

Following a Photochemical Reaction of Br_2 using Photoion and Photoelectron Momentum Spectroscopy

by

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Declaration of Authorship

I, Tian Wang, hereby certify that this thesis is entirely my own original work except where otherwise indicated. I am aware of the University of Ottawa regulations concerning plagiarism, including those regarding consequent disciplinary actions. Any use of the works of any other author, in any form, is properly acknowledged at their point of use.

List of Publications

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Abstract

When a chemical bond is breaking, the valence electrons within the bond undergo rearrangement, causing a corresponding rearrangement and separation of the atoms within a molecule. This process couples the motion of valence electrons and atoms, making it essential to concurrently visualize both in order to comprehend chemical reactions. However, obtaining complete information about these two different dynamics using a single observable presents a challenge. Over the past two decades, attosecond science has emerged as a means to generate multiple observables from a molecule by subjecting it to an intense femtosecond laser pulse, effectively disassembling it into electrons and ions. Additionally, the momentum distributions of photoions and photoelectrons contain intricate structures that offer valuable insights into the dynamic behavior of ions and electrons. This thesis explores the techniques for observing the atomic and valence electronic dynamics in the photochemical reaction of Br_2 by examining the momentum distributions of ions and electrons.

We first look at the electron momentum distribution and its subcycle interference structures. Here, we introduce a method for disentangling subcycle interference structure from non-adjacent quarter cycles by using orthogonal two-color laser fields.

Then we introduce a semiclassical model for simulating both atomic and molecular photoelectron spectra. For atomic ionization, various interference structures are comprehensively studied. In particular, we investigate the origin of fan-like interference structure by employing a time-variable soft-core Coulomb potential. For molecular ionization, our focus is on the photoionization of neutral Br_2 . We simulate photoelectron momentum distributions by taking into account various dynamic factors, such as molecular orbital structures, the ionization potential, and the internuclear distance. Furthermore, we conduct a comparative analysis of the electron momentum distributions between molecular Br_2 and atomic Br , aiming to elucidate the underlying reasons for their discrepancies.

At last, we will present our Br_2 pump-probe experiment, which encompasses the experimental techniques and results. We employed a cold target recoil ion momentum spectroscopy (COLTRIMS) apparatus to record the momentum spectra of ions and electrons from the ionization of dissociating neutral Br_2 molecules. When observing ions, we investigate the molecular orbital evolution during single ionization and the atomic separation during Coulomb explosion. In the case of electron observation, we analyze the electron momentum distributions stemming from single ionization and compare them with our simulation results. Our combined observations of ions and electrons provide a complete view of the photochemical reaction of Br_2 . We identify distinct transition stages, involving both molecular orbital evolution and structural transformation.

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Chapter 1

Introduction

*The more delicate the details are
by which we can follow nature on any path,
the richer and more lasting will the gains be
that we are able to draw from this perception.*

Max Planck

The manipulation of chemical reactions dates back nearly a million years to when our ancestors first started creating fire. However, our scientific comprehension of these reactions only began to take shape less than 300 years ago when pioneers like Dalton and Avogadro introduced the fundamental concepts of atoms and molecules to the world of science. While we have gained significant insights into the workings of nature, as Planck aptly pointed out, we continue to thirst for a deeper understanding. In modern science, we have come to recognize that the process of chemical reactions is intricately intertwined with complex dynamics at the atomic and valence electron levels.

In the realm of molecular quantum theory, valence electrons are distributed within entities known as molecular orbitals encircling the atomic nuclei. These molecular orbitals are constructed through the linear combination of atomic orbitals originating from each atom within a molecule. Consequently, the formation of molecular orbitals is contingent upon the relative proximity of atoms; only when two atomic orbitals draw near can they overlap to give rise to a molecular orbital. Otherwise, isolated atomic orbitals persist. Additionally, owing to the quantum property of superposition, two distinct types of molecular orbitals emerge: bonding molecular orbitals, resulting from constructive interference

between two atomic orbitals, and antibonding molecular orbitals, arising from destructive interference between two atomic orbitals.

Figure 1.1, utilizing the hydrogen molecular ion as an example, illustrates the contrasting mechanisms by which these two molecular orbital types are generated. There is a region of elevated electron probability between two atoms within the bonding molecular orbital, whereas a node devoid of electron density appears between atoms in the antibonding molecular orbital. Consequently, the filling of valence electrons in bonding molecular orbitals augments the attractive forces between the two atoms, promoting stability. Conversely, when valence electrons occupy antibonding molecular orbitals, the repulsive forces between the two atoms intensify. The equilibrium between these forces is what maintains the stability of the molecule. In a chemical reaction, the valence electrons undergo rearrangement, favoring the antibonding over bonding molecular orbitals, leading to the molecule's disintegration.

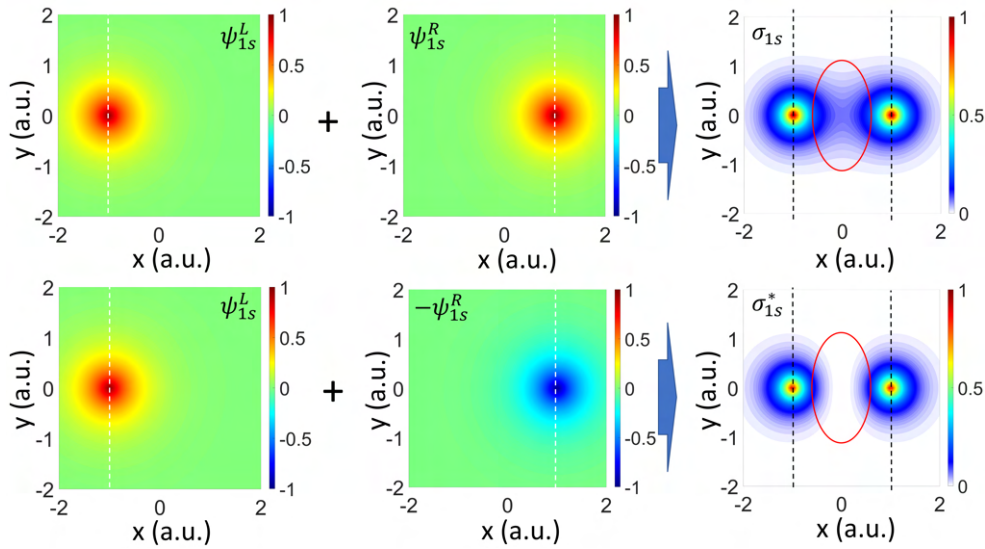


Figure 1.1: Formation of bonding MO and antibonding MO in H_2^+ . ψ_{1s}^L and ψ_{1s}^R are the ground state wavefunctions of two H atoms. σ_{1s} and σ_{1s}^* are the probability densities of bonding MO and antibonding MO which are calculated by $|\psi_{1s}^L + \psi_{1s}^R|^2$ and $|\psi_{1s}^L - \psi_{1s}^R|^2$ respectively. The red ellipses mark the electron probability densities between two atoms for the two different MOs. And the dashed vertical lines mark the nuclear positions of H atoms in each figure.

So, if we want to follow a chemical reaction and expect to obtain full knowledge of it, the best way is to observe the dynamics of both atoms and valence electrons at the same

time! Nowadays, the valence electron and nuclear dynamics can be probed individually by different ways: various methods in attosecond science can probe purely electronic dynamics in atomic [1] and molecular systems [2,3], while time-resolved structural-dynamics methods such as electron or X-ray diffraction and X-ray absorption can image atomic motion in specific dynamics [4]. Most recently, ultrafast electron diffraction has been demonstrated to simultaneously observe electronic and nuclear dynamics [5]. Until now, there has been a scarcity of research that can effectively observe and distinguish between the dynamics of both valence electrons and nuclei within a chemical reaction process simultaneously. This challenge can be attributed to the constraints of the available observation methods, which typically focus on individual entities such as electrons, photons, or specific ions. Valence electrons and nuclear behavior entail dynamic information that can manifest through various distinct observables, either separately or in combination. Therefore, it seems necessary to employ simultaneous measurement of multiple observables to unravel these distinct types of dynamics.

In this thesis, we have selected the light-induced dissociation of the bromine molecule as a representative example of a chemical reaction. In this particular reaction, a crucial step involves the excitation of one valence electron from the π bonding orbital to the σ anti-bonding orbital in Br_2 , triggered by the absorption of a single photon. To monitor this photochemical reaction, we have conducted a pump-probe experiment. In this experiment, a low-intensity (weak), ultraviolet pulse initiates the chemical reaction, and subsequently, a high-intensity, i.e., strong, infrared pulse probes the ensuing dynamics by ionizing the molecule. The high-intensity infrared pulse breaks the molecule, resulting in the generation of electrons and various types of ion fragments, whose properties can be measured to extract valuable information about the dynamics of this chemical reaction. To capture these multiple observables stemming from ionization, we employ a photoion-photoelectron coincident measurement technique known as COLd Target Recoil-ion Momentum Spectroscopy (COLTRIMS). COLTRIMS enables us to simultaneously record the momentum distributions of photoelectrons and various types of photoions. Consequently, we can investigate the time-resolved photoelectron and photoion momentum distributions to track the dynamic evolution of the photochemical reaction in Br_2 .

During the ionization event, both the photoelectron and photoion originate from the same molecule and are generated within the same laser pulse. Nevertheless, their characteristics in terms of their respective momentum distributions differ significantly. Typically, the photoelectron momentum distribution exhibits intricate interference patterns, while this is often not the case for the ion momentum distributions. This discrepancy arises from the fundamental distinctions between electrons and ions: electrons have considerably lower mass than ions, resulting in significantly larger de Broglie wavelengths. Furthermore,

by their very nature, photoelectrons report on the valence electron wavefunction, whereas photoions directly reflect the motion of the nuclear constituents of a molecule. Therefore, in this thesis, we will separately discuss the momentum distributions of photoelectrons and photoions.

Given the complexity of interference structures in photoelectron momentum distributions, we will begin by introducing a study focused on untangling intracycle interferences in photoelectron momentum distributions using orthogonal two-color laser fields. Subsequently, we will present a semiclassical model for simulating photoelectron momentum distributions and utilize it to disentangle intracycle interferences in atomic ionization. Additionally, we will extend this model to encompass molecular ionization and apply it to simulate electron momentum distributions arising from the dissociation of Br_2 . In the final section of this thesis, we will discuss the outcomes of our pump-probe experiment involving Br_2 .

This thesis will be organized as follows:

Chapter 2 will introduce the background and basic knowledge of strong field physics. The strong field ionization will be first discussed where various interference phenomena on photoelectron momentum distribution will be focused on. Then the strong field dissociation of a molecule will be introduced. In addition, other important strong field phenomena will also be briefly introduced.

Chapter 3 presents a combined experiment and theory resolving the finer details of intracycle interferences in the photoelectron momentum distributions using orthogonal two-color laser fields..

Chapter 4 introduces the semiclassical two step (SCTS) model for simulating photoelectron momentum distributions. This model will be first applied to atomic system and used to systematically disentangle intra- and intercycle interference structures in photoelectron momentum distribution. Then this model will be extended to the molecular case by considering molecular orbitals and molecular structure.

Chapter 5 covers the experimental knowledge needed to carry out a Br_2 pump-probe experiment using a COLTRIMS apparatus. The femtosecond laser system will be first shown, followed by the detailed introduction of COLTRIMS, including the data calibration procedure in a typical COLTRIMS experiment. Then, the optical setup is presented and the key procedures for an optical pump-probe experiment are introduced which includes the techniques for finding the temporal overlap and the intensity calibration for our laser pulses. At last, the preparation of Br_2 gas mixture, the precautions for using Br_2 gas and pulse intensity optimization for Br_2 experiment are shown.

Chapter 6 presents the results and analysis of our Br_2 pump-probe experiment. In this part, we will focus on the ion and electron observations respectively for following Br_2 's dissociation. We will combine our simulation results and experiment observations together in the analysis.

Chapter 7 provides a summary of the work discussed in this thesis.

Chapter 2

Background

2.1 Strong field ionization

In attosecond physics, ionization typically describes the process in which electrons are emitted from atoms or molecules upon absorbing photons. When the light intensity is low, this phenomenon can be comprehensively explained by Einstein’s photon theory. According to this theory, a single electron absorbs one photon’s energy to overcome the binding potential energy of the nucleus, subsequently gaining additional kinetic energy E_{kin} , as described by the equation:

$$E_{kin} = h\nu - W_0 \quad (2.1)$$

where h represents the Planck constant, and W_0 denotes the minimum energy required for electron removal. For atoms and molecules, this minimum energy corresponds to their ionization potential I_p . This theory inherently implies that the ionization rate is directly proportional to the light intensity, owing to the one-to-one relationship between photons and electrons. Einstein’s theory played a foundational role in the early development of quantum mechanics.

However, when examining strong laser fields, it has been revealed that a different scenario can occur as the light intensity becomes exceptionally high, and the electric field of light becomes comparable to the atomic or molecular Coulomb field that binds the electrons. In such circumstances, an intriguing phenomenon emerges: prior to ionization, a single electron can absorb multiple photons simultaneously. In this section, we will explore various mechanisms of strong-field ionization and provide the theoretical background, using atoms as illustrative examples.

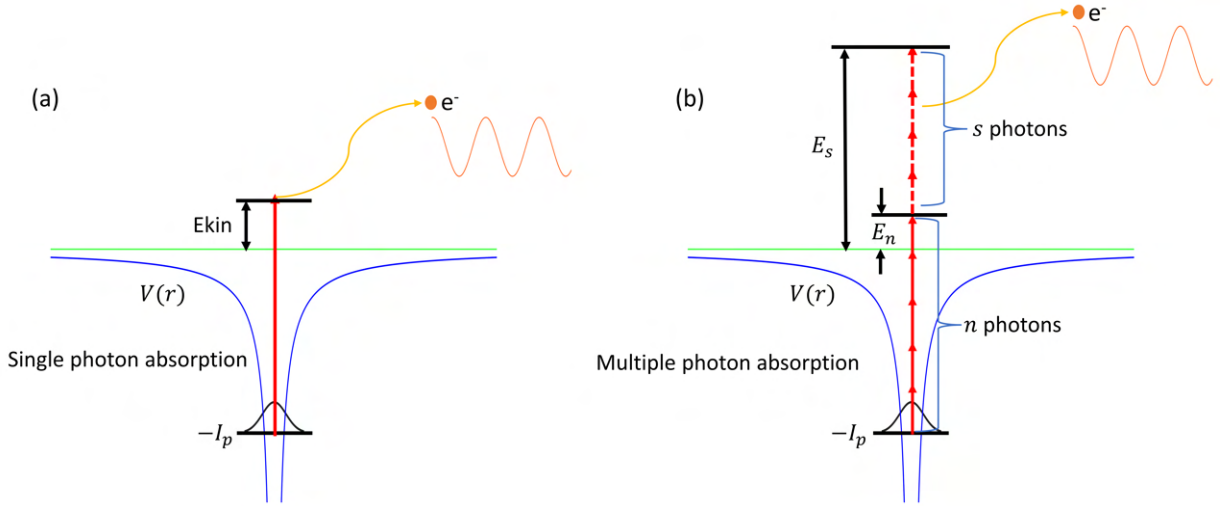


Figure 2.1: Single photon ionization (left) and multiphoton ionization (right). $V(r)$ represents the Coulomb field from the atomic nucleus. The solid red arrows symbolize the minimum number of photons required for ionization in each case. In multiphoton ionization, the dashed red arrows illustrate the additional photons that an electron can absorb. E_n represents the kinetic energy of the electron following the absorption of n photons, while E_s represents the electron kinetic energy after the absorption of $(n + s)$ photons.

2.1.1 Multiphoton ionization

Multiphoton ionization refers to the process of electron emission triggered by the absorption of multiple photons. Figure 2.1 illustrates a comparison between these two ionization mechanisms. In contrast to single photon ionization, which necessitates a single high-energy photon to elevate the electron from its bound state to the continuum state, multiphoton ionization requires the absorption of several lower-energy photons. Furthermore, owing to its multiphoton nature, the ionization rate associated with multiphoton ionization exhibits a nonlinear dependence on the light intensity. For the case of low intensity, the ionization rate w_n , associated with n photon absorption, can be approximated using the following expression:

$$w_n = \sigma_n I^n, \quad (2.2)$$

where σ_n is the n photon ionization cross section, I is the intensity, and n is the minimum number of photons required to free the electron.

Another characteristic of multiphoton ionization is the absorption of additional photons beyond the ionization threshold by the electron, a phenomenon often referred to as a

continuum-continuum transition. This unique photon absorption behavior becomes evident when examining the electron kinetic energy after ionization. As depicted in Figure 2.1, when the electron absorbs an additional s photons during the process of multiphoton ionization, its resulting kinetic energy can be expressed as follows:

$$E_s = (n + s)\hbar\omega - I_p \quad (2.3)$$

This predicts that the electron energy spectrum will have a comb structure spaced by one photon energy. The multiphoton ionization phenomenon is usually called above threshold ionization (ATI) and its comb structure has been observed and studied extensively [6].

2.1.2 Tunnel ionization

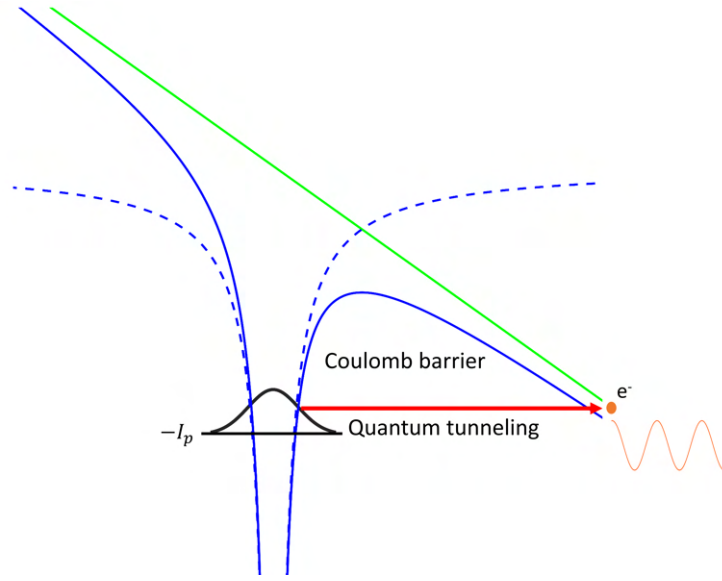


Figure 2.2: Effective potential and tunnel ionization resulting from intense light fields. The nuclear Coulomb potential in the absence of the field is represented by the dashed blue curve, while the solid green line illustrates the presence of the strong electric field. The solid blue curve represents the effective Coulomb barrier.

Up to this point, our discussion has revolved around the ionization process from the perspective of photons, which represents light as particles. However, as the light intensity reaches higher levels, it becomes possible for an electron to absorb multiple photons simul-

taneously. In such instances, it is more convenient to discuss the ionization event using a wave representation.

In the wave representation, the light field is treated as an oscillating electromagnetic wave. Additionally, strong field experiments typically utilize infrared laser pulses with wavelengths much larger than the scale of electron motion. Therefore, the electric dipole approximation is usually applicable, as long as the intensity does not lead to relativistic effects. Under these specific conditions, the Hamiltonian describing an electron within a strong light field can be expressed as follows:

$$\hat{H} = \frac{\mathbf{p}^2}{2m} + \hat{V}(\mathbf{r}) - \mathbf{e}\hat{E}(t) \cdot \mathbf{r}, \quad (2.4)$$

where $\hat{V}(\mathbf{r})$ is the Coulomb potential of ion core, and $\hat{E}(t)$ is the electric field of laser pulse. We can see that the electron is no longer confined only by the Coulomb potential but an effective potential:

$$V_{eff} = \hat{V}(\mathbf{r}) - \mathbf{e}\hat{E}(t) \cdot \mathbf{r}. \quad (2.5)$$

This effective potential has been shown in Figure 2.2. It can be seen that the Coulomb potential can be greatly suppressed by the electric field of intense light and forms a Coulomb barrier. Then the electron can directly pass through this Coulomb barrier by quantum tunneling effect! Hence, this ionization mechanism is called *tunnel ionization*.

2.1.3 Keldysh parameter

In order to categorize different ionization mechanisms, Keldysh introduced a dimensionless parameter in 1965 [7]:

$$\gamma = \sqrt{\frac{I_p}{2U_p}}, \quad (2.6)$$

where U_p is the ponderomotive potential:

$$U_p = \frac{F^2}{4\omega^2}. \quad (2.7)$$

Here, F is the laser field strength and ω is the laser frequency. In laser physics, the ponderomotive potential characterizes the cycle-averaged kinetic energy of an electron in the laser field.

By the parameter γ the applicable range of the two different ionization mechanisms can

be defined: multiphoton ionization occurs when $\gamma \gg 1$, while a picture of tunnel ionization can be well used when $\gamma \ll 1$. It can be seen from Equation 2.6 and Equation 2.7 that the tunnel ionization is usually more applicable for the laser field with high intensity and low frequency.

2.1.4 ADK model

Usually, most strong-field experiments are performed with infrared lasers and under moderate light intensity which corresponds to $\gamma \approx 1$. For this condition, tunnel ionization is found to be a good approximation to treat ionization. Moreover, the ionization rate of tunnel ionization can be well estimated by an analytical model which was first developed by Ammosov, Delone and Krainov in 1986 and is always referred to as ADK model. The fundamental form of the ADK ionization rate for a linearly polarized field is expressed as follows [8]:

$$w_{ADK}(t_0, v_\perp) \simeq \exp \left[-\frac{2\kappa^3}{|3F(t_0)|} \right] \exp \left[-\frac{\kappa v_\perp^2}{|F(t_0)|} \right], \quad (2.8)$$

where $\kappa = \sqrt{2I_p}$, $F(t_0)$ is the instantaneous electric amplitude of the laser field, and $v_\perp$ is the initial transverse velocity of the electron at the tunneling exit point. Here, the first exponential term originates from the width of barrier along the field direction, and the second term comes from the barrier width perpendicular to the field.

In a theoretical simulation for tunnel ionization, the ADK rate usually cooperates with another analytical model of calculating the tunneling exit point r_e . For example, in this thesis, The tunneling exit point r_e is calculated using the TIPIS approximation [9]:

$$r_e = \frac{I_p(t_0) + \sqrt{I_p(t_0)^2 - 4\beta_2 E(t_0)}}{2E(t_0)}, \beta_2 = 1 - \frac{\sqrt{2I_p(t_0)}}{2}, \quad (2.9)$$

where the Stark-shifted ionization potential is $I_p(t_0) = I_{p,0} + \frac{1}{2}(\alpha_N - \alpha_I)E(t_0)^2$, where α_N and α_I denote the static polarizability for the atom and the ion, respectively, and $I_{p,0}$ is the ionization potential without any shifts.

ADK model has been extended to give the ionization rate for an arbitrary initial velocity which has both the transverse and parallel components. In addition, the ADK model has also been extended to diatomic molecules by considering the properties of molecular orbital [10]. However, these ADK models with new features will not be discussed in depth in this thesis.

Nowadays, the ADK model is being widely applied to predict and analyze various strong field phenomena in strong laser experiments. For examples, the dependence of ionization rate on molecular alignment was first demonstrated by Zhao with application of molecular ADK model [11]. Subsequent experiments performed by Pavicic et al. strengthened our understanding on angular ionization of molecules by applying the ADK model as an analysis tool [12]. Moreover, the ADK model is also the foundation of many other theoretical models which are widely used in strong field physics [13–16]. For example, the ADK rate is embedded in the semiclassical model of simulating nonsequential double ionization [13, 17]. Most recently, the ADK model is applied in a semiclassical two step (SCTS) model, which reproduces various of interference structures in strong-field ionization [15]. The SCTS model and its application on disentangling interference structures in the photoelectron momentum distributions will be discussed in depth later.

2.1.5 Post-ionization dynamics: recollision

In an ionization event, the ionized electron will depart from its parent ion. However, as depicted in Figure 2.1(b), even after ionization, the electron remains capable of absorbing additional photons within the intense laser pulse. This signifies that the electron continues to be influenced by the light field while in the continuum. To understand this influence, the behavior of electrons in strong fields is often elucidated using classical trajectory concepts.

Figure 2.3 illustrates two types of trajectories for free electrons within a strong light field: (a) demonstrates that electrons ionized before the peak of the electric field will oscillate on one side of the nucleus, creating a gap between themselves and the nucleus, effectively preventing their return to the nucleus. These electrons are commonly referred to as "direct electrons." On the other hand, (b) shows that electrons ionized after a peak in the field can return to the nucleus following ionization. These electrons are known as "recollision" or "rescattering" electrons.

The recollision mechanism was initially formulated in a semi-classical three-step model by Paul Corkum in 1993 [18]. The inset in Figure 2.3(b) outlines the three-step model: in the first step, the electron is liberated through tunnel ionization; in the second step, it freely propagates while being influenced by the strong field; finally, in the third step, when the electric field changes direction, the electron returns to its origin and collides with its parent ion. One of the most significant predictions of the three-step model is the maximum photon energy attainable in high harmonic generation (HHG):

$$\hbar\omega_{max} = I_p + 3.17U_p. \quad (2.10)$$

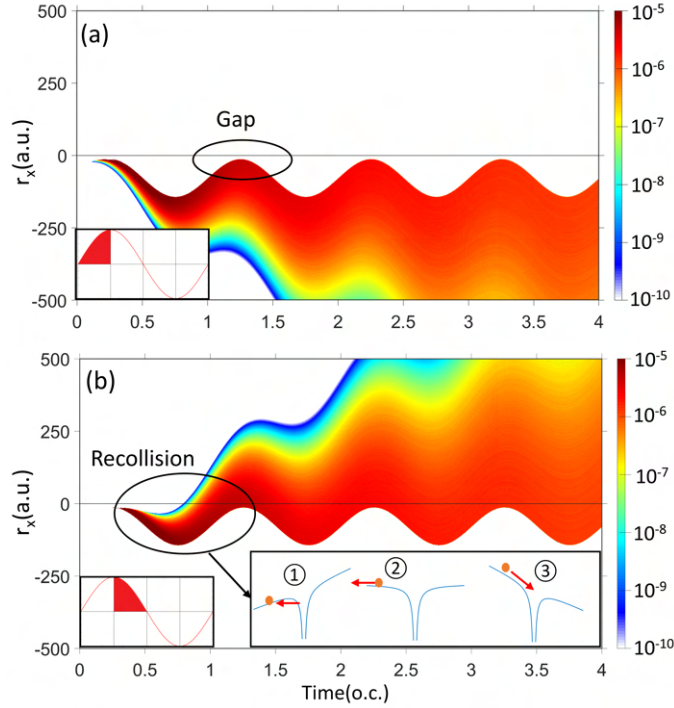


Figure 2.3: Electron trajectories from different quarter cycles: (a) the quarter cycle before a crest of electric field, and (b) the quarter cycle after a crest of electric field. The insets on the left lower corners of each panel indicate the quarter cycles where tunnel ionization happens. In (a), the black ellipse indicate that there is a gap between electron trajectories and the nucleus, while in (b), the black ellipse indicate the recollision trajectories of electron. Particularly, the inset on the right lower corner of panel (b) illustrates the three-step model.

In addition to high harmonic generation (HHG), the concept of recollision plays a pivotal role in numerous other significant phenomena within the realm of strong-field physics. These include high-order above-threshold ionization (ATI), non-sequential double ionization, and strong-field photoelectron holography. The three-step model provides a robust framework for comprehending all of these phenomena.

Presently, recollision and the three-step model have emerged as fundamental pillars of strong-field physics and attosecond science, underscoring their critical importance in advancing our understanding of these fields.

2.2 Interference in strong-field ionization

The particle-wave duality is a universal property of all matter. However, in the previous section, we primarily considered the electron solely as a particle when employing the photon absorption concept to elucidate multiphoton ionization or when introducing parameters like the electron's initial velocity and exit point in tunnel ionization. This prompts the question: where does the wave-like character of the electron come into play in strong-field ionization?

It is evident that quantum tunneling arises as a consequence of the electron's wave-like nature. However, the most important characteristic of a wave is the ability for interference. In fact, interference is manifest prominently in the energy spectrum and the momentum distribution of photoelectrons resulting from strong-field ionization. These interference patterns within the photoelectron momentum distribution are extraordinarily intricate and can be categorized into *intercycle* and *intracycle* interferences.

2.2.1 Intercycle interference: ATI peaks

As discussed in section 2.1.1, the photoelectron from strong-field ionization has a comb-like structure in energy where the teeth of the comb are spaced by one photon energy of laser field. A realistic photoelectron energy spectrum is shown in Figure 2.5(b) which agrees with this picture. On the other hand, these ATI peaks can also be interpreted in the time domain which has been shown in Figure 2.4. As shown in Equation 2.8, the tunnel ionization rate increases exponentially with the electric field strength, so the electron has the highest probability of ionization around each crest of the light wave. Thus, when the atom undergoes strong-field ionization, it will generate photoelectron wave packets at each crest of the electric field. Since they are from the same electron, these wave packets will interfere with each other if they hit on the same region of electron detector. Similar with Young's double slits interference, these crests of electric field will work as a set of temporal slits spaced by one optical cycle, thus when the wave packets from them interfere with each other, fringes appear in electron momentum space. Figure 2.5(a) shows an experimental photoelectron momentum distribution from ionization of Ar in a 800nm laser field. A ring-like interference structure can be clearly seen in this distribution. These ring structures are usually called ATI rings.

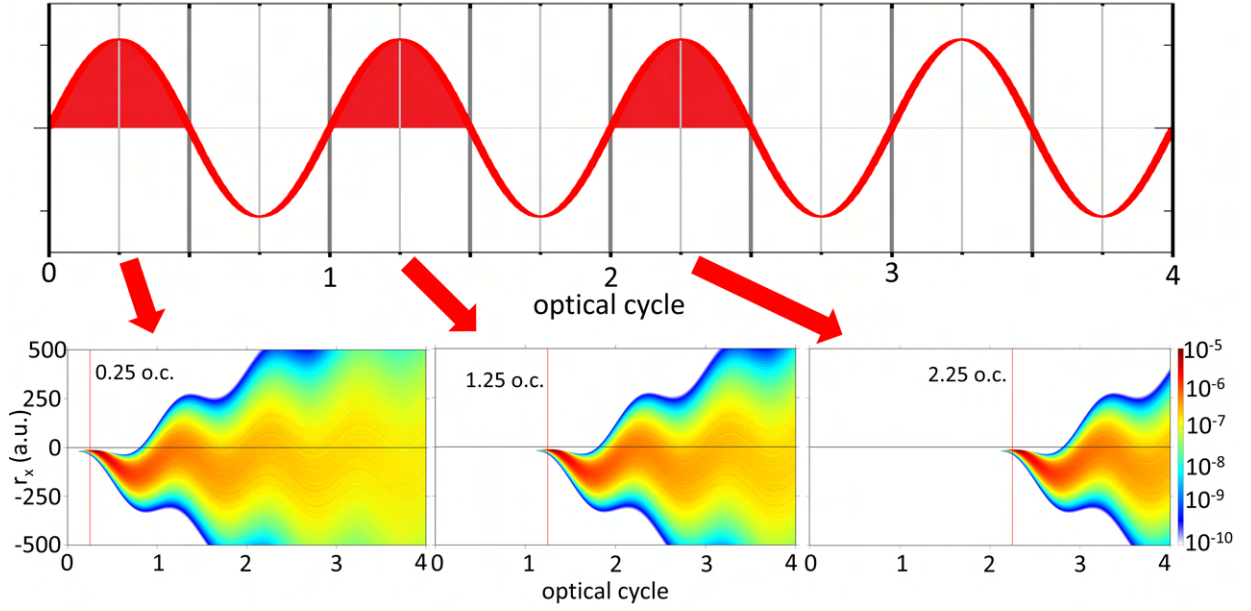


Figure 2.4: Upper panel: Illustrated is a diagram depicting the electric field of the laser pulse. The shaded regions in red represent three chosen half cycles during which electron ionization occurs. In the lower panel, electron paths from distinct optical cycles (*o.c.*) are presented. Specifically, trajectories originating from three half cycles (0.25 *o.c.*, 1.25 *o.c.*, and 2.25 *o.c.*) are showcased. Although the shapes of the trajectory distributions remain identical, they are offset by one optical cycle successively. Consequently, these trajectories yield the same momentum distribution, resulting in interference in the momentum space. While electrons can also undergo ionization in the unshaded half cycles, these trajectories are omitted for clarity.

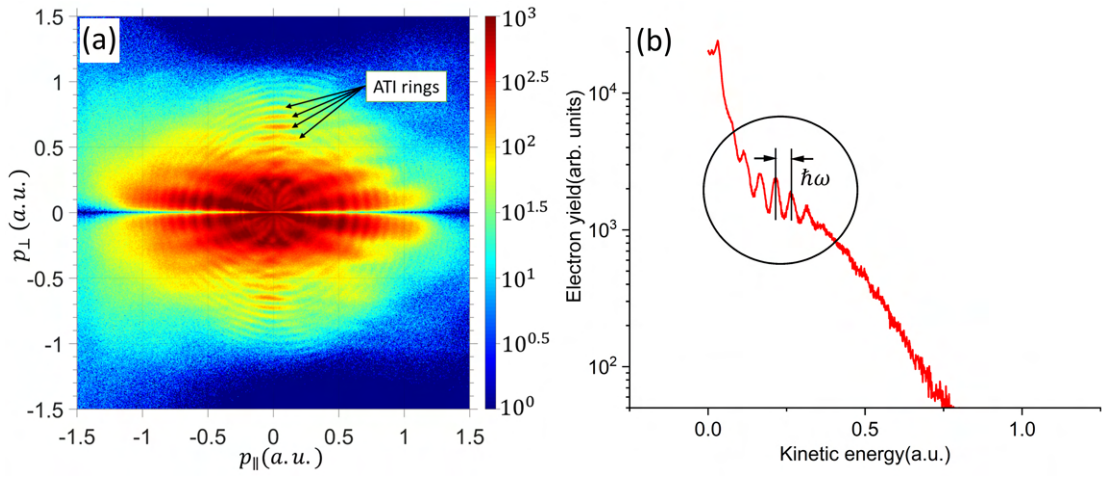


Figure 2.5: (a) Photoelectron momentum distribution from strong-field ionization of Ar with a 800 *nm* laser pulse. The solid white lines indicate the strong-field photoelectron holography fringes. The black arrows indicate the above-threshold ionization rings. Inside the dashed white circle are the so-called fan-like interference structure in the low momentum range. (b) Corresponding photoelectron energy spectrum. The black circle indicates the comb-like structure which is spaced by one photon energy $\hbar\omega$.

2.2.2 Intracycle interference

The intercycle interference comes from the translation symmetry of the optical wave in time: each optical cycle is identical to the next, which leads to several identical electron wave packets. Hence, the global ring-like interference fringes emerge in the momentum space. However, if we look into one optical cycle, such symmetry will be broken up, and other types of interference structures which have subcycle origin will emerge. Due to the diversity of electron dynamics within the laser field, there are various types of intracycle interference which we will discuss below.

2.2.2.1 Intracycle interference: strong-field photoelectron holography

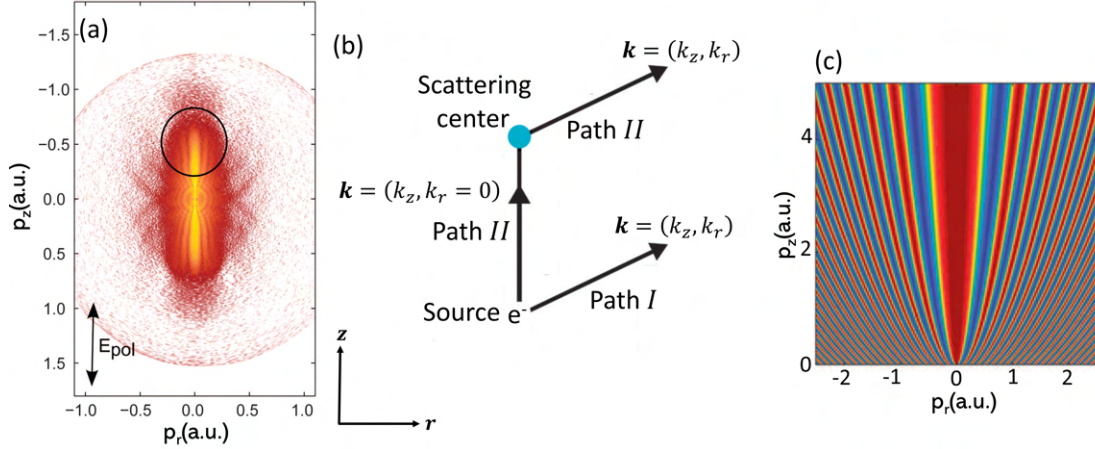


Figure 2.6: (a) Photoelectron momentum distribution from the ionization of metastable xenon under the laser condition: $\lambda_{laser} = 7\mu m$, *intensity* : $7.1 \times 10^{11} W/cm^2$. (b) Diagram illustrating the concept of electron holography. Two interfering paths with the same final momentum $\mathbf{k} = (k_z, k_r)$ are indicated. Path I is the reference wave, leaving the source with momentum $\mathbf{k} = (k_z, k_r)$. Path II is the signal wave, incident on the target with $k_r = 0, k_z = k = |\mathbf{k}|$ and scattering into $\mathbf{k} = (k_z, k_r)$. (c) Interference pattern generated by a Gaussian wave packet released at a distance $z_0 = 50$ atomic units (a.u.) toward a scattering center, with no laser field present. A hologram is created as a result of the interference between a scattering-signal wave packet and a direct-reference wave packet. Taken and adapted from [19].

The strong-field photoelectron holography (SFPH) originates from electron scattering on its parent ion during recollision process. The forward scattering version of SFPH was

first observed by Y. Huismans et al. in the ATI process from a metastable state of Xe in intensities of the order of 10^{11}W/cm^2 and a wavelength around $7 \mu m$ from a free electron laser [19]. Figure 2.6(a) displays the photoelectron momentum distribution. The interference patterns denoted by the black circle represent what is known as the strong-field photoelectron holography pattern. In Figure 2.6(b), we can observe its underlying interference mechanism. When the electron wave packet returns to its parent ion during the recollision event, a portion of it scatters due to interaction with the ion, while the other portion remains unscattered. Consequently, if both the scattered and unscattered wave packets eventually reach the same momentum, they will interfere with each other. This interference process can be regarded as a type of electron-based holography technology: the unscattered electron wave packet can be considered the reference wave, while the scattered wave packet serves as the signal wave. This interference results in the creation of fringe patterns resembling spider legs, which are nearly parallel to the polarization direction of the laser field, as illustrated in Figure 2.6(c). Subsequently, strong-field photoelectron holography (SFPH) was identified as a recurring phenomenon observable in various atomic and molecular targets when exposed to near-infrared laser fields [20–25].

The concept of holography provides a way to understand intracycle interference by regarding different electron trajectories as reference or signal electrons in the interference process. Usually, the un-scattered electron trajectories are treated as the reference, while the signal electron trajectories can be classified as two types: the forward scattering one and the backward scattering one. These reference and signal electrons can be born within different quarter cycles of the laser field, and, thereby lead to different intracycle interference mechanisms. Figure 2.7 shows different intracycle interference schemes and corresponding interference structures of photoelectron momentum distributions as identified by Bian et al. [26]. In this model, the Coulomb potential of ion core is not included. It can be seen that the different scattering mechanisms lead to very different interference patterns: the forward scattering generates fringes along the laser polarization direction or a set of ring-like structures, while the backward scattering leads to fishbone-like interference structures. This fishbone-like interference structure of backward SFPH was first observed in experiment by Haertelt et al. [27].

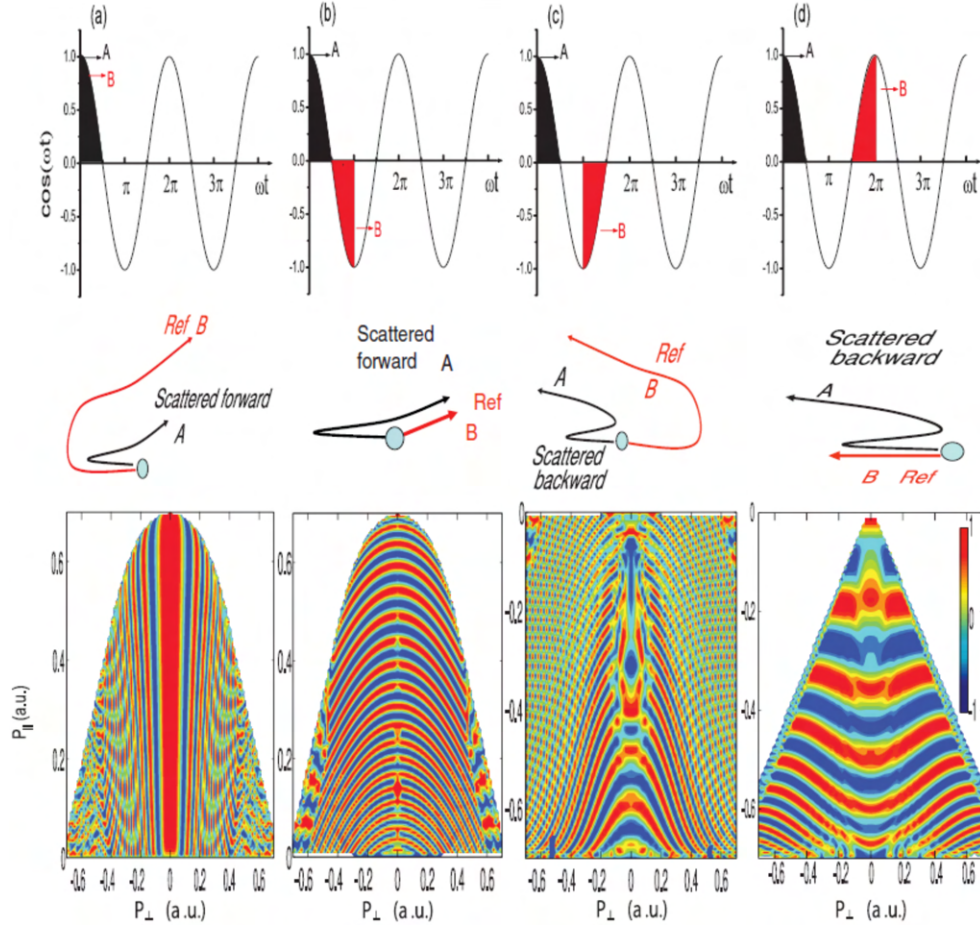


Figure 2.7: Sketch of different subcycle interference trajectories and the corresponding interferometric structures. A stands for the signal electron, B represents the reference electron. Reproduced from [26].

2.2.2.2 Intracycle interference: fan-like interference structure in low momentum range

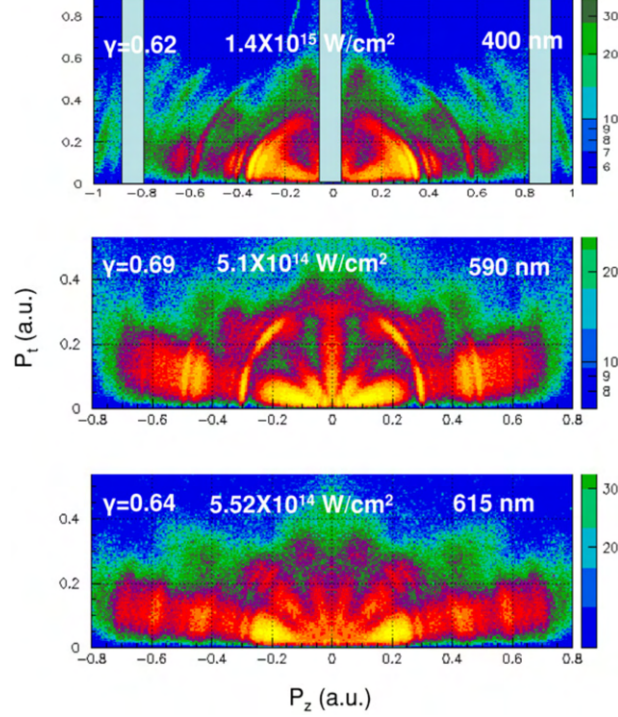


Figure 2.8: Photoelectron momentum distributions from strong-field ionizations of Ar for different wavelengths (400 nm, 590 nm, and 615 nm). The momentum components P_z and P_t are oriented parallel and perpendicular to the laser polarization. A fan-like structure appears within low momentum range: $|P_z| < 0.3$ a.u. for all three wavelengths. Reproduced from [28]

The fan-like interference structure is a type of interference which happens near the ionization threshold. Its characteristic is a set of radial interference fringes in the low momentum range of a photoelectron momentum distribution [28–30]. Figure 2.8 shows the fan-like interference structures in these early experimental observations [28]. It can be seen that the fan-like fringes are within a small momentum range: $|P_{z,r}| < 0.3$ a.u. which is the center part of photoelectron momentum distribution. Such a fan-like interference structure is also marked on the photoelectron momentum distribution of Figure 2.5.

Although the fan-like interference structure has been often observed in the last two decades [28, 29, 31], its detailed mechanism is controversial [20, 29, 32, 33]. Various theoret-

ical models have been applied to reproduce and interpret the formation mechanism from different angles of view [20, 34, 35]. The consensus is that such an interference process is due to the interplay between the laser field and the Coulomb potential. In this thesis, we study the fan-like interference structure by applying the semiclassical two-step model. Our simulation results demonstrate that this low-momentum interference arises from the interference between what we call *drifted* and *undrifted* electrons from opposite direct quarter cycles. This work will be discussed in detail in the chapter 4.

2.2.2.3 Intracycle interference: temporal double-slit interference

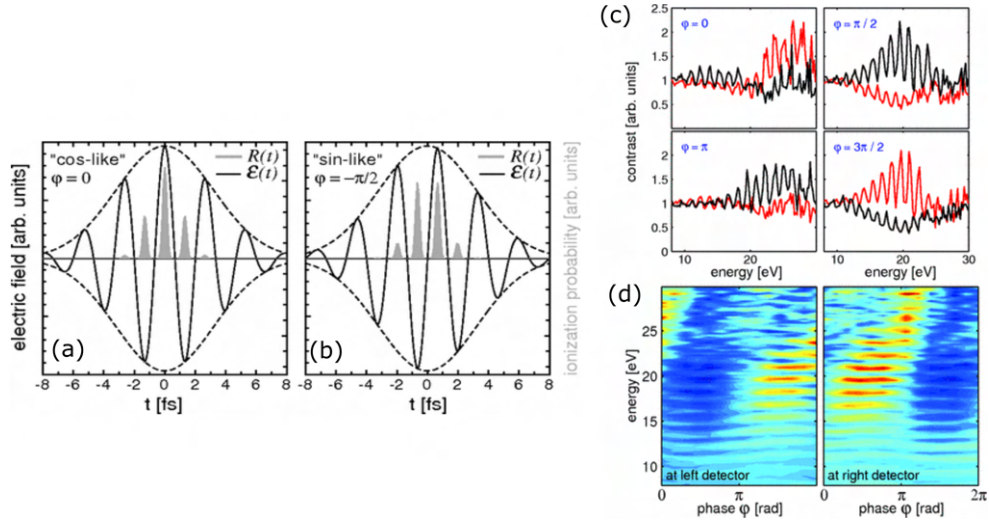


Figure 2.9: (a,b) Temporal variation of the electric field $E(t) = E_0(t) \times \cos(\omega t + \phi)$ of few-cycle laser pulses with phase $\phi = 0$ ("cos-like") and $\phi = -\pi/2$ ("sin-like"). Note: changing the phase by π only flips the direction of electric field but keeps its overall shape. (c) Photoelectron spectra of argon measured at the left (red line) and right (black line) detector using 6 fs laser pulses at an intensity of $1 \times 10^{14} \text{ W/cm}^2$ as a function of the carrier-envelope offset phase with $\phi = 0, \pi$ for cos-like pulses and $\phi = \pi/2, 3\pi/2$ for sin-like pulses. (d) The entire measurement where the fringe visibility is coded in false colors. The fringe positions and visibility vary as the phase ϕ of the pulse is changed. Taken and adapted from [36].

The concept of the temporal double-slit was first introduced to strong field physics in 2005 by F. Lindner et al. in a photoionization experiment using few-cycle laser pulses [36].

In their experiment, linearly polarized, carrier-envelope-offset phase(CEP) controlled, few-cycle, near infrared laser pulses were used to strong field ionize argon atoms. The energies of emitted photoelectrons were measured by two electron detectors in opposite directions. Figure 2.9 shows the shapes of few-cycle pulses with different CEP and the corresponding photoelectron energy spectra. In Figure 2.9(a,b) we can see that the electric fields of "cos-like" and "sin-like" pulses are completely different. Hence, the different wave form of electric field leads to different electron wave packets on the single-cycle time scale: the "cos-like" pulse generates a wave packet with the maximum amplitude at t_0 and two weaker wave packets at both sides of it, while within the "sin-like" pulse two wave packets with the same amplitude are generated where the vector potential is the same but the direction of the electric field is opposite. The clear interference fringes in Figure 2.9(c,d) are the result of the interference between the wave packets in the corresponding laser pulses. If we focus on the case of "sin-like" pulses with $\phi = \pi/2, 3\pi/2$, it can be seen that the two electron wave packets can lead to the most intense interference fringes although their initial emission directions are opposite. The reason that the two electron wave packets can interfere is the recollision: one electron wave packet will change its direction during recollision and finally reach the same detector with the other electron wave packet. Such interference phenomenon is called "temporal double-slit".

Subsequent studies using COLTRIMS and two-color pulses further extended the understanding of the temporal double-slit in the electron momentum distribution [37, 38]. The later research has demonstrated that each half cycle of the laser pulse releases a electron wave packet where half it goes into one direction and never recollide with the parent ion, while the other half can recollide with the parent ion. Hence, the quarter cycle where the ionized electron can not recollide can be treated as the direct quarter cycle, and the other quarter cycle where the recollision of electron can occur is the indirect quarter cycle. With the two concepts, the temporal double-slit can be treated as the interference between direct-quarter-cycle electron and indirect-quarter-cycle electron [37].

2.3 Molecular dissociation in a strong field

When a molecule is subjected to a strong laser field, the frequent absorption and stimulated emission of photons occur so rapidly that the molecule can no longer be treated as an isolated system separate from the laser field. Instead, the combined entity comprising the molecule and photons must be regarded as a unified system [39]. Within this system, the molecular ion produced after ionization can become inherently unstable, leading to subsequent dissociation. This dissociation process involves further interactions between

the molecule and the strong field. The manner in which coupling occurs, and consequently the dissociation mechanism, is determined primarily by two key factors: the laser intensity and its frequency [40].

Depending on the frequency of the laser field, the interaction between the molecule and light can be examined through two distinct frameworks. When the laser field operates at a frequency lower than the vibrational period of the molecule, the interaction can be aptly described using an adiabatic quasi-static model, wherein the potential energy surface (PES) of the molecule can be altered by the strong field [40, 41]. Conversely, when the laser wavelength shortens, consideration of the dressed-state molecule or the Floquet picture becomes necessary [40]. In this context, we will initially explore different dissociation mechanisms based on the Floquet picture. To simplify our discussion, we will use the simplest molecule, H_2^+ , as an example to illustrate various dissociation mechanisms within this framework.

2.3.1 Bond softening and above threshold dissociation

Figure 2.10 shows the photon-dressed PESs of the first two states (the ground state has σ_g symmetry, while the first excited state σ_u) for H_2^+ . The combined molecular and photon states are denoted by $|g/u, n\rangle$, where g or u describes the parity of molecular state and n describes the photon state. Here, a negative number n corresponds to photon absorption, while a positive number corresponds to photon emission. It can be seen that a one-photon dressing of the $|u, n\rangle$ state shifts it downward and cross the $|g, n\rangle$ state at the internuclear distance R_c . In the Floquet picture, when these two diabatic dressed states coupled together, two adiabatic dressed PESs form with an avoided crossing at R_c . Hence, the lower adiabatic dressed PES encounters a barrier to dissociation. The higher the laser intensity, the lower this barrier becomes.

With the laser field turned on, the vibrational states of the initial wavepacket are projected onto field-induced resonances. The dynamics of these resonances on the coupled dressed PESs decides the dissociation mechanism. For instance, when the resonances of high vibrational states coupled with the lower dressed state, indicated by the red arrow *BS* in Figure 2.10, the molecule can easily dissociate. Since this softens the molecular bond, this mechanism is often referred to as *Bond softening* (BS). On the contrast, if the resonances couple to the above PES, indicated by the red arrow *VT*, the resonance will be trapped in the potential well formed by two PESs. Hence, the latter mechanism is called *Vibrational trapping* (VT) or *Bond hardening* [42, 43].

When considering the states with more photon dressing, another dissociation mech-

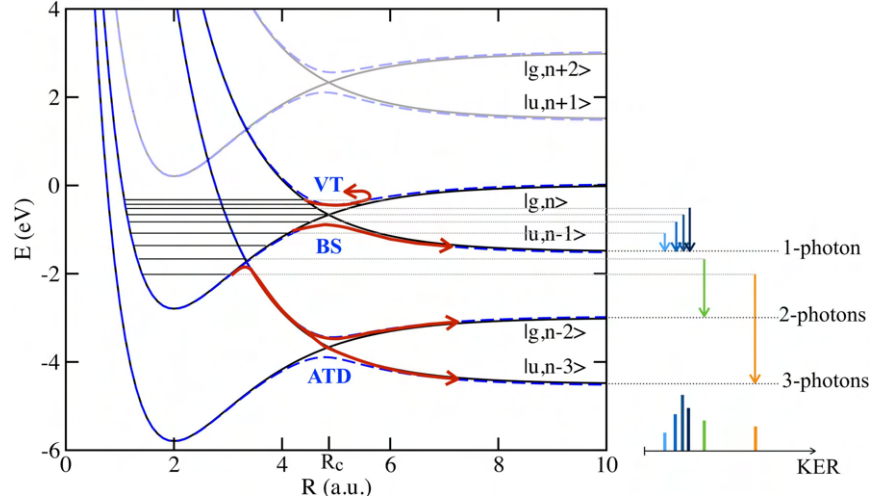


Figure 2.10: Potential energy curves of H_2^+ dressed by n photons in a 800nm laser field. The black curves and blue dashed curves are the diabatic and adiabatic dressed states respectively. The black solid lines denote the vibrational states in ground state. The red arrows show different dissociation mechanisms. BS indicates bondsoftening. VT vibrational trapping, and ATD above threshold dissociation. On the right-hand side, the photon-absorption pathways and corresponding kinetic energy release(KER) are shown. Taken from [40].

anism with higher kinetic energy release can occur. As shown in Figure 2.10, the low vibrational states of $|g, n\rangle$ state can couple to the $|u, n-3\rangle$ state through 3-photon absorption, or to the $|g, n-2\rangle$ state after reemitting one photon. This mechanism is called above-threshold-dissociation (ATD). ATD corresponds to the vibrational analog of above-threshold ionization. In both processes, more photons are absorbed than required to initiate the respective process, dissociation or ionization [40].

2.3.2 Charge resonance enhanced ionization

Charge resonance enhanced ionization (CREI) is an internuclear distance-dependent dissociative ionization phenomenon [40, 44].

Figure 2.11 illustrates its mechanism. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of H_2^+ are $1s\sigma_g$ and $2p\sigma_u$, respectively. When the laser intensity increases, the coupling between the laser field and the molecule is so intense that the molecular orbitals are distorted and mixed. Hence, the

localization of electron has to be considered and it is useful to re-express the molecular orbitals of H_2^+ in their localized basis: $\sigma_+ = \sigma_g + \sigma_u$ and $\sigma_- = \sigma_g - \sigma_u$. On the other hand, the combined molecular Coulomb potential and the electric field of laser pulse has to be considered since the strong coupling between molecule and laser field. Figure 2.11(a-c) show the combined potential. In such an effective potential, the Stark effect will up-shift the energy of σ_+ while down-shift the energy of σ_- . Consequently, at a specific distance, such as $R = 10$ atomic units (a.u.) as illustrated in Figure Figure 2.11(b), the energy of the Highest Occupied Molecular Orbital (HOMO) slightly exceeds the height of the central potential barrier. This situation results in the emergence of an additional ionization channel over the barrier, significantly amplifying the ionization process. The ionization rate of Charge Resonance-Enhanced Ionization (CREI) varies with distance and exhibits a dual-peaked structure, with the highest peak occurring at $R = 10a.u.$, as depicted in the right panel of Figure 2.11.

In comparison to other mechanisms such as bondsoftening and Above-Threshold Dissociation (ATD), CREI has the capacity to generate ion fragments characterized by much higher kinetic energy. This is attributed to the fact that CREI produces two bare protons that experience strong Coulomb repulsion. This process can be likened to an explosive event within the H_2 molecule and is often referred to as a *Coulomb explosion*.

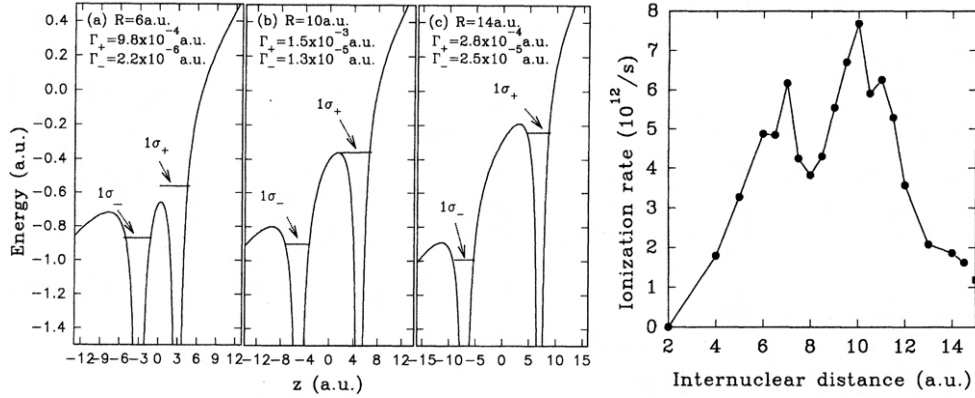


Figure 2.11: Charge resonance enhanced ionization. (a-c) Two molecular orbital levels for H_2^+ in the effective potential for different internuclear distance. Right panel shows the internuclear distance dependent ionization rate of H_2^+ . Adapted from [44].

2.3.3 Coulomb explosion

Coulomb explosion stands out as the most energetically intense dissociation process a molecule can undergo, as the term "explosion" suggests. In this mechanism, two or more electrons are ionized from the molecule, leading to the prompt separation of the resulting ion fragments. These fragments rapidly move away from each other due to the strong Coulomb repulsion between them. Given the inherent characteristics of Coulomb interaction, it is important to note that the kinetic energy released by the ion fragments is inversely proportional to the distance separating two such fragments:

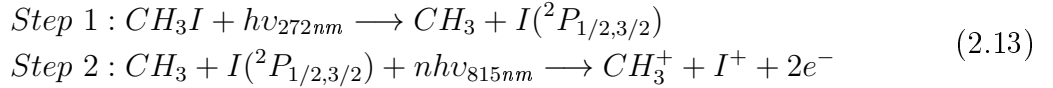
$$E_{KER} \propto \frac{k_e q_A q_B}{R_{AB}}, \quad (2.11)$$

where k_e is the Coulomb constant, q_A and q_B are the charges on the ion fragments A and B , and R_{AB} is the separation distance. From the momentum conservation law, the individual kinetic energy for each ion fragment can be expressed as:

$$E_A = \frac{m_B}{m_A + m_B} E_{KER}, E_B = \frac{m_A}{m_A + m_B} E_{KER}, \quad (2.12)$$

where m_A and m_B are the masses for two ion fragments respectively.

In order to illustrate the Coulomb-explosion feature in kinetic energy spectrum of ion, we take a pump-probe Coulomb-explosion experiment of CH_3I as the example [45]. In this experiment, the CH_3I is first photodissociated by a 272 nm, ultraviolet, pump pulse through single photon absorption. When the CH_3I starts dissociation, another 815 nm probe pulse is applied to double ionize the dissociating CH_3I after a time delay and induces Coulomb explosion. The complete dissociation process can be expressed as:



Where $I(^2P_{3/2})$ is the iodine atom in its ground spin-orbit state and $I(^2P_{1/2})$ is in the excited state. In *Step 1*, the absorption of UV photon will give an initial energy E_{UV} to the CH_3I molecule (for details, see [45]), and therefore leads to an initial relative velocity v_{rel} between two ion fragments. Hence, R_{AB} can be estimated by: $R_{AB} \sim R_{eq} + v_{rel}t$, where R_{eq} is the equilibrium separation of the charge centers in the initial undissociated molecule and t is the time delay between the pump pulse and the probe pulse. Thus, the

Equation 2.11 can be rewritten as follow:

$$E_{KER} \propto E_{UV} + \frac{k_e q_A q_B}{R_{eq} + v_{rel} t}. \quad (2.14)$$

In the experiment the momenta of CH_3^+ and I^+ are measured by a velocity-map-imaging spectrometer. Figure 2.12 shows the measured delay-dependent kinetic energy spectrum of CH_3^+ . We can see that the kinetic-energy calculation model 2.14 agrees well with the kinetic energy distributions of CH_3^+ . Hence, the kinetic energy structure indicated by the solid and dashed white curves show the Coulomb-explosion feature in a delay-dependent kinetic energy spectrum of ion.

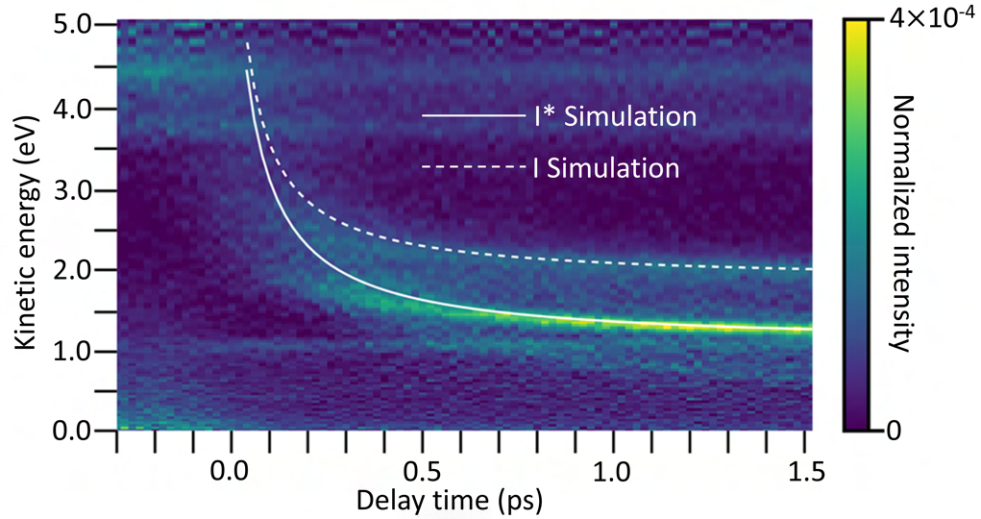


Figure 2.12: Delay-dependent kinetic energy spectrum of CH_3^+ in the pump-probe Coulomb-explosion experiment of CH_3I . The solid and dashed curves are the simulated kinetic energies of CH_3^+ by model 2.14 for two dissociation pathways which produce different iodine states: I ($^2P_{3/2}$) and I^* ($^2P_{1/2}$). Adapted from [45].

2.4 High harmonic generation

High harmonic generation (HHG) was first observed in 1988 by M. Ferray et al. [46]. It is a light-frequency conversion phenomenon in strong laser field: high-frequency photons are produced through the interaction between matter and intense, low-frequency laser pulse. Figure 2.13 illustrates the mechanism of HHG process by taking atomic ionization as the example. It can be seen that HHG originates from electron recollision. At first, the atom is ionized and an electron wavepacket is created in its continuum, which is expressed by Ψ_c in Figure 2.13(e). In the laser field, the electron wavepacket evolves and spreads. Eventually, the wavepacket is driven back and accelerated to its parent ion when the electric field changes its direction. In the final step, the returning wavepacket Ψ_c superposes with the ground state wavefunction Ψ_g . The expansion of the electron dipole moment $d_t = \langle \Psi | d | \Psi \rangle$ reveals a fast oscillation term:

$$d_h(t) = \langle \Psi_g | d | \Psi_c \rangle + c.c., \quad (2.15)$$

Where $\Psi = \Psi_g + \Psi_c$. Figure 2.14 shows the interference between the two wavefunctions Ψ_g and Ψ_c . We can see that at two adjacent moments, the electron density oscillates from one side to the other side, which induces an oscillation of dipole moment. The oscillation frequency of the dipole moment depends on the recombination energy: $\Omega(t_r) = W_r(t_r) + I_p$, where $W_r(t_r) = \mathbf{v}(t_r)^2/2$ is the kinetic energy of recolliding electron at the recollision time t_r . The higher the $\Omega(t_r)$, the faster the $d_h(t)$, and therefore the higher energy of the emitted harmonic photon [47, 48].

Figure 2.14 shows a typical HHG spectrum, which is from the ionization of neon within a 800 nm, $1.3 \times 10^{15} \text{ W/cm}^2$ laser field [49]. It can be seen that the frequency comb of HHG spectrum has a plateau structure followed by a cutoff. As shown in Equations 2.10 and 2.7, the position of harmonic cutoff is proportional to the ponderomotive energy U_p , and therefore to the peak electric field strength F^2 and the laser wavelength λ^2 .

In 2001, Pierre Agostini group first experimentally demonstrated that high harmonics corresponds to an attosecond pulse train of time domain [50]. In their experiment, both the amplitude and the phase of a harmonics were measured through two-photon, two-color photoionization. Figure 2.16 shows the reconstructed temporal intensity profile of high harmonics. It can be seen that these attosecond pulses in the train have a same duration of 250 as and are spaced by 1.35 fs which is the half cycle of the driving laser pulse ($\lambda_{laser} = 800 \text{ nm}$, $T_{cycle} \sim 2.7 \text{ fs}$). In the same year, Ferenc Krausz group produced isolated pulses of duration 650 as [51]. In their experiment, the electronic dynamics of 4p shell in krypton is traced by using attosecond soft-x-ray pulse and few-cycle visible pulse.

These works opened the window to the study of electron dynamics in atoms, molecules and matter in the condensed phase [52]. Since the first demonstration of isolated attosecond pulses and attosecond time-resolved spectroscopy, development of attosecond light sources has attracted great interests, and various methods have been proposed to generate ultra-broadband attosecond pulses [53]. So far, the shortest attosecond pulse has a duration of 43 as which was reported by Thomas Gaumnitz et al. in 2017 [54].

Besides enabling producing isolated attosecond pulses, HHG can also be utilized as a imaging tool [55]. One great examples is tomographic imaging of molecular orbitals. As shown in Equation 2.15, $d_h(t)$ is the transition dipole matrix element which describes the re-combination of returning electron to its original state. Hence, the harmonic spectrum inherently contains the information of the original wavefunction where the electron is ionized from. Measuring the harmonics spectrum in amplitude, phase, and polarization is a direct experimental determination of the Fourier components of the spatial wavefunction. In 2004 J. Itatani et al. first demonstrated tomographic imaging of the HOMO of N_2 molecule. In this work, the N_2 molecule is aligned at different angles with respect to the polarization of HHG probe pulse and the harmonic spectra from different alignment angles are measured as shown in Figure 2.17(a). In addition, the plane-wave amplitudes of the recolliding wavepacket are determined by the harmonic spectrum of argon. With these information from HHG, the HOMO of N_2 is reconstructed as shown in Figure 2.17(b). It can be seen that the reconstructed HOMO agrees well with the *ab initio* molecular calculation of Figure 2.17(c). In the past two decades the imaging techniques basing on high harmonics spectroscopy has been greatly extended for probing various atomic and molecular structures and dynamics such as tomographic imaging of complex molecule [56], electron hole dynamics in atom [57], Electronic charge transfer in molecules [58], and chemical reactions of molecules [59].

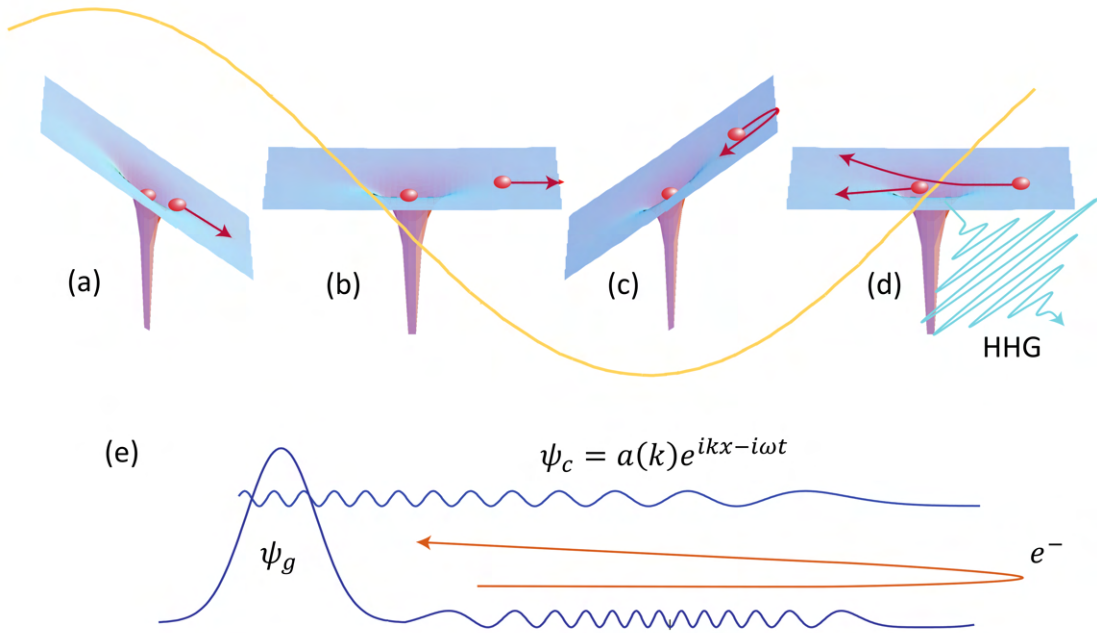


Figure 2.13: Mechanism of High harmonic generation. (a-d) Classical view of HHG by three-step model: (a) the electron is ionized (first step), (b) flies away, (c) reverses its flying direction (second step), (d) recombines with the ion and emits HHG photon (third step). (e) Same three-step process as (a-d) but with quantum view. Adapted from [47].

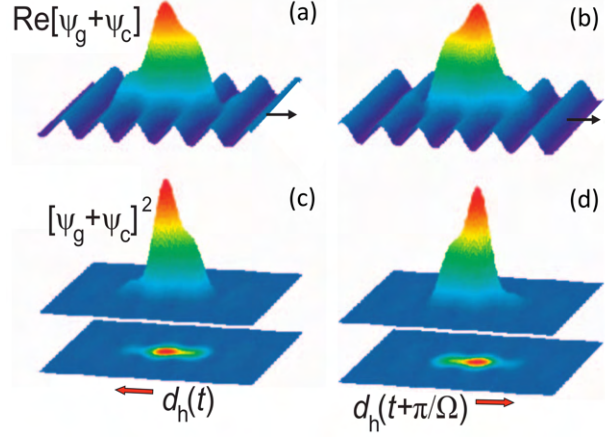


Figure 2.14: Interference of recolliding wave packet with the ground state part of the same electron wave function, at two adjacent moments of time: t for (a,c) and $t + \pi/\Omega$ for (b,d). (a,b) show the real part of total wavefunction, and (c,d) show the electron density. Adapted from [48].

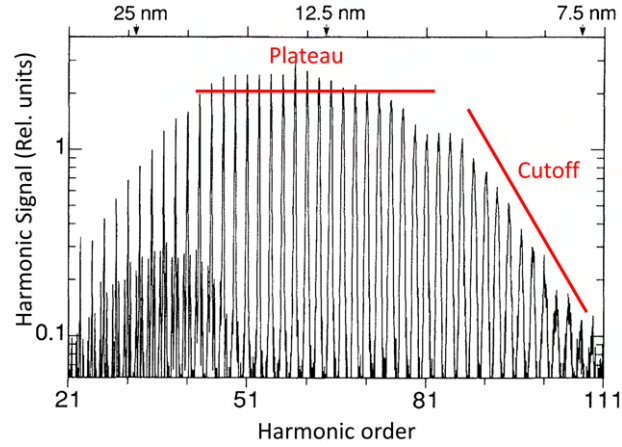


Figure 2.15: Harmonic spectrum of neon within 800 nm, $1.3 \times 10^{15} \text{ W/cm}^2$ laser field. The plateau and cutoff structure are indicated by red lines. Adapted from [49].

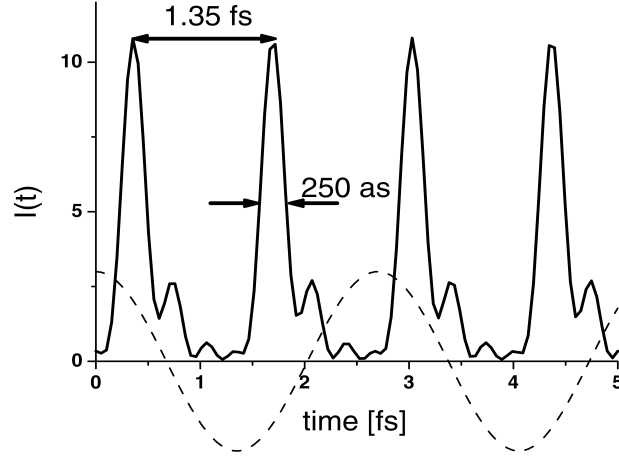


Figure 2.16: Temporal intensity profile of a sum of five harmonics from argon ionized by 800 nm, 40 fs laser pulse. Taken from [50].

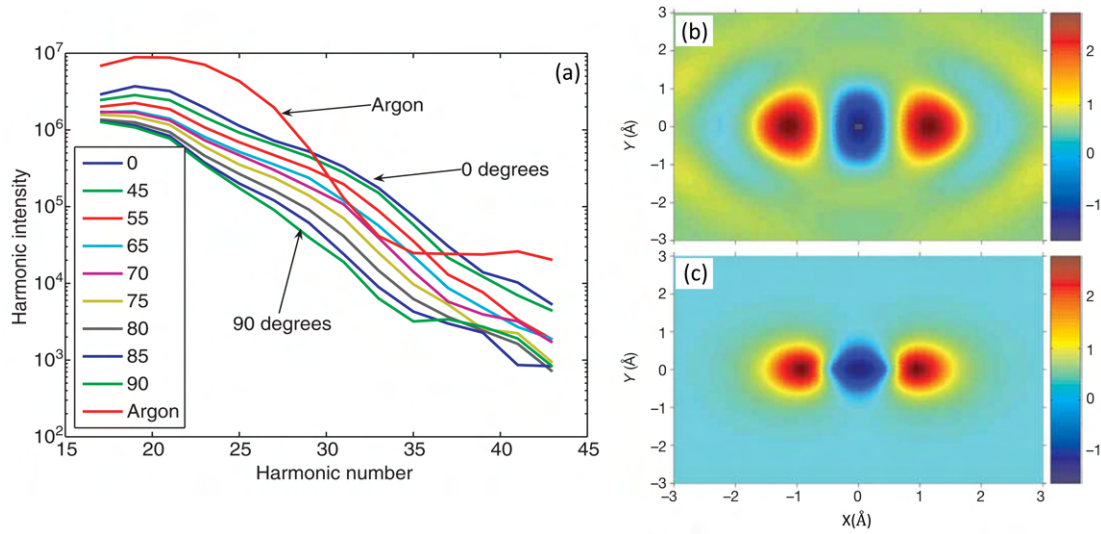


Figure 2.17: Reconstruction of N_2 HOMO by high harmonic spectra. (a) High harmonic spectra recorded for N_2 molecules at different alignment angles between 0° and 90° relative to the polarization axis of probe laser pulse. (b) Reconstructed wavefunction of the HOMO of N_2 . (c) The N_2 $2p\sigma_g$ orbital from an *abinitio* calculation. Adapted from [60].

2.5 Nonsequential double ionization

Nonsequential double ionization (NSDI) was first observed by Anne L’Huillier et al. in 1982 [61]. The observation on strong-field ionization of krypton reveals an unexpected “knee” structure in the Kr^{2+} yield as a function of the laser intensity. The later studies show that the “knee” structure of doubly-charged ion yield exists for all inert-gas atoms from xenon to helium [62–66]. Figure 2.18(a) shows the He ion yield curves reported in [64]. The solid curves are the simulation results by solving time dependent *Schrödinger* equation (TDSE) with the single-active-electron (SAE) approximation [67]. We can see that, around the intensity of $1 \times 10^{15} W/cm^2$, the observed He^{2+} yield is several orders higher than that of the simulation! This means the SAE approximation fails to describe double ionization in the strong field! On the other hand, the recollision model with the consideration of electron-ion interaction successfully reproduces the “knee” structure in He^{2+} yield curve [18] which is shown in Figure 2.18(b). Hence, the NSDI can be interpreted as a recollision induced process: when the first ionized electron is driven back to the parent ion by the laser field it can transfer its kinetic energy to the ion and lead to the ionization of the ion core, if the recolliding energy is higher than the second ionization potential of atom.

The success of the recollision model implies that the electron-electron correlation plays a key role in the NSDI process, since the energy transfer between recolliding electron and ion occurs on the level of electron-electron interaction. In 2000, Th. Weber et al. reported a striking evidence of electron-electron correlation in NSDI [68]. In this work, the momenta of two ionized electrons from argon are both measured by a COLTRIMS spectrometer. Figure 2.19(a,b) show the correlated electron momentum distributions for two different intensities. We can see that for the intensity of $3.8 \times 10^{14} W/cm^2$ the electron pairs mainly distribute in the first and the third quadrants, which means the two electrons from NSDI are highly correlated and tend to emit in the same direction. However, for the high intensity case of $15 \times 10^{14} W/cm^2$, the correlated electrons distribution is a uniform spot at the origin, which means the two electrons are ionized sequentially and therefore are less correlated.

An important progress for electron-electron correlation is the discovery of finger-like structure in the correlated electron momentum distribution. In 2007 A. Staudte (my supervisor) et al. first reported the experimental observation of finger-like structure in the double ionization of helium [69]. Figure 2.19(c,d) show the correlated electron momentum distribution from this experiment. It can be seen that two finger-like structures (indicated by yellow dots in Figure 2.19) appear in the first and third quadrants. The theoretical simulations reveal that this finger-like structure originates from the recoil collision between two electrons [17, 69]: when the first ionized electron recollide with a second electron in

the ion core, one electron will be strongly back scattered near the ion core.

Theoretical studies have significantly expanded our comprehension of electron-electron correlation within non-sequential double ionization and have provided valuable insights into the intricacies of recollision phenomena. For a more comprehensive overview of these advancements, one may refer to the comprehensive review by Wilhelm Becker et al. in 2012 [62].

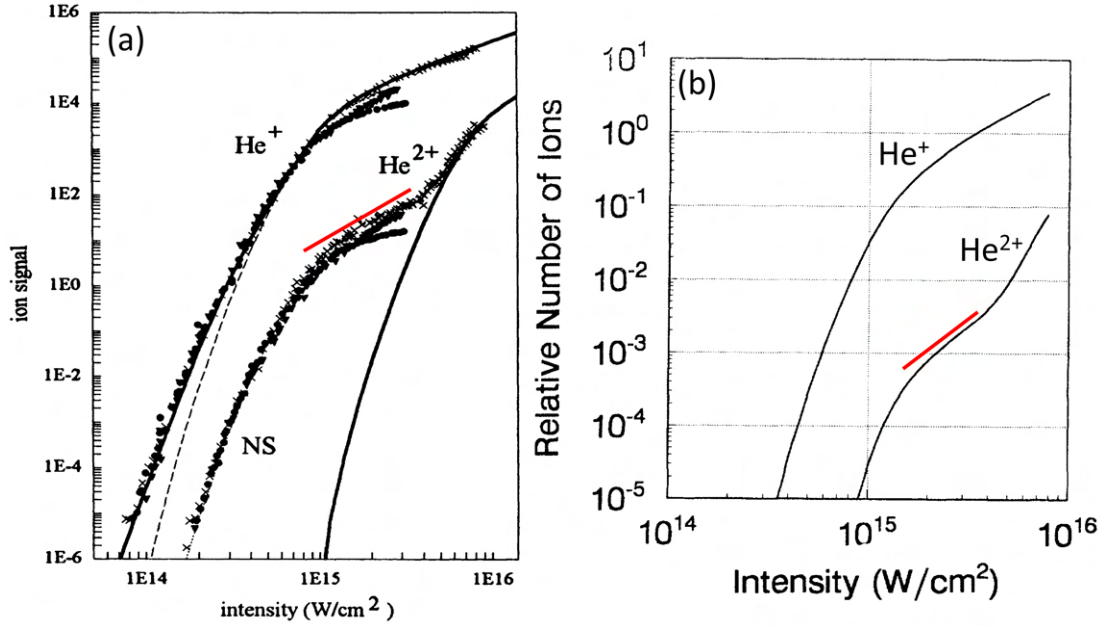


Figure 2.18: (a) Measured *He* ion yields for linear polarized, 100 *fs*, 780 *nm* light. The red line indicates the knee structure. Calculations are shown as solid (SAE-TDSE) and dashed (ADK) lines. (b) Calculations considering the recollision and electron-ion interaction. The red line indicates a similar knee structure with (a). Adapted from [64] and [18].

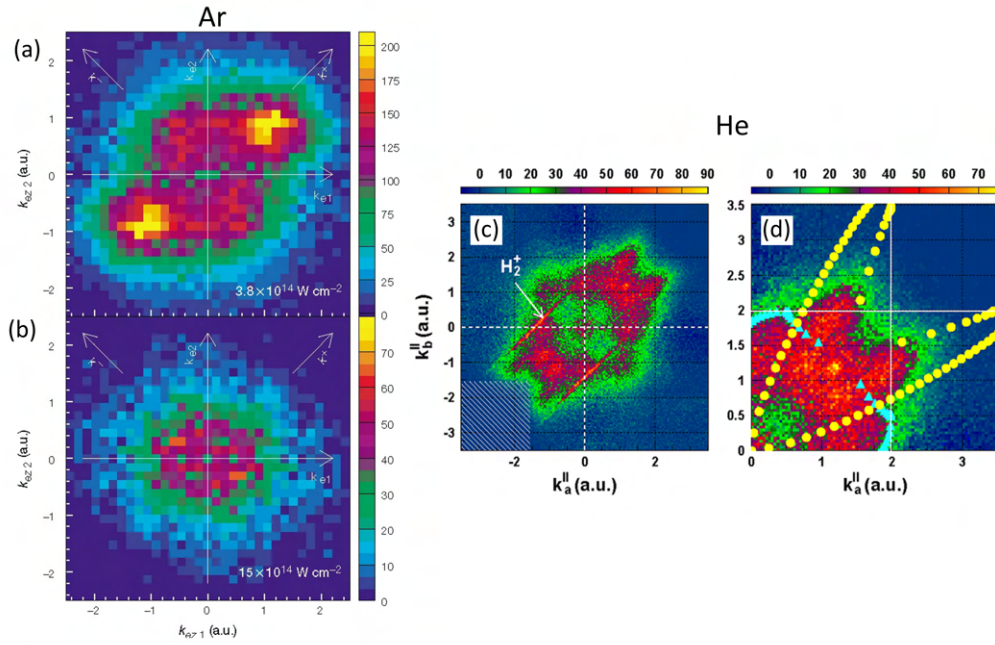


Figure 2.19: Correlated electron momentum distributions from argon under the low intensity (a) $3.8 \times 10^{14} \text{ W/cm}^2$ and the high intensity (b) $15 \times 10^{14} \text{ W/cm}^2$. (c) Correlated electron momentum distribution from helium. (d) Same as (c), only first quadrant is shown. Adapted from [68] and [69].

2.6 Recollision induced dissociation

The excitation energy for dissociation can also come from the recolliding electron driven by the strong field [70–72]. Figure 2.20 illustrates the dissociation of H_2^+ excited by the recollision in an intense laser field. After tunnel ionization of H_2 in the first step, the electron will oscillate in the laser field. The free electron can recollide with the H_2^+ , and, through inelastic scattering, excite a part of the nuclear wave packet from the $1s\sigma_g$ PES will be excited to the upper dissociative $2p\sigma_u$ PES which leads to dissociation. In this process, the later coupling between the two states through photon absorption at the tail end of the pulse can further enhance this dissociation channel [71]. In comparison to the no-recollision case, Rrecollision will lead to a broader and higher kinetic energy distribution of the ion fragment as shown in Figure 2.20(b). The dissociation higher energy is a direct consequence of the sub-optical cycle nature of recollision which necessarily projects the ground state vibrational wavepacket onto the steeper part of the dissociative $2p\sigma_u$.

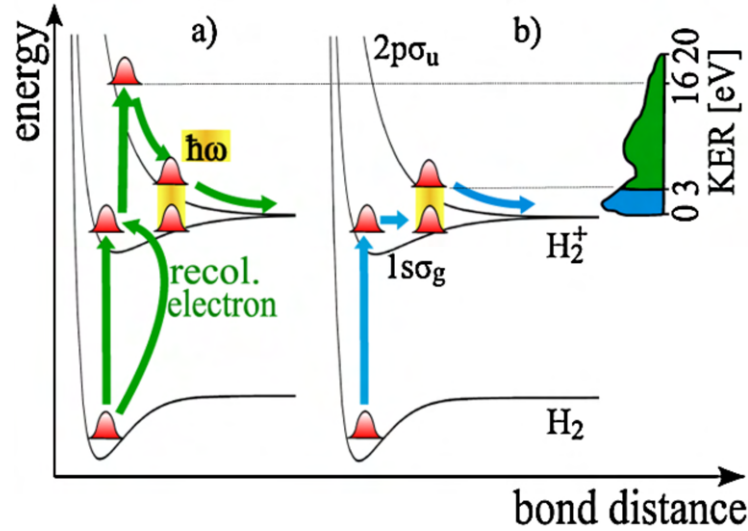


Figure 2.20: Illustration for dissociation of H_2^+ (a) with and (b) without a recolliding electron. The yellow shaded area is the region, where the laser can resonantly couple the two ionic states. Taken from [71].

2.7 Property of Br and Br_2

While Br_2 is, on one hand, a very simple molecule, because it consists of only two identical atoms and therefore lacks many degrees of freedom of more complex molecules. On the other hand, Br_2 is already quite challenging for theory to accurately calculate all possible electronic states, because of the number of electrons and the importance of relativistic effects. In this section we introduce the fundamental properties and electronic configurations of the molecule.

Elemental bromine exhibits two stable isotopes, namely ^{79}Br and ^{81}Br , with respective abundances of 50.686% and 49.314% [73]. Each bromine atom possesses 35 electrons, forming the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. Upon the formation of a Br_2 molecule by two bromine atoms, the $4p$ valence electrons contribute to molecular bonding, resulting in a ground X state with the electronic configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(2\sigma_u^*)^0$ [74].

Upon absorbing a photon with a wavelength of 400nm, Br_2 undergoes a transition in which a $1\pi_g$ electron is elevated to the $2\sigma_u$ orbital. This process enhances the repulsion force between the two atoms, leading to molecular dissociation. The resulting neutral dissociative state possesses an electronic configuration of $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^3(2\sigma_u^*)^1$ and corresponds to the C state $^1\Pi_u(1_u)$ of Br_2 . Figure 2.21 illustrates the simplified molecular orbital diagrams for the two neutral states of Br_2 .

Figure 2.22(a) displays the potential energy surfaces (PESs) of Br_2 . Notably, these PESs exhibit three distinct asymptotic energies due to the spin-orbit splitting in each Br atom, determined by different combinations of Br spin-orbit states. In Figure 2.22(b), the four lowest molecular states are depicted, namely $X^1\Sigma_g^+$, $^3\Pi_u(1_u)$, $^3\Pi_u(0_u^+)$, and $^1\Pi_u(1_u)$, with the last three states commonly referred to as the "A," "B," and "C" states, respectively [75]. Additionally, Figure 2.23 showcases the PESs of certain low-lying states of Br_2^+ .

The frequency dependence of the single photon transition to the C state has been measured by Martin J. Cooper et al. [76] and exhibits a characteristic absorption spectrum which is shown in Figure 2.24(a). The experiment shows that the A and B states are also accessible in a single photon absorption in a wavelength range of 450–600 nm, whereas the C state has an absorption maximum at around 410 nm. In our experiment, the pump light obtained by frequency-doubling our 800nm laser pulse has a center-wavelength of 400nm and the 5.5nm bandwidth [77], which perfectly falls into the absorption spectrum of the C state.

Due to the Π_u character of the C-state the photoexcitation from the Σ_g ground state

occurs for a light polarization perpendicular to the molecular axis. The earlier study by Cooper et al., using a time-of-flight mass spectrometer, first reveals this perpendicular transition feature by examining the velocity distribution of Br^+ from a pump-probe experiment [76]. In that experiment, the neutral Br atoms from Br_2 photolysis were ionized via three-photon ionization at 260 nm (4.5 eV) using a ultraviolet laser pulse. Figure 2.24(b,c) shows the velocity distribution of Br fragments. It can be seen that the ground state Br atoms from the C state dissociation are emitted along the perpendicular direction of the laser polarization. Moreover, we can see that even at 460 nm , when C and B state have similar cross sections according to Figure 2.24(a), they can be distinguished due to the dissociation energy and more importantly, the angular distribution.

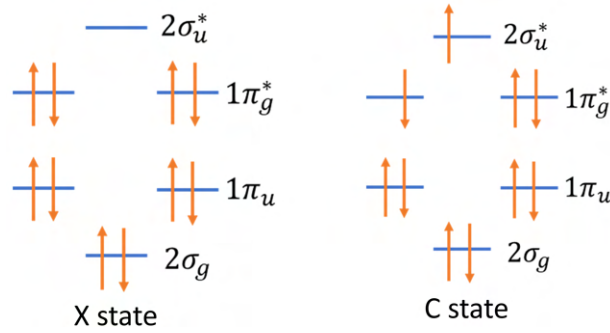


Figure 2.21: Simplified molecular orbital diagrams of the ground X state and dissociative C state of Br_2 .

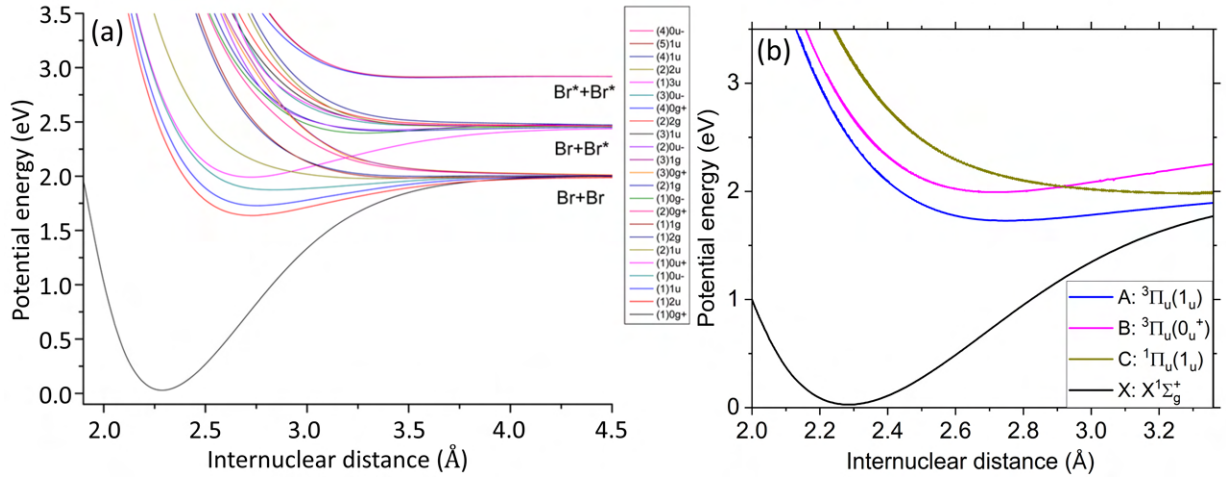


Figure 2.22: (a) Potential energy surfaces of Br_2 . Br and Br^* denote the $^2P_{3/2}$ and the $^2P_{1/2}$ atomic states respectively. (b) Magnification of (a) for presenting the states: ground state ($X^1\Sigma_g^+$), A state ($^3\Pi_u(1_u)$), B state ($^3\Pi_u(0_u^+)$), and C state ($^1\Pi_u(1_u)$). Adapted from [75].

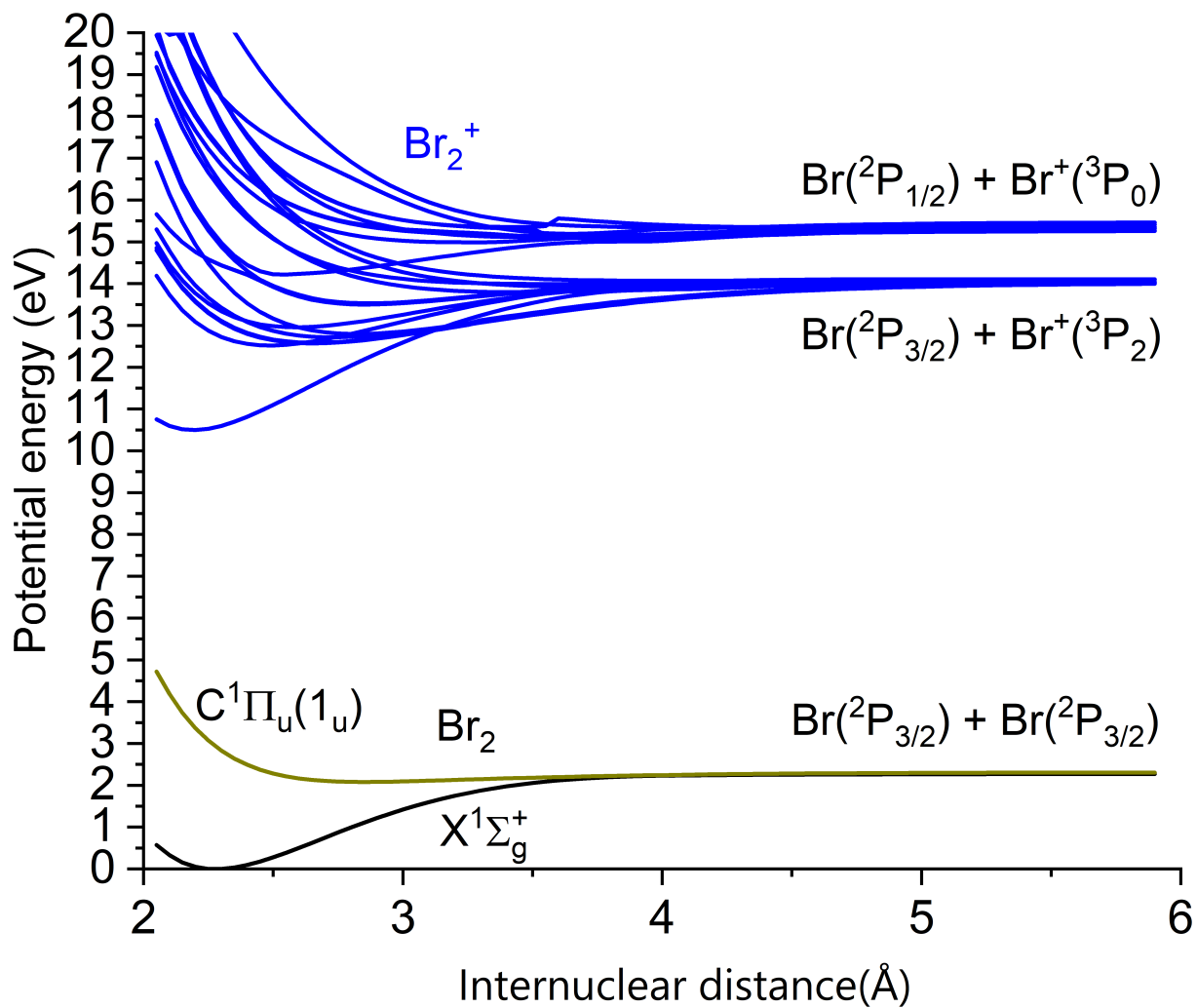


Figure 2.23: Potential energy surfaces of Br_2^+ . The ground state and C state of Br_2 are also presented. These are computed using CASPT2 with a large CAS active space, a relativistic VQZ ANO basis set and includes scalar relativistic corrections [78].

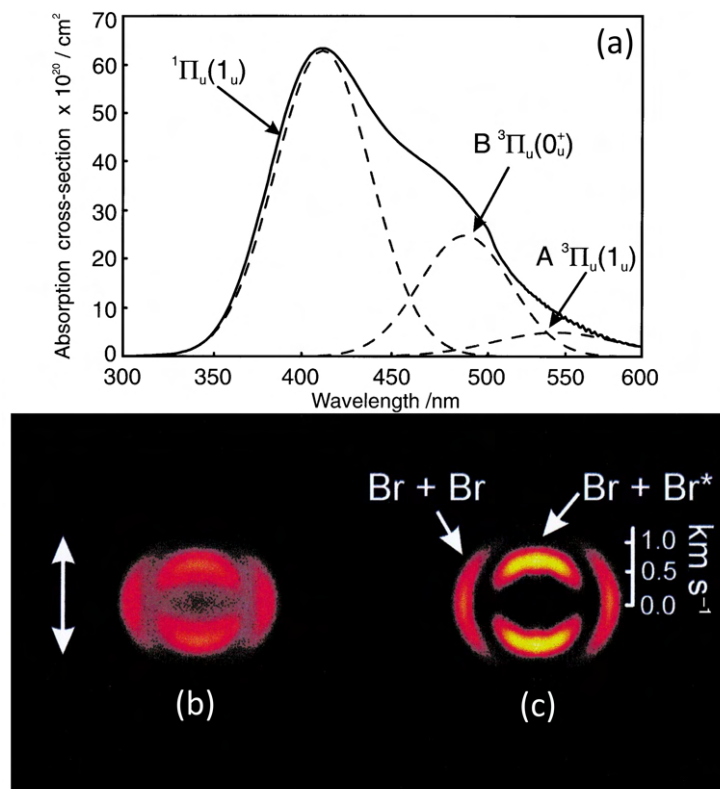


Figure 2.24: (a) Electronic absorption spectrum of Br_2 recorded over the wavelength range: 300 – 600 nm. The solid curve shows the total absorption spectrum from all contributions of three excitation states, while the dashed curves show the each contribution. Measured velocity distributions of Br fragments from 460 nm photolysis of Br_2 : (b) original 2D projection, (c) reconstructed 2D slice. The white arrow indicates the direction of laser polarization. In (b), two velocity sub-groups are indicated, which correspond to the formations of $Br + Br$ (outer ring) and $Br + Br^*$ (inner ring). The Br_2 molecules were unaligned with respect to the laser polarization. Hence, at 460 nm both absorption pathways to the C and B state were accessible. Adapted from [76].

2.8 Time-resolved dissociation of bromine molecule

The bromine molecule has been used as a prototype of studying chemical reaction since at least 1998. Various imaging methods with pump-probe experiment scheme have been utilized to follow the time evolutions of different physical observables during Br_2 's neutral dissociation process [59, 74, 79, 80]. So far, basing on different observables, these methods can be classified as three types: photoelectron energy spectroscopy, HHG spectroscopy, and ion kinetic energy spectroscopy.

2.8.1 Time-resolved dissociation of bromine molecule using photoelectron spectroscopy

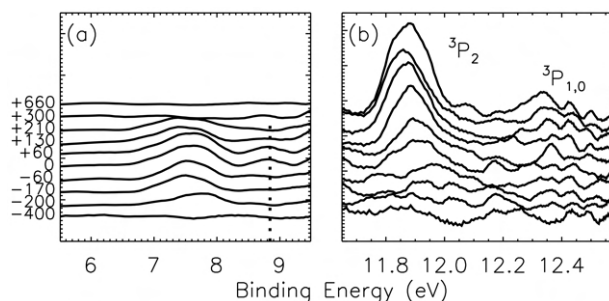
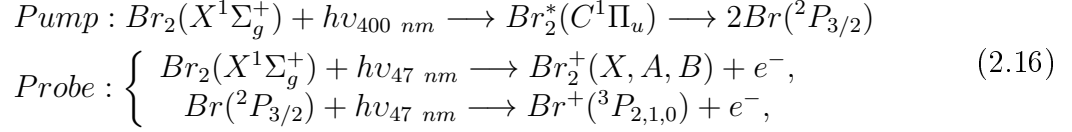


Figure 2.25: Electron binding energy versus delay time for a pump-probe experiment, where the pump is a 400nm, ultraviolet pulse and the probe is a 47nm, x-ray pulse. The binding energy is defined by $h\nu_{47nm} - E_{kin}$ where E_{kin} is measured electron energy. The delay time between two pulses are labeled by numbers in femtosecond on the vertical axis. In (b), the two binding energy peaks of Br 's two spin-orbit states: 3P_2 and $^3P_{1,0}$ appear at positive delay range. Taken and adapted from [79]

The first attempt to follow this reaction process was demonstrated in 2001 by measuring the photoelectron energy in a UV-pump x-ray-probe experiment [79, 81]. In this experiment, excited Br_2 molecules are prepared in the C state with 80 fs, 400 nm pulses, and a series of photoelectron spectra are obtained during dissociation with pulses of soft x-ray light (47 nm, 26.4 eV, 250 fs). The excitation scheme of the experiment is outlined

as follow:



Where $Br_2^+(X, A, B)$ are the ionic states prepared from the ground Br_2 . Here, we should note that there exists a spin rearrangement in Br^+ during the ionization of Br by 47 nm pulse, which leads to the detection of triplet state Br^+ .

Figure 2.25 illustrates the time-dependent binding energy spectrum. In Figure 2.25(b), as the delay time increases, two atomic energy peaks ($^3P_2, ^3P_{1,0}$) become evident. These peaks correspond to the established binding energies of the bare Br atom in the states $^3P_{2,1,0}$ [82], indicating the detection of dissociation product Br atoms. A subsequent investigation [83] significantly enhanced energy and time resolution, as depicted in Figure 2.26. The improved resolution reveals additional atomic states of Br , and all distribution branches converge to corresponding atomic states from various molecular states. The high resolution enables the resolution of ionic states $X' - S'$ originating from pump-excited Br_2 . These findings suggest that the time scale of C-state dissociation falls within the range of 40 – 85 fs.

2.8.2 Time-resolved dissociation of bromine molecule using HHG spectroscopy

In 2010, H. J. Worner et al pioneered the application of high-harmonic generation (HHG) spectroscopy to track the neutral dissociation of Br_2 [59]. Figure 2.27(a) illustrates their experimental approach, where a transient grating is formed through the interference of two 400 nm pump pulses. This grating consists of alternating horizontal planes of excited and unexcited Br_2 molecules. Subsequently, a powerful 800 nm probe pulse is employed to ionize these molecules, generating HHG from the two distinct groups of Br_2 molecules. The resulting high harmonics, characterized by different phases, interfere with each other, producing grating-diffraction patterns as depicted in the inset of Figure 2.27.

The grating formed by molecular excitation yields zero- and first-order diffraction, allowing for the extraction of the relative harmonic amplitude d_e/d_g and phase difference $|\phi_e - \phi_g|$ between harmonics originating from excited (e) and ground (g) state molecules. Control over the polarization of both the pump and probe pulses is a key aspect of this experiment. Given that the C state excitation involves a perpendicular transition, the

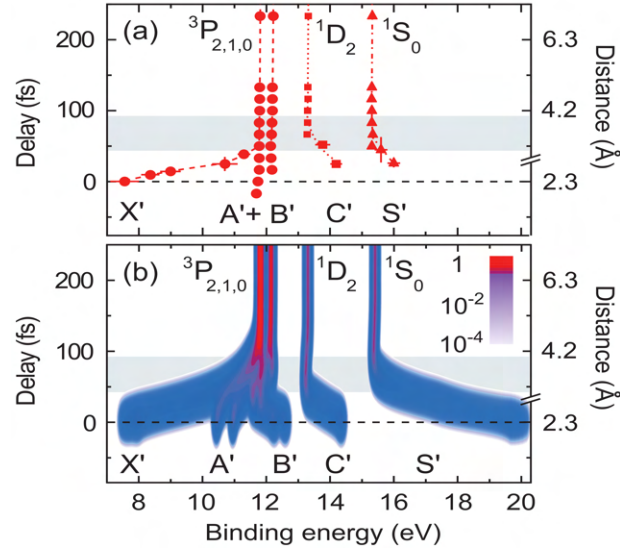


Figure 2.26: Electron's binding energy versus delay time spectrum in the UV-pump-x-ray-probe experiment for Br_2 neutral dissociation in [83]. (a) is the measured valence-electron binding energies versus delay and distance from the excited molecule (X'-S'), through a transition region (gray box) to the free atoms ($^3P_{2,1,0}$, 1D_2 , 1S_0). (b) Calculated time-dependent binding energies and photoelectron intensities. Taken from [83].

alignment between the dissociation direction and the probe polarization can be manipulated by adjusting the polarizations of the pump and probe pulses. In Figure 2.27(b), the two pulses are parallel, causing the probe pulse to be perpendicular to the dissociation. In contrast, in Figure 2.27(c), the two pulses are perpendicular, resulting in the probe pulse being parallel to the dissociation. For the unexcited Br_2 in the transient grating the molecular alignment is random, and therefore there is no relative alignment control between the molecule and the probe pulse. The delay-dependent amplitude and phase curves for two cases are shown.

The rapid phase variation observed within the initial 150 fs provides insight into the evolving electronic structure of the molecule during the dissociation process. As the delay increases, the phase eventually stabilizes at an asymptotic level around 1.8 rad. By employing the relationship $\Delta\phi_q \approx \Delta I_p \bar{\tau}_q$, where $\bar{\tau}_q$ represents the electron excursion time of recollision obtained from a classical calculation [18], the difference in ionization potential (ΔI_p) is estimated to be approximately 1.3 eV. This estimation aligns well with the known ionization potentials of Br_2 and Br . Consequently, the phase of high harmonic generation

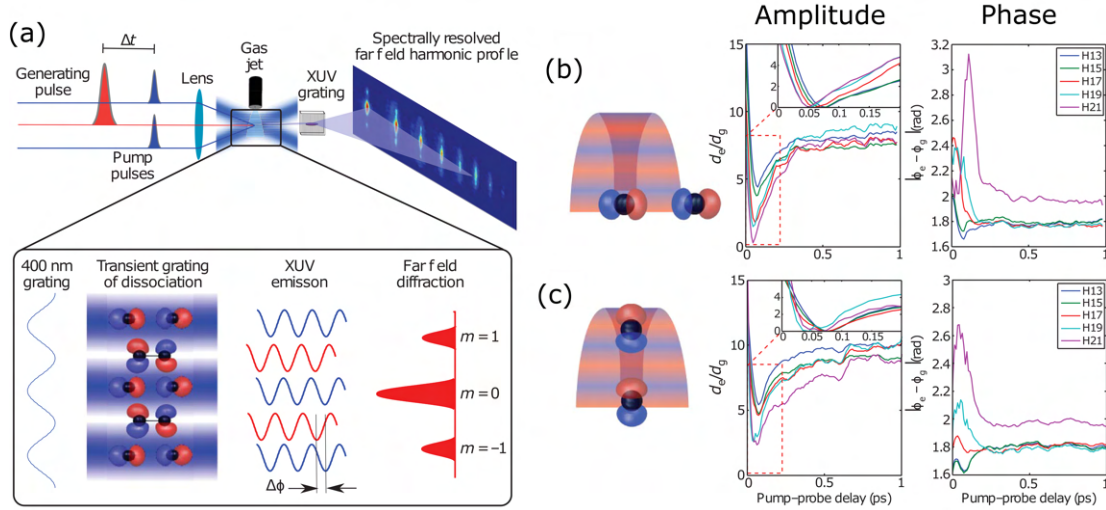


Figure 2.27: (a) Schematic of experiment for high-harmonic transient grating spectroscopy. Two synchronized 400nm pump pulses set up a transient grating of excitation in the molecular beam. A delayed 800nm probe pulse generates high harmonics from the excited sample. (b,c) high-harmonics amplitudes and phases of different-order harmonics for (b) perpendicular molecular alignment and (c) parallel molecular alignment relative to the polarization of probe pulse. Taken from [59].

(HHG) proves to be a valuable tool for tracking the transition in electronic structure from molecule to atom.

For the temporal evolution of the amplitude, a deep minimum appears for all harmonics around 51 fs. This minimum comes from the destructive interference between electron wave packet and the initial state wavefunction of molecule during recollision process. This destructive interference depends on the separation distance of two nuclei in Br_2 . Thus, the instantaneous bondlength of the stretching molecule is encoded with subcycle resolution in the amplitude of the high harmonic radiation.

The analysis of HHG phase and amplitude allows us to explore the time scale of Br_2 dissociation from two perspectives. If we define the conclusion of dissociation as the point when the structural transformation is complete, the HHG phase evolution indicates a dissociation time scale of approximately 150fs. This is evident as it directly captures the ionization potential of both the reactant Br_2 and the product Br . On the other hand, if we consider the conclusion of dissociation as the point where the two Br atoms no longer contribute to destructive interference with the recolliding electron, the HHG

amplitude indicates a more extended time scale exceeding 300 fs . We should note that both estimations on the dissociation time scale exceed that in [79,83].

2.8.3 Time-resolved dissociation of bromine molecule using ion spectroscopy

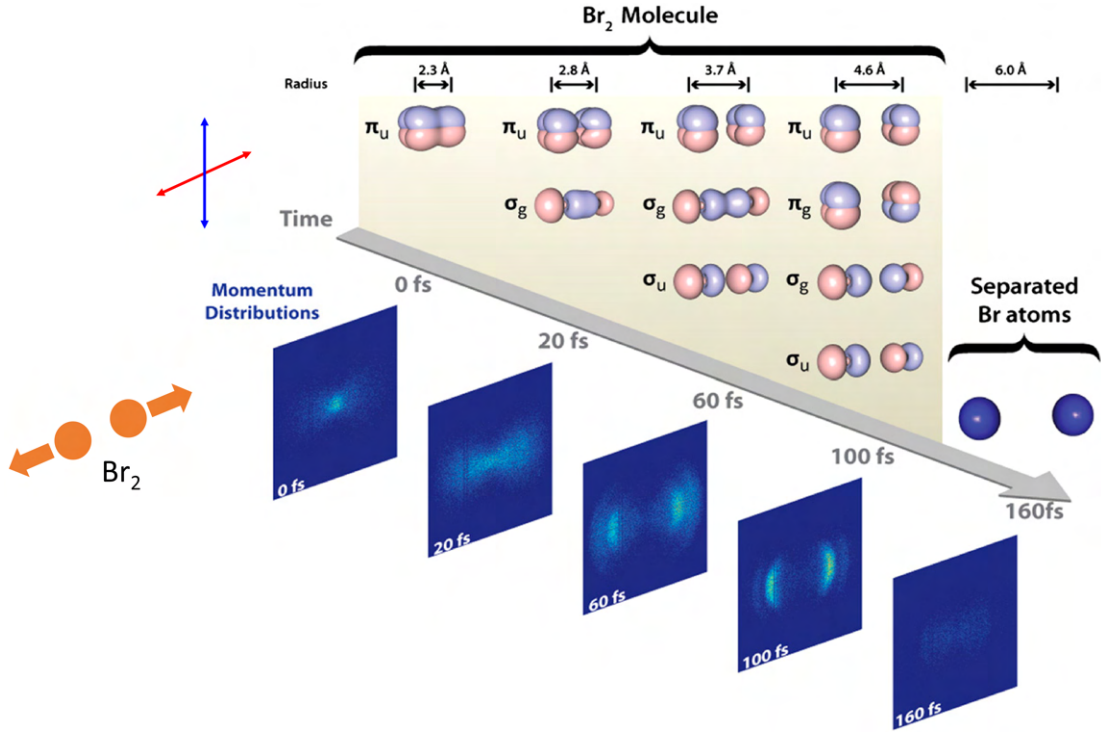
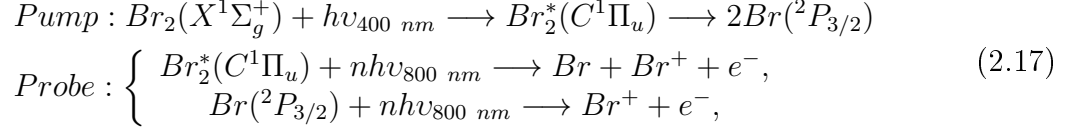


Figure 2.28: (upper panel) Molecular orbital evolution in neutral dissociation. (lower panel) delay-dependent Br^+ momentum distributions. The perpendicular polarization configuration of the two pulses are indicated by red and blue arrows. Taken and adapted from [74].

Besides photoelectron and high-harmonic generation (HHG) spectroscopy, the photoion can also function as suitable observables for visualizing the neutral dissociation of Br_2 . The initial exploration of the neutral dissociation of Br_2 through ion observation was carried out by Wen Li et al. in 2010 [74]. In this experiment, a pump-probe scheme is

implemented as follows:



In this setup, the time-delayed probe pulse ($\sim 4 \times 10^{13} \text{ W/cm}^2$, $\sim 30 \text{ fs}$) features a polarization perpendicular to that of the pump pulse ($\sim 2 \times 10^{11} \text{ W/cm}^2$, $\sim 40 \text{ fs}$). The momentum distribution of Br^+ , dependent on the delay, is measured using a COLTRIMS apparatus.

The fundamental understanding of the neutral dissociation process revolves around the participation of all valence orbitals within Br_2 in the dynamic process, as illustrated in Figure 2.28. When the probing pulse ionizes the dissociating Br_2^+ , it grants access to various molecular orbitals, resulting in the generation of wave packets along the potential energy surface associated with different Br_2^+ states. This, in conjunction with the kinetic energy accumulated in the C-state, gives rise to distinct KER profiles for the produced Br^+ ions.

For instance, at shorter time delays, the $2\sigma_g$ orbital remains unaltered, and the ionization of the $1\pi_g$ and $2\sigma_u$ orbitals only leads to the formation of bound ionic states. Consequently, the dissociation of Br_2 and the subsequent creation of Br^+ ions can solely occur through the ionization of the $1\pi_u$ orbital, resulting in low KER. These Br^+ ions with low KER are concentrated around the center in the Br^+ momentum distribution, as depicted in Figure 2.28.

As the dissociation process advances, Br_2^* acquires more kinetic energy on the PES of the C-state, allowing for the opening of dissociation channels involving the $2\sigma_u$ and $2\sigma_g$ orbitals. This, in turn, results in high KER Br^+ ions. In the Br^+ momentum distribution, this phenomenon is observed as a spreading momentum distribution in the dissociation direction as the time delay increases. Figure 2.29 presents an experimental representation of the Br^+ KER as a function of time delay, accompanied by a simulation result.

The simulation indicates that the KER spectrum reflects the evolving contributions from various molecular orbitals during the dissociation dynamics. This observation holds significance since all 10 valence electrons are implicated in these molecular orbitals, suggesting that the rearrangement of multiple electrons has been observed in the neutral dissociation process of Br_2 .

In 2013, another study employed the same pump-probe scheme to investigate the neutral dissociation of Br_2 [80]. In this experimental setup, both the 400 nm pump (with an intensity of approximately $1 \times 10^{12} \text{ W/cm}^2$ and a duration of over 100 fs) and the 800 nm

probe (with an intensity of approximately $5 \times 10^{13} \text{W/cm}^2$ and a duration of 100 fs) share a perpendicular polarization configuration, akin to the 2010 Br_2 experiment. However, it is worth noting that the time delay range between these two pulses is considerably longer in the more recent experiment, spanning over 2 picoseconds.

Figure 2.30 displays the KER spectrum of Br^+ ions as a function of the time delay. It is evident that, for the single ionization channel, the KER distribution exhibits a time-dependent characteristic, forming an elongated tail structure that persists for at least 2 picoseconds. This prolonged tail associated with the KER peak, which locates at approximately 1 eV , stands in contrast to previous observations of Li et al. data from 2010 [74]. In addition to the dominant low energy peak, Figure 2.30(b) also shows a high energy Br^+ channel whose KER decreases inversely with the delay time. This channel represents a Coulomb explosion process. The Coulomb explosion measures the increasing of interatomic distance between two Br atoms during the dissociation.

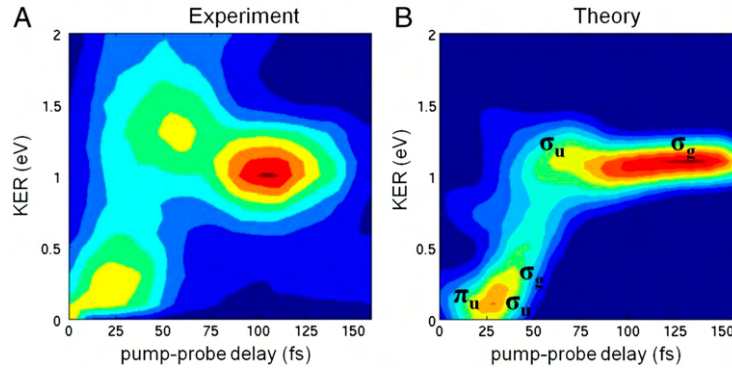


Figure 2.29: Experimental (A) and simulated (B) KER versus delay time spectra of Br^+ . At short time delays, Br^+ ions are generated predominantly by ionizing the $1\pi_u$ orbital of the molecule. After dissociating for 20 fs, the atoms have gained enough energy, hence, additional ionization channels of $2\sigma_g$ and $2\sigma_u$ orbitals are opened. Taken from [74].

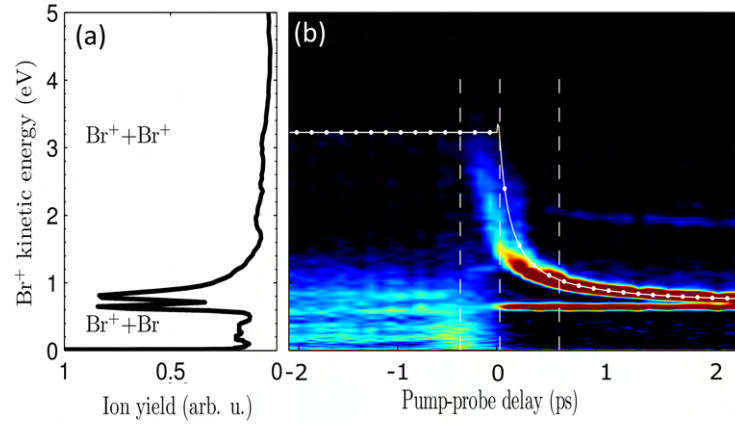


Figure 2.30: (a) Br^+ KER distribution of 2013 Br_2 experiment by integrating over time delay. The high-KER part and the low-KER part correspond to the double-ionization channel $\text{Br}^+ + \text{Br}^+$ and the single-ionization channel $\text{Br}^+ + \text{Br}$ respectively. (b) The delay-dependent KER spectrum of Br^+ in this experiment. The white interconnected dots show the ion energies predicted by a classical model. Taken and adapted from [80].

Chapter 3

Disentangling Intracycle Interferences in Photoelectron Momentum Distributions Using Orthogonal Two-Color Laser Fields

As discussed in Chapter 2, intracycle interference between electron trajectories is complex and can give rise to various characteristic structures in the photoelectron spectrum. Some of them are easy to observe in experiments, such as the fringes from strong-field photoelectron holography and the fan-like interference structures in the low momentum range. However, the temporal double-slit interference fringes are hard to observe in a single-pulse experiment, since they are always overwhelmed by the former two structures. In 2015, Richter et al [37] isolated the temporal double slit interferences by employing a orthogonally polarized two-color (OTC) laser pulse. In their experiment the authors perturbed the strong, linearly polarized 800 nm laser pulse with a weaker, orthogonally polarized, 400 nm laser pulse with about 1/10 of the intensity. The perturbing 400 nm field separates electron trajectories from neighboring half cycles in momentum space. By the fine control of the phase between the two laser pulses, the interferences is resolved for different quarter optical cycles.

In 2016, we collaborated with Markus Kitzler's team at the Technical University in Vienna. The project focused on their experimental measurement of photoelectron momentum spectra resulting from above-threshold ionization of argon using an OTC pulse. Notably, the OTC pulse employed had an unconventional feature: an inverted intensity

ratio, wherein the 400 nm pulse exhibited greater intensity than the 800 nm pulse, that is, an intensity ratio of 10 to 1 for 400 *nm* and 800 *nm*, respectively.

Upon analyzing the data, I discovered that this inverted ratio of field strengths offered a unique advantage: it enabled the isolation of interference patterns stemming from non-adjacent quarter cycles. Subsequently, in 2017, we published a paper (provided below) detailing these findings. In our research, we devised a photoelectron analysis method centered on the angularly resolved photoelectron energy, allowing us to separate the interference fringes originating from two non-adjacent quarter cycles.

Disentangling Intracycle Interferences in Photoelectron Momentum Distributions Using Orthogonal Two-Color Laser Fields

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We use orthogonally polarized two-color (OTC) laser pulses to separate quantum paths in the multiphoton ionization of Ar atoms. Our OTC pulses consist of 400 and 800 nm light at a relative intensity ratio of 10:1. We find a hitherto unobserved interference in the photoelectron momentum distribution, which exhibits a strong dependence on the relative phase of the OTC pulse. Analysis of model calculations reveals that the interference is caused by quantum pathways from nonadjacent quarter cycles.

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The momentum distributions of photoelectrons emitted during the interaction of intense laser pulses with atoms and molecules contain a wealth of information about the structure and field-induced attosecond dynamics in the target. This information can often be extracted by analyzing them in terms of semiclassical electron trajectories [1]. Within this semiclassical framework, the measured distributions can be understood as interferences of electron wave packets that reach the detector on direct or recolliding trajectories, giving rise to intercycle and intracycle fringes [2,3], holographic structures [4,5], and diffraction patterns [6–10]. Here, we use tailored laser fields, specifically orthogonally polarized two-color (OTC) fields [11], to gain control over the creation of interference structures in photoelectron momentum distributions. This permits us to experimentally disentangle a novel class of interference fringes from the many other structures in the measured distributions.

Interferences based purely on diffracting recolliding trajectories have been shown to provide structural information about the molecule with femtosecond temporal resolution [9,10,12]. On the other hand, interference fringes in the photoelectron spectrum arising from both direct and recolliding trajectories can be inverted to yield valence electron dynamics with attosecond resolution [3,5]. Two types of direct trajectories need to be distinguished for such an inversion: those launched with a periodicity of exactly one laser cycle giving rise to intercycle fringes, also referred to as above-threshold ionization peaks [13,14], and trajectories that originate from a single laser cycle, leading to intracycle interference fringes [2,3,15]. The resulting modulation of the intercycle peaks by the intracycle fringes can be interpreted as the diffraction of the emitted wave packets on a temporal grating [2]. Thus far, only intracycle fringes that originate from electron wave

packets emitted during adjacent quarter cycles of the optical wave—a situation that has been called the temporal double slit—have been considered theoretically [2,16–18] and observed in experiments [3,15,19,20].

In our experiment, OTC fields [11,21,22] are used for the generation of a tailored temporal grating for wave packet emission, which allows us to create and observe for the first time intracycle interferences from nonadjacent quarter cycles. The key to this achievement is the generation of an OTC field where the weak streaking component has half the frequency of the strong ionizing field component. Depending on the phase delay between the two colors, the two-dimensional character of the OTC fields maps the subcycle wave packet emission times into different regions of the momentum space. This solves the notorious problem of disentangling the different types of interference structures from measured photoelectron momentum distributions and allows the clear observation of the intracycle fringes from nonadjacent quarter cycles.

Disentanglement of different quantum paths using the two-dimensional mapping provided by OTC fields has been considered before [20,23–26]. Previously employed OTC pulses were generated by temporally overlapping an intense 800 nm pulse with a perpendicularly polarized 400 nm pulse of approximately equal [23,27–29] or weaker [30,31] peak intensity. In contrast, we invert the intensity ratio between long and short wavelength and use an intensity ratio of approximately 10:1 for 400 and 800 nm, respectively. Whereas multiphoton ionization in OTC pulses with a half-frequency streaking field has been investigated theoretically [32], our work explores this concept for the first time in an experiment.

In the experiment, OTC pulses were generated by combining *s*-polarized, 45 fs, 800 nm laser pulses, with

p -polarized, 45 fs, 400 nm pulses, in a collinear geometry at a repetition rate of 5 kHz, as described in Refs. [23,27]. The peak intensity in the isolated 800 and 400 nm pulses was estimated (uncertainty about 30%) as 0.2×10^{14} and 2×10^{14} W/cm², respectively. We used cold target recoil ion momentum spectroscopy (COLTRIMS) [33] to record the three-dimensional photoelectron momentum distribution of the single ionization of argon. Our COLTRIMS setup was described in detail previously [3,23,27]. In short, electrons and ions created in the laser focus were guided by weak uniform electric (1.54 V/cm) and magnetic (15.3 G) fields onto two multihit position- and time-sensitive detectors.

We define the field of the OTC pulse as [23]

$$\mathbf{E}(t) = \hat{E}_x f_x(t) \cos(\omega t) \mathbf{e}_x + \hat{E}_z f_z(t) \cos(2\omega t + \varphi) \mathbf{e}_z \quad (1)$$

with $\hat{E}_{x,z}$ and $f_{x,z}$ the peak field strengths and pulse envelopes along the 800 and 400 nm directions, respectively, ω the laser frequency of the 800 nm field, and φ the relative phase between the two colors. Figure 1 illustrates how the orthogonally superposed 800 nm field streaks the subcycle ionization in the 400 nm field. According to the simple man's model [34,35] the final electron momentum after the laser pulse is given by $\mathbf{p} = -\mathbf{A}(t_i)$ with $\mathbf{A}(t) = -\int_{-\infty}^t \mathbf{E}(t') dt'$ the laser field's vector potential and t_i the birth time of the electron (atomic units are used throughout, unless stated otherwise). Figure 1(a) depicts $\mathbf{A}(t)$ for each wavelength separately and for the two important limiting cases $\varphi = 1.5\pi$ and π . Figure 1(b) shows the corresponding

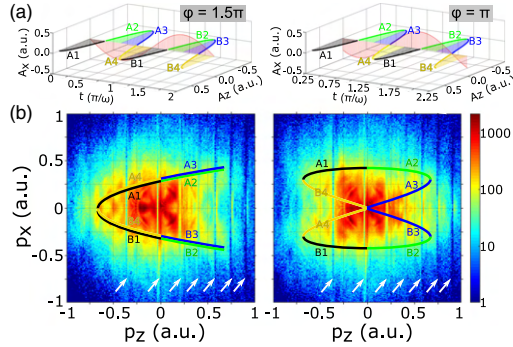


FIG. 1. (a) Vector potential of an OTC field for phase delays $\varphi = 1.5\pi$ (left) and $\varphi = \pi$ (right) over one optical cycle of the 800 nm field. The eight quarter cycles of the stronger 400 nm field are color coded and labeled by A1–A4 and B1–B4. The time window in each panel is adjusted to the reference quarter cycle A1. (b) Measured photoelectron momentum distributions of Ar ionized in a 45 fs OTC pulse, for the phase delays in (a). Superimposed on the momentum distributions is the simple man's prediction of the electron momentum, $\mathbf{p} = -\mathbf{A}(t_i)$, for $\mathbf{A}(t)$ from panel (a). The arrows mark nodes (experimental artifacts) caused by the spectrometer magnetic field [33].

measured photoelectron momentum distributions in the polarization plane of the OTC pulse. On top of the photoelectron momentum distributions we superimposed $\mathbf{p} = -\mathbf{A}(t_i)$ for t_i covering one optical cycle of the 800 nm field using the color code and labeling of Fig. 1(a).

In order to facilitate the analysis of the complex momentum distributions it is useful to transform the data into a polar coordinate system in the plane of polarization with the photoelectron energy E_{kin} as the radial coordinate. In Fig. 2(a) we have done this transformation for the data of Fig. 1(b). A polar angle of $\theta = 0^\circ$ corresponds to a momentum towards the right side, i.e., $p_{z,400 \text{ nm}} > 0$ and $p_{x,800 \text{ nm}} = 0$. Apart from the sharp line features due to the experimental artifacts (marked by arrows), both spectra show pronounced structures and differ significantly at $\theta = 180^\circ$. Whereas for a phase of $\varphi = \pi$ the photoelectron spectrum is only faintly structured, a rich interference carpet appears for a phase of $\varphi = 1.5\pi$. In the latter, a series of curved interference stripes is observed around $\theta = 180^\circ$ and, moreover, a few pronounced peaks can be discerned within the stripes. The variation of these structures with the OTC field shape is visualized in the movie provided in the Supplemental Material [36].

To understand these interference structures, we turn to the strong-field approximation (SFA) theory. In the SFA theory, the transition amplitude of the photoelectron from the initial bound state $|\psi_0\rangle$ to the final Volkov state $|\psi_{\mathbf{p}}^V\rangle$ with the final momentum $\mathbf{p}$ is given by [37,38]

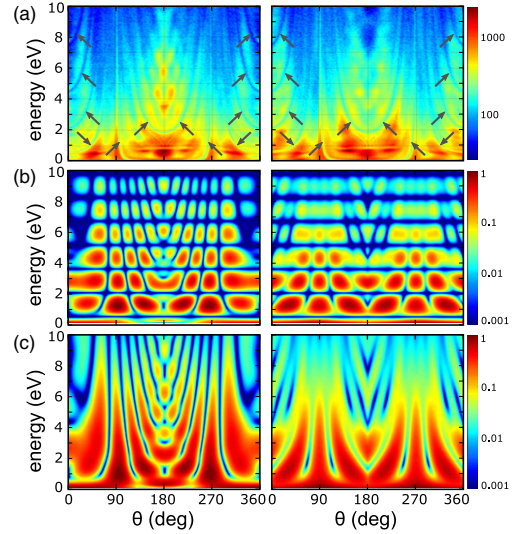


FIG. 2. Angle-resolved energy spectra of photoelectrons for a phase delay $\varphi = 1.5\pi$ (left) and $\varphi = \pi$ (right). (a) Experiment. (b) SFA calculation using Eq. (3). (c) SFA calculation with the OTC pulse restricted to one optical cycle of the 800 nm field. The arrows in (a) mark the experimental artifacts from Fig. 1(b).

$$M_{\mathbf{p}} = -i \int_{-\infty}^{\infty} dt \langle \mathbf{p} + \mathbf{A}(t) | \mathbf{r} \cdot \mathbf{E}(t) | \psi_0(r) \rangle e^{iS(\mathbf{p},t)}, \quad (2)$$

where $\mathbf{r} \cdot \mathbf{E}(t)$ is the laser-field-electron interaction, $S(\mathbf{p}, t) = -\frac{1}{2} \int_t^{\infty} dt' [\mathbf{p} + \mathbf{A}(t')]^2 + I_p t$ is the semiclassical action, and I_p denotes the ionization potential. For a sufficiently high intensity and low frequency of the laser pulse, the temporal integral in Eq. (2) can be evaluated with a high accuracy by the saddle-point method [39]. The corresponding transition amplitude then becomes

$$M_{\mathbf{p}} \sim \sum_s A_s(\mathbf{p}) e^{iS(\mathbf{p}, t_s)}, \quad (3)$$

where $A_s(\mathbf{p}) = \sqrt{2\pi i / (\partial^2 S_{\mathbf{p}} / \partial t_s^2)} \langle \mathbf{p} + \mathbf{A}(t_s) | \mathbf{r} \cdot \mathbf{E}(t_s) | \psi_0(r) \rangle$, and the index s runs over the relevant saddle points obtained by solving the saddle point equation $[\mathbf{p} + \mathbf{A}(t)]^2 = -2I_p$. Each saddle point corresponds to a quantum orbit. Physically, the transition amplitude $M_{\mathbf{p}}$ represents the coherent superposition of all quantum orbits [39,40]. Equation (3) thus provides an intuitive formulation of interference patterns in photoelectron spectra.

In Fig. 2(b) we show the photoelectron spectrum $d|M_{\mathbf{p}}|^2 / dE_{\text{kin}} d\theta$ calculated using Eq. (3) for the two phase delays $\varphi = 1.5\pi$ and π with slightly lower laser peak intensities than in the experiment $[0.15(1.5) \times 10^{14} \text{ W/cm}^2]$ for 800 (400) nm to achieve good agreement with the experimental data. This can be justified considering the experimental uncertainty. Our calculations reveal very distinct energy bands with a spacing of 1.55 eV, which are due to an intercycle interference that arises from the 800 nm component of the OTC field. Moreover, around $\theta = 180^\circ$ the photoelectron distribution for $\varphi = 1.5\pi$ features a much stronger ionization amplitude and more pronounced interference stripes than the distribution for $\varphi = \pi$. These features are in qualitative agreement with the experimental observations in Fig. 2(a).

In the following we will show that the distinct stripe structures around $\theta = 180^\circ$ are caused by a nonadjacent intracycle interference, the focus of this Letter. The temporal grating created by the 800 nm component dominates the calculated energy spectrum. This discrepancy is due to the fact that the simulation in Fig. 2(b) assumes a cw OTC field, whereas the experiment has a pulse envelope with a full width at half maximum of intensity of 45 fs. In order to remove the cw effect in the simulation, we follow a procedure that was used previously for a linearly polarized two-color field [3] and restrict the ionization time of quantum orbits in Eq. (3) to one cycle of the 800 nm field for the remainder of the discussion. The resulting photoelectron spectrum is shown in Fig. 2(c). Thereby, a better agreement with the experimental data is achieved. In comparison to Fig. 2(b), it is clear that the intercycle interference features from the 800 nm field, i.e., the above-threshold ionization structures with an energy

spacing of 1.55 eV, disappear. On the other hand, the prominent stripes around 180° , as observed in the experiment, still persist. The remaining discrepancies between the experimental data and the SFA simulation in different angle and energy ranges can be ascribed to the influence of the parent ion's Coulomb potential, which is neglected in the present SFA theory but in OTC fields can have a significant influence, in particular on the relative electron yields emitted along different directions [18].

To understand the origin of the interference structures around 180° observed for $\varphi = 1.5\pi$, we investigate the separate contributions of the emission time windows A1–A4 and B1–B4, introduced in Fig. 1, to the overall photoelectron spectrum. The simple man's mapping of electron emission time to the asymptotic emission angle θ in the polarization plane provided by the OTC field is shown in Fig. 3(a) for each quarter cycle of the 400 nm component. In agreement with this mapping, our SFA analysis shows that photoelectrons from the ionization time windows A2 and A3 will be mainly detected under angles $0^\circ < \theta < 90^\circ$ [Fig. 3(c)], whereas photoelectrons emitted

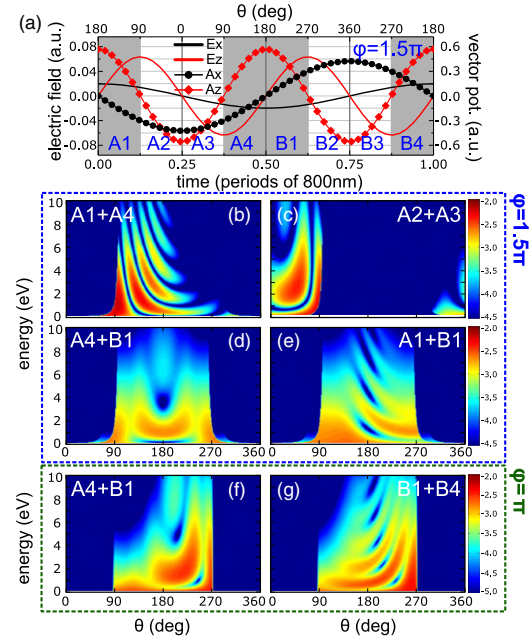


FIG. 3. (a) Electric fields (E_x, E_z) and vector potentials (A_x, A_z) for $\varphi = 1.5\pi$ within one cycle of 800 nm. A1–A4 and B1–B4 denote the different ionization time windows introduced in Fig. 1. The top axis shows the asymptotic emission angle θ of the photoelectron according to the simple man's model $\mathbf{p} = -\mathbf{A}(t)$. (b)–(g) SFA calculations for $\varphi = 1.5\pi$ [(b)–(e)] and $\varphi = \pi$ [(f),(g)] using Eq. (3) with quantum orbits from the different ionization time windows as indicated in the figures.

during A1 and A4 are observed as prominent stripes mainly within $90^\circ < \theta < 180^\circ$ [Fig. 3(b)]. Because of their quantum widths, the wave packets extend beyond the classically expected ranges. Since the vector potential of the 800 nm field (x direction) has the opposite sign for the A and B quarter cycles [see Fig. 3(a)], the SFA momentum distributions of photoelectrons emitted during the corresponding B quarter cycles ($B1 + B4$, $B2 + B3$) are exact mirror images of Figs. 3(b) and 3(c) about the 180° axis and are, thus, not explicitly shown in Fig. 3.

Comparing Fig. 3(c) with the left panel of Fig. 2(c), it becomes clear that the interference patterns at $0^\circ < \theta < 90^\circ$ are due to trajectories emitted from adjacent quarter cycles of the 400 nm field component (A2 and A3). This intracycle interference corresponds to the well-known temporal double slit and has been widely investigated in the literature [2,3,41,42]. In contrast, our analysis reveals that the stripes at $90^\circ < \theta < 270^\circ$ visible for $\varphi = 1.5\pi$ in Fig. 2(c) are from the interference of two kinds of orbits from nonadjacent quarters of the 400 nm field ($A1 + A4$, $B1 + B4$). This type of intracycle interference has not been observed or identified in experiment before, to the best of our knowledge. In fact, this intracycle interference of nonadjacent quarter cycle ionization also exists for a single-color field, see, e.g., Ref. [43]. However, in a single-color field, the two kinds of the intracycle interference structures appear in the same regions of the momentum space. Thus, the overlap of the two types of intracycle interferences obscures the nonadjacent intracycle interference. In contrast, the two-dimensional OTC field with a weaker half-frequency component drives the two orbits corresponding to the adjacent intracycle interference to different quarters of the photoelectron spectra, facilitating the detection of the nonadjacent intracycle interferences.

Our SFA simulations show that the interference stripes from this novel nonadjacent intracycle interference are much finer than those of the adjacent intracycle interference. The reason is that the ionization delays of the electron orbits for the nonadjacent intracycle interference are larger than those of the adjacent ones and, thus, the change of the corresponding action difference of the two orbits is more sensitive to the momentum of the photoelectron. This result is analogous to the double-slit interference [15], for which the stripe width on the screen is inversely proportional to the distance of the two slits. It is this novel intracycle interference, through which the fine and bent fringes at $90^\circ < \theta < 270^\circ$ for $\varphi = 1.5\pi$ are formed.

To further confirm this assessment, we plot in Figs. 3(d) and 3(e) other interference structures that can be observed in the range $90^\circ < \theta < 270^\circ$ and might contribute to the overall momentum distribution. These structures, which are intracycle [Fig. 3(d)] and intercycle interferences [Fig. 3(e)] of the 400 nm field emitted during quarter cycles $A4 + B1$ and $A1 + B1$, respectively, are broader and much weaker than the nonadjacent intracycle structures from $A1 + A4$

and, thus, cannot account for the experimentally observed sharp features. The intercycle structures from $A1 + B1$ somewhat contribute to the distinct peaks that are present on the background of these stripes around $\theta = 180^\circ$ in both the measured [Fig. 2(a)] and total SFA [Fig. 2(c)] distributions. However, the dominant contributions to these peaks come from the coherent superposition of the nonadjacent intracycle interferences, i.e., a superposition of the $A1 + A4$ structures from Fig. 3(b) with their mirrored counterparts from $B1 + B4$.

It is worth noting that the observation of the nonadjacent intracycle interference is strongly dependent on the phase delay of the OTC pulse [compare the left and right panels in Fig. 2(a) and also see the movie in the Supplemental Material [36]]. The reason is that by the variation of φ the OTC field shape changes, which results in completely different electron dynamics. To visualize this, we consider the OTC field with $\varphi = \pi$ shown in the right panel of Fig. 1(a). We first discuss the nonadjacent intracycle interferences of the 400 nm field originating from the quarter cycles $B1 + B4$, shown in Fig. 3(g). As can be seen, the intensity of the interference pattern is significantly reduced as compared to the corresponding one for $\varphi = 1.5\pi$ shown in Fig. 3(b). The reason is that for $\varphi = \pi$ electrons from $B1$ and $B4$ are mainly observed in different quarters of the momentum plane, i.e., $180^\circ < \theta < 270^\circ$ for $B1$ and $90^\circ < \theta < 180^\circ$ for $B4$ [cf. right panel of Fig. 1(a)]. In contrast, as the electron orbit from $A4$ is classically allowed for $180^\circ < \theta < 270^\circ$, it can interfere with that from $B1$ and, thus, the interference from the adjacent quarter cycles $A4 + B1$ becomes much more prominent than that from the nonadjacent ones, $B1 + B4$. The interference from the adjacent quarter cycles $A4 + B1$ [Fig. 3(f)], however, leads to much broader stripes and is also mainly observed at lower energy. As a result, no clear stripe structure related to the nonadjacent intracycle interference can be observed for $\varphi = \pi$, consistent with the experimental data in Fig. 2(a).

Concluding, we have demonstrated that the temporal grating in an OTC pulse can separate two classes of interfering intracycle quantum paths that evolve on two different time scales. In our experiment, the two-dimensional character of an OTC field with a weaker half-frequency component maps their contributions to different regions in momentum space facilitating their disentanglement. We envision that the coupling of subcycle time and space provided by OTC fields, as demonstrated by our experiment, can be exploited also for observing attosecond phenomena that lead to spatiotemporal variations of charge density. Careful analysis of intracycle interferences in OTC fields should thus permit the observation of subcycle variations of the ionization probability, caused, for example, by hole-wave packets after ionization [44]. This might be of particular interest for studying charge density oscillations in molecules that are properly oriented with respect to the spatiotemporal evolution of the OTC

field. We believe that photoelectron intracycle interferometry has a potential for resolving attosecond dynamics that is largely untapped. OTC pulses hold a key to unlock this potential.

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Chapter 4

Semiclassical model for strong field ionization

As discussed in the preceding chapter, the process of strong-field ionization is a dynamic phenomenon typically encompassing quantum tunneling and quantum propagation within the concurrently acting laser field and the Coulomb field of the parent ion. The quantum dynamics of this process can be theoretically computed by directly solving the time-dependent Schrödinger equation (TDSE). However, solving the TDSE is computationally demanding, particularly in a two-dimensional (2D) space, and the interpretation of results can be challenging. Consequently, various approaches have been introduced that rely on classical models to simulate the strong-field ionization process, offering a more computationally tractable and analytically accessible means of investigation [20].

Presently, there are several commonly used models for simulating photoelectron momentum distributions which take the parent ion's Coulomb field into account, such as the Coulomb quantum-orbit strong field approximation (CQSFA) [84], the quantum-trajectory Monte Carlo (QTMC) model [85,86], and the semi-classical two-step (SCTS) model [15,87]. These models can be categorized into two groups [20]: The CQSFA solves the inverse problem, which means it needs prior knowledge of the electron orbits. The QTMC and SCTS models, on the other hand, solve the direct problem, which means only the initial conditions are needed and the electron orbits are obtained by propagation in time. Due to the simplicity of solving the direct problem, we will use and discuss the SCTS model in this thesis.

This chapter will be organized as follows: at first, the algorithm of the SCTS model will be introduced, then we will apply the SCTS model to the hydrogen atom to disentangle

interferences in the photoelectron momentum distribution from strong-field ionization. At last, we will introduce the molecular SCTS model, then apply it with a light-molecule approximation to simulate photoelectron momentum distributions from different molecular orbitals of Br_2 during dissociation along the C-state.

4.1 Algorithm of semiclassical two-step model

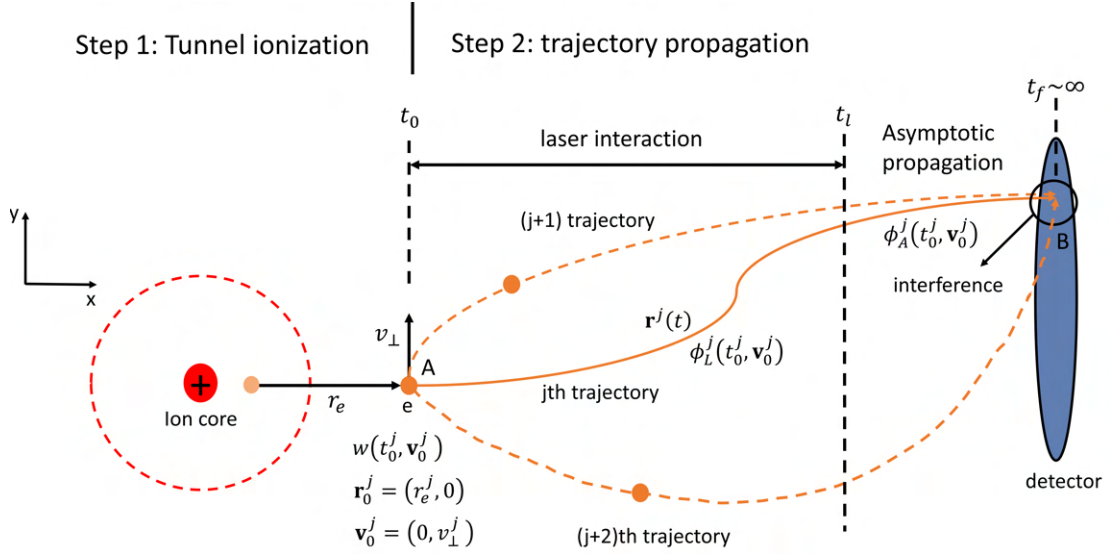


Figure 4.1: Illustration of semiclassical two-step model. The orange solid and dashed curves represent three different electron trajectories. Each trajectory has an initial state which is defined by $(w, r_e, v_\perp)$. Starting from ionization, each trajectory will accumulate a quantum phase Φ until it reach the detector.

The semiclassical two-step (SCTS) model is a Monte Carlo type simulation approach for strong-field ionization, involving calculating a vast number of electron trajectories. Figure 4.1 illustrates its calculation procedure. The semiclassical two-step model treats the strong field ionization process as two major steps: tunneling ionization and electron trajectory propagation. For the tunneling ionization step of the j th electron, the tunneling ionization rate $w(t_0^j, \mathbf{v}_0^j)$ at ionization time t_0 is determined by the Equation 2.8, and the tunneling exit point r_e^j is calculated using the Equation 2.9. In order to simplify the calculation, we have used a two-dimensional model. Then the initial coordinates of a tunneling electron on the x-y plane can be defined as: $(r_x^j = r_e^j, r_y^j = 0)$, while the initial velocity of the electron

will be: $\mathbf{v}_0^j = (v_x^j = 0, v_y = v_\perp^j)$. Here, we assume that the longitudinal velocity of the photoelectron at the tunneling exit point is zero.

For the electron trajectory propagation step, the tunneled electron will be driven by combined the laser field and the ion-core Coulomb field, which is well described by a classical dynamics. The Hamiltonian of the system is: $H(t) = \frac{1}{2}(\mathbf{p}^j)^2 + V(\mathbf{r}^j) + \mathbf{r}^j \cdot \mathbf{F}(t)$, where the Coulomb potential is $V(\mathbf{r})$. For atomic case, $V(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|}$, with Z the parent ion charge state. The electric field of the laser pulse is expressed as $\mathbf{F}(t) = \hat{\mathbf{e}}_x f(t) \sin(t)$, with the laser pulse being a half-trapezoidal envelope described by the envelope function $f(t)$:

$$\begin{cases} f(t) = 1, & t < T_p \\ f(t) = \cos\left(\frac{\pi(t-T_p)}{2T_t}\right)^2, & T_p < t < (T_p + T_t) \\ f(t) = 0, & \text{elsewhere} \end{cases} \quad (4.1)$$

where T_p is the duration of the plateau part, and T_t is the length of the $\cos^2$ tail.

The electric field of laser pulse is shown in Figure 4.2. In our simulation, depending on the purpose, the ionization will be restricted to the first four optical cycles which have a constant amplitude. For example, ionization during all four cycles will give us multi-cycle interference like ATI peaks. If ionization is restricted to the first optical cycle, we focus on the single-cycle dynamics like the recollision process. After the first four cycles, a cosine squared ramp with six cycles is applied to turn off the laser field slowly so that the carrier-envelope-phase effect can be minimized.

The classical dynamics of an electron is described by the canonical equations:

$$\frac{d\mathbf{r}^j}{dt} = \frac{\partial H}{\partial \mathbf{p}^j}, \quad \frac{d\mathbf{p}^j}{dt} = -\frac{\partial H}{\partial \mathbf{r}^j}, \quad (4.2)$$

where H is the Hamiltonian of the system. $\mathbf{p}$ and $\mathbf{r}$ are the momentum and position vectors of the photoelectron.

To simulate the quantum effect of electron propagation, Feynman's path-integral approach is employed. Figure 4.1 depicts various paths connecting the tunneling exit-point A to the hit position B on the detector. Numerous paths, labeled by j , exist between the two points, and each path contributes to the overall electron probability at point B with a distinct probability amplitude represented as:

$$\Gamma(\mathbf{r}^j(t)) \propto \exp\left(\frac{i}{\hbar} S(\mathbf{r}^j(t))\right), \quad (4.3)$$

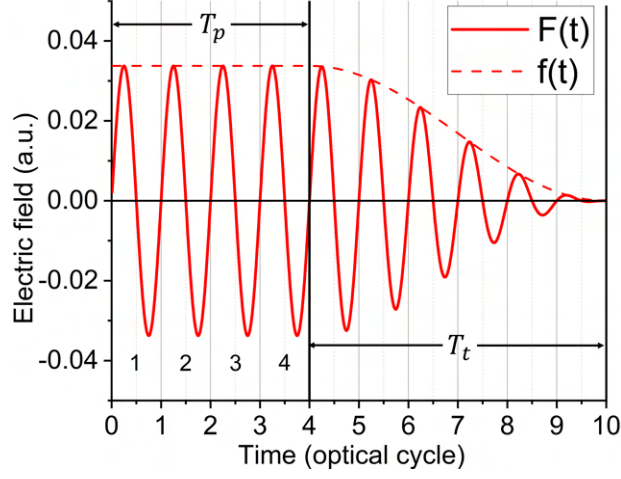


Figure 4.2: The electric field of the laser pulse is depicted by the solid curve, while the dashed curve represents the envelope function. The durations of the two parts of the pulse are denoted by T_p and T_t .

The classical action, expressed as $S(\mathbf{r}^j(t)) = \int_{t_0}^{t_f} L(\dot{\mathbf{r}}^j(t), \mathbf{r}^j(t)) dt$, is directly linked to a phase [88]: $\phi(\mathbf{r}^j(t)) = S(\mathbf{r}^j(t)) / \hbar$. The Lagrangian, denoted as $L(\dot{\mathbf{r}}^j(t), \mathbf{r}^j(t))$, is associated with the classical Hamiltonian:

$$L(\dot{\mathbf{r}}^j(t), \mathbf{r}^j(t)) = \mathbf{p}^j \dot{\mathbf{r}}^j - H(\mathbf{r}^j, \mathbf{p}^j), \quad (4.4)$$

The quantum effect of a trajectory is encapsulated in the phase $\phi(\mathbf{r}^j(t))$. However, this phase, connecting two points A and B in coordinate space, is not ideal for accurately simulating the momentum distribution in tunnel ionization. In the context of tunnel ionization, the phase of an electron trajectory should establish a connection between the tunneling exit-point in coordinate space and the electron final momentum in momentum space. To transform this coordinate-coordinate phase to the coordinate-momentum one, the different representations of semiclassical propagator has to be utilized under the semiclassical approximation [15]. The final form of the phase for tunnel ionization is as follow:

$$\begin{aligned} \Phi(t_0, \mathbf{v}_0^j) = & -\mathbf{v}_0^j \cdot \mathbf{r}^j(t_0) + I_p t_0^j \\ & - \int_{t_0}^{t_f} dt \left\{ \frac{\mathbf{p}^j(t)^2}{2} + V(\mathbf{r}^j(t)) - \mathbf{r}^j(t) \cdot \vec{\nabla} V(\mathbf{r}^j(t)) \right\}, \end{aligned} \quad (4.5)$$

where t_f is the time electron hits on the detector. Here, the temporal evolution of ground state has been added into the phase through the term $I_p t_0^j$. For the atomic Coulomb potential, $V[\mathbf{r}^j(t)] = -Z/|\mathbf{r}^j(t)|$, Equation 4.5 becomes:

$$\begin{aligned} \Phi(t_0, \mathbf{v}_0^j) &= -\mathbf{v}_0^j \cdot \mathbf{r}^j(t_0) + I_p t_0^j \\ &- \int_{t_0}^{t_f} dt \left\{ \frac{\mathbf{p}^j(t)^2}{2} - \frac{2Z}{|\mathbf{r}^j(t)|} \right\}, \end{aligned} \quad (4.6)$$

In a practical experiment of strong-field ionization, the atom undergoes interaction with a laser pulse over a time span of tens of femtoseconds. Following ionization, the electron obtains a momentum, denoted as $\mathbf{p}^j(t_l)$, where t_l signifies the conclusion time of the laser pulse. Then the electron will travel along a Kepler hyperbola until it reaches the detector. During this laser-free trajectory, the electron's momentum asymptotically approaches its ultimate momentum, denoted as $\mathbf{k}^j$. This convergence of asymptotic momentum occurs within a time scale of tens of nanoseconds and can be computed from the final motion state of electron, using classical mechanics formulas derived for hyperbolic motion [15]. For the electron ending in the motion state $(\mathbf{p}^j(t_l), \mathbf{r}^j(t_l))$ with energy E^j , the magnitude of the asymptotic momentum k^j can be determined,

$$\frac{(k^j)^2}{2} = \frac{\mathbf{p}^j(t_l)^2}{2} - \frac{Z}{|\mathbf{r}^j(t_l)|} = E^j, \quad (4.7)$$

and the angular momentum,

$$\mathbf{L}^j = \mathbf{r}^j(t_l) \times \mathbf{p}^j(t_l), \quad (4.8)$$

and the Runge-Lenz vector,

$$\mathbf{a}^j = \mathbf{p}^j(t_l) \times \mathbf{L}^j - \frac{\mathbf{r}^j(t_l)}{|\mathbf{r}^j(t_l)|}. \quad (4.9)$$

Finally, the asymptotic momentum vector is expressed as follow:

$$\mathbf{k}^j = k^j \frac{k^j (\mathbf{L}^j \times \mathbf{a}^j) - \mathbf{a}^j}{1 + (k^j)^2 (L^j)^2}. \quad (4.10)$$

The $\Phi(t_0, \mathbf{v}_0^j)$ and $\mathbf{k}^j$ of individual trajectories provide all the information for constructing the electron momentum distribution through interference. Here, the procedure of interference is carried out on a 2D momentum grid consisting of 1000×1000 bins. In

this procedure the ionization rates of all trajectories, leading to the same momentum $\mathbf{k}$, will be coherently added in corresponding bin:

$$P(\mathbf{k}) = \left| \sum_{j=1}^n \sqrt{w_{ADK}(t_0^j, \mathbf{v}_0^j)} \exp [i\Phi(t_0^j, \mathbf{v}_0^j)] \right|^2, \quad (4.11)$$

Where n is the number of trajectories falling into the momentum bin $\mathbf{k}$.

In the actual simulation, directly integrating Equation 4.6 is not applicable, since calculating over entire $t_f - t_l$ is time demanding. Considering the long time span of electron asymptotic propagation, we assume $t_f \sim \infty$, hence, the Equation 4.6 can be decomposed as:

$$\begin{aligned} \Phi(t_0, \mathbf{v}_0^j) &= \Phi_L^j(t_0^j, \mathbf{v}_0^j) + \Phi_A^j(t_0^j, \mathbf{v}_0^j), \\ \Phi_L^j(t_0^j, \mathbf{v}_0^j) &= -\mathbf{v}_0^j \cdot \mathbf{r}^j(t_0) + I_p t_0^j - \int_{t_0}^{t_l} dt \left\{ \frac{\mathbf{p}^j(t)^2}{2} - \frac{2Z}{|\mathbf{r}^j(t)|} \right\}, \\ \Phi_A^j(t_0^j, \mathbf{v}_0^j) &= - \int_{t_l}^{\infty} dt \left\{ \frac{\mathbf{p}^j(t)^2}{2} - \frac{2Z}{|\mathbf{r}^j(t)|} \right\} = - \int_{t_l}^{\infty} dt E^j - \int_{t_l}^{\infty} dt \frac{Z}{|\mathbf{r}^j(t)|}, \end{aligned} \quad (4.12)$$

Where $\Phi_L^j(t_0^j, \mathbf{v}_0^j)$ is the laser-atom interaction phase, and $\Phi_A^j(t_0^j, \mathbf{v}_0^j)$ is the electron asymptotic-propagation phase. It is evident that both integrals in $\Phi_A^j(t_0^j, \mathbf{v}_0^j)$ exhibit divergence, necessitating further treatment. Initially, referring to Equation 4.11, the interference among electron trajectories primarily relies on their phase difference. Within a momentum bin, trajectories share the same momentum $\mathbf{k}$ and consequently the same energy $E^j = E^{j'}$. Consequently, the phase difference, $-\int_{t_l}^{\infty} dt(E^j - E^{j'}) \sim 0$, permits the omission of the first integral of $\Phi_A^j(t_0^j, \mathbf{v}_0^j)$.

The second integral, expressed as $\int_{t_l}^{\infty} dt \frac{Z}{|\mathbf{r}^j(t)|}$, represents a phase originating from the Coulomb potential. This integral can be computed using the analytic Coulomb mapping for Kepler hyperbola, with an approximation made at the asymptotic limit as $t \rightarrow \infty$ [15]. The resulting asymptotic Coulomb phase is shown to be solely dependent on the electron's final motion state at the conclusion of the laser pulse. It takes the following form:

$$\Phi_C^j(t_l) = -Z\sqrt{b} \left[\ln g + \operatorname{asinh} \left(\frac{\mathbf{r}^j(t_l) \cdot \mathbf{p}^j(t_l)}{g\sqrt{b}} \right) \right], \quad (4.13)$$

where $b = 1/(2E^j)$, and $g = \sqrt{1 + 2E(L^j)^2}$.

Thus, for atomic ionization, the phase equation used in our SCTS model is as follow:

$$\Phi(t_0, \mathbf{v}_0^j) = -\mathbf{v}_0^j \cdot \mathbf{r}^j(t_0) + I_p t_0^j - \int_{t_0}^{t_l} dt \left\{ \frac{\mathbf{p}^j(t)^2}{2} - \frac{2Z}{|\mathbf{r}^j(t)|} \right\} + \Phi_C^j(t_l). \quad (4.14)$$

Our SCTS simulation is performed using 10^9 electron trajectories. For each trajectory, the ionization time is randomly assigned within the laser pulse, and its initial transverse velocity $v_{\perp}^j$ is randomly set within an interval of $(-v_{\perp}^{max}, v_{\perp}^{max})$, where $v_{\perp}^{max} = 3 \left(|\mathbf{F}(t_0)| / \sqrt{2I_p(t_0)} \right)^{\frac{1}{2}}$. After the initial conditions are defined, the Equation 4.2 of each tunneling electron is solved by using the symplectic method which can keep numerical stability for calculations over long time spans [89].

4.2 Disentangling interferences in the photoelectron momentum distribution from strong-field ionization

Disentangling interferences in the photoelectron momentum distribution from strong-field ionizationT. Wang^{1,*}, Z. Dube¹, Y. Mi¹, G. Vampa¹, D. M. Villeneuve¹, P. B. Corkum¹, Xiaojun Liu², and A. Staudte^{1,†}¹*Joint Attosecond Laboratory, National Research Council and University of Ottawa, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*²*State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Innovation Academy for Precision Measurement Science and Technology, Chinese Academy of Sciences, Wuhan 430071, China*

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Using the semiclassical two-step model for strong-field ionization, we theoretically investigate subcycle interference structures in the photoelectron momentum distribution. Specifically, we focus on the low-momentum fanlike interference structure. Employing a time-variable soft-core Coulomb potential, we demonstrate that the low-momentum interference arises from the interference between drifted and undrifted electrons from opposite direct quarter cycles. We also find that the main scattering in the nuclear Coulomb potential occurs just after ionization. Our findings suggest that the low-momentum region of the photoelectron spectrum is particularly sensitive to the ion potential and thereby offers another path to probe ultrafast electronic structure dynamics.

DOI: [10.1103/PhysRevA.106.013106](https://doi.org/10.1103/PhysRevA.106.013106)**I. INTRODUCTION**

In multiphoton ionization of atoms and molecules by intense multicycle laser pulses the photoelectron wave packets created at each crest of the optical wave interfere with each other, giving rise to a wealth of structures in the observable photoelectron momentum distributions [1–5]. Whereas some of these interferences arise directly from the symmetry of the optical wave driving the electron current, others inherently rely on the scattering in the parent ion's potential. These scattering interferences have a particular potential for revealing electronic structure and dynamics.

A prominent scattering interference structure is the so-called strong-field photoelectron holography [6,7]. It arises from the interference of two parts of the electron wave packet that are ionized within a fraction of a quarter optical cycle and are subsequently scattered differently in the parent ion's potential [8]. The holographic interference causes spider-leg-like fringes along the laser polarization direction in the photoelectron momentum distribution. This interference structure has been shown to be a powerful tool for probing fundamental strong-field processes [3,5,8–15], valence-shell electronic motion [16], and molecular structure and ultrafast dynamics [17–19] (see also Ref. [20] for a recent review of the topic).

Whereas holographic scattering is most distinct in the middle to high photoelectron momentum range due to the underlying recollision step, the low-momentum region of the photoelectron spectrum is especially affected by Coulomb scattering [21–23]. The observed fanlike interference structure in the lowest momentum range has been shown to reveal orbital symmetry [24] and has been found to originate in soft scattering of electron trajectories within 1/18 of the crest of an

optical cycle [25]. However, in contrast to holographic interferences, the potential of the fanlike low-momentum structure to access ultrafast dynamics remains largely unexplored.

Here, we employ a semiclassical two-step model [5,26] to resolve the subcycle interference of photoelectron wave packets by using a quarter-cycle interference scheme. Particularly, we focus on the fanlike interference structure in the low-momentum region of the photoelectron distribution to unveil its formation mechanism. The disentanglement of this interference structure is accomplished by considering its temporal structure and the Coulomb potential effect from the ion separately. We show that this structure originates in the interference between scattered and unscattered electron wave packets from different direct quarter cycles within a single optical cycle. Furthermore, our analysis reveals that the parent ion's influence on the scattered photoelectron is greatest only a short time after tunneling ionization and well before the moment of closest approach. Hence we believe that this specific structure can resolve ion dynamics on the sub-optical-cycle time scale.

II. METHOD

Presently, there are several commonly used models for simulating photoelectron momentum distributions which take the parent ion's Coulomb field into account, such as the Coulomb quantum-orbit strong-field approximation (CQSFA) [27], the quantum-trajectory Monte Carlo (QTMC) model [12,28], and the semiclassical two-step (SCTS) model [5,26]. These models can be categorized into two groups [20]: The CQSFA solves the inverse problem, which means it needs prior knowledge of the electron orbits. The QTMC and SCTS models, on the other hand, solve the direct problem, which means only the initial conditions are needed and the electron orbits are obtained by propagation in time. Due to the simplicity of solving the direct problem, we will use the SCTS model to study the photoelectron momentum distribution in this paper.

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The semiclassical two-step model treats the strong-field ionization process as two major steps: tunneling ionization and electron trajectory propagation. For the tunneling ionization step, the tunneling ionization rate at ionization time t_0 is determined by the Ammosov-Delone-Krainov (ADK) ionization rate [29]:

$$w_{\text{ADK}}(t_0, v_\perp) \simeq \exp\left[-\frac{2\kappa^3}{3|F(t_0)|}\right] \exp\left[-\frac{\kappa v_\perp^2}{|F(t_0)|}\right], \quad (1)$$

where $\kappa = \sqrt{2I_p(t_0)}$, $I_p(t_0)$ is the ionization potential of the atom, $F(t_0)$ is the instantaneous electric amplitude of the laser field, and $v_\perp$ is the initial transverse velocity of the electron at the tunneling exit point. The tunneling exit point r_e is calculated using the tunnel ionization in parabolic coordinates with induced dipole and Stark shift (TIPIS) approximation [30]:

$$r_e = \frac{I_p(t_0) + \sqrt{2I_p(t_0)^2 - 4\beta_2 F(t_0)}}{2F(t_0)}, \quad \beta_2 = Z - \frac{\sqrt{2I_p(t_0)}}{2}, \quad (2)$$

where Z is the ionic charge and the Stark-shifted ionization potential is $I_p(t_0) = I_{p,0} + \frac{1}{2}(\alpha_N - \alpha_I)F(t_0)^2$, where α_N and α_I denote the static polarizability for the atom and the ion, respectively, and $I_{p,0}$ is the ionization potential without any shifts. In order to simplify the calculation, we have used a two-dimensional model. Then the initial coordinates of a tunneling electron on the x - y plane can be defined as ($r_x = r_e$, $r_y = 0$), while the initial velocity of the electron will be $\mathbf{v}_0 = (v_x = 0, v_y = v_\perp)$. Here, we assume that the longitudinal velocity of the photoelectron at the tunneling exit point is zero.

For the electron trajectory propagation step, the tunneled electron will evolve classically within the laser field and the nuclear Coulomb field. The Hamiltonian of the system is $H(t) = \frac{1}{2}\mathbf{p}^2 + V(\mathbf{r}) + \mathbf{r} \cdot \mathbf{F}(t)$, where $V(\mathbf{r})$ is the nuclear potential, $\mathbf{F}(t) = \hat{\mathbf{e}}_x f(t) \sin(\omega t)$ is the electric field of the laser pulse, and ω is the circular frequency. Then the electron motion is described by the canonical equations

$$\frac{d\mathbf{r}}{dt} = \frac{\partial H}{\partial \mathbf{p}}, \quad \frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{r}}, \quad (3)$$

where H is the Hamiltonian of the system and $\mathbf{p}$ is the momentum vector of the photoelectron.

On its classically calculated path the photoelectron accumulates a phase Φ , which is calculated by [26]

$$\begin{aligned} \Phi(t_0, \mathbf{v}_0) = & -\mathbf{v}_0 \cdot \mathbf{r}(t_0) + I_p t_0 \\ & - \int_{t_0}^{\tau_f} dt \left\{ \frac{p(t)^2}{2} + V - \mathbf{r}(t) \cdot \vec{\nabla} V[\mathbf{r}(t)] \right\} \\ & + \Phi_f^C(\tau_f), \end{aligned} \quad (4)$$

where τ_f is the duration of the laser pulse and $V[\mathbf{r}(t)]$ is the ionic Coulomb potential. For a real Coulomb potential, $V[\mathbf{r}(t)] = -Z/|\mathbf{r}(t)|$. The asymptotic Coulomb phase $\Phi_f^C(\tau_f)$ has an analytical form [26]:

$$\Phi_f^C(\tau_f) = -Z\sqrt{b} \left[\ln g + \operatorname{asinh} \left(\frac{\mathbf{r}(\tau_f) \cdot \mathbf{p}(\tau_f)}{g\sqrt{b}} \right) \right], \quad (5)$$

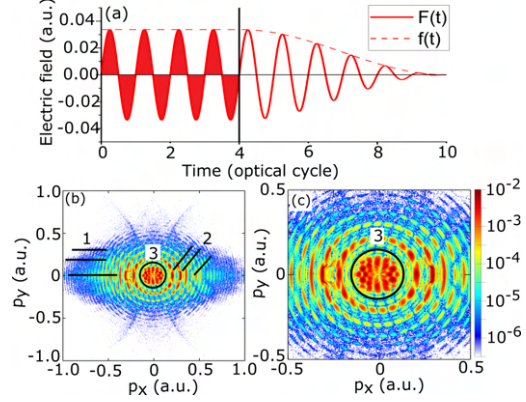


FIG. 1. (a) Electric field of the half-trapezoidal laser pulse. The solid red line is the electric field, and the dashed red line shows its envelope. The red shaded areas indicate the laser cycles where tunneling ionization is allowed. (b) Photoelectron momentum distribution for a H atom ionized by the laser pulse in (a) with wavelength $\lambda = 2000$ nm and peak intensity $I = 4 \times 10^{13}$ W/cm². The black lines indicate the strong-field photoelectron holography fringes (labeled “1”) and the temporal double slit fringes (labeled “2”). The black circle labeled “3” indicates the fanlike interference structure in the low-momentum range. (c) Magnification of (b).

where $b = 1/(2E)$ and $g = \sqrt{1 + 2EL^2}$. Here, E and L are the electron energy and angular momentum at the end of the laser pulse, respectively.

In this paper, we use a hydrogen atom as the model system to study subcycle photoelectron holography. Thus we set $Z = 1$, $I_{p,0} = 0.5$ a.u., $\alpha_N = 4.5$ a.u. [31], and $\alpha_I = 0.0$ a.u. In order to study the subcycle photoelectron dynamics independently of the carrier-envelope phase (CEP), a long laser pulse is ideal. Here, we use a laser pulse with a half-trapezoidal envelope, where the first four cycles have a constant field amplitude followed by a cosine squared turnoff over six cycles. We chose the specific form of the pulse envelope to minimize the effect of the CEP on the photoelectron distributions. The wavelength of the laser pulse is 2000 nm, and the peak intensity is 4×10^{13} W/cm². The electric field vector of our laser pulse is along the x direction, and its field strength versus time is shown in Fig. 1(a).

Our semiclassical two-step model simulation is performed using 10^9 electron trajectories. For each trajectory, the ionization time is randomly and uniformly assigned within the laser pulse, and its initial transverse velocity is randomly and uniformly set within an interval of $(-v_\perp^{\max}, v_\perp^{\max})$, where $v_\perp^{\max} = 3(|\mathbf{F}(t_0)|/\sqrt{2I_p(t_0)})^{1/2}$. After the initial conditions are defined, the Hamiltonian of each tunneling electron is solved by using the symplectic method, which can keep numerical stability for calculations over long time spans [32]. The asymptotic momentum distribution is calculated and recorded on a two-dimensional (2D) momentum grid with 1000×1000 bins, coherently adding the ionization rates of all

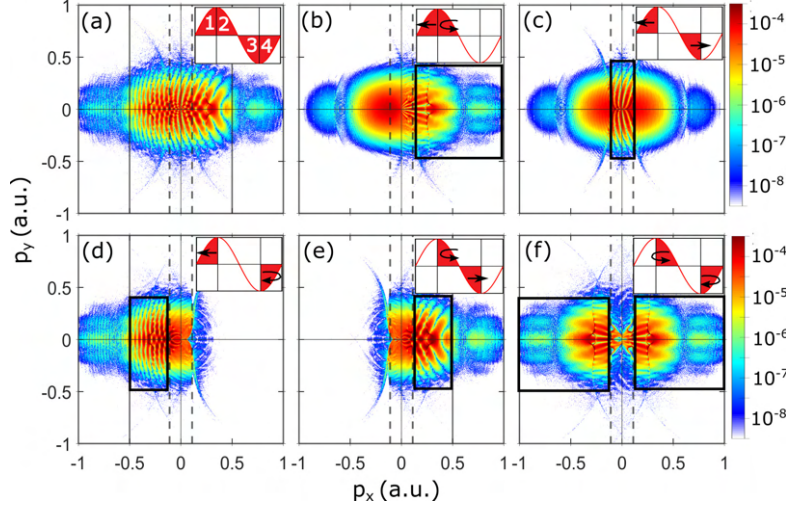


FIG. 2. Photoelectron momentum distributions with ionization restricted to different quarter-cycle (QC) combinations within the first optical cycle of the pulse shown in (a): (a) the complete optical cycle; (b) QCs 1 and 2, forward scattering holography; (c) QCs 1 and 3, low-energy interference structure; (d) QCs 1 and 4, extended temporal double slit; (e) QCs 2 and 3, temporal double slit; and (f) QCs 2 and 4, forward scattering holography. The quarter cycles are labeled as shown in the inset of (a). In (b)–(f), the insets indicate the quarter cycles (solid red) where tunneling ionization is permitted, and the black box indicates the main interference fringes. The straight and curved black arrows in each inset mark the direct and indirect QCs, and their directions mark the momentum directions of electrons ionized within corresponding QCs in the photoelectron momentum distribution.

trajectories:

$$P(\mathbf{k}) = \left| \sum_{j=1}^n \sqrt{w_{\text{ADK}}(t_0^j, \mathbf{v}_0^j)} \exp[i\Phi(t_0^j, \mathbf{v}_0^j)] \right|^2, \quad (6)$$

where j labels the electron trajectory, n is the total number of trajectories, and $\Phi(t_0^j, \mathbf{v}_0^j)$ is the phase of the j th trajectory.

III. RESULTS AND DISCUSSION

Figure 1(b) shows the calculated momentum distributions with ionization permitted only during the first four optical cycles of the laser pulse. We can clearly observe the dominant ring structure of the intercycle interference characteristic for above-threshold ionization (ATI). We can also distinguish several intracycle interference structures such as the strong-field photoelectron holography pattern [7], indicated by horizontal black lines (labeled “1”), and the temporal double slit fringes [33], indicated by 45° black lines (labeled “2”). Moreover, a fanlike interference structure [34] can be identified in the low-momentum part, indicated by a black circle (labeled “3”). The low-momentum part has been magnified in Fig. 1(c) to make the fanlike interference structure more visible. As we will show below, the fanlike interference structure (labeled “3”) extends to larger transverse momenta than indicated with the black circle but is obscured by ATI rings for the laser field parameters in Fig. 1.

In experiments, Fourier filtering can be employed to remove the dominant ATI structures and reveal subcycle interference structures [35]. Here, we can simply restrict ionization

to a single optical cycle, thereby removing any intercycle interference. In Fig. 2(a) we show the momentum distribution that is formed when ionization is restricted to the first optical cycle within the envelope in Fig. 1(a). Comparing with Fig. 1(b), the ATI rings are completely absent, and pronounced, vertical interference fringes emerge in the momentum range from -0.5 to 0.5 a.u.

In Figs. 2(b)–2(f), we now disentangle the momentum spectrum with respect to the contributions of the different quarter-cycle combinations within a single optical cycle. In each figure the main interference structure is indicated by a black box. Remarkably, the dominant modulations of the single-cycle photoelectron spectrum in Fig. 2(a) can be assigned to just three distinct quarter-cycle pairs, shown in Figs. 2(c)–2(e). Of these structures the ones in Fig. 2(e) can be recognized as the well-known temporal double slit [33,36]. The structure in Fig. 2(d) is a similar, but less known, larger double slit from nonadjacent quarter cycles, which manifests itself in narrower fringes. Finally, the quarter-cycle combination in Fig. 2(c) produces the low-energy vertical fringes. Figures 2(b) and 2(f) show the characteristic holographic fringes parallel to the laser polarization, which are almost indiscernible in the combined distribution [Fig. 2(a)]. Notably, Fig. 2(f) has a deficit of photoelectrons with $|p_x| < 0.1$ a.u. compared with the other cases.

To understand the lack of low-momentum electrons in Fig. 2(f), it is useful to classify the four quarter cycles by their trajectories. In the simple man’s model of recollision, the electron is treated fully classically, and the long-range Coulomb potential of the parent ion is ignored [37,38]. Within

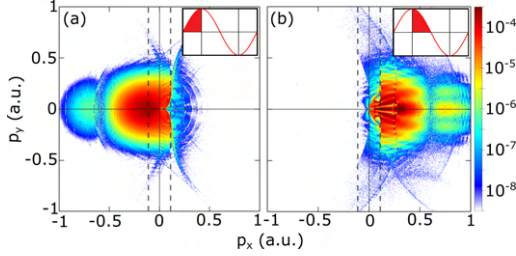


FIG. 3. Photoelectron momentum distributions from direct (a) and indirect (b) quarter cycles. The two black dashed lines indicate $p_x = -0.1$ a.u. and $p_x = 0.1$ a.u., respectively. The illustration in the right upper corner of each panel shows the quarter cycle where tunneling ionization happens.

this framework, the first and third quarter cycles [as indicated in Fig. 2(a)] are called *direct* quarter cycles, because the ionized electrons are driven directly away from the ion without a chance for recollision. The second and fourth quarter cycles are called *indirect* quarter cycles, because the ionized electrons are first driven back towards the parent ion, where they can *rescatter* in the ion potential, before traveling to the detector. The photoelectron momentum distributions of a single direct quarter cycle and a single indirect quarter cycle are shown in Fig. 3. Figure 2(f) is the only case without a direct quarter cycle, and thus the lack of low-momentum electrons must be due to rescattering. This can be further demonstrated by comparing the photoelectron momentum distributions of single direct and indirect quarter cycles. It can be seen that in Fig. 3(b) the electrons ionized from an indirect quarter cycle can hardly populate the low-momentum region: $|p_x| < 0.1$ a.u. compared with that in Fig. 3(a). On the other hand, Fig. 2(c) shows the only combination without an indirect, rescattering quarter cycle, exhibiting interference fringes in the low-momentum region. Such interference requires the electrons ionized within two different direct quarter cycles to achieve overlap in the momentum space. However, this is in contrast to the simple man's model, because the electric fields of the first and third quarter cycles are opposite; hence the ionized electrons within them will fly in different directions and cannot have the same momentum according to the simple man's model. In the following, we will focus on the low-momentum, vertical interference fringes and their origin beyond the simple man's model.

To begin, we introduce a soft-core potential to replace the $-Z/|r(t)|$ Coulomb potential in our simulation with a soft-core Coulomb potential $V[r(t)] = -\frac{Z}{\sqrt{(|r(t)|+\beta)^2}}$, where $\beta \geq 0$ is the soft-core parameter. A larger β means a shallower potential; thus $\beta = 0.0$ corresponds to a real Coulomb potential, and $\beta = \infty$ means no Coulomb potential. Here, we only investigate the effect of the Coulomb potential on the electron propagation after tunneling ionization; the effect of the ionic potential on quantum tunneling will not be considered. Hence the initial coordinates and probability of tunneling electrons will be calculated according to Eqs. (1) and (2). The evaluation of the asymptotic Coulomb phase $\Phi_f^C(\tau_f)$ uses the real Coulomb potential, because the ionized electron will be at a

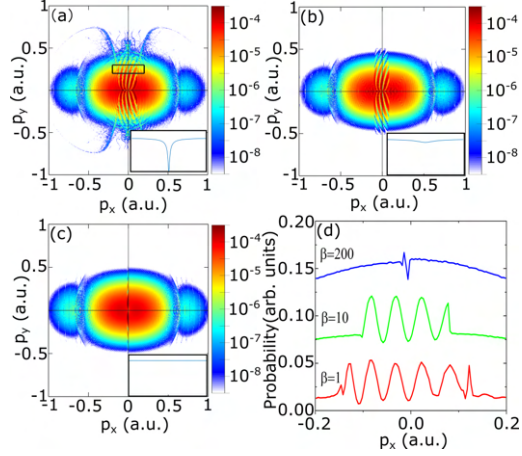


FIG. 4. Photoelectron momentum distributions with ionization restricted to the first and third quarter cycles for different soft-core Coulomb potentials, (a) $\beta = 1$, (b) $\beta = 10$, and (c) $\beta = 200$. (d) p_x integrated over a small window in p_y , $0.2 \text{ a.u.} < p_y < 0.3 \text{ a.u.}$ as indicated by the black box in (a). Note that the probability curves for $\beta = 10$ and $\beta = 200$ have been shifted upwards by 0.06 and 0.11, respectively, for a better visualization. The insets in (a)–(c) sketch the soft-core Coulomb potentials for different β .

large distance from the core at the end of the laser pulse and thus the soft-core parameter β can be neglected.

We now sample the tunneling electrons within the first and third quarter cycles in the ionization step and let the tunneled electrons propagate within the soft-core Coulomb potential. Figure 4 shows the momentum distributions for three different soft-core Coulomb potentials. We can see that a soft-core parameter $\beta = 1$ [Fig. 4(a)] produces almost identical distributions to a real Coulomb potential [Fig. 2(c)]. However, when β is increased to 10, the number of fringes is reduced as shown in Fig. 4(b). If we further increase β to 200, the low-momentum fanlike structure almost disappears as shown in Fig. 4(c).

Figure 4(d) shows the momentum distributions projected on the x axis for the three cases within a specific momentum range indicated by a black box in Fig. 4(a). The reduction of the low-momentum interference with increasing β demonstrates that it originates in the ionic potential.

To further understand the formation of the low-momentum interference, we now examine the electron trajectories as a function of β . Figures 5(a) and 5(b) show the time-dependent probability distributions $P(t, r_x)$ along the light polarization direction for $\beta = 0$ and $\beta = \infty$, respectively. Each figure contains 10^7 electron trajectories tunnel ionized during the first direct quarter cycle. After tunnel ionization, the electrons evolve in the combined laser and Coulomb field and form an oscillating cluster of electron trajectories in both cases.

For the real-Coulomb-potential case in Fig. 5(a), the cluster of electron trajectories oscillates and drifts toward the nucleus during its propagation and finally forms an upward propagation trend, indicated by an upward sloping black line. Such a drift

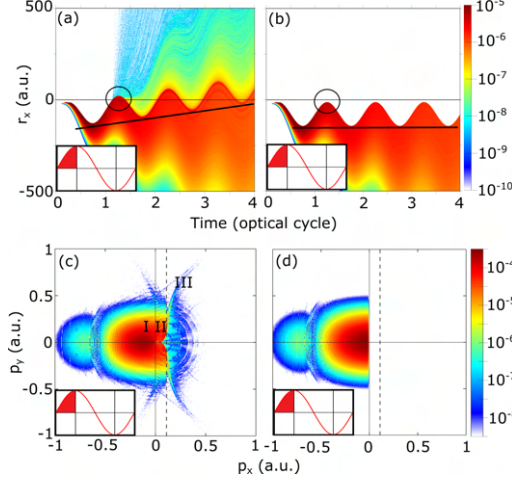


FIG. 5. Electron trajectory (a) and (b) and momentum distributions (c) and (d) from a single, direct quarter cycle. (a) and (c) are for the real-Coulomb-potential case, and (b) and (d) are for the no-Coulomb-potential case. In (c), the labels “I,” “II,” and “III” mark the undrifted, low-momentum drifted, and high-momentum drifted electrons, respectively. The insets indicate the quarter cycles (solid red) where tunneling ionization is permitted. The dashed vertical lines correspond to $p_x = 0.1$ a.u.

trend also makes it possible for electrons to recollide with the nucleus as indicated by the black ellipse.

For the zero-Coulomb-potential case in Fig. 5(b), the cluster of electron trajectories remains on one side of the nucleus and has a stable propagation trend which is indicated by a horizontal black line. Recollision cannot happen in this case, and a gap between trajectory cluster and nucleus remains, as indicated by the black ellipse. Intuitively, the drift of the electron bunch in the real-Coulomb-potential case is induced by the effect of the parent ion’s Coulomb attraction on the electrons after tunneling ionization.

The electron trajectory drift in position space will also have effect in momentum space. In Figs. 5(c) and 5(d) we compare the momentum distributions with and without Coulomb potential. In the presence of a Coulomb potential [Fig. 5(c)] the photoelectrons populate significantly the positive-low-momentum region, region II ($0 \text{ a.u.} < p_x < 0.1 \text{ a.u.}$), and to a much lesser extent even the positive-midmomentum region, region III ($0.1 \text{ a.u.} < p_x < 0.5 \text{ a.u.}$). In contrast, in the absence of a Coulomb potential [Fig. 5(d)] all electrons concentrate in the negative momentum range: $p_x < 0$.

Based on the above, we classify photoelectrons ionized within a direct quarter cycle as drifted and undrifted electrons. We refer to photoelectrons as undrifted if their final momenta are in the hemisphere allowed by the Coulomb-field-free model [region I in Fig. 5(c)]. Correspondingly, electrons in regions II and III will be called low- and high-momentum drifted electrons, respectively. Moreover, we can see that the high-momentum drifted electrons (region III) form a structure with two long legs which cover a large transverse momentum

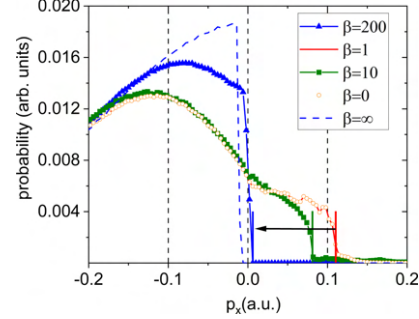


FIG. 6. Parallel momentum distributions of the first quarter cycle for different soft-core Coulomb potentials. Here, $\beta = \infty$ corresponds to the no-Coulomb-potential case.

range, while for the low-momentum drifted electrons (region II) the transverse momentum remains below 0.5 a.u.

Figure 6 illustrates how the soft-core parameter can gradually shift distribution from region I to regions II and III by plotting the momentum component p_x parallel to the polarization for several soft-core parameters. It can be seen that all the spectra for $\beta = 0, 1, 10, 200$ cover at least a part of the positive-low-momentum space below 0.1 a.u. The cutoffs in the low-momentum range, indicated by solid vertical lines, reveal that with increasing parameter β , the low-momentum coverage area decreases from about 0.1 a.u. to near-zero momentum as indicated by the black arrow.

In Fig. 7 we now illustrate how the two direct quarter cycles within one optical cycle contribute to the creation of the low-momentum interferences. Figures 7(a) and 7(b) show

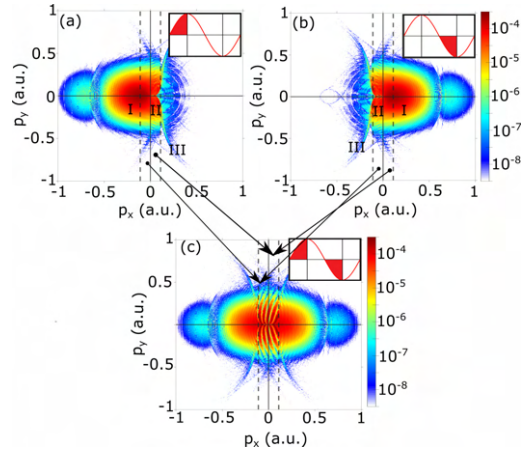


FIG. 7. Illustration of the interference scheme for the formation of the low-momentum fanlike interference structure. (a) and (b) Photoelectron momentum distributions for the first and third quarter cycles, respectively. The labels “I,” “II,” and “III” mark the undrifted, low-momentum drifted, and high-momentum drifted electrons, respectively. (c) Combined photoelectron momentum distribution of the two quarter cycles.

the momentum distributions for $\beta = 1$, and the first and third quarter cycles, respectively. Only in the coherent combination of the two quarter cycles shown in Fig. 7(c) does the fanlike interference pattern become visible in the low-momentum region. Notably, the high-momentum drifted electrons in region III do not visibly interfere with the undrifted electrons of the opposite quarter cycle.

Now that we have established that the Coulomb potential plays a key role in the formation of the low-momentum fanlike interference structure through low-momentum drifted electrons, we want to see whether the influence of the Coulomb potential can be correlated with specific parts of the electron trajectory [39]. In order to examine how the Coulomb field affects specific parts of the photoelectron trajectory, we now introduce a time-variable, soft-core Coulomb potential:

$$V(\mathbf{r}) = \frac{-Z}{\sqrt{[r + \beta(r)]^2}}, \quad \begin{cases} \beta = 0, & t < T_c \\ \beta = 200, & t > T_c \end{cases} \quad (7)$$

where T_c is defined as the time when the Coulomb potential is effectively turned off by setting a large soft-core parameter $\beta = 200$. Here, we choose four values for $T_{c,n}$, namely, $T_{c,n} = 3/4, 1, 3/2$, and 2 optical cycles. In addition, we want to point out that due to the insensitivity of undrifted electrons to the Coulomb potential as shown in Figs. 5(c) and 5(d), such time-dependent Coulomb potential and time partitions allow us to examine the effect of the Coulomb potential on the drifted electrons which are only from one direct quarter cycle.

In Fig. 8(a) we show the trajectories for a fixed $\beta = 0$ with the four critical times indicated. The chosen values for T_c divide the third-quarter-cycle trajectories into three different stages: In stage I, the electrons have just been ionized and begin to fly away from the nucleus through the action of the laser field. In stage II, the electrons are slowed down and pulled back towards the nucleus. Finally, in stage III, the electrons have their first return to the parent ion.

Figures 8(b)–8(e) show the distributions of the four times, $T_{c,n}$, when the Coulomb field is switched off. Whereas for $T_{c,1}$ in Fig. 8(b) the negative-momentum part of the low-momentum fanlike interference structure is completely missing, the cases $T_{c,2}$ [Fig. 8(c)], $T_{c,3}$ [Fig. 8(d)], and $T_{c,4}$ [Fig. 8(e)] exhibit an almost identical fanlike interference structure in the low-momentum range. This means that the formation of the low-momentum fanlike interference structure is largely complete before $T_{c,2}$. Thus the Coulomb field acts on the electrons just when they begin to fly away from the nucleus within 0.25 optical cycles.

In addition, the variable Coulomb potential allows us to narrow down the time window for the creation of the thin leglike structures [indicated by black ellipses in Figs. 8(d) and 8(e)] that are present in all momentum distributions featuring a Coulomb potential. While the leglike structure is absent before $T_{c,2}$ [if compared with Figs. 8(b) and 8(c)], a right-sided leg structure has formed by $T_{c,3}$ [Fig. 8(d)], and it is fully recovered after two full optical cycles [Fig. 8(e)]. Thus, in contrast to the fanlike low-momentum structure, the formation of the high-momentum legs occurs at one full optical cycle after ionization. Specifically, the leglike structures originate

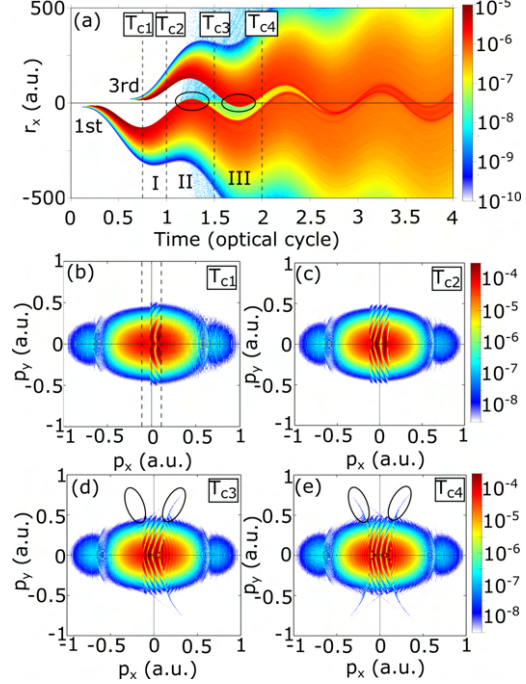


FIG. 8. Time partition of the electron dynamics after tunneling ionization and photoelectron momentum distributions for different critical time. (a) Electron trajectory distribution. The four black dashed lines correspond to times: $3/4, 1, 3/2$, and 2 optical cycles. The labels “I,” “II,” and “III” mark the three dynamics stages of the ionized electrons born within the third quarter cycle. The two black ellipses mark where the recollisions happen. (b)–(e) Photoelectron momentum distribution for the four critical times. In (d) and (e), the black ellipses mark the thin leglike structures.

in the large-angle scattering that can occur when the electron returns to the origin [black ellipses in Fig. 8(a)].

IV. CONCLUSION

In conclusion, we investigated the photoelectron momentum distributions of strong-field ionization in a 2000-nm laser field using the semiclassical two-step model. First, we disentangled various subcycle interference structures by resolving the contributions from different quarter-cycle combinations within one optical cycle. These distributions revealed several key subcycle interference structures of multiphoton ionization, among them a new extended temporal double slit and a low-momentum interference structure. We then studied the temporal and dynamical origin of the low-momentum interference structure. We found that it is caused by electrons that are born in opposite direct quarter cycles and undergo soft scattering in the parent ion’s Coulomb potential. Our analysis shows that the soft scattering occurs before the first turning point of the electron trajectory. We also identified large-angle (hard) scattering in the trajectories from direct quarter cycles at the moment of closest return.

Our results hold promise for the detection of electronic structure dynamics in the low-energy part of the photoelectron spectrum. Ultrafast postionization dynamics such as spin-orbit wave packets [40], or charge migration [41], cause a change in the ionic charge distribution and thus will leave a signature in the low-energy part of the photoelectron momentum spectrum. Using polarization-gated laser pulses not only will allow us to suppress other, purely symmetry-driven interferences [42] but also will enable ultrafast angular probing of the parent ion's charge distribution.

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4.3 Molecular semiclassical two-step model

4.3.1 Tunnel ionization in Molecules

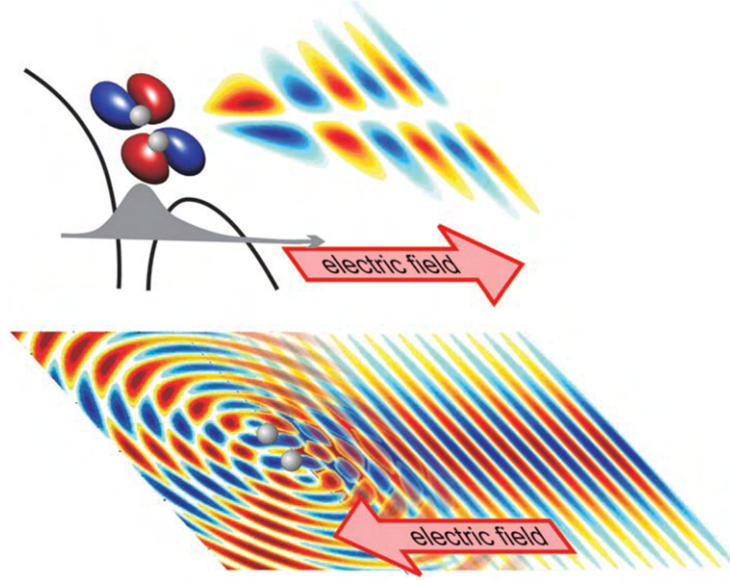


Figure 4.3: Tunneling produces a filtered projection of MO. Adapted from [90].

Comparing with the case of a hydrogen atom, the complexity of molecular ionization is that molecule has multiple Coulomb potentials and molecular orbitals. The two-center Coulomb potential of Br_2 can be expressed as follow:

$$V(x, y) = -\frac{Z_1}{\sqrt{x^2 + (y - \frac{R_0}{2})^2}} - \frac{Z_2}{\sqrt{x^2 + (y + \frac{R_0}{2})^2}} \quad (4.15)$$

Where R_0 is the internuclear distance, and $Z_1 = Z_2 = 0.5$ are the ionic-charges for two ion cores to make sure the long-range potential has the character of singly charged ion. Here, we align the Br_2 to be along the y axis which is perpendicular to the laser polarization direction to simulate the alignment case in our Br_2 experiment.

Due to the presence of the two-center potential as outlined in Equation 4.15, it is essential to employ Equation 4.5 for integrating the phase during the interaction between the laser pulse and the molecule, rather than relying on Equation 4.14.

Molecular orbitals can exhibit various shapes and phase structures. One approach to incorporate these characteristics in the ionization process involves treating tunnel ionization as a filter in momentum space. As depicted in Figure 4.3, during tunneling ionization, the molecular orbital is projected onto the outgoing wave, imprinting its amplitude and phase structure onto the continuum. The typical representation of this orbital projection involves a filter for the perpendicular component, $p_{\perp}$, of the orbital. The tunneled wave packet can be expressed as [90]:

$$\Psi(\mathbf{p}) \propto \langle \mathbf{p} | \Psi_i \rangle \exp \left(-\frac{\sqrt{I_p}}{\sqrt{2}F} p_{\perp}^2 \right), \quad (4.16)$$

where the first term, $\langle \mathbf{p} | \Psi_i \rangle$, is the initial wave function in the momentum space, and the exponential factor is the filter function caused by the tunnel barrier which is formed by the binding potential and the laser field. Here, to keep the consistency with our atomic SCTS model, we employ the Equation 2.8 to describe tunneling filter, and obtain the tunneled wave packet:

$$\Psi(\mathbf{p}) \propto \langle \mathbf{p} | \Psi_i \rangle \exp \left[-\frac{\kappa^3}{|3F(t_0)|} \right] \exp \left[-\frac{\kappa p_{\perp}^2}{2|F(t_0)|} \right], \quad (4.17)$$

where $\kappa = \sqrt{2I_p}$. It can be seen that the effect of the potential barrier, formed by Coulomb potential and laser field, along the laser polarization on the wave packet is also included through the first exponential term. Thus, the ionization rate for each electron trajectory is expressed as follow:

$$w(t_0^j, \mathbf{v}_0^j) \propto M(v_{\perp}^j) \exp \left[-\frac{2\kappa^3}{|3F(t_0)|} \right] \exp \left[-\frac{\kappa v_{\perp}^{j2}}{|F(t_0)|} \right], \quad (4.18)$$

where

$$M(v_{\perp}^j) = \int |\Psi_i(p_{\perp} = v_{\perp}^j, p_{\parallel})|^2 dp_{\parallel} \quad (4.19)$$

and the vector $\mathbf{v}_0^j$ is defined as $(v_x^j = 0, v_y^j = v_{\perp}^j)$, with $v_{\perp}^j$ being randomly assigned using the same method as discussed for the atomic SCTS model. The term $M(v_{\perp})$ represents the transverse velocity distribution of the initial wave function of the molecular orbital.

The remaining challenge is to obtain the molecular orbital in momentum space. To simplify the simulation of molecular orbitals, we employ an analytical form which was proposed for light diatomic molecules by Vladimir Usachenko et al. [91]. In this approach, the $\pi_{g,u}$ and $\sigma_{g,u}$ molecular orbitals in coordinate space are derived through a linear combination of atomic $2p$ orbitals. Subsequently, the orbitals in momentum space can be computed using the Fourier transform.

During the neutral dissociation of Br_2 , the molecular orbitals evolve into atomic orbitals, as illustrated in Figure 4.4. In this context, we follow the approach outlined in reference [74]. However, we focus specifically on the π_u orbital within the 0 – 25 fs timeframe, the σ_u orbital within 50 – 75 fs , and the σ_g orbital towards the end. These intervals are highlighted by three red circles. The rationale behind this selection is that these three orbitals are expected to be more easily observable in experiments compared to the three orbitals that are "too-close" within the 0 – 50 fs timeframe. Therefore, we utilize the momentum forms of these selected orbitals below:

$$\phi_{1\pi_u}(\mathbf{p}, \mathbf{R}) = \frac{i2^5 p \kappa_n^{7/2} \sin(\theta)}{\pi \sqrt{2} (p^2 + \kappa^2)^3} \frac{\cos[(\mathbf{p} \cdot \mathbf{R})/2]}{\sqrt{2[1 + S_{2p_x}(R)]}}, \quad (4.20)$$

$$\phi_{3\sigma_u}(\mathbf{p}, \mathbf{R}) = \frac{i2^5 p \kappa_n^{7/2} \cos(\theta)}{\pi \sqrt{2} (p^2 + \kappa^2)^3} \frac{\cos[(\mathbf{p} \cdot \mathbf{R})/2]}{\sqrt{2[1 + S_{2p_z}(R)]}}, \quad (4.21)$$

$$\phi_{3\sigma_g}(\mathbf{p}, \mathbf{R}) = \frac{i2^5 p \kappa_n^{7/2} \cos(\theta)}{\pi \sqrt{2} (p^2 + \kappa^2)^3} \frac{\sin[(\mathbf{p} \cdot \mathbf{R})/2]}{\sqrt{2[1 + S_{2p_z}(R)]}}. \quad (4.22)$$

where $\kappa = \sqrt{2I_p}$, R is the internuclear distance, and θ is the polar angle of electron with respect to the internuclear distance: $\cos(\theta) = (\mathbf{p} \cdot \mathbf{r})/pR$. The overlap integrals S_{2p_x} and S_{2p_z} of $2p$ orbitals are:

$$S_{2p_x}(R) = [1 + \kappa R + \frac{2}{5}(\kappa R)^2 + \frac{1}{15}(\kappa R)^3] \exp(-\kappa R), \quad (4.23)$$

$$S_{2p_z}(R) = [1 + \kappa R + \frac{1}{5}(\kappa R)^2 - \frac{2}{15}(\kappa R)^3 - \frac{1}{15}(\kappa R)^4] \exp(-\kappa R). \quad (4.24)$$

It is important to note that these orbitals we are discussing are not the true representation of Br_2 , as the actual orbitals are formed by $4p$ atomic orbitals, not $2p$. Moreover, the significant relativistic effect in Br_2 can impact the shapes of molecular orbitals. However, when it comes to strong field ionization, the primary factors are the symmetry and node structure of the orbitals [22, 92, 93]. Therefore, we maintain that these simplified molecular orbitals, with the correct symmetry, can still offer valuable predictions.

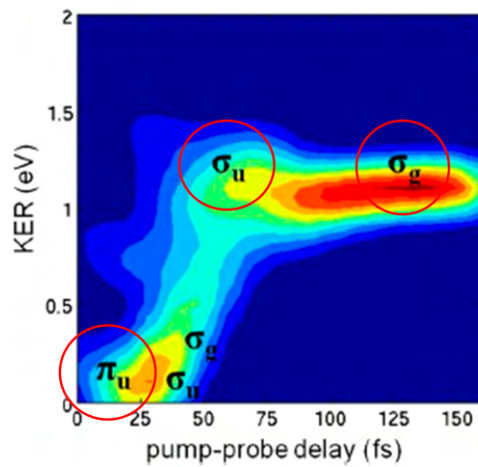


Figure 4.4: Simulated KER of Br^+ as a function of delay time for probing the neutral dissociation of Br_2 . The contributed molecular orbitals are indicated on the KER-delay distribution. The three molecular orbitals $\pi_u\sigma_u$ and σ_g are indicated by red circles. Adapted from [74].

4.3.2 Implementation of Br_2 SCTS model

In addition to changes in the symmetries of molecular orbitals, the internuclear distance R and ionization potential I_p will also change as Br_2 undergoes neutral dissociation. We estimate that R_0 will increase from the ground state equilibrium internuclear distance of $2.28 \text{ \AA}$ to $4.6 \text{ \AA}$ as Br_2 dissociates into σ_u and σ_g states [74]. However, regarding I_p , there is currently no information on its evolution during neutral dissociation. Therefore, we make the simple assumption that I_p will decrease from the value of 12.44 eV for the π_u orbital of Br_2 to 11.81 eV for the neutral Br atom. The summary of these initial state settings is presented in Table 4.1. The molecular orbitals ψ_i of Br_2 with these initial state settings are illustrated in Figure 4.5(a-c). It is worth noting that the molecular alignment is configured to be perpendicular to the laser polarization, as the neutral dissociation of Br_2 involves a perpendicular-transition process.

Table 4.1: Initial states for our SCTS simulations considering the different symmetries of Br_2 .

MO	R_0	I_p
π_u	$2.28 \text{ \AA}$	12.44 eV
$\sigma_{u,g}$	$4.6 \text{ \AA}$	11.81 eV

The molecular orbitals $\langle \mathbf{p} | \Psi_i \rangle$ corresponding to the specified initial-state configurations are illustrated in Figure 4.5(a-c). In this depiction, the molecular alignment is configured to be perpendicular to the laser polarization, aligning with the fact that the neutral dissociation of Br_2 is characterized by a perpendicular-transition process. The transverse velocity distributions $M(v_\perp)$ of these molecular orbitals are depicted by the blue curves in Figure 4.5(d-f). The wave functions and transverse velocity distributions reveal the node structures of different molecular orbital symmetries. In Figure 4.5(a-c), the different phases of the lobes are indicated by the various colors on the lobes of the molecular orbital. The different lobes separated by a node have a π phase difference. Here, we set the phase of the red color lobe to be $\phi_{mol} = \frac{\pi}{2}$, and the phase of the blue color lobe to be $\phi_{mol} = -\frac{\pi}{2}$. The phase structures for different molecular orbitals are also indicated in their transverse velocity distributions.

For the phase integration, due to the presence of the two-center potential as outlined in Equation 4.15, it is essential to employ Equation 4.5 for integrating the phase during the interaction between the laser pulse and the molecule, rather than relying on Equation 4.14. Furthermore, the total phase takes into account the phase of the lobe from which

the electron is ionized:

$$\Phi_{tot.}(t_0, \mathbf{v}_0^j) = \Phi(t_0, \mathbf{v}_0^j) + \phi_{mol}^j \quad (4.25)$$

where ϕ_{mol}^j is the phase the electron obtained from the molecular orbital lobe.

The impact of the tunneling filter on the transverse momentum is depicted in Figure 4.5 (illustrated by the red curves in panels d-f). Here, the transverse velocity dependent ionization rates $w(v_\perp)$, for different molecular orbitals, are calculated at the peak electric field strength of the laser field. It is evident that tunneling significantly suppresses the overall transverse momentum distribution, allowing only the central momentum range of $-1.0 \text{ a.u.} < p_\perp < 1.0 \text{ a.u.}$ to contribute. This implies that, in the case of Br_2 , the inner lobes of a molecular orbital contribute the most to strong field ionization. For instance, the σ_u orbital in Figure 4.5 exhibits a distinct four-lobe structure with the outer two lobes having higher probability than the inner ones. However, following quantum tunneling, the ionization rates of the inner lobes surpass those of the outer ones by two orders of magnitude!

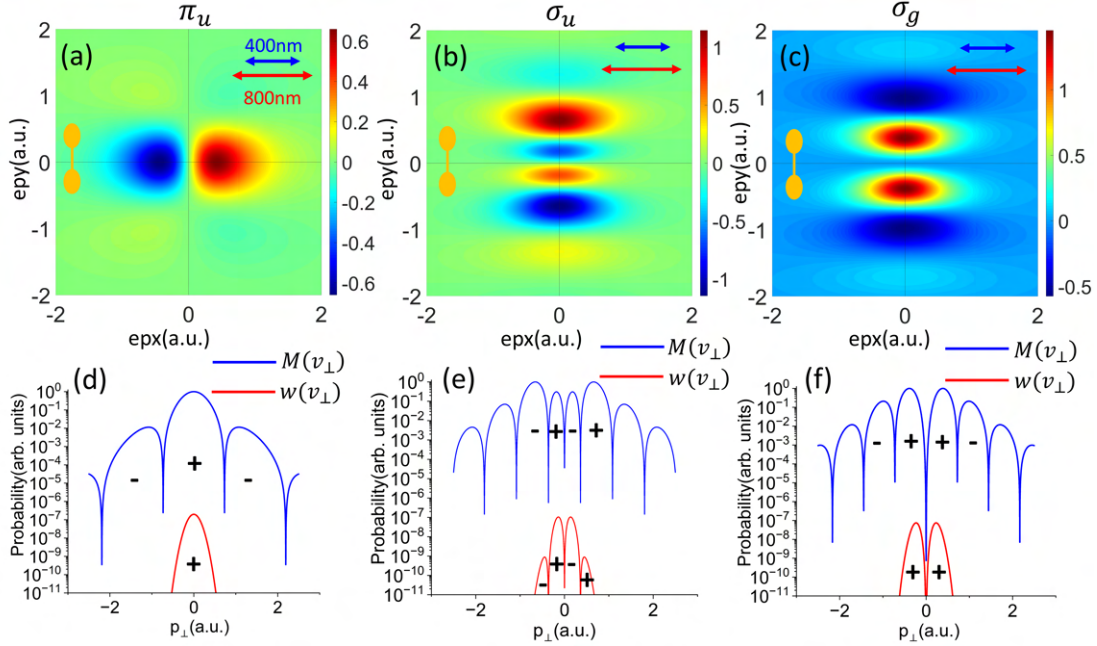


Figure 4.5: Different molecular orbitals in momentum space of Br_2 , $\langle \mathbf{p} | \Psi_i \rangle$, in light-molecule-approximation: (a) π_u orbital, (b) σ_u orbital, and (c) σ_g orbital. The color value represents the value of the Imaginary part of the wave functions in the Equations 4.20, 4.21, and 4.22. The blue and red color indicate the different phases of different molecular orbital lobes. The polarization configurations of blue and red laser pulses are indicated by blue and red arrows. The dissociating Br_2 is perpendicular to the laser polarization. (d-f) transverse velocity distributions $M(v_\perp)$ (blue curve) of these molecular orbitals and corresponding transverse velocity dependent ionization rate $w(v_\perp)$ (red curve) at the peak electric field strength of the laser field. The phase of molecular orbital lobe is indicated by $\pm$ signs: $+$ is for $\phi_{mol} = \frac{\pi}{2}$, and $-$ is for $\phi_{mol} = -\frac{\pi}{2}$.

4.3.3 I_p dependent ATI rings

Figure 4.6(a-c) shows the simulated photoelectron momentum distributions from different molecular orbitals of Br_2 . We can see that these distributions all have clear ATI rings and strong-field holography fringes. Furthermore, the normalized differential (ND) plots in Figure 4.6(d-f) show the differences between different molecular orbitals. The ND plot is calculated by:

$$ND = \frac{D_{sig} - D_{ref}}{D_{sig} + D_{ref}} \quad (4.26)$$

where the signal distribution D_{sig} and the reference distribution D_{ref} are both normalized.

The most apparent difference in the momentum distributions of the π_u orbital and the σ_g and σ_u orbitals is the presence of alternating blue-red rings in Figure 4.6(d,e). These rings signify a shift in energy between the sets of ATI peaks of the π_u orbital on one side and the σ orbitals on the other. As per Equation 2.3, this energy shift is attributed to the difference in ionization potential (I_p) between the two orbitals.

The shift in the ATI peaks results in distinct structures in the low momentum region for the different molecular orbitals. Illustrated in Figure 4.7, within the momentum range of $0.3 \text{ a.u.} < |p_{x,y}| < 0.3 \text{ a.u.}$, the π_u orbital exhibits a pronounced contrast with the σ_u orbital: the former displays a substantial ring-like structure, while the latter showcases a fan-like pattern concentrated around the origin. This structural disparity contributes to a blue inner ring in the ND plot, as depicted in Figure 4.7(c). The I_p dependence of the low momentum structure is exemplified in Figure 4.8 by examining the π_u orbital with varying ionization potential. It is evident that as the I_p increases from 0.434 a.u. to 0.457 a.u., the fan-like structure gradually transforms into a thick ring-like structure.

Figure 4.6(e) reveals the presence of a blue inner ring in the ND plot between the π_u and σ_g orbitals within the low momentum region. Consequently, the distinctive features of both the thick ring structure in the electron momentum distribution and the blue inner ring structure in the ND plot can be considered characteristic of the π_u orbital. These characteristics will serve as valuable indicators for identifying the π_u orbital in our Br_2 experiment.

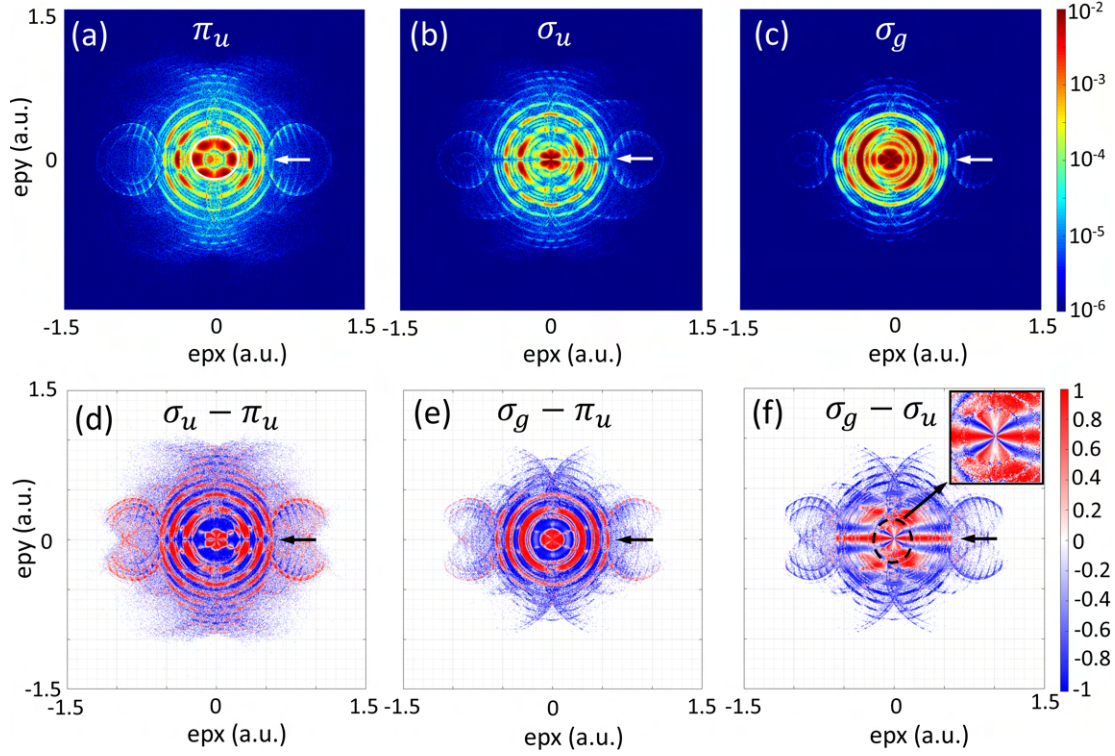


Figure 4.6: Simulated distributions of photoelectron momentum for distinct molecular orbitals are illustrated: (a) π_u orbital, (b) σ_u orbital, and (c) σ_g orbital. The laser pulse, with a wavelength of $\lambda = 800 \text{ nm}$ and intensity $I = 5 \times 10^{13} \text{ W/cm}^2$, is polarized perpendicular to the molecular axis of Br_2 . As indicated by the white arrows, the photoelectron momentum distributions for the π_u and σ_u orbitals display a central finger structure aligned with the laser polarization, while the σ_u orbital exhibits a minimum. (d-f) Displayed are normalized differential plots contrasting these photoelectron momentum distributions, with black arrows emphasizing distinct holography-induced structures in the normalized differential plots. The inset of panel (f) highlights a fan-like structure in the low momentum range: $|ep_{x,y}| < 0.2 \text{ a.u.}$.

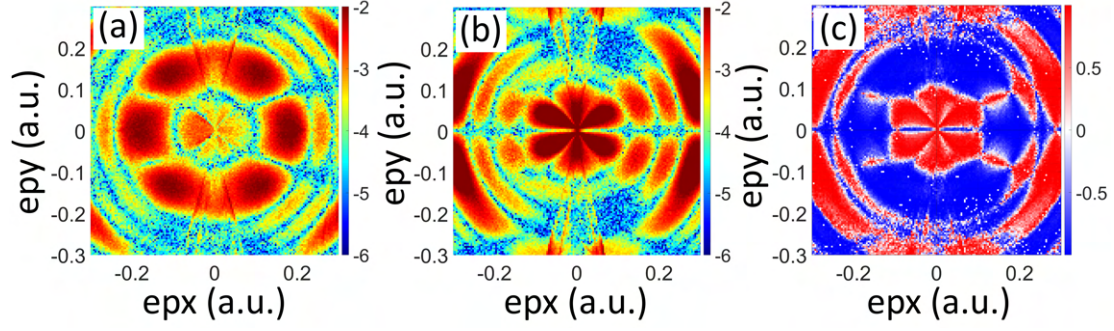


Figure 4.7: Low momentum regions of the data shown in (a) Figure 4.6(a), (b) Figure 4.6(b), and (c) Figure 4.6(d).

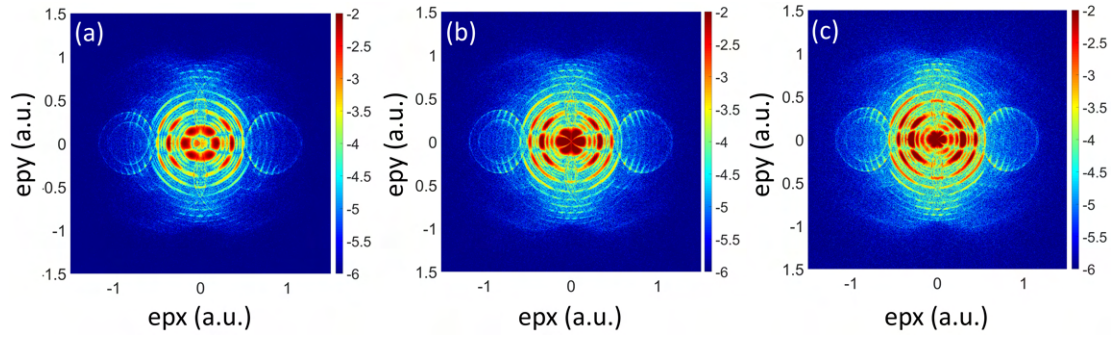


Figure 4.8: Electron momentum distributions for the π_u orbital with different I_p values: (a) $I_p = 12.44\text{eV}$, (b) $I_p = 12.12\text{eV}$, (c) $I_p = 11.81\text{eV}$.

4.3.4 Molecular-orbital-phase effect on strong-field-holography finger

Upon examining the strong field holographic interferences in 4.6(a-c), we find that both π_u and σ_g orbitals exhibit a central peak around $epy = 0$ a.u., as denoted by the white arrows. In contrast, the σ_u orbital displays a minimum at the same position. This discrepancy arises from variations in the phase structures of these molecular orbitals. Illustrated in Figure 4.5(d-f), the σ_u orbital features opposing phases in the two lobes near $p_\perp = 0$ a.u., whereas there is no phase change for the other two orbitals. Consequently, the absence of the central peak in the σ_u orbital can be attributed to destructive interference between electrons originating from the two lobes surrounding $p_\perp = 0$ a.u..

The strong field holography fringes originate in the electron scattering on the nucleus. Electrons possessing substantial initial transverse momentum tend to evade the nucleus upon their return, resulting in a minimal contribution to holography fringes. Examining the middle finger in Figure 4.6(a,c), it becomes apparent that it emerges at $epy = 0$ a.u. with a relatively narrow transverse momentum range. This middle finger is a consequence of electrons being ionized within a small initial transverse momentum vicinity around 0 a.u.. Therefore, when the two lobes of the orbital on either side of $p_\perp = 0$ a.u. exhibit opposite phases, as depicted in Figure 4.9(a), destructive interference occurs within a limited momentum range (indicated by the shaded area). This interference suppresses the middle finger, resulting in a minimum at $epy = 0$ a.u., as illustrated in Figure 4.9(b). In contrast, Figures 4.9(c-d) depict the scenario of the σ_g orbital, revealing constructive interference around $p_\perp = 0$ a.u. due to the identical phases of the two orbital lobes.

The molecular orbital-dependence of the central holographic peak is evident in the ND plots of the electron momentum distributions between the various molecular orbitals, as depicted in Figure 4.6(d-f). Additionally, the ND plot contrasting σ_u and σ_g orbitals reveals a fan-like pattern (depicted in the inset of Figure 4.6(f)) within a narrow momentum range of $|ep_{x,y}| < 0.2$ a.u.. This unique fan-like structure arises from the distinct phase structures inherent in the two molecular orbitals.

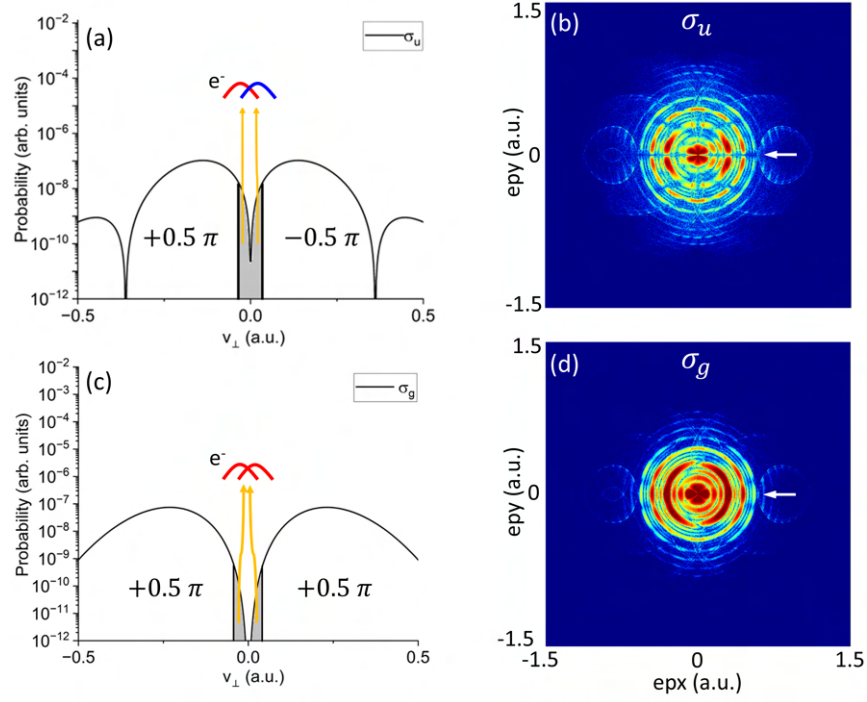


Figure 4.9: Visualization of the interference choices within the low initial transverse momentum range for two molecular orbitals: destructive interference for the σ_u orbital and constructive interference for the σ_g orbital. Panels (a) and (c) show the distributions of the initial transverse momentum, while panels (b) and (d) present the corresponding 2-dimensional photoelectron momentum distributions.

4.3.5 Difference of molecular and atomic ionization in electron momentum distribution: transverse-momentum-enhancement

In addition to the molecular orbital evolution, the neutral dissociation of Br_2 involves a process of structural transformation, wherein the two-center molecule ultimately transitions into single-center atoms. Common sense suggests that such a structural change should alter the structures induced by rescattering in the electron momentum distribution. This is because rescattering occurs on the nucleus, and any modification of the Coulomb center will impact the trajectory of electrons scattered on it. To explore this effect, we conducted simulations of electron momentum distributions by varying the internuclear distance R_0 . Equation 4.15 reveals that when $R_0 = 0$, V becomes an atomic potential, while $R_0 \neq 0$ corresponds to the molecular scenario. In this context, our focus is solely on the internuclear-distance effect. Therefore, we exclude consideration of the MO structure in the initial stages, concentrating only on I_p and R_0 to simulate the physical properties of a molecule or atom. Consequently, if we exclusively consider the initial molecular orbital π_u and the final atomic orbital $4p$, their initial ionization parameters are as follows: In Figure

Table 4.2: Initial states for SCTS simulations only considering molecular and atomic structure.

Orbital	R_0	I_p
$Br_2(\pi_u)$	$2.28\overset{\circ}{A}$	12.44eV
$Br(4p)$	$0.0\overset{\circ}{A}$	11.81eV

4.10 we show the electron momentum distributions from the π_u orbital of Br_2 and the $4p$ orbital of Br . Two simulation approaches were employed, each involving the restriction of ionization to different optical cycles. The first approach, a multi-cycle type, confines ionization events to four optical cycles, while the second, a single-cycle type, limits ionization to a single optical cycle.

In the multi-cycle simulations, Figure 4.10(c) illustrates that the ND plot exhibits a structure of shifted ATI-rings and a blue, inner ring structure reminiscent of Figure 4.6(d,e). These features arise from the ionization potential differences for the two orbitals. Notably, the ND plot in the multi-cycle simulation reveals an enhancement in the high transverse momentum segment (within the black ellipse: $0.4 \text{ a.u.} < ep_y < 1.0 \text{ a.u.}$), indicating that atomic bromine can produce electrons with larger momentum in the perpendicular direction.

Conversely, in single-cycle simulations, all structures relevant to above-threshold ionization vanish. However, the enhancement at high transverse momentum becomes more pronounced, as demonstrated in Figure 4.10(f). This implies that the observed transverse momentum enhancement originates from the dynamics associated with single-cycle ionization.

In Figure 4.11, we aim to emphasize the distinctive features originating from both multi-cycle and single-cycle processes on ND plots. To achieve this, we present radial momentum distributions derived from the ND plots by integrating the total difference values at p_r , where $p_r = \sqrt{e_{p_x}^2 + e_{p_y}^2}$. The distribution associated with the multi-cycle scenario (blue line in Figure 4.11(a)) exhibits an oscillation structure aligning with the shifted ATI-ring pattern. The first minimum is at $p_r = 0.2$ a.u., corresponding to the blue-inner ring structure in the ND plot. For larger momenta, the average ND rises in conjunction with the oscillation amplitude until $p_r \approx 0.6$ a.u..

Conversely, the distribution for the single-cycle case (red line in Figure 4.11(a) and (b)) lacks oscillations and does not exhibit a minimum at $p_r = 0.2$ a.u.. It is evident that the increase in the radial momentum distribution begins around $p_r = 0.3$ a.u. and forms two peaks. To retrieve the center positions of these peak-like distributions we apply standard Gauss peak fitting on each peak respectively and obtain two positions: $p_r = 0.65$ a.u. (red dashed curve in Figure 4.11(b)) and $p_r = 0.93$ a.u. (green dashed curve in Figure 4.11(b)), aligning with the transverse-momentum enhancement observed in Figure 4.10(f). Moreover, the Gauss single-peak fittings shown in Figure 4.11(a-b) display a general enhancement peak feature in the atomic ionization case. In this thesis, all Gauss peak fittings are standard and empirical to identify a peak structure without any justification for the shape of the distribution.

In summary, the peak structure in the high radial-momentum region signifies a critical distinction between a molecule and an atom in terms of electron momentum distribution. It provides a means to identify the structural transformation of Br_2 neutral dissociation in experimental observations.

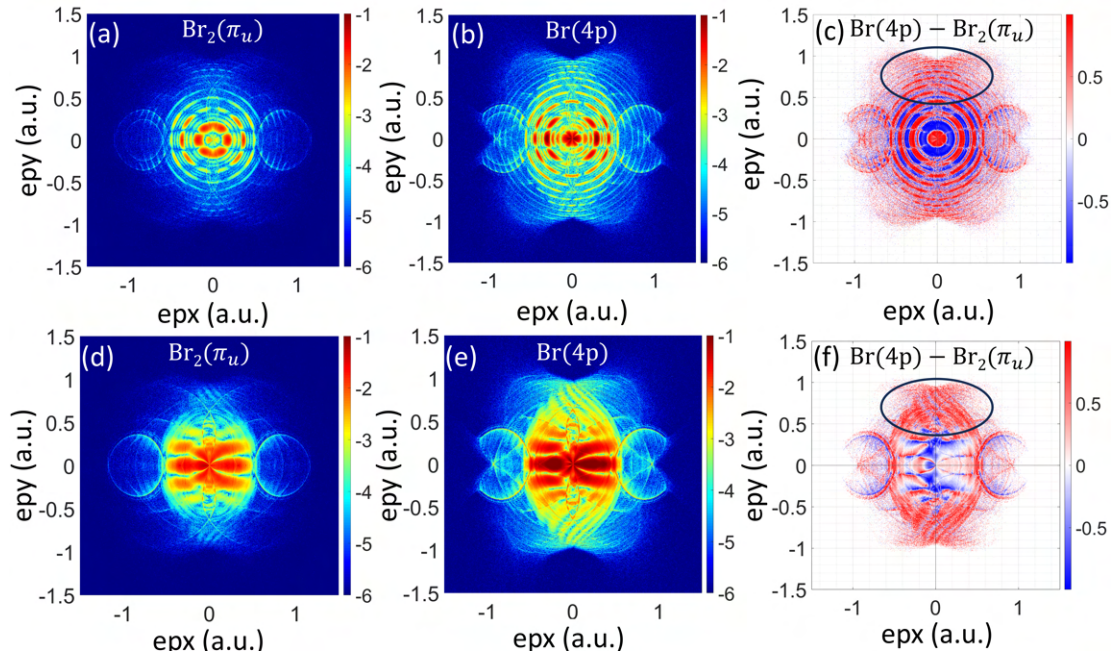


Figure 4.10: Electron momentum distributions for Br_2 molecule and Br atom. (a,b) are multi-cycle simulations and (d,e) are single-cycle simulations. (c) and (f) are the ND plots. The black ellipses indicate the transverse-momentum enhancement.

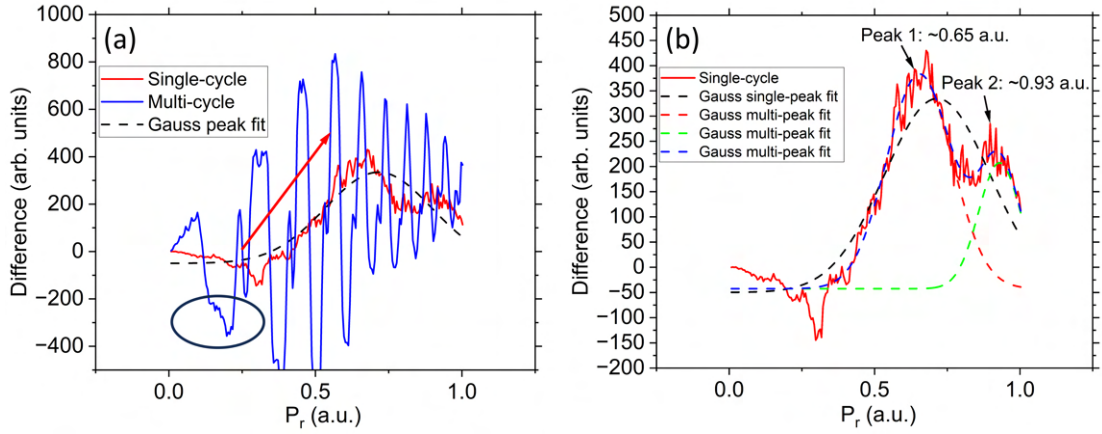


Figure 4.11: Radial momentum distributions of the ND plots in Figure 4.10(c) and (f). In panel (a) the blue curve is the radial momentum distribution from the multi-cycle simulations. The red curve from the single-cycle simulations are displayed as comparison. The black dashed curve is the Gauss single-peak fitting for the radial momentum distribution of the single-cycle simulations. In panel (b) the radial momentum distribution of single-cycle simulations is enlarged. The black dashed curve shows the Gauss single-peak fitting. The blue curve is a Gauss multi-peak fitting. The Gauss single-peak fittings by red and green curves for the two peaks reveal two peak positions at $p_r = 0.65$ a.u. and $p_r = 0.93$ a.u..

4.3.5.1 Effect of ion charge distribution on photoelectron transverse-momentum-enhancement

The increase in transverse momentum during atomic ionization is attributed to differences in target structure, ionic charge, or ionization potential, as these represent the sole distinctions between atoms and molecules in our simulation. Figure 4.12 illustrates the distinct target structures in the two scenarios. Notably, in atomic ionization, a single ion core carries a +1 charge, whereas in molecular ionization, the +1 charge is distributed across two ion cores. Following the established convention in theoretical studies of strong-field ionization [21,94], the +1 charge is assumed to be evenly shared between the two ion cores, as depicted in Figure 4.12(a). To investigate the impact of ionic charge on transverse momentum enhancement, we conduct single-cycle simulations on both molecules and atoms, varying the ionic charge for each case.

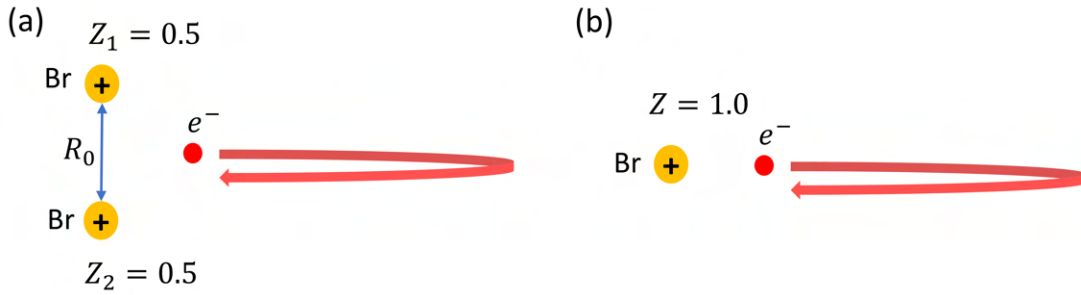


Figure 4.12: Target structure for molecular (a) and atomic (b) simulations. The ionic charges of each ion core are denoted by Z_1 , Z_2 , and Z for the two scenarios. The electron recollision trajectory is highlighted by the red curved arrows.

Figure 4.13 displays the radial momentum distributions of ND plots featuring various ionic charge configurations for the two scenarios. In this context, the electron momentum distribution with $Z_1 = Z_2 = 0.5$ serves as the reference for the molecular case, while $Z = 0.5$ is the reference for the atomic case. It is important to note that, in each case, the ionization potential remains constant, allowing for the exclusive exploration of the effect of ionic charge.

The initial parameters for both cases are summarized in Table 4.3. In Figure 4.13, it is evident that both scenarios exhibit a peak enhancement structure beyond $p_r = 0.5$ a.u.. This observation indicates that all the considered ionic charge configurations result in a transverse momentum enhancement when compared to their respective reference momentum distributions.

Table 4.3: Initial states for investigating the ionic-charge effect on transverse-momentum-enhancement.

Case	I_p	R_0	$Z, Z_{1,2}$
Molecule	12.44 eV	$2.28 \text{ \AA}$	varying
Atom	11.81 eV	$0.0 \text{ \AA}$	varying

In the context of molecular ionization, it is evident that the height of the enhancement peak increases proportionally to the ionic-charge asymmetry. The configuration with $Z_1 = 1.0, Z_2 = 0.0$ exhibits the highest asymmetry, concentrating all the charge in a single ionic core. Conversely, the configuration with $Z_1 = 0.6, Z_2 = 0.4$ demonstrates a lower asymmetry, approaching the symmetrical configuration of $Z_1 = Z_2 = 0.5$. This observation implies that the transverse momentum enhancement is contingent upon electron scattering on one ionic core within a molecule, with the charge of that ionic core dictating the scattering intensity. Specifically, a ionic core carrying more charge leads to a greater scattering of electrons in the transverse direction.

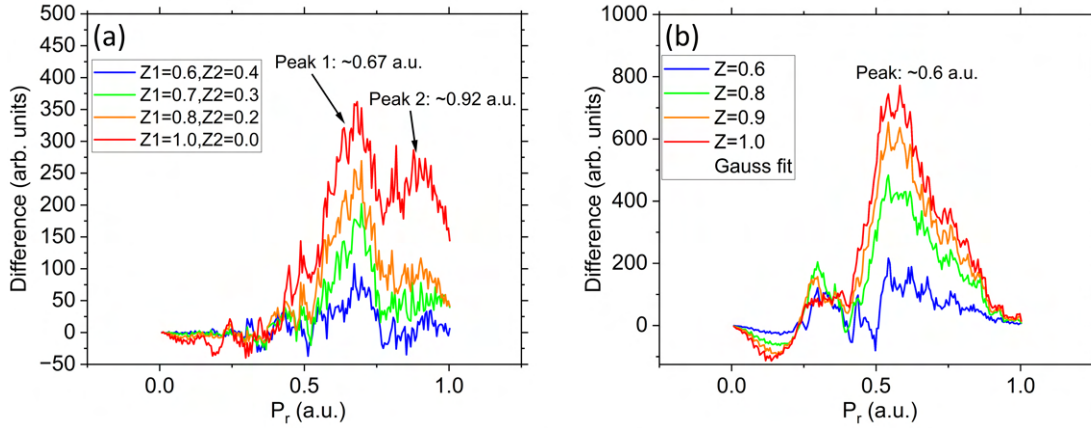


Figure 4.13: Radial momentum distributions of ND plots with different ionic charge configurations for molecular ionization (a) and atomic ionization (b).

In the case of atomic ionization, where there is a singular ionic core, we can observe the growth of the transverse momentum enhancement in tandem with the increase in ionic charge on that single ionic core. This observation aligns with the above analysis for the molecular case.

When comparing the two scenarios depicted in Figure 4.13, it is notable that the ra-

dial momentum distributions for molecular ionization exhibit a double-peak structure. The higher peak is positioned around 0.67 a.u. , while the lower peak is approximately at 0.92 a.u. . In contrast, the atomic ionization case displays a single sharp peak. Interestingly, the distribution for Br_2 and Br in Figure 4.11(b) mirrors the same double-peak structure observed in the molecular ionization case. This implies that the origin of the double-peak structure lies in the reference electron momentum distribution corresponding to the charge configuration of $Z_1 = Z_2 = 0.5$.

Figure 4.14 presents the electron momentum distributions for the two cases with different ionic charge configurations. Both scenarios exhibit a distinct transverse momentum enhancement feature in the ND plots between the two momentum distributions, consistent with the observation in Figure 4.10. Furthermore, the horizontal finger-like fringes in the ND plots indicate that the ionic charge also influences the strong-field holography fingers. Specifically, in Figure 4.14(d,e), it is evident that the strong-field holography fingers become more pronounced with $Z = 1.0$ compared to $Z = 0.5$.

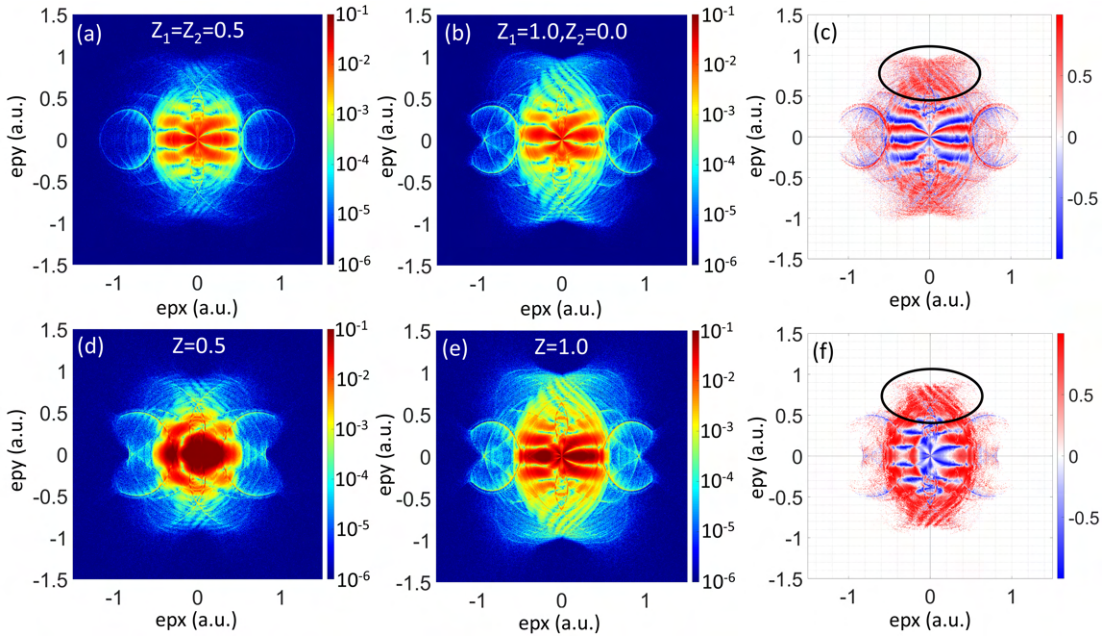


Figure 4.14: Electron momentum distributions of different ionic-charge configurations for molecular ionization (a-c) and atomic ionization (d-f). (c) and (f) are the ND plot between two momentum distributions for each case. The black ellipses indicate the transverse-momentum enhancement.

4.3.5.2 Effect of ionization potential on photoelectron transverse-momentum-enhancement

In this section, we explore the impact of the ionization potential on the transverse momentum enhancement. As indicated in Table 4.4, the ionization potential undergoes a change from 12.44 eV to 11.81 eV when a Br_2 molecule transforms into a Br atom. To illustrate the I_p effect on the electron momentum distributions presented in Figure 4.10, we maintain control over the internuclear distance R_0 and the ionic charge configurations for both molecular and atomic cases. We then vary the I_p and generate the ND plot between the electron momentum distributions with different I_p . The electron momentum distributions with $I_p = 12.44$ eV serve as the reference distributions. The initial parameters are summarized as shown in Table 4.4. In Figure 4.15(a), the radial momentum distributions of ND

Table 4.4: Initial states for investigating the ionization-potential effect on transverse-momentum-enhancement. The ionization potentials for the reference (ref.) and the signal (sig.) electron momentum distributions are indicated.

Case	R_0	$Z, Z_{1,2}$	I_p
Molecule	$2.28\overset{\circ}{A}$	$Z_1 = 1.0, Z_2 = 0.0$	ref.:12.44 eV, sig.: 11.81 eV
Atom	$0.0\overset{\circ}{A}$	$Z = 1.0$	ref.:12.44 eV, sig.: 11.81 eV

plots for the two cases are presented. Notably, a single peak is observed at a low radial momentum of 0.54 *a.u.*, a marked deviation from the patterns observed in Figure 4.11(b) and Figure 4.13(a). In Figure 4.15(b), the ND plot for the atomic case similarly does not exhibit a transverse momentum enhancement feature in the high radial momentum range of 0.5 *a.u.* $< p_r < 1.0$ *a.u.*, contrasting the observations in Figure 4.10 and Figure 4.14. These findings indicate that the difference in ionization potential between Br_2 and Br does not lead to transverse momentum enhancement.

4.3.5.3 Effect of internuclear distance on photoelectron transverse-momentum-enhancement

In this section, we will demonstrate the influence of the internuclear distance the transverse momentum enhancement. Given the focus on molecular ionization, we set the electron momentum distribution at the equilibrium distance of $R_0 = 4.3$ *a.u.* for Br_2 as the reference distribution. The ionic charge distribution of $Z_1 = Z_2 = 0.5$ will be kept constant. The only variation we will consider is the internuclear distance R_0 .

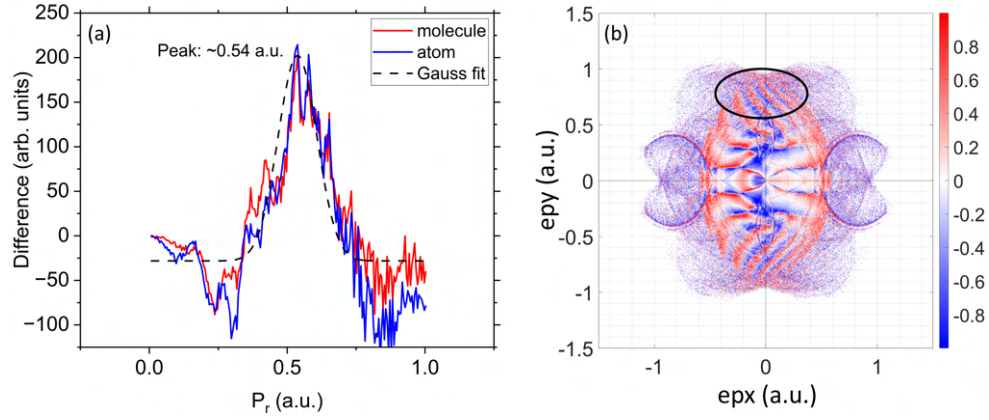


Figure 4.15: (a) Radial momentum distributions of ND plots for molecular and atomic ionization cases. The black dashed curve of the single-peak Gauss fitting shows the peak position at about 0.54 a.u. . The Gauss peak fitting is standard and empirical to identify a peak structure. (b) The ND plot between the two electron momentum distributions for atomic ionization case.

In Figure 4.16, we show the radial momentum distributions of normalized distribution (ND) plots, each corresponding to a different internuclear distance. Notably, there is an observable increase in the height of the enhancement peak as the internuclear distance decreases. Moreover, it can be seen that the position of the enhancement peak is around $p_r = 0.7 \text{ a.u.}$

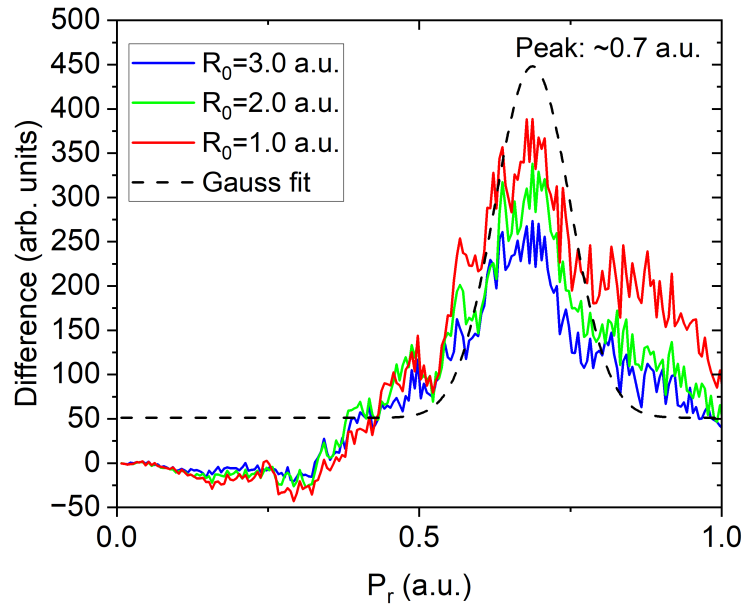


Figure 4.16: Radial momentum distributions of ND plots with different internuclear-distance in Br_2 ionization. The black dashed curve is the single-peak Gauss fitting for the radial momentum distribution of $R_0 = 1.0$ a.u., which indicates a peak position of about 0.7 a.u.. The Gauss peak fitting is standard and empirical to identify a peak structure.

4.3.6 Summary for the molecular SCTS model

In summary, we have expanded the atomic semiclassical two-step model by incorporating molecular orbitals and molecular geometry into our framework. To address various aspects of the Br_2 experiment, we conducted two types of molecular simulations.

The first simulation type incorporates molecular orbitals, utilizing a simplified analytical formula to describe these orbitals. This simulation focuses on interference phenomena originating from molecules. Predictions are made for electron momentum distributions from distinct orbital symmetries of Br_2 during its neutral dissociation. For intercycle interference, we explored ionization potential-dependent ATI-ring structures and identified a characteristic inner ring structure for the π_u orbital of Br_2 . In the realm of intracycle interference, diverse strong-field holography finger structures arising from different Br_2 molecular orbitals are elucidated by analyzing the phase structure of the orbitals. Our findings illustrate that constructive and destructive interferences from orbital phases contribute to the formation of distinct strong-field holography finger structures.

The second simulation type hones in on the scattering effects induced by molecular nuclei in electron momentum distributions, excluding molecular orbitals from consideration. Through simulations of the electron momentum distributions of both Br_2 molecules and Br atoms, we identify a transverse momentum enhancement structure for the atom. We systematically explore the impacts of ionic charge, ionization potential, and internuclear distance on this enhancement structure. Our results underscore the pivotal role of ionic charge in shaping this structure, while the internuclear distance of the molecule also exerts an influence on the enhancement structure.

Chapter 5

Experiment techniques

In this Chapter we will introduce the techniques employed in our experiments to resolve the photodissociation of Br_2 . The technical part of the experiment can be divided into the optical part, which involves the production of femtosecond laser pulses of different color with a variable delay, on one side, and the molecular target preparation and fragment detection on the other.

5.1 Laser system

The process of strong field ionization and molecular dissociation demands the utilization of high-intensity laser fields. Currently, the most commonly employed method to generate such intense laser fields combines Kerr-lens modelocking (KLM) with chirped pulse amplification (CPA). KLM harnesses the optical Kerr effect within a titanium-doped sapphire (Ti:Sapphire) crystal to produce ultrashort laser pulses [95–98]. As shown in Figure 5.1(a), the Kerr effect induces self-focusing through self-amplitude modulation, thereby enhancing the alignment between the central mode TEM_{00} and the crystal. This enhancement allows for the preferential amplification of the TEM_{00} mode within the oscillator. However, it is important to note that the self-phase modulation caused by the Kerr effect will lead to pulse elongation, necessitating subsequent dispersion compensation.

The femtosecond laser pulses generated by the oscillator are subsequently amplified using chirped pulse amplification (CPA) to attain higher intensity levels [99, 100]. Figure 5.2 illustrates the underlying concept of CPA. Initially, the laser pulses are temporally stretched through the use of a grating pair. These stretched pulses are then directed into

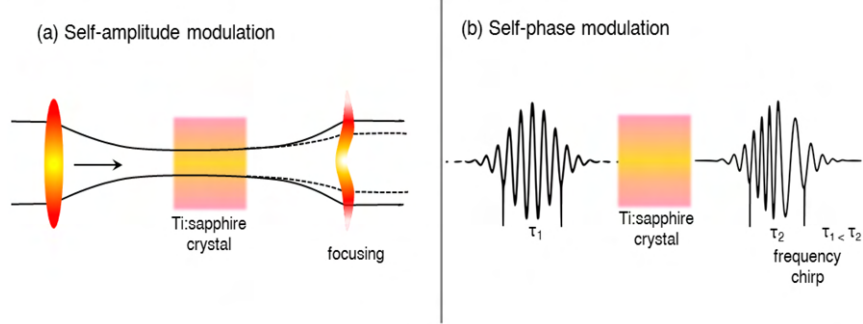


Figure 5.1: Illustration of self-amplitude and self-phase modulation induced by nonlinear optical Kerr effect in a Ti:sapphire crystal. (a) Self-amplitude modulation enhances mode-locking by self-focusing effect, hence, compress the pulse. (b) Self-phase modulation results in an elongated pulse due to increased chirp.

another Ti:Sapphire cavity, where their energy is increased. Finally, the picosecond pulses are recompressed back to the femtosecond scale while maintaining high energy levels. In our experiment, we employed a commercial Ti:Sapphire laser system, specifically the Coherent Legend Elite Cryo model. The laser system is initially seeded by a Ti:Sapphire oscillator, the Coherent Micra, which delivers 800 nm pulses with a duration of $20\text{ femtoseconds (fs)}$ and an energy of 1 nanojoule (nJ) at a repetition rate of 80 MHz . To further enhance the pulse energy, we employed two amplification stages.

The first amplification stage consists of a stretcher, a regenerative amplifier (Regen), and a single-pass amplifier (SPA). Both the Regen and SPA are pumped by an Evolution HE 75 system, providing 25 W of power at a 10 kHz repetition rate for each of the two amplifiers. The picosecond pulses generated at the output of this stage have an energy of $1.1\text{ millijoules (mJ)}$ at a 10 kHz repetition rate, or an average output power of about 11 W .

The second amplification stage, a Coherent Cryo system, includes an additional SPA pumped by a second Evolution HE 75 system, delivering 50 W of power. After passing through both amplification stages, the pulses are compressed in an integrated grating compressor. Thus, we obtained laser pulses with a wavelength of 800 nm , a pulse duration of 25 fs , and an energy of 1.6 mJ at a 10 kHz repetition rate. The complete laser system is schematic illustrated in Figure 5.3.

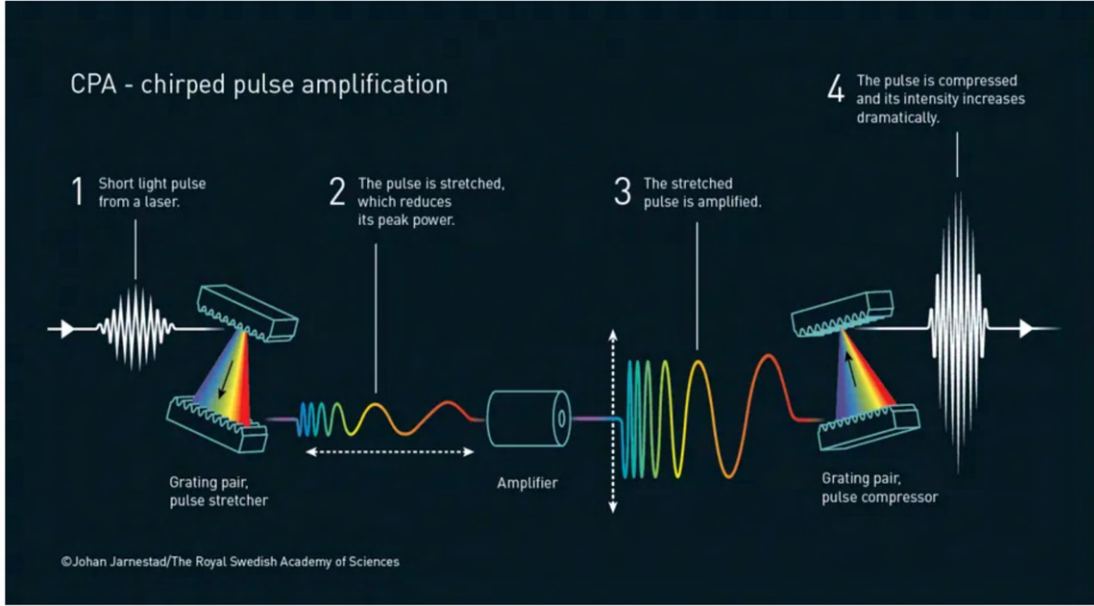


Figure 5.2: Illustration of chirped pulse amplification: The input pulse is first stretched temporally and spectrally, then it is amplified, finally, it is compressed. Taken from [101].

5.2 COLTRIMS

COLTRIMS, short for "COLd Target Recoil Ion Momentum Spectroscopy," is a well-established technique [102], which we employed in this work to measure the momenta of ions and electrons generated when a cold target interacts with a strong laser pulse. The measurement principle of COLTRIMS is depicted in Figure 5.4.

The process begins with an atomic or molecular beam operating at high stagnation pressure, which is directed through a small nozzle with a diameter of $30\text{ }\mu\text{m}$. The nozzle is mounted to a cold-finger, which can be cooled with a Helium refrigerator (Leybold COOLPAK 4000). However, in our case, we did not use the capability to precool the gas. This expansion of the pressurized gas through the nozzle into a high vacuum (10^{-4} mBar) creates a supersonic expansion. A skimmer (diameter $300\text{ }\mu\text{m}$) positioned several millimeter above the nozzle selects the coldest portion of the expanding gas. When the cold gas jet is introduced into the spectrometer, a laser beam is precisely focused onto it using a 5cm parabolic mirror.

The spectrometer consists of a vertical stack of copper electrodes that generate a uniform electric field. Within this electric field, both electrons and ions are directed toward

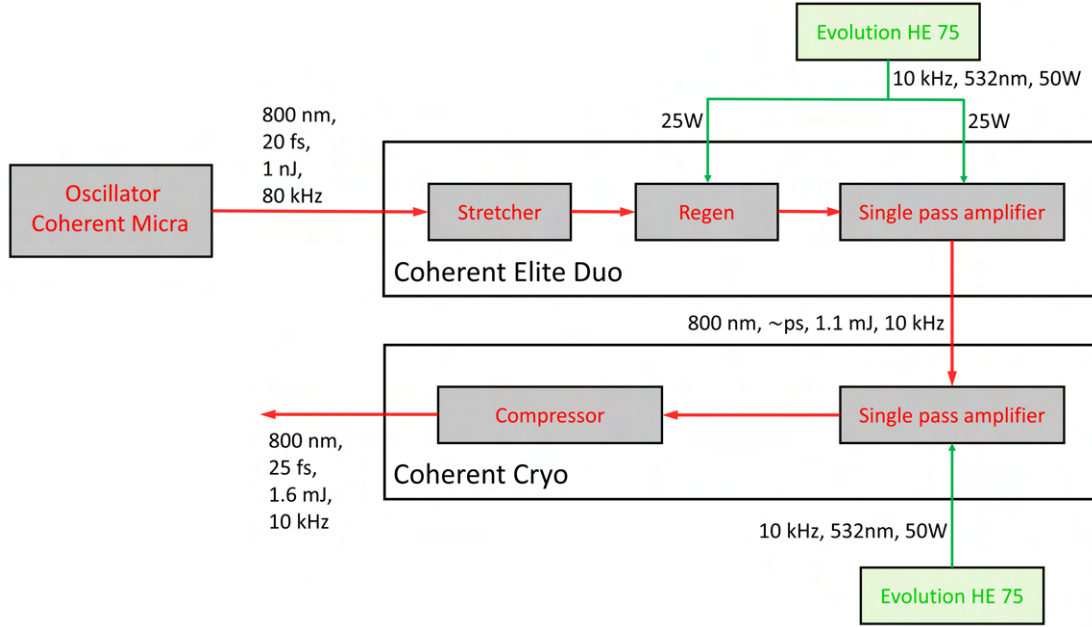


Figure 5.3: Illustration of the Ti:Sapphire laser system in JASLab. It contains an oscillator and two amplification stages.

their respective detectors located at opposite ends of the spectrometer. The detectors record the positions of impact and the arrival times, which are then converted into three-dimensional momenta for both electrons and ions.

To enhance electron detection, two Helmholtz coils are placed around the vacuum chamber to create an additional uniform magnetic field parallel to the electric field. This significantly dramatically increases the solid angle for electron detection such that 4π detection is achieved for electron energies up to 30 eV . Given the high laser field intensity (approximately 10^{14} W/cm^2) used in our experiment, nearly all atoms and molecules within the focal volume have a high probability of ionization. Therefore, maintaining an ultra-high vacuum (UHV) environment (approximately 10^{-10} mbar) is imperative to maintain an ionization rate of around 0.1 ion per laser pulse. This condition is necessary to be able to reliably correlate photoelectrons with their photoions. Even when photoelectron-photoion correlation is not required, such as in Coulomb explosion experiments, there is still the need to mitigate the detrimental influence of space charge effects on the momentum resolution.

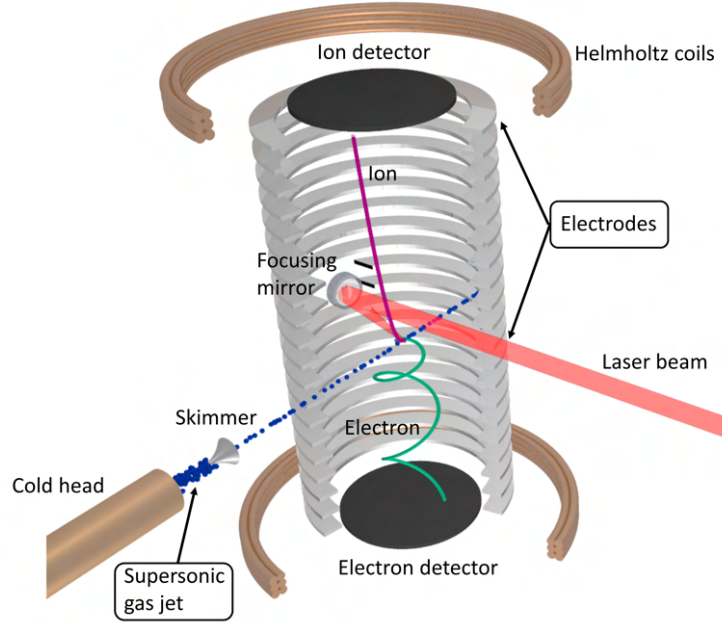


Figure 5.4: Schematic diagram of a COLTRIMS apparatus

5.2.1 Vacuum chambers

One of the most prominent components of a COLTRIMS apparatus is a system of interconnected vacuum chambers. The design schematics of these chambers are depicted in Figure 5.5. The source chamber, housing the gas nozzle and skimmer, is responsible for generating the cold molecular beam. Following this, the collimator chamber, equipped with a piezo-electric slit with an aperture of $0 - 300 \mu m$, further collimates the molecular beam before it enters the main chamber. The main chamber, serving as the core of the setup, houses the spectrometer along with electron and ion detectors. Finally, the dump chamber functions as the destination for the molecular beam once the measurements are complete.

To achieve ultra-high vacuum (UHV) conditions within the main chamber, a series of turbo-molecular pumps are employed across these chambers. Specifically, the source chamber utilizes two pumps with flow rates of $200 l/s$ and $500 l/s$, the collimator chamber relies on a single pump with a flow rate of $200 l/s$, and the main chamber employs two pumps with flow rates of $200 l/s$ and $500 l/s$. These pumps are effective in reducing the chamber pressure to approximately $10^{-9} mbar$. In the case of the main chamber,

an additional cryogenic pump is utilized to further decrease the pressure to around $< 10^{-10}$ mbar.

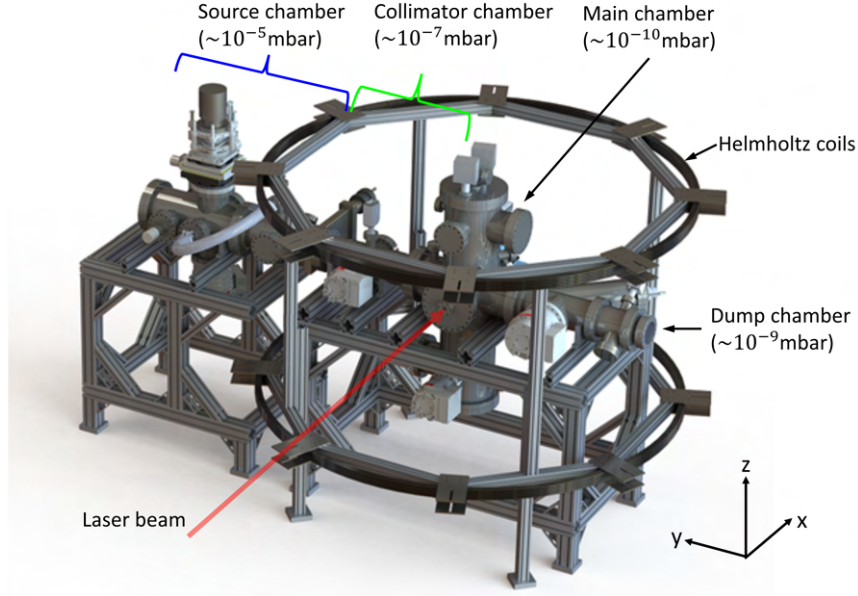


Figure 5.5: Rendering of the vacuum chambers in our COLTRIMS apparatus. The operational pressures for each chamber are indicated. In the lower right corner, three black arrows establish the coordinate system for COLTRIMS. Adapted from [103].

5.2.2 Gas jet

In a COLTRIMS experiment, the molecular beam is cooled through a process known as supersonic expansion, achieved by expanding the gas from a high-pressure volume into a vacuum. This process creates a zone of silence [104], where all gas molecules move at the same speed without interacting, effectively reducing the internal temperature of the gas to a few Kelvin. Figure 5.6 illustrates the structure of the zone of silence resulting from supersonic expansion.

Our COLTRIMS jet apparatus is shown in Figure 5.7. It consists of a cold head attached to a long cold finger, with a removable nozzle plate mounted to the end of it. In the actual setup, the cold finger is connected to a helium compressor to pre-cool the cold head and gas before it passes through the nozzle. Additionally, a heater is attached to the cold finger near the nozzle to preheat the gas if necessary. For instance, in our Br_2 experiment, we

disable the helium supply to the cold finger and regulate the heater to maintain the cold head at approximately 40°C . This is done to prevent nozzle clogging from Br_2 .

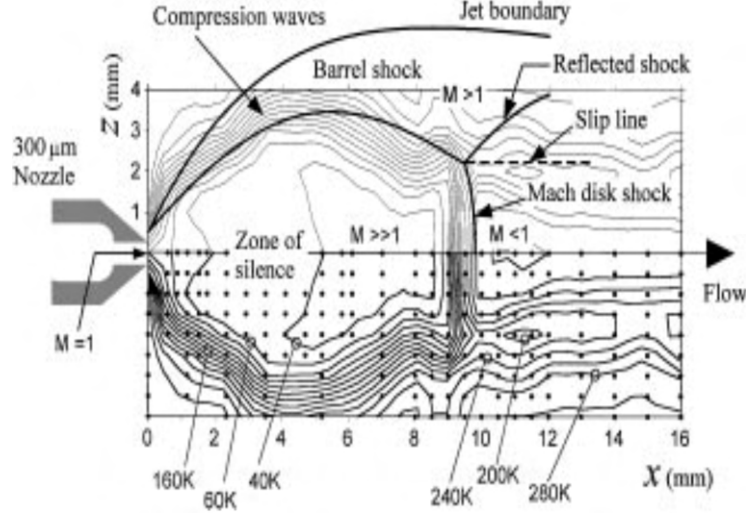


Figure 5.6: Raman mapping of isothermal lines from a gas jet. Taken from [104].

5.2.3 Detectors

In our COLTRIMS spectrometer, the electron and ion detectors utilize either two or three microchannel plates (MCP) in combination with a delayline detector. Figure 5.8(a) illustrates the design layout of the COLTRIMS spectrometer. Positioned in front of the delayline detector, the MCP serves to amplify signals generated by electrons or ions upon impact, while the delayline detector receives these signals from the MCP and measures the two-dimensional coordinates of the impact points. Furthermore, the MCP also measures the arrival times of the charged particles, thus providing valuable time-of-flight (TOF) information for both electrons and ions.

The MCP is a thin glass wafer, typically a one to two millimeters thick, containing numerous narrow channels that are oriented at a slight angle of 0° to 15° relative to the normal surface. Figure 5.8(b) illustrates the operational concept of the MCP. The two metallic-coated surfaces of the MCP are subjected to a high voltage, with the backside acting as the anode attracting electrons. When an electron impacts the inner wall of a channel, it generates multiple secondary electrons, resulting in a cascade of electron

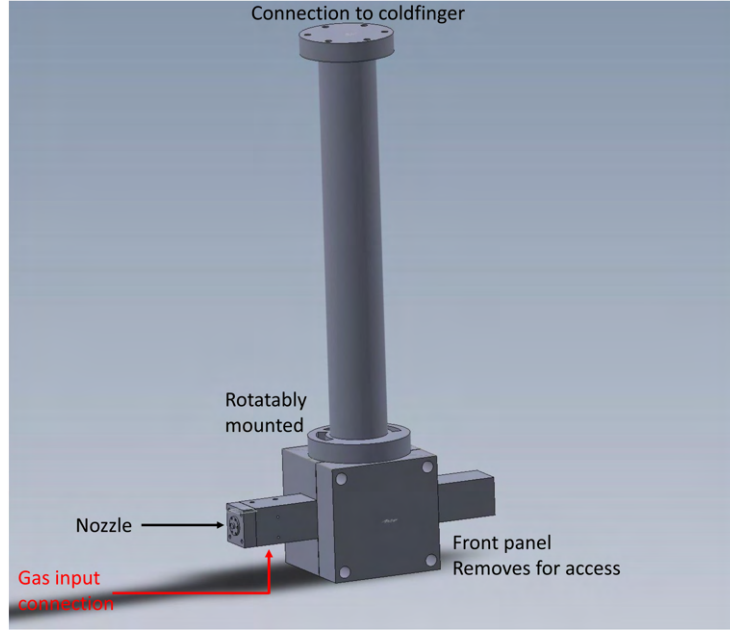


Figure 5.7: The jet apparatus in COLTRIMS. A solid copper rod which is mounted to the cold finger of the cold head holds a rotationally adjustable clamp for the nozzle assembly. The front panel is removable for ease of access, and the jet can slide along its output axis as needed. All parts are made of copper. Adapted from [105].

emissions through reflections within the channel, ultimately creating an electron shower out of the back side.

As shown in Figure 5.8(c), the delay line anode comprises three layers of copper wires arranged in a hexagonal configuration. Each layer consists of a pair of wires, one carrying a signal and the other serving as a reference line, wound around a holder plate in such a manner that the base plate facing the MCP features evenly spaced parallel wires. When the electron shower from the MCP reaches these layers of delay lines, it generates six voltage pulses that commence propagating along the wire directions, as indicated by the black arrows in Figure 5.8.

For a single layer of the delay line, the principle of position measurement is elucidated in Figure 5.9. Two voltage pulses propagate in opposite directions from the electron impact location, arriving at the two ends of the wire at distinct times, denoted as t_1 and t_2 . The initial position within the delay line coordinate system can be determined by:

$$x_0 = s \cdot (t_1 - t_2), \quad (5.1)$$

where s is a scale factor which can be determined during the data analysis process. The combination of any two delay lines provides the capability to determine the two-dimensional position of a charged particle fragment, and the inclusion of an additional layer serves to decrease the dead-time between successive particle impacts, and improving the effectiveness of multi-hit data acquisition [106].

Where s is a scale factor which can be determined in the data analysis presedure. Any two delay lines can give the two-dimensional position of a charged fragmenet and the additional layer reduces the dead-time between particle hits and improves multihit readout [106].

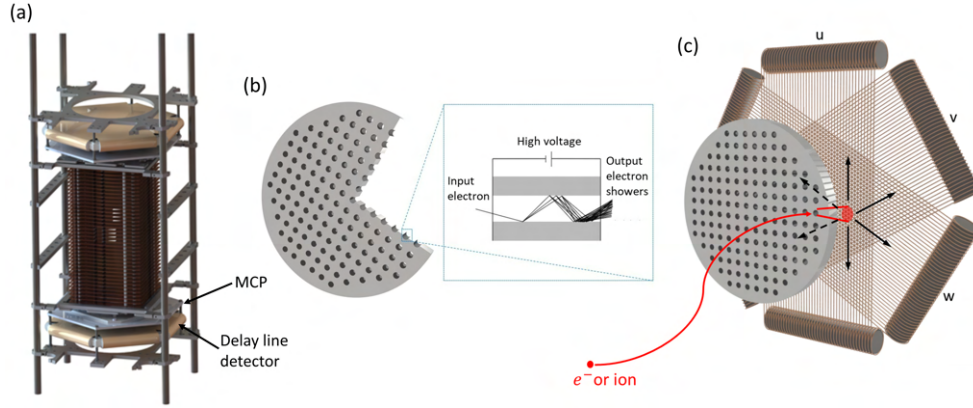


Figure 5.8: Detection system of COLTRIMS. (a) Design schematic of the COLTRIMS spectrometer. (b) Illustration of MCP and its working principle. (c) Illustration of the working process of delay line anodes cooperating with MCP: When an electron or ion hits on the MCP, an electron shower from the electron avalanche emits to the delay line anodes stack, then six electron pulses start to travel along the wire directions indicated by black arrows. Adapted from [105].

5.2.4 Signal processing

The impact signals generated by the MCP and the delay line anode are in the form of voltage dips. These weak, GHz signals require careful processing, involving filtering, amplification, and ultimately conversion to digital format for collection by a computer. The schematic representation of the signal processing circuitry can be seen in Figure 5.10.

In the first step, the voltage signals from the MCP and the delay line anode are individually decoupled and amplified, with careful matching of impedances between the decoupling

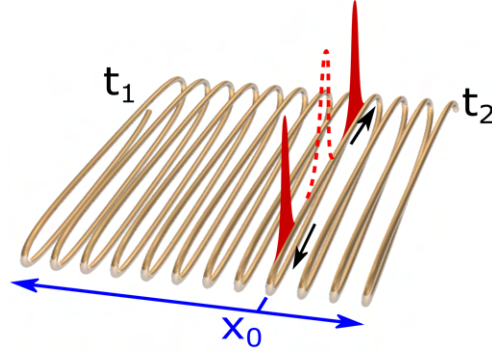


Figure 5.9: Position measurement by a single delay line. When an electron shower from MCP hits the delay line at a position, two voltage pulses are generated and propagate to the opposite directions. The arrival times at the two ends, t_1 and t_2 , are measured. The difference between the arrival times gives the position along the wire, and thus the position of the hit in the direction perpendicular to the wire (x_0 along the blue arrow). Adapted from [103].

circuit and the cables to minimize electronic reflections. The amplification increases the signal height from a few millivolt to the 1 V level.

The second step involves constant fraction discrimination (CFD) applied to the pulses. Given that signal pulses have varying amplitudes, relying solely on pulse height for triggering would introduce significant uncertainty. Therefore, a constant fraction of each pulse's height is utilized as the trigger. In practice, the pulse is divided into two copies, with one of them being amplified, inverted, and delayed by 80% of the signal's rise time. The superposition of these two pulse copies yields a zero crossing point, which serves as the trigger. Following the CFD, the voltage signals are converted into standardized logic signals conforming to the Nuclear Instrument Module standard (NIM).

Finally, the NIM signals are transmitted to a PC for data collection. We have two separate, yet synchronized Time-to-Digital Converter (TDC) computer card that digitize the signals from both detectors. The software responsible for recording this data is COBOLD and developed by RoentDek GmbH, a small spin-off company from the University of Frankfurt, Germany. COBOLD records the detector hit data in an event-by-event manner into a list mode file (LMF). Additionally, COBOLD offers basic online data visualization and analysis capabilities.

In our COLTRIMS experiment, the LMF file containing the detector data is further processed using a C++ based program code called LMF2Root. Using this program, the

detector data is consolidated, and missing signal can be reconstructed. Ultimately the goal of this step in the data analysis is to have reliable impact positions and MCP values for each ion and electron detected in every laser shot. This stage is also referred to as the "first-stage analysis," which encompasses calibration procedures for both detectors.

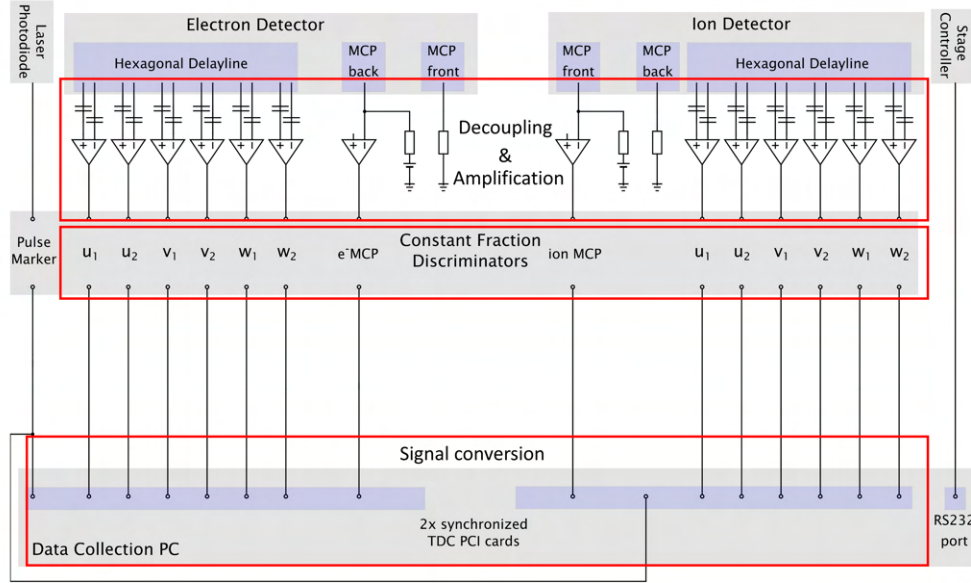


Figure 5.10: Diagram of signal processing (see text for details).

5.2.5 Calculation of momenta

Following the initial stage of analysis, there will be a subsequent second-stage analysis that involves extracting the Time-of-Flights (TOFs) of electrons and ions from the LMF file. It also calculates their momenta by taking into account the hit positions and TOFs. The coordinate system is illustrated in Figure 5.5. The two-dimensional hit position on the detector yields momentum information within the xy -plane, while the TOF measurement provides momentum information along the z -direction. As a result, a three-dimensional momentum vector for each charged fragment can be constructed.

As previously discussed, within the spectrometer, a consistent electric field and an even magnetic field are both present. Consequently, the overall force acting on a particle with

charge q and velocity $\vec{v}$ is the combination of the Lorentz force $\vec{F}_L$ and the electrostatic force $\vec{F}_E$:

$$\begin{aligned}\vec{F} &= \vec{F}_E + \vec{F}_L \\ &= q \cdot (\vec{v} \times \vec{B} + \vec{E}) \\ &= q \cdot \begin{pmatrix} v_y B_z - v_z B_y + E_x \\ v_z B_x - v_x B_z + E_y \\ v_x B_y - v_y B_x + E_z \end{pmatrix}.\end{aligned}\tag{5.2}$$

Both $\vec{E}$ and $\vec{B}$ are along z direction, thus, the above equation can be simplified to:

$$\vec{F} = q \cdot \begin{pmatrix} v_y B \\ -v_x B \\ E \end{pmatrix}\tag{5.3}$$

Now the initial velocity $\vec{v}$ needs to be determined.

5.2.5.1 Electron momentum

Within the spectrometer, electron's TOF and hit position are determined by $\vec{E}$, $\vec{B}$, and the length of acceleration region for electron: $l_{a,e}$.

On the z direction which is the TOF direction, electron's equation of motion is:

$$l_{a,e} = \frac{1}{2} \frac{q_i}{m_e} E t_{tof,e}^2 + \frac{p_{e,z}}{m_e} t_{tof,e}\tag{5.4}$$

$$p_{e,z} = \frac{l_{a,e} m_e}{t_{tof,e}} - \frac{1}{2} q_e E t_{tof,e}\tag{5.5}$$

It is evident that the computation of $p_{e,z}$ is straightforward. Nevertheless, in cases where the spectrometer has a "drift" region without an electric accelerating field, the calculation becomes more involved, necessitating the use of an iterative algorithm. In our COLTRIMS setup, there is no such drift region.

In the x-y plane, the motion of electrons is primarily influenced by the magnetic field

$\vec{B}$. As a result, solving Equation 5.3 will yield the following:

$$\begin{pmatrix} \dot{v}_{x,e} \\ \dot{v}_{y,e} \end{pmatrix} = \frac{q_e}{m_e} B \begin{pmatrix} v_{y,e} \\ -v_{x,e} \end{pmatrix}. \quad (5.6)$$

This yields the following coupled equations of motion:

$$\begin{pmatrix} p_{x,e} \\ p_{y,e} \end{pmatrix} = \frac{1}{2} m_e \omega_{gyr} \cdot \begin{pmatrix} \frac{x_e}{\xi} - y_e \\ \frac{y_e}{\xi} + x_e \end{pmatrix} \quad (5.7)$$

where

$$\omega_{gyr} = \frac{q_e}{m_e} B = \frac{2\pi}{T_{gyr}}, \quad (5.8)$$

and T_{gyr} is electron gyration period in the $\vec{B}$ field, and

$$\xi = \tan\left(\frac{1}{2} \omega_{gyr} t_{tof,e}\right). \quad (5.9)$$

5.2.5.2 Ion momentum

In the case of ions, the influence of the magnetic field can be disregarded since ions are significantly heavier than electrons, and the magnetic field $\vec{B}$ in our experiment is of low intensity ($|\vec{B}| < 15 \text{ Gauss}$). Consequently, there is no force acting on the xy -plane, and the ion's momentum $p_{xy,i}$ is directly correlated with its final position $r_{xy,i}$ on the detector.

$$\begin{pmatrix} p_{x,i} \\ p_{y,i} \end{pmatrix} = m_i \cdot \begin{pmatrix} \frac{r_{x,i}}{t_{tof,i}} \\ \frac{r_{y,i}}{t_{tof,i}} \end{pmatrix} \quad (5.10)$$

On the z direction, similar with electron case, ion's equation of motion is:

$$l_{a,i} = \frac{1}{2} \frac{q_i}{m_i} E t_{tof,i}^2 + \frac{p_{i,z}}{m_i} t_{tof,i} \quad (5.11)$$

$$p_{i,z} = \frac{l_{a,i} m_i}{t_{tof,i}} - \frac{1}{2} q_i E t_{tof,i} \quad (5.12)$$

Where $l_{a,i}$ is the length of acceleration region for ion.

5.2.6 Data calibration

As previously mentioned, a COLTRIMS experiment comprises two distinct data analysis stages. The first stage of analysis is primarily focused on calibrating the two delay line detectors. Within this stage, various parameters such as timesum offsets, delay line scale factors, and third-layer offsets are calibrated, achieved through both manual adjustments and automatic configuration settings within the input file of the LMF2Root program. This stage is primarily technical in nature and does not involve the fundamental field parameters of the spectrometer.

Conversely, the second stage of the analysis is dedicated to calibrating the two crucial parameters of COLTRIMS: the electric field and magnetic field intensities. Additionally, this stage includes the relative rotation of the two detectors, and the calibration of the time-of-flights for both electrons and ions. Once all these parameters have been accurately calibrated, the second stage analysis proceeds to calculate momenta and populate all relevant histograms that hold significance in the context of physics.

5.2.6.1 Ion and electric field calibration

To establish the calibration for the electric field intensity, it is necessary to utilize Time-of-Flights (TOFs) of various ion species. Figure 5.11 displays the TOF spectrum of ions obtained from a Br_2 experiment. By considering their relative abundances and characteristic shapes, one can deduce the TOF peaks corresponding to major ion species. For a given ion species, its ensemble-averaged initial momentum in the z -direction should be approximately zero: $p_{i,z} \sim 0$. Consequently, using Equations 5.11, it becomes straightforward to derive the following relationship:

$$t_{tof,peak} = \sqrt{\frac{m_i}{q_i}} \sqrt{\frac{2l_{a,i}}{E}} \quad (5.13)$$

By selecting ion species with differing charge states and, consequently, distinct mass-charge ratios m/q , it becomes possible to compute the slope $k = \frac{l_{a,i}}{E}$ and the ion TOF offset t_0 through a linear regression. The approximate length of the acceleration region $l_{a,i}$ is already known based on the spectrometer design. As a result, through the calibration process that sets each ion's peak momentum to zero, it becomes feasible to determine the spectrometer electric field strength E .

Refinements can be made to fine-tune the value of $l_{a,i}$. A criterion for assessing the calibration accuracy involves scrutinizing the momentum conservation of ions and electrons in the z -direction. As illustrated in Figure 5.12, the correlated distribution of ion and electron momenta along the diagonal signifies that: $p_{i,z} + p_{e,z} = 0$. If everything is well calibrated the diagonal is centered and symmetric.

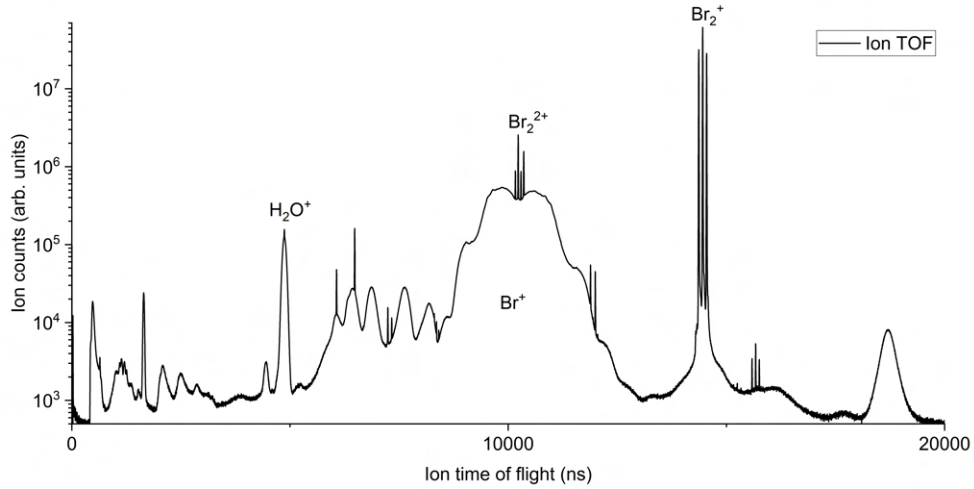


Figure 5.11: Time of flight spectrum of ions in Br_2 experiment. The ion species H_2O^+ , Br^+ , Br_2^{2+} , and Br_2^+ are indicated.

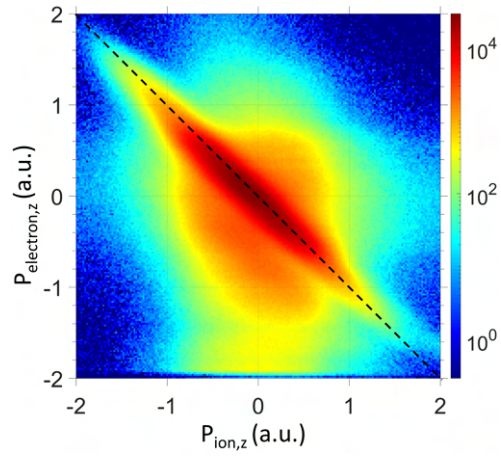


Figure 5.12: Correlated momentum distribution of Br_2^+ and corresponding electron in single ionization of Br_2 . The diagonal line is indicated by black dash line. The major part of the distribution is well along this line.

5.2.6.2 Electron and magnetic field calibration

Within a magnetic field, electrons perform a spiral motion, called cyclotron-trajectories, as illustrated in the rendered image of the spectrometer in Figure 5.4. All electrons begin their trajectory at the origin, i.e., the laser focus. As the electrons travel in the electrostatic and magnetostatic field of the spectrometer, their trajectories begin to spread across the xy -plane according to their initial momentum distribution. However, at integer multiples of the gyration period T_{gyr} , i.e., $t_{tof,e} = n \cdot T_{gyr}$, all electrons will return to the origin of detector. If the trajectory strikes the detector at such a time, the result will be a narrow distribution on the detector, referred to as a "node". The temporal spacing between two consecutive nodes corresponds precisely to the gyration period, enabling us to calculate the magnetic field intensity using Equations 5.8. For every experiment, we conduct a separate procedure to calibrate the magnetic field by adjusting the electric field of the spectrometer, known as a "wobble scan."

In addition to the magnetic field calibration, electron offsets must undergo further calibration, which involves two steps: position offset and temporal offset adjustments. As illustrated in Figure 5.14(a), the position offset for each direction must be compensated to ensure that the wiggled distribution is centered at the zero position. The temporal offset is corrected in Figure 5.14(b) by aligning the electron's momentum distribution with the origin.

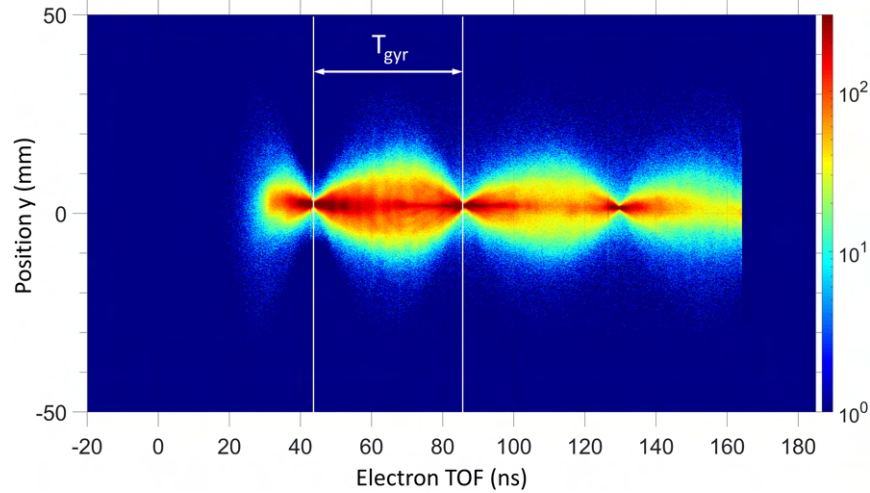


Figure 5.13: Distribution of electron hit position versus electron time of flight. The first and second nodes are indicated by white vertical lines. The spacing between them is gyration period T_{gyr} .

The accurate calibration of the gyration period and the precise adjustments of the electron offsets play an essential role in the resolution of fine interference patterns in the photoelectron momentum distribution. One way to assess the quality of calibration is by examining the Above-Threshold Ionization (ATI) rings, as these concentric rings are extremely sensitive to even minor offsets. Figure 5.15 illustrates well-calibrated electron momenta with distinct ATI rings.

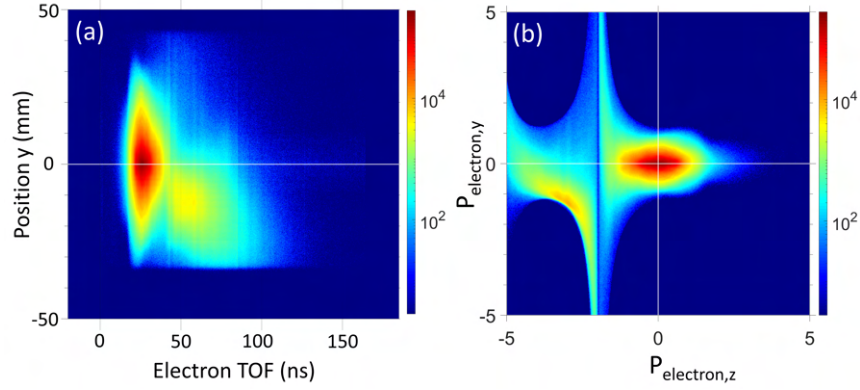


Figure 5.14: Offset calibration for electron. (a) Distribution of electron hit position versus electron time of flight. (b) electron momentum distribution on yz -plane. For (a), the vertical position of the distribution is approximately at $y = 0$. For (b), the center of electron momentum distribution is at the origin.

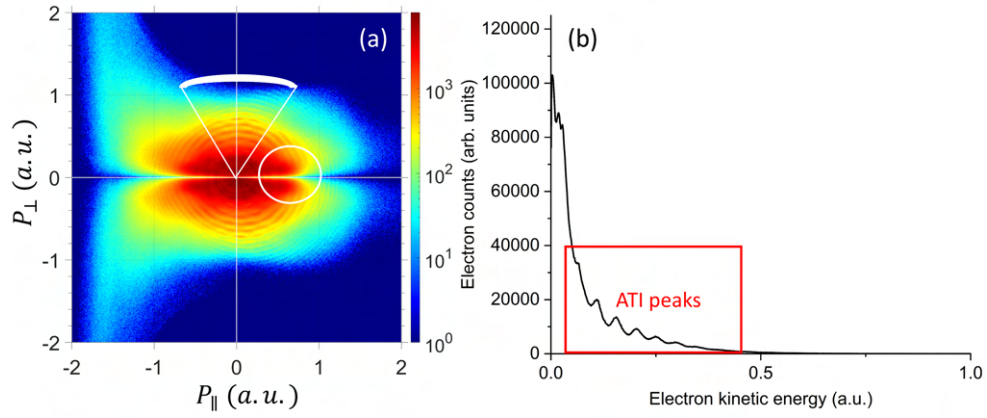


Figure 5.15: (a) Photoelectron momentum distribution from single ionization of Br_2 . The distribution exhibits distinct ATI rings across the entire distribution. To generate a cleaner ATI peak representation, we exclude the regions with strong field holography features (enclosed within the white ellipse) characterized by high intensity. Instead, we integrate only the electrons within the white vertical fan to obtain the ATI electron energy spectrum. (b) Electron energy spectrum resulting from ATI. The presence of distinct ATI peaks enclosed within the red box signifies a successful electron momentum calibration.

5.3 Pump-probe optical setup

5.3.1 Pump-probe beam path

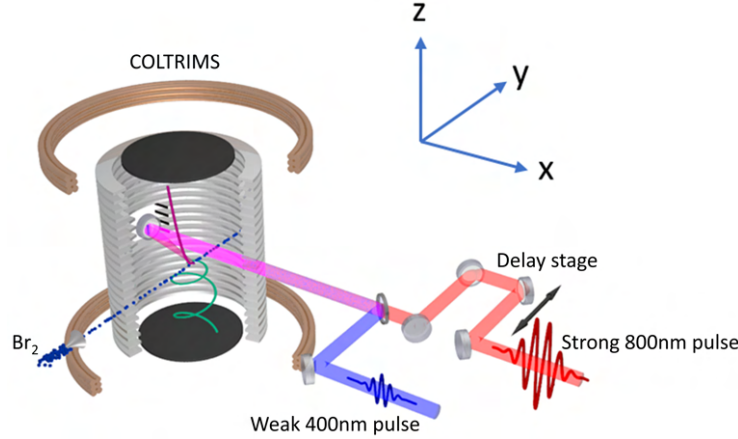


Figure 5.16: Schematic representation of the Br_2 pump-probe experiment conducted with COLTRIMS. In this setup, a 400 nm pulse with low intensity is responsible for inducing Br_2 into its neutral dissociation state, while a powerful 800 nm pulse in a strong field ionizes it. The ions and electrons produced as a result of both ionization and dissociation processes are then captured and analyzed using the COLTRIMS apparatus.

The schematic of our pump-probe optical arrangement is depicted in Figure 5.16. This setup involves two pulses: a feeble 400 nm pulse and a potent 800 nm pulse, both possessing the same vertical polarization orientation. The strong red pulse can be delayed using a computer-controlled delay stage. In this pump-probe configuration, the Br_2 is strongly field-ionized in a direction perpendicular to that of neutral dissociation. This represents a significant distinction when compared to previous studies [74, 80].

Figure 5.17 shows our Br_2 pump-probe scheme in the view of potential energy surfaces (PES). First, a wave packet is prepared on the C state PES of Br_2 through single photon absorption of the weak 400 nm pulse at initial time t_0 . After an interval of Δt the wavepacket travels from its initial position x_0 to x_1 , and then the strong 800 nm pulse arrives to further lift the wave packet to a dissociative PES of Br_2^+ through multiphoton absorption. At last, the Br_2^+ breaks up into a neutral Br atom, a singly charged Br^+ ion, and an electron. Hence, the dynamical information along the C state will be encoded in the Br^+ ion and the photoelectron, which will be observed coincidentally by our COLTRIMS spectrometer.

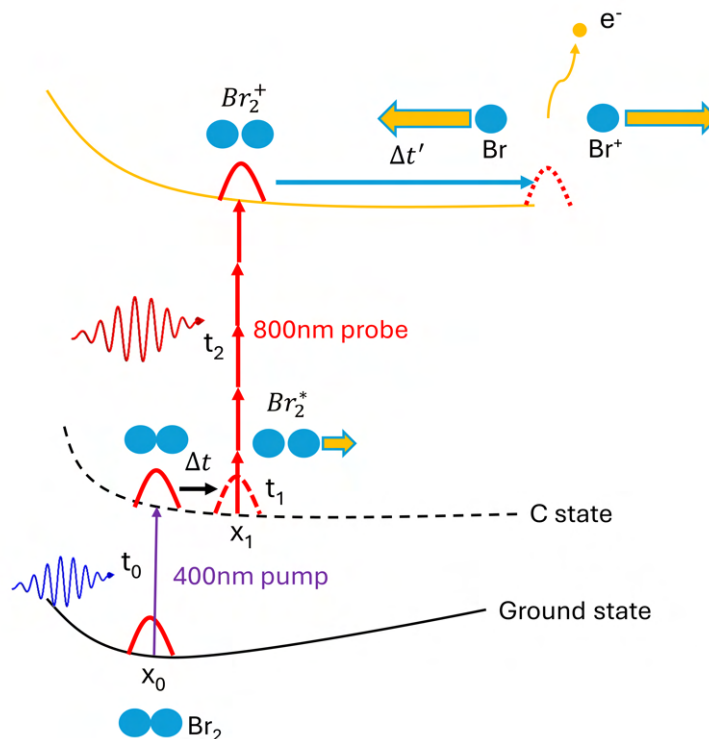


Figure 5.17: Pump-probe scheme in the view of potential energy surfaces of Br_2 and Br_2^+ . The potential energy surfaces of Br_2 ground state, C state, and a dissociative state of Br_2^+ are sketched. Br_2^* represents the neutral dissociating Br_2 along its C state. The 400 nm pulse and the 800 nm pulse are sketched in the blue and the red color respectively.

In practice, the C-state dissociation of Br_2 is quite rare, but obtaining good photoion and photoelectron spectra demands a high level of data statistics. Thus, precise control over the two pulses is paramount to maximize the pump-probe efficiency. Moreover, employing short pulses is always preferred to enhance time resolution in delay-dependent experiments. To meet these demands, we have designed our pump-probe beam path as depicted in Figure 5.18. At first, the diameter of the input 800 nm beam is halved using a telescope at the very beginning. This action enlarges the focal volume of both the pump and probe pulses by approximately fourfold, significantly expanding the interaction region with the molecular beam and thereby increasing data statistics. Subsequently, the beam is split into two arms: the upper arm passes through a BBO crystal to generate a 400 nm beam via frequency doubling, while the lower arm proceeds with a translation stage. The 400 nm beam undergoes two reflections between a pair of chirped mirrors to precompensate the

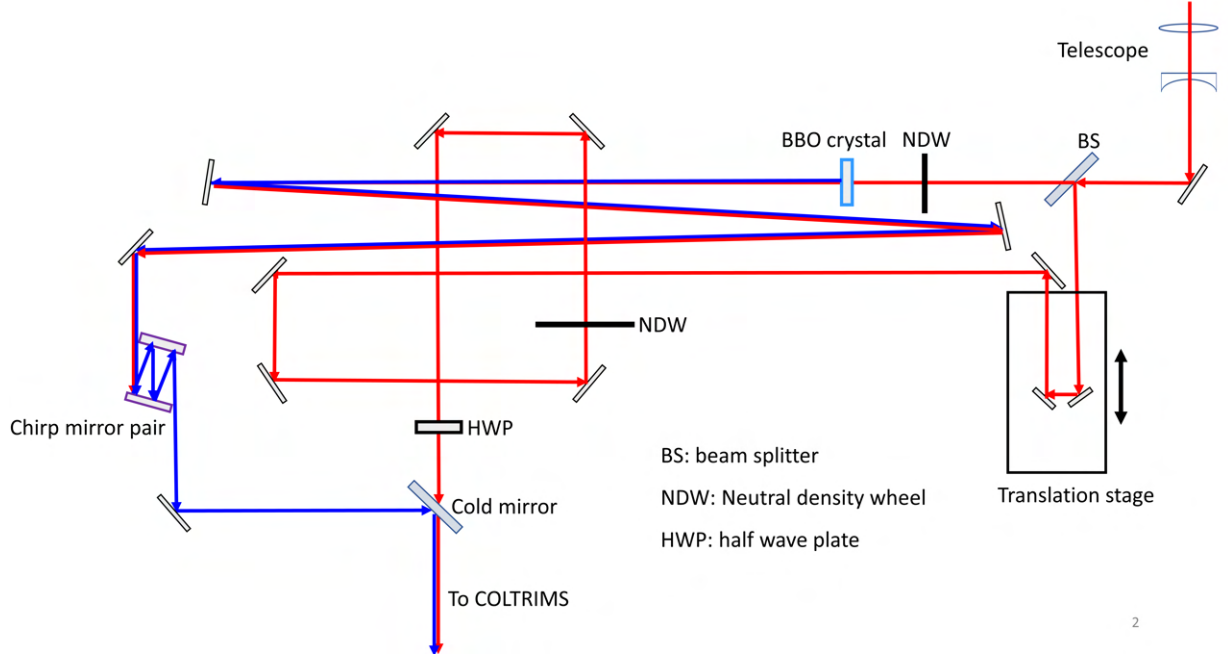


Figure 5.18: Detailed beam path of Br_2 pump-probe interferometer.

dispersion of the short pulse and to eliminate the remaining 800 nm component. The 800 nm probe beam incorporates a half-wave plate to control its polarization direction, with the aim to align the 800 nm and the 400 nm beam. The intensities of the two arms are independently controlled by two neutral density wheels. Prior to entering the COLTRIMS spectrometer, the two beams are combined using a cold mirror. The optical setup of this pump-probe interferometer is visualized in Figure 5.19.

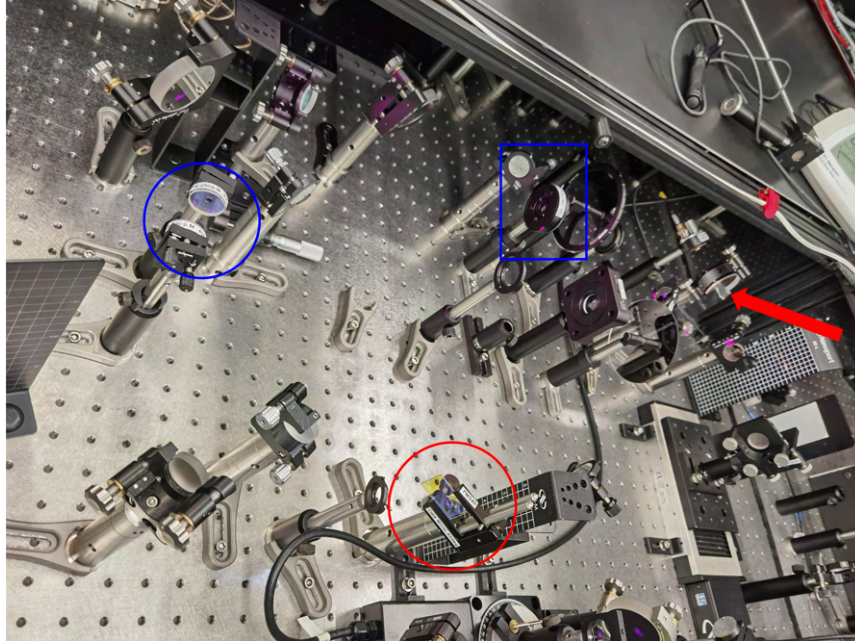


Figure 5.19: Realistic optical setup of Br_2 pump-probe interferometer. The blue circle, the blue rectangle, and the red circle indicate the chirp mirror pair, the BBO crystal, and the recombination cold mirror respectively. The red arrow indicates the input direction of the 800 nm laser beam.

5.3.2 Temporal overlap of two pulses

Spatial and temporal overlap of the two pulses are stringent requirements for a pump-probe interferometer. In this context, we will specifically address the temporal overlap. In our experiment, we achieve temporal overlap through a two-step process.

The first step is conducted outside the COLTRIMS chamber, utilizing a plasma method illustrated in Figure 5.20. In this method, the combined two beams are tightly focused in the air. The strong 800 nm pulse generates a plasma, which modulates the refractive index of the surrounding air. If the 400 nm pulse arrives at the plasma region afterward, it scatters off the plasma and produces a diffraction pattern on the blue pulse's beam profile. Consequently, around the temporal overlap position, one can observe alternating appearances and disappearances of this diffraction pattern by adjusting the delay stage. This diffraction pattern can also serve to evaluate spatial overlap: perfect spatial overlap ensures that any fine adjustments to one mirror in the interferometer result in minimal changes to the diffraction pattern.

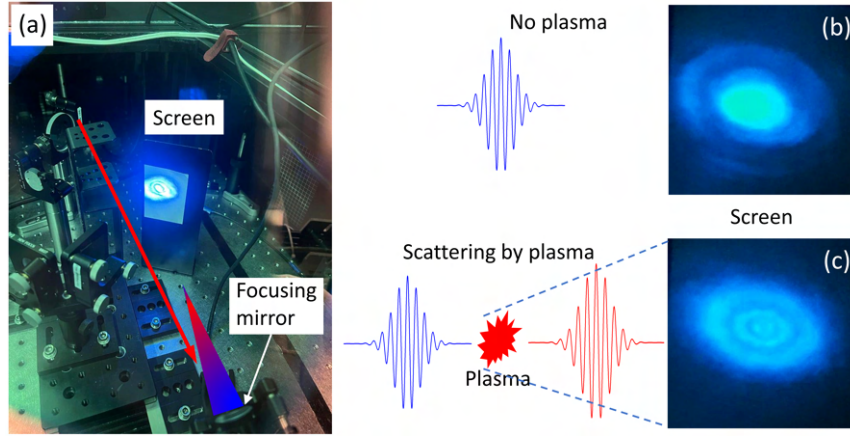


Figure 5.20: Plasma-based method for determining temporal overlap. (a) Experimental configuration: The two combined beams are focused in air using a parabolic mirror with a focal length of 5 *cm*. The intense 800 *nm* pulse create a plasma. A screen placed in the far field captures the beam profile of the 400 *nm* pulse. The beam profile of the 400 *nm* pulse is shown in (b) when the 400 *nm* pulse arrives first, or when the ionizing 800 *nm* pulse is blocked, and in (c) when the 800 *nm* pulse creates the plasma before arrival of the 400 *nm* pulse. The diffraction of the 400 *nm* pulse on the plasma generates an interference pattern, visibly distinct from the profile shown in (b).

The precise position of temporal overlap is subsequently determined using COLTRIMS. In our experiment, we employ the strong-field ionization yield as an indicator of temporal overlap between the two pulses. When the two pulses are perfectly overlapped, the total electric field is enhanced, leading to an increase in the ionization rate. Figure 5.21 illustrates the ionization counts as a function of delay-stage position. A sharp peak is observed at approximately 0.06 *mm*, which corresponds to the precise temporal overlap position.

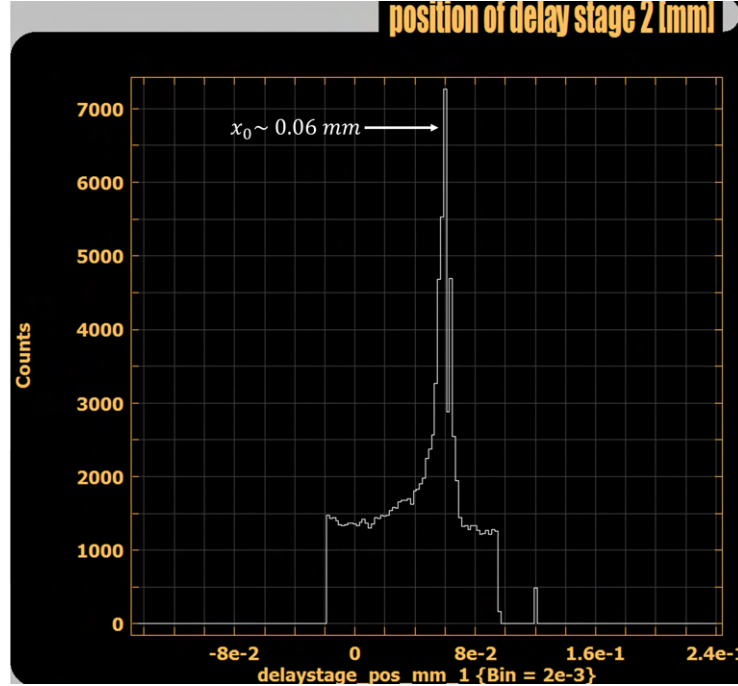


Figure 5.21: Determining the temporal overlap position through strong-field ionization yield: The presence of a distinct peak, which stands more than 5 times higher than the baseline, suggests that the temporal overlap position is approximately at $x_0 = 0.06 \text{ mm}$.

5.3.3 Intensity calibrations

5.3.3.1 Intensity calibration of 800nm pulse

In our experiment, we deduce the peak intensity of the 800 *nm pulse in-situ* from the measured photoelectron momentum distribution. This can be done in with linear polarization, but this approach suffers from a poor resolution. Circular polarization, on the other hand, has been shown to give an accuracy in the intensity measurement of only a few percent [107]. Hence, it has become common practice in COLTRIMS experiments to calibrate the peak intensity by converting the linearly polarized 800 nm beam into a circularly polarized (CP) field and by analyzing the photoelectron momentum distribution resulting from strong-field ionization. Figure 5.21(a) illustrates the electron momentum distribution, which exhibits a ring-like structure. This ring arises from the drift momentum of the *direct* electrons, as recollision events are suppressed in a circularly polarized field. The motion of these direct electrons obey Newton's equations, making it straightforward to calculate. Employ-

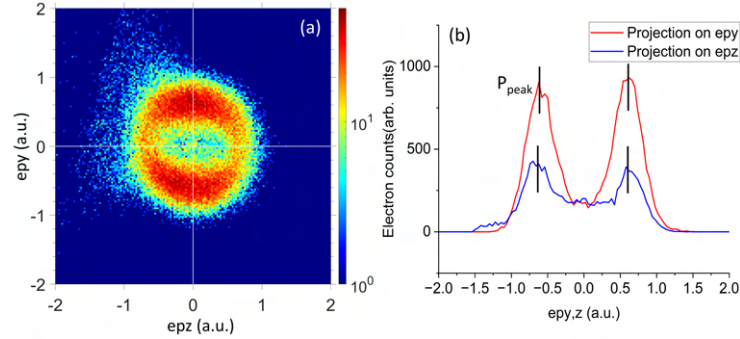


Figure 5.22: Intensity calibration using a circularly polarized field. (a) 2-dimensional momentum distribution of photoelectrons resulting from the ionization of D_2 . (b) projections of this distribution along two momentum axes. The presence of double peaks in both projections is highlighted by black bars.

ing the long-pulse approximation, we can express the maximum electron momentum as: $P_{peak} = \frac{E_0}{\sqrt{2}\omega}$, where E_0 represents the peak strength of the electric field, and ω denotes its circular frequency. Consequently, the laser intensity is determined as: $I = 2\omega^2 P_{peak}^2$, and for an 800 nm pulse, $I[(10^{14}\text{W}/\text{cm}^2)] \approx 2.2776 P_{peak}^2 [a.u.]$. In practical terms, P_{peak} is determined by fitting the double peaks depicted in Figure 5.22(b) using Gaussian functions.

5.3.3.2 Intensity calibration of 400nm pulse

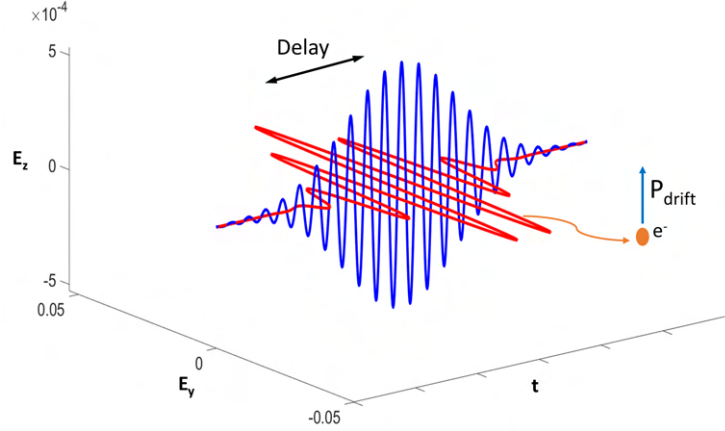


Figure 5.23: Orthogonal two color pulses for 400nm intensity calibration. The electric fields of strong 800nm-pulse(in y-direction) and weak 400nm-pulse(in z-direction) are shown. The free electron ionized by red pulse obtains a drift momentum P_{drift} in z direction from the blue pulse.

While circularly polarized fields prove effective for calibrating the intensity of 800 nm pulses, we encounter significant challenges when attempting to calibrate the intensity of 400 nm pulses using the same approach. This is primarily due to the weaker nature of 400 nm pulses and their shorter wavelength, which results in insufficient electron momentum generation. Our solution to this issue involves the utilization of orthogonal two-color (OTC) fields, as illustrated in Figure 5.23.

In this method, a high-intensity 800 nm (red) pulse is responsible for ionizing argon atoms to provide an ample supply of free electrons. Subsequently, the weak electric field of the blue pulse imparts a drift momentum to these free electrons in a direction perpendicular to the 800 nm pulse. By varying the time delay between these two pulses, the electric field of the 400 nm (blue) pulse can be effectively scanned by the free electron current originating from the red pulse. This approach enables us to access the electric field of the 400 nm pulse in a subcycle manner. To introduce such fine delays, we employ a silica window mounted on a rotational stage.

Figure 5.24(a) displays the electron momentum distribution in the z -direction as a function of delay. An evident oscillatory pattern is observed, which corresponds to the

electric field of the 400 *nm* pulse. Subsequently, we calculate the average center momentum of this distribution for each delay point and represent it in Figure 5.24(b).

The maximum energy a free electron can attain in a laser field is $2U_p$ (corresponding to a maximum momentum of $2\sqrt{U_p}$). Consequently, the momentum separation between the farthest two peaks should be $4\sqrt{U_p}$. Utilizing Equation 2.7, we can then compute the intensity of the 400 *nm* pulse as: $I = 4\Delta ep_z^2\omega^2$, where Δep_z represents the maximum amplitude of the momentum oscillation, and ω is the circular frequency of the 400 *nm* pulse.

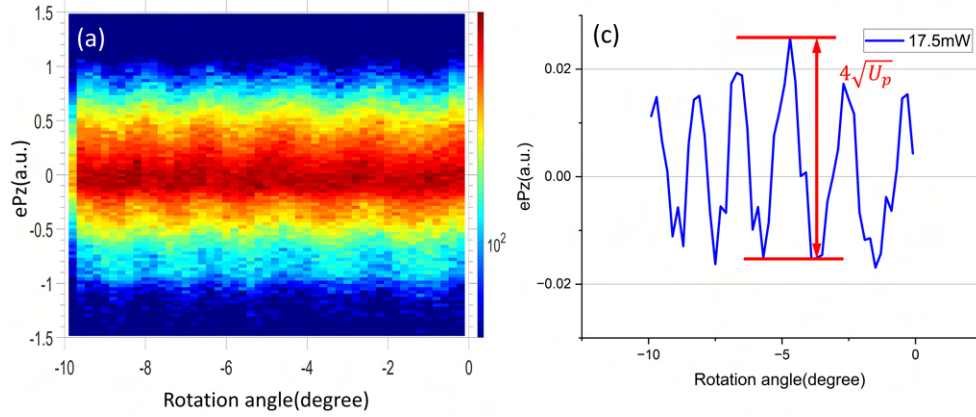


Figure 5.24: (a) delay-dependent electron momentum dustrubution in z direction. (b) average center momentum of the distribution in (a).

5.4 Br_2 gas supply and safety procedures

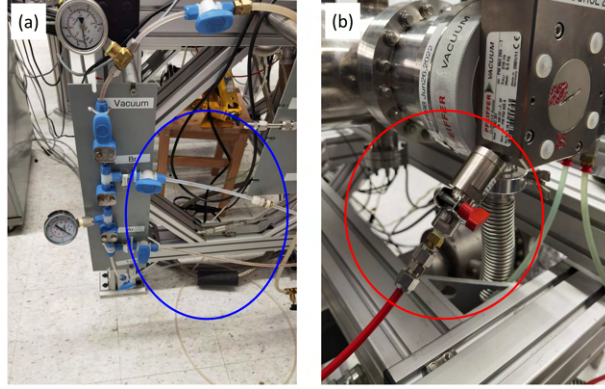


Figure 5.25: (a) Manifold for Br_2 gas supply. The manifold and Br_2 gas line in blue ellipse are all made of teflon. (b) Sealing gas valve (in red circle) installed on the turbo pump of source chamber.

The initial and critical step in conducting a Br_2 experiment involves the preparation of a Br_2 gas cylinder. This step holds paramount importance as it necessitates a delicate balance. On one hand, it is essential to ensure an ample presence of Br_2 in the gas jet to facilitate a sufficient number of neutral dissociation events. On the other hand, it is equally crucial to safeguard the experimental setup from the highly corrosive nature of Br_2 gas.

To strike this balance, a 1% Br_2 concentration is introduced into a helium gas carrier. Given that the intensity of the probe pulse in our experiment remains relatively low ($I < 10^{14} \text{W/cm}^2$), helium remains un-ionized, allowing for exclusive probing of Br_2 . Additionally, helium functions as a buffer gas, aiding in maintaining the Br_2 jet at lower temperatures.

Despite substantial dilution, it is observed that the Br_2 gas mixture still exhibits a relatively high chemical reaction rate with metal surfaces, leading to complete Br_2 consumption or potential damage to the experimental setup. To address this concern, several precautionary measures must be implemented initially, as outlined below:

- (a) All components within the gas supply line must be constructed from Teflon, and the interior surface of the gas cylinder should be coated with Teflon. Figure 5.25(a) provides a visual representation of the Teflon manifold and gas supply line.

- (b) Both the gas cylinder and the pressure regulator require a Br_2 passivation coating, even though the entire gas line is constructed from Teflon. This implies that the initial few Br_2 fills will be essentially wasted until all potential metal surfaces within the gas line have undergone chemical reactions with Br_2 . This step is indispensable; otherwise, no ionization signal from Br_2 can be detected!
- (c) The turbo pumps located within the source chamber must be safeguarded by introducing a sealing gas. Failure to do so could result in their malfunction during the experiment. In our specific experimental setup, nitrogen gas is introduced into the turbo pump via a sealing gas valve, as illustrated in Figure 5.25(b).

Another crucial step in the gas supply process is to minimize the moisture content within the Br_2 gas mixture. This precaution is essential due to the chemical reaction that occurs between Br_2 and water molecules, which has the potential to deplete a significant amount of Br_2 :



The primary source of moisture is the surrounding air. Therefore, the process of filling Br_2 should be carried out in an environment that is isolated from atmospheric air. To achieve this, a Br_2 filling bubbler is employed, and a series of meticulous filling procedures have been devised, as illustrated in Figure 5.26. The underlying concept is to utilize a dense atomic gas such as Xe or Ar as a sealing gas to create a barrier between the Br_2 liquid and the surrounding air.

As depicted in Figure 5.27(a), it is evident that the product HBr from Equation 5.14 becomes dominant, and the desired observable Br^+ is significantly suppressed in this scenario. However, when the sealing gas Xe is utilized, as shown in Figure 5.27(b), the HBr^+ peak disappears.

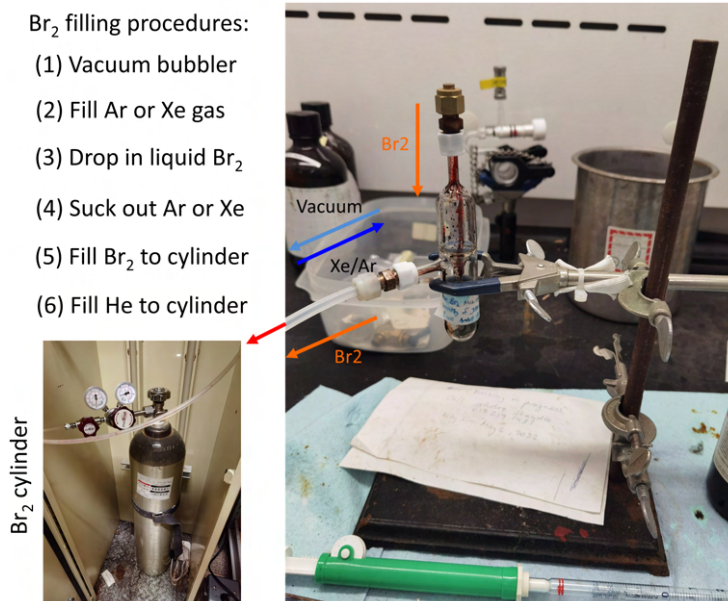


Figure 5.26: Br₂ filling bubbler and precedures.

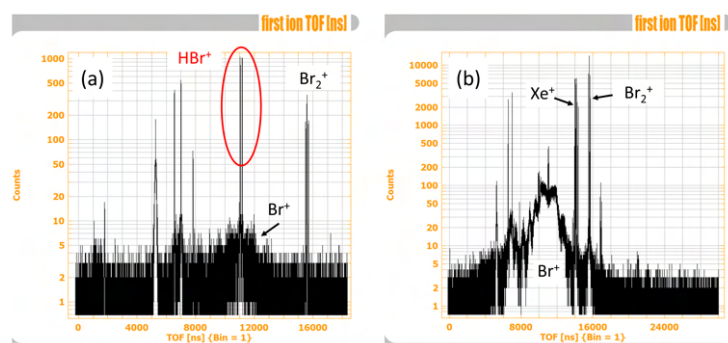


Figure 5.27: Ion TOF spectra for (a) without Xe/Ar sealing gas, and (b) with Xe/Ar sealing gas.

5.5 Pulse intensity optimization for Br_2 's neutral dissociation

The C-state dissociation of Br_2 occurs through a single-photon process, necessitating that the 400 nm pump pulse be kept sufficiently weak to avoid any multi-photon absorption. However, achieving good statistical data requires a higher number of neutral dissociation events, i.e., the excitation to the C-state. A high excitation yield translates to a need for higher intensity. Therefore, finding the optimal intensity for the 400 nm pulse is crucial.

To determine the optimized conditions for the excitation, we assess the Kinetic Energy Release (KER)-delay spectra under various intensities of the 400 nm pulse. An example with two different pulse powers is presented in Figure 5.28. As observed in Figure 5.28(b), the characteristic long-tail structure of the dissociation of the neutral [80] becomes more prominent, indicating improved neutral dissociation at a power level of 3.5 mW , or 350 nJ per pulse. Furthermore, a broad background signal underneath the Br^+ time-of-flight becomes more prominent at this pulse power. As we will discuss in the next chapter, this background is formed by high energy Br^+ who are created through two-photon excitation and subsequent high energy dissociation and even double ionization, which leads to Coulomb explosion. It is worth noting that higher intensity also leads to increased background signals around time zero, which is less than ideal. Nevertheless, these background signals can be effectively filtered out during the subsequent data analysis stage.

Consequently, in our experiment the 400 nm pump pulses used for exciting the C-state of Br_2 have a pulse energy of 350 nJ and a pulse duration of approximately 40 fs . They are focused to an intensity of approximately $I \approx 10^{10}$ W/cm^2 .

For our 800 nm probe pulse, we have determined that its intensity should not exceed 10^{14} W/cm^2 . Going beyond this intensity threshold would result in the signal from the C-state dissociation of the neutral molecule being overshadowed by the dissociative ionization originating from the ground state Br_2^+ . The dissociative ionization is a process that is independent of the pump pulse and is solely caused by the probe pulse: within the 25 fs , 800 nm probe the Br_2 molecule is first ionized and then further multiphoton-excited into dissociative states of the Br_2^+ . Therefore, to minimize this contribution, we have chosen to set the probe pulse intensity to approximately 5×10^{13} W/cm^2 .

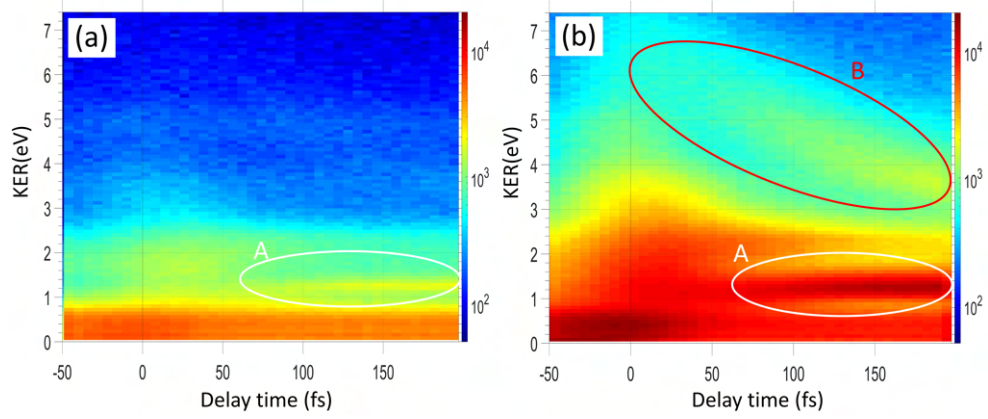


Figure 5.28: KER-delay spectra of Br^+ for two power levels of 400 nm pump pulses: (a) 250 nJ/pulse, (b) 350 nJ/pulse. In both panels, the "long-tail" feature, signifying C-state dissociation probed through single ionization, is highlighted by a white ellipse labeled as A. Additionally, in Panel (b), a distinct structure arising from Coulomb explosion manifests in the high KER range, which is marked by a red ellipse labeled as B.

Chapter 6

Experiment results and analysis

In this chapter, we present and discuss the results of our Br_2 experiment. We begin by outlining the methodology for tracking the Br_2 neutral dissociation through the observation of Br^+ ions. These ion spectra serve as the initial indicators of neutral dissociation, enabling us to selectively concentrate on and analyze the neutral dissociation events. Building on our understanding of the ion spectrum associated with neutral dissociation, we then illustrate how to track Br_2 neutral dissociation through the observation of electrons, which constitutes the central focus of this thesis. To interpret the observed photoelectron spectra, we employ the molecular semiclassical two-step (SCTS) model introduced in Chapter 3. Our findings demonstrate that a comprehensive understanding of both nuclear and valence electron dynamics can be achieved by independently observing ions or electrons, thereby establishing two complementary approaches to our investigation.

In our Br_2 pump-probe experiment, the observations of ions and electrons impose distinct time-delay range requirements, despite originating from the same dissociation process. On the ion side, confirmation of neutral dissociation involves identifying the reaction product, the Br atom. Consequently, a pump-probe delay range of several hundred femtosecond needs to be scanned, extending well beyond the conclusion of neutral dissociation. Conversely, on the electron side, sufficient statistics is crucial for rendering structures in the 2-dimensional electron momentum distribution visible. Therefore, the focus is on the detailed transition process from Br_2 molecule to the Br atom, specifically during neutral dissociation. To accommodate these diverse requirements, three separate Br_2 experiments are conducted:

Extended delay scan: This represents a pump-probe experiment encompassing a substantial delay range (-2 ps to 1 ps), covering both extensive positive and negative

delay intervals. This delay range gives a birds-eye view of the pump-probe experiment, allowing to follow the dissociation to very large distances. The sizable negative delay range enables the observation of vibrational wave packet dynamics in Br_2^+ induced by a strong red pulse.

Short delay scan: In this pump-probe experiment, a relatively limited delay range (-50 fs to 200 fs) is scanned, in order to precisely capturing the transformation of molecular to atomic orbitals, the breaking of the molecular bond, in the Br_2 neutral dissociation. This scan provides optimal statistical data for both ions and electrons, enabling the time-resolving of electron momentum distributions.

Probe-only scan: This scan is a single-pulse experiment where the 400 nm pump beam is blocked, and only the 800 nm probe beam is allowed to enter the vacuum chamber. In order to simplify comparison with the other two experiments, the delay stage for the probe pulse is operational, covering the same delay range as the extended delay scan. The probe-only scan serves to eliminate the background signal of dissociating Br_2 caused by the 800 nm pulse and mitigates any fluctuations resulting from the movement of the delay stage.

6.1 Following the neutral dissociation of Br_2 by observing the Br^+ ion

6.1.1 Identification of dissociation channels

In the Br_2 pump-probe experiment, various dissociation processes can be initiated by either the 400 nm pump or by the 800 nm probe pulse. In fact, the much stronger 800 nm pump pulse is expected to produce the most of the dissociation fragments. These dissociation processes are distinguishable by analyzing the Br^+ momentum distribution, as depicted in Figure 6.1. Figure 6.1(a) illustrates the distribution from the probe-only experiment featuring only the intense, 800 nm pulse, while Figure 6.1(b) showcases the distribution resulting from the full pump-probe experiment.

In both of these distributions, the majority of ions fall within the momentum range of $130 \text{ a.u.} < ip_z < 130 \text{ a.u.}$ and exhibit a multi-lobe structure along the polarization direction. These Br^+ ions result from dissociation processes solely induced by an 800 nm pulse. Within this set, the low momentum segment (labeled "1") arises from bond softening (BS), while the lobes with higher momentum (labeled "2") originate from above-threshold dissociation (ATD). In addition to these low momentum channels along the polarization

direction, the outer ring structure with very high momentum (labeled "3" at $p_z > 150$ a.u.) is attributed to the Coulomb explosion (CE) process, which is triggered by double ionizing the ground state of Br_2 .

Moving to Figure 6.1(b), although Br^+ ions along the polarization direction dominate the distribution, two shifted thin rings in the perpendicular direction are evident (within the white rectangle, labeled "4"). These rings, absent in Figure 6.1(a), are indicative of the neutral dissociation (ND) channel. In Figure 6.1(c), a magnification plot of these rings reveals one ring centered at $p_z = 0$ a.u. (solid line), while the other shifts from zero by approximately 16 a.u. (dashed line). The discrepancy between the two rings is attributed to the isotope effect of bromine. During data calibration, a specific isotope mass is assumed for Br^+ (here, $m(Br^+) = 81$ amu), leading to an error in the measurement of the other isotope species (^{79}Br) and resulting in a momentum shift from zero. While this isotope effect is inevitable and introduces an isotope background in any ion spectrum, it does not impact the kinetic energy release (KER)-delay spectrum of Br^+ .

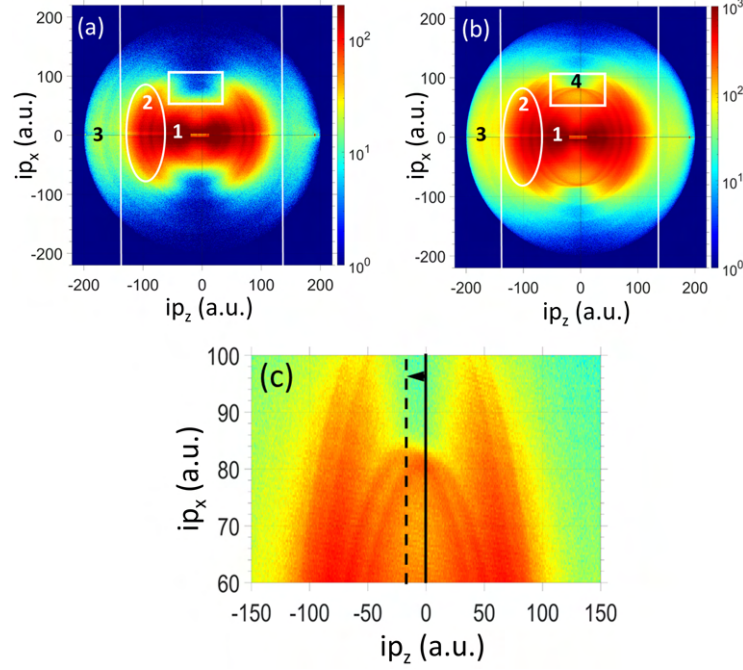


Figure 6.1: Br^+ momentum distributions from the (a) probe-only scan, and the (b) short delay scan. The 800 nm probe pulses in the two experiments are identical. In the probe-only experiment the delay-stage is moving with the same parameters as in the extended delay scan experiment. In (a,b) we indicate the Br^+ momentum ranges corresponding bond-softening (1), above threshold dissociation (2), Coulomb explosion (3), and the neutral dissociation (4). The two vertical white lines indicate the momentum value $p_z = \pm 130$ a.u.. In (b), the thin double rings from neutral dissociation (4) are indicated by a white rectangle. (c) magnification of the neutral dissociation structure in (b). The black dashed line corresponds to $ip_z = 16$ a.u..

6.1.2 Delay-dependent Br^+ momentum distributions

An intuitive approach to understanding the process of neutral dissociation is to look at the delay-dependent Br^+ momentum distributions. Illustrated in Figure 6.2, four specific delay times are chosen from the KER-delay spectrum of Br^+ ions, capturing various stages of the dynamics: $T_1 = 20$ fs represents the negative delay range when neutral dissociation has not initiated; $T_2 = 0$ fs signifies the moment Br_2 is pumped; $T_3 = 50$ fs corresponds to a moderate delay time when neutral dissociation is still in progress, while $T_4 = 170$ fs denotes a large delay time when the neutral dissociation is expected to be complete based on simulations [74]. In the following, we call the neutral dissociation to be "complete" or "concluded" when the molecular bond is irreversibly broken, that is, when the energy between the neutral and the singly ionized system does not change with increasing time or internuclear separation. Figure 6.3 displays the Br^+ momentum distributions at the four

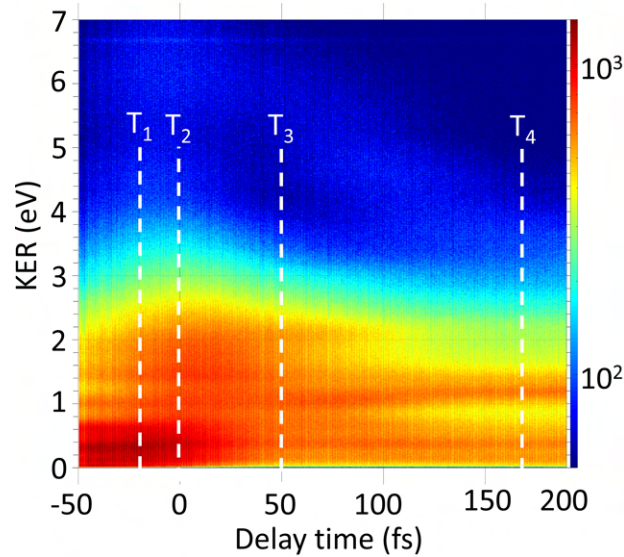


Figure 6.2: Original KER-delay spectrum of Br^+ . The four time points for plotting Br^+ momentum distributions are indicated by: $T_1 = -20$ fs, $T_2 = 0$ fs, $T_3 = 50$ fs, and $T_4 = 170$ fs.

delay times mentioned above. Notably, the two thin rings in the perpendicular direction become increasingly distinct with the progression of delay time. Particularly noteworthy is the clarity of the double-shifted rings at T_4 , 170 fs, indicating that these Br^+ ions originate from the ionization of neutral Br atoms post-neutral dissociation.

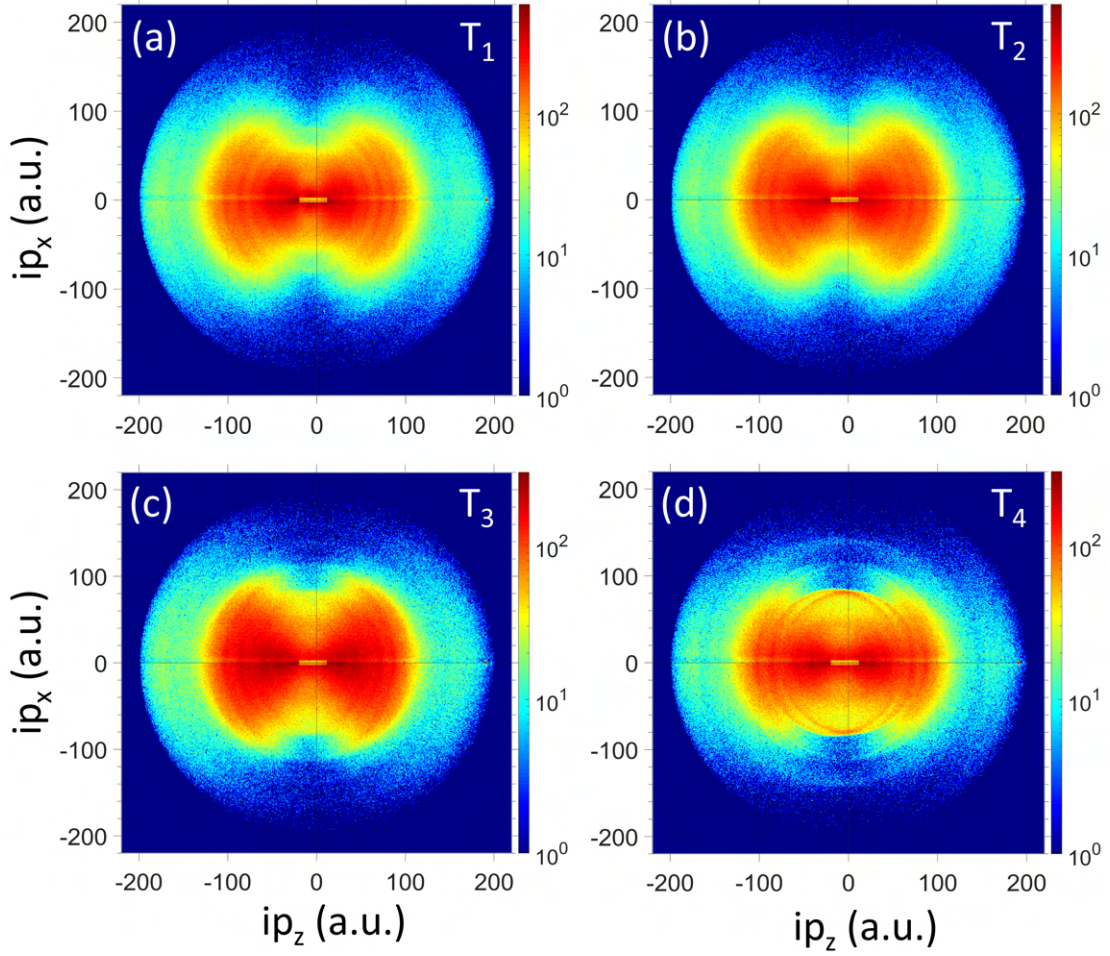


Figure 6.3: Delay-dependent Br^+ momentum distributions. The four momentum distributions are obtained by integrating Br^+ around a small time window $\Delta t = 10$ fs at each time point: (a) $T_1 = -20$ fs, (b) $T_2 = 0$ fs, (c) $T_3 = 50$ fs, and (d) $T_4 = 170$ fs.

6.1.3 Neutral dissociation selected by cone-cut filter

While observable, the double rings of the neutral dissociation in the Br^+ momentum distribution are obscured by a significant background from above threshold dissociation and bondsoftening, which originate solely from the 800 nm probe pulse. To reduce this background we implement a filtering process in the data analysis stage which can be treated as a post-processing step. To this end, a momentum filter in the polar angle θ along the time-of-flight axis is applied to the Br^+ ions. As illustrated in Figure 6.4(a), the filter divides the 3-dimensional momentum space into two cones with their peaks meeting at $p_z = 0$. Along the z -axis within the cones, we find primarily the Br^+ which are produced via ATD and BS, whereas in the gap between the two cones, the Br^+ from the Br_2 neutral dissociation (ND) can be found.

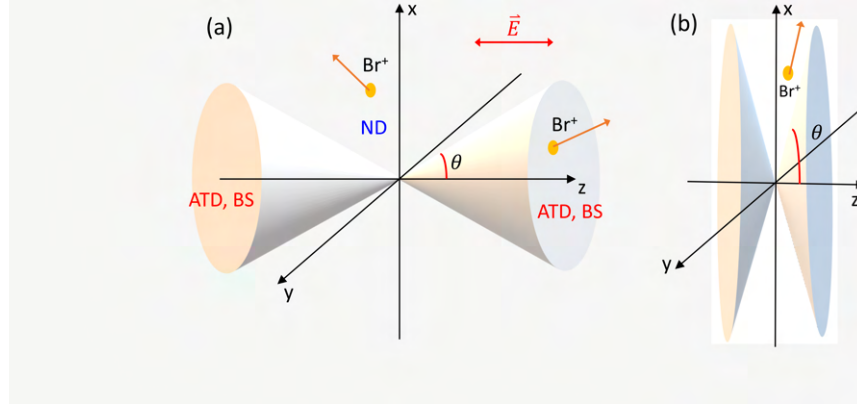


Figure 6.4: Illustration of cone-cut momentum filter for Br^+ . (a) cone-cut filter with a small cone angle $\theta = 30^\circ$ and (b) cone-cut filter with a large cone angle $\theta = 60^\circ$. The electric field $\vec{E}$ is along the z direction. The different dissociation channels are indicated in different regions of the two cones: the Br^+ ions from ATD and BS channels are within the cones, while the Br^+ ions produced from ND channel are within the gap between the two cones.

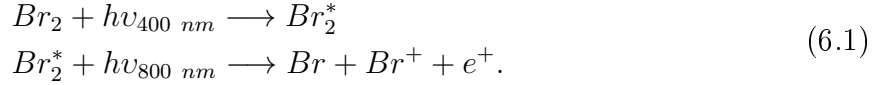
The cone angle θ controls the sizes of these two regions. For instance, with a large angle setting, as depicted in Figure 6.4(b), the region for neutral dissociation becomes very narrow, causing the momentum of Br^+ to align more perpendicularly to the laser polarization direction. By eliminating ATD and BS Br^+ , the ND Br^+ can be observed individually with minimal ATD and BS background.

A comparison of Br^+ momentum distributions obtained with two cone angles is presented in Figure 6.5. For $\theta = 30^\circ$, a clear double ring structure with a substantial angular

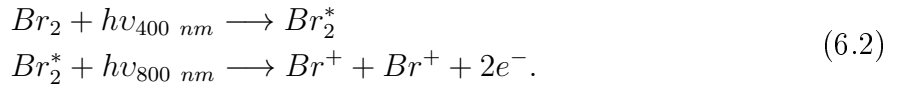
span is visible. However, its KER-delay spectrum is somewhat blurred due to saturation from ATD background. Conversely, in the case of $\theta = 60^\circ$, only a subset of Br^+ ions around the perpendicular direction is selected. Consequently, a distinct branch-like structure (within the white dashed rectangle) emerges, originating exclusively from the neutral dissociation of Br_2 .

In the extended delay scan, the clarity of the neutral dissociation structure is enhanced, as depicted in Figure 6.7(b). Notably, the long-tail structure extends over 1 ps after the 400 nm excitation, aligning with observations in [80]. In Figure 6.7(c), background Br^+ ions from the probe pulse are further eliminated by normalizing the differential between Figure 6.7(a) and Figure 6.7(b). The KER-delay spectra in both Figure 6.7(b) and 6.7(c) exhibit two major structures labeled as "A" and "B".

In contrast, for the probe-only scan, the KER-delay spectrum in Figure 6.7(a) displays no apparent time-dependent features, and the Br^+ momentum distribution in Figure 6.6(a) lacks the presence of the double rings in the perpendicular direction. These observations suggest that structures A and B represent two distinct dissociation channels directly mapping the neutral dissociation process of Br_2 . Structure A, characterized by relatively low kinetic energy release (KER) and high population, is attributed to the single ionization of dissociating Br_2 :



The structure B, on the other hand, exhibits a high kinetic energy release, and therefore is a Coulomb explosion process, which originates in the double ionization of Br_2 by the probe pulse:



In Figure 6.8 we compare structure A with the simulation results presented in [74]. Notably, the resemblance between the two kinetic energy release (KER)-delay spectra lends support to the conclusion drawn in [74]: the KER-delay structure of the single ionization channel can effectively track the molecular orbital evolution during the Br_2 neutral dissociation. Furthermore, the evident Coulomb explosion structure B in Figure 6.7 indicates that changes in internuclear distance during Br_2 neutral dissociation can also be discerned through the observation of Br^+ .

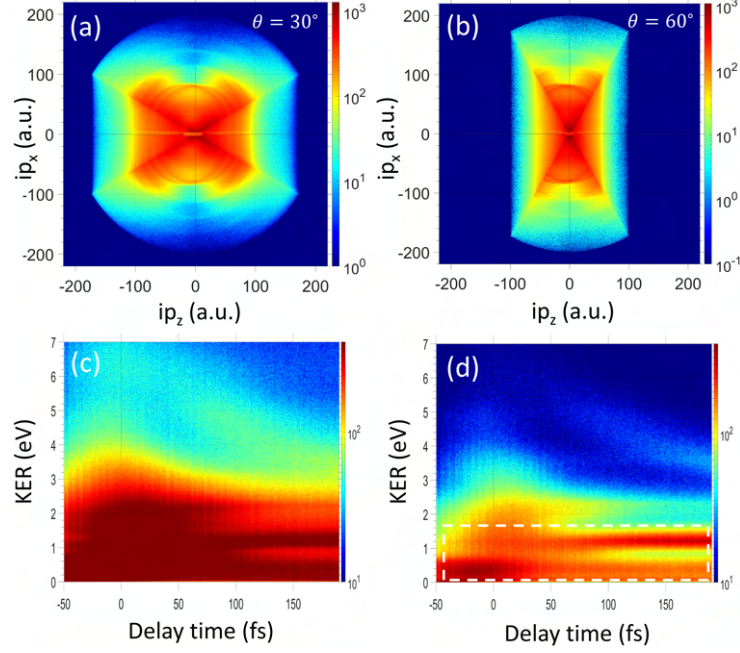


Figure 6.5: Br^+ momentum distributions and KER-delay spectra for different cone angles: (a,c) $\theta = 30^\circ$ and (b,d) $\theta = 60^\circ$. In (d), the white dashed rectangle indicates a branch-like structure, which starts from a spot around 0 fs and rises with delay time, finally reaches a constant KER level and forms a long-tail.

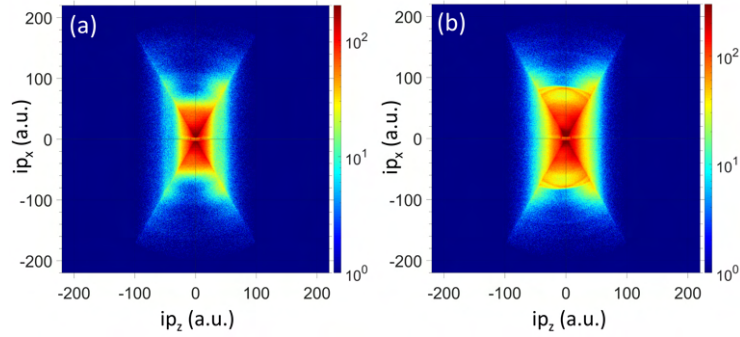


Figure 6.6: Br^+ momentum spectra for probe-only scan (a) and pump-probe scan (b). Here, the same cone-cut filter ($\theta = 60^\circ$) is applied to both cases.

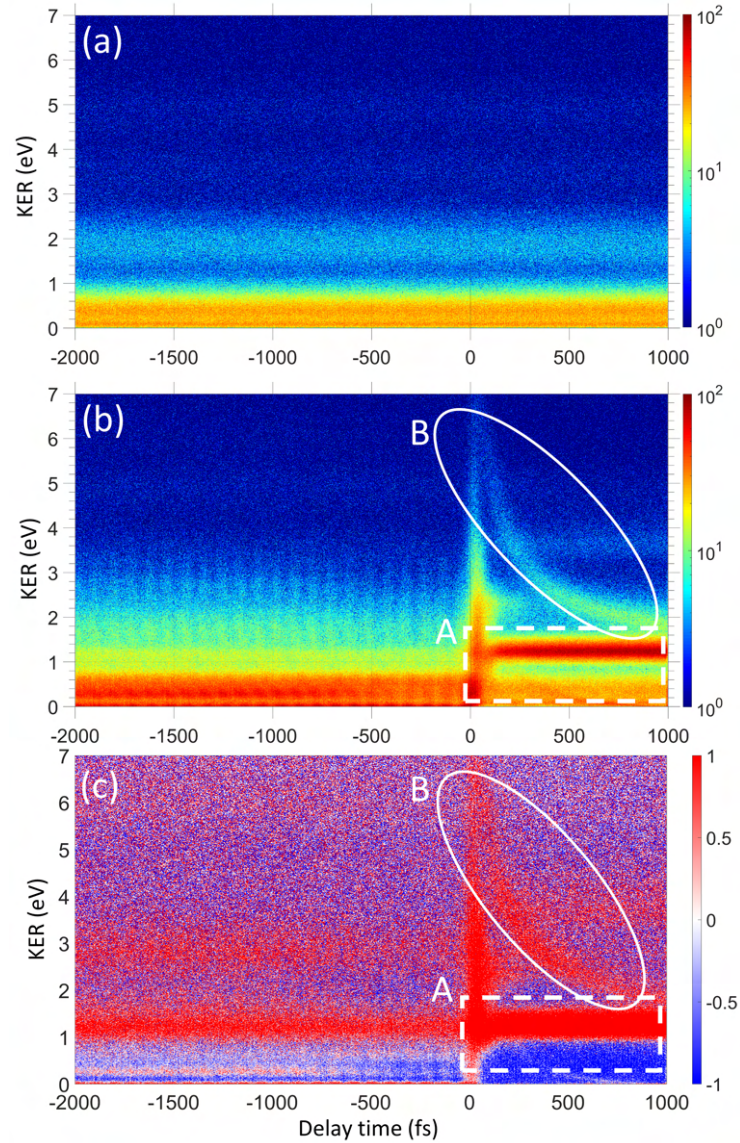


Figure 6.7: KER-delay spectra of proble-only scan (a) and long-delay pump-probe scan (b). (c) is the normlized differential plot between the two spectra. In (b,c), the neutral dissociation probed by single ionization is indicated by a dashed white rectangle labelled “A”, and the Coulomb explosion is indicated by a white ellipse labelled “B”.

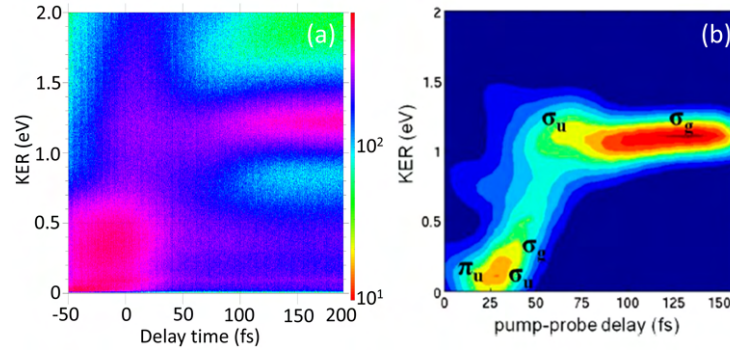


Figure 6.8: Comparing the KER-delay spectrum of single ionization channel (a) with simulation result (b) in [74]. Note a different colorbar is used to enhance the structure A in Figure 6.7.

6.2 Following the neutral dissociation of Br_2 by observing the photoelectron

6.2.1 Molecular frame photoelectron momentum distributions

In the previous section, we discussed the Br^+ momentum spectra in the laboratory coordinate system. However, when it comes to photoelectrons, the molecular coordinate system is typically preferred. This preference arises because ionization naturally occurs at the single molecular level, and the random molecular alignments in a gas jet can obscure structures in the electron momentum distribution. Consequently, a three-dimensional alignment of the molecule becomes necessary. Instead of physically aligning the Br_2 molecules in the experiment, we opt to select molecules with favorable alignment and then transform the measured data into the molecular frame.

To achieve this, we first select a subset of Br^+ ions oriented around the perpendicular direction of the z -axis (polarization direction), restricting the polar emission angle to $(120^\circ > \theta > 60^\circ)$, as illustrated in Figure 6.4(b). In the second step, we calculate the azimuthal ion emission angle α of the Br^+ ions in the xy -plane. We rotate both ion and electron momentum components in the xy -plane using a rotation matrix: $\mathbf{ip}' = \mathbf{R}(\alpha)\mathbf{ip}$ and $\mathbf{ep}' = \mathbf{R}(\alpha)\mathbf{ep}$ as depicted in Figure 6.9.

Figure 6.10 displays the rotated ion momentum distribution, denoted as $\mathbf{ip}'$. It is evident that all the Br^+ ions have been successfully aligned with the positive x -axis through this rotation. This same rotation matrix, denoted as $\mathbf{R}(\alpha)$, is also applied to the electrons. As a result, in conjunction with the stringent ion momentum constraints in the xy -plane, our coordinate system now coincides with the molecular frame.

Figure 6.11 illustrates the electron momentum distribution arising from the single ionization channel of dissociating Br_2 (as defined in Equation 6.1) within the molecular coordinate system. Noticeably, this transformation preserves the distinct ATI rings and strong field holography patterns. However, it is worth noting that these interference patterns are not as pronounced as those seen in the single ionization of Ar, as shown in Figure 2.5. We attribute this difference to the distinction between atoms and molecules: atoms do not face alignment issues, whereas even slightly misaligned molecules can still obscure some of the finer interference features, despite the alignment-selection procedures carried out on Br_2 .

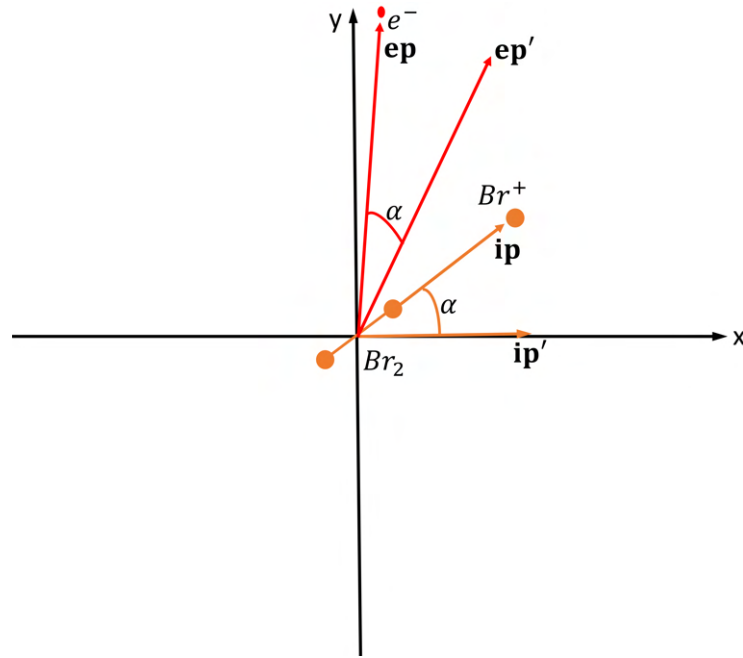


Figure 6.9: Illustration of electron momentum rotation. $\mathbf{ip}$ denotes the measured momentum of Br^+ with the azimuthal angle α . $\mathbf{ip}'$ represents the momentum of Br^+ after undergoing rotation to align with the x -axis. The electron momentum, $\mathbf{ep}$, undergoes rotation through the application of the rotation matrix $\mathbf{R}(\alpha)$, resulting in the transformed momentum $\mathbf{ep}'$.

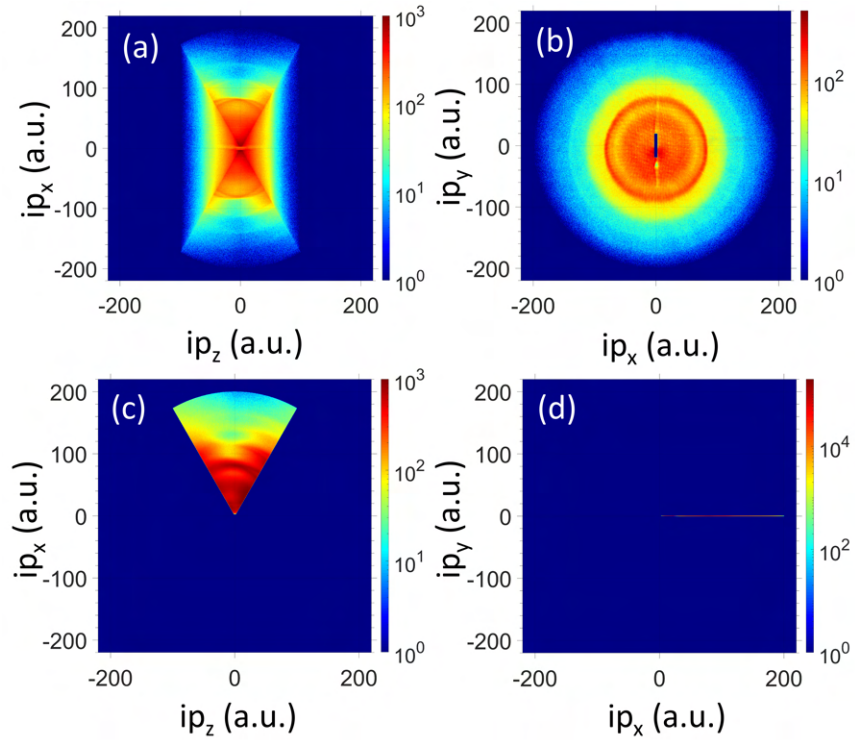


Figure 6.10: Br^+ momentum distributions (a,b) before and (c,d) after applying the rotation matrix $\mathbf{R}(\alpha)$.

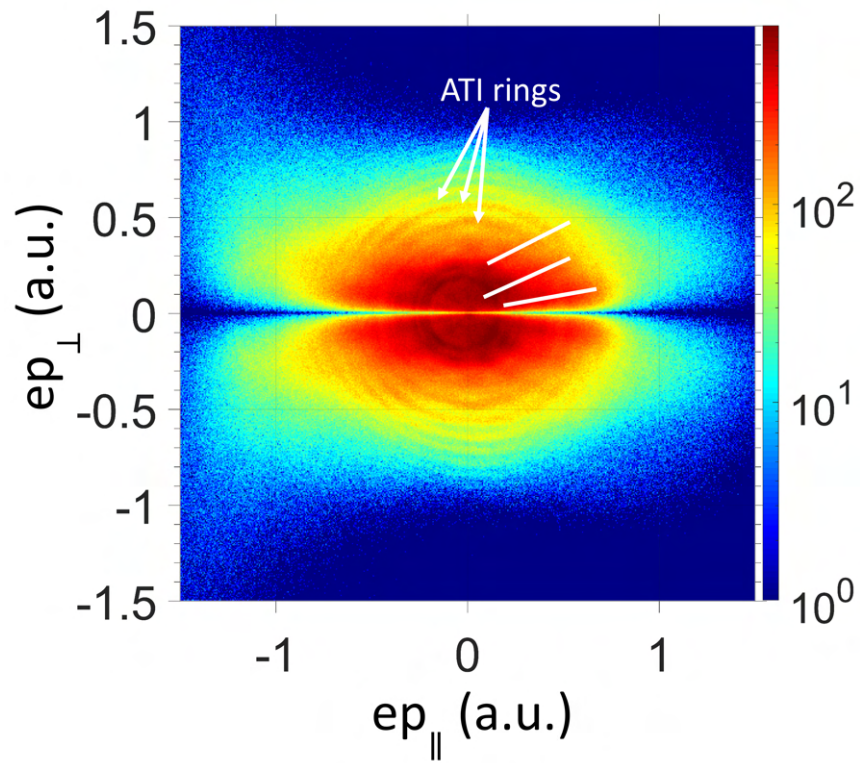


Figure 6.11: Electron momentum distribution from single-ionization channel of dissociating Br_2 . The ATI rings and the strong-field-holography fingers are indicated by white arrows and white lines respectively.

6.2.2 KER-delay dependent electron momentum distributions

The Br^+ KER-delay spectrum within the single ionization channel not only allows us to trace the evolution of molecular orbitals through ionization but also provides a means to isolate the photoelectrons produced from the dissociating C-state. Equation 6.1 represents the case that one electron is ionized during the dissociation of Br_2 . When compared to the double ionization channel described in Equation 6.2, the single ionization process retains more coherent characteristics, such as various interference structures, which would otherwise be obscured by the interaction of two distinct electrons in double ionization.

In Figure 6.12 we show that neutral dissociation occurs with the progression of both delay time and KER. Consequently, to capture the distinct dynamic stages involved, we must partition the KER-delay spectrum. However, the detailed understanding of how the neutral dissociation unfolds within the KER-delay space remains elusive. Therefore, we propose a division of neutral dissociation into five stages, corresponding to five KER-delay zones in Figure 6.12. This partitioning is based on the structure of the KER-delay distribution, which commences from a low-KER ($KER < 0.7$ eV) and low-delay (-25 fs $<$ delaytime < 25 fs) region (hence, the first zone) and progresses through a transition to a constant level (the last zone) exceeding 1 eV. The detailed KER and delay parameters for the zone partition can be arbitrary. Here, our specific parameters for this partitioning are provided in Table 6.1.

Table 6.1: Delay and KER parameters of different KER-delay zones.

Zones	Delay(fs)	KER(eV)
Zone 1	(-25,25)	(0.15,0.7)
Zone 2	(-20,75)	(0.7,1.0)
Zone 3	(50,100)	(1.0,1.4)
Zone 4	(100,150)	(1.0,1.5)
Zone 5	(150,200)	(1.0,1.5)

In Figure 6.13, we observe the electron momentum distributions corresponding to the five distinct KER-delay zones. Notably, there are discernible differences between these zones. For instance, Zone 1 exhibits a significantly more pronounced inner ring structure compared to the other zones, while Zone 4 and Zone 5 display clearer finger-like structures and inner fan-shaped patterns. Furthermore, the high transverse momentum region (0.5 a.u. $< |ep_{\perp}| < 0.8$ a.u.) becomes progressively more intense as we transition from one zone to the next.

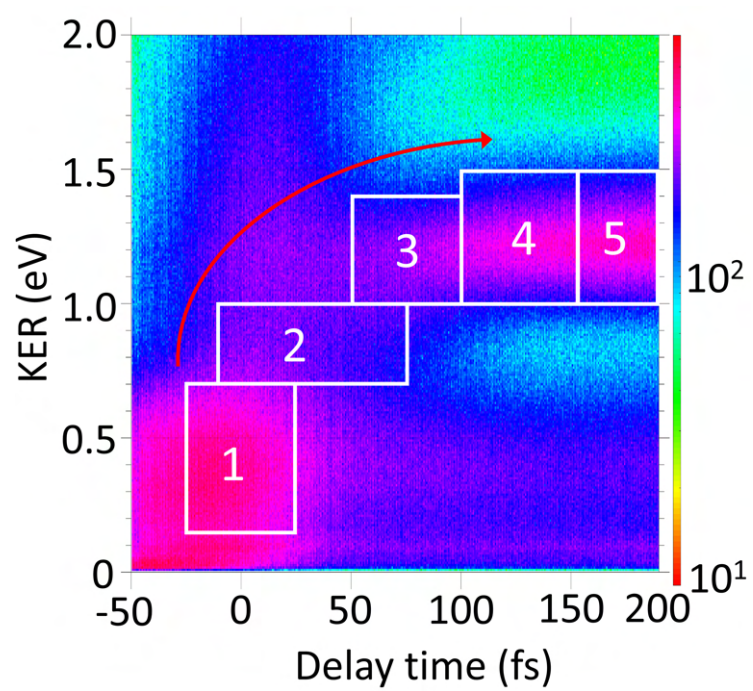


Figure 6.12: Zone-partition of KER-Delay spectrum.

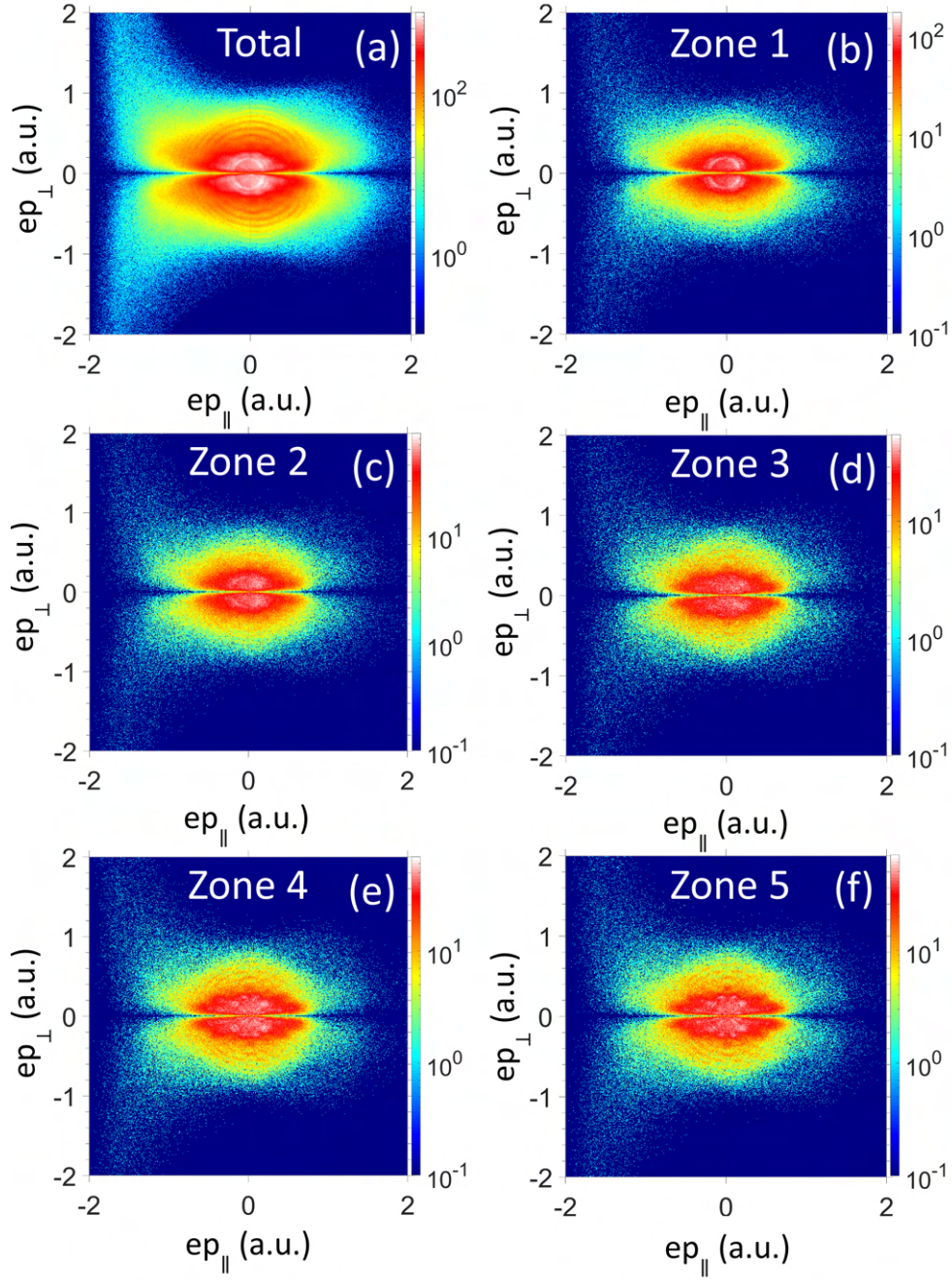


Figure 6.13: Electron momentum distributions from different Delay-KER zones. (a) is the distribution from all single ionization events of neutral dissociating Br_2 .

6.2.3 KER-delay dependent normalized differential plots of electron momentum distributions

In order to better observe the changes in KER-delay dependent electron momentum distributions, we further make the normalized differential (ND) plots between these distributions:

$$\begin{aligned} D'_{sig}(\mathbf{p}) &= \frac{D_{sig}(\mathbf{p})}{N_{sig,tot}}, \quad D'_{ref}(\mathbf{p}) = \frac{D_{ref}(\mathbf{p})}{N_{ref,tot}}, \\ ND(\mathbf{p}) &= \frac{D'_{sig}(\mathbf{p}) - D'_{ref}(\mathbf{p})}{D'_{sig}(\mathbf{p}) + D'_{ref}(\mathbf{p})}, \end{aligned} \quad (6.3)$$

where $D_{sig}(\mathbf{p})$ and $D_{ref}(\mathbf{p})$ are the signal and reference momentum distributions, respectively, and the primed ones are their normalized distributions. For normalization step, every pixel of each momentum distribution is divided by the total electron counts of respective distribution: $N_{sig,tot}$ or $N_{ref,tot}$, such that the distribution will sum to 1 when integrated over all momentum space.

In this context, we establish the distribution of Zone 1 as the common reference distribution, denoted as $D_{ref}(\mathbf{p})$, and then generate the ND (Normalized Difference) plots for each of the zones, which are presented in Figure 6.14. It can be seen that all the ND plots exhibit a blue inner ring, albeit with varying intensities. Specifically, the blue ring in Zone 2 appears notably weaker than in the other three zones. Moreover, the high transverse momentum region (enclosed within the dashed black ellipse) displays differing levels of red intensity across the different zones. Starting from Zone 2, the red intensity gradually increases and reaches its peak in Zone 4 and 5. These features observed in the ND plots of the electron momentum distributions can be understood based on our simulation results discussed in Chapter 4.

Figure 6.15 provides a comparison between the ND plot of Zone 5 and the ND plots obtained from two types of molecular-atomic SCTS (Strong-Field Coulomb-Three-Step) simulations: the multi-cycle simulation (depicted in Figure 6.15(b)) and the single-cycle simulation (illustrated in Figure 6.15(c)). Clearly, the blue inner ring structure is faithfully reproduced in the multi-cycle simulation. As previously discussed in Chapter 4, this blue inner ring structure arises from the ionization potential (Ip) difference between the Br atom and the π_u orbital of the Br_2 molecule. Concerning the high-transverse-momentum part, the single-cycle simulation exhibits the most similar enhancement feature to the experimental results, although the multi-cycle simulation also reproduces a similar feature, albeit somewhat blurred by ATI-rings.

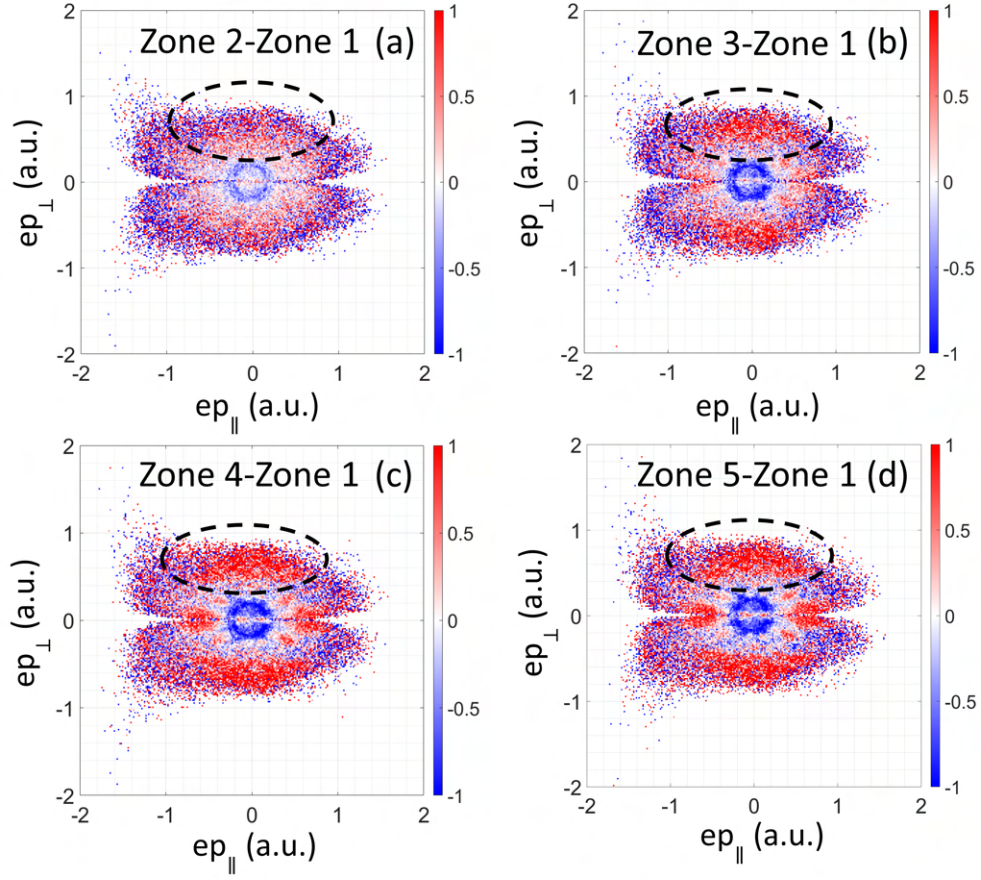


Figure 6.14: ND plots for the electron momentum distributions from different KER-delay zones. The black dashed ellipse indicates the feature of transverse-momentum-enhancement.

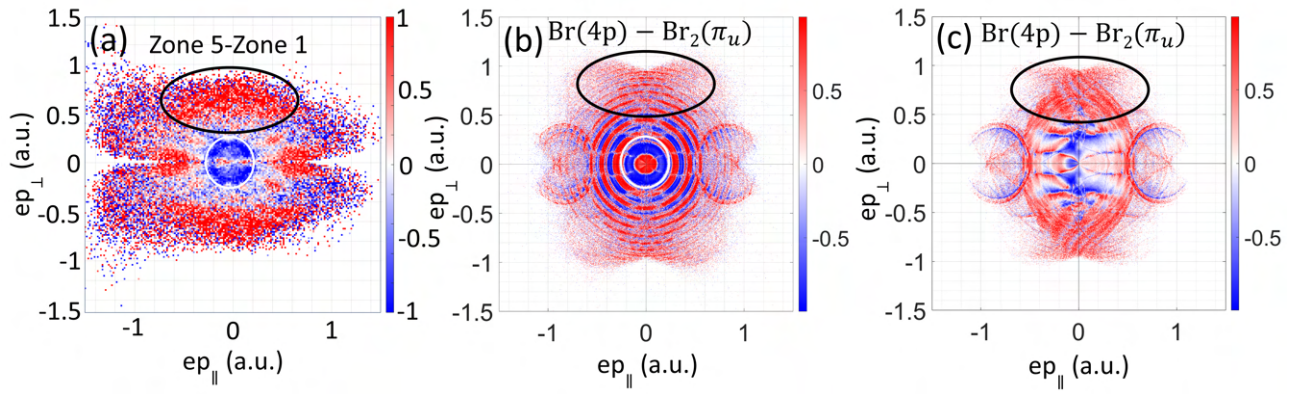


Figure 6.15: Comparison of ND plots from the experiment (a) and simulations (b-c). (b) is from the multi-cycle simulations of Br_2 ionization and Br ionization. And (c) is the same spectrum but from the single-cycle simulations.(see Section 4.3.5)

6.2.4 Radial momentum distributions of ND plots

Similar to the ND-plot analysis presented in Chapter 4, we aim to quantitatively highlight the characteristics of these five zones in the photoelectron momentum distributions by examining their radial momentum distributions.

In Figure 6.16(a), the experimental radial momentum distributions of the ND plots for Zone 2-5 are depicted. Notably, all four distributions exhibit a valley at low momentum and a peak at the high momentum end. When compared with the SCTS simulation results shown in Figure 6.16(b), we observe that the radial momentum of the valley precisely aligns with that derived from the multi-cycle simulation, at $ep_r = 0.2$ a.u.. Furthermore, the ND plot of Zone 5 minus Zone 1 in Figure 6.15(a) displays a similar blue inner-ring structure to that observed in Figure 6.15(b). These congruences between the experimental data and simulation results indicate that the π_u orbital is distinguishable by its I_p difference when compared to other orbitals during the process of neutral dissociation.

Concerning the peak structure observed at the high-momentum end, both the experimental data and the single-cycle simulation reveal that it emerges when $ep_r > 0.4$ a.u. and diminishes at $ep_r = 1.0$ a.u.. As discussed in Section 4.3.5, we have learned that this peak structure corresponds to the enhancement of transverse momentum in the ionization of the *Br* atom. The transverse momentum enhancement feature is also discernible in the ND plot shown in Figure 6.15(a), as indicated by the black ellipse. Consequently, the transition from the *Br*₂ molecule to the *Br* atom can be detected through the analysis of electron momentum distributions in our experimental setup.

A good agreement between experiment and simulated results on the enhancement peak should include the peak shape, the peak position, and the peak amplitude. However, we find our single-cycle simulation clearly differ from the experimental results. The first difference pertains to the peak shape: the simulation indicates a double-peak structure, whereas the experiment only displays a single peak. This peak shape difference also leads to the different peak positions as shown in Figure 6.17: the experimental single peak located between the double peaks of single-cycle simulation. The second difference relates to the peak amplitude: the simulation yields a difference value exceeding 300 at the peak, whereas the experiment records a maximum difference value of approximately 100, particularly for Zone 4 and 5. We believe that these variations in peak shape might arise from the contrast between a realistic Coulomb potential of ion-core and the theoretical one employed in our simulation. The presence of multiple electrons surrounding nuclei can potentially offset a portion of the Coulomb attraction force from the ion-core through the screening effect, thereby potentially diminishing or altering the scattering in the transverse direction. Moreover, a screened ion-core Coulomb potential may contribute significantly

to the differences in peak amplitudes. We suggest that a more accurate model for the ion-core Coulomb potential, which considers the multi-electron screening effect, may be necessary to achieve quantitative agreement with experimental observations. Additionally, we suspect that the background noise in our experimental setup may obscure certain peak features, further contributing to the disparities observed in comparison to the simulation results.

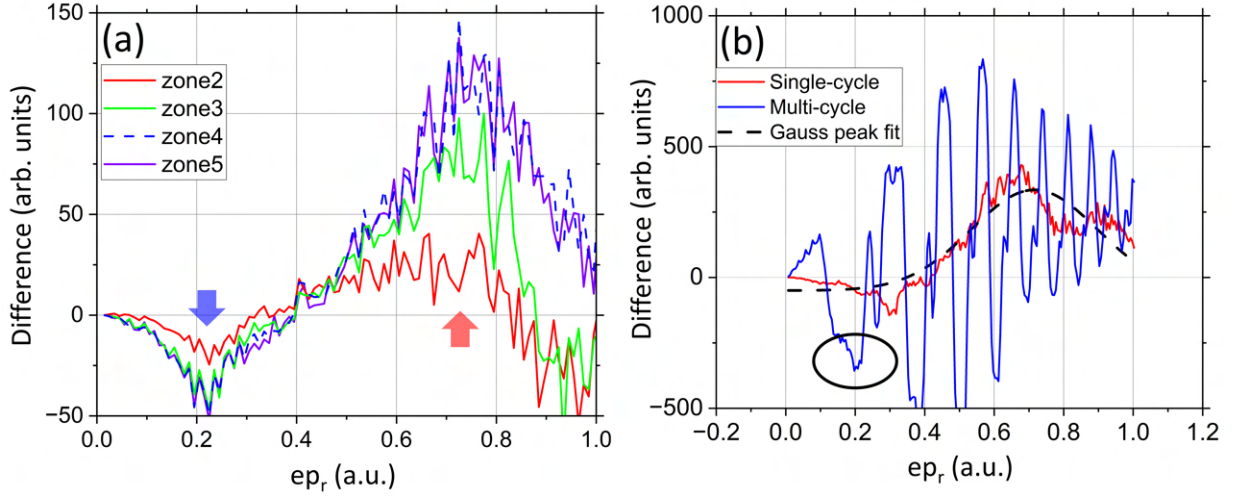


Figure 6.16: Comparison of the radial momentum distributions of the ND plots derived from both experimental data (a) and simulations (b). In panel (a), the ND plots are generated by comparing the electron momentum distributions of Zone 2-5 with the reference distribution of Zone 1. The blue downward arrow and the red upward arrow signify the valley structure characterized by a decrease in intensity and the peak structure characterized by an increase in intensity, respectively. In panel (b), the ND plot is derived between the atomic ionization of Br with the molecular ionization of Br_2 , as detailed in Section 4.3.5. The black ellipse indicates the radial momentum corresponding to the valley structure observed in the low momentum region.

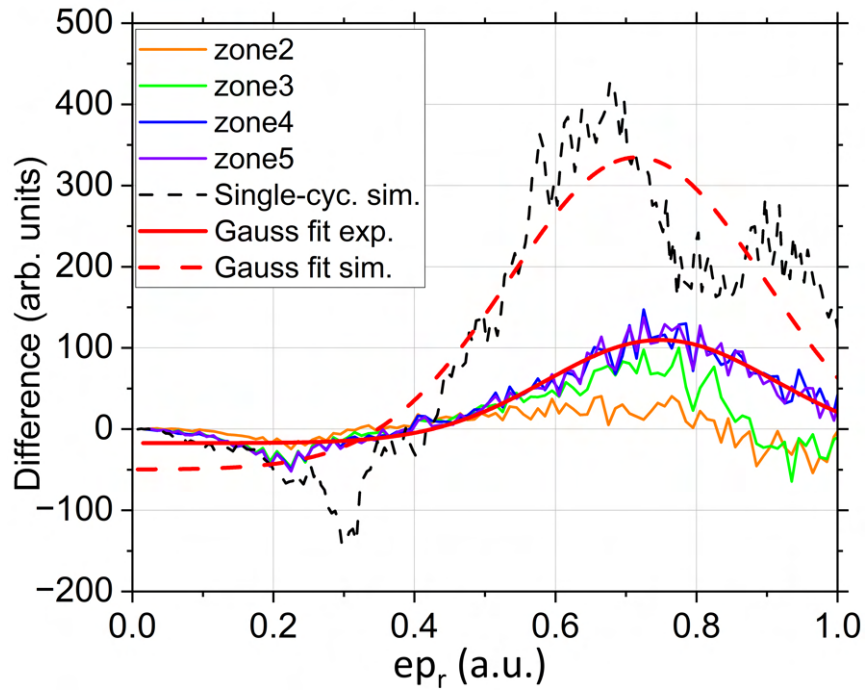


Figure 6.17: Detailed comparison between the radial momentum distributions of ND plots from experiment and the single-cycle simulations for molecular Br_2 and atomic Br . (see Section 4.3.5).

6.2.5 Identification of dynamical stages of Br_2 neutral dissociation

As elaborated in Section 4.3.5, the radial momentum distributions within ND plots encapsulate both molecular orbital information via the shifted ATI-rings, and molecular structural information through the transverse momentum enhancement. Consequently, these distributions serve as a distinctive tool for delving deeper into the neutral dissociation process of Br_2 , unveiling its various dynamic phases. In the following, we explore these radial momentum distributions within two distinct regions: the low momentum region ($0.0 \text{ a.u.} < p_r < 0.4 \text{ a.u.}$) and the high momentum region ($0.4 \text{ a.u.} < p_r < 1.0 \text{ a.u.}$).

As illustrated in Figure 6.18(a), within the low momentum region, Zone 2 exhibits a valley minimum that is notably higher than those observed in the other Zones. This disparity implies that the molecular orbital composition in Zone 2 differs from that in the other Zones. In Zone 2, there still exists some contribution from the π_u orbital, resulting in a less pronounced contrast with Zone 1. Conversely, in Zones 3-5, the π_u orbital has completely disappeared and is no longer contributing to the photoelectron signal, leading to a substantial disparity with Zone 1. By integrating this observation with the simulation outcome shown in Figure 2.29(b) [74], we deduce that the variation in the valley minimum reflects the evolution of the molecular orbital composition, transitioning from the π_u orbital to $\sigma_{u,g}$, and ultimately to the atomic $4p$ orbital. Zone 2, therefore, acts as an intermediate stage in this evolution of the molecular dissociation.

In Figure 6.18(b), we observe a broad enhancement in the high momentum region for each delay-KER zone. Notably, Zone 2 exhibits the lowest enhancement nearly aligning with the horizontal zero line, implying that the particular structure within Zone 2 closely resembles that in Zone 1. Thus, the dominance of the Br_2 molecular structure is evident in Zone 2. As we progress towards Zone 4 and Zone 5, the enhancement attains its maximum amplitude and maintains this level, indicating the completion of neutral dissociation and the dominance of Br atomic structure.

Furthermore, the high KER enhancement in Zone 3 is situated between Zones 2 and 4/5, suggesting that Zone 3 serves as a transitional phase between molecular and atomic structures. To elucidate the amplitude variation of these structures, we turn to our analysis through SCTS simulations. As elucidated in Section 4.3.5 of Chapter 4, the peak associated with the transverse momentum enhancement experiences an increase with higher ionic charge asymmetry and a decrease with internuclear distance. The enhancement observed in Zone 2 and Zone 3 imply that it increases with an increase in internuclear distance before reaching the atomic state. Consequently, we posit that the effective ionic charge distribution on the two Br atoms is responsible for the variation in the strength of the enhancement.

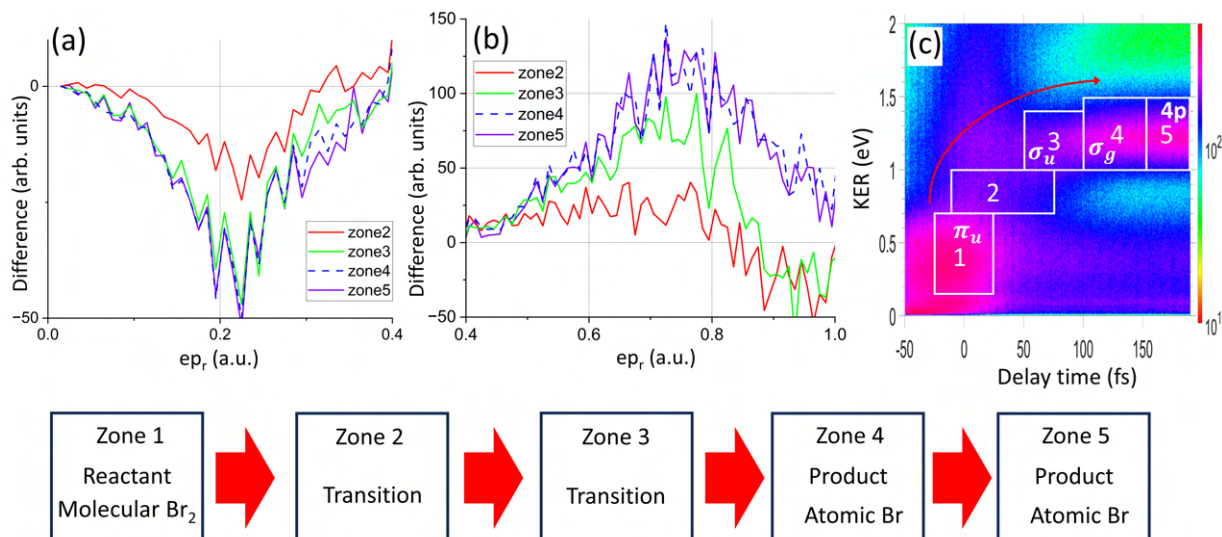


Figure 6.18: Dynamical stages identification for Br_2 's neutral dissociation. The radial momentum distributions of the ND plots in Figure 6.16 are examined in two regions: (a) the low radial momentum region ($0.0 \text{ a.u.} < p_r < 0.4 \text{ a.u.}$), and (b) the high radial momentum region ($0.4 \text{ a.u.} < p_r < 1.0 \text{ a.u.}$). (c) presents the KER-delay spectrum. Five KER-delay zones are indicated by the label “1-5”. The major contributed molecular orbitals in zones 1,3, and 4 are indicated basing on the simulation results in [74] (see Figure 6.8). For zone 5, the dissociation ends, hence, only atomic $4p$ orbital contributes the ionization.

Figure 6.19 provides an illustration of how the effective ionic charge on two Br atoms changes during the process of Br_2 neutral dissociation, divided into three distinct stages. In the initial stage (Zone 1 and Zone 2), the dissociation is just commencing, and Br_2 remains in its molecular state, characterized by a small internuclear distance. Consequently, when Br_2 is ionized, the remaining charge can evenly redistribute between the two atoms, resulting in a symmetric ionic charge configuration: $Z_1 = Z_2 = 0.5$.

Conversely, in the final stage, one Br atom is ionized while the other remains intact. Given the considerable separation between the two Br atoms at this stage, the remaining charge on one atom cannot redistribute to the other, leading to the most asymmetric ionic charge configuration: $Z_1 = 1.0, Z_2 = 0.0$. During the intermediate stage, the ionic charge configuration falls between the two extreme cases mentioned above. The internuclear distance between the two atoms is too small to cause an effective localization of the charge, yet not small enough to facilitate an equal distribution of the remaining charge. This results in a moderate level of ionic charge asymmetry.

Based on the simulation results discussed in Section 4.3.5.1, we ascertain that the asymmetric ionic charge configuration in Zone 3 gives rise to a peak higher than those observed in Zone 1 and Zone 2 (characterized by symmetric ionic charge configurations) but lower than the peaks in Zone 4 and Zone 5 (associated with atomic ionization). Therefore, the distinct peak structures observed in different zones can be attributed to the effective ionic-charge configuration post-ionization.

Furthermore, we notice that the low momentum valley structure in Zone 3 closely resembles that of Zone 4 and Zone 5, implying that the molecular orbital composition remains relatively stable as dissociation reaches Zone 3. Consequently, the differences in high momentum peaks observed in Zone 3 suggest that Zone 3 serves as a transitional stage in the structural evolution, wherein the molecular structure of Br_2 has nearly transitioned to the atomic configuration.

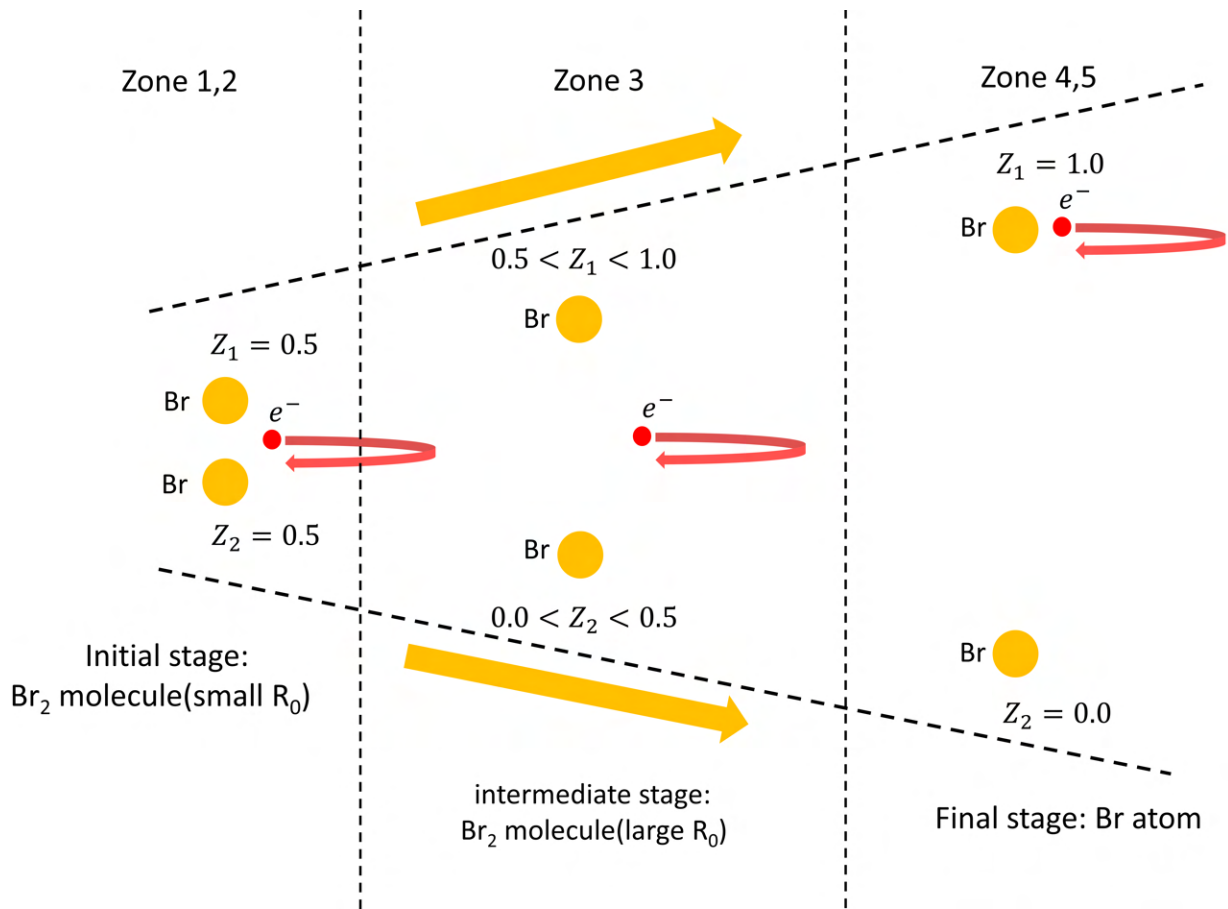


Figure 6.19: The graphic illustrates how the effective ionic charge on two Br atoms changes as Br_2 undergoes neutral dissociation. The red curved arrows in the image highlight instances of electron recollision in a strong laser field.

6.3 Observing vibrational wave packets on two spin-orbit states of Br_2^+

In the preceding sections, our observations have been focused solely on Br^+ ions in the perpendicular direction, enabling us to study the dissociation of neutral Br_2 along the C-state without interference from other dissociation pathways. In this section, we will present our observations of Br^+ ions aligned with the laser polarization direction.

6.3.1 Mechanism of pumping and probing vibrational wave packet in Br_2^+

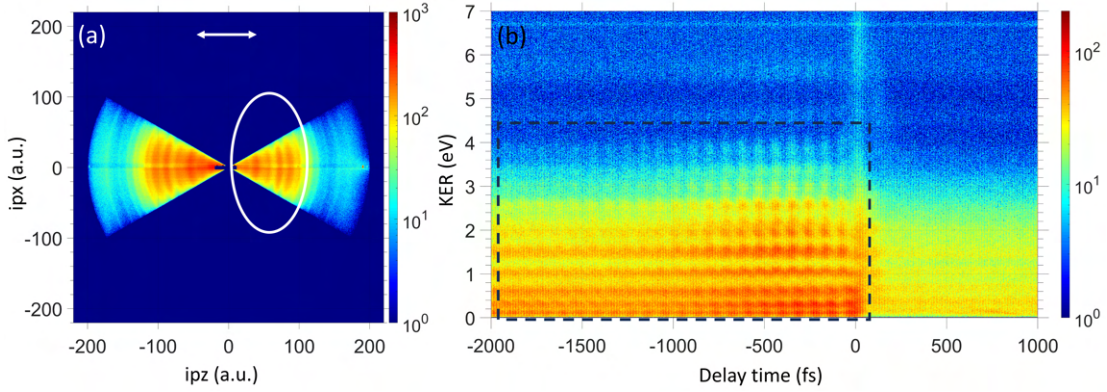


Figure 6.20: (a) Br^+ momentum distribution of the Br^+ ions along the polarization direction. (b) corresponding KER versus delay spectrum. In (a), the white arrow shows the laser polarization direction, and ellipse indicates the multi-rings structures along the polarization direction. In (b), the black dashed rectangle indicates the oscillation structure in the negative delay range.

In order to exclusively observe the Br^+ ions aligned with the polarization direction, we implemented a filter in the ion emission angle of $\theta < 30^\circ$ and $\theta > 150^\circ$. Such a constraint retains all ions within two narrow cones along the polarization direction while eliminating all others, representing the reverse procedure compared to the conical filter discussed in Section 6.1.3. In Figure 6.20(a), the Br^+ momentum distribution resulting from this cone-cut filter is displayed. Within the momentum range of $|ip_z| < 100$ a.u., we observe two sets of multi-ring structures. These structures bear resemblance to the bond-softening and above-threshold dissociation phenomena described in Section 6.1.1. However, it is

noteworthy that these multi-ring structures correspond to a long-time oscillation pattern within the KER distribution, particularly in the negative delay range, as outlined by the black dashed rectangle in Figure 6.20(b). This implies that these Br^+ ions originate from vibrational wave packets rather than a static ground state.

Considering that the weak, 400 nm pulse follows the strong 800 nm pulse in the negative delay range, it is evident that the vibrational wave packets are generated within the Br_2^+ manifold of states through strong-field ionization of groundstate Br_2 . Subsequently, the 400 nm pulse induces the dissociation of Br_2^+ and thereby produces Br^+ . Given the relatively low intensity of our 400 nm pulse (as discussed in Section 5.5), we believe that the dissociation induced by the blue pulse occurs through a single or two-photon transition process.

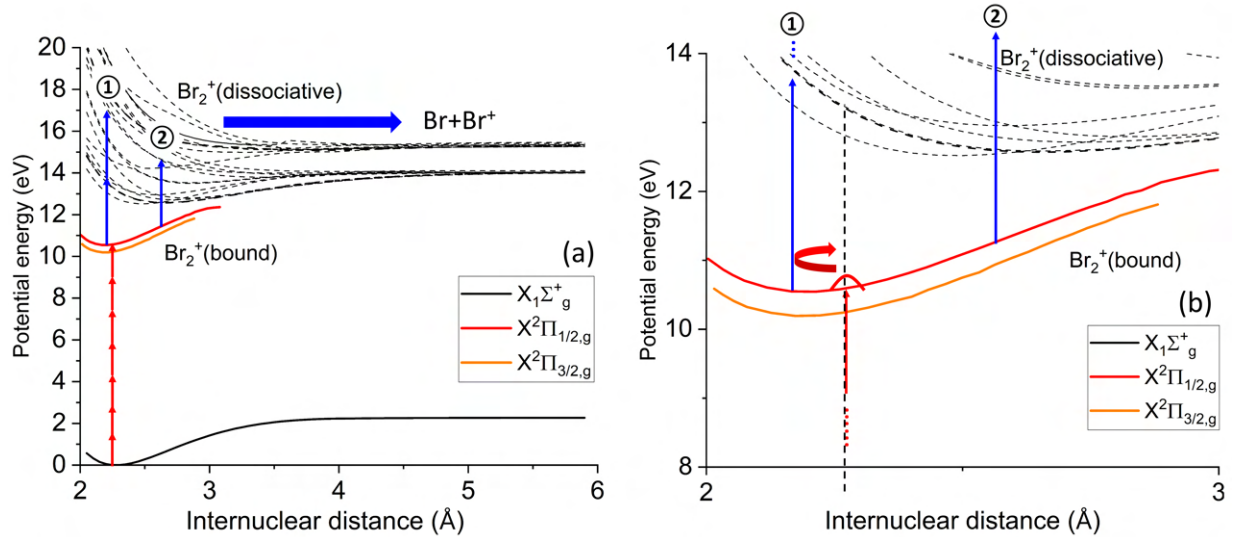


Figure 6.21: Illustration of probing the vibrational wave packet of Br_2^+ with the weak, 400 nm pulse. (a) Potential energy surfaces of Br_2 and Br_2^+ . The strong-field ionization of Br_2 is indicated by multiple red arrows. The two-photon and single-photon transition channels induced by blue pulse are indicated by “1” and “2” respectively. (b) Magnification of (a). The black dashed line indicates the equilibrium internuclear distance of Br_2 .

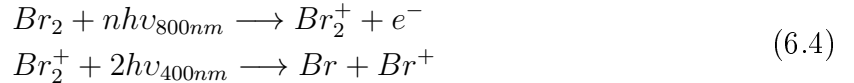
Figure 6.21 illustrates the probing mechanism of a vibrational wave packet in Br_2^+ using a weak, 400 nm pulse. Br_2^+ ground state is spin-orbit split into $X^2\Pi_{1/2,g}$ and $X^2\Pi_{3/2,g}$ states, shown by the red and yellow potential energy surface. When Br_2 undergoes strong field ionization by the intense, 800 nm pulse, two separate vibrational wave packets are being created on these two states.

After ionization, the weak, 400 *nm* pulse allows for either a two-photon absorption (designated as "1") or a single-photon channel (designated as "2") between the bound state and a dissociative state of Br_2^+ . These transitions tend to occur at a specific internuclear distance where one or two photons of 400 *nm* wavelength are resonant. Thus, when the bound vibrational wave packet reaches this resonance, it undergoes further excitation to reach the dissociative state, leading to the generation of a *Br* atom and a Br^+ ion. The Br^+ ions are subsequently measured using COLTRIMS (Cold Target Recoil Ion Momentum Spectroscopy).

Upon examining the internuclear distances, associated with the two transition channels within the blue pulse, a notable disparity becomes evident. The two-photon transition channel favors a position near the equilibrium internuclear distance of Br_2 , primarily due to the substantial transition energy that allows Br_2^+ to access high energy dissociative potential energy surfaces at shorter internuclear distances. Conversely, the single-photon transition channel can only excite the bound wave packet when it is located far from the equilibrium distance.

It is worth noting that when a wave packet travels over a significant distance, it can quickly lose coherence, potentially disrupting its profile. However, as indicated by the KER-delay spectrum in Figure 6.20(b), the vibrational motion persists for approximately 2 picoseconds. This suggests that the wave packet must oscillate within a limited displacement range around the equilibrium distance.

Hence, we conclude that the two-photon transition channel dissociates the Br_2^+ ion, and the process of pumping and probing the vibrational wave packet in Br_2^+ can be described as follows:



6.3.2 Fourier analysis of KER-delay spectrum

To extract frequency information from the oscillating KER distribution depicted in Figure 6.20(b), we employ the Fourier Transform (FT). This allows us to examine the oscillation dynamics of individual KER peaks shown in Figure 6.22(a). Specifically, we focus on the KER distribution within a time window of -2000 fs to 0 fs delay and apply a Hann window to minimize spectrum leakage.

In Figure 6.22(b), we present the FT amplitude spectrum, revealing two distinct frequency components: the most prominent component at 0 cm^{-1} , stemming from the constant background, and a column of discrete peaks at a frequency of around 360 cm^{-1} .

These peaks correspond to the oscillations within the KER-vs-delay distribution and align with the frequencies of the nine KER peaks in Figure 6.22(a). Upon closer inspection, we find that these peaks can be separated into two groups that are slightly shifted in frequency.

At first, we classify these KER peaks as two groups: the peaks with ($KER < 0.8$ eV) are defined as low KER and those with ($KER > 0.8$ eV) are high KER. To provide a quantitative assessment of the frequencies associated with the two groups of KER peaks, we construct frequency distributions for each KER peak, as depicted in Figure 6.23. This analysis highlights that the low KER peaks exhibit lower frequencies compared to the high KER peaks. Through Gaussian fitting of these frequency peaks, we obtain the center frequencies for these KER peaks as listed in Table 6.2. The two frequencies thus obtained closely match those of the two spin-orbit states in Br_2^+ : 361.2 cm^{-1} for $X^2\Pi_{1/2,g}$ and 364.9 cm^{-1} for $X^2\Pi_{3/2,g}$ [108]. Furthermore, it is evident that the frequencies of the low KER peaks correspond to the $X^2\Pi_{1/2,g}$ state, while the frequencies of the high KER peaks align with the $X^2\Pi_{3/2,g}$ state.

Consequently, in our Br_2 experiment, by observing various KER peaks of Br^+ , we can simultaneously and individually track the two vibrational wave packets associated with two closely spaced spin-orbit states.

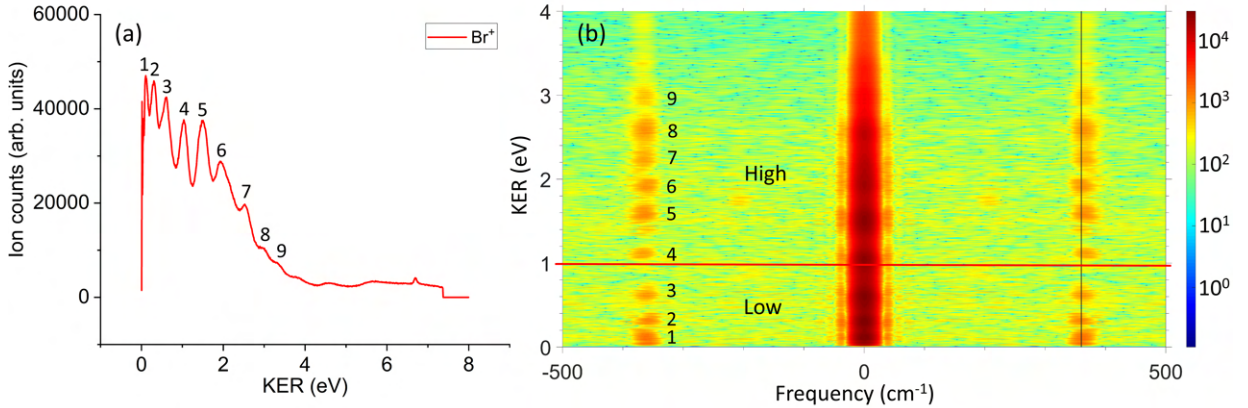


Figure 6.22: (a) Br^+ KER distribution by integrating over the entire delay time. (b) FT amplitude spectrum of KER-delay spectrum in Figure 6.20(b). The black vertical line corresponds 360 cm^{-1} . The 9 KER peaks are labeled in both spectra. The red horizontal line at 1 eV separates the KER peaks into two groups: low KER peaks and high KER peaks.

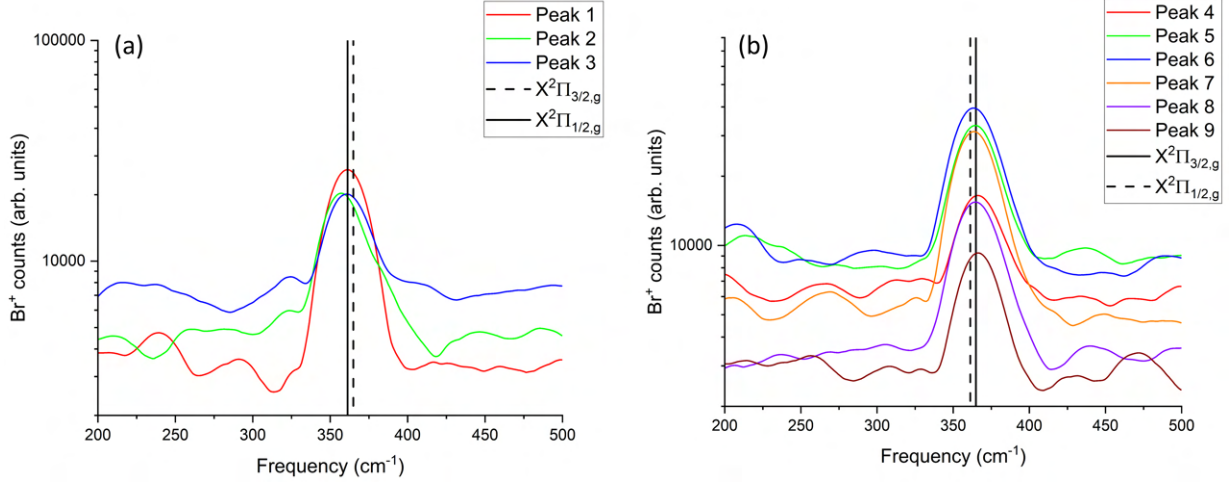


Figure 6.23: Frequency distributions for the KER peaks: (a) Low-KER peaks, (b) high-KER peaks. The vibrational frequencies of the two spin-orbit states $X^2\Pi_{1/2,g}$ and $X^2\Pi_{3/2,g}$ are indicated by solid and dashed lines in (a), while indicated by dashed and solid lines in (b).

Table 6.2: Central frequencies of the oscillating KER peaks obtained from a Gauss fit in Figure 6.23.

KER peak No.	1	2	3	4	5	6	7	8	9
KER (eV)	0.1	0.3	0.6	1.0	1.5	1.9	2.5	3.0	3.3
Frequency(cm^{-1})	361.2	357.5	360.5	366.5	364.5	363.5	363.5	364.5	366.5

Chapter 7

Conclusion

Understanding chemical reactions necessitates the simultaneous observation of atomic and valence electron dynamics within a molecule. The now well-established techniques of attosecond science provide the capability to dissect a molecule into its constituent ion and electron components, enabling the investigation of atomic and electronic motions concurrently.

In this thesis, our chosen subject of study is the photochemical reaction of Br_2 , which we examine through a pump-probe experiment utilizing photoion and photoelectron momentum spectroscopy. Given the intricacies of photoelectron spectroscopy, our initial focus was on untangling intracycle interference phenomena in strong-field ionization. This encompassed both experimental and theoretical efforts. Subsequently, we expanded our simulation model to include the case of molecule Br_2 and embarked on our Br_2 pump-probe experiment.

By combining our experimental findings with molecular simulation results, we conducted an analysis of the electron momentum distributions and tracked the photochemical reaction of Br_2 using ion and electron momentum spectroscopy. Consequently, our conclusions will revolve around two key aspects: the exploration of interference phenomena in strong field ionization and the observation of the photochemical reaction of Br_2 through photoion and photoelectron momentum spectroscopy.

In Chapter 3, we illustrated that it is possible to discern interference arising from non-adjacent quarter cycles in the photoelectron momentum distribution. This was achieved by utilizing two-color laser pulses with orthogonal polarizations, where the intensities of the 400 nm and 800 nm components were in a ratio of 10:1. In the experimental aspect of our research, we introduced a novel angle-resolved electron energy spectrum as a means

to visualize the intricate intracycle interference patterns within the electron momentum distribution. In the theoretical component of our study, we employed strong-field approximation theory to simulate these intracycle interference structures resulting from different combinations of quarter cycles.

The remarkable agreement observed between our experimental results and the simulations underscores the clarity with which intracycle interference structures can be elucidated. This approach treats interference as a composite of quantum pathways originating from various quarter cycles occurring within a single optical cycle.

In the first part of Chapter 4, we delved into a comprehensive exploration of intracycle interference structures within atomic ionization. This involved a meticulous examination of all feasible combinations of quarter cycles. Our primary focus here was on the intriguing fan-like interference structure found in the low-momentum region. Employing a time-variable soft-core Coulomb potential, we were able to establish that this low-momentum interference phenomenon arises from the interplay between electrons that have undergone drift and those that have not, specifically stemming from opposite direct quarter cycles. Furthermore, our investigations revealed that the principal scattering in the nuclear Coulomb potential occurs shortly after ionization. These findings underscore the sensitivity of the low-momentum region in the photoelectron spectrum to the ion potential, offering an additional avenue for probing ultrafast electronic structure dynamics.

The second part of Chapter 4 extends our model to molecules through the utilization of a semiclassical two-step model tailored for molecules. To this end, we took into consideration the molecular geometry and molecular orbitals. Our simulations, designed to replicate the electron momentum distributions observed in our Br_2 experiment, comprised two distinct approaches.

In the first type of simulation, we incorporated the phase structures of molecular orbitals, concentrating on unraveling the interference phenomena linked to the neutral dissociation of Br_2 . For intracycle interference, we explored the molecular orbital-dependent strong field holography patterns. Regarding intercycle interference, our modeling led to the identification of ionization potential-dependent ATI-ring structures within the low momentum range. Specifically, we identified a distinctive inner ring structure in the electron momentum distribution of Br_2 π_u orbital, making this orbital discernible in the observable photoelectron distributions.

In the second type of simulation, we directed our attention to the scattering events involving the nuclei of the Br_2 molecule and the Br atom, focusing solely on the molecular geometry. Through a comparison of electron momentum distributions between Br_2 molecules and Br atoms, we observed an enhanced transverse momentum feature in the

case of atoms. Upon a thorough examination of factors influencing this structure, we ascertained that the ionic charge plays a pivotal role in its formation. Furthermore, we demonstrated that, in the context of molecular ionization, an increase in the asymmetry of ionic charge between the two nuclei significantly amplifies this distinctive structure.

In Chapter 5, we presented a comprehensive overview of our experimental methods for conducting a pump-probe experiment involving Br_2 . This encompassed photoion and photoelectron momentum spectroscopy, and included detailed descriptions of our optical setup and COLTRIMS apparatus.

Finally, in Chapter 6, we presented a detailed discussion of the results obtained from our Br_2 experiment. In the measurements of the photoions, we employed a filter in the emission angle to selectively isolate Br^+ ions from the C-state dissociation of Br_2 and eliminate any interference from other dissociation processes. By scrutinizing the delay-dependent KER spectrum of Br^+ , we isolated two ionization channels that provide complementary insights into photodissociation of Br_2 : single ionization and Coulomb explosion. The KER-delay structure associated with single ionization compared well with the findings of previous research, confirming that it serves as a reliable indicator of the moment when the molecular bond breaks, that is when the molecule has transformed into two independent atoms. Simultaneously, the distinct Coulomb explosion structure evident in our KER-delay spectrum underscored the ability to track the increasing internuclear distance well after the electronic structure has transformed from a molecular one to an atomic one. However, whereas previous modeling of the experiment predicted the evolution of the molecular orbitals during dissociation, details of bond-breaking in a photodissociation are not directly observable in ion-momentum spectroscopy alone and require the simultaneous measurement of photoelectron spectra.

Consequently, in the second part of Chapter 6, we focussed on the delay-dependent electron momentum distributions arising from the C-state dissociation of Br_2 . The normalized differential plots of these electron momentum distributions revealed a distinct inner ring structure, mirroring the results obtained from multi-cycle simulations for Br_2 molecules and Br atoms in Chapter 4. Consequently, we were able to discern the presence of the π_u orbital through the I_p -dependence of the ATI-rings. Further examination of the radial momentum distributions revealed a gradual reduction in the contribution of the π_u orbital as the dissociation progressed. Additionally, we observed the emergence of high momentum structures in the radial momentum distributions and proposed that this suggested a structural transition from molecular Br_2 to atomic Br . Drawing upon our simulation findings, we attributed the structures to the increasing asymmetry in the ionic charge distribution between the two Br atoms as the internuclear distance grows. In conclusion, we identified the dynamic stages of the C-state dissociation, identifying two transitional phases related

to evolution of the molecular orbitals. These combined ion-electron observations demonstrate the qualitative advantage over observations based solely on ions, offering a more detailed perspective on photochemical reactions.

Finally, in the last part of Chapter 6, we studied the bound vibrational wave packets that were produced on the ground state of Br_2^+ through strong field ionization by the 800 *nm* pulse. Instead of focusing on Br^+ ions in the perpendicular direction, we shifted our attention to Br^+ ions aligned along the laser polarization direction. The KER-delay spectrum associated with these Br^+ ions unveiled a conspicuous oscillatory structure in the negative delay range. We postulated that these wave packets were generated through strong-field ionization induced by the strong, 800 *nm* pulse and subsequently probed via a two-photon transition process facilitated by the weak, 400 *nm* pulse. Our Fourier analysis further revealed that the oscillation frequencies of the low and high KER peaks corresponded to the vibrational wave packets found on the $X^2\Pi_{1/2,g}$ and $X^2\Pi_{3/2,g}$ states, respectively.

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APPENDICES

Appendix A

Symplectic algorithm for integrating Hamiltonian equations

In chapter 4, the hamiltonian equations 4.2 are integrated by the symplectic algorithm which is a numerical solving method specialized for integrating hamiltonian equations. It is an efficient algorithm and can keep numerical stability for calculations over long time span.

Generally, the hamiltonian $H(\mathbf{p}, \mathbf{q})$ of an electron in strong laser field can be splitted as:

$$H(\mathbf{p}, \mathbf{q}) = H_1(\mathbf{p}) + H_2(\mathbf{q}, t) \quad (\text{A.1})$$

Where $H_1(\mathbf{p}) = \frac{\mathbf{p}^2}{2}$ is the kinetic energy term, and $H_2(\mathbf{q}, t) = \mathbf{V}(\mathbf{q}) + \mathbf{q} \cdot \mathbf{E}(t)$ represents the Coulomb potential combined with the time-dependent interaction between electron and laser field. Here, we adopt a fourth-order symplectic algorithm which has a form as

follow:

$$\begin{aligned}
\mathbf{p}_1 &= \mathbf{p}^n + c_1 \tau \left(\frac{\partial H_2}{\partial \mathbf{q}} \right)_{\mathbf{q}_n, t}, \mathbf{q}_1 = \mathbf{q}^n + d_1 \tau \left(\frac{\partial H_1}{\partial \mathbf{p}} \right)_{\mathbf{p}_n} \\
t_1 &= t + \tau d_1 \\
\mathbf{p}_2 &= \mathbf{p}_1 + c_2 \tau \left(\frac{\partial H_2}{\partial \mathbf{q}} \right)_{\mathbf{q}_1, t_1}, \mathbf{q}_2 = \mathbf{q}_1 + d_2 \tau \left(\frac{\partial H_1}{\partial \mathbf{p}} \right)_{\mathbf{p}_1} \\
t_2 &= t_1 + \tau d_2 \\
\mathbf{p}_3 &= \mathbf{p}_2 + c_3 \tau \left(\frac{\partial H_2}{\partial \mathbf{q}} \right)_{\mathbf{q}_2, t_2}, \mathbf{q}_3 = \mathbf{q}_2 + d_3 \tau \left(\frac{\partial H_1}{\partial \mathbf{p}} \right)_{\mathbf{p}_2} \\
t_3 &= t_2 + \tau d_3 \\
\mathbf{p}^{n+1} &= \mathbf{p}_3 + c_4 \tau \left(\frac{\partial H_2}{\partial \mathbf{q}} \right)_{\mathbf{q}_3, t_3}, \mathbf{q}^{n+1} = \mathbf{q}_3 + d_4 \tau \left(\frac{\partial H_1}{\partial \mathbf{p}} \right)_{\mathbf{p}_3}
\end{aligned} \tag{A.2}$$

Where $c_1 = 0$, $c_2 = c_4 = \alpha$, $c_3 = \beta$, $d_1 = d_4 = \frac{\alpha}{2}$, $d_2 = d_3 = \frac{\alpha+\beta}{2}$, $\alpha = \left(2 - 2^{\frac{1}{3}}\right)^{-1}$, and $\beta = 1 - 2\alpha$.