$) associated with the acceleration of the electron in the continuum essentially cancels out. However, a contribution associated with the difference in ionization potential ($\Delta I_p = -1.58$ eV) between Br₂ ($I_{p,\text{HOMO}} = 10.55$ eV) and Xe ($I_p = 12.13$ eV) remains: $\Delta\Phi_P(q) = -\Delta I_p \tau_q$ [11, 21, 22], τ_q being the calculated classical electron excursion time associated with the short trajectory harmonic order q . As a result, we can extract a relative phase $\Delta\Phi_{\text{Mol-Ref}}(q, \theta)$ between the molecule (HOMO is the molecular reference point) and the reference atom due to both the photorecombination (R) and possibly the ionization (I) steps [8, 9]:

$$\begin{aligned}\Delta\Phi_{\text{Mol-Ref}}(q, \theta) &= \Delta\Phi_{\text{Mix}}(q, \theta) - \Delta\Phi_P(q) \\ &= \Delta\Phi_R(q, \theta) + \Delta\Phi_I(q, \theta).\end{aligned}\tag{2}$$

At this point we could also remove the recombination phase of the reference xenon atom, which we calculated and show in the SI sect. II.A. Instead, we will leave the experimentally determined amplitude and phase of bromine relative to xenon, see Fig. 5 (a) and (b), and include the calculated xenon recombination amplitude and phase into the theoretical model, which we describe below.

At the laser intensity $I_{\text{probe}} = 1.5 \times 10^{14}$ W/cm² used in the experiment, multiple molecular orbitals of Br₂ (HOMO, HOMO-1 and HOMO-2) can significantly participate to HHG [8, 23, 24]. Indeed, a strong-field approximation calculation [25] on atoms with $I_{p,\text{HOMO}} = 10.55$ eV, $I_{p,\text{HOMO-1}} = 13.09$ eV and $I_{p,\text{HOMO-2}} = 14.62$ eV shows that, although HOMO emits the strongest for $q \leq 15$, the contributions from HOMO-1 and HOMO-2 become dominant for $q \geq 17$ (see SI Fig. S6(b)). In order to simulate the experiment, we coherently add the contributions from HOMO, HOMO-1 and HOMO-2 along the lines of refs. [8, 24], using molecular photorecombination dipoles obtained by quantum scattering calculations [26, 27]; refer to SI sect. III for details on the theoretical model. To be consistent with our definition of $\Delta\Phi_{\text{Mol-Ref}}(q, \theta)$ retrieved experimentally, see eq.(2), we also take HOMO as the molecular reference point and include the ionization potential differences relative to HOMO when calculating the expected photorecombination dipole relative phase $\Delta\Phi_R(q, \theta) = \Phi_{\text{Mol},R}(q, \theta) - \Phi_{\text{Ref},R}(q)$, see SI eqs. (S10-S12). In Fig. 5(c)-(e), we show the progressive contribution of each HOMO to the total relative amplitude (d) and phase (e).

The calculated amplitude and phase in Fig. 5(d) and (e) are in good agreement with the LAPIN experimental results in Fig. 5(a) and (b). Our calculations reveal that HOMO-1

is responsible for the amplitude and phase mainly peaking at $\theta = 90^\circ$, see Fig. 5(c) lower panel. An amplitude minimum in the vicinity of $q=21$ and $\theta = 0^\circ$, accompanied by a rapid local phase variation with increasing q , is observed experimentally. The position of this minimum ($q=21$) is consistent with the two-center interference model [28]; a similar feature around $q=23$ was also observed in the recombination dipole of aligned CO_2 measured by the RABBIT technique [7], Br_2 and CO_2 having the same ordering of valence molecular orbitals. However, the dependence of that spectral feature on laser intensity [8] and wavelength [24] in CO_2 instead supports the participation of multiple orbitals [23]. Here, our calculations in Fig. 5(d)-(e) qualitatively reproduce this spectral minimum and rapid phase variation observed experimentally in Fig. 5(a)-(b): it also originates from the interplay between the Br_2 HOMO and HOMO-2.

For quantitative agreement between experiment and theory (Fig. 5(b) and (e)), we need to add an overall constant $\Gamma \approx -0.9 \pi$ to the calculated recombination phase $\Phi_{\text{Mol},R}(q, \theta) - \Phi_{\text{Ref},R}(q)$. Based on eq. (2), this suggests an additional constant phase difference between the emission from HOMO and xenon, $\Gamma \approx -0.9 \pi$. While the concept of an ionization phase is not yet fully understood [8, 9], $\Delta\Phi_I \approx -0.9 \pi$ would explain the overall shift between the experiment and the model. As a result, comparing LAPIN measurements to our model allows to report an additional, previously unaccounted for, phase difference between the emission of two species in mixed gases experiments [18, 19, 22]. This needs to be further investigated by more detailed modeling which could include multielectron attosecond dynamics and sub-cycle laser-driven population evolution of the electron-hole first created by ionization [8, 9]. Our results on Br_2 support previous results in CO_2 where no ionization phase is observed between the XUV emission from different molecular orbitals [8].

In conclusion, we have combined two all-optical techniques, namely two-source harmonic phase and mixed gas interferometries, allowing us to first solve for the two-dimensional (q, θ) molecular high-harmonic photorecombination dipole amplitude and phase relative to that of a reference atom. Although we demonstrated the LAPIN technique using 30 fs laser pulses, unlike RABBIT [14], it will work for few-cycle pulses where individual harmonics are not resolved. Accessing these quantities is especially important for the development of single-molecule imaging by high harmonic generation [10–13]. LAPIN is applicable to any molecular systems that can be expanded in the gaseous phase, these include: aligned [20], three-dimensionally aligned [29] and oriented [30] polyatomic molecules. Finally, combining

LAPIN with time-resolved homodyne high-harmonic spectroscopy [31, 32] now provides all necessary information for time-resolved tomographic imaging of a chemical reaction.

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Supplementary Information for Linked Attosecond Phase Interferometry for Single-Molecule Imaging

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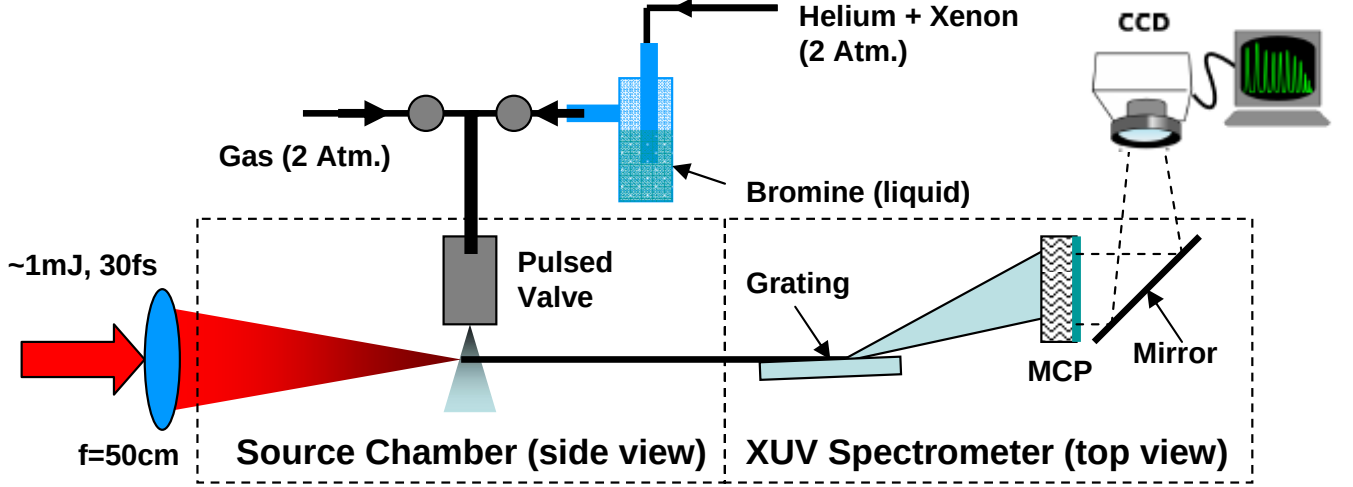


Figure S1. The high harmonics experimental setup composed of a source chamber and an XUV spectrometer. Bromine (Br_2) vapors are injected in a supersonic gas jet using a carrier gas (helium + xenon) that flows through liquid Br_2 .

I. EXPERIMENTAL SETUP

A. General

To perform the experiment, we use the output of a Ti:Sapphire multi-pass laser system (32 fs, 800 nm, 50 Hz, 12 mJ per pulse). An optical setup that both splits and recombines laser pulses for pump-probe experiments precedes the high-harmonic vacuum chamber. As seen in Fig. S1, we generate the high-harmonic radiation in a source chamber (pulsed valve, 250 μm orifice, total backing pressure is $P_{\text{back}}=2$ atm.) and measure spectra using an XUV spectrometer (a grazing incidence XUV grating, a microchannel plate detector backed by a phosphor screen, and a camera readout).

Bromine (Br_2) is a liquid at room temperature. In order to inject the bromine molecules through the pulsed valve (Parker Hannifin) into the chamber, a carrier gas (helium) was bubbled through the liquid Br_2 . Due to helium's high ionization potential of 24.6 eV, no high harmonic generation signal from helium is observed at the probe intensity $I_{\text{probe}} = 1.5 \times 10^{14} \text{ W/cm}^2$ employed in the experiment. In the second part of the experiment, mixed gas interferometry, we prepare a mixture of helium + xenon which provides a vapor pressure ratio r of Xe: Br_2 of $0.2:1.0 \pm 10\%$ at the gas jet. The error on r is attributed to measuring gas pressures in the preparation of the Xe+He carrier gas. The partial vapor pressure of Br_2 at $T=22^\circ$ Celsius is ~ 29 kPa (~ 0.3 atm.) [1]. In these conditions, high-harmonic signal is obtained from both Br_2 and xenon, providing an homodyne interference between the emission of each species [2, 3], see Fig. 3 of the main paper.

B. Sign convention and harmonic phase interferometry

In order that others are able to use and reproduce the present results, it is necessary that we establish our conventions regarding phases. In particular, since we are often measuring phase *differences*, the ordering of the contributions is important. Whenever we use a phase difference such as $\Delta\phi$, we use the order of molecule minus atom, e.g. $\Delta\phi = \phi_{\text{mol}} - \phi_{\text{ref}}$.

We use the time-dependent Schrodinger equation to establish the sign of the time propagator,

$$\psi(t) = e^{-iHt}\psi(0) = e^{-iEt}\psi(0). \quad (\text{S1})$$

Here H is the Hamiltonian and E is the eigenenergy for a time-independent Hamiltonian. This also defines the sign of the Fourier transform kernel to be $e^{i\omega t}$ [4].

We now define our sign convention for the Strong Field Approximation (SFA) [5] as follows, where we explicitly

include the energy of the neutral and the ion [6].

$$\begin{aligned} d(t) = & -i \int d\mathbf{k} \int_0^t dt_1 \left\langle \psi_N \left| e^{iE_N t} \mathbf{r} e^{-iE^+(t-t_1)} e^{-iS_v(t,t_1)} \right| \mathbf{k} + \mathbf{A}(t), \psi^+ \right\rangle \\ & \times \left\langle \mathbf{k} + \mathbf{A}(t_1), \psi^+ \left| \hat{V}_L(t_1) e^{-iE_N t_1} \right| \psi_N \right\rangle \end{aligned} \quad (\text{S2})$$

Here, $\psi_N(1\dots n)$ is the n -electron ground state of the neutral atom, E_N is the total energy of the neutral, $\psi^+(1\dots n-1)$ is the $(n-1)$ -electron wave function of the ion following ionization, E^+ is the total energy of the ion, $V_L = xE_L(t_1)$ is the interaction Hamiltonian due to the laser field, and $S_v(t, t_1) = \int_{t_1}^t (\mathbf{k} + \mathbf{A}(t''))^2 dt''/2$ is the Volkov phase of the electron in the continuum. If we substitute the ionization potential $I_p = E^+ - E_N$, the phase terms become

$$\phi = -S_v(t, t_1) - I_p(t - t_1). \quad (\text{S3})$$

Both S_v and I_p are positive, so this overall term will be negative.

We now define our sign convention for the harmonic phase $\Phi_{Mol}(q, \theta)$. The high harmonic generation process is composed of three steps: ionization, acceleration, and photorecombination [7]. Each step contributes to the total spectral amplitude $|D_{Mol}(q, \theta)|$ and phase $\Phi_{Mol}(q, \theta)$ of the emitted single-molecule real-valued high-harmonic dipolar XUV field E_{Mol} , where θ is the molecular alignment angle and q is the harmonic order at frequency $\Omega = q\omega_0$ with ω_0 being the central frequency of the driving laser field. Following the convention introduced in refs. [8, 9], in the spectral domain, we define the emitted field as:

$$E_{Mol}(q, \theta) = |D_{Mol}(q, \theta)| e^{i\Phi_{Mol}(q, \theta)}. \quad (\text{S4})$$

Using a thin gas jet in the experiment allows us to minimize propagation effects [10] and, therefore, to measure at the XUV detector a signal $S_{Mol}(q, \theta)$ proportional to the single-molecule intensity $|E_{Mol}|^2$. Since we are interested in the relative change of the signal with θ or q , we drop the proportionality sign and directly use the equality:

$$S_{Mol}(q, \theta) = |E_{Mol}(q, \theta)|^2. \quad (\text{S5})$$

The amplitude $|D_{Mol}|$ can be computed directly from the measured HHG spectrum: $|D_{Mol}(q, \theta)| = \sqrt{S_{Mol}(q, \theta)}$. The two-dimensional spectral phase $\Phi_{Mol}(q, \theta)$ of the XUV emission, however, is not readily accessible. We must specify that, for a given alignment angle θ , we refer here to $\Phi_{Mol}(q, \theta)$ as the spectral phase linking adjacent harmonics as can be measured by RABBIT [11–13] or FROG-CRAB [14]. This spectral phase is responsible for the temporal profile of the XUV emission on the attosecond timescale. On the other hand, the detailed variation of the phase over the bandwidth of a given harmonic order q will give access to the femtosecond temporal profile of the XUV emission, see ref. [4] for a detailed description. This finer structure in the harmonic phase can be measured via femtosecond optical techniques adapted to the XUV domain (high-harmonic SPIDER [15] and FROG-CRAB [14]). Next, we shall describe how harmonic phase interferometry allows us to measure $\Phi_{Mol}(\theta; q)$, the variation of the harmonic phase with molecular alignment angle.

In harmonic phase interferometry (HPI), the interference between the emitted fields from the top source aligned (E_{top}) and bottom source randomly aligned (E_{bottom}) molecules creates an interference in the far field at the XUV detector, see Fig. S2. Both sources are waves traveling to the right with, in addition, the top source also carrying information about the angular-dependent harmonic phase which we denote here as $\Phi_{HPI}(\theta; q)$. Following the phase sign convention in eq. S4 to describe the macroscopic high-harmonic field, the emissions from the top and bottom sources are written:

$$E_{top}(\theta; q) \propto e^{i(kr_1 - \Omega t)} e^{i\Phi_{HPI}(\theta; q)}, \quad E_{bottom}(\theta; q) \propto e^{i(kr_2 - \Omega t) + i\Phi_q}, \quad (\text{S6})$$

where we have introduced an arbitrary constant spectral phase Φ_q for the bottom source which acts as a local oscillator here. By varying the molecular alignment angle from $\theta = 0^\circ$ to 90° in the top source only, we observe the fringes moving along the vertical direction on the XUV detector. The phase difference determines the position of the fringes. Let us consider the central fringe ($r_1 = r_2$) at $\theta = 0^\circ$. If it moves up when increasing θ , this means that, since the phase difference remains the same: $\Phi_{HPI}(\theta) - \Phi_q + k(r_1 - r_2) = \Phi_{HPI}(\theta = 0^\circ) - \Phi_q$. Since $(r_1 - r_2) < 0$, this straightforwardly means $\Phi_{HPI}(\theta) - \Phi_q > 0$. In other words, when the fringes move in the upper direction at the detector, the phase $\Phi_{HPI}(\theta; q)$ increases.

We understand from this analysis that, having aligned the molecules in the bottom source instead, the fringes would have moved in the opposite direction. We carefully imaged the laser foci of both the two-source probe and alignment pulses, as seen in Fig. S2(b), to confirm that we were indeed aligning the top source. We also had to carefully examine the entire XUV spectrometer imaging system in order to determine the sense of motion of the fringes.

Harmonic Phase Interferometry

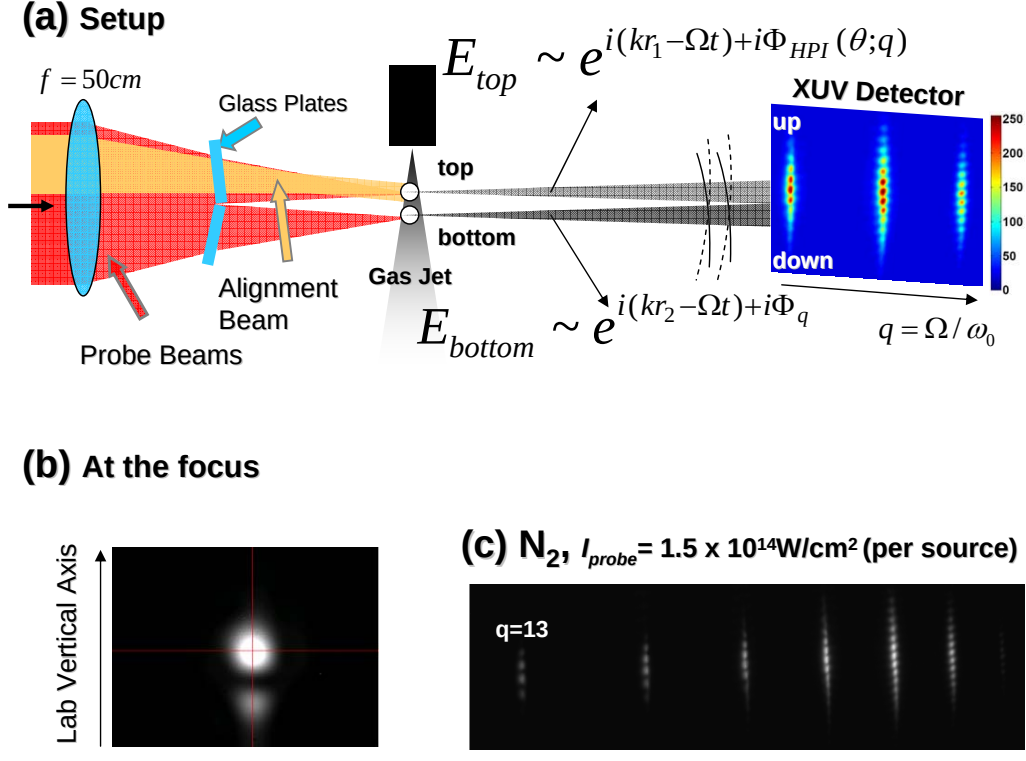


Figure S2. Spectral harmonic phase interferometry (HPI) of aligned Br_2 molecules. (a) Two XUV sources created in a supersonic gas jet interfere in the far field. We laser-align the molecules in the top source only and observe the interference fringes moving as a function of alignment angle θ , providing a measurement of the high-harmonic spectral phase $\Phi_{HPI}(\theta; q)$, see text for details. (b) We image the laser foci of both 2-source probe and alignment pulses using an imaging system and a ccd camera, confirming that we align the molecules in the top source only. (c) A typical high-harmonic spectrum (averaged over 50 laser shots) as seen on the detector.

Since the macroscopic response restricts the emission from randomly aligned molecules (bottom source) to be polarized parallel to the driving field, the motion of the fringes provides a measurement of the phase of the parallel (to the driving laser field) component of the electromagnetic field E_{top} emitted from aligned Br_2 molecules. We have performed polarimetry measurements (not presented here) which indicate that the perpendicular component from aligned Br_2 is small ($\leq 10\%$ in intensity). In other cases, stronger perpendicular emission could affect the measurement in part by changing the fringes' visibility [16].

The position of the fringes in the vertical direction (at the XUV detector, see Fig. 2(c)) is averaged over 1000 laser shots at each molecular angle θ . Molecular alignment (in the top source only) is obtained by the nonadiabatic interaction of a non-ionizing and stretched (~ 130 fs, $I_{align} = 3 \times 10^{13} \text{ W/cm}^2$) laser pulse with the gas-phase molecules [17]. This pulse comes 0.5 ps earlier to provide prompt molecular alignment. For each given harmonic q -order, the position of the fringes is obtained by first integrating horizontally (over the spectral width of a given harmonic) the averaged signal on the detector and then, by spatially Fourier transforming the profile along the vertical direction [18]. The extracted phase, which we denote as $\Phi_{HPI}(\theta; q)$, is the phase of this transform, where 2π corresponds to the distance between two bright (or dark) fringes. We arbitrarily choose $\Phi_{HPI}(\theta=0; q)=0$ since there is no connection made between adjacent harmonics in this measurement. We plot the results for each measured harmonic order $q=13$ to 23 (~ 20 -35eV) in Fig. 2(b) of the main paper.

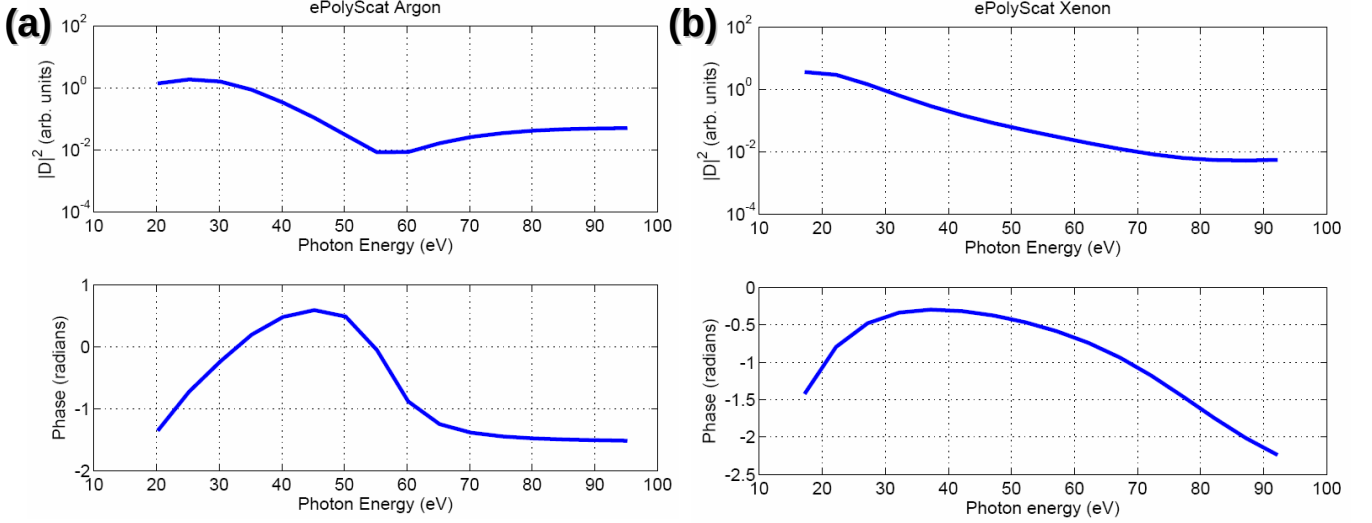


Figure S3. The amplitude squared ($S_{Ref,R}(q)$, top panel) and phase ($\Phi_{Ref,R}(q)$, lower panel) of the photorecombination (R) differential cross section as calculated by ePolyScat [19, 20] for (a) argon (Ar) and (b) xenon (Xe).

II. MIXED GASES INTERFEROMETRY

A. Xenon as reference Atom

In the second step of the LAPIN procedure, mixed gases interferometry, xenon acts as a θ -independent homodyne local oscillator against which we measure the molecular harmonic phase $\Phi_{Mol}(q, \theta)$ of the Br_2 molecules. We choose xenon as a reference because it has a polarizability and an ionization potential ($I_p=12.13$ eV) similar to Br_2 ($I_{p,\text{HOMO}}=10.55$ eV, $I_{p,\text{HOMO}-1}=13.09$ eV and $I_{p,\text{HOMO}-2}=14.62$ eV) [21], offering similar ionization dynamics. Having a reference atom with a much smaller ionization potential ($I_{p,\text{Ref}}$) than the molecule's ($I_{p,\text{Mol}}$) could engender macroscopic phase mismatch effect due to the large amount of free electrons created by ionization. At the opposite extreme, if $I_{p,\text{Ref}}$ is much larger than $I_{p,\text{Mol}}$, the reference atom emission will be too small for accurate interferometry. We selected the molar ratio $r \approx 0.20$ in order to approximately balance the HHG emission from xenon and bromine.

Ideally, to make the molecular amplitude and phase retrieval the most straightforward, one would use a reference atom with flat high-harmonic photorecombination (R) amplitude $\sqrt{S_{Ref,R}(q)}$ and phase $\Phi_{Ref,R}(q)$ in the spectral range of interest, $q=13$ to 23 (~ 20 - 35 eV). It is not quite the case for xenon as shown in Fig. S3(b). Later, we will use this calculated differential photorecombination cross section (we take the complex conjugate of the output from ePolyScat [19, 20]) to compute the theoretical relative amplitude $\sqrt{S_{Mol}(q)/S_{Ref}(q)}$ and relative phase $\Phi_{Mol,R}(q, \theta) - \Phi_{Ref,R}(q)$. We will compare those to the experimentally retrieved values by LAPIN, see Fig. 5(a) and (b) of the main paper. In Fig. S3(a), we display the calculated signal $S_{Ref,R}(q)$ (top panel) and phase $\Phi_{Ref,R}(q)$ (lower panel) of argon. We verified the reliability of the calculation by reproducing the argon Cooper minimum in the vicinity of ~ 55 eV [22].

B. The Amplitude and Phase Retrieval Procedure

The signal from the gas mixture is a coherent sum of the emission from both molecular and atomic reference species [3]:

$$S_{Mix}(q, \theta, r) = S_{Mol}(q, \theta) + r^2 S_{Ref}(q) + 2r \sqrt{S_{Mol}(q, \theta)} \sqrt{S_{Ref}(q)} \cos \Delta \Phi_{Mix}(q, \theta) \quad (\text{S7})$$

where $r \sim 0.2$ is the Xe/ Br_2 molar fraction in the gas jet. We directly measure $S_{Mol}(q, \theta)$ (the HHG spectrum for the bromine molecules alone as a function of molecular alignment angle θ) and $S_{Mix}(q, \theta)$ (the HHG spectrum for the mixture of the bromine molecules and the reference xenon atoms as a function of molecular alignment angle).

The bromine molecules are entrained in a helium carrier gas in the pulsed valve gas expansion. We only add about $\sim 4\%$ by pressure of xenon to the helium, which has negligible effect on the gas expansion. However, we cannot directly measure the HHG spectrum from the reference atom alone $S_{Ref}(q)$ as in other experiments [3, 23], because the pulsed

valve operation is different without the presence of Br₂ vapors. Instead, we separately record the HHG spectra of the bromine molecules alone ($S_{Mol}(q, \theta)$) and of the gas mixture ($S_{Mix}(q, \theta)$). This not only removes the difficulty in matching gas expansion conditions with and without Br₂ molecules, but also means that we do not need to know the precise ratio of gas pressures r : our fitting procedure uniquely determines $r^2 S_{Ref}(q)$.

We normalize eq. (S7) by the XUV signal from Br₂ molecules alone $S_{Mol}(q, \theta)$ (see Fig. 3(b) of the main paper, both $S_{Mol}(q, \theta)$ and $S_{Mix}(q, \theta)$ are the respective raw signals normalized by the raw signal from aligned molecules at $\theta = 0^\circ$, i.e., $S_{Mol}(q, \theta = 0^\circ) = 1$) and obtain the ratio $R_{Mix}(q, \theta, r)$:

$$R_{Mix}(q, \theta, r) = 1 + r^2 \frac{S_{Ref}(q)}{S_{Mol}(q, \theta)} + 2r \sqrt{\frac{S_{Ref}(q)}{S_{Mol}(q, \theta)}} \cos \Delta\Phi_{Mix}(q, \theta) \quad (S8)$$

Here $\Delta\Phi_{Mix}(q, \theta) = \Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)$ is defined as the phase difference between the emission from the aligned molecules $E_{Mol}(q, \theta)$ and that of the reference atom $E_{Ref}(q)$.

We separately record the HHG spectra of the bromine molecules alone ($S_{Mol}(q, \theta)$) and of the gas mixture ($S_{Mix}(q, \theta)$). In eq. S8 we know all quantities except for $r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$. Therefore we seek to solve for these two unknowns. For each harmonic order q , we have 21 measurements at different molecular angles θ . Therefore there is sufficient information to determine both $r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$, provided that we parameterize the phase. However the mixed gas measurement alone is not able to determine the sign of the phase due to the cosine function.

In mixed gases interferometry, an ambiguity on the phase arises because $\cos \Delta\Phi_{Mix}(q, \theta)$ is symmetric around $\Delta\Phi_{Mix}(q, \theta) = 0$ [23]. Two solutions, $\pm \Delta\Phi_{Mix}(q, \theta)$, can satisfy eq. S8, thereby accessing only $|\Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)|$ and leaving the *directionality* of $\Phi_{Mol}(q, \theta)$ undetermined. McFarland et al. [23] had to make assumptions about the direction of the phase difference in order to extract the molecular phase. However, we recall that in the first interferometry step (HPI) we measured the *directionality* (up or down) of $\Phi_{HPI}(\theta; q)$, corresponding also to a measurement of the *directionality* of $\Phi_{Mol}(q, \theta)$ based on our definition of E_{Mol} above, see eq. (S4). Therefore we can use the redundant information provided by the HPI measurement to lift the sign ambiguity of the phase. For this purpose, we combine both experimental measurements, $\Phi_{HPI}(\theta; q)$ and $R_{Mix}(q, \theta)$, into a global fitting procedure. This procedure of combining two phase measurements has been given the acronym LAPIN: Linked Attosecond Phase INterferometry.

We parameterize the phase difference using even (0-6) Legendre polynomials P_{2i} ,

$$\Delta\Phi_{Mix}(q, \theta) = \left| \sum_{i=0}^3 a_{2i} P_{2i}(\theta) \right|$$

This parameterization fulfills the symmetry requirements at parallel ($\theta=0^\circ$) and perpendicular ($\theta=90^\circ$) alignments. Using 4 Legendre polynomials is sufficient to match the HPI measurements, but in principle higher orders can be included if necessary.

For each harmonic order q , we then need to extract 4 angular parameters a_{2i} and the single value of $r^2 S_{Ref}(q)$. Since there are 21 angular measurements made at each harmonic order q , the system is overdetermined. We apply a nonlinear least-squares fitting procedure to extract the parameters. This procedure seeks to minimize the error function between the fit and the measurement. We include both the mixed gas measurement and the HPI measurement into the error function L_q which is defined as the sum of the residuals,

$$L_q = w_1 \sum_{\theta} |R_{Calc}(q, \theta) - R_{Mix}(q, \theta)| + w_2 \sum_{\theta} |\Delta\Phi_{Mix}(q, \theta) - \Delta\Phi_{Mix}(q, \theta = 0^\circ) - \Phi_{HPI}(\theta; q)| \quad (S9)$$

where $R_{Calc}(q, \theta)$ is the calculated ratio using eq. (S8) and the 5 fitting parameters, and $\sum_{\theta}$ denotes summation over the 21 angular measurements. w_1 and w_2 are weighting factors chosen to, respectively, give more importance to the mixed gases or the harmonic phase interferometry measurements. We use $w_1 = w_2 = 1$ to equally take into consideration both interferometry steps. Below, we will discuss the effect of changing w_1 and w_2 .

In Fig. S4(a), we show the general fitting procedure for the case of $q=17$. We obtain $R_{Mix}(q = 17, \theta, r = 0.2)$ (triangles pointing down) from dividing the signal from the mix $S_{Mix}(q = 17, \theta)$ (diamonds) by the one from molecules alone $S_{Mol}(q = 17, \theta)$ (open circles). Every point is averaged over 1000 laser shots and the $\pm$ error bars on raw measurements are obtained by calculating the standard deviation at each point. We solve eq. (S9) and obtain both the reference atom signal $r^2 S_{Ref}(q = 17)$ and the relative angular phase $\Delta\Phi_{Mix}(q = 17, \theta)$ (crosses). The quality of the fit is seen here in the overlap of R_{Calc} (solid line) with R_{Mix} . We observe that the extracted phase $\Delta\Phi_{Mix}(q = 17, \theta)$ (cross) is almost identical (in modulation depth) as $\Phi_{HPI}(\theta; q = 17)$ (dashed line). This confirms the consistency between the two interferometry steps. From the total solution ($r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$) and using eq. (S8), we

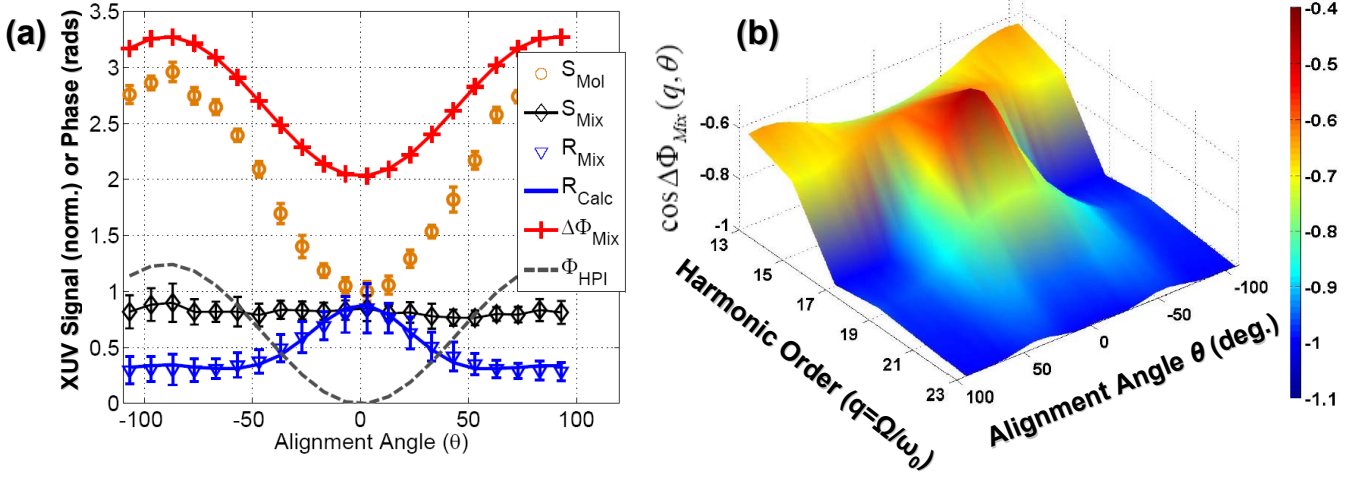


Figure S4. (a) Fitting procedure for $q=17$, see text for details. (b) The retrieved value for $\cos \Delta\Phi_{Mix}(q, \theta)$, see eq. (S8) below, showing that the interference between Br_2 and xenon is destructive over the full (q, θ) range covered in the experiment.

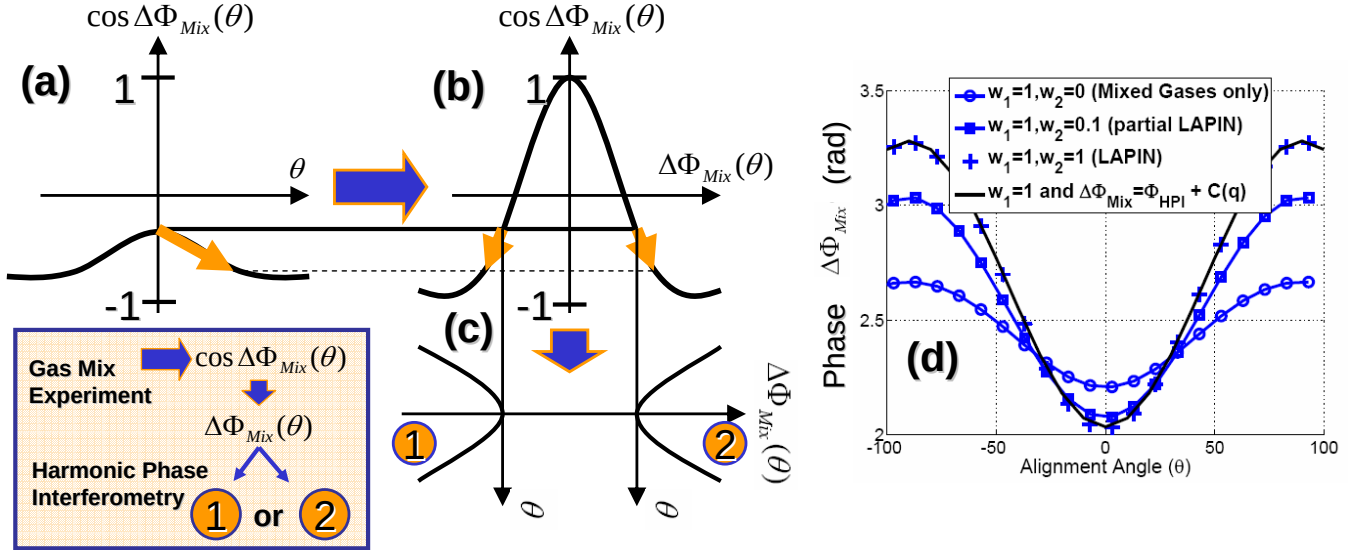


Figure S5. (a) One can extract $\Delta\Phi_{Mix}(q, \theta)$ by mixed gas interferometry only. (b) However, two solutions for $\Delta\Phi_{Mix}(q, \theta)$ are possible since $\cos \Delta\Phi_{Mix}(q, \theta)$ is symmetric around $\Delta\Phi_{Mix} = 0$. (c) The harmonic phase interferometry step allows to unequivocally determine the curvature (case 1 or 2) of $\Delta\Phi_{Mix}(q, \theta) = \Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)$. (d) Effect of changing the relative weights in the global LAPIN fitting procedure for $q=17$.

compute the value of $\cos \Delta\Phi_{Mix}(q, \theta)$, which is shown in Fig. S4(c). The result confirms that the interference between aligned Br_2 molecules and xenon is strongly destructive, consistent with the raw mixed gases measurements presented in Fig. (3) of the main paper.

We have also solved for $\Delta\Phi_{Mix}(q, \theta)$ based solely on (A) mixed gas interferometry ($w_1=1, w_2=0$). In that case, we manually used the HPI measurement to lift the ambiguity of the sign of $\Delta\Phi_{Mix}(q, \theta)$, see Fig. S5(a)-(c). For example, in Fig. S5(d), we select the solution where the phase increases with increasing (starting at $\theta=0^\circ$) molecular angle (circles), the other solution being symmetric with $\Delta\Phi_{Mix}(q, \theta)=0$ or π (not shown). The LAPIN ($w_1=1, w_2=1$) solution is also shown (crosses). We also explored the (B) procedure where we would take $\Delta\Phi_{Mix}(q, \theta) = \Phi_{HPI}(\theta; q=17) + C(q)$, that is, shifting vertically by a constant phase $C(q)$ determined from mixed gas interferometry. This would usually give a solution (black solid line) close to the LAPIN ($w_1 = w_2=1$) solution (crosses). As expected, decreasing the weight ($w_1=1, w_2=0.1$) given to the first interferometry step (HPI), pulls the solution (squares) back towards the mixed gases only (circles).

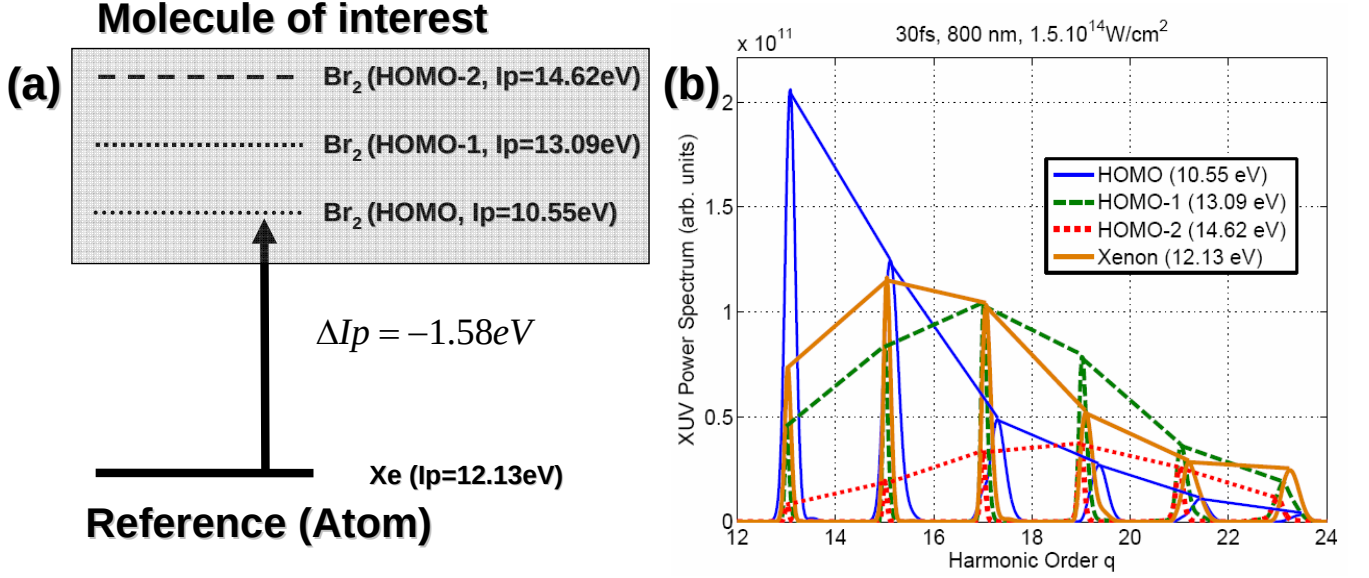


Figure S6. (a) The highest occupied molecular orbitals of Br_2 have similar ionization potentials. Throughout this work, both experimentally and theoretically, we always measure the amplitude and phase of the XUV emission from aligned Br_2 molecules (above) relative to a reference Xenon atom (below). (b) Calculated high-harmonic spectra from atomic-like species of ionization potentials of the Br_2 HOMOs, where we used a gaussian pulse of full width at half maximum of 30fs (centered on 800nm) and peak intensity $I_{\text{probe}} = 1.5 \times 10^{14} \text{ W/cm}^2$.

Overlap between the R_{Calc} solution and R_{Mix} is always observed: all different solutions for $\Delta\Phi_{\text{Mix}}(q, \theta)$, see Fig. S5(d), are accompanied by different retrieved amplitudes $r\sqrt{S_{\text{Ref}}}$ which all lie inside the range $\pm 50\%$ of the LAPIN solution. The case of $q=17$ in Fig. S5(d) presents the strongest difference between the two extrema solutions (A) and (B) discussed above. We attribute the discrepancies between the (A) and (B) extrema solutions to various possible reasons: a small orthogonal component of E_{Mol} provides an extra term not accounted for in eqs. (S7) and (S8), and the different generation conditions between the HPI and mixed gases steps (1 source vs 2 sources) probe molecules from slightly different locations in the gas jet expansion (e.g. different degrees of alignment).

In general, for all harmonic orders q , we observe that the LAPIN solution ($w_1=1, w_2=1$) falls between the (A) and (B) extrema and that all solutions are similar (modulation depth and location on the vertical phase axis). First, this confirms the consistency between the measurements from individual interferometry steps and second, most importantly, justifies using the LAPIN procedure for finding a unique solution that simultaneously takes both measurements into account.

III. THEORY: PARTICIPATION OF MULTIPLE MOLECULAR ORBITALS

At the laser intensity $I_{\text{probe}} = 1.5 \times 10^{14} \text{ W/cm}^2$ used in the experiment, multiple highest occupied molecular orbitals (HOMO) can significantly participate to the high harmonic generation process [18, 24]. In Br_2 , HOMO, HOMO-1 and HOMO-2, have similar vertical ionization potentials ($I_{\text{p,HOMO}}=10.55 \text{ eV}$, $I_{\text{p,HOMO-1}}=13.09 \text{ eV}$ and $I_{\text{p,HOMO-2}}=14.62 \text{ eV}$), see Fig. S6(a). In order to estimate the contribution from each orbital, we use the Strong Field Approximation (SFA) along the lines of ref. [25], where we use the Yudin-Ivanov model [26] for the instantaneous ionization rate, and treat each molecular orbital as an atomic emitter [27] with a flat photorecombination cross section ($=1$). We observe that although HOMO emits the strongest for $q \leq 15$, the contribution from HOMO-1 and HOMO-2 becomes dominant at $q \geq 17$, see Fig. S6(b).

In order to simulate the experiment, we need to coherently add the contributions from HOMO, HOMO-1 and HOMO-2 which we denote respectively with the indices $j = 0 - 2$. Using the SFA framework, we write the total complex molecular frame dipole along the lines of refs. [18, 28]:

$$D_{\text{Mult}}(q, \alpha) = \sqrt{c_0(q)^2 I_0(\alpha)} R_0(q, \alpha) e^{i\phi_0(q)} + \sqrt{c_1(q)^2 I_1(\alpha)} R_1(q, \alpha) e^{i\phi_1(q)} + \sqrt{c_2(q)^2 I_2(\alpha)} R_2(q, \alpha) e^{i\phi_2(q)} \quad (\text{S10})$$

where the normalized spectral weights $c_j(q)^2$ (see Fig. S7(a)) are obtained by normalizing the atomic XUV spectra

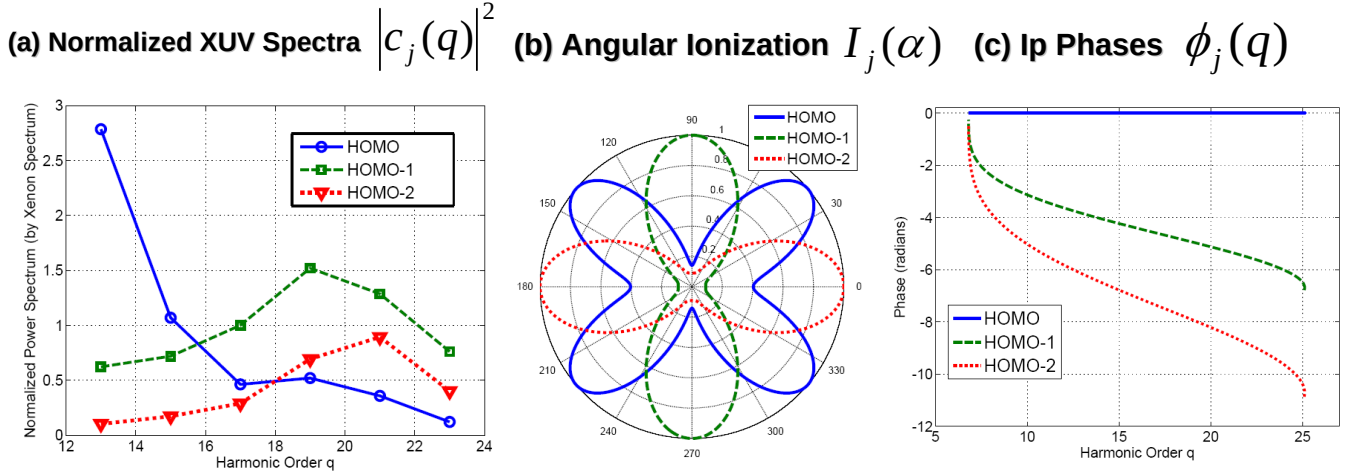


Figure S7. (a) High-harmonic spectral contribution from each orbitals from an SFA calculation with atomic species (b) The corresponding molecular frame ionization profiles taken from ref. [18] and (c) the additional phase due to the difference in ionization potential of each orbitals with respect to HOMO ($\Delta I_{p,0}=0$).

by the one of xenon in Fig. S6(b), and the R_j are the complex recombination dipoles. α denotes the angle between the molecular axis and the laser polarization in the molecular frame (throughout the paper, we have chosen θ as the angle between the alignment distribution axis and the laser polarization in the laboratory frame, not to confuse with the opposite notation in ref. [29]). The angular ionization profiles $I_j(\alpha)$ are chosen to contain the signature of the corresponding molecular orbitals [18] (see Fig. S7(b)) and the phases $\phi_j(q) = -\Delta I_{p,j}\tau_q$ (see Fig. S7(c)) carry the effect of the different ionization potentials associated to each orbitals with respect to HOMO [2, 5, 30], τ_q being the classical electron excursion time associated with the short trajectory harmonic order q for HOMO. We use $\Delta I_{p,0}=0$ to be consistent with our definition of the retrieved phase in the main paper, where HOMO is the molecular reference point when compared to the reference atom, see Fig. S6(a).

The complex molecular frame differential photorecombination dipoles $R_i(q, \alpha)$ are obtained by ePolyScat calculations [19, 20]. We calculate Hartree-Fock orbitals using Gaussian using a cc-pVTZ basis set for bromine. These orbitals are then used as input to ePolyScat to calculate the transition moments from bound states to continuum electrons of various kinetic energies. We include only the parallel (to the driving field) polarization component and take the complex conjugate of the ePolyScat (photoionization) output.

We obtain the calculated laboratory frame relative XUV amplitude $\sqrt{S_{Mol}(q, \theta)}/\sqrt{S_{Ref}(q)}$ (see Fig. S8(c)) by performing a coherent convolution of the molecular frame emission D_{Mult} with the alignment distribution $A(\theta', \phi')$ [31]:

$$\sqrt{S_{Mol}(q, \theta)}/\sqrt{S_{Ref}(q)} = \left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{Mult}(q, \alpha(\theta', \phi', \theta)) A(\theta', \phi') \sin\theta' d\phi' d\theta' \right| / \sqrt{S_{Ref,R}(q)}. \quad (S11)$$

α is the angle between the laser polarization (linear) and the molecular axis, θ is the angle between the main axis of the prolate alignment distribution $A(\theta', \phi')$ and the laser polarization, and (θ', ϕ') are, respectively, the angles with respect to the distribution axis and in a plane perpendicular to that axis. The angles are related via a frame transformation [29]: $\cos \alpha = \cos \theta \cos \theta' - \sin \theta \sin \theta' \sin \phi'$. We use an alignment distribution $A(\theta', \phi')$ of degree of alignment $\langle \cos^2 \theta' \rangle = 0.55$, based on our experimental conditions ($P_{back}=2$ atm., $T_{rot}=30-40$ K, $I_{align} = 3 \times 10^{13}$ W/cm²) and supported by a time-dependent Schrödinger equation calculation of prompt alignment in these conditions for Br₂ [32]. The corresponding alignment distribution $A(\theta')$ has an analytical form [29] and the dependence on ϕ' is lost by cylindrical symmetry. The missing Ω^2 prefactor in eq. (S11) [31] is implicitly included via the calculated spectral (purely real) amplitudes $c_j(q)$ in eq. (S10) and cancels out since eq. (S11) is a ratio. In this manner, we express the reference atom amplitude $\sqrt{S_{Ref}(q)}$ as a product of the contribution from the ionization step, included implicitly via the normalized coefficients $c_j(q)$ described earlier, and the photorecombination step via $\sqrt{S_{Ref,R}(q)}$ shown in Fig. S3(b) (top panel).

The calculated laboratory frame photorecombination (R) phase difference between the molecule and the reference

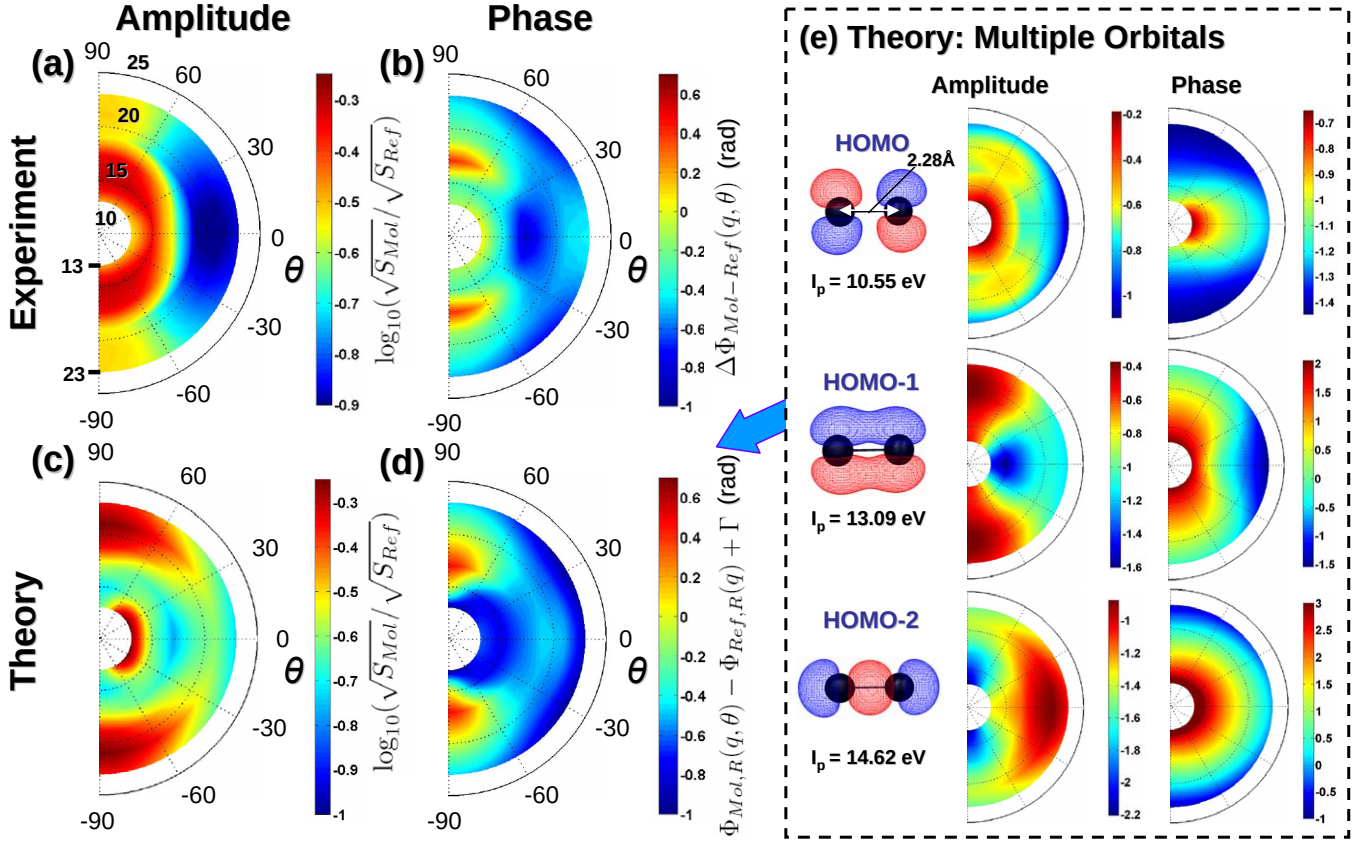


Figure S8. (a)-(d) are reproduced (unnormalized) from Fig. 5 of the main paper. (e) The calculated laboratory frame relative amplitudes (left) and phases (right) from individual orbitals, notice the varying color scales. We use eqs. (S10-S12) and consider the contribution from each orbitals: HOMO ($j=0$, top), HOMO-1 ($j=1$, middle) and HOMO-2 ($j=2$, bottom).

atom (see Fig. S8(d)) is then obtained in the following way:

$$\begin{aligned} & \Phi_{Mol,R}(q, \theta) - \Phi_{Ref,R}(q) = \\ & \arg \left[\int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{Mult}(q, \alpha(\theta', \phi', \theta)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right] - \Phi_{Ref,R}(q) \end{aligned} \quad (S12)$$

$\Phi_{Ref,R}(q)$ is shown in Fig. S3(b).

In Fig. S8(e), we show the individual contribution of each molecular orbital ($j = 0-2$ in eq.(S10)) to the total relative amplitude (eq.(S11)) and phase (eq.(S12)) to which we add the constant $\Gamma \approx -0.9\pi$. We note that Br_2 and CO_2 have the same sequence of valence molecular orbitals. Our calculated amplitudes and phases in Fig. S8(e) compare qualitatively well with other calculations made in CO_2 using a different approach for calculating the photorecombination dipole moments [18].

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Chapter 6

Conclusions and Perspectives

In high harmonic generation, the strong driving laser field imposes its coherence on the atomic or molecular system involved. This is an important guideline we follow, throughout this thesis, to contribute originally to the new field of high-harmonic spectroscopy. In particular, we develop new attosecond techniques that allow the coherent detection of single-molecule chemical dynamics, refer to chapter 4. We also explore different aspects of high-harmonic spectroscopy, helping to establish it as a novel, ultrafast, and fully coherent atomic and molecular spectroscopy. Next, in section 6.1, we summarize the original findings contained in each chapter (2 to 6) and discuss, along the way, possible applications relevant to the emerging field of attosecond science. Other related (unpublished) work conducted during this Ph.D will be mentioned. We finish by presenting our current progress towards this thesis' initial main goal (section 1.5) of imaging a chemical reaction in section 6.2.

6.1 Contributions to High-Harmonic Spectroscopy and Attosecond Science

High harmonic generation is a highly nonperturbative process, refer to theory sections 1.2-1.3. However, we show in the first article (publication 7) of chapter 2 that a perturbative

nonlinearity can still be developed around it upon the application of another laser field. This bridges the conceptual gap between perturbative nonlinear optics (NLO), introduced in the 1960s [39, 126], and nonperturbative NLO, introduced in the 1990s [43, 49] for high harmonic generation. It opens a route to transfer the powerful wave-mixing techniques of perturbative NLO to high intensity, highly nonlinear phenomena.

Possible applications of perturbative NLO techniques to high-harmonic spectroscopy include implementing noncollinear wave-mixing pump-probe schemes such as transient grating or Box-CARS [127]. In chapter 4, we implement the transient grating scheme: two noncollinear and synchronized pump-pulses are used to launch molecular dynamics later probed by high harmonic generation. In this case, the noncollinear photon momentum, initially put in the medium by the simultaneous presence of the two pump pulses, manifests itself by spatially diffracting the high-harmonic emission. In another case, when two or more laser fields are simultaneously present to drive high harmonic generation, the off-axis direction of the high-harmonic emission can be predicted straightforwardly using conservation laws (publication 7). It is unclear, however, if high-harmonic photons emitted from excited molecules will carry the momentum signature from a single (or multiple delayed) pump pulse(s) in a noncollinear optical spectroscopy such as Box-CARS. This area remains unexplored but could potentially make wave-mixing concepts useful to attosecond science investigations in photo-excited atomic or molecular systems.

One important technological outcome from the noncollinear two-color HHG experiment (publication 7) is its utility as an all-optical high-harmonic radiation beam splitter. By selecting the angle at which the weaker 'perturbation' field ($\sim 10^{-1}I_0$ in intensity) intersects the laser focus of the strong driving field (I_0 in intensity) in the generation medium, the off-axis direction of the high-harmonic emission can be controlled. This scheme can be used to spatially decouple the high-harmonic light from the driving laser beams, a particularly attractive scheme for high-repetition rate cavity-assisted HHG [118].

We estimate that the noncollinear HHG scheme can be directly implemented towards two types of experiments, see Fig. 6.1: (a) for attosecond interferometry and (b) all-attosecond pump-probe experiments. In the first case (a), high-harmonic photons emitted at the same frequency, but dispersed vertically, could be reunited using a recombination

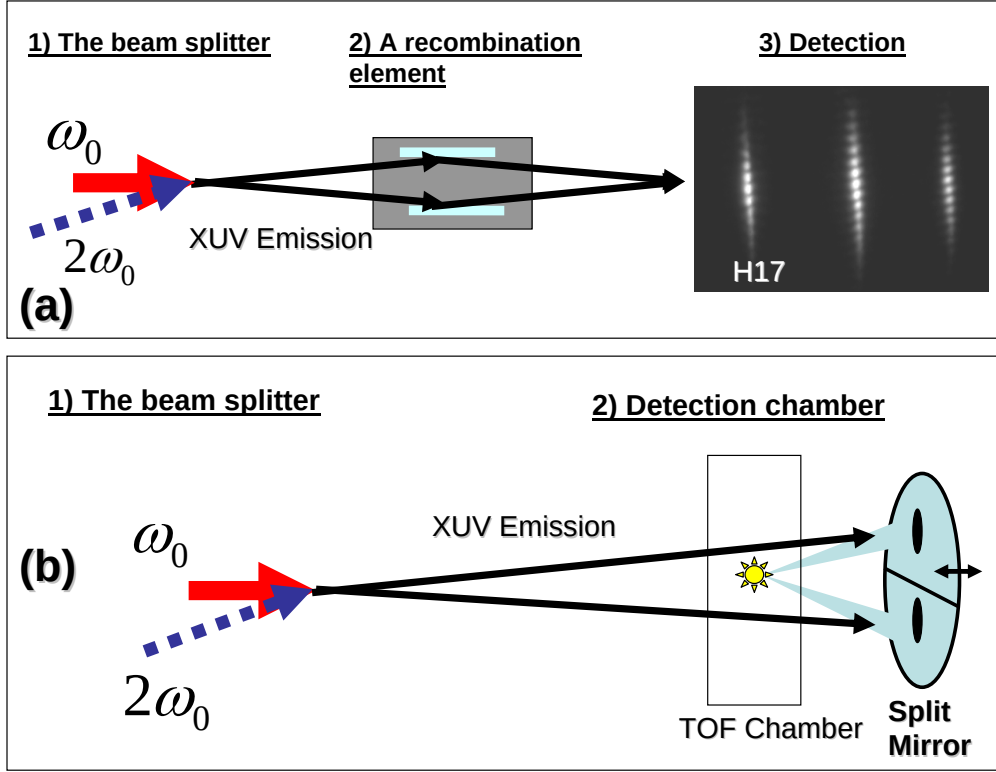


Figure 6.1: An all-optical XUV beam splitter for (a) attosecond interferometry or (b) all-attosecond pump-probe experiments, see text for details. The beam splitter is an outcome of the original work presented in publication 7.

element made of mirrors, see middle of Fig. 6.1 (a), on the light detector for performing frequency-resolved interferometry experiments. As a proof of principle, in the far right of Fig. 6.1 (a), we show the resulting interference pattern (on the detector) of two high-harmonic sources created in a gas jet. Please refer to chapter 5 for a description of the two-source harmonic phase interferometry (HPI) setup. One could study the phase shifts introduced by reflexion on one surface of the recombination element undergoing dynamics: for example, a surface undergoing ultrafast femtosecond demagnetization [128].

Another application of the XUV beam splitter would be for attosecond-pump and attosecond-probe spectroscopy. Provided that a sufficient amount of XUV radiation is emitted both in the upper and lower vertical direction from the propagation axis of the

fundamental beam (ω_0 is horizontal), the XUV light can be sent directly to a split mirror before being focused in a charged-particle TOF (time-of-flight) detection chamber to perform all-attosecond pump-probe photoionization measurements, as shown in Fig. 6.1 (b). A similar pump-probe scheme was achieved in ref. [129] using a diffuse high-harmonic beam generated by a single color laser beam. Further investigation on the spatial dependence of the noncollinear emission spectral phase is required in order to, ultimately, implement this technique to single attosecond pulses pump-probe experiments.

Still in chapter 2, the first experimental observation of even harmonic orders from oriented molecules is reported in publication 16. Here, it is the coherence imposed by the strong laser field between the emission of successive attosecond pulses that allows us to probe valence electrons asymmetry on a single-molecule scale. The background-free detection of even harmonics is applicable to any molecule or time-resolved chemical reaction realizable experimentally in the gas phase. Disentangling the origin of the asymmetry, however, either in the relative spectral amplitude or phase of the attosecond pulses, is not straightforward. It requires an *a priori* knowledge of the degree of orientation achieved experimentally: our current efforts in determining the actual mechanism underlying two-color laser field orientation [130, 131] will shed light on this aspect (publication 13).

In chapter 3 we contribute to the large class of experiments where HHS was first developed in the early 2000s: high harmonic generation in field-free aligned molecules [35]. In the first article (publication 4), we add to this particular area by performing one of the first experiments in aligned molecules at longer (than 800nm) driving laser field wavelengths. In particular, this piece of work provides additional evidence for the participation of multiple molecular orbitals. This is currently a hot research topic in all spectroscopies encompassing Strong Field Ionization (SFI) as it would (always) underlie attosecond electron dynamics [25, 33]. In high-harmonic spectroscopy, it is via the ionization step (step 1) that electronic coherence between the highest-lying valence orbitals would be introduced by the strong driving laser field and lead to attosecond electron wave packets. To summarize, the study presented in publication 4 reveals that both dynamical (laser-dependent) and structural (laser-independent) properties of aligned molecules are probed by high-harmonic spectroscopy. Varying the driving laser field wavelength is an efficient way of disentangling and controlling the participation of multiple molecular or-

bitals [25, 63] and, for the purpose of molecular imaging, accurately identifying the object wave function $\Psi_g(\mathbf{r})$ to be imaged via high-harmonic tomographic imaging (section 1.4).

Also in chapter 3, in the second article (publication 15), we show how the blurring effect coming from imperfect alignment, as typically achieved in the laboratory frame, can be removed. In particular, the presented deconvolution procedure allows us to identify that the spectral minimum (~ 42 eV) in aligned N_2 molecules is a Cooper-like minimum, as supported by state-of-the-art quantum scattering photorecombination calculations. It originates from the coherent contribution of two recombining partial waves, a universal feature already known from photoionization [41] and expected to often occur in high-harmonic spectroscopy of aligned molecular and atomic [132] targets. The deconvolution approach will significantly improve the angular resolution of high-harmonic molecular imaging when alignment averaging is important. We discuss, in section 1.3.3, how this procedure can be further improved for the complete (polarization, amplitude and phase) retrieval of the molecular frame high-harmonic dipolar field.

In chapter 4, we introduce homodyne high-harmonic spectroscopy of chemical reactions in the gas phase. We first study a prototypical chemical reaction: the photodissociation of diatomic Br_2 molecules into two neutral Br atoms. This pump-probe experiment reminds us of the old problem in femtochemistry where rarely more than 10-15% of the molecules can typically be single-photon excited by a short femtosecond laser pulse. In the first article (publication 6), we understand how this limitation can be turned into a major advantage: we use the unexcited molecules as a local oscillator against which we coherently detect –homodyne interference– the high-harmonic emission from excited molecules. In the second article (publication 5), implementing the transient grating scheme to photo-excite molecules allows us to disentangle both the relative amplitude and phase between excited and unexcited molecules. We observe that the amplitude encodes the internuclear separation while the phase records the attosecond dynamics of the electrons, giving access to the evolving ionization potential and electronic structure of the bond-breaking molecule. In the third article of chapter 4 (publication 9), we apply the transient grating technique to the photodissociation of NO_2 , allowing us to observe previously unseen (but predicted) population transfer dynamics via a conical intersection [133]. In general, our results confirm the versatility of high-harmonic spectroscopy at

measuring ultrafast chemical dynamics in a novel and coherent fashion, even when only a small fraction of the molecules in the sample are excited and undergoing dynamics.

High-harmonic spectroscopy is sensitive to the electronic character of high-lying participating molecular orbitals, via their corresponding photorecombination transition dipole matrix elements. Photorecombination is related to the time-reversed photoionization process: they are proportional based on detailed balancing [65, 73, 74]. We enforce this close relationship between photoionization and photorecombination by observing, in general, relatively good agreement between experiments (photorecombination) and calculations (photoionization) done in the SFA framework [25]. On this, we present various successful examples, these include the cases of: argon (publications 1, 8), N₂ (publication 15), CO₂ (publication 4), CO (publication 16) and Br₂ (publication 14).

We highlight that time-resolved high-harmonic spectroscopy (TRHHS) extends well-established time-resolved photoelectron spectroscopy (TRPES) [27, 28], based on charged particle detection, to a fully coherent one, based on light characterization. The novel aspects offered by TRHHS include: (1) the coherent homodyne detection advantage, (2) the simultaneous access to broad photoelectron spectra in a single laser shot as well as, (3) the possibility of angström-size tomographic orbital imaging. For more details, see a comparative review between TRHHS and TRPES in ref. [30]. In the spirit of comparing TRHHS as a probe of molecular dynamics to other widely used photoelectron spectroscopy techniques, we explore single-photon (in the range of 266-310 nm) photodissociation of SO₂ with TRHHS, two-photon ionization TRPES [27], and above threshold ionization (ATI) [134]. Preliminary results indicate that the sensitivity of each method to probing the same dynamics is dissimilar (publication 19).

In order to reconstruct a molecular wave function $\Psi_g(\mathbf{r})$ by high-harmonic tomographic imaging, the corresponding high-harmonic photorecombination dipole matrix elements,

$$\mathbf{R}_g(\Omega, \theta) = \langle \Psi_g(\mathbf{r}; \theta) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle, \quad (6.1)$$

need to be fully determined (polarization, amplitude and phase), please refer to sect. 1.4 for details. The spectrally-resolved polarization and amplitude can be both measured

by polarimetry, see section 1.3.3. However, this measurement only reveals the relative phase between the parallel ($R_{\parallel}(\Omega, \theta)$) and perpendicular ($R_{\perp}(\Omega, \theta)$), with respect to the driving laser field linear polarization, components of the emission for a given point in the (Ω, θ) coordinate space. The spectral (Ω) and angular (θ) variation of each component of the photorecombination phase ($\Phi_{R_{\parallel} \text{ or } \perp}(\Omega, \theta) = \arg[R_{\parallel \text{ or } \perp}(\Omega, \theta)]$) still remains to be measured for each polarization component.

In chapter 5, we accomplish this latter task by combining two all-optical attosecond techniques, namely, two-source harmonic phase and mixed gases interferometries. We call our technique LAPIN for: Linked Attosecond Phase Interferometry (publication 14). We use it to fully determine the two-dimensional photorecombination spectral phase $\Phi_{R_{\parallel}}(\Omega, \theta)$ from aligned (Br_2) molecules with respect to the one of a reference atom (Xe). Polarimetry measurements (not shown in this thesis) indicate us that the parallel component ($R_{\parallel}(\Omega, \theta)$) dominates in the two-dimensional (Ω, θ) range covered in the experiment, the perpendicular one ($R_{\perp}(\Omega, \theta)$) being small ($\leq 10\%$ in intensity). We support our experimental findings on $\Phi_{R_{\parallel}}(\Omega, \theta)$ with state-of-the-art quantum scattering photorecombination calculations, thereby, spectrally and angularly, resolving the participation of multiple molecular orbitals in aligned Br_2 . We should emphasize here that our results on aligned Br_2 confirm recent ones on aligned CO_2 [25], both molecules having the same sequence of valence orbitals with similar ionization potential differences between them. Our results are therefore important for the generalization of high-harmonic spectroscopy as a probe of molecular structure and, possibly, multi-electron attosecond dynamics launched by strong field ionization [25, 35].

The two-dimensional photorecombination phase $\Phi_R(\Omega, \theta)$ is an important quantity that has only either been approximated or partially measured in the past [35]: LAPIN (publication 14) unambiguously solves this problem for the first time. For this reason, we believe this technique will be key for the further development of molecular high-harmonic tomographic imaging. LAPIN is applicable to any molecular system that can be aligned in the gas phase; for example, we have considered extending it to larger polyatomic systems such as aligned benzene (C_6H_6 , publication 20). Furthermore, LAPIN presents significant technological advantages such as being an all-optical and in-situ technique: it does not require to photoionize a second gas sample with the high-harmonic radiation as do the

well-established ex-situ techniques like RABITT [135, 136] and FROG-CRAB [137].

6.2 Towards Time-Resolved Tomographic Imaging

In this thesis, we develop a general procedure for time-resolved tomographic imaging of valence electrons involved during a chemical reaction. For this, we need to fully characterize (polarization, amplitude and phase) the photorecombination dipole $\mathbf{R}_e(\Omega, \theta, \Delta t)$ of excited molecules undergoing chemical dynamics, see section 1.4 for details on the general tomographic reconstruction procedure:

$$\mathbf{R}_e(\Omega, \theta, \Delta t) = \langle \Psi_e(\mathbf{r}; \theta, \Delta t) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle, \quad (6.2)$$

where $\Psi_e(\mathbf{r}, \Delta t)$ is the valence electronic wave function, Δt is the moment of observation in the chemical reaction initiated at $\Delta t = 0$ and we use the subscript e to refer to the photo-excited molecules that are undergoing dynamics. We apply our procedure to a prototypical reaction: the photodissociation of Br_2 into two neutral Br atoms by single-photon excitation (400 nm), refer to chapter 4.

Our procedure is twofold. First, in chapter 4, the coherent detection advantage of homodyne high-harmonic spectroscopy, along with the implementation of the transient grating scheme for photo-exciting molecules, allows us to retrieve both the time-resolved relative amplitude and phase of the high-harmonic emission from excited (e) molecules with respect to a given local oscillator –here, being the emission from unexcited (g) molecules. This operation is illustrated in Fig. 6.2 (a). As will be shown later, this operation can be executed at all alignment angles θ , provided that the chemical reaction is aligned with respect to the laser (linear) polarization. Second, in chapter 5 (LAPIN), we fully characterize (polarization, amplitude and phase) the high-harmonic emission from aligned unexcited (g) molecules with respect to another local oscillator, –here, the emission from a reference atom– see Fig. 6.2 (b). Therefore, by combining both the LAPIN technique (chapter 5) and transient grating high-harmonic spectroscopy (chapter 4) on aligned molecules, we establish a pathway for the complete characterization of the high-harmonic photorecombination dipole matrix elements from excited molecules,

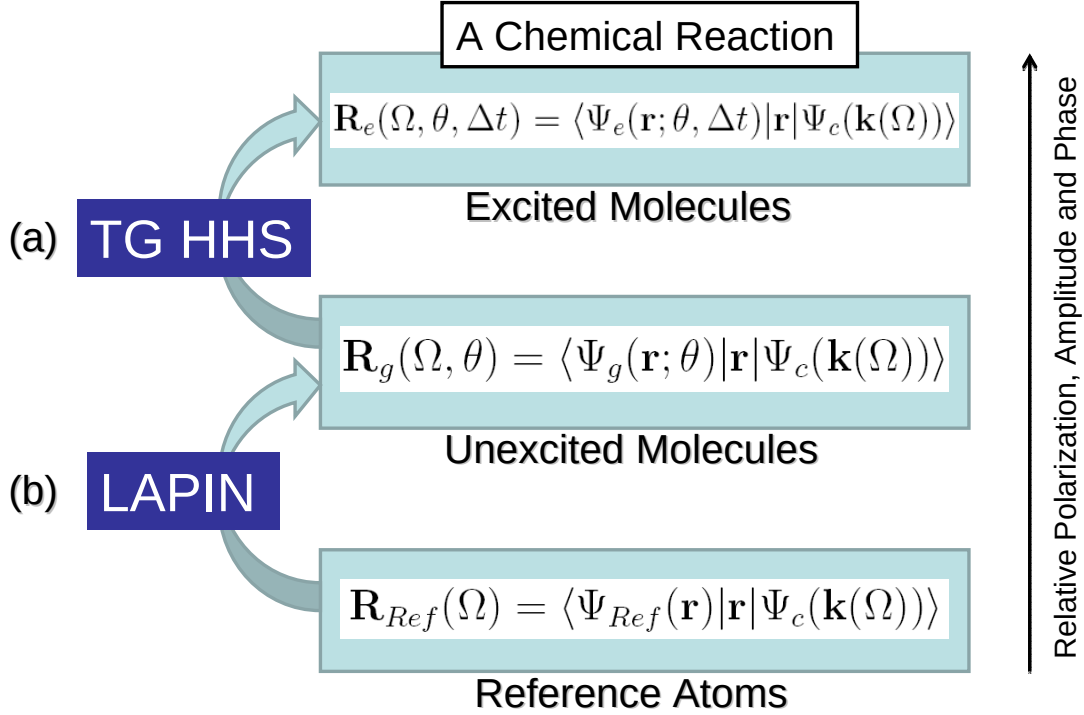


Figure 6.2: A summary of this thesis' main goal (see section 1.5): the full characterization (polarization, amplitude and phase) of the photorecombination dipole $\mathbf{R}_e(\Omega, \theta, \Delta t) = \langle \Psi_e(\mathbf{r}; \theta, \Delta t) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle$ of molecules undergoing chemical dynamics (upper panel). This quantity is needed for time-resolved tomographic imaging (TRTI) of the evolving valence electronic wave function $\Psi_e(\mathbf{r}, \Delta t)$ involved in a chemical reaction. (a) Transient grating high-harmonic spectroscopy (TG HHS), see chapter 4, measures the high-harmonic emission from excited (*e*) molecules relative to unexcited and aligned ground state (*g*) molecules. (b) The LAPIN technique, see chapter 5, characterizes the emission from aligned molecules relative to that of reference atoms. Altogether, (a) and (b) provide a pathway for retrieving $\mathbf{R}_e(\Omega, \theta, \Delta t)$ relative to that of a reference atomic target $\mathbf{R}_{Ref}(\Omega)$, necessary for TRTI (see section 1.4).

$\mathbf{R}_e(\Omega, \theta, \Delta t)$, with respect to the one from an atomic target.

The choice of atomic emission as a reference, see lowest panel in Fig. 6.2, is justified by the its angular (θ) independence and usually readily approximable (by calculation) spectral (Ω) dependence. This is especially important to, ultimately, extract $\mathbf{R}_e(\Omega, \theta, \Delta t)$

with respect to flat two-dimensional (Ω, θ) amplitude and phase profiles, as required for tomographic imaging (sect. 1.4). Polarimetry measurements on the emission from excited molecules is also required. Here, in the particular case of the prototypical photodissociation of Br_2 , preliminary results (not shown here) suggest that the emission from both aligned unexcited (g) and excited (e) molecules are mostly polarized parallel to the driving laser field in the (Ω, θ) range covered in the experiment.

In order to measure the complete three-dimensional map of the photorecombination dipole $\mathbf{R}_e(\Omega, \theta, \Delta t)$, we perform transient grating high-harmonic spectroscopy, see Fig. 6.2 (a), on laser-aligned (θ) molecules. This ultimate 4-beam experiment is illustrated in Fig. 6.3 (a): a first laser pulse field-free aligns (sect. 1.3.3) molecules prior to applying the transient grating pump-probe scheme. This 4-beam experiment is applicable to studying a broad range of chemical dynamics in aligned molecular samples. However, one important limitation may arise: the chemical reaction should be faster than the field-free alignment dynamics. It is the case, here, where prompt alignment dynamics of Br_2 is fairly slow (0.5-1.0 picosecond) compared to the bond breaking dynamics (~ 200 fs).

We performed the 4-beam experiment on aligned Br_2 molecules as schematically shown in Fig. 6.3 (b). The single-photon excitation (400 nm) being a perpendicular transition, we keep both pump pulses perpendicular to the aligned molecules and rotate all of them together to probe the chemical reaction at different angles θ and delays Δt , leaving the polarization of the HHG probe pulse unchanged. As a proof of principle, in appendix E, we show preliminary (unpublished) results of the 4-beam experiment investigating the prototypical photodissociation of Br_2 . At two different delays, $\Delta t = 150$ and 450 fs, we observe (see Fig. E.1) significant differences in the retrieved angular (θ) profile of the relative amplitude and phase of the high-harmonic emission between excited (e) and unexcited (g) molecules.

By combining the earlier LAPIN (chapter 5) measurements with these latter results, along the framework presented in Fig. 6.2, we can now go forward with the tomographic reconstruction of the electronic valence orbital of dissociating molecules, $\Psi_e(\mathbf{r}, \Delta t)$, in a time-resolved (Δt) fashion. We are currently working on the first frames.

Assembling these images will reveal how valence molecular electrons react to chemical bond breaking, that is, how they spatially redistribute as the molecular bond distance

increases with dissociation time Δt , giving us new insights on how nuclear and electronic molecular degrees of freedom are coupled together. These are fundamental questions left only partially answered by femtochemistry, see section 1.1. Here, the spatial resolution of our experimental reconstruction of the wave function $\Psi_e(\mathbf{r}, \Delta t)$ is given by the shortest electron de Broglie wavelength available, the cutoff harmonics having $E(q = 23) \sim 40\text{eV}$, of about 2 angströms, refer to Fig. 1.9. Improving the spatial resolution by increasing the cutoff energy E is clearly at hand with the development of new laser sources, see section 1.4. The current temporal resolution of each movie frame, which is about 30-40 fs here, can also be straightforwardly improved with the use of shorter pump and probe laser pulses. We believe that improving the spatiotemporal resolution of this overall procedure will become an intensive area of research in attosecond science [35].

In this thesis, we concentrate on using the high harmonic generation process as an in-situ probe of molecular dynamics to, ultimately, image valence electrons in a time-resolved fashion. The temporal resolution of this technique remains limited by the shortest driving pulse duration available, typically on the order of few femtoseconds. However, high harmonic generation, the workhorse of attosecond science, provides means to produce broad bandwidth light pulses that can, in turn, support few tens of attoseconds in duration. Using these pulses in ex-situ experiments will break the 1 femtosecond temporal resolution barrier.

While femtochemistry has been explored extensively before the year 2000s, the 1999 Nobel Prize in Chemistry was awarded to Ahmed Zewail "for his studies of the transition states of chemical reactions using femtosecond spectroscopy", attochemistry, now becomes reality. The direct control and observation of electronic motion on the attosecond timescale will be revealed, it is just around the corner. The work presented in this thesis, which combines aspects of femtosecond and attosecond spectroscopies, points in that direction.

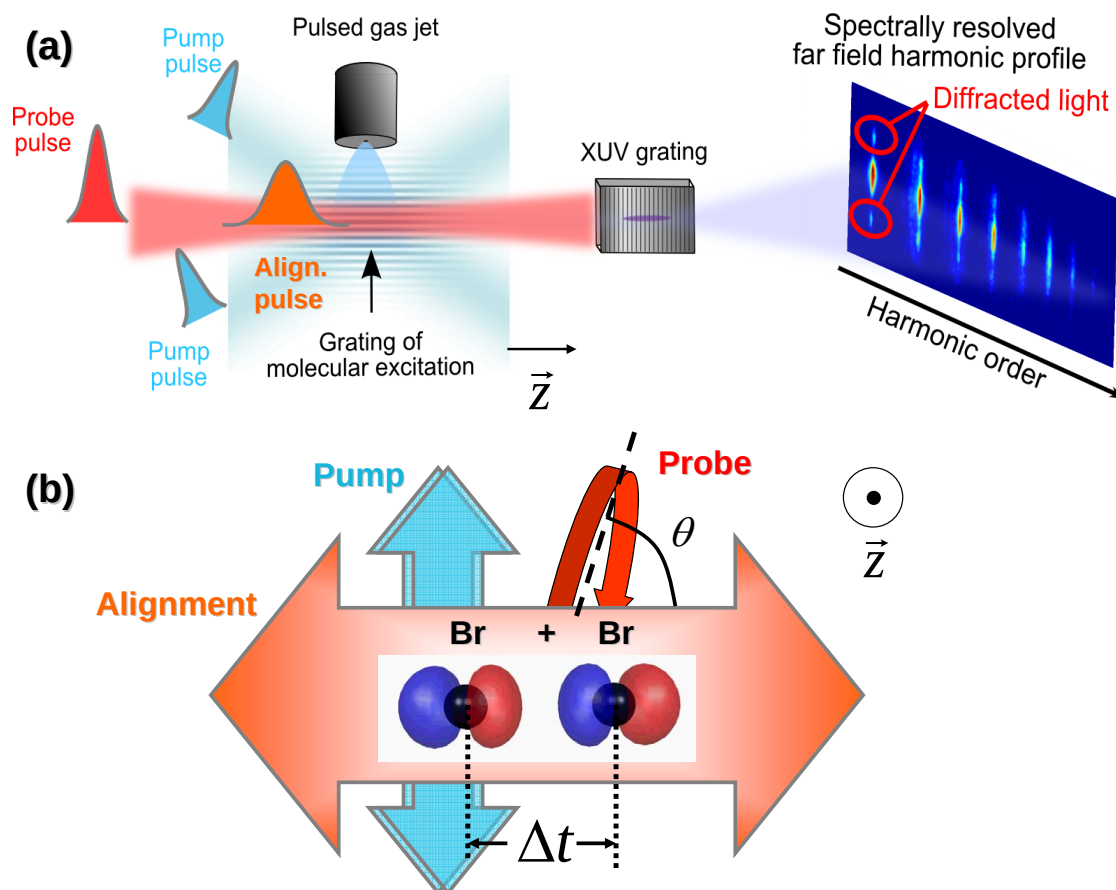


Figure 6.3: The ultimate 4-beam experiment for time-resolved tomographic imaging of a chemical reaction. (a) A first laser pulse field-free aligns (θ) the molecular ensemble prior to applying the transient grating high-harmonic spectroscopy (TG HHS) scheme presented in chapter 4. We record the high-harmonic signal at all molecular angles θ and pump-probe delays Δt of interest after the pump pulses initiated the reaction, leaving the polarization of the HHG probe pulse unchanged. (b) The 4-beam experiment is applied to the prototypical photodissociation of Br_2 into two neutral Br atoms. The single-photon excitation (at 400 nm) being a perpendicular transition, we keep both pump pulses polarizations perpendicular to the aligned molecules and rotate both the alignment and pump pulses altogether to probe the chemical reaction at different alignment angles θ and delays Δt . Next, after retrieval of the full photorecombination dipole of excited molecules, $\mathbf{R}_e(\Omega, \theta, \Delta t)$ (see Fig. 6.2), tomographic images of the valence electrons involved in a chemical bond breaking, $\Psi_e(\mathbf{r}, \Delta t)$, can be assembled (see section 1.4.2 for details) to make a molecular movie.

Appendix A

Experimental Setup and Methods

A.1 FemtoLab 2 at the National Research Council

The experimental work presented in this thesis (2005-2011) was performed in FemtoLab 2, room 0024, at the National Research Council Canada (CNRC), 100 Sussex Drive, Ottawa. In the process (2008), the laboratory officially became part of a collaborative infrastructure between the university of Ottawa and CNRC: the Joint Attosecond Science Laboratory (JASLab). This Ph.D thesis was co-supervised by David M. Villeneuve (JASLab Program Leader) and supervised by Paul B. Corkum (JASLab Director).

In Fig. [A.1](#), we can see the high harmonic generation chamber at NRC (Atto 1) in FemtoLab 2 when in operation. We will now describe all parts of the experimental setup, as well as techniques, used to accomplish all the work presented in this thesis.

A.2 The Laser Source

The femtosecond laser source is a custom-built [\[138\]](#) chirped pulse amplification [\[139\]](#) system. The front end of the system, see Fig. [A.2](#) is composed of (a) a master oscillator cavity (Femtolasers) providing ~ 15 fs, few nanojoules laser pulses centered around 790nm at a ~ 82 MHz repetition rate. On a daily basis, mode-locking is obtained by a

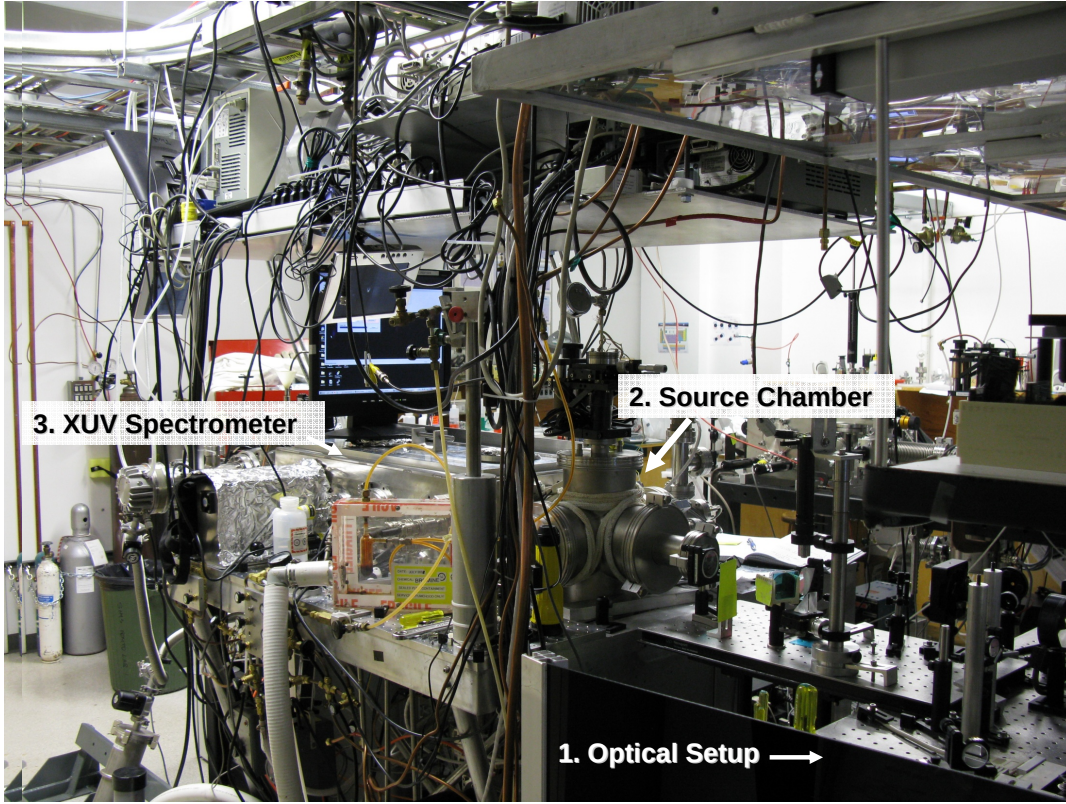


Figure A.1: The Atto 1 high harmonic generation chamber in FemtoLab 2 at CNRC.

small movement (preserving alignment) of a mirror in the cavity. These pulses are then stretched (to ~ 100 picoseconds) in (b) an Offner stretcher before being amplified for the first time in (c) a 10-pass Ti:Sapphire preamplifier. From the amplified train of pulses (after the first 5 passes) only a single pulse is selected by a pockel cell at a repetition rate (50 Hz) of the flash-lamp pump laser (Quanta Ray, 300 mJ per pulse at 532 nm) and then sent back on the same optical path for 5 more passes. During my thesis, I have spent a significant amount of time re-aligning this pre-amplifier: mostly due to the failure or changes in the beam parameters of the pump laser, which occasionally caused damages to the Ti:Sa crystal (see TiS2 in Fig. A.2 (c)). At the output of the pre-amplifier, the typical energy per pulse is ~ 2.5 mJ, a modified double-pass Faraday oscillator [138] outcouples the amplified pulses.

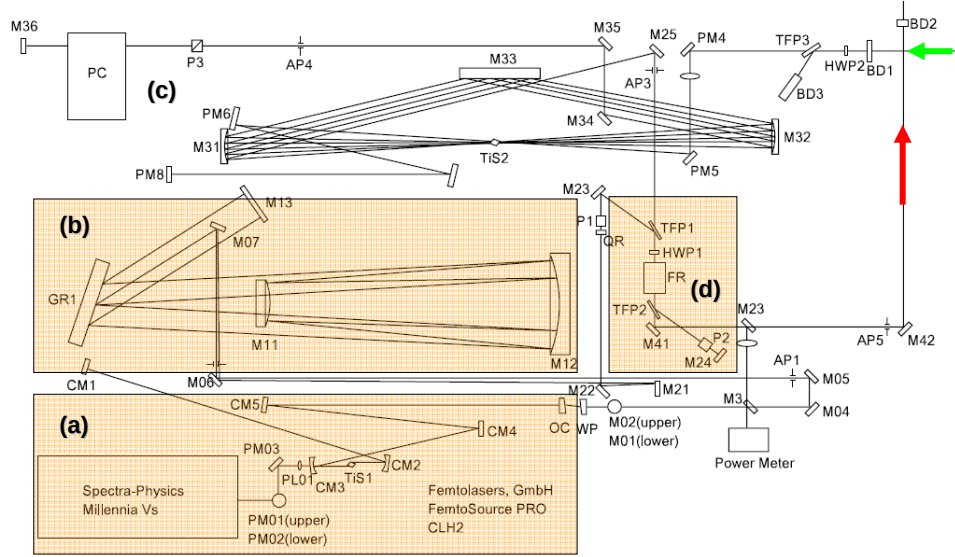


Figure A.2: Front end of the chirped pulse amplification laser system, adapted from ref. [138]: (a) the master oscillator, (b) Offner stretcher, (c) Ti:Sapphire 10-pass preamplifier and (d) Faraday isolator.

The laser output is further amplified in a 2 (or 3)-pass bow-tie configuration power amplifier, see Fig. A.3. We typically have ~ 20 -30 mJ per pulse after amplification. Short femtosecond pulses are then obtained using a grating compressor (two gratings and a roof-top mirror). On a daily basis, we get linearly polarized pulses of $\sim 32 \pm 5$ fs (measurement done using a single-shot autocorrelator) in duration and 10-15 mJ of energy per pulse.

A.3 High Harmonic Generation in the Laboratory

A.3.1 General Optics Layout

The compressed laser output is split and recombined using a standard Mach-Zehnder interferometer (see Fig. A.4, region 1), before being focused in the high-harmonic chamber (region 2). The versatile optics layout shown in Fig. A.4 is used throughout this thesis work, with small occasional modifications. In this configuration all laser beams (pump

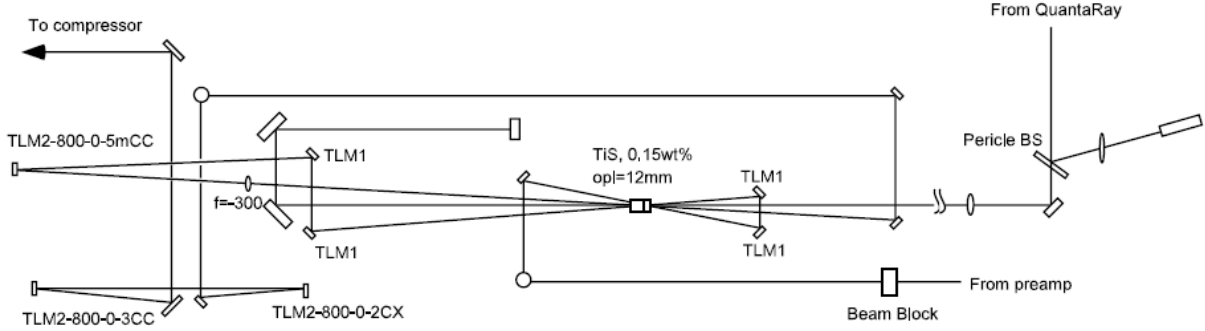


Figure A.3: The Ti:Sapphire 3-Pass power amplifier [138]. Usually operated in the 2-pass configuration for this thesis' work.

and probe) are collinear. For saving laser output, an alternative to the use of a 50/50 beamsplitter (BS2) for recombining beams (near the chamber) is a noncollinear scheme, where beams are recombined using separate mirrors and made parallel before the focusing element (lens or mirror) to overlap in the high harmonic chamber.

In all pump-probe experiments, the spatial overlap of pulses under the gas jet is verified using an imaging system composed of an movable mirror (and attenuators), intercepting beams before the entrance window of the chamber, an objective and a CCD camera. The temporal overlap can be found by looking at interference fringes on beam cards, or a photodiode for long delays (≥ 10 ns). However, we use a more general technique, applicable to any multi-color beams: we generate a plasma in air by focusing one of the stronger beams and seek for the other colors to diffract from that plasma. The earlier arrival of the stronger beam is confirmed when diffraction is observed. Optimizing the overlap of beams in the gas jet can be accomplished by looking directly at the high harmonic signal and optimizing the effects of the (usually much weaker) pump pulse. Routinely, for alignment experiments, we start by aligning nitrogen (N_2) around its half rotational revival: we improve the overlap of pump (alignment) and probe (HHG) pulses by optimizing the extinction of the signal at anti-alignment. For this, one is better to have (1) manual control on a translation stage for adjusting the delay between pump and probe pulses, (2) direct access (real-time monitoring) to the signal produced in the chamber and finally, (3) at least one robust and stable mount for adjusting the spatial

APPENDIX A. EXPERIMENTAL SETUP AND METHODS

overlap between pulses in the chamber. To my experience, it is by combining all these elements that one can efficiently perform accurate pump-probe experiments. Having a daily routine is key to systematically detect any unusual changes to the signal and therefore to the experimental setup.

The transient grating experiments presented in chapter 4 required a different optical setup: two pulses are used to photo-excite molecules in a non-collinear geometry, the setup is described in appendix B.

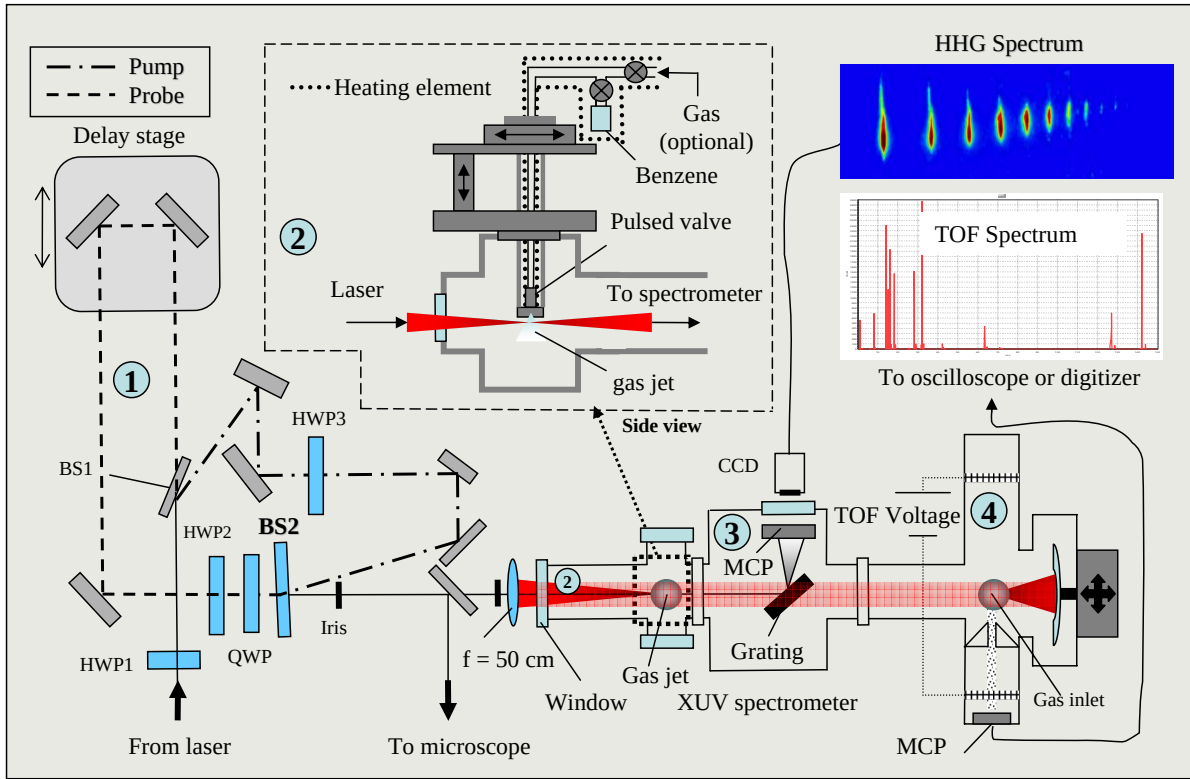


Figure A.4: Schematic of the high harmonic generation experimental chamber and optics layout. (1) The Mach-Zehnder-type interferometer used to derive the pump (alignment) and probe (HHG) pulses from the laser source. (2) The high-harmonic light is generated in the source chamber and detected in (3) the XUV spectrometer, a second differentially-pumped chamber. (4) Ionization measurements can be done in a linear Time-of-Flight (TOF) chamber, by removing the XUV spectrometer and changing, accordingly, the optics at the entrance of the chamber.

A.3.2 The High-Harmonic Chamber

High harmonic radiation is generated in the source chamber (see Fig. A.4, region 2) and detected in a second, differentially pumped chamber (region 3). We often use a spherical mirror ($f=50\text{cm}$) to focus all laser beams in the chamber. Alignment through the chamber, all the way to the XUV spectrometer (region 3), is accomplished using irises placed before and after the chamber (the beam is intercepted by a mirror in the spectrometer (region 3) and sent outside the chamber on another iris).

The high harmonic radiation is produced in a thin ($\sim 1\text{ mm}$ thick) supersonic gas jet. This allows us to minimize detrimental macroscopic effects due to the propagation of the XUV radiation: the measured signal corresponds to the single-molecule response [93]. We operate a pulsed valve (General Valve-Parker Hannifin) with $\sim 2\text{ atm.}$ of backing pressure. This provides a density of $\sim 10^{17}/\text{cm}^3$ and allows to produce relatively rotationally cold (30-50 K) molecules [89]. We use a trigger signal from the preamplifier to synchronize the valve with the arrival of laser pulses. When in operation, the source chamber is maintained at $\sim 10^{-4}\text{ Torr.}$ The gas jet orifice is usually placed $\sim 1\text{ mm}$ above the focus and $\sim 3\text{-}5\text{ mm}$ after the focus along the propagation direction to favor the short trajectories [48], refer to chapter 1 for a description of the short trajectories. Next, the high harmonic radiation propagates through a differential pumping pinhole before entering the spectrometer (region 3) maintained at $\sim 10^{-5}\text{ Torr.}$

The radiation is detected using an XUV spectrometer (Fig. A.4, region 3) composed of a vertical slit at the entrance ($\sim 200\text{-}500\text{ }\mu\text{m}$ opening), a grazing incidence (angle $\approx 87^\circ$) diffraction grating and a micro-channel plate detector backed by a phosphor screen. Spectral images (the phosphor screen) are captured by a CCD (12-bit) camera placed outside the chamber. The entire acquisition system interface uses the Visual Studio environment (initially written by Jérôme Lévesque in 2001-2003) and compilation of HHG spectra is achieved mostly using LabVIEW subroutines.

If we remove the focusing optics at the entrance of the high harmonic chamber and the XUV spectrometer, we can perform time-of-flight mass spectrometry in another attached chamber, see Fig. A.4, region 4. A gate valve separates this chamber from the XUV spectrometer (region 3). In the TOF chamber, we use lower gas densities (an effusive jet).

Mass-spectrometry not being possible in the high-harmonic source chamber because of the (too high) gas densities used, the TOF chamber allowed us to learn and confirm important information about the ionization dynamics and time scales for the photodissociation of several molecules (Br_2 , NO_2 and SO_2), as presented in chapter 4.

A.3.3 Other Experimental Details

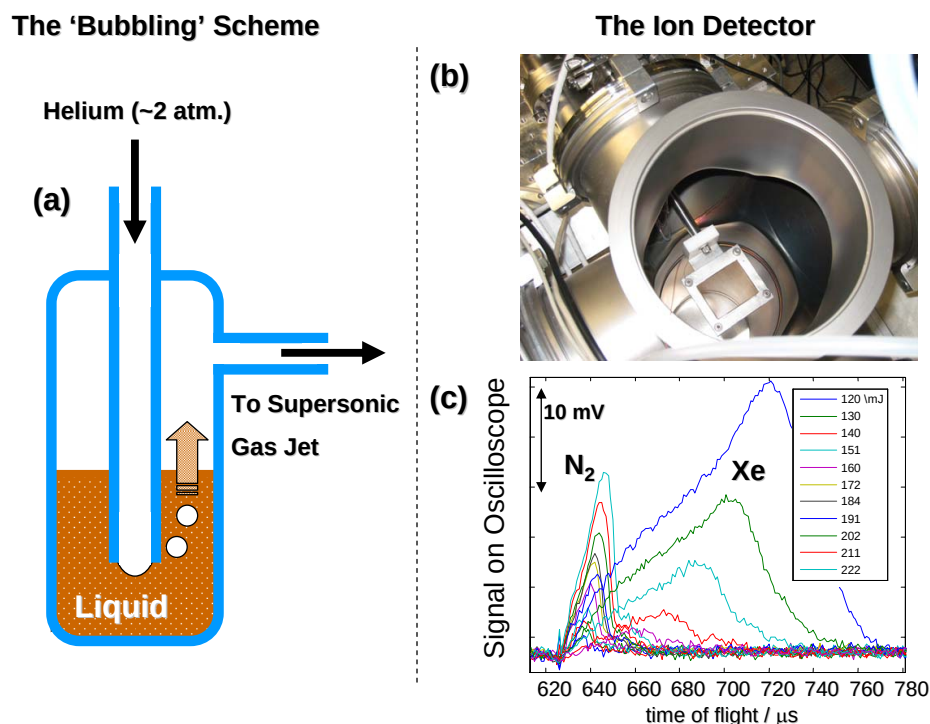


Figure A.5: (a) The glass flask used for the 'bubbling scheme', allowing to bring vapors to the gas jet using a carrier gas (He). (b) The ion detector (square mesh), (c) ion traces measured (oscilloscope) using 8 fs pulses centered on 800 nm (publication 1) for different pulse energies in microjoules (see legend).

Corrosive gases such as Br_2 , NO_2 and SO_2 are studied in the experimental setup, therefore, precautions needed to be taken with the gas pumping systems. To that purpose, high-vacuum turbo pumps are purged with dinitrogen (N_2) and the backing pri-

mary roughing pumps are operated with synthetic oil, the oil being filtered in real-time to minimize corrosion. An interesting anecdote is that the original research proposal suggesting to study the photodissociation of Br_2 in the gas phase was rejected because its feasibility was put in doubt; few years later, it led to our understanding of homodyne detection of ultrafast dynamics using high-harmonic spectroscopy and the corresponding publications 5, 6 and 9.

We performed experiments on molecules that are liquid at room temperature using the system presented earlier in Fig. A.4. Our first candidate was benzene (in 2005). The liquid molecules were put in a flask that was then heated to about $\sim 80^\circ\text{C}$ to provide sufficient vapor pressure at the supersonic gas jet. For better safety and correct operation of the pulsed valve, we needed to change our design when using bromine (Br_2) molecules. We implemented what we call the 'bubbling scheme' where a carrier gas (helium) is bubbled through the liquid Br_2 , see Fig. A.5 (a). This allowed us to keep a higher (than with pure vapors only) total backing pressure at the pulsed valve, making the pulsed valve operate normally and providing sufficient high-harmonic signal for performing pump-probe experiments. Using a carrier gas also improves the degree of molecular alignment achieved through the supersonic gas expansion. We thank Mike Vandenhoff from the 'Glass Shop' at CNRC for the flasks.

In the quest of better understanding chemical dynamics experiments probed by HHG (chapter 4), we installed an ion detector directly in the high-harmonic source chamber, see Fig. A.5(b). Preliminary measurements suggested linearity between the collected signal and the amount of ions generated in the laser focus. Further investigation on a similar detector support these findings [140]. Due to the velocity spread of the molecules in the gas expansion, mass resolution is hardly attainable with the short (~ 10 cm) time-of-flight region available. The high density ($\sim 10^{17}/\text{cm}^3$) plasma of ionized atoms and/or molecules in the gas jet will also contribute to making mass resolution difficult. Nonetheless, we could clearly distinguish the mass spectra of xenon ($M_{Xe} \sim 135$) and nitrogen ($M_{N_2}=14$) as shown in Fig. A.5 (c).

Measuring the ionization rate in the high harmonic chamber is highly valuable. It can help to calibrate the laser peak intensity [57] as well as to follow pump-probe processes such as molecular alignment [77, 141]. In chapter 4, we show how simultaneous mea-

measurements of the ionization rate and the high-harmonic signal (publication 6) became a strong indication of homodyne interference taking place in chemical reactions probed by high harmonic spectroscopy.

A.4 The Optical Parametric Amplifier

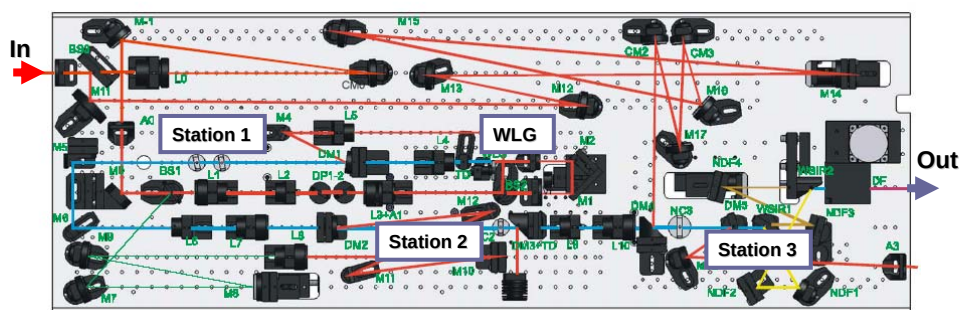


Figure A.6: The optical parametric amplifier (HE-TOPAS-C from Light Conversion).

One avenue to improve the cutoff energy of high-harmonic spectra is to increase the wavelength of the driving laser field, see chapter 1. To that purpose, we use an optical parametric amplifier (OPA) seeded by a part (~ 8 mJ per pulse) of the Ti:Sa laser system (described above) output. In the summer of 2009, I was in charge of operating an OPA: we measured our first spectra using longer (than 800 nm) wavelength. A schematic of the various elements in the OPA (HE-TOPAS-C from Light Conversion) is shown in Fig. A.6. Using this apparatus in our laboratory directly led to an important contribution to the field of high-harmonic spectroscopy of aligned molecules (see publication 4).

Appendix B

Optical Setup for Transient Grating Spectroscopy

In order to photo-excite molecules in a transient grating (TG) geometry, we need to produce two pump pulses which must then be overlapped in both time and space with the probe (high harmonic generation) beam. First, see Fig. B.1, we divide the laser output using a beam splitter or the combination of a half wave-plate and a thin film polarizer. This leaves a portion of the energy for the probe pulse and the rest of the energy is used to produce the two pump pulses. We show here the case where we generate the second harmonic of the fundamental using a BBO-I crystal, we have an adjustable telescope to diminish the beam size by a factor 2 for better nonlinear conversion. A similar setup was also used for preparing a TG of excitation at ~ 266 nm. We remove the remaining fundamental by making two reflections on high 800 nm transmission dichroic mirrors. Two pump pulses are then obtained via reflection on a 50/50 beam splitter (BS). Both beams are sent to separate manually controllable delay lines, M1 adjusts for the parallelism between beams (separated by ~ 3 -4 cm). A rotating periscope brings both beams to the height of the probe pulse and makes them now separated vertically. The near-field overlap of both pump pulses and the probe is achieved on a dichroic 2-inch mirror near normal incidence. All co-propagating beams are sent to the chamber. In the TG configuration, we use a 2-inch UV protected aluminum spherical focusing mirror at the entrance of the chamber.

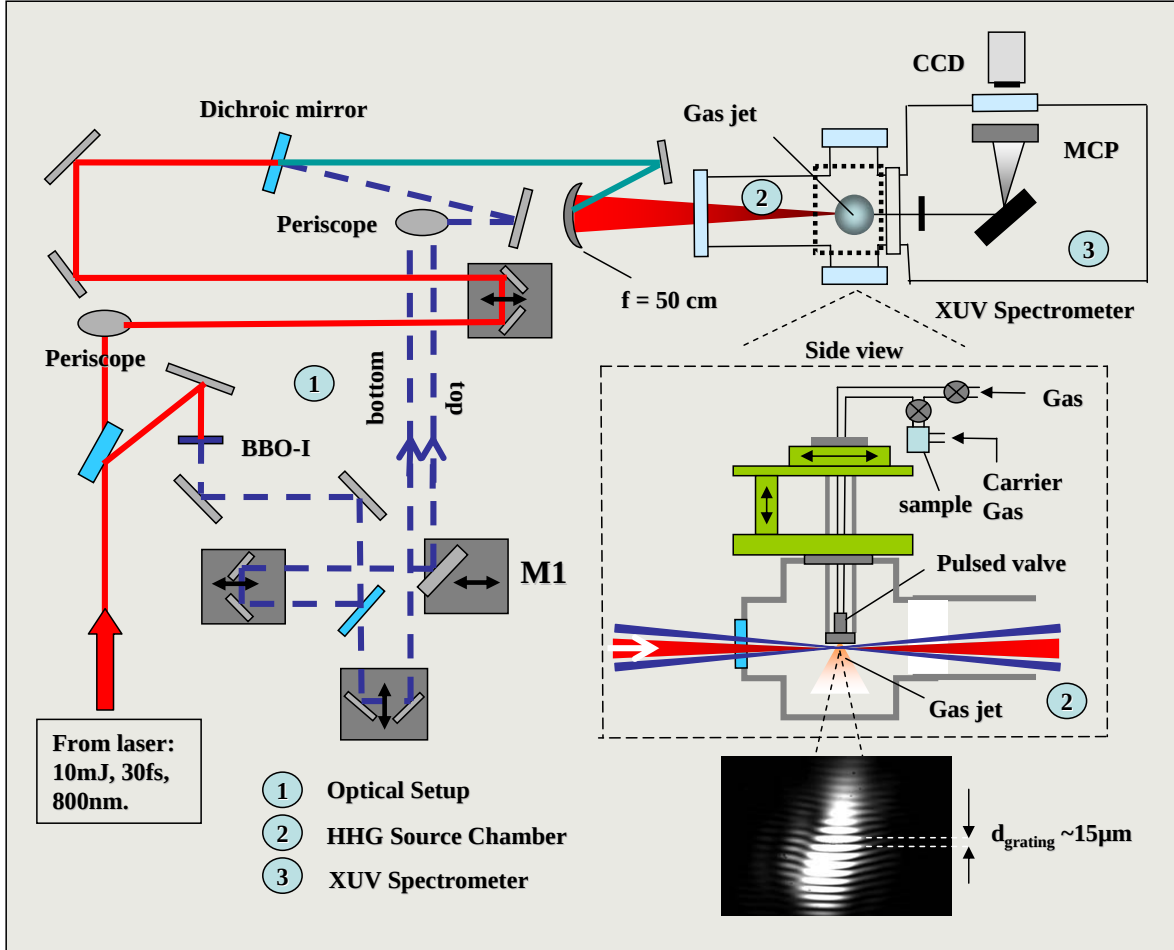


Figure B.1: Transient grating optical setup and high harmonic chamber.

For the 4-beam experiment, see section 6.2, the alignment beam is derived in the arm of the probe pulse (red) in Fig. B.1. Both alignment and probe beams are superposed spatially. The polarization of both the alignment and pump (blue) beams are controlled via half wave plates in each respective arms. After rotation, all beams undergo only near-normal incidence reflections to preserve their (linear) polarization state.

Appendix C

Calibration of the XUV Spectrometer

We present a general procedure for calibrating the XUV spectrometer presented in chapter [A](#), see Fig. [A.4](#) (region 3).

Grating Calibration

1. Description

The grating used in the HHG chamber is the specific model ‘Hitachi 001-0266’ (nominal groove number of 1200 grooves/mm). Briefly, grazing incidence is used to reduce absorption and the surface is made concave in order to minimize astigmatism across one flat spectral plane [1,2]. The layout is as follows [3]:

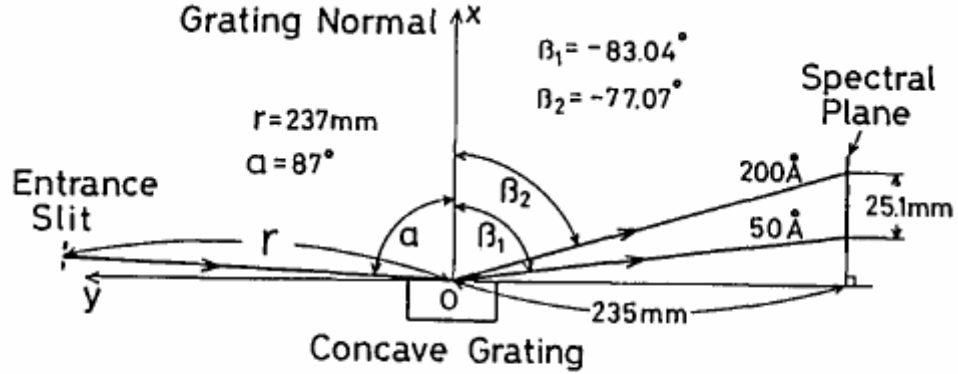


Fig. 1. Schematic and design specifications for the flat-field grazing-incidence spectrograph using a mechanically ruled aberration-corrected concave grating: 1200 grooves/mm; $R = 5649$ mm; $50 \times 30\text{-mm}^2$ ruled area.

In our setup, a MCP backed by a phosphor screen sits in the spectral plane. Recording of HHG spectra is made by taking a picture, with a CCD camera, of the phosphor screen.

In figure1 above, the x-position “L” of the HHG spectrum in the spectral plane can be computed using the grating equation and the corresponding geometric parameters:

$$m\lambda = \sigma_0(\sin\alpha + \sin\beta),$$

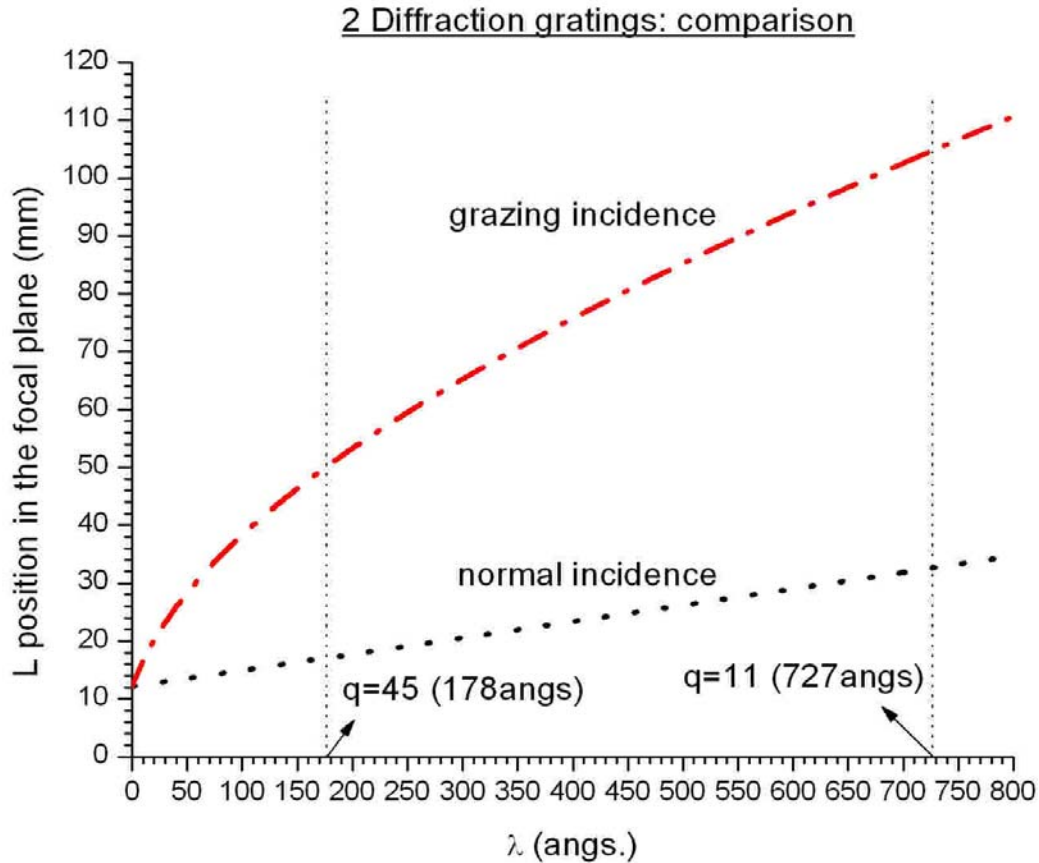
$$L = -235 \cot\beta,$$

For sake of comparison, I also considered the case of a normal incidence grating of the same nominal groove number. Its dispersion is given by the usual equation:

$$m\lambda = \sigma_0 \sin \theta$$

Where $\theta=0^\circ$ corresponds to $\beta=-\alpha=-87^\circ$.

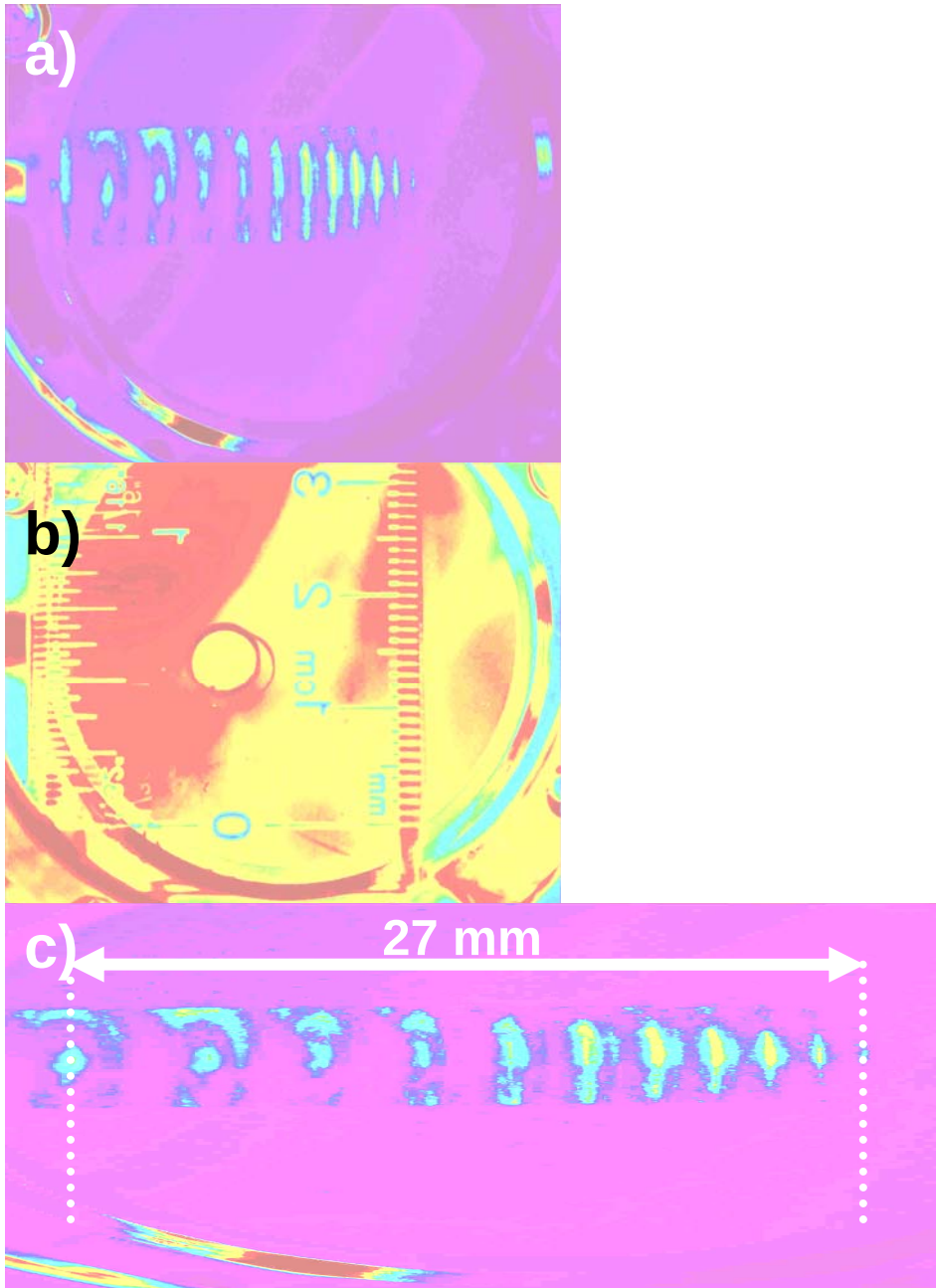
Here is a plot of the first order diffraction ($m=1$) comparing normal and grazing incidences for the same nominal number $\sigma_0=1200$ grooves/mm. We can see that the grazing incidence grating is more dispersive. It confirms that one cannot simplify the analysis of the grazing incidence to the normal case. We proceed to calibration.



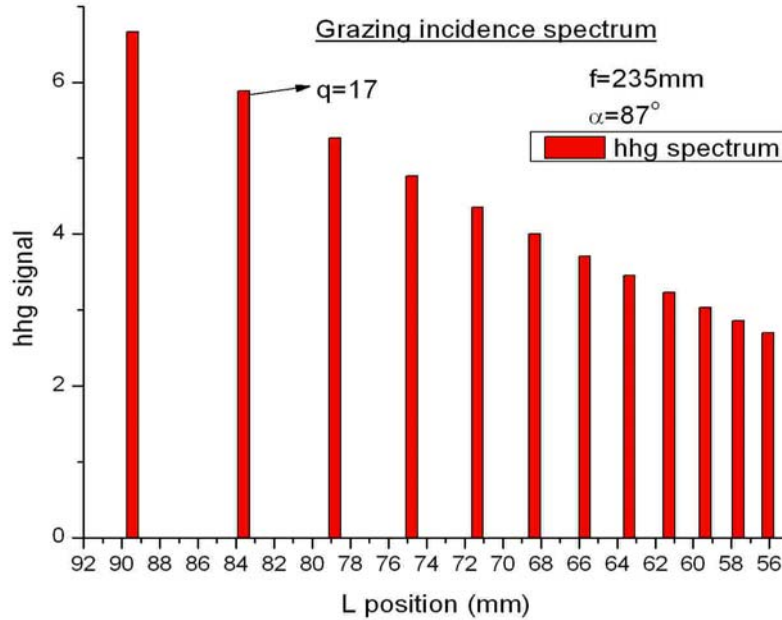
2. Calibration

The goal is to label the harmonic numbers “q” seen in the spectral plane. The procedure is relatively simple. First (2.1), one needs a real spectrum picture (~ 10 harmonic lobes or more) on which the real physical distance is known. For this purpose, the known diameter of the MCP can be used if seen on the HHG spectrum picture (I used a picture of the MCP with a ruler on top, see next). Second (2.2), a theoretical HHG spectrum showing the “qth” harmonic orders and their real “L” physical position must be calculated ($m=1$). This theoretical spectrum must be scaled to the real spectrum. Finally, one should slide the theoretical spectrum on the real one until they match. “Et voilà!” -[4].

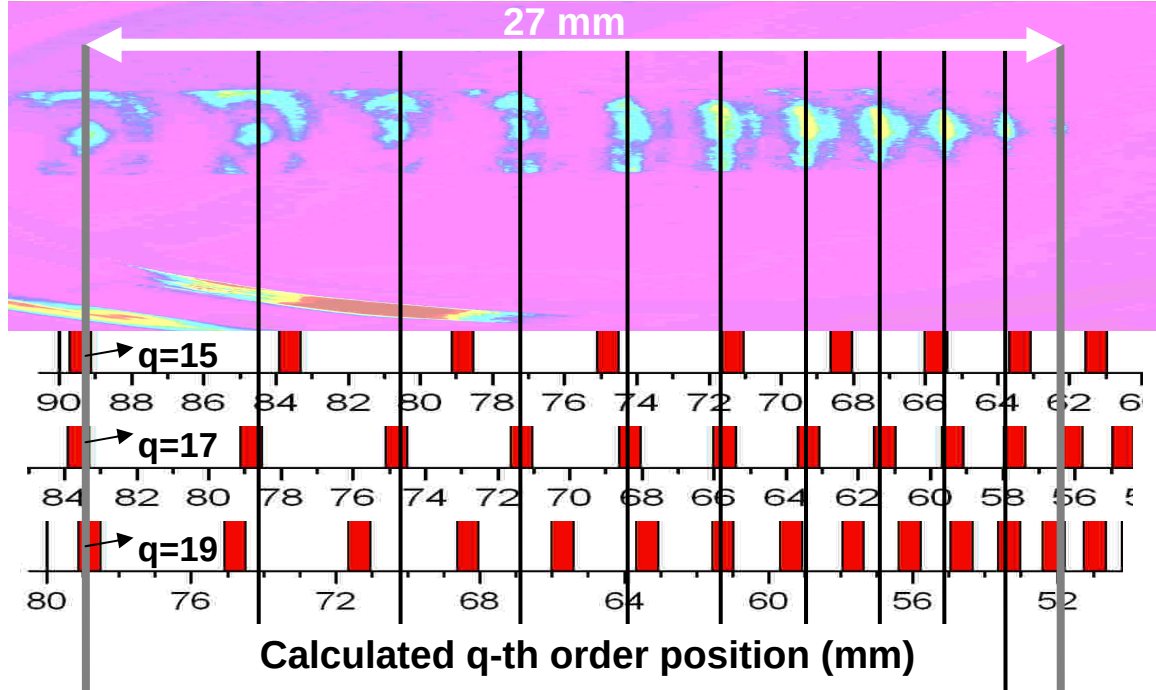
2.1: I started with 2 identical images in size: the first one is a real spectrum (a) and the second, (b) is a picture of the MCP with a length reference on it. The 2 images must be of same size and not be rescaled to start. The image processing software of your choice (I used Origin7/ImageProcessing) can be used to treat these images and attribute real physical spacing between harmonic lobes on the real spectrum. Once this is done, the scaled spectrum can be manipulated as needed (c).



2.2: I generated a theoretical spectrum. I assumed $f=235\text{mm}$ and $\alpha=87^\circ$: f is the distance from the normal of the grating to the spectral plane and α is the incidence angle as shown in fig1.

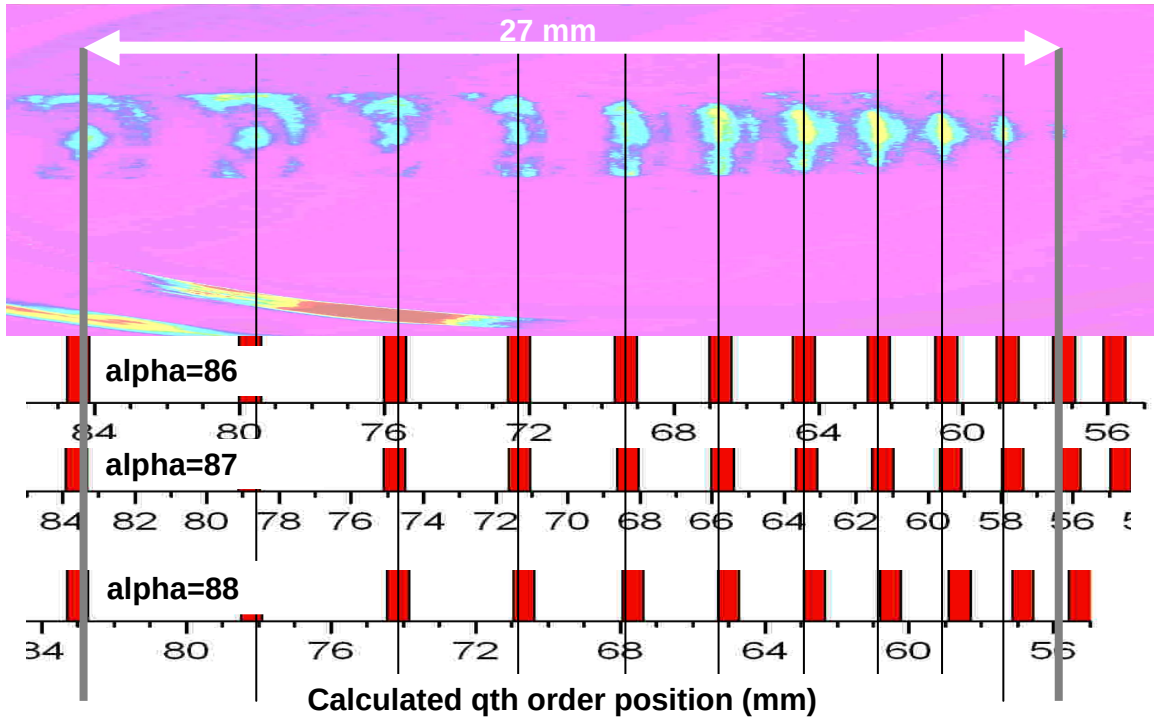


2.3: The real and calculated spectra are horizontally scaled so that they correspond by 1:1 ratio in real physical (lab) length. Then, they are superposed:

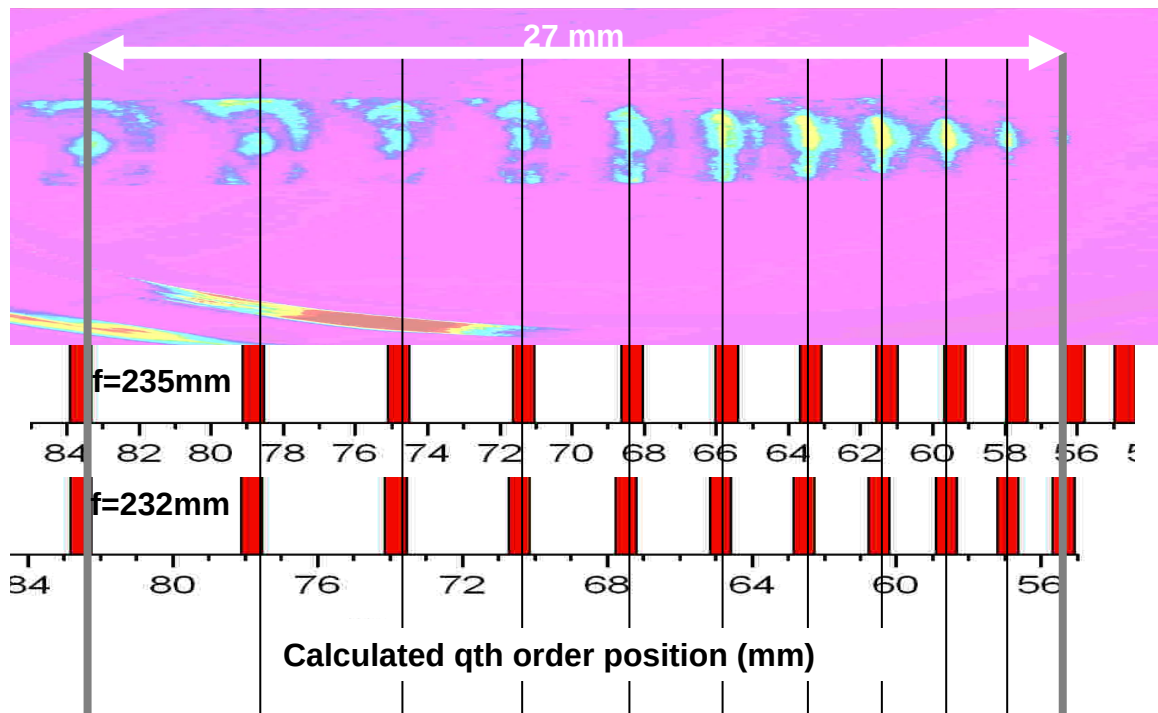


The best overlap is found with the first harmonic on the left being $q=17$. In principle, the calibration can be different since the real values of α and f are not known here. I tried different values of α and f in what follows.

2.4: Comparison: Different α 's.



2.5: Comparison: Different f 's, $\alpha=87^\circ$.



The value of α ($=87^\circ$) is critical for minimizing astigmatism in the spectral plane [1-3]. This should be once taken care of at the installation of the grating. The distance f can be different from 235 mm and affect linearly the spread of the spectrum. In our setup, f is probably smaller than 235mm. In the end, the best overlap of the real and calculated spectra is, without ambiguity, when $q=17$ is the first harmonic on the left.

3. Summary

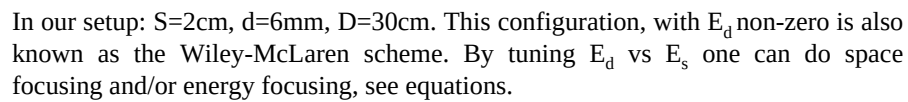
The harmonic orders have been labelled for a specific x-position of the MCP in the focal plane.

In the lab, we have $q=17$ first on the left when the MCP controller arm is at position 24mm.

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Wiley-McLaren TOF Chamber



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Linear Wiley-McLaren TOF chamber Equations

Useful formulas [1,2]:

$$U_0 = \text{kinetic}E(\text{eV})$$

$$m = \text{mass}(\text{a.u.})$$

$$(s, d, D) = \text{lengths}(\text{cm})$$

$$(t_x) = \text{time}(\mu\text{s})$$

$$t_{\text{back}} = \frac{1.02 \cdot (2mU_0)^{1/2}}{qE_s} = \frac{S \cdot 1.02 \cdot (2mU_0)^{1/2}}{qV_s}$$

$$d_{\text{back}} = -\frac{U_0}{qV_s} S$$

$$t_{s(U_0=0), \text{slow}, \text{fast}} (\mu\text{s}) = 1.02 \frac{(2m)^{1/2}}{qE_s} [(U_0 + q s E_s)^{1/2} \pm (U_0)^{1/2}] =$$

$$1.02 \frac{S(2m)^{1/2}}{qV_s} [(U_0 + \frac{qV_s}{2})^{1/2} \pm (U_0)^{1/2}]$$

$$U = U_0 + q s E_s + q d E_d = U_0 + \frac{qV_s}{2} + qV_d$$

$$t_d = 1.02 \frac{(2m)^{1/2}}{qE_d} [U^{1/2} - (U_0 + q s E_s)^{1/2}] = 1.02 \frac{d(2m)^{1/2}}{qV_d} [U^{1/2} - (U_0 + \frac{qV_s}{2})^{1/2}]$$

$$t_D = 1.02 \frac{(2m)^{1/2} D}{2U^{1/2}}$$

[1]: W. C. Wiley and I. H. McLaren, Rev. of Sci. Instr. **26**, 12 (1955).

[2]: I derived them too...!

Figure D.2: TOF Wiley-McLaren scheme equations.

Appendix E

4-Beam Experiment: Preliminary Results

In Fig. E.1, we present preliminary results on the relative amplitude D_e/D_g and phase $\Phi_e - \Phi_g$ of the high-harmonic dipoles of excited (e) and unexcited (g) molecules at two different delays in the photodissociation of Br_2 (chapter 4): (a) $\Delta t=150$ fs and (b) $\Delta t=450$ fs. $D(\Omega, \theta) = |D(\Omega, \theta)|e^{i\Phi(\Omega, \theta)} = \sqrt{I(\Omega, \theta)}P(\Omega, \theta)R(\Omega, \theta)$, see eq. 1.28 in section 1.3. These results are obtained using the 4-beam configuration explained in Fig. 6.3 of the conclusion chapter 6. We consider the emission from excited molecules to be polarized only parallel to the driving field (linear) polarization, as supported by preliminary polarimetry measurements (not shown) on both excited and/or unexcited Br_2 molecules. To obtain the relative amplitude D_e/D_g and phase $\Phi_e - \Phi_g$ in Fig. E.1, we use eqs. (11)-(16) of the supplementary information (SI) of publication 5, see chapter 4.

At the two different delays presented here, $\Delta t=150$ and 450 fs, we observe significant differences in the retrieved angular (θ) profile of the relative amplitude D_e/D_g and phase $\Phi_e - \Phi_g$ of the high-harmonic emission between excited and unexcited molecules. Moreover, these results are consistent with earlier results obtained with unaligned molecules, see publication 5. When combining the earlier LAPIN (chapter 5) measurements with these latest results, refer to Fig. 6.2, we obtain a complete characterization of:

$$\mathbf{R}_e(\Omega, \theta, \Delta t) = \langle \Psi_e(\mathbf{r}; \theta, \Delta t) | \mathbf{r} | \Psi_c(\mathbf{k}(\Omega)) \rangle. \quad (\text{E.1})$$

APPENDIX E. 4-BEAM EXPERIMENT: PRELIMINARY RESULTS

We can now go forward with the tomographic reconstruction of the electronic valence orbital $\Psi_e(\mathbf{r}, \Delta t)$ of dissociating molecules in a time-resolved (Δt) fashion. We are currently working on the first frames of the Br_2 photodissociation.

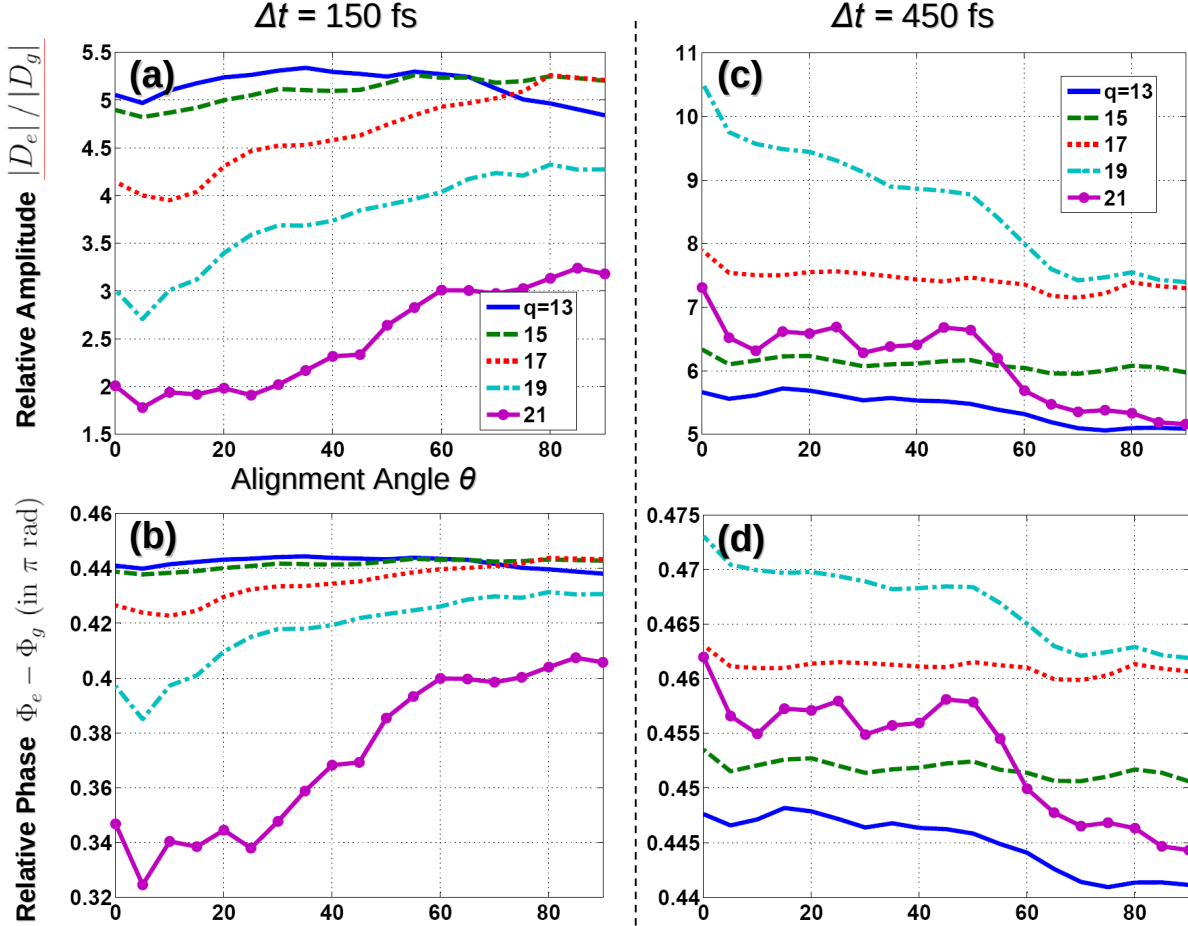


Figure E.1: Coherent imaging of the prototypical photodissociation (400 nm) chemical reaction: $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$. Here, we present preliminary results of the 4-beam experiment (section 6.2) on the relative amplitude D_e/D_g and phase $\Phi_e - \Phi_g$ between the high-harmonic emission from excited e and unexcited g aligned molecules, see text for details. At two given pump-probe delays, respectively $\Delta t=150$ fs or 450 fs, we show the alignment (θ) dependence of the relative amplitude in (a) or (c) and, phase in (b) or (d).

Appendix F

Units and Constants

Constants

List of frequently used constants [61]

Quantity	Symbol	Value	Unit
Speed of light	c	299 792 458	m/s
Electric field constant	ϵ_0	$8.854\,187\,817 \dots \times 10^{-12}$	A s/(V m)
Planck constant	h	$6.626\,069\,3(11) \times 10^{-34}$	J s
	$\hbar = \frac{h}{2\pi}$	$1.054\,571\,68(18) \times 10^{-34}$	J s
Elementary charge	e	$1.602\,176\,53(14) \times 10^{-19}$	C
Rydberg constant	$R_\infty = \frac{\alpha^2 m_e c}{2h}$	109 737.315 685 25(73)	cm ⁻¹
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$0.529\,177\,210\,8(18) \times 10^{-10}$	m
Mass of the electron	m_e	$9.109\,382\,6(16) \times 10^{-31}$	kg
Constant of Avagadro	N_A	$6.022\,141\,5(10) \times 10^{23}$	mol ⁻¹
Boltzmann constant	k	$1.380\,650\,5(24) \times 10^{-23}$	J/K

Atomic units

List of atomic units [\[61\]](#)

Quantity	Symbol	Value	Unit
Electric charge	e	$1.602\,176\,53(14) \times 10^{-19}$	C
Mass	m_e	$9.109\,382\,6(16) \times 10^{-31}$	kg
Action	$\hbar$	$1.054\,571\,68(18) \times 10^{-34}$	J/s
Length	a_0	$0.529\,177\,210\,8(18) \times 10^{-10}$	m
Energy	E_h	$4.359\,744\,17(75) \times 10^{-18}$	J
Time	$\frac{\hbar}{E_h}$	$2.418\,884\,326\,505(16) \times 10^{-17}$	s
Force	$\frac{E_h}{a_0}$	$8.238\,722\,5(14) \times 10^{-8}$	N
Velocity	$\frac{a_0 E_h}{\hbar}$	$2.187\,691\,263\,3(73) \times 10^6$	m/s
Electric potential	$\frac{E_h}{e}$	$27.211\,384\,5(23)$	V
Electric field	$\frac{E_h}{a_0 e}$	$5.142\,206\,42(44) \times 10^{11}$	V/m

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Curriculum Vitae

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Education

1995-2000	Secondary education, École Secondaire Hormisdas-Gamelin, Gatineau (Buckingham), Canada
2000-2002	Studies of Natural Sciences at the Cégep de l'Outaouais, Gatineau, Canada
2002-2005	Studies of physics (B.Sc.) at the University of Ottawa, Ottawa, Canada
2003	Summer research studentship on the "Coulomb Explosion of Buckminsterfullerene in a Strong Laser Field" in the group of Prof. T. Brabec in Ottawa, Canada
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2005	B. Sc. Physics with Honours thesis on "Non-adiabatic Laser Alignment of Benzene" in the group of Prof. P. B. Corkum at the Joint Attosecond Science Laboratory, University of Ottawa and National Research Council Canada, Ottawa, Canada
2005-	Ph.D. Physics in the group of Prof. P. B. Corkum at the Joint Attosecond Science Laboratory (JASLab), University of Ottawa and National Research Council Canada

Other activities

2000	Finalist at provincial (Québec) "Expo Science Bell", project on "Le mouvement perpétuel", Chicoutimi, Canada
2002-2004	Triathlon (6 events), ON and QC, Canada
2002-2007	Teaching assistantship at the undergraduate level in experimental physics at the University of Ottawa
2007	Participation to the first Attosecond Summer School, Physikzentrum Bad Honnef, Germany, 20 to 25 May 2007.

Awards and Distinctions

2003-2004	Summer Scholarship of the Natural Sciences and Engineering Research Council of Canada
2005	"Summa Cum Laude" B. Sc. Honours in Physics at University of Ottawa
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Languages

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Invited Talks

1. Non-Collinear Wave-Mixing in High Harmonic Generation
Advanced Laser Light Source (ALLS) Annual Meeting, Mont-Gabriel (QC), Canada, February 2010.
2. Molecular Frame High Harmonic Generation
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3. Génération d'harmoniques dans le référentiel moléculaire
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4. Non-Collinear Wave-Mixing in High Harmonic Generation
Cross-Boarder Workshop on Laser Science 2010, Waterloo (ON), Canada, June 2010.
5. An All-Optical XUV Beamsplitter for Attosecond Pump and Probe Experiments
Photonics North 2011, Ottawa, Canada, May 2011.
6. An All-Optical XUV Beamsplitter for Attosecond Pump and Probe Experiments
Cross-Boarder Workshop on Laser Science 2011, Rochester NY, USA, June 2011.
7. Hot Topic Talk: Linked Attosecond Phase Interferometry (LAPIN) for Single-Molecule Imaging
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Poster Presentations

1. High Harmonic Generation in Aligned Benzene
Gordon Research Conference (GRC) on Multiphoton Processes 2006, Tilton (NH), USA, June 2006.
2. Dynamical Orbital Tomographic Imaging
CIPI AGM 2008, Banff (AB), Canada, May 2008.
3. Dynamical Orbital Tomographic Imaging
American Physical Society DAMOP 2008, State College (PA), USA, May 2008.
4. Molecular Frame High Harmonic Generation
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5. Molecular Frame High Harmonic Generation
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6. High Harmonic Generation Meets Perturbation Theory
Gordon Research Conference (GRC) on Multiphoton Processes 2010, Tilton (NH), USA, June 2010.
7. An All-Optical XUV Beamsplitter for Attosecond Pump-Probe Experiments
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