



MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES



DIRECTIONAL DISSOCIATION OF MOLECULES BY SPATIALLY AND TEMPORALLY MODIFIED LASER FIELDS

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Ph.D. THESIS

Department of Physics

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Saba Arife KARAKAŞ

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ÖZET

UZAYSAL VE ZAMANSAL OLARAK MODİFİYE EDİLMİŞ LAZER ALANLARI İLE MOLEKÜLLERİN YÖNLÜ AYRIŞMASI

Bu tezde ultra-hızlı fiziğin dört temel konusuna dair sonuçlar ile bu sonuçların teorik temelleri anlatılmaktadır. Bu konular ele alınırken lazer atması hem uzaysal hem de zamansal olarak çeşitli şekillerde modifiye edilmiştir.

Ayrışmanın şiddet bağımlılığında öncelikle basit olarak hangi ayrışma kanalının hangi şiddette açıldığı gösterilmiştir. Bu hesaplamalarda sistem bir nanotip civarına taşınarak bu nanotipin ayrışma kanallarına etkisi de incelenmiştir.

İkinci kısımda iki-döngülü, gausyen zarflı lazer atmasına bir son-atma eklenmiştir. Burada motivasyon, gerçek deneysel ortamlarda temiz bir lazer atmasının oluşturulmasının çok zor olmasıdır. Bu zorluk nedeni ile görece zayıf bir son-atma eklenecek bu atmanın sonuçlara etkisi teorik olarak irdelenmiştir. Bu son-atmanın, zaman ölçeklerinin uzun olmasından dolayı BS ve özellikle ZPD kanallarını etkilediği ve bu iki kanalın üstüste geldiği düşük KER bölgesinde ayrışmayı ve ayrışma asimetrisini modifiye ettiği görülmüştür.

Cıvıtlı ultra kısa lazer atmaları konusunda “Atma Genişliği Korunan Cıvıtlama” ismi verilmiş olan cıvıtlama şekli teorik olarak önerilmektedir. Bu yeni mekanizma ile cıvıtılanmış lazer atmalarının ayrışma verimini ve ayrışmadaki asimetriyi kuvvetli bir şekilde modifiye ettiği bulunmuştur. Cıvıltı arttıkça ayrışma veriminin arttığı ve cıvıltı ile lineer bağımlı şekilde düşük enerjilere kaydığı görülmüştür. Bu pozitif cıvıltı için ATD kanalının şiddetlenerek düşük enerjilere doğru kaydığını göstermektedir.

İzotop etkisinin ayrıntılı araştırılması ile ayrışma verimine ve asimetriye dair önemli sonuçlar elde edilmiştir. Bu kısımda sistem metalik bir nanotipin civarına taşınmıştır. Bu sayede sistemin uzay-bağımlı bir elektrik alan ile ayrışması sağlanmıştır. Kütle- nin artması ile ayrışma veriminin düştüğü, ancak ayrışma piklerinin daha yüksek enerjilere doğru, kütle numarasına lineer bağımlı olarak kaydığı gözlenmiştir. Tezde ayrıca uzay-bağımlı yakın alanın sonucu olarak oluşmuş olan asimetri kontrastı da ayrıntılı olarak incelenmiştir.

ABSTRACT

DIRECTIONAL DISSOCIATION OF MOLECULES BY SPATIALLY AND TEMPORALLY MODIFIED LASER FIELDS

In this thesis, the results of the four fundamental subjects of ultra-fast physics and the theoretical foundations of these results are explained. In addressing these issues, laser pulse has been modified in various ways, both spatially and temporally.

In the intensity dependence of dissociation, it has been shown in a simple way which dissociation channel is opened at which intensity. In these calculations, the system was moved around a nanotip and the effect of this nanotip on the dissociation channels was also examined.

In the second part, a post-pulse is added to the two-cycle, ultra-short laser pulse with gaussian-envelope. The motivation here is that it is very difficult to create a clean laser pulse in real experimental settings. Because of this difficulty, a relatively weak post-pulse is added and the effect of this pulse on the results was examined theoretically. This post-pulse has been observed to affect the BS and especially the ZPD channels due to the long time scales and modifies the dissociation and asymmetry in the low KER region where these two channels overlap.

In the case of chirped ultra-short laser pulses, the form of chirping, called “Pulse-Width Maintained Chirping”, is theoretically proposed. This shows that for positive chirp, the ATD channel shifts towards low energies.

With detailed investigation of the isotope effect, important results were obtained regarding the dissociation yield and asymmetry. In this part, the system has been moved around a metallic nanotip. In this way, the laser interacted with both the molecule and the nanotip, and the system was dissociated by a space-dependent electric field by creating a space-dependent near field around the nanotip. Both heteronucleus and homonucleus isotopes of the hydrogen molecule have been studied. It has been observed that the dissociation yield decreases with the increase in mass, but the dissociation peaks shift towards higher energies, with a linear dependence on the mass number. In the thesis, the asymmetry contrast formed as a result of the space-dependent near field is also examined in detail.

CLAIM FOR ORIGINALITY

DIRECTIONAL DISSOCIATION OF MOLECULES BY SPATIALLY AND TEMPORALLY MODIFIED LASER FIELDS

In this thesis, four different problems subjected to atto physics and atto-nano physics are discussed. These problems are intensity dependency of molecular dissociation, post pulse effect on molecular dissociation, chirp effect on molecular dissociation and isotope effect on molecular dissociation near metallic nanotips. In the first problem addressed in this thesis, the intensity effect on molecular dissociation is clearly shown for the first time. In second problem, new phenomena called as “Post-Pulse” is defined and investigated for the first time. In third problem, a novel schema for chirping a laser pulse, called as “Pulse-Width Maintained Chirping Schema”, is proposed and effects of this new schema is investigated thoroughly. In the forth problem, for the first time, isotope effect is discussed in the perspective of molecular dissociation near metallic nanotip.

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Saba Arife KARAKAŞ

ABBREVIATIONS

ADK Ammosov-Delone-Krainov

ATD Above Threshold Dissociation

BS Bond Softening

CEP Carrier Envelope Phase

FC Franck-Condon

FFT Fast Fourier Transform

FT Fourier Transformation

KER Kinetic Energy Release

MO-ADK Molecular-Ammosov-Delone-Krainov

PES Potential Energy Surface

PP Post-Pulse

QM Quantum Mechanics

TDSE Time Dependent Schrödinger Equation

TLP Transform Limited Pulse

ZPD Zero Photon Dissociation

SYMBOLS

$\mathbf{D}_2^+$ Duterium Diatomic Cation

$\mathbf{DT}^+$ Deuterium Tritium Cation

$\mathbf{H}_2^+$ Hydrogen Diatomic Cation

$\mathbf{HD}^+$ Hydrogen Deuterium Cation

$\mathbf{HT}^+$ Hydrogen Tritium Cation

$\mathbf{T}_2^+$ Tritium Diatomic Cation

$\mathbf{1s}\sigma_g$ Gerade State

$\mathbf{2p}\sigma_u$ Ungerade State

$\mathbf{H}_2$ Hydrogen Diatomic Molecule

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1. INTRODUCTION

The advent and steady evolution of ultra-short intense laser sources and momentum imaging techniques, have placed the research in the fields of attosecond physics, especially the ultrafast strong-field-matter interaction in general and photo-dissociation and ionization processes in particular attention [2–15]. The simplest molecules available, i.e., the molecular hydrogen, its isotopes and their ionic companions, have been used as standard models to examine the underlying complex dynamics arising when they are illuminated by strong and short light fields. Particularly interesting phenomena, such as bond softening and above-threshold dissociation have been experimentally demonstrated successfully in these elementary molecular systems [5, 11, 12, 15–17]. Electron localization has been observed in real time during molecule dissociation with recent experiments [18]. Amongst the knobs available to manipulate and control these phenomena, laser peak intensity, carrier envelope phase, and pulse duration have predominantly been used [8, 19–21]. It is possible, however, to manipulate the temporal and spectral shape of the driven laser sources [22], thanks to the spectrally broad bandwidth of femtosecond pulses. Therefore physics behind the strong-field-matter interactions for hydrogen molecule and its cation is widely investigated [2–17, 23, 24]. Especially, the Bond Softening (BS) and Above Threshold Dissociation (ATD) have been observed in the experiments for H_2 and H_2^+ [5, 11, 12, 15–17].

The hydrogen molecule has an interesting characteristic when it comes to the isotope effect. The hydrogen atom nearly doubles its mass by taking an additional neutron. There is no other molecule in the universe that nearly doubles and triples its mass via its first and second isotopes. This is the strongest isotope effect known by the human-beings and both theory and experiment take advantages of this fact. Also, the isotopes of this tiny molecule are the intermediate steps to the more complicated molecules, such as Li_2 , H_2O , CH_4 , NH_3 , etc. In addition, there are ongoing investigations about photo-dissociation of larger, organic molecules such as proteins, DNA, etc [25–34]. Many molecules, whether

they are diatomic or not, can be modeled as diatomic, with one atom on one side and the remaining group on the other with suitable effective potentials. Therefore investigating the phenomena with the heteronucleus isotopic molecules of hydrogen, namely HD^+ , HT^+ , D_2^+ , DT^+ and T_2^+ , bridges the gap between hydrogen molecule and more complex molecules and helps to understand and explain the physics behind several phenomena. Thus, the control and manipulation of vibrational and electronic dynamics in isotope molecules of hydrogen are widely investigated [8, 35–38].

On the other hand, there is a research field called as nanoscale physics which studies to understand and manipulate the physical phenomena occurs at nanoscale. This area of research focuses on particles, molecules, materials, metamaterials, etc. One may check references to reach some of recent reviews for the applications of nanoscience in optoelectronics [39], nonlinear plasmonics [40, 41], surface plasmons [42], medical implants [43].

Together with these, recently the two emerging research area, namely attosecond physics and nanoscale physics begin to unite. Even though both attosecond physics and nanoscale physics are well established, their emergence holds a lot of open questions. Some of these questions are answered such as the dissociation of H_2^+ in the vicinity of nanotips [44, 45], altering conductivity of dielectrics with ultra-short pulses [46], controlling driving electron currents [47], managing electron emission induced by light from nanoparticles and nanotips [48–52] and subcycle drive photoemission from solids [53–56], observing dissociation of molecules near metallic structures real-time and real space [57].

In this thesis, we go beyond aforementioned phenomena and introduce new control mechanisms on directional dissociation during strong-laser-matter interactions. First we briefly investigated the intensity-dependence of dissociation channels. Then we consider laser pulse shapes modified in different ways, both spatially and temporally. One of the temporal modification is named as “Post-Pulse”. This kind of laser pulse consists of two successive ultra-short and strong laser pulses first of which is responsible to induce dissociation in the molecule. The second laser pulse is created to mimic the noisy laser pulses in a

real experiment. Even though a clean, phase-stabilized ultra-short laser pulse is desired to better understand the processes in molecules, this is often not the case in an experiment. Therefore we begin to investigate the effect of a post-pulse theoretically to gain a better understanding in the experimental results. Then we consider another temporally modified laser pulse and study the outcomes from the interactions with phase-stabilized, ultra-short, chirped laser pulses and molecules. To do so, we propose a new chirping schema [58]. Finally, we study a spatially modified laser field. In this case we move the laser-matter system into the vicinity of a nanotip. This way the laser pulse interacts not only with the molecule, but also with the nanotip, as well. Occurring from this interaction, due to the surface plasmon resonance in the nanotip, a spatially-inhomogeneous field is shaped. We systematically take this spatial inhomogeneity into account in our calculations.

This thesis is arranged as follows: In second section, we revise the theoretical foundations of strong-laser-matter interactions. In third section, our results are given. Conclusion is discussed in the forth section. In appendices, vibrational level energies and KER-CEP maps generated in this thesis are shown for all the molecules considered.

2. THEORY

In this section, we describe the fundamentals and theory of the ultra-short laser pulse and molecule interactions we considered in the thesis. We first review the ultra-short laser pulses and the laser-matter interaction dynamics and continue with the quantum mechanical explanations of diatomic molecules. To make the process more realistic, we will assume that the molecular cations occur dynamically by the ionization of parent molecules. We calculate the ionization rates and ionization times and start the TDSE calculations at these times. We prepare the initial nuclear wave functions as the superposition of different vibrational levels by use of Franck-Condon coefficients.

2.1. Time Dependent Schrödinger Equation

Evolution of a quantum mechanical system over time is described by time dependent Schrödinger equation (TDSE). It is a second order partial differential equation. In atomic units ($e = \hbar = m_e = 1$) this equation is written as,

$$i\frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t) \quad (2.1)$$

In this thesis this equation is used to determine the behaviour of molecules interacting with laser pulses under different conditions. One of these conditions is the chirp, the varying frequency of the laser pulse over time and the other one is near field effect caused by a nanostructure interacting with a laser field. The other one of these conditions is Post-Pulse (PP). PP is a satellite pulse following the ultra-short laser pulse. Lastly we have investigated the isotope effect on dissociation near metallic nanotip.

2.2. Ultra-short Laser Pulses

An electric field pulse whose duration is equal or less than a picosecond (10^{-12} s) are defined as an ultra-short laser pulse. This time-scale is less than the vibration period of a molecule and is the order of electron ionization, resonant transition, etc. Ultra-short

pulses are sometimes called femtosecond pulses. Ultra-short laser frequencies cover a broad spectrum, typically ranging between infrared and ultra-violet, and ultra-short pulses are produced by various sources. Ti-sapphire lasers are amongst the most common ones and emits tunable radiation between red and near-infrared (i.e., $\sim 800\text{-}1000\text{ nm}$) [59]. In a fundamental perspective, the time-scale of such pulses match well with the electron dynamics of atoms, molecules and solids with which, *e.g.* time-resolved measurements and inducing/probing electronic processes are performed. Therefore, the advances in femtosecond lasers lead to the birth of ultra-short pulse, non-linear optics. And many various applications/technologies are made possible in fundamental research, materials and biotechnology, etc., thanks to the ultra-short pulses. Some of the fundamental application are; high-order harmonic generation [60–63], tomographic orbital imaging [64, 65], attosecond metrology [66–68], coherent chemical reaction control [8], etc.

The mathematical form of the time-dependent laser pulse can simply be written as,

$$E(t) = E_0 f(t) \cos(\omega_0 t + \phi), \quad (2.2)$$

where $f(t)$ is the pulse envelope (to encapsulate the ultra-short pulse) and cosine term is the carrier of the pulse. ω_0 is the angular frequency, where $\omega_0 = 2\pi/T$, and ϕ is the Carrier-Envelope Phase (CEP) of the pulse (see Figure 2.1). In case CEP is temporally stabilized, becoming a transform-limited pulse, $\phi = \phi_0$ is a constant. In order to reflect the experimental measurements depending on the conditions, different functional forms of $f(t)$ can be chosen as the envelope; such as Gaussian, sin-squared or trapezoidal, etc, given as,

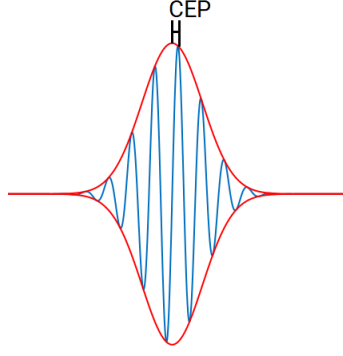


Figure 2.1 A diagram showing the carrier-envelope phase (CEP) between two ultra short pulses.

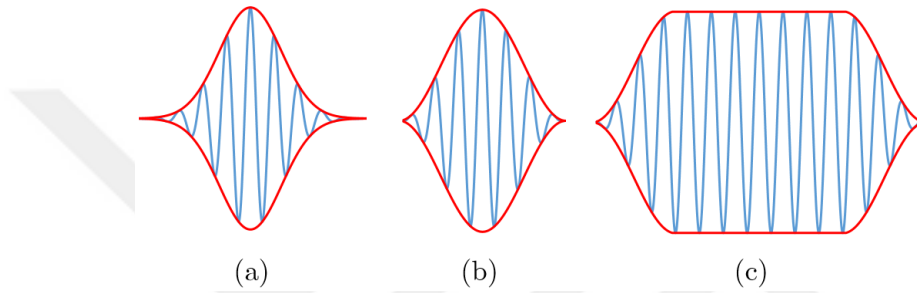


Figure 2.2 Laser pulses with (a) Gaussian, (b) sin-squared and (c) trapezoidal envelopes.

$$\text{Gaussian Envelope : } f(t) = \exp(-t^2/\tau^2) \quad (2.3)$$

$$\text{Sin-squared Envelope : } f(t) = \sin^2(t\pi/\tau) \quad (2.4)$$

$$\text{Trapezoidal Envelope : } f(t) = \begin{cases} \sin^2(t\pi/\tau), & \text{first } n \text{ cycles} \\ \text{constant}, & \text{middle } m \text{ cycles} \\ \sin^2(t\pi/\tau), & \text{last } k \text{ cycles} \end{cases} \quad (2.5)$$

One may change the rising and falling edges of trapezoidal envelope with Gaussian terms. Pictorial representations with different envelopes of an ultra-short pulse is portrayed in Figure 2.2.

Based on perturbation theory, the laser field impacts matter via the coupling term $\vec{p} \cdot \vec{E}$, where $\vec{p}$ is the dipole moment of the matter and $\vec{E}$ is the field vector. If we assume that $\vec{E} = E_0 \cos(\omega_0 t) \hat{e}_z$, i.e. a linearly polarized light, and $\vec{p} = \vec{r}$, then $\vec{p} \cdot \vec{E} = z E_0 \cos(\omega_0 t)$.

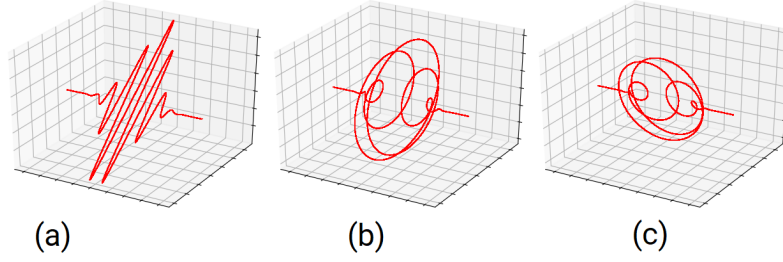


Figure 2.3 Laser pulses with (a) linear, (b) circular and (c) elliptical polarizations.

2.3. Chirped Laser Pulses

Chirp is a spectral property of laser pulses which can be defined as the change of the frequency over time. A laser pulse gains chirp during propagating a transparent medium due to the nonlinearities and chromatic dispersion. In semiconductor lasers or amplifiers chirp can be acquired from refractive index changes essential to density changes of the carrier [69]. All in all to chirp a laser pulse, fibers and grating pairs can be used experimentally [70]. Mathematically speaking chirp is the higher order term in the wave function.

$$E(t) = E_0 f(t) \cos \left(\omega_0 t + \phi_0 + \frac{4 \ln(2) \eta}{\tau^2} t^2 \right), \quad (2.6)$$

where E_0 is the peak-intensity, $f(t)$ is the envelope, ω_0 is the frequency, ϕ_0 is the CEP, τ is the duration of the laser pulse, respectively. η is a dimensionless parameter which indicates the degree of frequency change over time, *i.e.* the chirp parameter. For positive values of η , higher frequencies come later in the tail of the laser pulse whereas for the negative chirp parameters the lower frequencies are in the falling edge of the pulse. Therefore a blue(red)-shift occurs for positive(negative) chirp values. Figure 2.4 shows the temporal shape of zero (Transform Limited Pulse, TLP), positive and negative chirped laser pulses with Gaussian envelope.

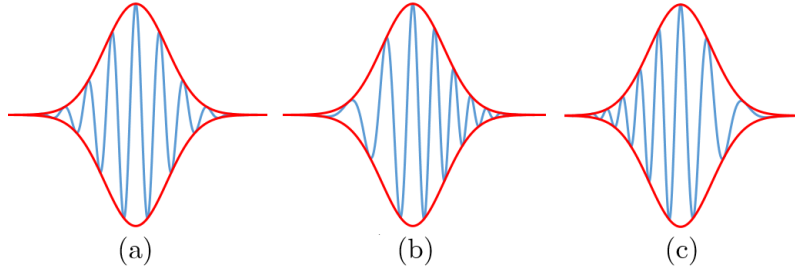


Figure 2.4 Two-cycle laser pulses with (a) zero, (b) positive and (c) negative chirp values with Gaussian envelope.

2.4. Numerical Solution of the Time-Dependent Schrödinger Equation for Diatomic Cation

To solve the dynamics of laser-matter interactions we employed the numerical solutions of the time-dependent Schrodinger equation (TDSE) based on the interaction of a linearly polarized laser field with a molecule. This equation is written as,

$$\hat{H}(\vec{r}, R, t)\Psi(\vec{r}, R, t) = i\frac{\partial}{\partial t}\Psi(\vec{r}, R, t) \quad (2.7)$$

where r and R stands for the electronic and nuclear coordinates, respectively. In the next sections, we introduce the approximations we made on Equation 2.7. Solution of Equation 2.7 leads to electronic and nuclear dynamics of the diatomic molecules we considered.

2.5. Born-Oppenheimer Approximation: Field-Free Hamiltonian of a Diatomic Cation

The field-free Hamiltonian of the diatomic cation (such as H_2^+) contains kinetic and potential energy terms for nuclei and electron:

$$\begin{aligned} \hat{H} &= \hat{T}_e(\vec{r}) + \hat{T}_n(R) + V_e(\vec{r}, R) + V_n(R) \\ &= -\frac{1}{2\mu_e}\nabla^2 - \frac{1}{2\mu_n}\frac{\partial^2}{\partial R^2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z^2}{R} \end{aligned} \quad (2.8)$$

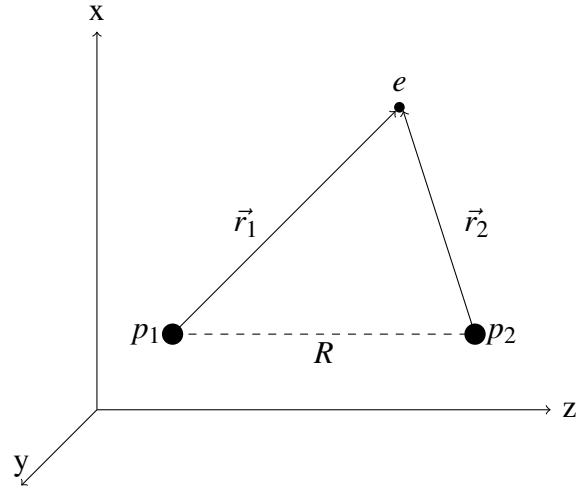


Figure 2.5 Diatomic molecular cation system

where the first and second terms of the Hamiltonian is the kinetic energy of the electronic and nuclear motion, respectively. $\mu_n = M_p/2$ and $\mu_e = 2M_p/(2M_p + 1)$ are the reduced mass of the nuclei and electron, respectively, and M_p is the nuclear mass. Third and forth terms in the Hamiltonian are electron-nuclei interaction potentials and the last term is the Coulomb potential of the inter-nuclear interactions. Coordinate definitions are shown in Figure 2.5.

We apply Born-Oppenheimer approximation to solve the time-independent Schrödinger equation. Born-Oppenheimer approximation is the principle realizes that the time scales of electron and nucleus motions are different, one is much faster than the other. Based on this approximation, the total wave function of the system can be separated as the wave functions of electron and nucleus as, $\Psi_{total} \simeq \psi_e \psi_n$, with which, we can write our total wavefunction as

$$\Psi_{total}(\vec{r}, R) = \psi_e(\vec{r}; R) \psi_n(R). \quad (2.9)$$

Using this approximation in the Schrödinger equation yields the separation of field-free

Hamiltonian into electronic and nuclear parts as follows:

$$\hat{H}_e \psi_e = E_e \psi_e, \quad (2.10)$$

$$\hat{H}_n \psi_n = E_n \psi_n, \quad (2.11)$$

and more explicitly one can write,

$$\left[-\frac{1}{2\mu_e} \nabla^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z^2}{R} \right] \psi_e(\vec{r}; R) = E_e(R) \psi_e(\vec{r}; R) \quad (2.12)$$

$$\left[-\frac{1}{2\mu_n} \frac{\partial^2}{\partial R^2} + E_e(R) \right] \psi_n(R) = E_n \psi_n(R), \quad (2.13)$$

for electronic and nuclear Schrödinger equations, respectively.

2.6. Model Diatomic Molecule

To solve Equations 2.12 and 2.13 is very challenging even numerically due to the degrees of freedom. Even for the simplest molecule on Earth, H_2^+ , there are 2 nuclei and an electron ,i.e. there are 9 degrees of freedom of this system. Mathematically speaking, these much degrees of freedom express the number of equations one has to solve. To simplify this system, we may consider a model diatomic molecule. In order to modify the Hamiltonian of the system first we shift the origin of the coordinate system (see Figure 2.6). Simplification will be done in electronic kinetic and potential terms.

$$\begin{aligned} V_e &= -\frac{Z}{r_1} - \frac{Z}{r_2} = -\frac{Z}{\sqrt{x^2 + y^2 + (z + R/2)^2}} - \frac{Z}{\sqrt{x^2 + y^2 + (z - R/2)^2}} \\ &\approx -\frac{a}{\sqrt{b(R) + (z + R/2)^2}} - \frac{a}{\sqrt{b(R) + (z - R/2)^2}} \end{aligned} \quad (2.14)$$

$$\hat{T}_e = -\frac{1}{2\mu_e} \nabla^2 \approx -\frac{1}{2\mu_e} \frac{\partial^2}{\partial z^2}. \quad (2.15)$$

Simplification in the kinetic term arise from that z-direction is chosen for the polarization

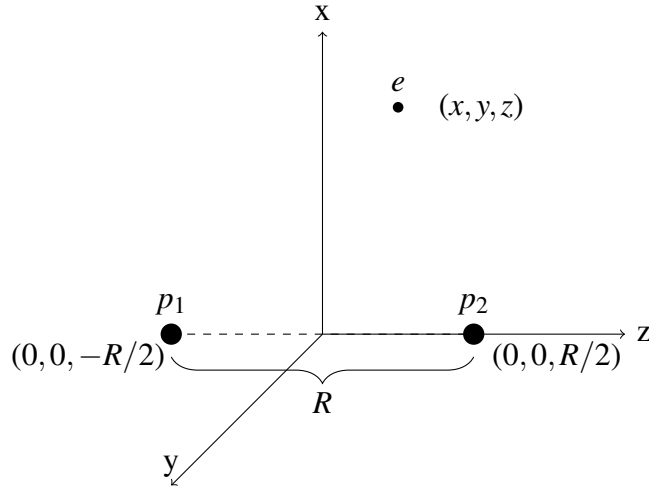


Figure 2.6 Diatomic molecular cation system in shifted coordinates.

of the laser pulse. Therefore it is assumed that the electron has non-zero momentum only in z -direction. Hence the Hamiltonian of this simplified model molecule is stated as,

$$\hat{H}_n = \hat{T}_n(R) + V_n(R) = -\frac{1}{2\mu_n} \frac{\partial^2}{\partial R^2} + \frac{Z^2}{R}, \quad (2.16)$$

$$\begin{aligned} \hat{H}_e &= \hat{T}_e(z) + V_e(z, R) \\ &= -\frac{1}{2\mu_e} \frac{\partial^2}{\partial z^2} - \frac{a}{\sqrt{(z - R/2)^2 + b(R)}} - \frac{a}{\sqrt{(z + R/2)^2 + b(R)}}. \end{aligned} \quad (2.17)$$

Please note that electronic Hamiltonian depends on R -coordinate, parametrically. Therefore Equation (2.10) can be solved for a constant value of R to obtain electronic wave function. By calculating electronic wave functions for all the possible nuclei arrangements, nuclei solution can be introduced which is enacted from effective potentials, so-called Potential Energy Surfaces (PES). These potentials result from the population and the energy of the electronic eigenstates.

$a = 0.251$ is a scale parameter and $b(R)$ is a function to accurately reproduce the three dimensional potential energy curves of the molecular cation.

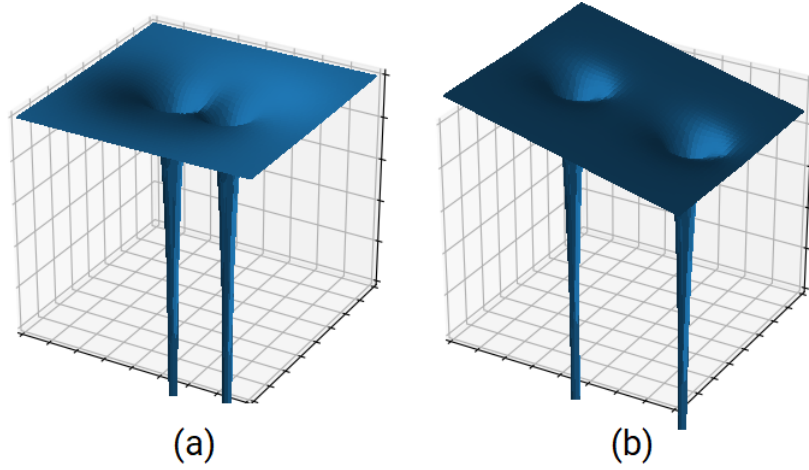


Figure 2.7 Potentials formed by hydrogen molecule during the dissociation triggered by a laser field. Molecular potential (a) before the laser pulse arrives. (b) when the laser pulse is at its peak.

2.7. A Molecule Interacting with A Laser Pulse

When a laser pulse hits a molecule, it bends the potential created by the atoms in the molecule according to the direction of the electric field. In Figure 2.7 (b) this bend is shown. Since the electric field in a laser pulse changes both its magnitude and its direction within time, this bend occurs as a shake of the molecular potential. And during this shake, atoms begin to move away from each other.

The Hamiltonian for a molecule interacting with a laser pulse can be written as,

$$\hat{H} = \hat{T}_e(z) + \hat{T}_n(R) + V_n(R) + V_e(z, R) + V_L(z, R, t), \quad (2.18)$$

where the first two terms are the kinetic energy terms of electron and nuclei, respectively, third term is the potential between two nucleus, fourth term is the potential between nuclei and electron and the last term is the laser-matter interaction term. For uniform linearly polarized laser field and matter interactions the last term can be written as [71],

$$V_L(z, R, t) = E(t) \left[\frac{m_1 - m_2}{m_1 + m_2} R + \frac{m_1 + m_2 + 2}{m_1 + m_2 + 1} z \right] \quad (2.19)$$

which also accounts the mass asymmetry. Here, m_1 and m_2 are the nuclear masses. In this

thesis, only the length-gauge representation of laser potential is in use unless otherwise stated. To propagate the time-dependent wave-function we use,

$$\Psi(z, R; t + \delta t) = \exp(-i\hat{H}\delta t)\Psi(z, R; t) \quad (2.20)$$

We have splitted the hamiltonian into nuclear and electronic parts,

$$\Psi(z, R; t + \delta t) = \exp(-i\hat{H}_n\delta t)\exp(-i\hat{H}_e\delta t)\Psi(z, R; t) + \mathcal{O}([\hat{H}_n, \hat{H}_e]) \quad (2.21)$$

and from Padé approximation we may rewrite the time propagation operator as,

$$\Psi(z, R; t + \delta t) \approx \frac{1 - i\hat{H}_n\delta t/2}{1 + i\hat{H}_n\delta t/2} \frac{1 - i\hat{H}_e\delta t/2}{1 + i\hat{H}_e\delta t/2} \Psi(z, R; t), \quad (2.22)$$

where $\hat{H}_n$ is the nuclear and $\hat{H}_e$ is the electronic Hamiltonian. At this point we need to first update the wave function using only electronic Hamiltonian. Then we may apply the nuclear Hamiltonian. The order of this operation does not matter since the commutator of electronic and nuclear Hamiltonians vanishes. Let us give a name to the first update operation as,

$$(1 + i\hat{H}_e\delta t/2)\Psi'(z, R; t + \delta t/2) = (1 - i\hat{H}_e\delta t/2\hbar)\Psi(z, R; t), \quad (2.23)$$

$$(1 + i\hat{H}_n\delta t/2)\Psi(z, R; t + \delta t) = (1 - i\hat{H}_n\delta t/2\hbar)\Psi'(z, R; t + \delta t/2), \quad (2.24)$$

where $\Psi'(z, R; t + \delta t/2)$ is the intermediate solution step named as half-time wave function. Note that we have used an intermediate step to update the wave function. Now we may apply the finite difference rule on a grid to obtain update equations for Ψ . The 2nd order finite difference rule for an ordinary function follows as,

$$\frac{d^2f}{dx^2} = \frac{f_{j+1} - 2f_j + f_{j-1}}{\delta x^2} + \mathcal{O}(\delta x^2) \quad (2.25)$$

By applying finite difference rule one may get,

$$\begin{aligned} & \left(1 + i\frac{\delta t}{2} \left(V_e + \frac{1}{\mu_e \delta z^2}\right)\right) \Psi'_{s+1/2,j,k} - i\frac{\delta t}{4\mu_e \delta z^2} (\Psi'_{s+1/2,j+1,k} + \Psi'_{s+1/2,j-1,k}) \\ &= \left(1 - i\frac{\delta t}{2} \left(V_e + \frac{1}{\mu_e \delta z^2}\right)\right) \Psi_{s,j,k} + i\frac{\delta t}{4\mu_e \delta z^2} (\Psi_{s,j+1,k} + \Psi_{s,j-1,k}) \end{aligned} \quad (2.26)$$

$$\begin{aligned} & \left(1 + i\frac{\delta t}{2} \left(V_n + \frac{1}{\mu_n \delta R^2}\right)\right) \Psi_{s+1,j,k} - i\frac{\delta t}{4\mu_n \delta R^2} (\Psi_{s+1,j,k+1} + \Psi_{s+1,j,k-1}) \\ &= \left(1 - i\frac{\delta t}{2} \left(V_n + \frac{1}{\mu_n \delta R^2}\right)\right) \Psi'_{s+1/2,j,k} + i\frac{\delta t}{4\mu_n \delta R^2} (\Psi'_{s+1/2,j,k+1} + \Psi'_{s+1/2,j,k-1}) \end{aligned} \quad (2.27)$$

These equations are tridiagonal matrix equations. To visualize, we rewrite the first one in matrix form as,

$$\begin{pmatrix} 1+\beta & -\alpha & 0 & 0 & \cdots \\ -\alpha & 1+\beta & -\alpha & 0 & \cdots \\ 0 & -\alpha & 1+\beta & -\alpha & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & -\alpha & 1+\beta \end{pmatrix} \Psi' = \begin{pmatrix} 1-\beta & \alpha & 0 & 0 & \cdots \\ \alpha & 1-\beta & \alpha & 0 & \cdots \\ 0 & \alpha & 1-\beta & \alpha & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \alpha & 1-\beta \end{pmatrix} \Psi, \quad (2.28)$$

where $\beta = i\frac{\delta t}{2} \left(V_e + \frac{1}{2\mu_e \delta z^2}\right)$ and $\alpha = i\frac{\delta t}{4\mu_e \delta z^2}$. To write the second equation in matrix form is simple with slightly different α and β values. Since we begin by the known time-step, RHS of Equation (2.28) is straightforward. Therefore this equation can be solved by diagonalisation of the LHS. After this step, one may apply the nuclear Hamiltonian to Ψ' similarly, to obtain the updated Ψ in time.

In this thesis, the simulation box is $z \in (-100, 100)$ a.u. and $R \in (0, 25)$ a.u. with $dz = 0.1$ a.u. and $dR = 0.1$ a.u.. Time propagation runs for ~ 37 fs with time step $dt = 0.0135$ a.u..

2.8. Two-Level System for Hydrogen Cation

Hydrogen cation is simple enough of a molecule that can be described with only its first two PES levels, which is called as gerade ($1s\sigma_g$) and ungerade ($2p\sigma_u$) states [8]. This is also realized from the fact that first two energy states are energetically well separated from upper energy states. Gerade and ungerade states are shown in Figure 2.8. These states are obtained by changing the distance between the nuclei and resolving the Hamiltonian for fixed intermolecular distance using Shooting method [72]. Using the two-level simplification, one may expand the full wave function for the internuclear distance and the electronic coordinate in terms of the lowest-lying electronic states, as,

$$\Psi_{total}(r, R; t) = |g\rangle \Psi_g(R; t) + |u\rangle \Psi_u(R; t), \quad (2.29)$$

where $|g\rangle$ is $1s\sigma_g$ state, $|u\rangle$ is $2p\sigma_u$ state, Ψ_g nuclear wavepacket corresponding to $1s\sigma_g$ state and Ψ_u nuclear wavepacket corresponding to $2p\sigma_u$ state. Here the molecule is assumed to be aligned with the polarization axis of the laser field. Inserting this ansatz into the TDSE one gets the coupled equations as ([73, 74]),

$$i\frac{\partial}{\partial t} \begin{pmatrix} \Psi_g(R; t) \\ \Psi_u(R; t) \end{pmatrix} = \begin{pmatrix} -\frac{1}{M} \frac{\partial^2}{\partial R^2} + V_g(R) & V_{gu}(R) \\ V_{gu}^*(R) & -\frac{1}{M} \frac{\partial^2}{\partial R^2} + V_u(R) \end{pmatrix} \begin{pmatrix} \Psi_g(R; t) \\ \Psi_u(R; t) \end{pmatrix} \quad (2.30)$$

where $V_g(R)$, $V_u(R)$ are the potentials corresponding to the $1s\sigma_g$ and $2p\sigma_u$ states and $V_{gu}(R)$ is the coupling between them.

2.9. Origin of Asymmetry: Two-Level Case

Considering the two-level model for directional control of dissociation, we can write the electronic wave-function in terms of gerade and ungerade states, their relative populations and phase as [75],

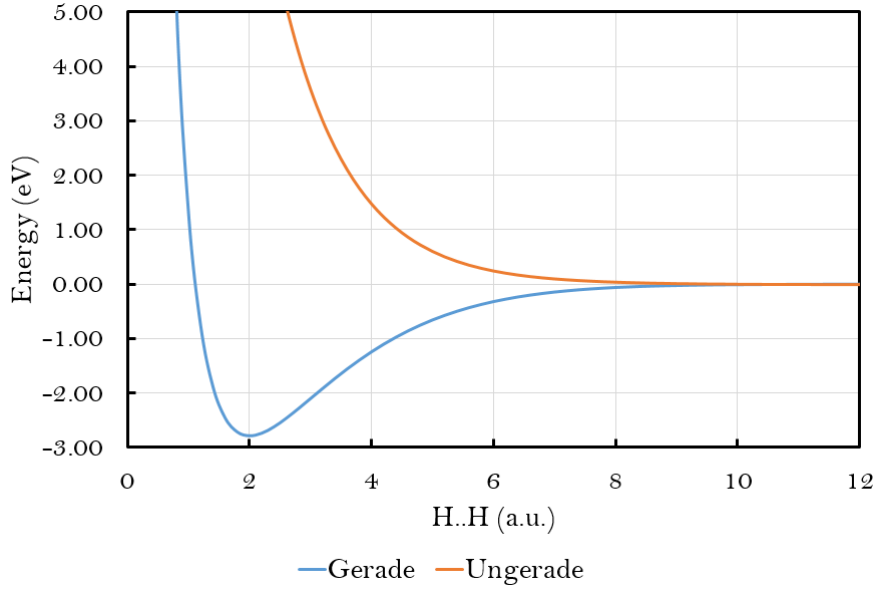


Figure 2.8 Potential energy curves for hydrogen molecular cation. Only gerade and ungerade states are shown.

$$|\Psi_e\rangle = c_g|g\rangle + e^{-i\phi}c_u|u\rangle \quad (2.31)$$

where $c_g(E;t) \equiv c_g$ and $c_u(E;t) \equiv c_u$ are the probability amplitudes of the gerade and ungerade states, respectively. For amplitudes of the left and right side dissociations we have,

$$c_L = \frac{1}{2}(c_g + e^{-i\phi}c_u), \quad (2.32)$$

$$c_R = \frac{1}{2}(c_g - e^{-i\phi}c_u). \quad (2.33)$$

Therefore, the probabilities of finding the electron on the left/right are found from,

$$P_L = |c_L|^2 = \frac{1}{4}(|c_g|^2 + |c_u|^2 + c_g^*c_ue^{-i\phi} + c_gc_u^*e^{i\phi}), \quad (2.34)$$

$$P_R = |c_R|^2 = \frac{1}{4}(|c_g|^2 + |c_u|^2 - c_g^*c_ue^{-i\phi} - c_gc_u^*e^{i\phi}), \quad (2.35)$$

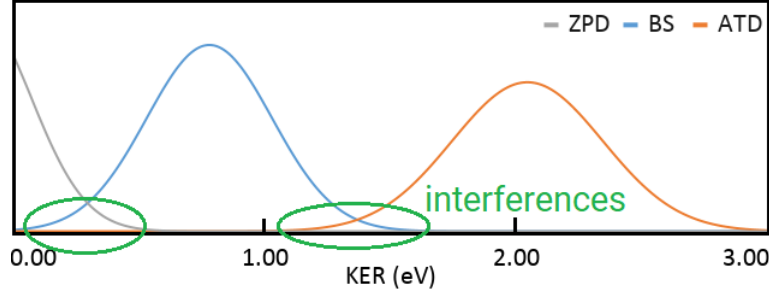


Figure 2.9 Representative channel contributions to KER and the interference regions of ZPD, BS and ATD channels.

where the third and forth are the interference terms in both equations. From Equations 2.34 and 2.35, total probability of directional dissociation is found to be,

$$P_{total} = P_R + P_L = \frac{1}{2}(|c_g|^2 + |c_u|^2), \quad (2.36)$$

and similarly the asymmetry of dissociation becomes,

$$A(E, \phi) = \frac{P_L - P_R}{P_L + P_R} = \frac{Re(c_g^* c_u e^{-i\phi})}{|c_g|^2 + |c_u|^2}. \quad (2.37)$$

Two fundamental pieces of information emerge from this expression. First of all, it follows that $A \propto \cos(\phi)$, meaning that asymmetry of dissociation, in other words electron localization, varies with the phase. Second, while the dissociation depends on the amplitudes of electronic states, asymmetry is related to the interference (or level of mixing) of different electronic-states, with the same energy, during dissociation.

2.10. Dissociation Channels and Asymmetry

When the time length of laser pulse is shortened, CEP becomes important and causes new physical phenomena.

After directional dissociation, electron localizes to the one of the nuclei. There is no asymmetry between the localization in left or right¹ nuclei if the pulse is long. But when the pulse is shortened, the destiny of the electron is determined by the laser parameters.

¹Left and right labels are just our choice. One may prefer to label the nuclei as up-down or 1-2... etc.

For the dissociation process triggered by short laser pulses, an asymmetry occurs in the localization of electron. This asymmetry stems from the interference of different dissociation channels. When laser pulse is short enough, dissociation occurs through more than one channel and these channels get round to mix with each other. This way gerade and ungerade levels blend and asymmetry happens. This asymmetry is calculated by the flux through two virtual detectors placed on the left and the right of the molecule, as,

$$A(E, \phi) = \frac{P_L(E, \phi) - P_R(E, \phi)}{P_L(E, \phi) + P_R(E, \phi)}, \quad (2.38)$$

where $P_{R/L}$ is the directional dissociation probability through the right and the left virtual detectors and subscripts R and L stand for right and left, respectively. Different dissociation mechanisms abovementioned are the Above Threshold Dissociation (ATD), the Bond Softening (BS) and the Zero Photon Dissociation (ZPD). ATD, BS and ZPD occur via,

$$\text{ATD : } 1s\sigma_g + 3\omega \rightarrow 1p\sigma_u \rightarrow 1s\sigma_g + \omega, \quad (2.39)$$

$$\text{BS : } 1s\sigma_g + \omega \rightarrow 2p\sigma_u, \quad (2.40)$$

$$\text{ZPD : } 1s\sigma_g + 0\omega \rightarrow 1s\sigma_g, \quad (2.41)$$

respectively. Interferences of ATD - BS and BS - ZPD occur in 1.0 - 1.5 eV and 0.0 - 0.3 eV energy intervals for hydrogen cation. At these energy values, dissociation occurs more powerfully and also the asymmetry is observed [8, 76, 77].

In Figure 2.10, ATD, BS and ZPD channels are shown diagrammatically. Here, laser field dressed electronic states become adiabatic due the high intensity, allowing efficient dissociation via different channels, as demonstrated in Figure 2.10.

2.11. Vibrational Levels of H_2^+ , D_2^+ and T_2^+ and Adiabatic Energy Curves

Adiabatic energy curves are formed when a laser pulse hits the molecule. During this interaction, the ungerade state is down-shifted by number of the photon energy according

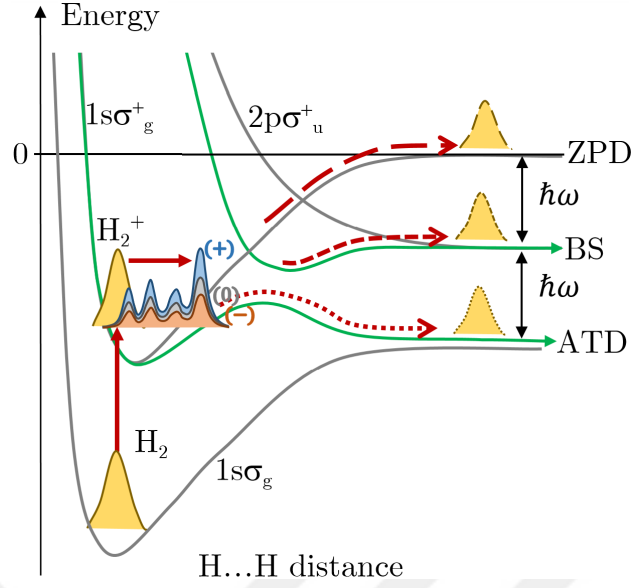


Figure 2.10 Diagram for dissociation channels.

to the dissociation process and an avoided crossing between gerade and ungerade states is shaped. This case called as “diabatic process”. The avoided crossing is being opened as the intensity of the pulse increases. Thereby the dissociation processes can occur adiabatically.

In Figure 2.11, vibrational levels of hydrogen, deuterium and tritium (orange lines) are shown as well as the gerade-ungerade states (blue lines), shifted-ungerade state by one-photon (black line) and adiabatic curves (grey lines). Vibrational states are obtained by Fourier Grid Hamiltonian method [78, 79].

Adiabatic curves are obtained as [80],

$$V_{\pm} = \frac{1}{2} \left(V_g + V_u - \hbar\omega \pm \sqrt{(V_g - V_u + \hbar\omega)^2 + (\hbar\omega_R)^2} \right), \quad (2.42)$$

where $\hbar\omega_R = \langle 1s\sigma_g | \vec{E} \cdot \vec{d} | 2p\sigma_u \rangle$, ω_R is Rabi frequency [81–83], $\vec{d}$ is transition dipole moment, $\vec{E}$ is laser pulse. Rabi frequency is a measure to identify the strength of radiative coupling which can be used for high intensity regime.

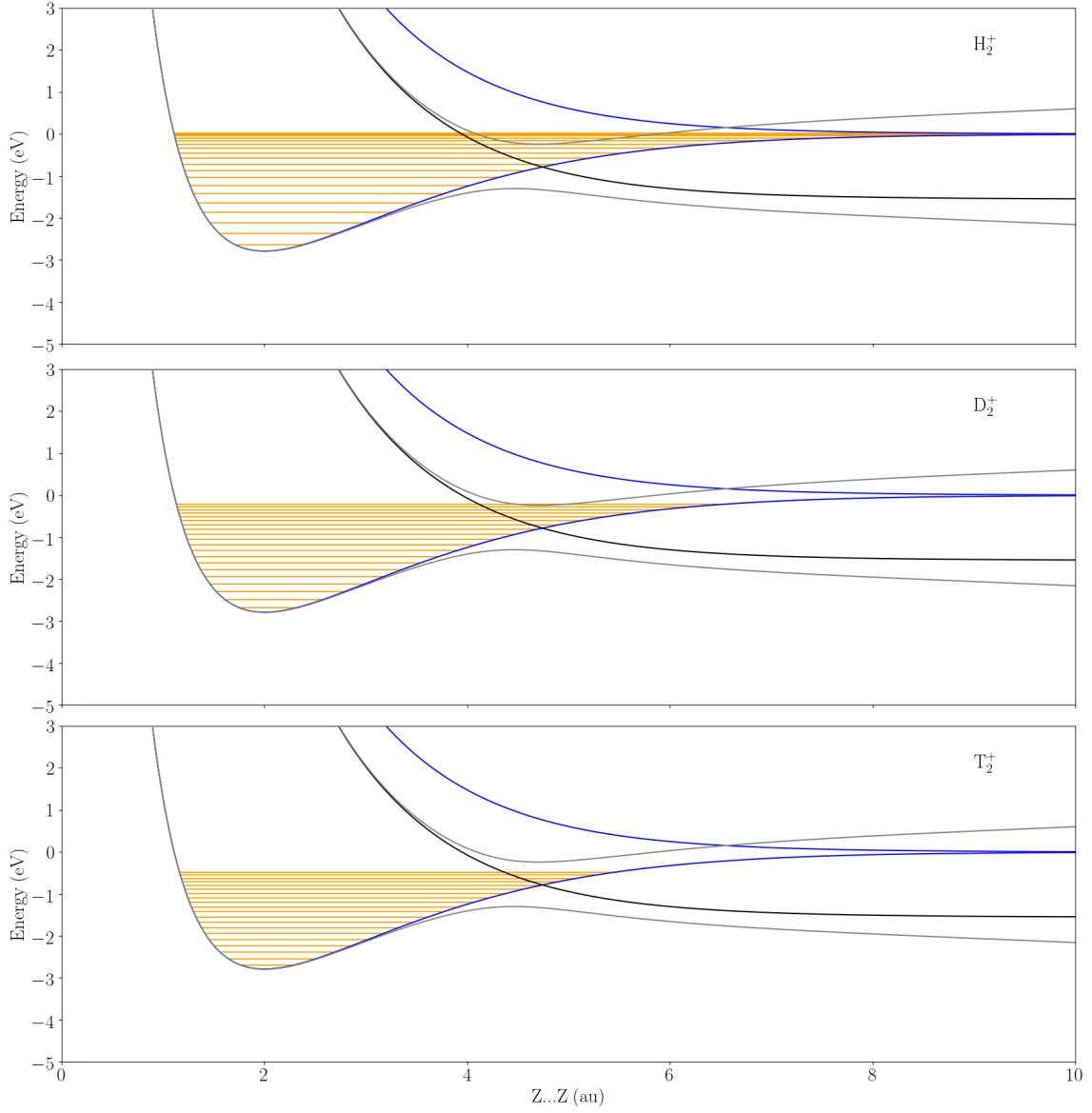


Figure 2.11 Vibrational levels, gerade state, ungerade state, diabatic and adiabatic potential curves for hydrogen, deuterium and tritium. Laser form is same as Figure 2.2 (a) with intensity is $I = 10 \text{ TW/cm}^2$.

2.12. Permanent Electronic Dipole Moments of Heteronucleus Isotopes of Hydrogen Molecular Cation.

For molecules considered in this thesis, there are no charge difference in their nuclei. But for heteronucleus molecules, masses of the nuclei are different from each other. This makes the geometrical center and charge center different for heteronucleus molecules. Therefore the molecule gains a permanent electronic dipole moment which enables the

transitions between same electronic state [84, 85]. The transition moment elements are given by,

$$\mu_{v,v'} = -\frac{m_L - m_R}{2(m_L + m_R)} \langle v' | R | v \rangle, \quad (2.43)$$

where $m_{L/R}$ is the mass of Left/Right nucleus and v is the vibrational level. To obtain the transition dipole moment between the same electronic state one should consider $v = v'$ and this yields,

$$\mu_{vv} = -\frac{m_L - m_R}{2(m_L + m_R)} R. \quad (2.44)$$

For homonucleus molecules, this expression obviously vanishes and for heteronucleus molecules, the corresponding numerical values are given in **Table 2.1**.

Molecule	Dipole Moment (De)
HD ⁺ (left oriented)	0.85
HD ⁺ (right oriented)	-0.85
HT ⁺ (left oriented)	1.27
HT ⁺ (right oriented)	-1.27
DT ⁺ (left oriented)	0.51
DT ⁺ (right oriented)	-0.51

Table 2.1 Permanent dipole moments for heteronucleus molecules.

2.13. Initial Nuclear Wave-packet of the Molecular Cation

Another result from the fact that the electronic processes occur much faster than the nuclear one in the hydrogen molecule is that one can assume that the first ionization from the parent molecule occurs instantaneously in comparison with the nuclear motion. Therefore the transition is vertical from the ground state of hydrogen molecule to the ground state of the hydrogen molecular cation as shown in Figure 2.12(a). As a consequence, the wavepacket is populated on certain vibrational levels with different probabilities as given in Figure 2.12 (b). Franck-Condon (FC) principle determines how likely to locate the wavefunction to which vibration level. The FC factors are determined from

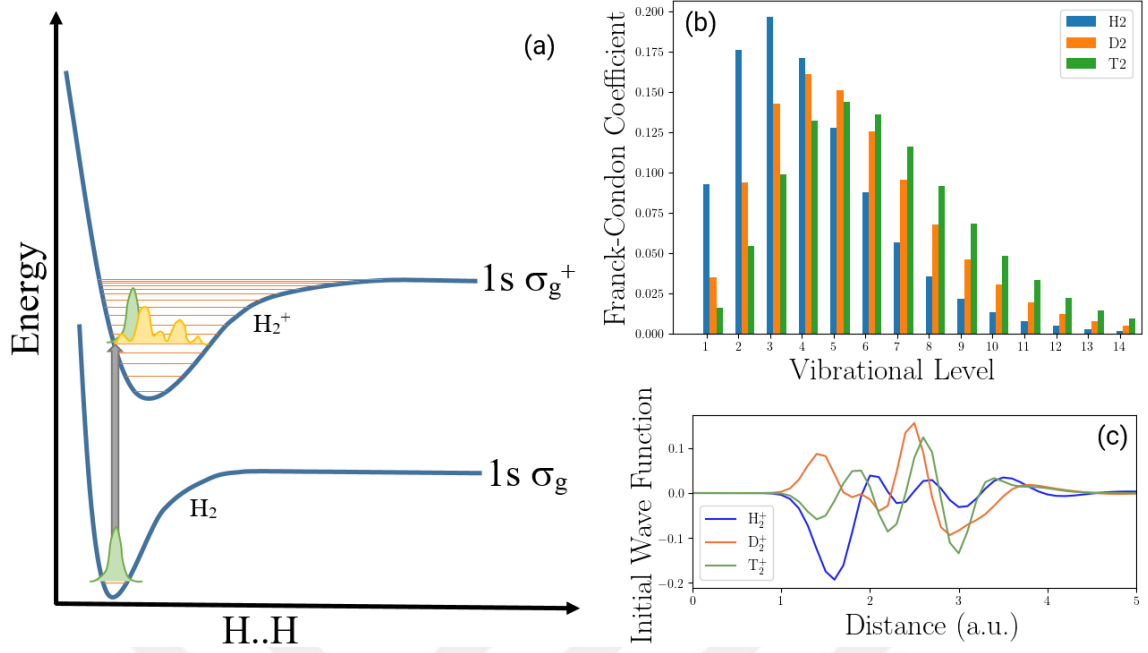


Figure 2.12 (a) Scheme for transition from the gerade state of hydrogen molecule to the gerade state of hydrogen molecular cation. (b) Franck-Condon coefficients for the transition of hydrogen, deuterium and tritium molecules to their cations. (c) Initial wave functions for hydrogen, deuterium and tritium cations.

$|\langle H_2^+, v | H_2, 0 \rangle|^2$ for H_2^+ and then the FC-weighted initial wave-function becomes,

$$|\Psi\rangle = \sum_v f_v |\Psi_v\rangle, \quad (2.45)$$

where $|\Psi_v\rangle$ is the vibrational state of molecular cation and $|0\rangle$ is the ground level of parent molecule. After the first ionization of the parent molecule, the cation is created and we start the TDSE calculations at this time point. Based on Equation 2.45, the initial nuclear wave-packet of the molecular cation is constructed as a superposition of the wave function of vibrational states with use of the probabilities (see Figure 2.12(c)).

2.14. Molecule Ionization

In some experimental scenarios interaction with laser pulse begins with the molecule not the ion. Ion, or the cation in our case, is produced during the interaction with laser pulse. To imitate this situation, one may begin to model the dissociation process from the birth of the cation. To determine the birth moment of the cation Ammosov-Delone-Krainov

method extended for molecules can be used. Ammosov-Delone-Krainov (ADK) method is the model to calculate the ionization probabilities in time for ionization of atoms via tunnelling [86] during the interaction with a laser pulse. In 2002, [87] extends this model to the tunnelling ionization of the molecules. This extended model is called as Molecular-Ammosov-Delone-Krainov (MO-ADK).

The tunnelling ionization rate in a static field is obtained as [87],

$$w_{stat}(E_0) = \frac{B^2(m)}{2^{|m|}|m|!} \frac{1}{\kappa^{2Z_c/\kappa-1}} \left(\frac{2\kappa^3}{E_0} \right)^{2Z_c/\kappa-|m|-1} \exp(-2\kappa^3/3E_0), \quad (2.46)$$

where E_0 is the peak field strength of the field, m is the magnetic quantum number, Z_c is the effective Coulomb charge and $\kappa = \sqrt{2I_p}$ where I_p is the ionization potential. Here $B(m)$ is calculated as,

$$B(m) = \sum_l C_l Q(l, m), \quad (2.47)$$

where $Q(l, m)$ is the coefficient of the spherical harmonics along the direction of $\theta \sim 0$,

$$Q(l, m) = (-1)^m \sqrt{\frac{(2l+1)(l+|m|)!}{2(l-|m|)!}}, \quad (2.48)$$

with l being the angular momentum quantum number of the electron. Equation 2.46 can be generalized to the nonstatic electric fields as follows,

$$w(E_0) = \left(\frac{3E_0}{\pi\kappa^3} \right)^{1/2} w_{stat}(E_0). \quad (2.49)$$

2.15. Accumulation of Ionization Rates

In this thesis, we use MO-ADK to determine how strong and when the first ionization occurs in parent molecule. We have started TDSE calculations at these time points and mix their results by using the ionization rates at relative times. There are two different aspects to mix the results. One of which is the incoherent calculations. We have considered that the first ionization finished before the dissociation begins. In this aspect, the two physical phenomena are independent from each other. Therefore the calculations started

from different times and the results are summed via mixture rates, as follows;

$$\hat{O}_{total}^{incoherent}(E) \propto \int w_{ion}(t_i) \hat{O}(E, t_i) dt_i. \quad (2.50)$$

where $\hat{O}$ is any physical observable.

In the opposite extreme, we consider a maximal coherence between the launched wave-packets. Hence, we calculate an approximate H_2^+ wave-function as

$$\begin{aligned} \Psi(\mathbf{r}, R, t) &= \Psi_1(\mathbf{r}, R, t; t_1) + \\ &\int w_{ion,rel}(t_i) H(t - t_i) \Psi_i(\mathbf{r}, R, t; t_i) dt_i \end{aligned} \quad (2.51)$$

as the coherence accumulation, where $\Psi_i(\mathbf{r}, R, t; t_i)$ is the wave-function of H_2^+ launched at t_i , $H(t - t_i)$ is the Heaviside step function and $w_{ion,rel}(t_i) = w_{ion}(t_i)/w_{ion}(t_1)$ is the relative ionization rate of H_2 . However, as we approximate the integration in Equation 2.50 with a summation, it is also convenient to approximate the integral in Equation 2.51. In this case, Equation 2.51 can be written as,

$$\begin{aligned} \Psi(\mathbf{r}, R, t) &= \Psi_1(\mathbf{r}, R, t; t_1) \\ &+ \sum_n w_{ion,rel}(t_n) H(t - t_n) \Psi_n(\mathbf{r}, R, t; t_n) \end{aligned} \quad (2.52)$$

where $t_n = nT(t)/2$. Thus, the energy-dependent dissociation probability for a maximal coherent case is calculated from

$$P_{tot,coh}(E) \propto w_{ion}(t_1) P(E). \quad (2.53)$$

We base the first part of our calculations and results on the incoherent accumulations of the wave-packet by eliminating the interference of the wave-packets in order to elaborate the impact of individual cations. In the second part we calculate the impact of coherent

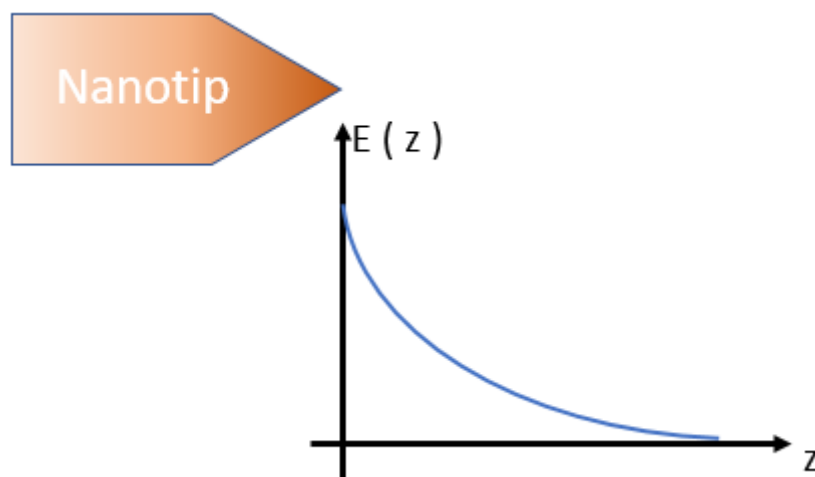


Figure 2.13 Near-field effect due to the laser-nanotip interaction near the nanotip. The arised electric field depend on the distance. The gradient in the nanotip represents the charge distribution.

accumulation of the wave-packets. In all cases, we assumed that launched wave-packets are initially in the FC distributed vibrational levels on the $1s\sigma_g$ states.

2.16. Enhanced Near-Fields of The Metallic Nanotips

In the vicinity of a metallic nanotip, the laser field not only interact with the molecule but also interact with the nanotip itself. This interaction creates an additional electric field due to the cumulative movement of the free electrons inside of the metallic nanotip. The laser field wafts the free electrons inside of the metallic nanotip to the one side of the nanotip. This situation creates charge excrescence at both side of the nanotip, one of which is negative and the other is positive. In consequence of this charge excrescence an extra, distance-dependent electrical field arises. Hence this electric field is spatially inhomogeneous. This electrical field is called “The Near-Field” and is visualised in Figure 2.13. This electrical field contributes to the laser field and creates a distance dependency in the total electrical field.

To mathematically express the near-field one may use the formula, $E(z) \sim \exp(-z/d)$, where d is the decay length [88–90]. As d goes to infinity, the electrical field becomes less and less inhomogeneous.

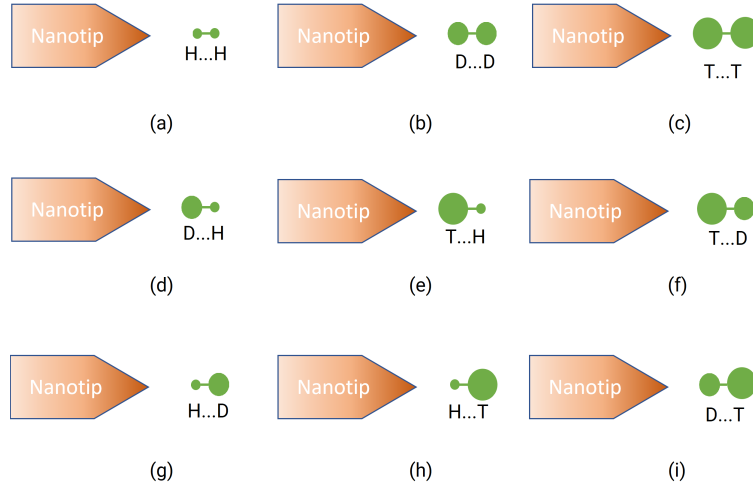


Figure 2.14 Alignments for different molecules subjected to this thesis. (a) (b) (c) Homonucleus (d) (e) (f) left oriented heteronucleus (g) (h) (i) right oriented heteronucleus molecules.

2.17. Potential Term in The Vicinity of A Metallic Nanotip

When an additional electric field occurs in the surrounding of the molecule we study, we need to take into account this field, as well. To do so, we have to modify the electric field part in the Hamiltonian such as [91],

$$V_L(z, t) = \int_0^z E(z', t) dz' - \int_0^R [E(z'/2, t) - E(-z'/2, t)] dz'. \quad (2.54)$$

In this thesis, the decay length is treated as the inverse of the inhomogeneity parameter, *i.e.* the curvature radius of the metallic nanotip and inhomogeneity parameter is scanned from 0.000 au^{-1} , no inhomogeneity, to 0.032 au^{-1} , max inhomogeneity.

2.18. Molecule Alignments with respect to the Nanotip

In this thesis, molecules are assumed to be aligned with the polarization direction of the laser pulse. This is also the direction of the nanotip strike.

In Figure 2.14 alignments for all the molecules subjected to this thesis are shown. Heteronucleus molecules are considered in two different alignments, one of which is named as “left-oriented” and the other one is “right-oriented”. Left-oriented molecules are the

ones with the heavy atom placed closer to the nanotip (see Figure 2.14 (d) (e) (f)) and for the right-oriented ones, heavy atom placed further away from the nanotip (see Figure 2.14 (g) (h) (i)). The system with the most anisotropy is left-oriented HT^+ . For this molecule, heavy atom is subjected to higher electric field and this is the molecule with most mass difference.

2.19. Molecule Ionization in Near Field

Because of the fact that the electric field is modified by the near field effect in the vicinity of a nanotip we need to revise the MO-ADK calculations. Due to that the near field depends on the spatial coordinate, we average its contribution over the space as a first order approximation. The position of the nanotip and the calculation grid is shown in Figure 2.15.

Near field of a nanotip is mathematically represented as [88–90],

$$E_{\text{near field}} \propto e^{-R_0 z}, \quad (2.55)$$

where R_0 is the inhomogeneity parameter defined as,

$$R_0 = 1/d. \quad (2.56)$$

Here d is the decay length. Other part of the electric field depends on the time and acts like constant for near field. If we average the near field over the space we get,

$$\langle E_{\text{near field}} \rangle \propto \frac{1}{2z_{\text{max}}} \int_{-z_{\text{max}}}^{z_{\text{max}}} e^{-R_0 z} dz = \frac{1}{R_0 z_{\text{max}}} \sinh(R_0 z_{\text{max}}). \quad (2.57)$$

For the full electric field used in isotope effect calculations, we get,

$$\langle E \rangle = \frac{E_0}{R_0 z_{\text{max}}} \sinh(R_0 z_{\text{max}}) \exp\left(-4 \ln(2) \frac{t^2}{(2\tau)^2}\right) \cos(\omega t + \phi). \quad (2.58)$$

For the cases with nanotip, inhomogeneity parameter is showed up in the equation.

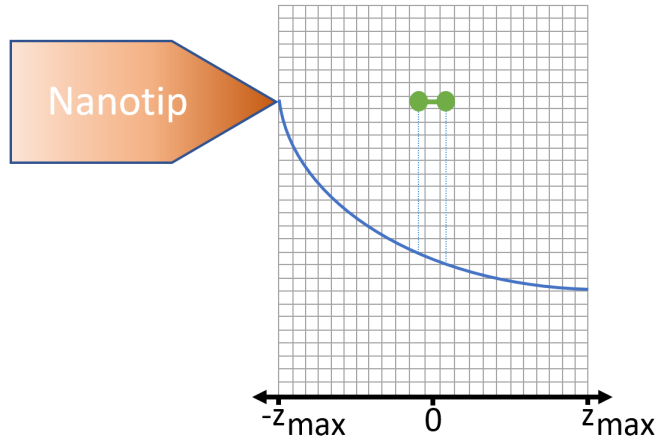


Figure 2.15 Grid position according to the nanotip considered in this thesis.

2.20. Extracting Physical Observables

To extract physical observables related to the directional control of dissociation such as kinetic energy release and momentum distribution, we use virtual detector method [92, 93]. This method considers the time-dependent behaviour of the wavepacket at a fixed space point, R_d , which can be defined as “position of virtual detector”. In this method, the spatial array needed to extract the momentum distribution is reduced significantly. Also this method is faster than Fourier Transformation (FT).

In the viewpoint of Quantum Mechanics (QM), the wavepacket in any representation contains all the necessary information about a physical system. For example, the momentum distribution of a system is given by the FT of the wavefunction that expresses the system, such as;

$$\Phi(k) = \frac{1}{(2\pi)^{3/2}} \int \Psi(r) \exp(-ikr) dr. \quad (2.59)$$

According to this formula, the momentum distribution depends on the global behaviour of the wavefunction. Therefore, the momentum distribution information can be extracted from the time dependence of an outgoing wavepacket at a fixed point in coordinate space. Here by “space point”, one should deduce a literal grid point for a 1D problem, an array for a 2D problem and a hypersurface for 3+ dimensional problems.

Let us rewrite the wavefunction as,

$$\Psi(\vec{r}, t) = A(\vec{r}, t) \exp(i\phi(\vec{r}, t)), \quad (2.60)$$

where $A(r, t)$ is real, time-dependent amplitude and $\phi(r, t)$ is a real time-dependent phase. To extract the information at a given position r_d which is contained by the wavefunction, one can consider current density, j , at r_d of an outgoing particle of mass m , in general;

$$\vec{j}(\vec{r}_d, t) = \frac{1}{2im} \left(\Psi^*(\vec{r}_d, t) \vec{\nabla} \Psi(\vec{r}, t)|_{\vec{r}=\vec{r}_d} - \Psi(\vec{r}_d, t) \vec{\nabla} \Psi^*(\vec{r}, t)|_{\vec{r}=\vec{r}_d} \right). \quad (2.61)$$

One may substitute Equation 2.60 in above formula to get,

$$\vec{j}(\vec{r}_d, t) = \frac{1}{\mu} \rho(\vec{r}_d, t) \vec{\nabla} \phi(\vec{r}_d, t), \quad (2.62)$$

where $\rho(\vec{r}_d, t)$ is the density probability. The momentum in terms of the phase is,

$$\vec{k}(\vec{r}_d, t) = \vec{\nabla} \phi(\vec{r}_d, t). \quad (2.63)$$

Now we may apply a binning/histogramming procedure to acquire the momentum distribution. The probability of finding the number of events ΔN with momenta k within a small momentum interval Δk around a momentum value k_i is given by,

$$\Delta N(k_i) = \Delta k \int_0^\infty dt j(r_d, t), \quad \text{for } k \in [k_i - \frac{\Delta k}{2}, k_i + \frac{\Delta k}{2}]. \quad (2.64)$$

In the limit of infinitesimal momentum intervals, this equation contains a Dirac delta function and becomes,

$$\begin{aligned} \left. \frac{dN}{dk} \right|_{k=k'} &= \int_0^\infty dt j(r_d, t) \delta(k' - k(r_d, t)) \\ &= \sum_m \int_0^\infty dt j(r_d, t) \frac{\delta(t - t_m)}{|\frac{dk}{dt}(t_m)|}, \end{aligned} \quad (2.65)$$

where k' is the momentum at t_m . To obtain Kinetic Energy Release KER distribution, $P(E)$, we have used the following formula;

$$P(E)|_{E=k'^2/2\mu} \propto \int dt j(r_d, t) \delta(k' - k(r_d, t)). \quad (2.66)$$

2.21. Contrast

When the directional control of dissociation process is transferred to the vicinity of a nanotip, the asymmetry is effected from the resultant local near field and “asymmetry in asymmetry”, *i.e.* the contrast occurs [45]. Contrast is directly proportional to the difference between the maximum and the minimum of the asymmetry and is defined as,

$$C = \frac{A_{max} - (-A_{min})}{A_{max} + (-A_{min})}. \quad (2.67)$$

2.22. Volume Averaging

In a real experiment laser pulse is focused to a really small area, yet its intensity changes within that area. Therefore not all of the molecules are subjected to the laser pulse of the same intensity. The ones that relatively away from the focal center are interacting with a relatively less intense laser field. This effect is called as “volume effect” (see Figure 2.16) and to compare the theoretical results with experimental ones in a healthier way, theorists should emulate this effect as well [94, 95].

To model this effect, we can average the results of different volumes where the intensity of the laser pulse is assumed to be constant.

$$P_{total} = \int \frac{P(I)dI}{\sqrt{I}} \approx \sum_I \frac{P(I)}{\sqrt{I}} \delta I, \quad (2.68)$$

where P is the dissociation probability of molecules and I is the intensity of laser pulse.

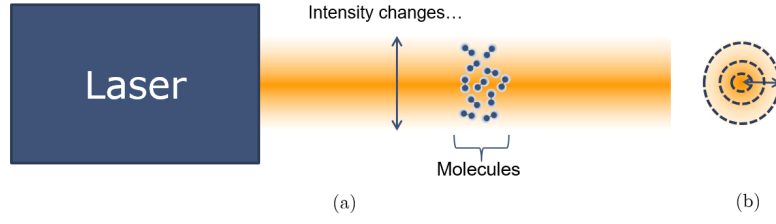


Figure 2.16 Visualization for Volume Effect. (a) Sketch for an experimental setup. (b) Cross-section of laser pulse.

2.23. Semi-classical model

Yavuz et al. have recently devised a simple semi-classical model to complement the underlying mechanisms of molecular dissociation. The model is based on the dynamics of a model “classical” particle driven by the electric field, however certain “non-classical” electronic transitions due to quantum-mechanical photon absorptions are allowed([45]). The classical equations of motion are defined as follows:

$$\mu_p \ddot{R} = -\frac{\partial}{\partial R} W(R, t) = -\frac{\partial}{\partial R} [V_{g,u}(R) + V(R, t)] \quad (2.69)$$

Here μ_p is the reduced proton mass, $D_g(R)$ and $D_u(R)$ are the gerade and ungerade states, respectively, and $V(R, t)$ is the field-matter interaction potential. We solved 2.69 by velocity-Verlet algorithms. The model enables classical simulations of dissociation *via* different channels. For each case, the non-classical transitions are allowed at the critical dynamical bond length, R' , at which the energy difference matches the multiple of the incident photon-energy, i.e. $V_u(R') - V_g(R') = n\hbar\omega_0$. To simplify the problem we solely focused on the diabatic transitions. For each dissociation channel certain level of bond stretching is required. For diabatic BS; net one photon transition ($g \rightarrow u$) occurs at 4.7 Å. For diabatic ATD; three photon transition occurs first at 3.3 Å ($g \rightarrow u$), followed by a one photon release at 4.7 Å ($u \rightarrow g$). Finally ZPD is the dissociation channel *via* stretching the bond distance with no net photon absorption.

As an example, we studied the field-induced semi-classical dissociation dynamics of H_2^+ *via* BS channel. The results are shown in Figure 2.17. Here we assumed that the particle

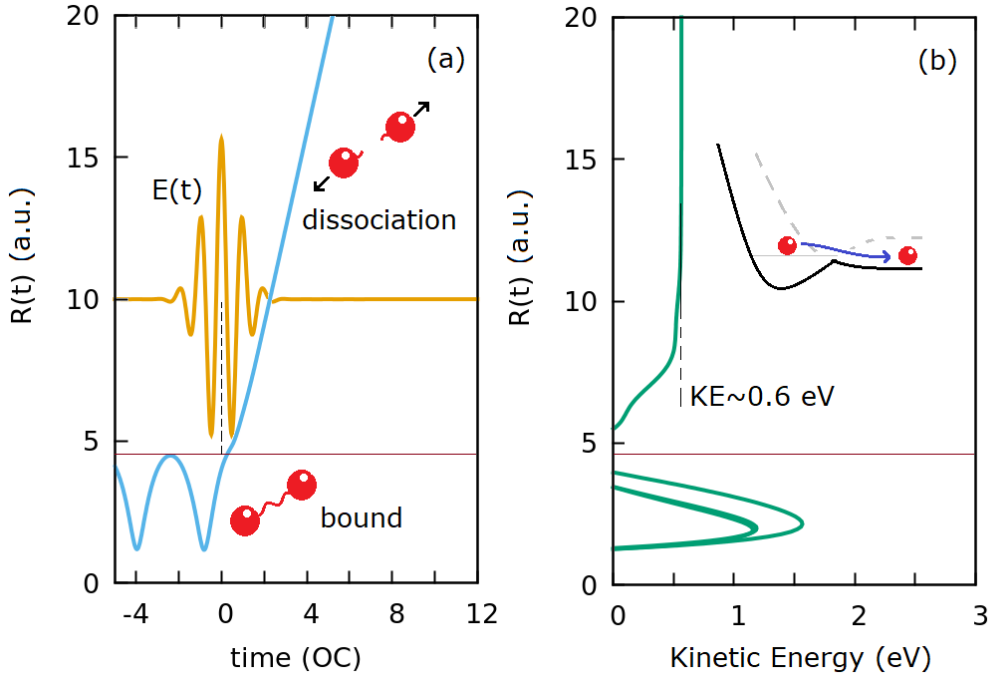


Figure 2.17 Field-induced semi-classical dissociation dynamics of H_2^+ via BS channel. (a) Time-dependence of the bond distance. Bound and dissociated regions are indicated. The electric field used is also shown. (b) Corresponding trajectory of the semi-classical particle. For $R > 10$ a.u. distances dissociation occurs with kinetic energy of ~ 0.6 eV. A gaussian pulse with two-cycle duration at FWHM and intensity of $10 \text{ TW}/\text{cm}^2$ is used. An initial velocity of $1.24 \times 10^{-2} \text{ a.u.}$ is taken (see text).

is initially in the non-classical $v = 9$ vibrational state. For H_2^+ this corresponds to a $E = 1.91 \text{ eV}$ energy and $1.24 \times 10^{-2} \text{ a.u.}$. In our simulations, during the motion of the initially bound semi-classical particle, once $R = 4.7 \text{ \AA}$, then ($g \rightarrow u$) transition occurs at $t = 0$. This means that the particle subsequently experiences a repulsive force resulting in an induced dissociation as shown in Figure 2.17(a). The corresponding kinetic energy of dissociation is found to be $\sim 0.6 \text{ eV}$, as shown in Figure 2.17(b). Quantum mechanical calculations as well as experimental measurements have shown that kinetic energy release from the $v = 9$ vibrational state of H_2^+ via BS channel is around 0.8 eV . Thus, our simple semi-classical simulation agrees fairly well.

3. RESULTS AND DISCUSSION

3.1. Dissociation of H_2^+ by Femtosecond Pulses

We first calculate the KER of dissociation of H_2^+ by a femto-second pulse. We used a two-cycles Gaussian-type pulse with 800 nm wavelength. This corresponds to a pulse with a 5.4 fs duration at FWHM. Figure 3.1(a)-(b) show the KER spectra of the H_2^+ molecule for two different laser intensities, namely $I = 20 \text{ TW/cm}^2$ and $I = 300 \text{ TW/cm}^2$. The initial vibrational state is chosen to be the lower vibrational state, $v = 0$. For the low laser intensity case, e.g. $I = 20 \text{ TW/cm}^2$, the initial-state, $v = 0$, lies well below the threshold for the 1ω -crossing (i.e., BS), which is the dominant dissociation channel. Thus, in the KER plot of Figure 3.1(a) we observe only contributions from vibrational-excitations. For $I = 20 \text{ TW/cm}^2$, the adiabatic threshold for KER is $v = 5$ (corresponding to a $\sim 0.1 \text{ eV}$) and higher v levels are hence allows the molecule to dissociate. As seen in Figure 3.1(a), a more or less continuous $P(E)$ distribution in the region of energies $0 \sim 1.5 \text{ eV}$ are observed. They primarily originate from BS channel, where these indistinguishable peaks, with an increasing trend, come from $v \sim 5-9$ vibrational level dissociations. Here, $v = 9$ is also the threshold for the diabatic BS. Beyond 0.8 eV , i.e. for $v > 9$, KER of dissociation again decreases as these levels are non-resonant and, more importantly, prone to vibrational-trapping (see Figure 3.1(c)). On the other hand, the weak shoulders above 1.5 eV are either from higher-order dissociation channels or due to the broad spectral width of the pulse (*vide infra*). At higher laser intensities, e.g. $I = 300 \text{ TW/cm}^2$ (Figure 3.1(b)), the influence of the plasmon-enhanced field on the KER spectra is much more pronounced. The adiabatic potential surface of the $1s\sigma_g$ state is highly suppressed and the initial level $v = 0$ can easily undergo to a dissociation via tunneling. Namely, the dissociation probability $P(E)$ is greatly enhanced in the KER range $1 - 2 \text{ eV}$, which may originate from the ATD channel. The broad spectral bandwidth of a 2-cycle fs pulse (see Figure 3.1) leads to sampling of continuous photon energies within $\Delta\omega_0 \simeq 0.2 \text{ eV}$ for a central 1.55-eV pulse. This results in contributions to KER from different vibrational

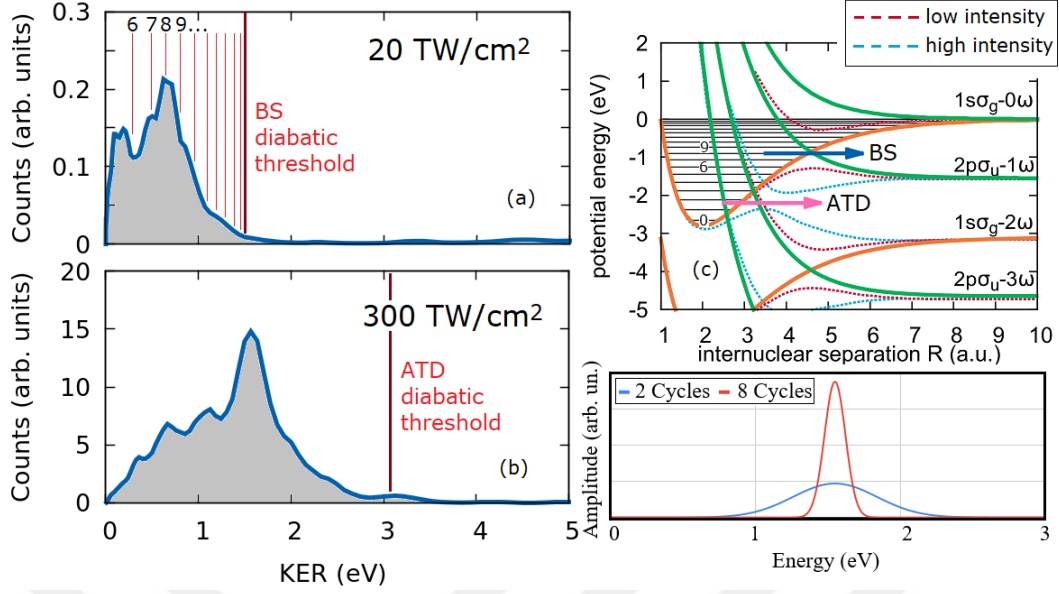


Figure 3.1 KER distribution of the dissociation of H_2^+ at low (a), and high (b) intensities. Red vertical lines in (a) represents the BS-channel vibrational comb. A Gaussian-type laser with a two-cycle pulse at FWHM and CEP $\phi = 0$ is used. (c) Diabatic and adiabatic potential curves at low and high intensities. (d) Spectral distribution of a two-cycle and eight-cycle pulse.

channels with continuous distributions with $\Delta E_{\text{KER}}(\nu) = \hbar\Delta\omega_0$, instead of discrete KER peaks (here, ΔE_{KER} is the broadening in KER). This is the source of indistinguishable distributions we observed in Figure 3.1(a)-(b).

The intensity dependence of KER of H_2^+ dissociation exhibit interesting phenomena, as shown in Figure 3.2(a). The graph clearly show the emergence of the higher order channels with increasing intensity. For relatively weak fields within $10 - 20 \text{ TW}/\text{cm}^2$, one can see that BS channel contribute predominantly to KER, evident from the maxima occurring around 0.8 eV and the span of dissociation upto $\sim 1.5 \text{ eV}$. To support this finding we calculated the dissociation probabilities for fixed field intensity as a function of initial vibrational level. The results are shown in Figure 3.2(b). We see that the maximum dissociation occurs at $\nu = 9$, corresponding to KER at 0.82 eV in the diabatic limit, which is consistent with our findings for low intensities. As the intensity is increased upto around $200 \text{ TW}/\text{cm}^2$, the KER range is still within 0-1.5 eV, suggesting that BS channel is still the dominant one. But the maxima is reduced to lower KERs, for instance, around $100 \text{ TW}/\text{cm}^2$ intensity the maximum is $\sim 0.5 \text{ eV}$. This can be attributed to lowering of the

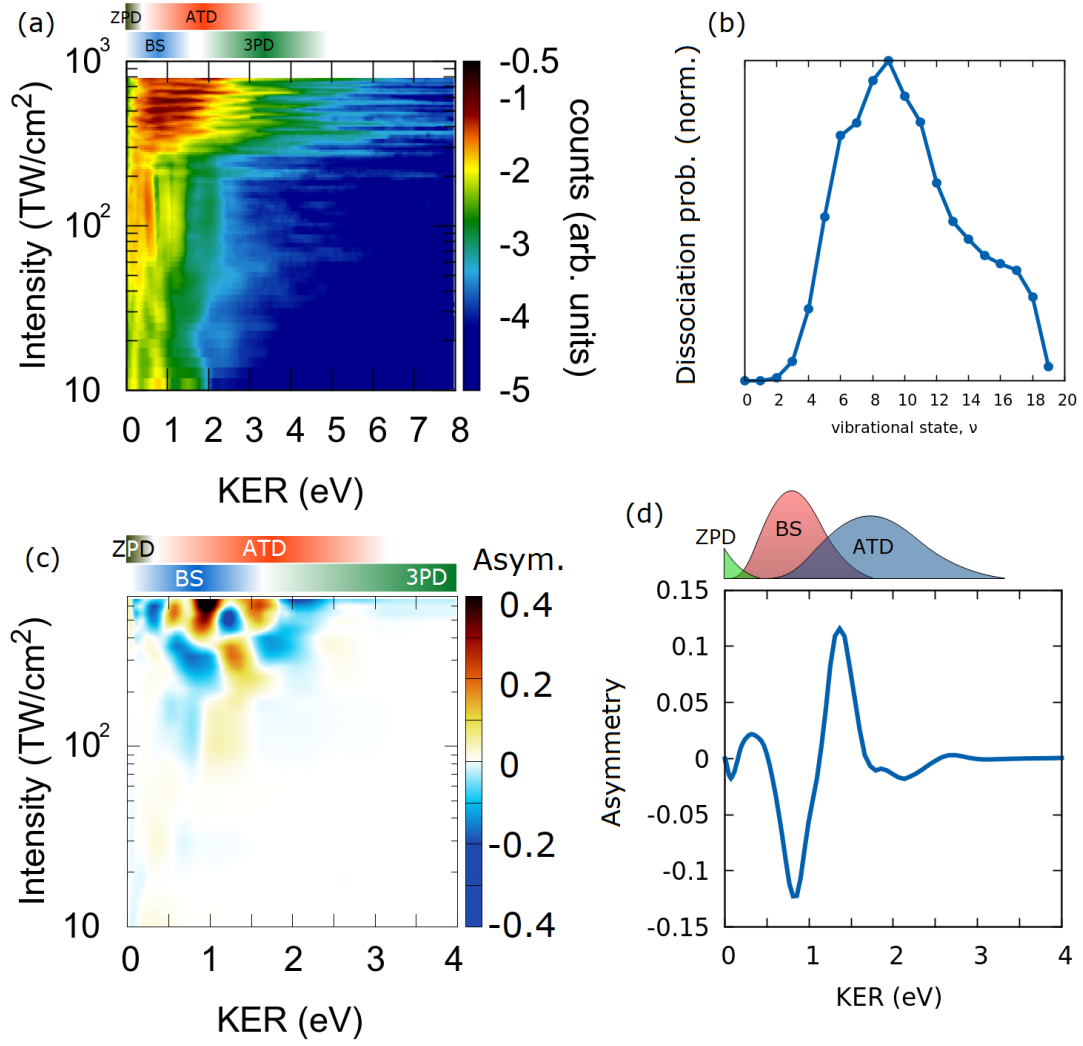


Figure 3.2 (a) Intensity dependence of the KER of dissociation of H_2^+ . (b) Dissociation probabilities as a function of the initial vibrational state. (c) Intensity dependence of the KER of dissociation asymmetry. Volume averaged asymmetry, based on (c). (d-top) A diagram representing the possible distributions of ZPD, BS and ATD channels with their interferences leading to KER dependence of asymmetry. A Gaussian-type laser with a two-cycle pulse at FWHM and CEP $\phi = 0$ is used.

adiabatic potential barrier with increasing intensity (see the diagram in Figure 3.1(c)), allowing dissociation even from lower vibration levels. Finally, there is an obvious opening of the ATD channel above 300 TW/cm², since strong dissociation occurs between 0-3 eV for this region.

Figure 3.2(c) shows the intensity dependence of asymmetry of H_2^+ . Since asymmetry is established when different dissociation channels interfere, we see that for low intensities

there is weak asymmetry at very low KER due to overlap of ZPD-BS channels. As the intensity is increased we see that asymmetry is increased and due to the emergence of BS-ATD channel overlap asymmetry occurs around 1 eV. We also calculated the volume-averaged asymmetry and the results are shown in Figure 3.2(d). The graph shows that the asymmetry is enhanced when ZPD-BS and BS-ATD channels interfere (see also the diagram on top of Figure 3.2(d)).

3.2. Influence of Post-Pulse on Directional Control of Dissociation

To better understand/characterize the electronic processes in molecules, a single, noise-free, clean and phase-stabilized ultra-short pulse is often desired (see *e.g.* Figure 3.3(a)). However, this is a major challenge experimentally and, therefore, we first attempted to theoretically understand the influence of a post-pulse to directional dissociation [96]. With this, we anticipate that if a satellite (pre- or post-pulse) pulse could be used in a controllable manner, their presence can be engineered for the electronic processes, which adds a new dimension to the field. The mathematical form of the laser field we prepared is as follows:

$$E(t) = E_0 f_0(t) \cos(\omega_0 t + \phi) + E_{pp} f_{pp}(t - \Delta t) \cos(\omega_0 t + \phi_{pp}), \quad (3.1)$$

where the first term is the main pulse and the second term is the post-pulse; Δt is the time-delay between pulses. E_0 and E_{pp} are the field amplitudes, $f_0(t)$ and $f_{pp}(t + \Delta t)$ are the pulse envelopes and ϕ and ϕ_{pp} are the CEP of the main pulse and post-pulse, respectively. We chose a main pulse with 5.7fs and a post-pulse with 8fs duration and time-delay is chosen to be 18 fs, as shown in Figure 3.3(a)-(b). The intensity of the main pulse is 150 TW/cm² and the amplitude of the post-pulse 5 fold weaker than the main pulse, corresponding to $I_{pp} = 6$ TW/cm². Comparing Figure 3.3(c) and (d), we observed that with the presence of a post-pulse, dissociation is coherently enhanced in the low KER region, for which ZPD and BS channels are responsible. High KER regions, where ATD is effective, are clearly not effected by the post-pulse.

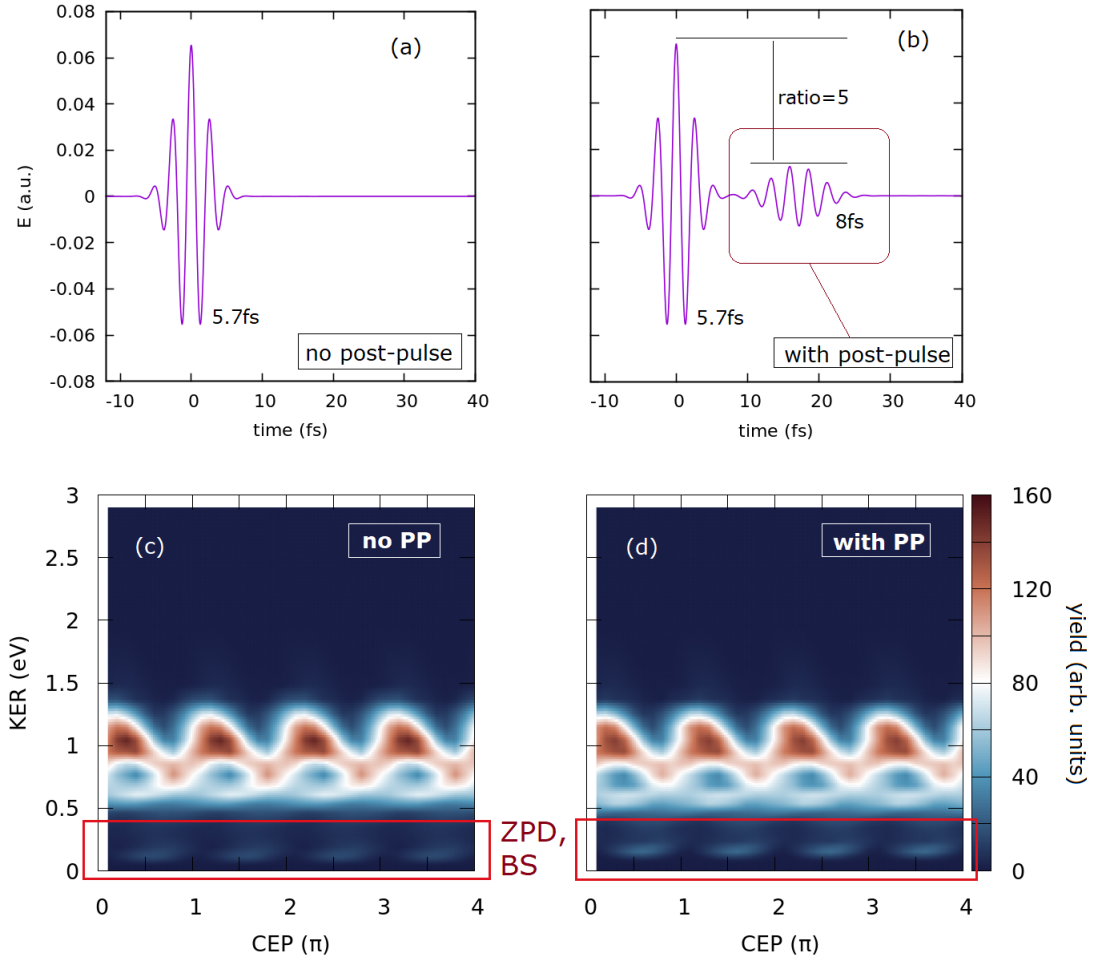


Figure 3.3 Time-profile of a fs pulse: (a) single-shot and (b) with post-pulse. (c) CEP-KER maps of directional dissociation with (c) and without (d) a post-pulse (PP). 18fs time-delay, 1:5 ratio and 8fs at FWHM is used for the post-pulse. Field intensity is $150\text{TW}/\text{cm}^2$. Low KER regions are highlighted.

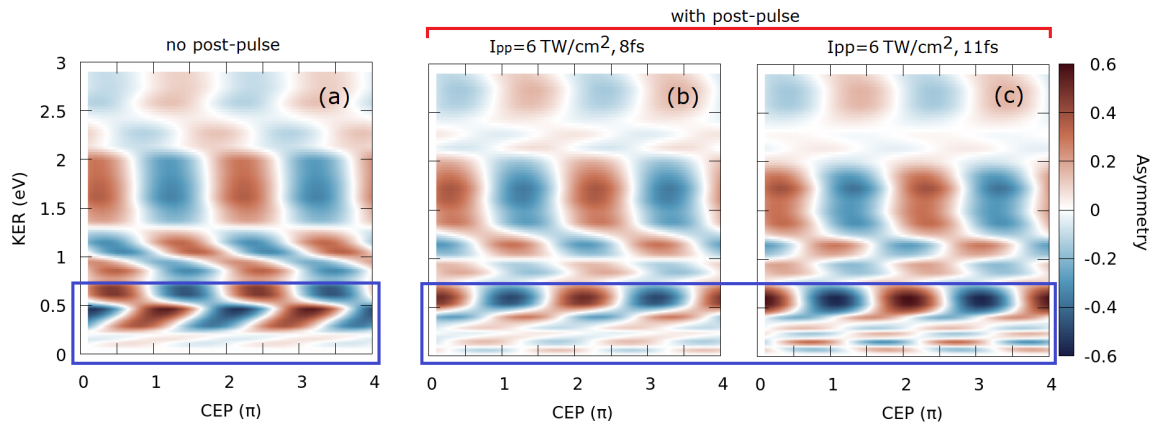


Figure 3.4 CEP-KER variations of asymmetry for (a) single main pulse (i.e., no post-pulse) and with post-pulse for (b) 8 fs, (c) 11 fs duration at FWHM. The laser parameters are the same as in Figure 3.3. Low KER regions are highlighted.

We then calculated the dissociation asymmetry of directional control. The results are shown in Figure 3.4. We observed that high KER regions are typically not effected by the post-pulse, whereas there is a systematic variation in the low KER regions with the inclusion of the post-pulse. Specifically, near 0.2 eV there is a substantial increase in directional asymmetry with the post-pulse. Since the overlap of ZPD-BS channels are responsible for the observed asymmetry in this region, the results suggests that both channels are collectively affected by the post-pulse. We suspect that the moment of electronic transition and the stretching of the molecule at this moment is the reason for the observed variation in directional dissociation. To support this finding we performed semi-classical simulations introduced in 2.23.. As shown in the Figure 3.5, ATD channel is activated earliest and BS channel comes later, since in the diabatic limit ATD starts at around $R = 3.3$ Å and BS starts at around $R = 4.7$ Å (see Figure 3.1(c)). Since no net photon is absorbed, a classical bond-breaking occurs in ZPD. Therefore considering the time-scale of dissociation; $ATD < BS < ZPD$, *e.g.* the time-scale of ZPD is the slowest. Thus, we see from Figure 3.5 that the reason why the ATD channel (or high KER regions) are not effected by the post-pulse is that, dissociation via ATD occurs so early that it finishes already before the post-pulse comes in. In contrast, ZPD occurs in a longer time-scale that it continues as long as the post-pulse sweeps the molecule. Since both BS and ZPD channels are effected considerably by the pulse-pulse, the variation in directional asymmetry in the low KER region due to the BS-ZPD overlap.

3.3. Directional control of Dissociation via CEP-Controlled Chirped Laser Pulse

In this section, the directional dissociation via CEP-controlled chirped laser pulses will be discussed under two main titles. First we investigated two-level system for Hydrogen molecular cation with CEP-controlled chirped laser pulse to gain preliminary understanding about the system. Then we solved the TDSE to fully analyze the chirp effect on molecular dissociation.

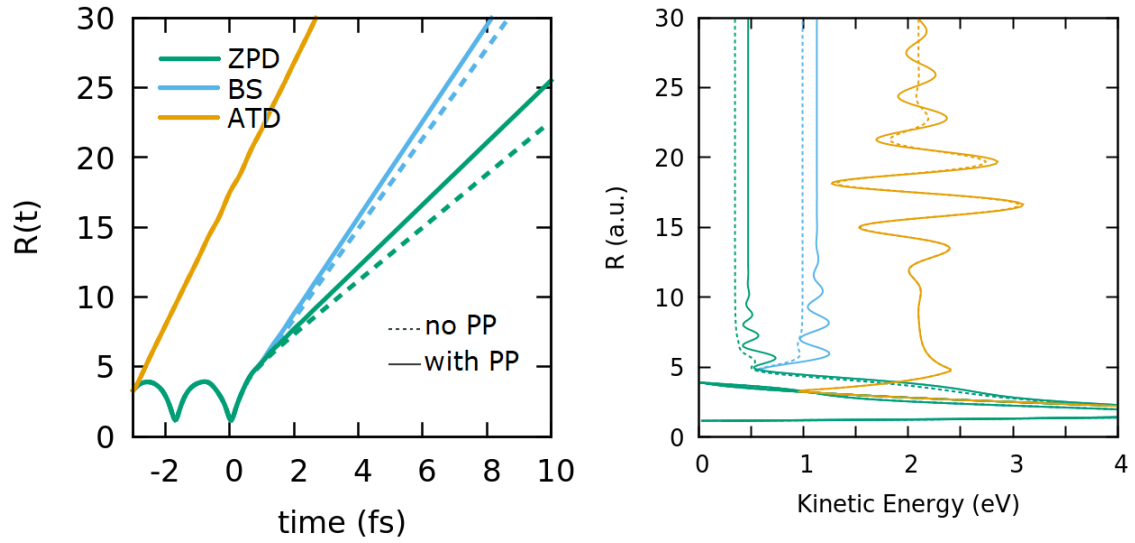


Figure 3.5 Post-Pulse (PP) simulation results with the semi-classical model of different dissociation channels; ZPD, BS and ATD. (a) Variation of the dynamical inter-molecular distance, $R(t)$. (b) Trajectory of dissociation with and without a post-pulse.

3.3.1. Analyze of the chirped laser pulse

Due to the group-delay dispersion (gdd), i.e. derivative of the group delay with respect to the frequency,

$$gdd(\omega) = \beta/2(\omega - \omega_0)^2, \quad (3.2)$$

chirping a laser pulse introduces polychromy and increases the temporal pulse bandwidth by,

$$\tau = (1 + \eta^2)\tau_0, \quad (3.3)$$

and reduces the intensity by,

$$I = I_0/(1 + \eta^2), \quad (3.4)$$

with τ_0 being the total duration and I_0 being the intensity of the transform limited pulse and η is the chirp parameter (see Figure 3.6). Diminution in intensity and elongation in pulse duration is something we don't desire. Because in this case total dissociation is suppressed due to pulse-elongation [1] and lower intensities suppress ATD channel.

Also, this factor hinders the CEP-control which is crucial for observing the asymmetry. To overcome these issues, as shown in Figure 3.6, we keep the temporal duration and the intensity of the chirped pulse constant in our calculations. The mathematical forms of our transformations are shown by,

$$(1 + \eta^2)\tau_0 \rightarrow \tau', \frac{I_0}{(1 + \eta^2)} \rightarrow I'. \quad (3.5)$$

The graphical representations of the procedure we introduce, namely pulse-width maintained chirping, is shown in Figure 3.7. Therefore, if one wants to perform the experiment of the calculations in this thesis, the individual need to begin with suitable intensity and duration values to end up with 150 TW/cm² as intensity and 5.4 fs as duration. The initial duration and intensity values are shown in Figure 3.7. The Fourier Transform (FT) of the wavefunction yields its spectral form. To analyze spectral forms, we have performed a Fast Fourier Transform (FFT) on the chirped laser pulse. The FT of a function, $f(t)$ is given as,

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \exp(-i\omega t) dt. \quad (3.6)$$

Here we consider the waveform as the function we want to transform. Therefore, the function we get is,

$$F(\omega) = \int_{-\infty}^{\infty} E_0 \exp(-4 \ln(2) t^2 / (2\tau)^2) \cos\left(\omega t + \phi_0 + \frac{4 \ln(2) \eta t^2}{\tau^2}\right) \exp(-i\omega t) dt. \quad (3.7)$$

When FT applied to the chirped pulses we used in our calculations, optical shapes are obtained as given in Figure 3.8. We only consider the second half of the laser pulse for Fourier Transform due to that we started the TDSE calculations from the peak of the laser pulse. Because we only consider the half of the laser pulse, the shapes in Figure 3.8 are not an exact Gaussian rather a disturbed one. Also peaks in Figure 3.8 shift to lower wavelength or higher angular frequency by chirp.

Pulse-width Maintained Chirping

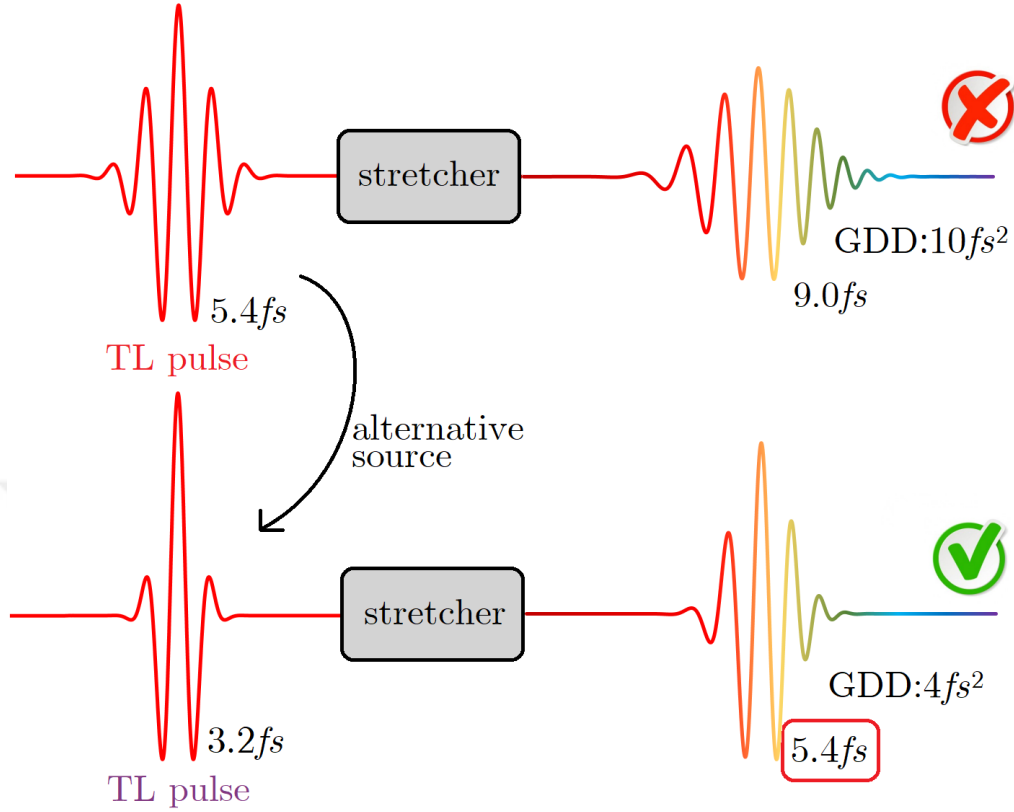


Figure 3.6 Chirping the laser pulse, introduces polychromy, reduces intensity and elongates the pulse duration. These factors suppresses the dissociation [1]. In order to overcome this issue, we suggest a “Pulse-width Maintained Chirping” schema.

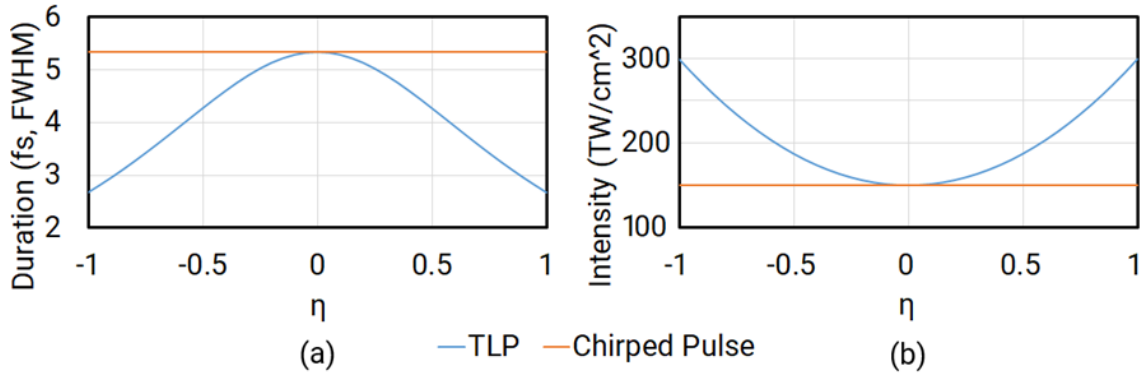


Figure 3.7 (a) Initial duration and (b) initial intensity values necessary in an experiment.

Because we use chirped laser pulses, phase of the pulse changes over time with,

$$\phi(t) = \phi_0 + \frac{4 \ln(2) \eta t^2}{\tau^2}. \quad (3.8)$$

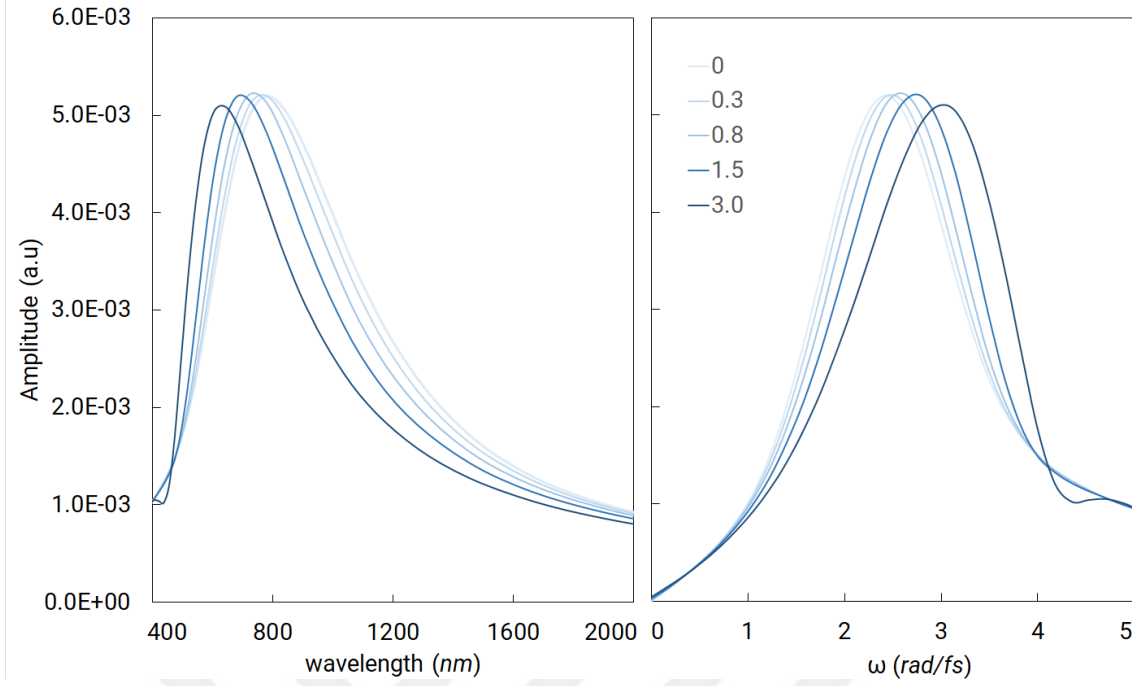


Figure 3.8 Fourier transforms of laser pulses with different chirp values.

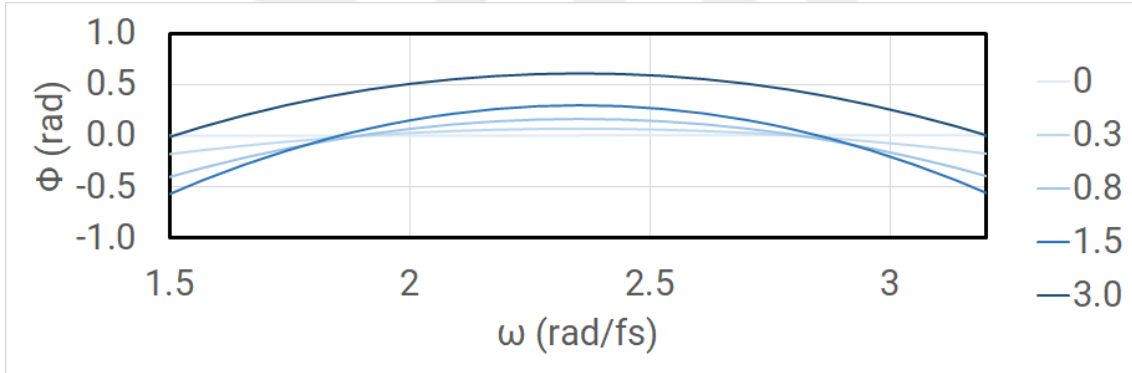


Figure 3.9 Spectral forms of pulses with different chirp values.

After the FT, one may extract the phase by using the imaginary and the real parts of the transformed function as,

$$\phi(\omega) = \text{Arctan} \left(\frac{\text{Im}(F(\omega))}{\text{Re}(F(\omega))} \right). \quad (3.9)$$

We have shown the ω variation of the phase in Figure 3.9. For $\eta = 0$ we have got a constant line at $\phi_0 = 0$. For other η values shape is negative-quadratic.

3.3.2. Two-level model calculations

For a preliminary understanding of the chirp effect on CEP-controlled directional dissociation, we first investigated the two-level model for the dissociation of H_2^+ with chirped laser pulses, based on the ansatz that the wave-function is expanded in terms of attractive ground $1s\sigma_g$ (gerade) and repulsive first excited $2p\sigma_u$ (ungerade) states. Here we consider a perturbative chirping, *i.e.* $|d\omega(t)/dt| \ll 1$. For a clear understanding, we take the initial wave-packet to be at the electronically excited *ungerade* state, since, otherwise a large residue of the initial state would remain in the ground state. We start the calculations on the peak of the envelope of the laser pulse because of the fact that we know from the MO-ADK calculations that the 1st ionization of a neutral hydrogen molecule occurs at the peak time with most probability. This means that the hydrogen cation molecule is mostly created at the peak time of the laser pulse. As we can see in Figure 3.10 for negative chirp values the temporal width of the pulse gets narrower and for positive chirp values it gets wider. To determine the inter-state transitions and dynamical origin of such transitions (*i.e.*, adiabatic, diabatic, or mixed dynamics), we calculate the avoided-crossing passage probability by the Landau-Zener formula as

$$P_{diabatic}(R, t) = \exp(-\pi V_{ug}(R)^2 / (4\pi\omega_0\mu(R)E(t))), \quad (3.10)$$

where $V_{ug}(R)$ is the coupling between states such as,

$$V_{ug}(R) = V_u(R) - V_g(R). \quad (3.11)$$

When $V_{ug}(R)^2 \gg \omega_0\mu(R)E(t)$ the transition is fully adiabatic and when $V_{ug}(R)^2 \ll \omega_0\mu(R)E(t)$ it is fully diabatic. Figure 3.10 shows that, the fully adiabatic part, where the wave-packet stays in the ungerade state, finishes at ~ 2.5 fs and fully diabatic part starts at ~ 6.2 fs for the TL pulse, where the wave-packet occasionally jumps between the states, *i.e.* at the zero-crossings of the field (see Figure 3.10(c)). For positive(negative) chirp values, these happen earlier(later). For positive chirp, higher frequencies appear later in the falling

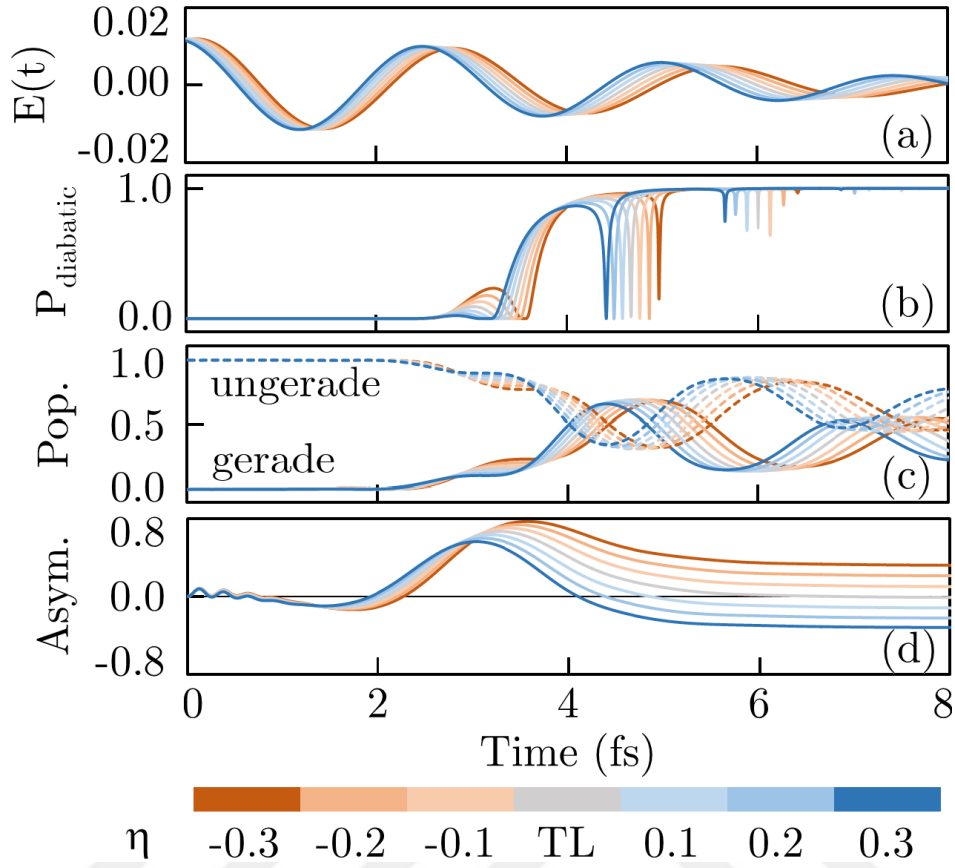


Figure 3.10 Chirp effect on the directional dissociation of H_2^+ in a two-level system. All grey(blue)[brown] lines for transform limited(positively chirped)[negatively chirped] pulses. (a) Temporal variation of the chirped pulse. $\phi_0 = 0$. (b) Landau-Zener probability from adiabatic to diabatic process. (c) Left(solid) and right(dashed) populations over the ungerade and gerade states. (d) Asymmetry change by chirp. It changes sign with the change in the sign of chirp.

edge, resulting in a more rapid change per cycle (see Figure 3.10(a)). Electronic transitions happen earlier, maximum transition probability per-cycle is reduced and localization is established in the left nucleus ($A < 0$), after when the electron population freezes out (see Figure 3.10(d)). For negative chirp, falling edge is at lower frequencies; the electronic transitions happen later and maximum transitions per-cycle are increased, resulting in an increased asymmetry in the mixed(adiabatic+diabatic) dynamics part (*i.e.*, within 2 – 6 fs). The electron localization is therefore established in the right nucleus ($A > 0$). Regardless of the sign of chirp, absolute asymmetry is enhanced relative to that of the TL pulse and a linear variation of asymmetry with chirp in the form of $A \propto -\eta$ is found (see

Figure 3.10(d)) [58].

3.3.3. MO-ADK calculations for neutral hydrogen molecule

By using Equation 2.49, we obtained the peak ionization rates and their occurrence moments. Then we have started the TDSE calculations at these moments and we combined the results via ionization rates in both coherent and incoherent manner. Figure 3.12 shows the time-dependent ionization rates, $w_{ion}(t)$, of H_2 , forming H_2^+ , subjected to an ultra-short chirped laser field. We have found that the first ionization from the neutral hydrogen molecule occurs mainly at three moments one of which corresponds to the peak time and the other two correspond to the second-most-strong time of the laser field. The ionization appears to have three peaks separated by a half-cycle. There are two second-most-strong peaks in a whole laser pulse and we name the ionization probability peaks corresponds to these moments as “satellite peak”s. Main peak is at $t = 0$ and two satellite peaks at the rising and falling edge of the laser field. The ionization rate at peak time is relatively stronger than the other two satellite peaks (see Figure 3.11 (a)). With change of the chirp from negative to positive, while the main peak stands steady, both of the satellite peaks slide linearly to a later time. On the other hand, for earlier satellite, the height gets higher and for the later satellite, it gets shorter as the chirp changes negative to positive. Figure 3.11(b) shows the CEP dependence of the ionization time, t_i , of the main and the second main peak for TL and a positively chirped pulse, $\eta = 0.7$. As CEP variates, main peak and satellite peaks shifts to later times with the carrier’s peak and while main peak loses power, first satellite peak gains it. When CEP is equal to π , the power of main peak and satellite peak are met. And for CEP values greater than π , satellite peak becomes main peak. As shown in Figure 3.11(c), the instantaneous ionization rate at t_i , *i.e.* $w_{ion}(t_i)$, of the main and second main peak oscillate with ϕ_0 with π periodicity. The oscillations of the main peak are almost unaffected by the chirp, except around $\phi = \pi/2$, but the second main peak is significantly left shifted. The peaks unite at $\phi = \pi/2$ since these two peaks become identical (due to the time profile of the laser field at $\phi = \pi/2$) and are separated by a

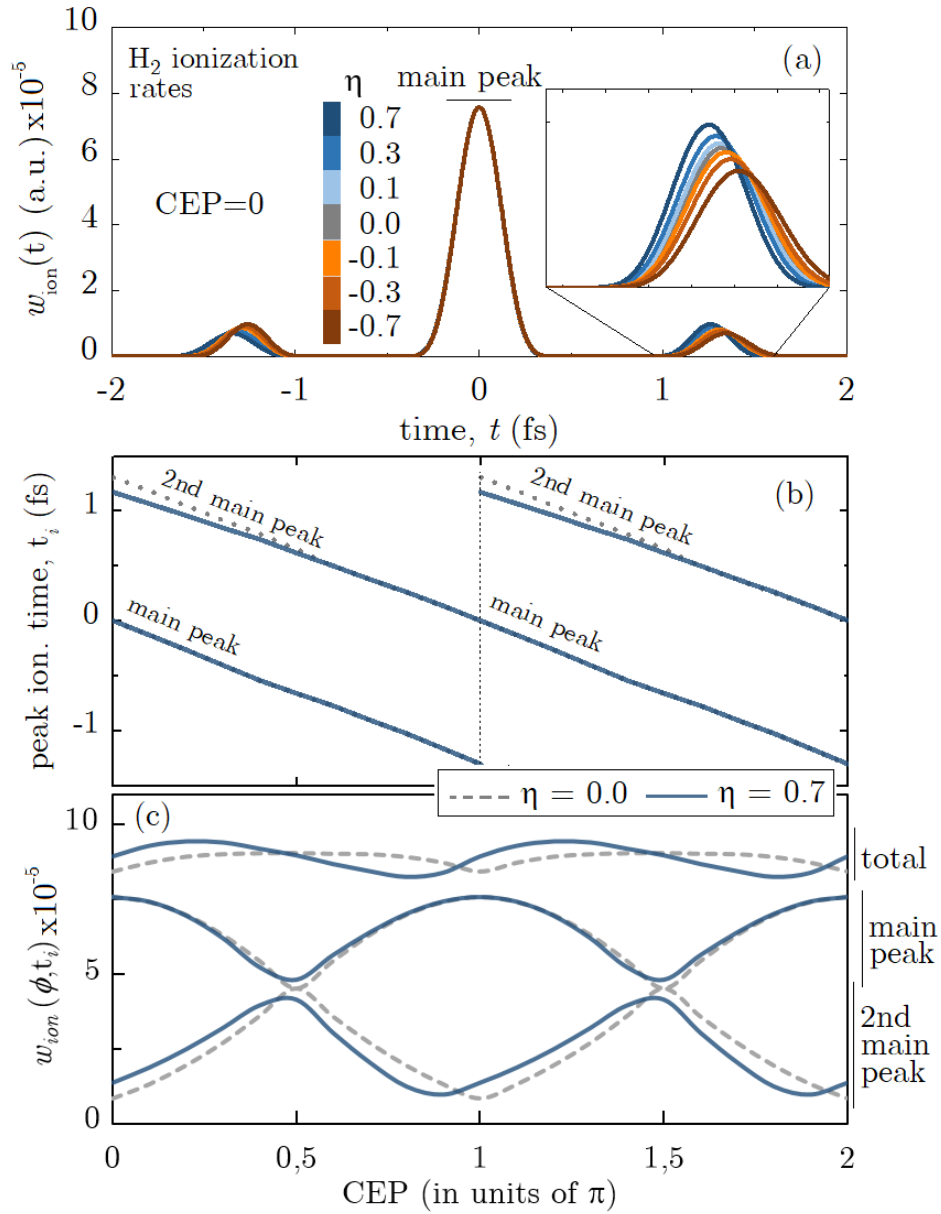


Figure 3.11 MO-ADK calculated time-dependent ionization rates of H₂, forming H₂⁺, by a chirped laser field. (a) Temporal variation of the ionization rates, $w_{ion}(t)$, in $-2 \text{ fs} < t < 2 \text{ fs}$ for different chirp values. Inset is a zoom to the temporal range $1 \text{ fs} < t < 1.6 \text{ fs}$. (b) Ionization time, t_i of the main and second main peak as a function of CEP for TL and positively chirped pulse. (c) Ionization rates of the main and second main peak at $t = t_i$ as a function of CEP. “total” corresponds to the sum of the ionization rates of these two peaks. An 800 nm Gaussian pulse with two-cycles at FWHM and $I=150 \text{ TW/cm}^2$ is used.

half-cycle at this phase.

Figure 3.12 shows the time variation of the ionization probability. We see that ionization probability for hydrogen molecule begins to increase when first second-most-strong peak

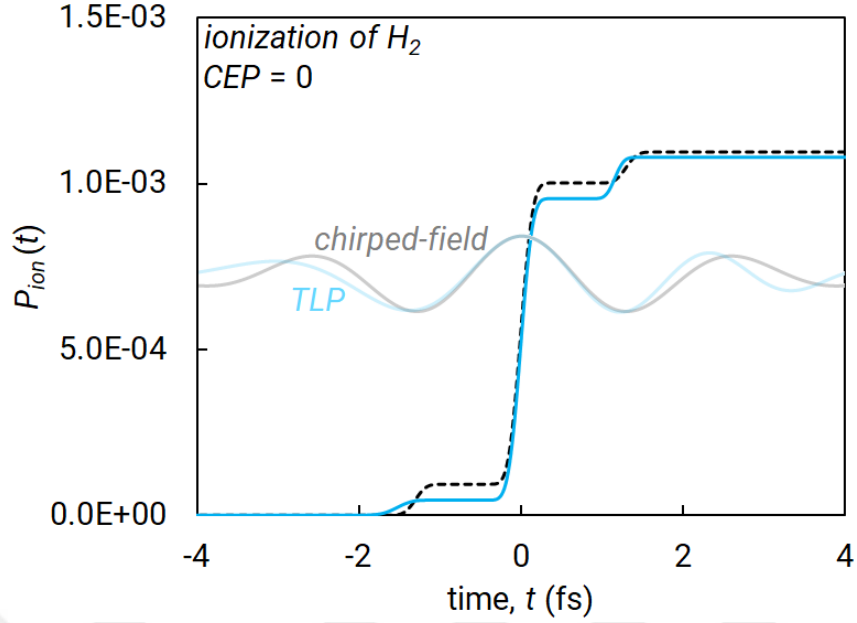


Figure 3.12 First ionization probability of H_2 obtained by MO-ADK calculations with chirped pulse and TLP

time arrives. Then a plateau occurs for a short period of time. When the peak of the pulse turns to come, raising in the ionization probability boosts and gets even higher. And after a small plateau again, for the second second-most strong peak time, we see another gain in first ionization probability. Due to the delay in the second-most-peaks for chirped pulse, the increment for these parts starts a little bit later for chirped pulse. The important thing here is that, first ionization probability goes upper for chirped pulse then TLP around the first second-most-strong peak time, resulting in a higher population on H_2^+ vibrational levels. Because of this difference, the first ionization probability ends up at a little bit higher value for chirped pulse.

3.3.4. TDSE results for the CEP-controlled chirped laser field

In this section the results for chirped-field-induced directional dissociation obtained from Time Dependent Schrödinger Equation (TDSE) is discussed. We first calculate the temporal variation of the dissociation asymmetry for different chirp values relative to the values obtained by the TL pulse. As shown in Figure 3.13, we first assume that H_2^+ is populated by the ionization of H_2 at the peak of the pulse at $t = 0$ for each case for a

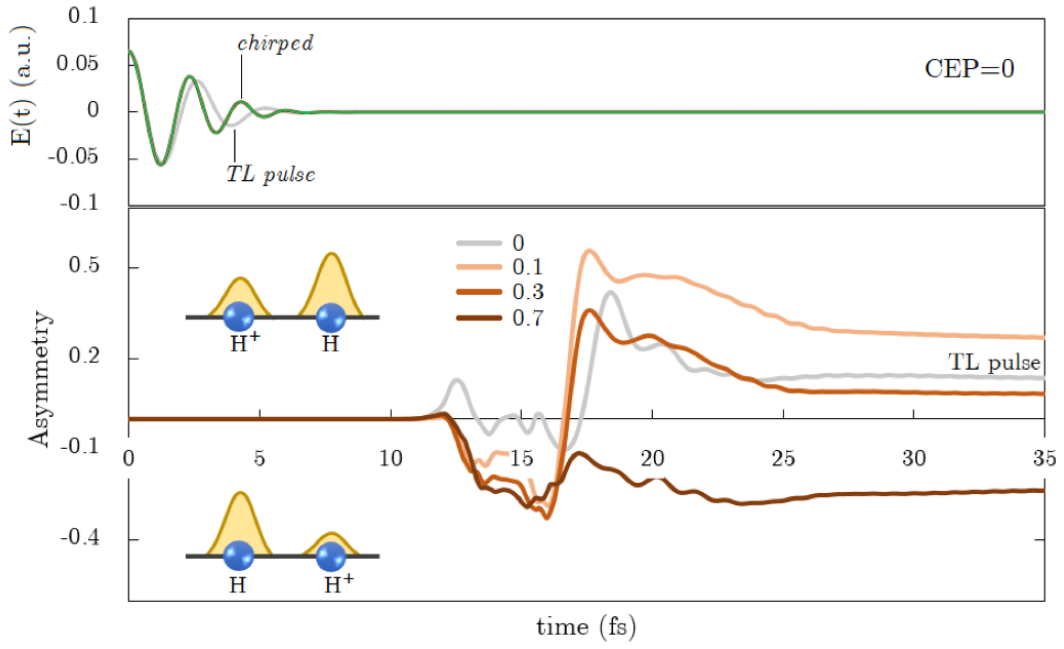


Figure 3.13 (Top) time variation of transform-limited (TL) pulse and chirped pulse for zero CEP case. (bottom) Variation of asymmetry with respect to time for different chirp parameters.

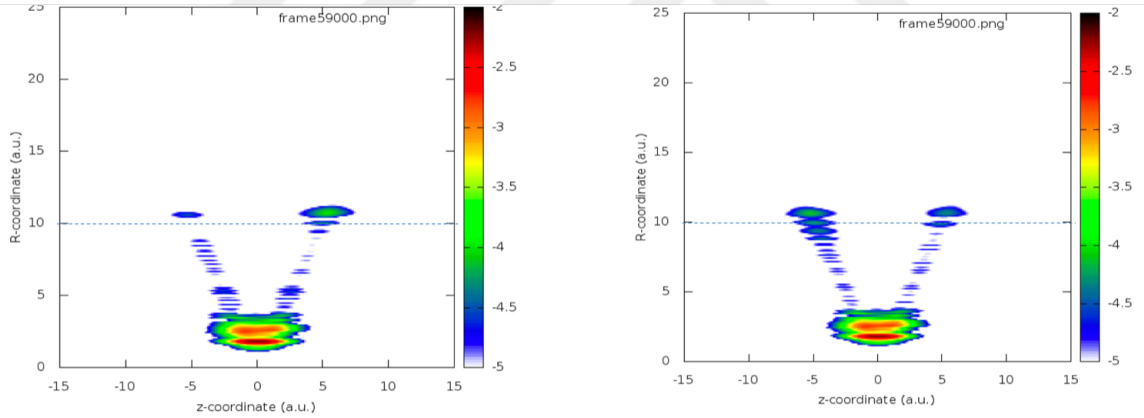


Figure 3.14 Snapshot of the wave-packet probability distributions near the maximum intensity instant, for the case of (left) transform-limited pulse $\eta = 0$, and (right) chirped pulse, $\eta = 0.7$. Horizontal dashed lines indicated the position of the virtual detectors.

rational comparison. With the TL pulse, asymmetry oscillates starting from $t = 12$ fs and converges beyond $t = 25$ fs, at which the asymmetry is established. The time difference between the peak of the pulse and the time when sizable asymmetry occurs, results from the fact that it takes some time for the dissociative wave-packet to reach the detector at $R = 10$ a.u. (see Figure 3.14 for a clear understanding). With chirp, the wave-packet os-

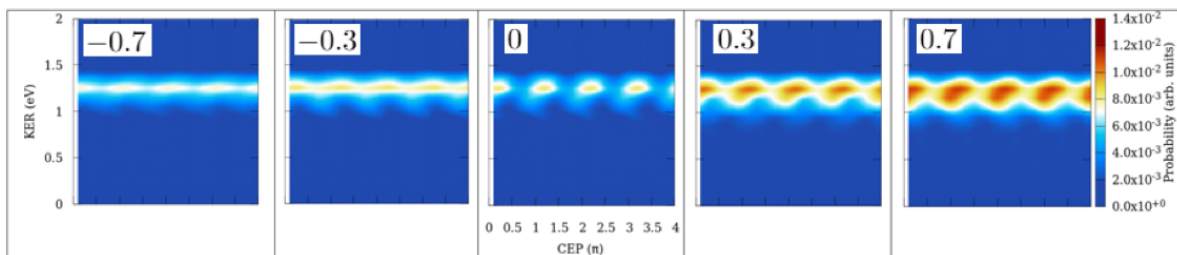


Figure 3.15 KER-CEP maps of directional dissociation for different values of chirp; from negative to positive values.

cillations are disturbed, relative to the TL pulse, and we observed a linear increase in the amplitude of the initial sizeable asymmetry around $t = 13$ fs. This causes different levels of oscillations at later times resulting in chirp dependent asymmetry. Figure 3.14 shows the snapshots of the wave-packet distribution for TL vs. chirped pulse when $t \simeq 15$ fs. The figures show that, while the large portion of the incoming dissociating wave-packet is localized at the right-side for the TL pulse driving case, the situation is reversed and the localization occurs at the left-side for the chirped pulse. This leads to asymmetries with opposing signs for TL vs. chirped pulse, which supports our findings in Figure 3.13. Figure 3.15 shows KER-CEP maps of dissociation probability for various chirp values. For each case, we see peaks around KER=1.3 eV oscillating with CEP. The periodicity of these oscillations are π , as expected. Starting from zero chirp, we see that the dissociation increases(decreases) with increasing positive(negative) chirp. Interestingly, the diagonal stripes lean towards the right-side with positive chirp, whereas it leans towards the left side with negative chirp. The figure clearly shows the strong coherent control over the dissociation reaction in molecules with chirped pulses.

3.3.5. Directional Dissociation and asymmetry in incoherent accumulation

There is a linear increase in the directional dissociation probability by chirp which can be seen in Figure 3.17(a). The increase is even more dramatic within the KER range of 1.0-1.3 eV. The maximum of the distribution appears to be left shifted, consistent with the recent experiments for longer pulses [97, 98]. To understand such variations, we have calculated the level-resolved contributions to dissociation. Different channels, launched by

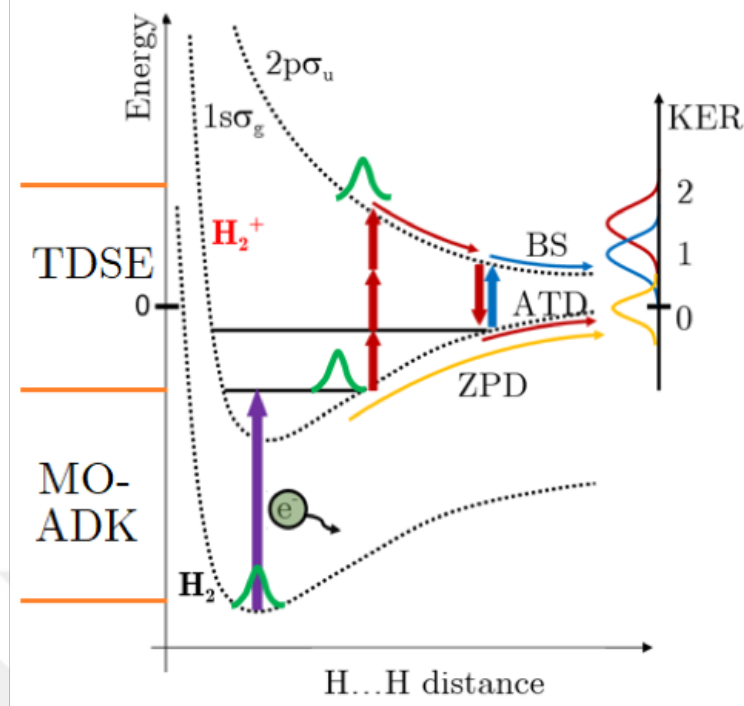


Figure 3.16 A diagram showing our procedure for the calculations: starting from the ionization of H_2 , modelled by MOD-ADK, we simulate the dissociation of H_2^+ by TDSE. Different strong channels leading to wave-packet dissociation and KER spectrum by absorbing different number of photons are also shown.

photon transitions between electronic states and at different vibrational states, contribute to dissociation, as shown in Figure 3.16. Identification of these channels through KER is necessary to determine the physical mechanism responsible for dissociation [16]. Typically, in the low (i.e., 0 – 3 eV) KER region three major electronic transitions between the ground ($1s\sigma_g$) and the first excited state ($2p\sigma_u$) lead to dissociation; (i) zero-photon dissociation (ZPD): $1s\sigma_g + 0\omega \rightarrow 1s\sigma_g$ transition, i.e., absorption of net zero-photons, (ii) bond softening (BS): $1s\sigma_g + \omega \rightarrow 2p\sigma_u$, i.e., absorption of net one-photon and (iii) above-threshold dissociation (ATD): $1s\sigma_g + 3\omega \rightarrow 2p\sigma_u \rightarrow 1s\sigma_g + \omega$, i.e. absorption of net two-photons. Therefore, $E_{KER} = n\omega - |E_v|$ yields the energy of the dissociating wave-packet from different channels, where E_v is the vibrational energy and n is the number of net absorbed photons. Here, to eliminate the time-dependence of the laser frequency due to chirp, we considered a time-averaged frequency as, $\langle\omega\rangle = \omega_0 + \eta/\tau$ for the analysis of the results. First, $\langle E_{KER} \rangle = n[\omega_0 + \eta/\tau] - |E_v|$, in fact, enounce that the kinetic-energies

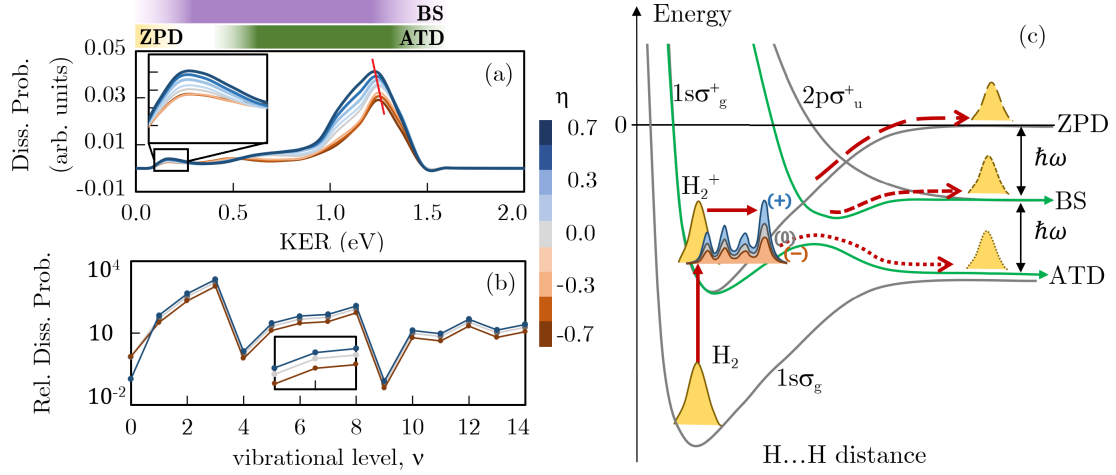


Figure 3.17 (a) Variation of CEP-integrated KER spectra of dissociation by chirp. Inset: Zoom in to the 0.1-0.3 eV interval. (b) Contributions to the dissociation from different vibrational levels. Inset: Zoom in to the 5-7th vibrational states. (c) Energy curves of diabatic (grey) gerade and ungerade states (green) and possible BS and ATD dissociation channels. Diagram also illustrates how positive (+), transform-limited (0) and negative (-) chirp influence vibrational population transfer to the same vibrational state, based on (b).

of the dissociating wave-packet is independent of chirp, since lower(higher) vibrational levels would *in turn* contribute to KER if positive(negative) chirp is used. To demonstrate; for a TL pulse ($\eta/\tau = 0$) with $\lambda = 800 \text{ nm}$ (and $\omega_0 = 1.55 \text{ eV}$), the KER of H_2^+ dissociation through the BS ($n = 1$) channel is launched from the $v = 5$ and higher levels. But when $\eta/\tau = 0.1 \text{ eV}$ and $\omega_0 = 1.55 \text{ eV}$, this threshold becomes $v = 4$. Therefore, the variation of KER spectra with chirp is caused by the variations in vibrational excitations. To support this, we calculated the chirp-dependence of the dissociating vibrational population rates based on the projections of the dissociating wave-packet to each vibrational state, v , for positive, TL and negative chirp values. As shown in Figure 3.17(b), and with the help of the diagram in Figure 3.17(c), we find that the vibrational levels are coherently de-populated with positive(negative) chirp relative to the TL pulse. Its effect is more pronounced within the KER range 1.0-1.3 eV, since both $v > 9$ rendering the BS channel and first few v rendering the ATD channel (of which are at high populations) collectively contribute this KER range (see Figure 3.17(a)-(c)). We also calculated the chirp-dependent dissociation probabilities by simulating wave-packet propagation at different initial vibrational levels. As shown in Figure 3.18, further increase in positive chirp

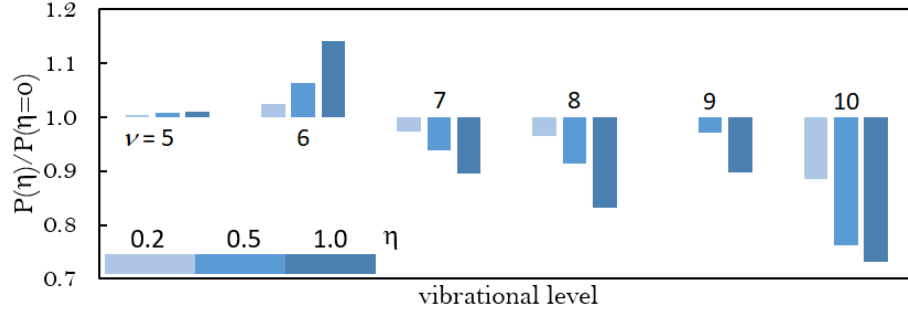


Figure 3.18 Vibrational-level resolved dissociation probabilities of H_2^+ for different chirp pulses relative to the TL pulse.

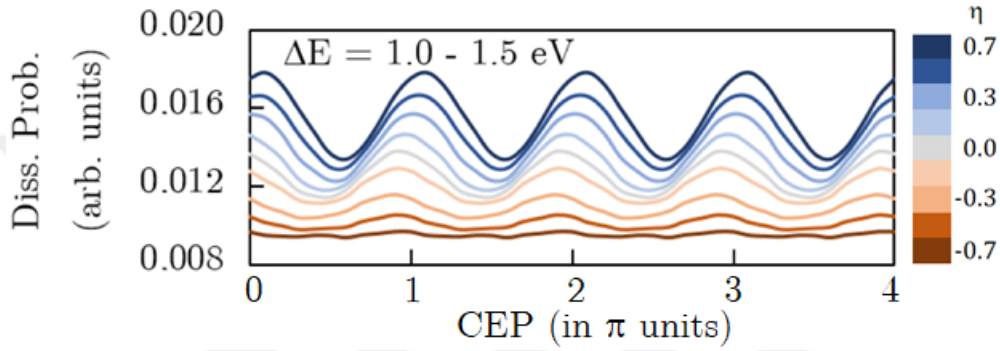


Figure 3.19 CEP variations of KER-integrated directional dissociation probability for different chirp parameters. The KER range is chosen to be 1.0-1.5 eV. The colour scheme for chirp parameters is the same as in Figure 3.17.

results in slight relative increase in the dissociation from the $v = 5$ level. Dissociation from this level is weak in all cases since, it lies slightly above the dressed electronic states ($\hbar\omega_0 = 1.55$ eV, $|E_5| = 1.44$ eV). In contrast, dissociation increase from $v = 6$ with chirp is more pronounced ($|E_6| = 1.24$ eV). For higher levels $v \geq 7$, dissociation is decreased with increasing chirp. To conclude, the variation of KER in the dissociation probability is directly related to the variations in vibrational population transfer by chirp and to the dissociation channel.

When we average the directional dissociation probability within the 1.0-1.5 eV interval, we obtain the CEP variation of dissociation probability, which is given in Figure 3.19. Dissociation probabilities oscillate with CEP and the amplitude of the oscillations increase with increasing chirp as well as the phase of the CEP (namely, phase-of-phase) dependence increase with chirp. Both BS and ATD channels contribute to dissociation in this KER region.

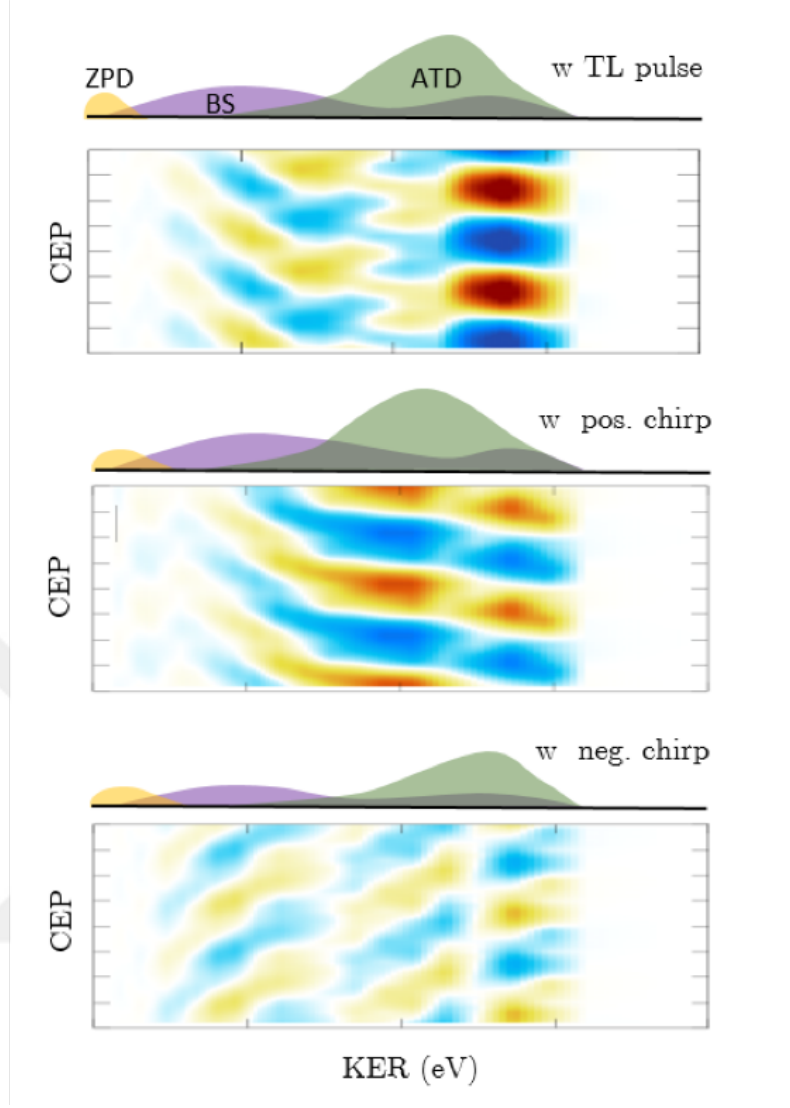


Figure 3.20 KER-CEP maps of asymmetry for (top) TL pulse, (middle) positive ($\eta = 0.7$) and (bottom) negative ($\eta = -0.7$) chirp values. At the top of each figure, a scenario-wise distributions of channel contributions leading to the calculated KER-CEP maps are shown.

We next calculate the CEP-dependence of dissociation probability and electron-localization asymmetry in ultra-short chirped laser pulses. The energy-resolved electron-localization asymmetry, $A(E, \phi)$, is computed from $A = (P_R - P_L)/(P_R + P_L)$ with the help of Equation 2.7, where $P_{R/L}(E, \phi)$ corresponds to directional dissociation through the right/left. Chirped CEP is indeed time-dependent having the analytical form $\phi(t, \eta) = \phi_0 + \eta t^2/\tau^2$, where $\eta t^2/\tau^2$ can be considered as the instantaneous phase variation in CEP, *i.e.* “phase-of-phase” [99]. To comprehend how chirp affects the CEP dependency of dissociation

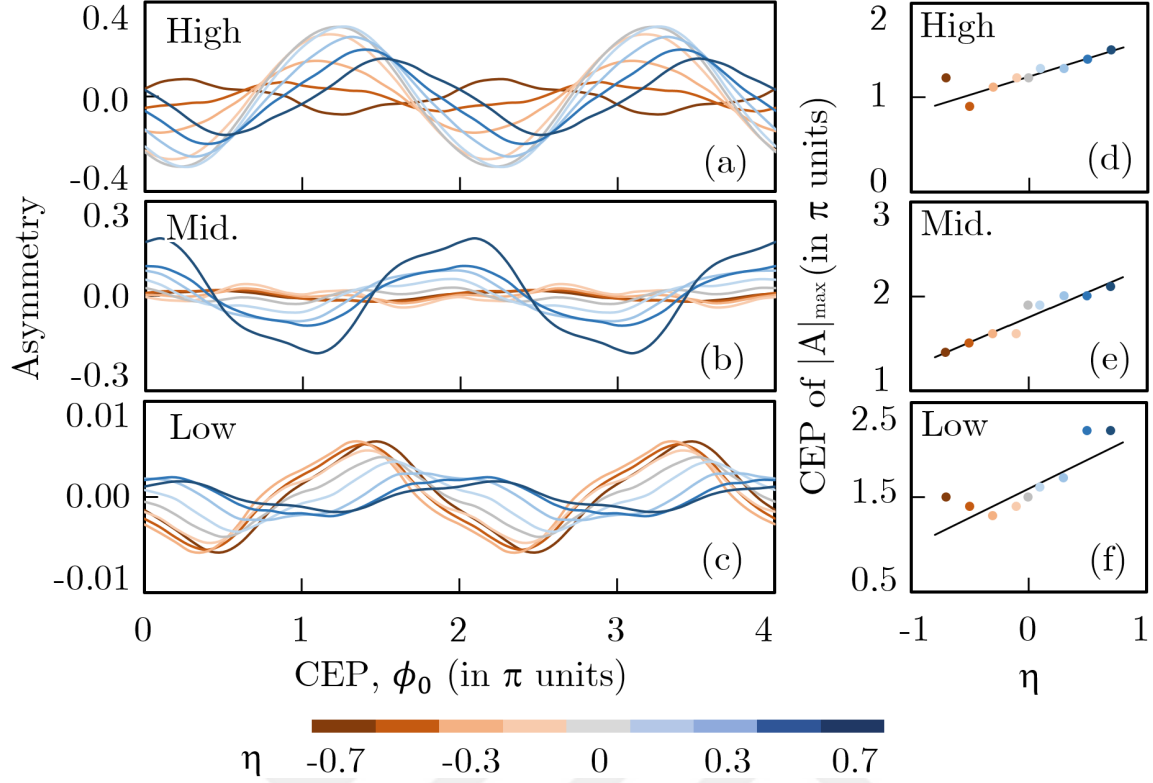


Figure 3.21 Averaged asymmetry plots over different KER regions. (a) High (1.3 - 1.5 eV) (b) middle (0.8 - 1.0 eV) (c) low (0.1 - 0.3 eV) energy regions.

probability and asymmetry, we time-averaged the chirped CEP as a first-order approximation and found that $\langle \phi(t, \eta) \rangle = \phi_0 + 4\eta/3$. This indicates that the phase-of-phase typically varies linearly by $4\eta/3$ with chirp [58].

We calculate the KER-CEP maps of the dissociation and asymmetry for various chirp values and present CEP variation of asymmetry results with KER integration over different energy ranges presented in Figure 3.21. First, Figure 3.20 shows the impact of zero, positive and negative chirp values on asymmetry. One can see a strong chirp modulations in the CEP-dependent asymmetry. Asymmetry maps for the negative chirp consists of uphill diagonal weak stripes modulating with CEP and increasing KER as shown in Figure 3.20 (a). However, these stripes appears to be downhill for the positive chirp with enhanced asymmetry (*vide infra*).

Figure 3.21 shows the CEP variations in the chirp dependent KER-integrated asymmetry for different KER regions. For high-energy region the amplitude of asymmetry of direc-

tional dissociation linearly decreases and CEP-dependence right-shifts for both positive and negative chirps. For the mid-energy region the amplitude linearly enhances and the CEP-dependence right-shifts from negative upto positive chirp. Finally, in contrast to the mid-energy case, for low-energy region the amplitude of asymmetry reduces and right-shifts. Specifically, a linear-fitting of the η variation in the CEP positions of the maxima for the 1.3-1.5 eV region, 0.8-1.0 eV region and 0.1-0.3 eV region (see Figure 3.21) gave a slope of 1.21 ± 0.09 , 1.40 ± 0.12 and 1.92 ± 0.45 , respectively, which are consistent with $4/3$ ($\simeq 1.33$) in the first-order approximation for CEP, *i.e.* $\langle \phi(t, \eta) \rangle = \phi_0 + 4\eta/3$. Based on these considerations, one can, in general, approximate the CEP variation of asymmetry for a certain chirp in the form of $A(\phi, \eta) \simeq A_0(\eta) \cos(\phi)$, where $\phi = \phi(\eta)$ (see Figure 3.21).

Even though there is a linear relationship between the chirp and the CEP-dependence of asymmetry, it is clear that the mechanism behind the right-left shifts and the variation in the amplitudes for different chirp values and for different KER regions is much more complicated as presented in Figure 3.20. But, apparently, from our analysis of the dissociation probability and its relation to the dissociation pathways show that they are playing the central role here. Besides, in general, interferences between states with different parity, e.g. between gerade and ungerade states in case of H_2^+ , are needed to achieve asymmetry in electron localization [37]. Such superpositions can be reached by interferences of different dissociation paths such as ZPD and BS or BS and ATD. However, as in our case, this asymmetry can also be established in a single dissociation path with varying photon-transition energies in chirped pulses. The ZPD-BS interference and BS-ATD interference produce asymmetry in the low and the remaining (mid and high) regions, respectively. For the low KER (0.1-0.3 eV), $v \simeq 5-7$ levels contribute to BS and very high v values contribute to ZPD in ultrashort pulses, but their probabilities are low (see Figure 3.17(b)). The decreasing amplitude in the asymmetry from negative to positive η observed for the low KER in Figure 3.20 is due to the systematic increase in the dissociation from BS relative ZPD in this KER region. In other words, increasing

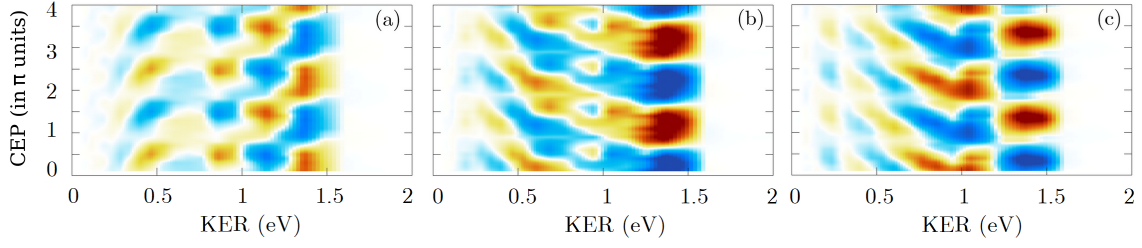


Figure 3.22 Asymmetry maps for (a) negative ($\eta = -0.7$) (b) transform limited ($\eta = 0$) and (c) positive ($\eta = 0.7$) chirp values.

dissociation from BS relative to ZPD results in an overall decrease in the overlap of ZPD-BS KER regions. This is also evident from the systematic increase in the dissociation in the low KER region shown by the inset of Figure 3.17(a). For the high KER range (1.3-1.5 eV) the asymmetry of the negative chirp (in Figure 3.20(a)) decreases relative to TL pulse, which can be attributed to the decreasing dissociation rate for both BS and ATD in this region. The decrease in the asymmetry for the positive chirp – even though dissociation rate increases – is due to the shift of ATD to lower KER region, resulting in reducing BS-ATD overlap. These are also in compliance with increasing asymmetry around mid KER region 0.8-1.0 eV for positive chirp as well as weak asymmetry for the negative chirp in the same region relative to the TL pulse, as shown in Figure 3.20.

3.3.6. Asymmetry in coherent accumulation

In this part, with the aid of Equation 2.52 and Equation 2.53, we calculate the dissociation and asymmetry of H_2^+ in chirp pulses by considering a coherent accumulation of the wave-packets, i.e., assuming that the individually launched H_2^+ wave-packets dynamically interfere within the laser pulse. We calculated the dissociation using Equation 2.66 and the asymmetry via $A = (P_R - P_L)/(P_R + P_L)$. The KER-CEP maps in Figure 3.23 shows that the overall appearances for different chirp values are similar to those we obtained for the incoherent case shown in Figure 3.20, which suggests that the energetic contributions of the dissociating pathways responsible for the KER-CEP maps in the coherent accumulations are nearly the same as of the incoherent case. However, looking at the fine structures and comparing them with those in Figure 3.20, we observe that there are slight

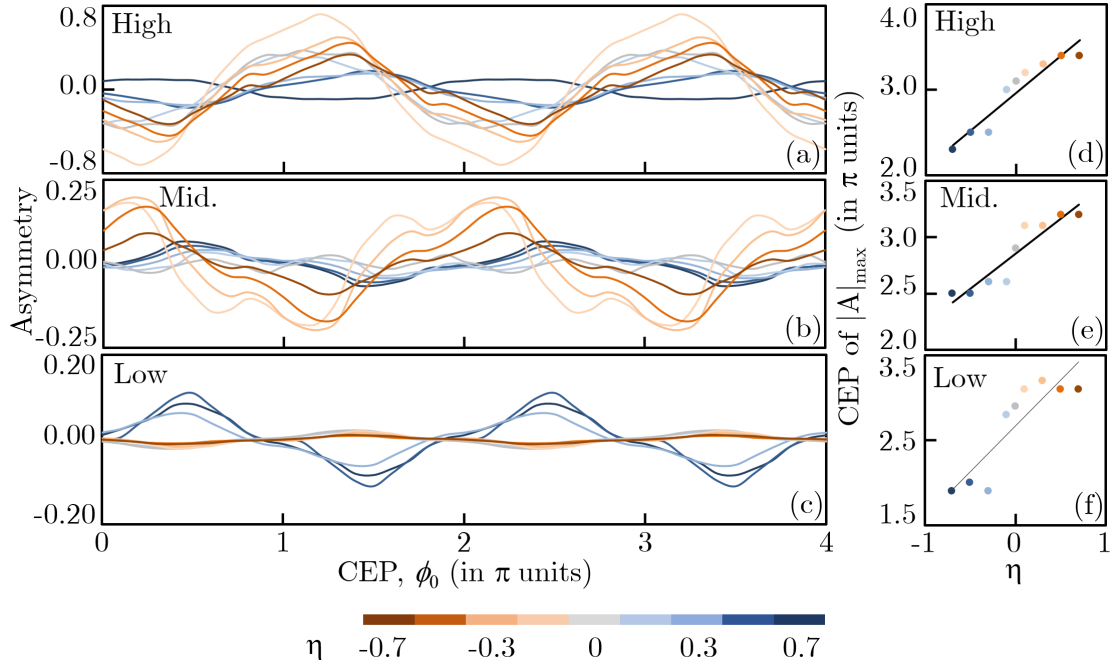


Figure 3.23 CEP variations for asymmetry averaged over different KER regions. (a) High (1.3 - 1.5 eV) (b) middle (0.8 - 1.0 eV) (c) low (0.1 - 0.3 eV) energy regions.

differences in asymmetry between incoherent and coherent cases around half integer π values of CEP but the difference is less for the integer π values. This stems from the fact that for the latter a sole strong peak at $t = 0$ predominantly contributes (see Figure 3.11) to the dissociative ionization process.

There is still CEP-dependent oscillations in asymmetry for different KER regions and we observed a linear relationship between η and CEP for the coherent case, as shown in Fig. Figure 3.23. Fit results in consequence of coherent calculations give slopes 2.77 ± 0.32 , 1.94 ± 0.29 and 3.38 ± 0.70 for high (1.3 - 1.5 eV), middle (0.8 - 1.0 eV) and low (0.1 - 0.3 eV) KER regions, respectively. The results are systematically higher than those of the incoherent accumulation and also the first-order approximation for the phase-of-phase (*i.e.*, $\langle \phi(t, \eta) \rangle = \phi_0 + 4\eta/3$) appears to underestimate the slopes (*i.e.*, $4/3$) for the coherent case. Specifically, the correlation between η and asymmetry seems to be relatively weak in the low energy range for both incoherent and coherent accumulations due to very fine-scale oscillations and complexity in the asymmetry with KER in this range.

In conclusion, we have investigated the chirp effect on CEP-controlled dissociation and

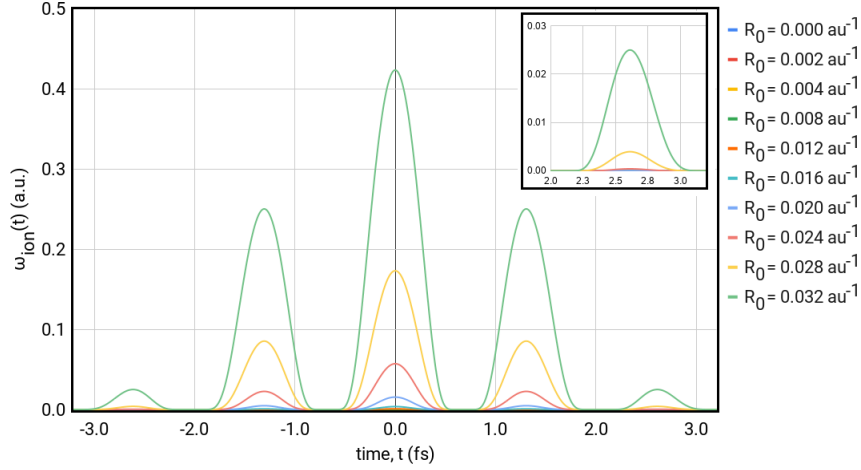


Figure 3.24 MO-ADK ionization rates in the vicinity of a nanotip. Inset is the zoom for right additional satellite peak. See the text for details.

asymmetry and found that exploiting the chirp modulates electron localization during dissociation. Dissociation is enhanced by chirp and CEP dependence of both the dissociation and the asymmetry shift with the chirp parameter. We find that ZPD, BS and ATD pathways are selectively induced depending on the sign and value of chirp and their interferences alternatively contribute to the KER spectra. We explored the dissociation dynamics in the context of incoherent and coherent accumulations of the individual H_2^+ wave-packets launched at different phases, arising from the strength of the wave-packet interferences. We found a linear relationship between the chirp and asymmetry in electron localization for both cases. We anticipate that our results for the chirped pulses provide an alternative perspective in the sub-cycle control of electron dynamics in molecular reactions.

3.4. Isotope Effect on Dissociation in the Vicinity of a Nanotip

3.4.1. H_2 ionization in the vicinity of a nanotip

In this section MO-ADK calculations with a nanotip are under discussion. In Figure 3.24, we see the first ionization rate of hydrogen molecule and its isotope molecules varied in time. Unlike the case in plain laser pulse [87], there is additional two satellite peaks shows up for $R_0 = \{0.024, 0.028, 0.032\} \text{ au}^{-1}$ and in total, there are five peaks for these

Figure 3.25 CEP variation of MO-ADK ionization rates in the vicinity of a nanotip. Increase in the nanotip inhomogeneity results in a boost in the strength of ionization rate. See the text for details.

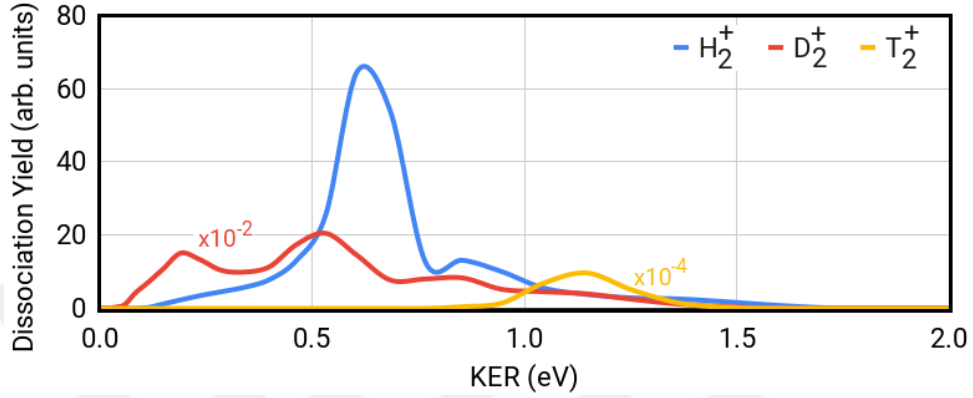


Figure 3.26 KER variation in dissociation yield of H_2^+ , D_2^+ and T_2^+ . A two-cycle at FWHM, 10 TW/cm^2 peak intensity Gaussian-shaped ultra-short laser pulse is considered.

inhomogeneity values. The reason behind these occurrence is the order of stiffening in electric field for these inhomogeneity values. The order of strengthening is so high that even for the descending and ascending parts of the laser pulse is enough to ionize the base molecule. Other than that, there are three peaks for all of other inhomogeneity values. And in general, we see a boost in all of the peaks by the rise of the inhomogeneity values.

In Figure 3.25 we see the CEP variation of MO-ADK rates for all the isotope molecules and the hydrogen molecule. Main peak and second peak show opposite characters by CEP variation. While main peak is in its maximum, second peak minimizes and vice versa. On the other hand, there is a strong shift in ionization rate with inhomogeneity to higher values.

3.4.2. Isotope effect on directional dissociation

In this section, we present the results for dissociation for H_2^+ and its homonucleus isotopes. We begin our calculations with a relatively weak intensity case (10 TW/cm^2) to explain the physics behind the dissociation. For such low intensities typically BS channel

is dominant. In this preliminary calculation, we have not considered ionization from parent molecule. Therefore we assume that the cation is populated before the interaction with few-cycle laser field (i.e., at $t = -\infty$). We consider an initial FC-averaged wave-function as the nuclear wave-function. Under these conditions, the adiabatic energy curves take the form as shown in Figure 2.11. This makes it possible for H_2^+ to dissociate from $v = 6$ th level to $v = 12$ th level. This is compatible with the dissociation profile we see in Figure 3.26 for hydrogen. Also we see from Figure 3.26 that the KER of dissociation maximum corresponds to that from the $v = 8$ th level. For deuterium, we observe dissociation within 0.2-1.2 eV which results from the dissociation from $v = 8$ th-18th levels. For 0.5 eV, there is a maximum in Figure 3.26 and this maximum is connected with the dissociation from the $v = 10$ th level. Finally, for tritium we observe that the dissociation predominantly occurs at ~ 1.15 eV and the lower energy channels are suppressed. Based on the analysis shown in Figure 2.11 we see that no vibrational levels can contribute to this dissociation via BS. Therefore we speculate that the source of dissociation is the ATD channel from the $v = 5$ th-10th levels. On the other hand, there is a dramatic decrease in dissociation yield as the reduced mass increases. This can simply be explained by the increasing mismatch between the timescale of laser pulse period (2.7 fs) and molecular vibrational period of a cation ($T \simeq 2\pi \sqrt{\frac{\mu}{k}} \simeq 14 \text{ fs} \sqrt{\frac{A}{2}}$, where μ and A are the reduced mass and mass-number for the diatomic cation.). In order to complement our findings, we also performed two level model calculations for isotopes presented in Section 2.8. Figure 3.27 shows the time-dependent wave-packet probability distributions of H_2^+ , D_2^+ and T_2^+ cations. We assume that in all cases the wave-packet is initially in the ungerade state and the field-induced ionization occurs at the peak of the field and dissociation is established for $R > 10 \text{ \AA}$. With these, Figure 3.27 clearly shows that the dissociation of H_2^+ occurs faster and that of T_2^+ slower.

Next we consider the full-size case, i.e. we include the field-induced ionization of parent molecule into our calculations and perform volume averaging to mimic a realistic experimental case. The intensity range is chosen from 10 TW/cm^2 to 150 TW/cm^2 for volume

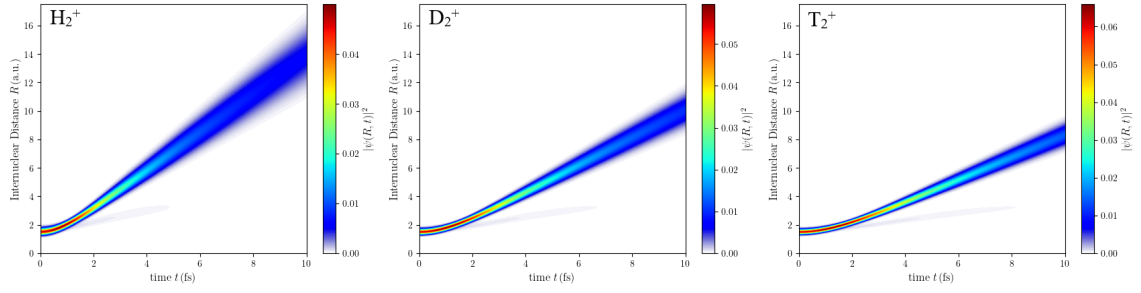


Figure 3.27 Dissociation probabilities for hydrogen, deuterium and tritium cations. Dissociation occurs slower as the reduced mass of the molecule gets higher.

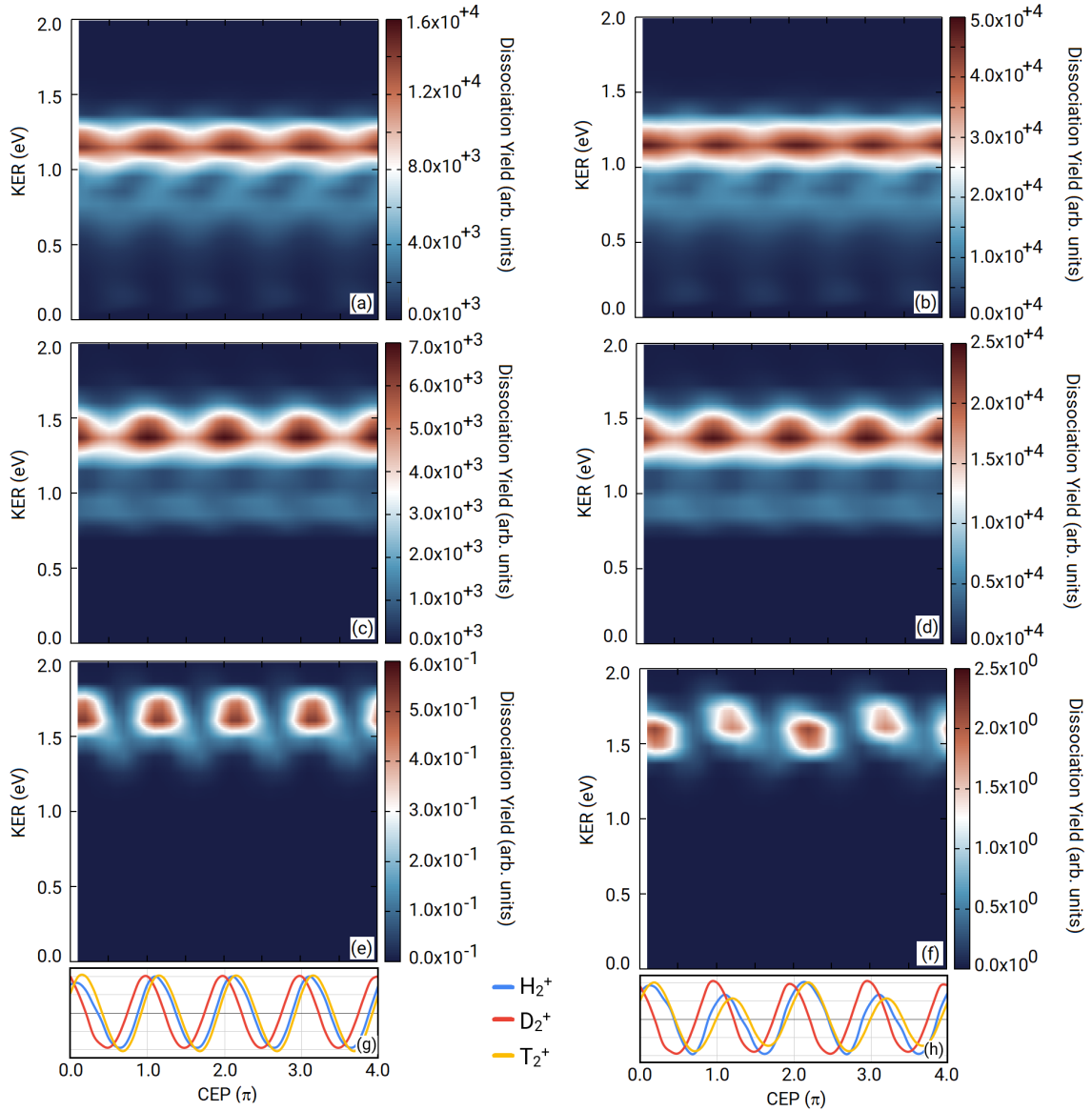


Figure 3.28 KER-CEP maps of dissociation for H_2^+ ((a)-(b)), D_2^+ ((c)-(d)) and T_2^+ ((e)-(f)) without nanotip ($R_0=0.000\text{a.u.}^{-1}$) (1st column) and with nanotip ($R_0=0.008\text{a.u.}^{-1}$) (2nd column).

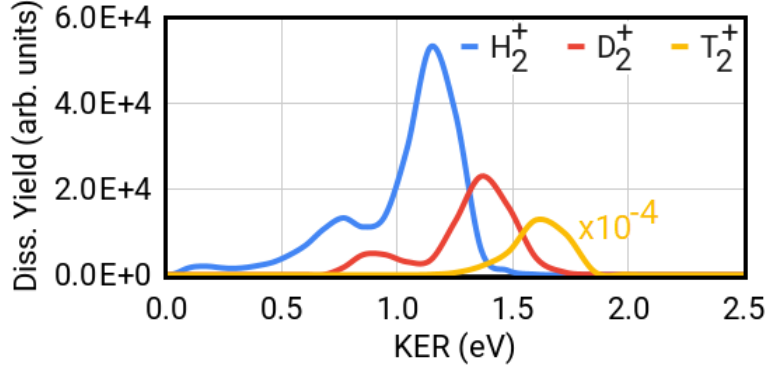


Figure 3.29 CEP-integrated dissociation yield for different hydrogen cation isotopes. The field parameters are the same as in Figure 3.28.

averaging with a total of eight steps within this range. For each intensity value we scan forty CEP values between 0 and 2π . For each intensity and CEP values, two main starting times are considered. For each case, 10 inhomogeneity values are used. In total, we considered 9 different isotopes. Thus, a total of 57600 TDSE calculations are done in parallel. Each calculation takes ~ 4.5 hours, which corresponds to nearly 30 CPU years of run time.

The CEP-KER maps for dissociation of H_2^+ , D_2^+ and T_2^+ are given in Figure 3.28. Before we dive deep into the inhomogeneity effect we would like to analyse the isotope effect with a perturbative inhomogeneity. Therefore we choose to present the KER-CEP maps of dissociation with homogeneous field, i.e. inhomogeneity is zero, and perturbed-inhomogeneous field, i.e. inhomogeneity is relatively small, 0.008 a.u.^{-1} .

For hydrogen, we observed that the maximum of dissociation is around 1.2 eV and the CEP variation has a,

$$P(E, \phi) = P(E, \phi + \pi), \quad (3.12)$$

periodicity. Also, there are small bumps at around 0.7 eV and 0.2 eV for hydrogen. Dissociation yield systematically reduces as the reduced mass increases as shown in Figure 3.28 (a), (c), (e), which can again be attributed to the increasing mismatch between the timescales of laser-field and vibrational periods. The maximum of dissociation shifts to higher KER with increasing reduced mass. For deuterium, it is 1.4 eV and for tritium,

it is 1.6 eV, consistent with the literature [100]. Also, the dissociation yield in low KER regions are systematically suppressed as the reduced mass increases. These observations can also be seen in the CEP-integrated plot for hydrogen, deuterium and tritium in Figure 3.29. Similar to hydrogen, the CEP variations of deuterium and tritium both have a π periodicity. However, we observed that, the CEP oscillations become more strong as the reduced mass increases. To quantify this effect, we used a contrast parameter in the form $(P_{max} - P_{min})/(P_{max} + P_{min})$, similar to Hua *et al.* [100]. We found that the contrast is 0.07, 0.19 and 0.42 for hydrogen, deuterium and tritium cations, respectively.

When the field inhomogeneity is perturbatively incorporated, as shown in Figure 3.28 (b), (d), (f), we first observed that the position of the maxima are largely maintained and the dissociation yield increases in all cases with field inhomogeneity. Similar to the homogeneous case, the dissociation from lower KER is suppressed. On the other hand, field inhomogeneity has a dramatic effect on CEP variation [45]. The π -periodicity is clearly broken and the periodicity manifests itself as 2π . Although, this is not clear from Figure 3.28 (b) and (d), the break in the π -periodicity can be seen from Figure 3.28 (f). To demonstrate the 2π -periodicity for all isotopes, we calculated the KER-integrated CEP variation of dissociation yield within KER ranges 1.0-2.0 eV. To better visualise this effect, we employed the formula, $(P(\phi) - P_{avg})/P_{avg, max}$. The results are shown in Figure 3.28 (g) and (h). Again, Figure 3.28 (h) clearly shows that a conventional π -periodicity is broken and it manifests itself with different variations for different isotopes. We also calculated the contrast in CEP variation with field inhomogeneity using the aforementioned contrast parameter and found values as 0.05, 0.17 and 0.45 for hydrogen, deuterium and tritium cations, respectively. Thus, our results show that field inhomogeneity and isotopes are both have strong controls over the directional dissociation.

In order to generalize, we also calculated the dissociation from heteronucleus isotopic cations in addition to the homonucleus ones. As shown in Figure 3.30, the reduction in dissociation yield with increasing reduced mass can be clearly seen for homogeneous case ($R_0=0.000$ a.u.⁻¹). Dissociation is systematically enhanced with different field inho-

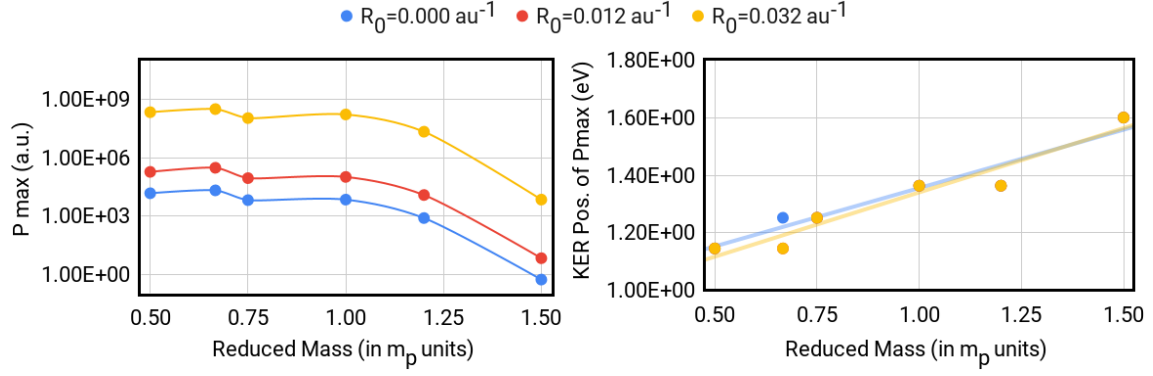


Figure 3.30 (a) Maximum dissociation yield, $P_{\max}$ and (b) the corresponding KER value of diatomic cations as a function of reduced mass.

mogenities and the reduction in the dissociation yield is maintained.

Figure 3.30 (b) shows the KER position of the maximum dissociation as a function of reduced mass. The results show that there is an almost linear increase in KER position. Therefore we fit the values to a linear function and found that it is in the form $A/10 + 1$, where A is the mass number of the diatomic cation.

Dissociation in homonucleus molecules:

We calculated the CEP integrated KER distributions of diatomic molecules near the nanotip. The full maps of these results are shown in the Appendix section. Figure 3.31 shows the escalating dissociation probability with rising field inhomogeneity values. For all values, there is a peak arising from the intersection of two dissociation channels, namely ATD and BS around 1.15 eV for hydrogen. And there is a second rise in low energy regime which corresponds to BS and ZPD channels around 0.2 eV. With increasing field inhomogeneity, the dissociation is systematically enhanced, but the KER profiles are largely maintained for hydrogen cation. The influence of field inhomogeneity is more apparent for deuterium and tritium cations as shown in Figure 3.31 (b)-(c). First the peaks of the dissociation are shifted by 0.2 eV and 0.5 eV for deuterium and tritium relative to that of hydrogen cation, respectively. Similarly, the dissociation is enhanced with increasing field inhomogeneity. However we observed that there is a clear evidence that field inhomogeneity has a strong control over the dissociation at low-KER region for deuterium and tritium. In addition, dissociation is also dramatically enhanced for high KER of tritium. The strong

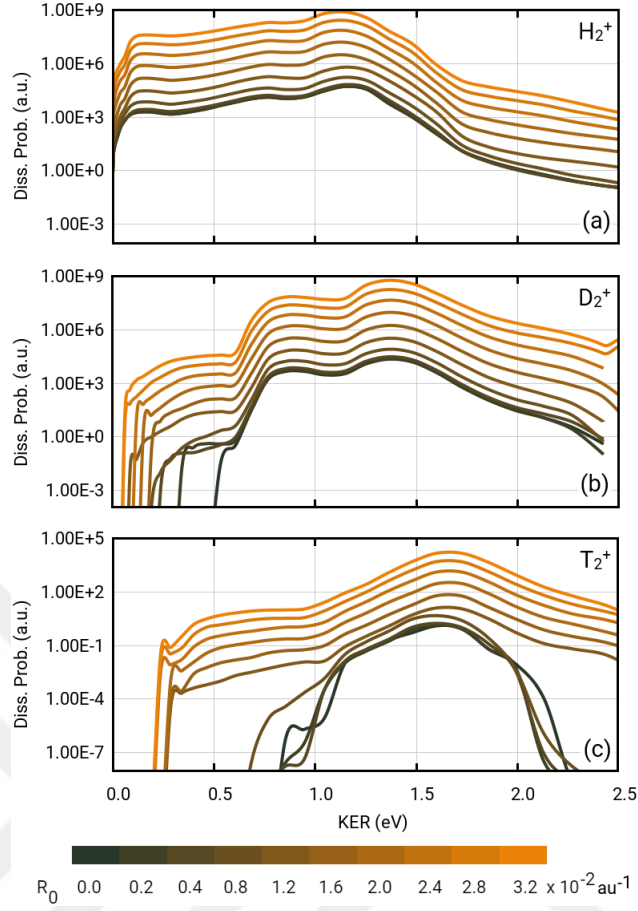


Figure 3.31 Dissociation probability with respect to KER of (a) H_2^+ , (b) D_2^+ and (c) T_2^+ for inhomogeneous field.

control of field inhomogeneity at low KER is attributed to the longer length scale of ZPD channel that decently matches with the length scale of spatial field inhomogeneity [45]. In other words, for ZPD channel, the molecule is so stretched that it feels the field enhanced by the plasmonic field. On the contrary, the apparent modification of field inhomogeneity at very high KER in tritium led us believe that the dissociation is influenced by field inhomogeneity when the dissociating wave-packet is in gerade state which is the case for ZPD and ATD channels.

Dissociation in heteronucleus molecules:

Figure 3.32 shows the CEP integrated KER distributions of dissociation for heteronucleus molecules. Due to broken mass symmetry, we calculated cases where either the lighter or the heavier atom is close to the nanotip. We called these as “left-oriented” or

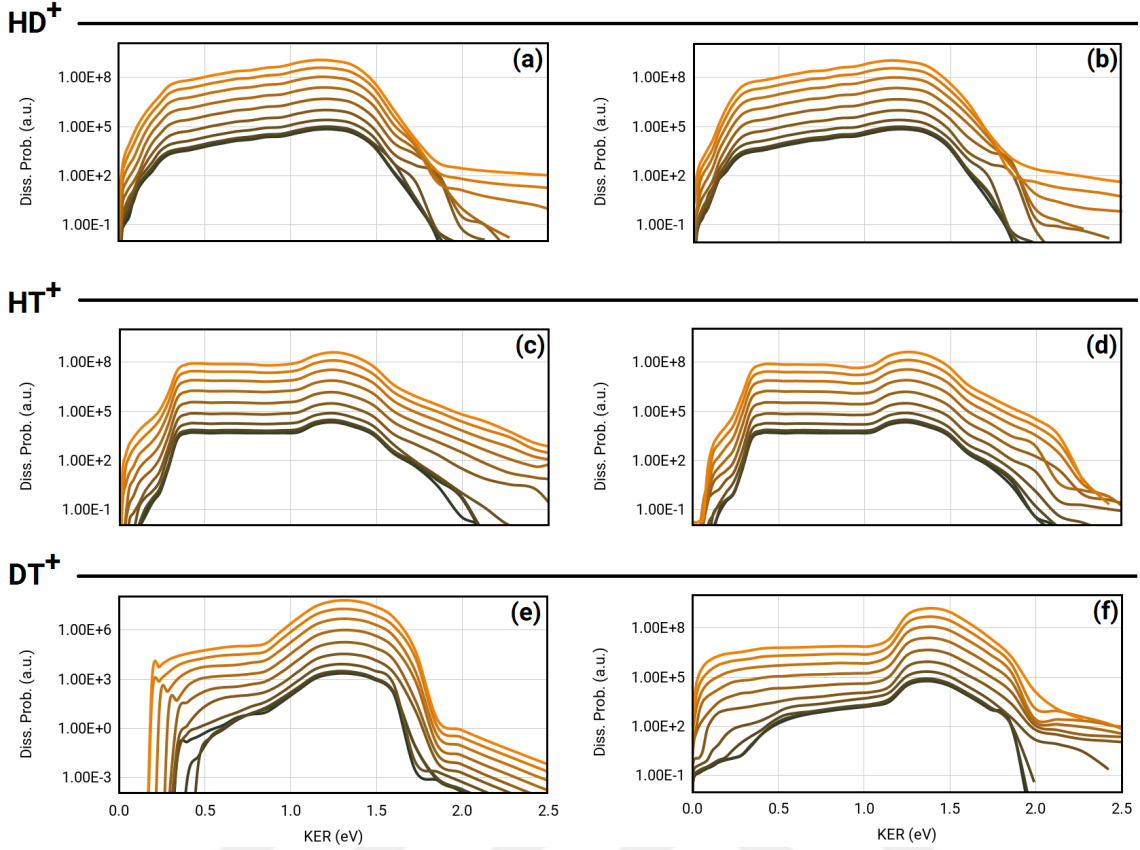


Figure 3.32 KER variations of dissociation yield for left-oriented ((a)-(c)-(e)) and right-oriented ((b)-(d)-(f)) HD^+ ((a)-(b)), HT^+ ((c)-(d)), DT^+ ((e)-(f)).

“right-oriented” cases. We observed that increasing field inhomogeneity always enhances dissociation but for some cases it obviously effects the KER profile of dissociation at different KER regions. This difference is relatively small for both HD^+ and HT^+ as shown in Figure 3.32 (a)-(d). For left-oriented DT^+ the dissociation is typically 2 orders of magnitude lower than the right-oriented case (see Figure 3.32 (e)-(f)), since in the former case tritium atom is closer to the nanotip. For right-oriented DT^+ , the dramatic modification in high KER (> 2.0 eV) is due to the ATD channel and comparing left- and right-oriented DT^+ , there is an apparent difference in the low KER region caused by the ZPD channel.

3.5. Isotope Effect on Asymmetry

Next we calculated the directional control of dissociation in different isotopes and focused on asymmetry based on the full numerical solution of TDSE presented in Section

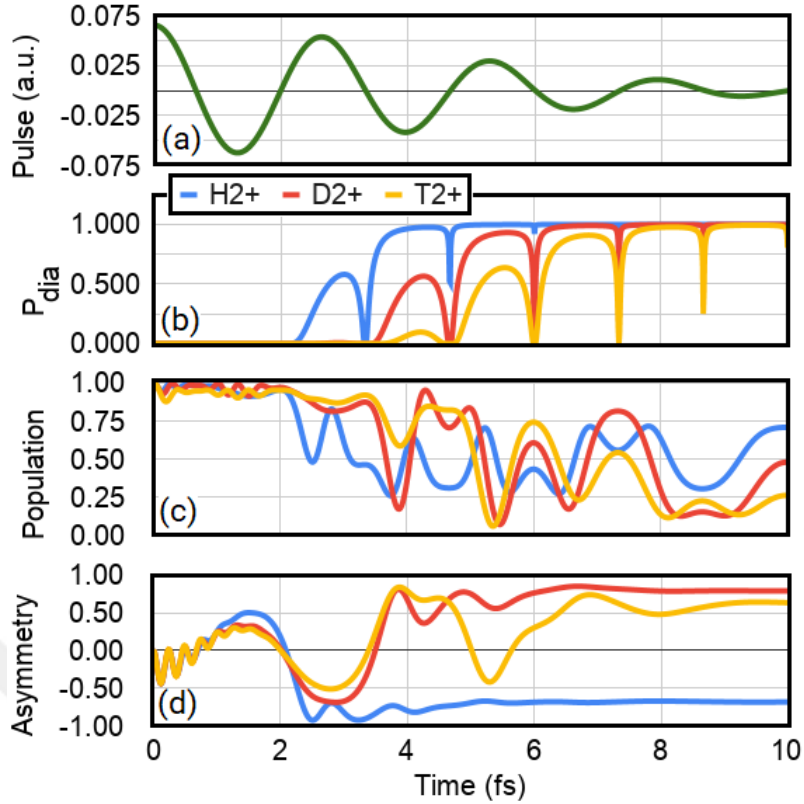


Figure 3.33 Isotope effect on the directional dissociation of H_2^+ in a two-level system. All blue(red)[yellow] lines for hydrogen(deuterium)[tritium] cation. (a) Temporal variation of the laser pulse. $\phi_0 = 0$. (b) Landau-Zener probability from adiabatic to diabatic process. (c) Ungerade populations. (d) Isotope effect on asymmetry change in time.

2.7. The incoming laser pulse couples with the nanotip and creates a local, spatially inhomogeneous field due to surface plasmon resonance. Therefore, the field is enhanced near the nanotip surface. This causes potentially an alternative dissociation control in molecules, since the molecular motions (vibrational, electronic, etc.) are coupled with the spatial inhomogeneity. When the main axis of the diatomic molecule perfectly aligns with the apex axis of the nanotip, the dissociation will be maximized. These effects have been first demonstrated by Yavuz *et al.* [44, 45]. In this thesis, we go beyond and explored the isotope effect of such process. First, we investigated the dissociation triggered by laser pulse in H_2^+ , D_2^+ and T_2^+ molecules with only their first two levels. These two levels are called as gerade and ungerade states. The initial wave function is assumed to be in ungerade state. This choice is made due to the fact that, otherwise, much of the wavefunction stays at gerade state and it becomes hard to observe the process and the physics behind it.

We have calculated the diabatic probability by use of the Landau-Zener formula and see that the beginning of the mixed state (diabatic and adiabatic state) shifts to later times as the reduced mass increases. During mixed era (adiabatic-diabatic mixed), transitions between gerade and ungerade state causes the asymmetry. Because the starting time of mixed era shifts to later times as the reduced mass increases, the settlement in asymmetry occurs later times for Deuterium and the latest for Tritium. Such as in the chirped pulse case, we see instantaneous downs in diabatic transition probability at the moments when the intensity of laser pulse is zero which indicates that the adiabatic transitions occur transiently at these moments. Also the intensity of these downs gets bigger as the reduced mass decreases, meaning the transitions happens more dramatically for molecules with higher mass. Because the adiabatic transitions end earlier for hydrogen molecule (at 5 fs, see Figure 3.33), the gerade and ungerade states do not find time to get mixed one more time which eventuates in the negative asymmetry sign. But for deuterium and tritium, adiabatic-diabatic mixture lasts longer and thus the sign of asymmetry is positive for these molecules.

Asymmetry in homonucleus molecules:

We then calculated the time variation of asymmetry and the results are shown in Figure 3.34 using the full numerical solution of TDSE. For a homogeneous field ($R_0 = 0$), we observed that the asymmetry first oscillates roughly for 15 fs for hydrogen, 20 fs for deuterium and 25 fs for tritium. This can be attributed to the slowing timescale of molecular motions. The starting time of the oscillations are also shifted which is again related to the slowing wave packet motion. We found that the asymmetry of directional dissociation significantly reduced by increasing isotope mass. We suggest that the reduction in asymmetry is due to the weakening in the field strength at the moment of dissociation for increasing isotope mass. When we shift the CEP by π , we observed that for all isotopes the variation of asymmetry is exactly the same as that of zero CEP, but the direction of dissociation is opposite. In other words, there is a $A(\phi = 0) = -A(\phi = \pi)$ inversion

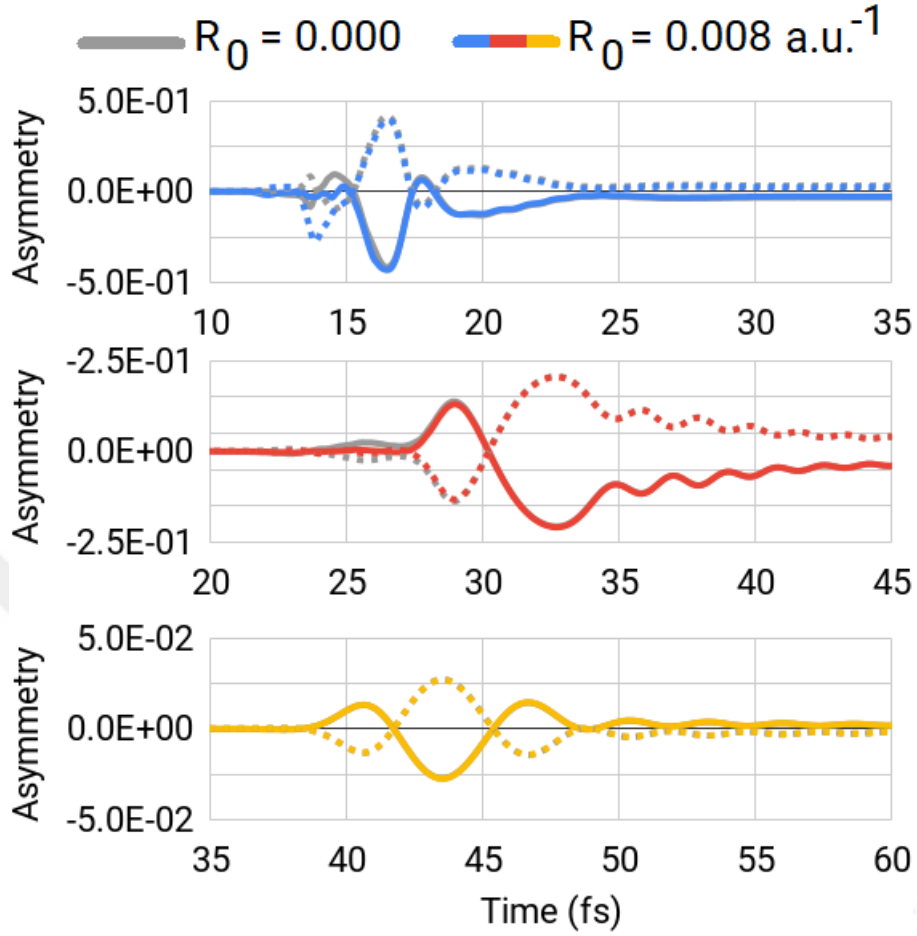


Figure 3.34 Asymmetry variation in time for Hydrogen, Deuterium and Tritium cations for CEP = 0 (solid-lines) and CEP = π (dotted-lines), without (grey) and with (colour) nanotip.

symmetry, which means that a π change in CEP fully drives the dissociation in the opposite direction for homogeneous fields. When we incorporated the field inhomogeneity ($R_0 = 0.008 \text{ a.u.}^{-1}$) we saw that its impact systematically decreases for increasing mass. The time profile of these asymmetry oscillations are modified and the aforementioned inversion symmetry is broken. Based on the parameters we chose, we observed that the asymmetry is dynamically modified in the vicinity of a nanotip, but the asymmetry is established nearly in the same direction in all cases. This can be due to the field parameters we chose. In the next sections, we will comprehensively show that the field inhomogeneity typically enhances the dissociation asymmetry. For homogeneous fields, it should be obvious that $A(\phi = 0) - (-A(\phi = \pi)) = 0$, meaning that the inversion symmetry is fulfilled,

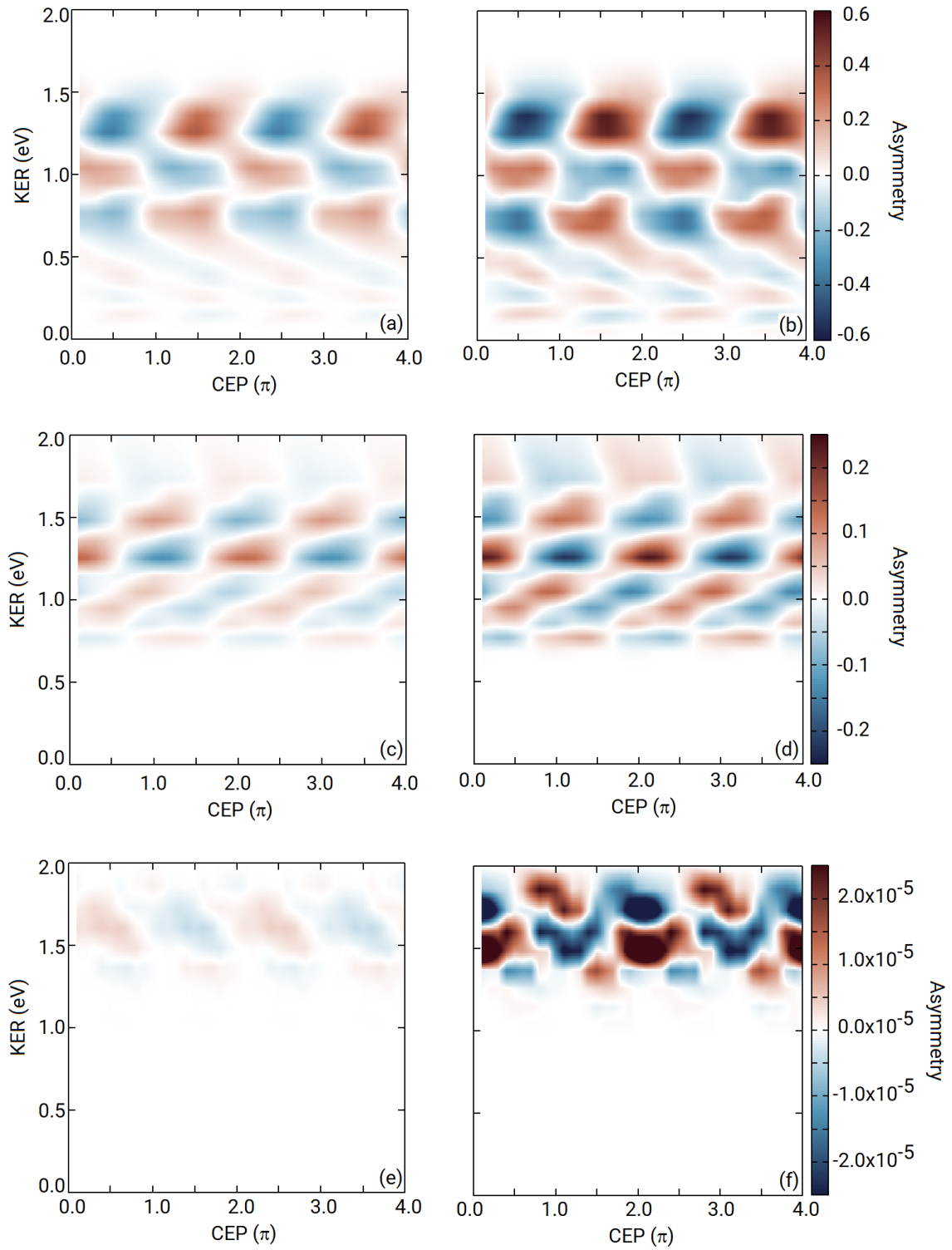


Figure 3.35 KER-CEP maps of asymmetry in the dissociation of H_2^+ (1st-row), D_2^+ (2nd-row) and T_2^+ (3rd-row) without nanotip (1st-column) and with nanotip (2nd-column).

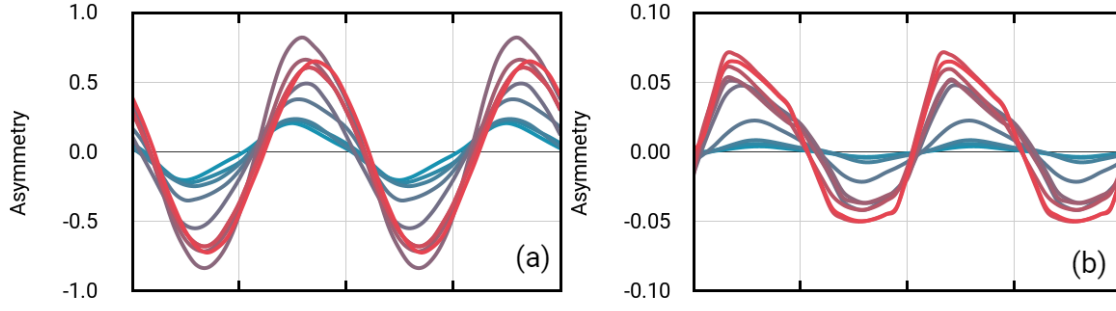
in other words the contrast in asymmetry is zero. However, as Yavuz *et al.* [45] showed field inhomogeneity introduces asymmetry contrast due to non-uniform spatial distribution

of the plasmon enhanced field near the nanotip. We found that the contrast in asymmetry reduces with isotope mass, *i.e.* $H_2^+ > D_2^+ > T_2^+$ (see Section 3.5.1. for details).

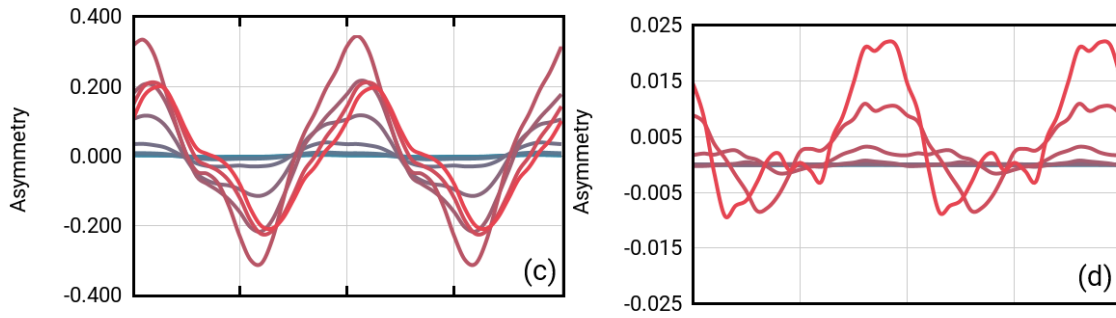
Figure 3.35 (a), (c) and (d) show the KER-CEP maps of directional asymmetry in H_2^+ , D_2^+ and T_2^+ in homogeneous fields, respectively. We found strong variation in asymmetry with isotope mass. Typical asymmetry is maximum for H_2^+ and it decreases with increasing isotope mass. We observed that the strong CEP variation in asymmetry is around 1.2-1.3 eV consistent with the maximum KER position of dissociation in H_2^+ shown in Figure 3.28 (a). This asymmetry is caused by the BS-ATD overlap. Weak variation in asymmetry near 0.7 eV and 0.2 eV is also consistent with the dissociation yield shown in Figure 3.28 (a). For D_2^+ and T_2^+ we observed almost no apparent asymmetry in low KER regions, since dissociation vanishes shown in Figure 3.28 (c) and (d). The field inhomogeneity ($R_0 = 0.008 \text{ a.u.}^{-1}$) enhances asymmetry in all isotopes, but the difference between the homogeneous and inhomogeneous cases increase with isotope mass. In other words, we observed a large impact on asymmetry of T_2^+ even with a low R_0 . We also observe that the R_0 also breaks the π -periodicity in absolute asymmetry, which also introduces contrast in asymmetry [45]. We found that the contrast in asymmetry reduces with increasing isotope mass.

Next, we calculate the KER integrated CEP dependent asymmetries for H_2^+ , D_2^+ and T_2^+ and for various values of field inhomogeneity, R_0 , over different energy regions. The entire set of KER-CEP maps are shown in the Appendix section. The results are shown in Figure 3.36. In all cases, one can clearly see that the asymmetry is more rapidly enhanced in one direction than the other. For instance, for T_2^+ in high energy region, asymmetry is increased up to 0.003 in the positive direction whereas the asymmetry is increased up to 0.001 in the negative direction. Normally, for either direction the magnitude of asymmetry should be the same for homogeneous fields. Therefore we observed again that the asymmetry has contrast for inhomogeneous fields. The asymmetry is systematically reduced for increasing isotope mass. This can be due to the reduction in either the dissociation yield or the overlap of ATD-BS for the high KER regions and BS-ZPD for low KER

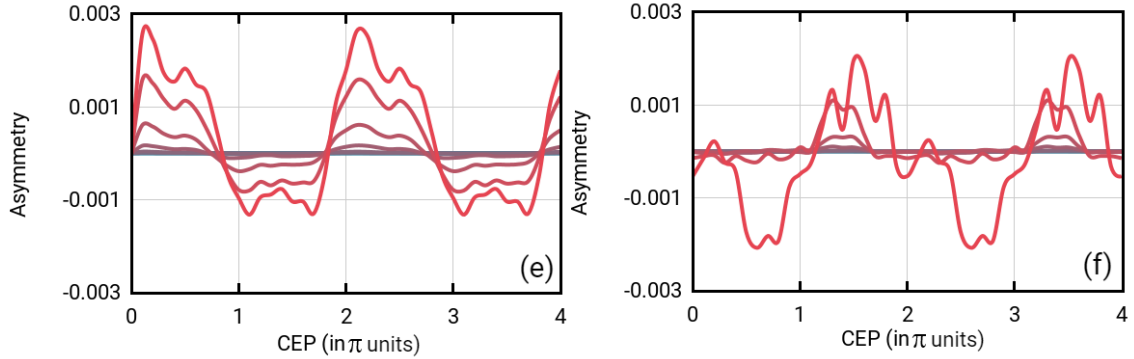
Hydrogen



Deuterium



Tritium



R_0 0.0 0.2 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 $\times 10^{-2} \text{ au}^{-1}$

Figure 3.36 CEP variation of asymmetry in electron localization during dissociation of hydrogen cation in (a)/(c)/(e) high and (b)/(d)/(f) low energy intervals.

regions. We also observed that, interestingly the asymmetries for homonucleus molecules are shifted as the mass increases. Relative to H_2^+ , the “phase-of-phase” of D_2^+ is roughly $\pi/2$ and of T_2^+ is roughly π . This corresponds to $\Delta\phi = \pi(A - 1/2)$, where A is the mass number.

Asymmetry in heteronucleus molecules:

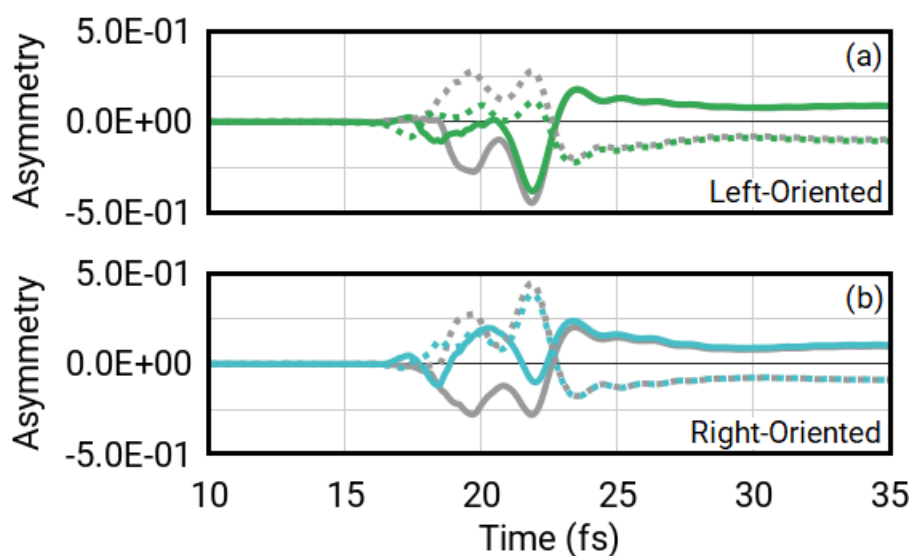


Figure 3.37 Asymmetry variation in time for (a) left-oriented and (b) right-oriented HD^+ cation with CEP=0 (solid-lines) and CEP= π (dotted-lines) without (grey) and with (colour) nanotip.

In this section, we studied directional control of dissociation in heteronucleus diatomic molecules where the masses of the left and the right nucleus are different. This mass asymmetry manifests itself as a different way of directional control. For instance, the inversion in dissociation asymmetry is broken with the inversion of the laser field (shifting CEP by π) even in the homogeneous case. We can consider this mass asymmetry as a prototype of more complex systems, where typically mass distribution around a chemical bond is not homogeneous. One simple example can be methane (CH_4) molecule where in one bond there is CH_3 group on one side and H on the other side. Therefore there is a 15:1 mass ratio around the bond for CH_4 . Then, for instance, an efficient abstraction of hydrogen in such complex molecule can be controlled by ultra-short lasers. To demonstrate the effect of mass asymmetry in directional dissociation, we calculated the time dependent asymmetry in HD^+ in a homogeneous field. The results are shown in Figure 3.37 with grey lines. Here one can first see that for a fixed orientation of the molecule (either left- or right-orientation) the time variation of asymmetry for zero CEP is clearly different from that with π . For the left-oriented case, where the deuterium is on the left side, asymmetry is converged to 0.08 for zero CEP, meaning that dissociation occurs dominantly to the

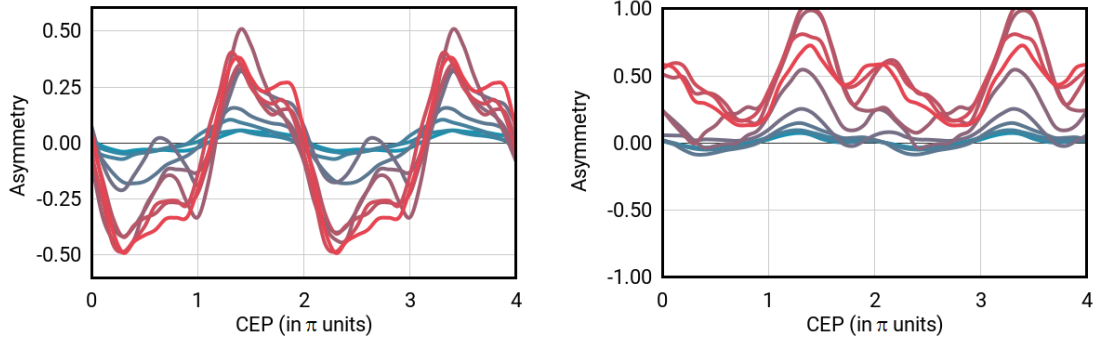
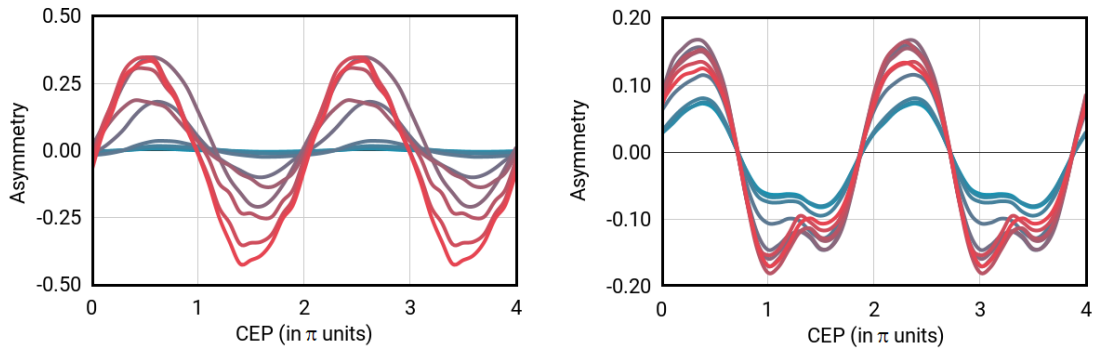
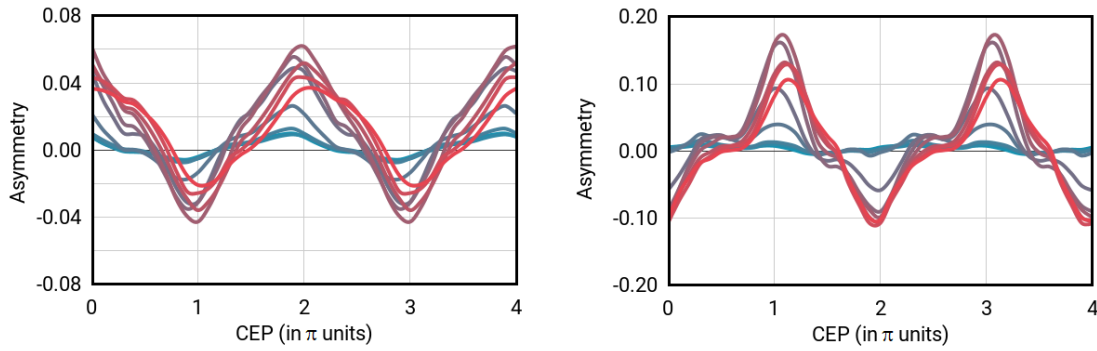
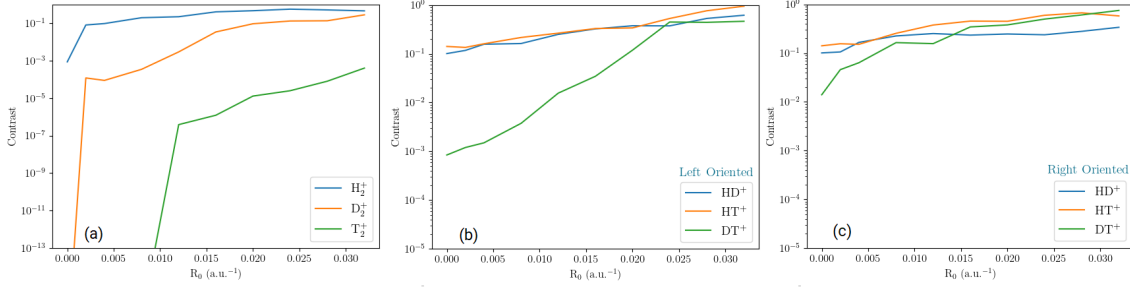
HD⁺**HT⁺****DT⁺**

Figure 3.38 KER integrated CEP variations of asymmetry for heteronucleus molecules in high KER region.

left, *i.e.* via deuterium side. However, when CEP is shifted by π , asymmetry converges to -0.10, via hydrogen side. When the orientation of HD⁺ is reversed, the asymmetry for zero and π CEPs are also reversed. In other words, if A_L and A_R are the asymmetry for left- and right-orientation, then one can see that $A_L(\phi) = -A_R(\phi + \pi)$. This symmetry again is clearly broken by field inhomogeneity as shown in Figure 3.37.

Figure 3.38 shows the KER-integrated CEP variation of asymmetries for HD⁺, HT⁺ and

Low KER



High KER

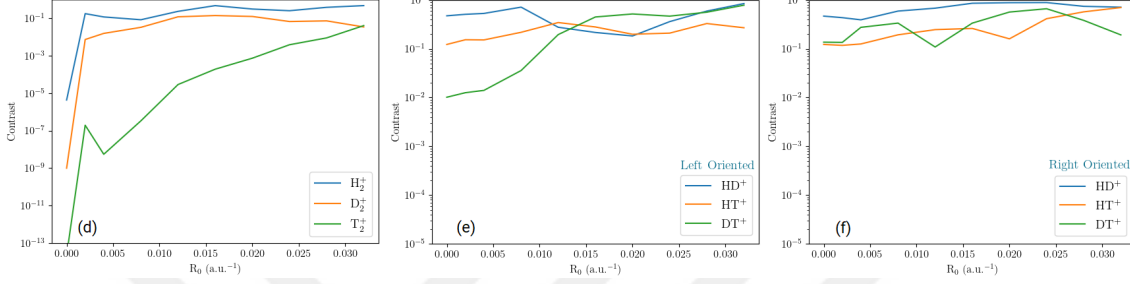


Figure 3.39 inhomogeneity variation in contrast for high ((a)-(b)-(c)) and low ((d)-(e)-(f)) energy regions. For homonucleus molecules, contrast reduces with increasing nucleus mass. For heteronucleus molecules, no dramatic change with mass is observed. See the text for detail.

DT^+ cations interacting with an inhomogeneous field. The inhomogeneity values are chosen between 0.000 to 0.032 a.u.^{-1} . Since there is a mass asymmetry in these diatomic molecules, we considered cases where either heavier nuclei or lighter nuclei is closer to the nanotip. The former case is called as “left-oriented” and the latter is called as “right-oriented”. Comparing Figure 3.38 (a) and (b), we observed that there is a dramatic difference in asymmetry variation in HD^+ . The right-orientation asymmetry is systematically enhanced in the positive direction. As the mass of the heavier nuclei is increased from D to T, the asymmetry variation is reduced both for left- and right-orientation as shown in Figure 3.38 (c) and (d). Also the phase of asymmetry oscillations is shifted by π . The asymmetry variation is further reduced for DT^+ both for left- and right-orientation.

3.5.1. Contrast analysis

Contrast analysis is done following the Equation 2.67 for two different energy regions. R_0 variation in contrast for all molecules in high and low energy regions are shown in

Figure 3.39. For homonucleus molecules, variation in contrast by R_0 is exponential and the increase in contrast is observed for all cases, contrast variation is more rapid as the isotope mass increases for both high and low KER regions as shown in Figure 3.39 (a) and (d). On the contrary, the variation in contrast by R_0 for heteronucleus molecules is typically weak for both low and high KER regions and left- and right-orientations. We suspect that for heteronucleus molecules the permanent dipole plays the central role here and compensates the dramatic variation in contrast.

3.5.2. Semi-classical dissociation calculations

From our previous quantum mechanical calculations, we showed that dissociation is primarily effected by the isotopes; (i) dissociation is reduced as well as (ii) dissociation occurs at higher KER ranges with increasing nuclear mass. Also, (iii) the asymmetry in directional dissociation is observed at higher KER values as well as (iv) variation in asymmetry is reduced with increasing mass. To complement these four findings and to address the mechanism behind the channel-dependent of dissociation by different isotopes, we employed the semi-classical model we mentioned in Section 2.23. The system is assumed to be in the $R = 2a.u$ initially with a sufficient initial momentum. The semi-classical dynamics are solved for different dissociation channels. All channels are activated in H_2^+ at a very short time frame, *i.e.* within $2 - 3 fs$. ZPD exhibit a slow dissociation dynamics resulting in a small momentum. We observed no ZPD for D_2^+ and T_2^+ , most likely due due to the field parameters we picked. BS occurs almost at the same time for different isotopes but, in contrast, ATD occurs very early for both D_2^+ and T_2^+ comparing with the ATD of H_2^+ which occurs at the rising edge of the pulse. Even so, the momentum of both BS and ATD channels are systematically increased with isotope mass. We observed a strong overlap in dissociating momentum values in BS-ATD channels for H_2^+ around $p = 10 a.u.$, corresponding to $1.5eV$, consistent with TDSE calculations shown in Figure 3.15 and Figure 3.35. The overlap is systematically reduced for D_2^+ and T_2^+ , which may be the reason for reduced asymmetry for these systems relative to H_2^+ shown in Figure 3.35.

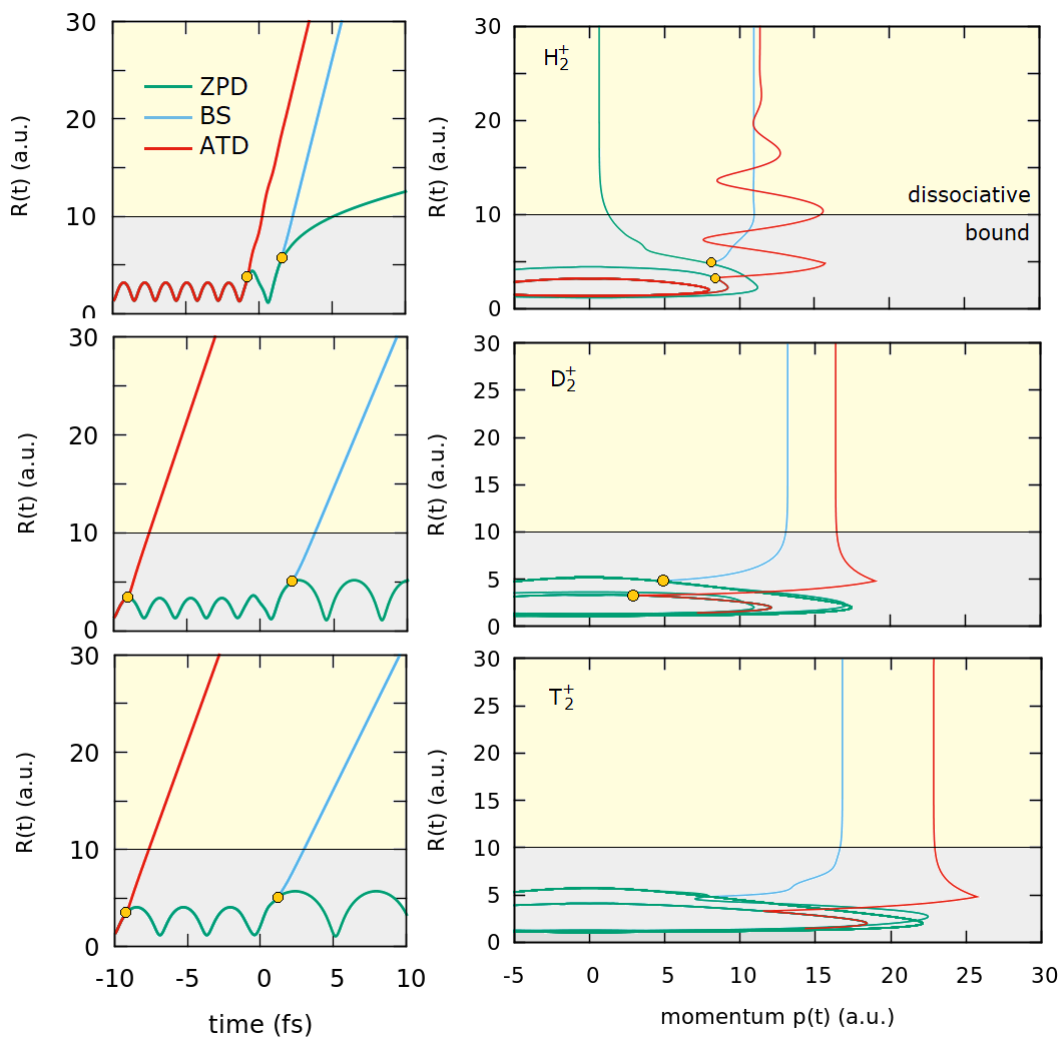


Figure 3.40 (left column) Channel-dependent semi-classical simulations for the time-variation in the inter-atomic distances, $R(t)$, of diatomic cations. (right column) Semi-classical trajectories of molecular dissociation: the circles mark the moments of non-classical electronic transitions via photon absorption/emission. In all cases only the ZPD, BS and ATD channels are taken into account.

4. CONCLUSION

In this thesis, photo-separation of molecules is the subject. Researched phenomena can be grouped under four subjects. First of which is the dependence of dissociation channels to the intensity of laser pulse. We observed that certain dissociation channels are opened as the intensity increases.

The second main subject is the influence of Post-Pulse on directional control of dissociation. The motivation here is to gain a deeper understanding about the experimental results. Essentially, a clear, ultra-short, phase-stabilized laser pulse is desired to control the dissociation in molecules. However, this is experimentally challenging and there usually is a satellite pulse following the main laser pulse in an experiment. Therefore we focus on the effect of this satellite pulse on the dissociation. We observed that the overlap of ZPD-BS channels is influenced by the presence of post-pulse and the effect manifests itself as increment in dissociation yield in the 0.0-0.5 eV KER region. Also, asymmetry is modified by the post-pulse and the tilted stripes change in this low KER region. While for no post-pulse case the tilts are to the right, when the post-pulse introduced the direction of tilts become to the left. This tells us that the post pulse modifies the KER dependence on asymmetry for a certain CEP value.

Third subject of this thesis is the influence of chirped pulses on the dissociation channels. Chirping a laser pulse weakens and elongates the laser pulse which is the case results in very low dissociation yield. To overcome this issue, we propose an alternative way of chirping called as “Pulse-width maintained chirping schema”. In this schema, the experimentalist should begin a narrower and more intense laser pulse to obtain a suitable, chirped laser pulse. The desired pulse width is 5.4 fs at FWHM and the intensity is taken to be 150 TW cm^{-2} in this thesis. We begin our analysis by calculating the first ionization rates and times using chirped laser pulses. We see that the main peak in the ionization rate is not affected by chirp, but the satellite peaks shifts to later times as the chirp parameter decreases. CEP variation of the peak ionization times is nearly linear. After designated

the first ionization times and rates we numerically solved the TDSE for ultra-short, phase stabilized, chirped laser-matter interaction. We assume that the cationic hydrogen is populated at peak times obtained from the first ionization calculations. We accumulate the results in two different ways, one of which is coherent and the other is incoherent. We systematically consider the chirp values from -0.7 to 0.7 and investigate the change in dissociation yield and asymmetry. We observed that the dissociation yield linearly increases as the chirp value changes from negative to positive. We showed that this is due to the systematic increase in the populations at vibrational levels by chirp parameter. CEP variation of dissociation is sinusoidal for all chirp values. But its amplitude is suppressed as the chirp value decreases. For asymmetry, we begin to analyze how the time variation is affected by chirp. We see a strong modification depending on chirp parameter. Even though the oscillations begin at the same time for all of the chirped laser pulses, the time profiles of them are quite different and asymmetry settles down at different values for different chirp parameters. Asymmetry even changes sign for certain chirp values. Thereby, our chirping schema provides a strong directional control on dissociation. We also investigate the KER-CEP maps with positive chirp, TLP and negative chirp cases. We observe that the dissociation channels are suppressed by negative chirp. Then we integrate the asymmetry over different energy regions to analyze the CEP dependence of it. We see that the maximum of asymmetry shifts with chirp parameter and the relationship is linear, meaning the “phase-of-phase” is a 1st-order polynomial of chirp parameter. We also showed that the coherence and incoherence accumulation yields the similar results.

Finally we investigate the isotope effect on the directional control of dissociation in the vicinity of a nanotip. Again, we begin with the ionization from neutral parent molecules. We observed that, as the inhomogeneity increases, the ionization rates enormously enhanced whereas the ionization times at peak ionization rates stay same. Also, two additional, considerably large satellite peaks occur for inhomogeneities greater than 0.024 a.u.^{-1} . Then we numerically propagate the the system using TDSE and Páde approximation with a two-cycle laser pulse of relatively low intensity (10 TW/cm^2). For such

low intensities, BS is the typically dominant channel for dissociation. In this preliminary calculations, we have not consider the first ionization from parent molecule and volume averaging. Under these circumstances, for H_2^+ , dissociation from $v = 6 - 12$ levels, for D_2^+ , dissociation from $v = 8 - 18$ levels are possible. These are compatible with the dissociation profile seen in Figure 3.26 for hydrogen and deuterium. But for tritium, we see that the dissociation occurs around 1.15 eV and lower energy contributions are highly suppressed. Therefore we see that there is no contribution via BS channel from vibrational levels. Thus we speculate that the dissociation occurs via ATD from $v = 5 - 10$ levels. Also we see that the dissociation yield dramatically decreases as the reduced mass increases which can be explained by the increasing time-scale mismatch between the laser and the molecular vibrational period of the cation. To support this, we have considered two-level calculations for H_2^+ and homonucleus isotopes and see that the dissociation occurs slower for molecules with higher total (or reduced) mass. Finally, we address the full-size problem with high intensity laser near a metallic nanotip. This time we have considered the first ionization from neutral parent molecule for all of the homonucleus and heteronucleus isotopes. We have assumed that the main peak intensity of the Gaussian-type, two-cycle at FWHM laser pulse is 150 TW/cm^2 and that the intensity decreases as the molecule moves away from the focus of the laser and include the volume averaging to our calculations. We start the simulations at the ionization times corresponding to the peaks of the main and the first-satellite ionizations from parent molecules and we accumulate the results incoherently using the ionization rates. We systematically change inhomogeneity from 0.000 a.u.^{-1} to 0.032 a.u.^{-1} . We first observed that the dissociation is highly decreased as the reduced mass increases. However, for all molecules, as inhomogeneity increases, the dissociation yield increases as well. Also the KER position of peak of the dissociation yield shifts to higher KER values with increasing reduced mass. The relationship is almost linear and fits to the form of $A/10 + 1$, where A is the mass number of the molecule. We also see that the ZPD and BS channels are modified by the field inhomogeneity as the reduced mass increases. This can be attributed that for ZPD,

the molecule is so stretched that it is more effected by the field inhomogeneity and for both ZPD and ATD channels, we speculate that the gerade state is the state influenced by field inhomogeneity. For asymmetry, we again begin with two-level calculations. We see that the adiabatic transitions open later as the molecular mass increases. Populations during the transitions are massively modified and so that the asymmetry. Next we consider simple case TDSE solutions. In homonucleus molecules, asymmetry has π -anti-symmetry, i.e. shifting CEP by π do not variate the asymmetry, only changes its sign. Introducing the field inhomogeneity breaks this symmetry. This causes a contrast in asymmetry. And we found that the contrast in asymmetry reduces with isotope mass. Next we calculated the KER integrated CEP dependence of asymmetries and we see a “phase of phase” roughly $\Delta\phi = \pi(A - 0.5)$ where A is the mass number of the molecule. For heteronucleus molecules, there is $A_L(\phi) = -A_R(\phi + \pi)$ symmetry, meaning that the asymmetry for left oriented molecule is anti symmetrically equal to the asymmetry for right oriented molecule with a shifted CEP by π . We show that this anti symmetry breaks once the inhomogeneous fields introduced. We also see that, when the heteronucleus molecule is turned around from one orientation to the other, the asymmetry shifts by π . For contrast in asymmetry for homonucleus molecules, we show that the contrast reduces as the molecule mass increases. However, for heteronucleus molecules we see more or less same characteristic in contrast of asymmetry. We think that this modifications root from the permanent dipole moments of heteronucleus molecules.

REFERENCES

1. A. Csehi, G. J. Halasz, L. S. Cederbaum, and A. Vibok, "Tracking the photodissociation probability of d_2^+ induced by linearly chirped laser pulses," *J. Chem. Phys.*, vol. 144, no. 7, p. 074309, 2016.
2. A. M. Sayler, P. Q. Wang, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, "Determining laser-induced dissociation pathways of multielectron diatomic molecules: Application to the dissociation of o_2^+ by high-intensity ultrashort pulses," *Phys. Rev. A*, vol. 75, p. 063420, Jun 2007.
3. H. G. Breunig, A. Lauer, and K.-M. Weitzel, "Control of branching ratios in the dissociative ionization of deuterium chloride," *J. Phys. Chem. A*, vol. 110, no. 20, pp. 6395–6398, 2006.
4. J. McKenna, A. M. Sayler, B. Gaire, N. G. Johnson, E. Parke, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, "Intensity dependence in the dissociation branching ratio of nd^+ using intense femtosecond laser pulses," *Phys. Rev. A*, vol. 77, p. 063422, Jun 2008.
5. K. Sändig, H. Figger, and T. W. Hänsch, "Dissociation dynamics of H_2^+ in intense laser fields: Investigation of photofragments from single vibrational levels," *Phys. Rev. Lett.*, vol. 85, pp. 4876–4879, Dec 2000.
6. I. D. Williams, P. McKenna, B. Srigengan, I. M. G. Johnston, W. A. Bryan, J. H. Sander-son, A. El-Zein, T. R. J. Goodworth, W. R. Newell, P. F. Taday, and A. J. Langley, "Fast-beam study of h_2 ions in an intense femtosecond laser field," *J. Phys. B*, vol. 33, pp. 2743–2752, jul 2000.
7. I. Ben-Itzhak, P. Q. Wang, J. F. Xia, A. M. Sayler, M. A. Smith, K. D. Carnes, and B. D. Esry, "Dissociation and ionization of H_2^+ by ultrashort intense laser pulses probed by coincidence 3d momentum imaging," *Phys. Rev. Lett.*, vol. 95, p. 073002, Aug 2005.
8. M. F. Kling, C. Siedschlag, A. J. Verhoef, J. I. Khan, M. Schultze, T. Uphues, Y. Ni, M. Uiberacker, M. Drescher, F. Krausz, and M. J. J. Vrakking, "Control of electron localization in molecular dissociation," *Science*, vol. 312, no. 5771, pp. 246–248, 2006.
9. L. J. Frasinski, J. H. Posthumus, J. Plumridge, K. Codling, P. F. Taday, and A. J. Langley, "Manipulation of bond hardening in H_2^+ by chirping of intense femtosecond laser pulses," *Phys. Rev. Lett.*, vol. 83, pp. 3625–3628, Nov 1999.
10. A. Assion, T. Baumert, U. Weichmann, and G. Gerber, "Photofragmentation of na_2^+ in intense femtosecond laser fields: From photodissociation on light-induced potentials to field ionization," *Phys. Rev. Lett.*, vol. 86, pp. 5695–5698, Jun 2001.
11. J. McKenna, M. Suresh, D. S. Murphy, W. A. Bryan, L.-Y. Peng, S. L. Stebbings, E. M. L. English, J. Wood, B. Srigengan, I. C. E. Turcu, J. L. Collier, J. F. McCann, W. R. Newell, and I. D. Williams, "Intense-field dissociation dynamics of d_2 molecular ions using ultra-fast laser pulses," *J. Phys. B*, vol. 40, pp. 2607–2619, jun 2007.
12. J. H. Posthumus, J. Plumridge, L. J. Frasinski, K. Codling, E. J. Divall, A. J. Langley, and P. F. Taday, "Slow protons as a signature of zero-photon dissociation of h_2 in intense laser fields," *J. Phys. B*, vol. 33, pp. L563–L569, jul 2000.

13. D. Pavičić, T. W. Hänsch, and H. Figger, “Vibrationally resolved strong-field dissociation of D_2^+ in ion beams,” *Phys. Rev. A*, vol. 72, p. 053413, Nov 2005.
14. B. Feuerstein, T. Ergler, A. Rudenko, K. Zrost, C. D. Schröter, R. Moshhammer, J. Ullrich, T. Niederhausen, and U. Thumm, “Complete characterization of molecular dynamics in ultrashort laser fields,” *Phys. Rev. Lett.*, vol. 99, p. 153002, Oct 2007.
15. P. Q. Wang, A. M. Sayler, K. D. Carnes, J. F. Xia, M. A. Smith, B. D. Esry, and I. Ben-Itzhak, “Dissociation of H_2^+ in intense femtosecond laser fields studied by coincidence three-dimensional momentum imaging,” *Phys. Rev. A*, vol. 74, p. 043411, Oct 2006.
16. J. H. Posthumus, “The dynamics of small molecules in intense laser fields,” *Reports on Progress in Physics*, vol. 67, pp. 623–665, apr 2004.
17. J. McKenna, A. M. Sayler, F. Anis, B. Gaire, N. G. Johnson, E. Parke, J. J. Hua, H. Mashiko, C. M. Nakamura, E. Moon, Z. Chang, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, “Enhancing high-order above-threshold dissociation of h_2^+ beams with few-cycle laser pulses,” *Phys. Rev. Lett.*, vol. 100, p. 133001, Apr 2008.
18. H. Xu, Z. Li, F. He, X. Wang, A. Atia-Tul-Noor, D. Kielpinski, R. T. Sang, and I. V. Litvinyuk, “Observing electron localization in a dissociating h_2^+ molecule in real time,” *Nature Communications*, vol. 8, p. 15849, Jun 2017.
19. A. S. Alnaser and I. V. Litvinyuk, “Subfemtosecond directional control of chemical processes in molecules,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 50, p. 032002, jan 2017.
20. H. Li, X. Gong, K. Lin, R. de Vivie-Riedle, X. M. Tong, J. Wu, and M. F. Kling, “Sub-cycle directional control of the dissociative ionization of h_2 in tailored femtosecond laser fields,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 50, p. 172001, aug 2017.
21. H. Ibrahim, C. Lefebvre, A. D. Bandrauk, A. Staudte, and F. Légaré, “ H_2 : the benchmark molecule for ultrafast science and technologies,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 51, p. 042002, jan 2018.
22. A. M. Weiner, “Femtosecond pulse shaping using spatial light modulators,” *Rev. Sci. Instrum.*, vol. 71, no. 5, pp. 1929–1960, 2000.
23. X. M. Tong and C. D. Lin, “Dynamics of light-field control of molecular dissociation at the few-cycle limit,” *Phys. Rev. Lett.*, vol. 98, p. 123002, Mar 2007.
24. F. He and U. Thumm, “Dissociative ionization of h_2 in an attosecond pulse train and delayed laser pulse,” *Phys. Rev. A*, vol. 81, p. 053413, May 2010.
25. T. W. Gorczyca, M. F. Hasoglu, and S. T. Manson, “Photoionization of endohedral atoms using r -matrix methods: Application to $xe@c_{60}$,” *Phys. Rev. A*, vol. 86, p. 033204, Sep 2012.
26. M. Tashiro, “Theoretical treatment of molecular photoionization based on the r -matrix method,” *Journal of Physics: Conference Series*, vol. 388, p. 022077, nov 2012.

27. M. Ilchen, S. Deinert, L. Glaser, F. Scholz, J. Seltmann, P. Walter, and J. Viefhaus, "Photoelectron angular distribution studies of the outer valence states of N_2 ," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 45, p. 225102, nov 2012.
28. A. Rouzée, A. G. Harvey, F. Kelkensberg, D. Brambila, W. K. Siu, G. Gademann, O. Smirnova, and M. J. J. Vrakking, "Imaging the electronic structure of valence orbitals in the XUV ionization of aligned molecules," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 47, p. 124017, jun 2014.
29. D. S. Brambila, A. G. Harvey, Z. Mašín, J. D. Gorfinkiel, and O. Smirnova, "The role of multichannel effects in the photoionization of the NO_2 molecule: an ab initio r-matrix study," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 48, p. 245101, nov 2015.
30. G. VanGysegghem, T. W. Gorczyca, and C. P. Ballance, "Near-threshold photoionization of molecular nitrogen," *Journal of Physics: Conference Series*, vol. 635, p. 112102, sep 2015.
31. W. J. Brigg, A. G. Harvey, A. Dzarasova, S. Mohr, D. S. Brambila, F. Morales, O. Smirnova, and J. Tennyson, "Calculated photoionization cross sections using quantemol-n," *Japanese Journal of Applied Physics*, vol. 54, p. 06GA02, may 2015.
32. A. Gallego, U. Sezer, M. Arndt, and M. Mayor, "Long-pulse laser launch and ionization of tailored large neutral silver nanoparticles with atomic mass assignment," *Nanoscale*, vol. 9, pp. 9175–9180, 2017.
33. U. . G. Sezer, P. . Kriegleder, M. . Debiossac, M. . Shayeghi, A. . Arndt, M. . Felix, L. . Mayor, and M. Beilstein, "Selective photodissociation of tailored molecular tags as a tool for quantum optics," *J. Nanotechnology*, no. 8, pp. 325–333, 2017.
34. K. A. Larsen, T. N. Rescigno, T. Severt, Z. L. Streeter, W. Iskandar, S. Heck, A. Gatton, E. G. Champenois, R. Strom, B. Jochim, D. Reedy, D. Call, R. Moshhammer, R. Dörner, A. L. Landers, J. B. Williams, C. W. McCurdy, R. R. Lucchese, I. Ben-Itzhak, D. S. Slaughter, and T. Weber, "Photoelectron and fragmentation dynamics of the $\text{h}^+ + \text{h}^+$ dissociative channel in NH_3 following direct single-photon double ionization," *Phys. Rev. Research*, vol. 2, p. 043056, Oct 2020.
35. V. Roudnev, B. D. Esry, and I. Ben-Itzhak, "Controlling HD^+ and H_2^+ dissociation with the carrier-envelope phase difference of an intense ultrashort laser pulse," *Phys. Rev. Lett.*, vol. 93, p. 163601, Oct 2004.
36. D. Ray, F. He, S. De, W. Cao, H. Mashiko, P. Ranitovic, K. P. Singh, I. Znakovskaya, U. Thumm, G. G. Paulus, M. F. Kling, I. V. Litvinyuk, and C. L. Cocke, "Ion-energy dependence of asymmetric dissociation of D_2 by a two-color laser field," *Phys. Rev. Lett.*, vol. 103, p. 223201, Nov 2009.
37. V. Roudnev and B. D. Esry, "General theory of carrier-envelope phase effects," *Physical Review Letters*, vol. 99, no. 22, p. 220406, 2007.
38. K. Liu, Q. Zhang, P. Lan, and P. Lu, "Anomalous isotopic effect on electron-directed reactivity by a 3- μm midinfrared pulse," *Opt. Express*, vol. 21, pp. 5107–5116, Feb 2013.

39. M. Kumar, S. Varshney, and S. Kumar, “Emerging nanoscience with discotic liquid crystals,” *Polymer Journal*, Sep 2020.
40. N. C. Panoiu, W. E. I. Sha, D. Y. Lei, and G.-C. Li, “Nonlinear optics in plasmonic nanostructures,” *Journal of Optics*, vol. 20, p. 083001, jun 2018.
41. A. V. Krasavin, P. Ginzburg, and A. V. Zayats, “Free-electron optical nonlinearities in plasmonic nanostructures: A review of the hydrodynamic description,” *Laser & Photonics Reviews*, vol. 12, no. 1, p. 1700082, 2018.
42. N. Maccaferri, S. Meuret, N. Kornienko, and D. Jariwala, “Speeding up nanoscience and nanotechnology with ultrafast plasmonics,” *Nano Letters*, vol. 20, no. 8, pp. 5593–5596, 2020. PMID: 32787183.
43. T. Yarlagadda, S. Sharma, P. K. Yarlagadda, and J. Sharma, “Recent developments in the field of nanotechnology for development of medical implants,” *Procedia Manufacturing*, vol. 30, pp. 544 – 551, 2019. Digital Manufacturing Transforming Industry Towards Sustainable Growth.
44. I. Yavuz, M. F. Ciappina, A. Chacón, Z. Altun, M. F. Kling, and M. Lewenstein, “Controlling electron localization in H_2^+ by intense plasmon-enhanced laser fields,” *Phys. Rev. A*, vol. 93, p. 033404, 2016.
45. I. Yavuz, J. Schötz, M. F. Ciappina, P. Rosenberger, Z. Altun, M. Lewenstein, and M. F. Kling, “Control of molecular dissociation by spatially inhomogeneous near fields,” *Phys. Rev. A*, vol. 98, p. 043413, Oct 2018.
46. M. Schultze, E. M. Bothschafter, A. Sommer, S. Holzner, W. Schweinberger, M. Fiess, M. Hofstetter, R. Kienberger, V. Apalkov, V. S. Yakovlev, M. I. Stockman, and F. Krausz, “Controlling dielectrics with the electric field of light,” *Nature*, vol. 493, 2013.
47. A. Schiffrin, T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J. V. Barth, R. Kienberger, R. Ernstorfer, V. S. Yakovlev, M. I. Stockman, and F. Krausz, “Optical-field-induced current in dielectrics,” *Nature*, vol. 493, 2013.
48. S. Zherebtsov, T. Fennel, J. Plenge, E. Antonsson, I. Znakovskaya, A. Wirth, O. Herwerth, F. Süßmann, C. Peltz, I. Ahmad, S. A. Trushin, V. Pervak, S. Karsch, M. J. J. Vrakking, B. Langer, C. Graf, M. I. Stockman, F. Krausz, E. Rühl, and M. F. Kling, “Controlled near-field enhanced electron acceleration from dielectric nanospheres with intense few-cycle laser fields,” *Nature Physics*, vol. 7, 2011.
49. M. Krüger, M. Schenk, and P. Hommelhoff, “Attosecond control of electrons emitted from a nanoscale metal tip,” *Nature*, vol. 475, pp. 78–81, Jul 2011.
50. G. Herink, D. R. Solli, M. Gulde, and C. Ropers, “Field-driven photoemission from nanostructures quenches the quiver motion,” *Nature*, vol. 483, pp. 190–193, Mar 2012.
51. B. Piglosiewicz, S. Schmidt, D. J. Park, J. Vogelsang, P. Groß, C. Manzoni, P. Farinello, G. Cerullo, and C. Lienau, “Carrier-envelope phase effects on the strong-field photoemission of electrons from metallic nanostructures,” *Nature Photonics*, vol. 8, pp. 37–42, Jan 2014.

52. F. Süßmann, L. Seiffert, S. Zherebtsov, V. Mondes, J. Stierle, M. Arbeiter, J. Plenge, P. Rupp, C. Peltz, A. Kessel, S. A. Trushin, B. Ahn, D. Kim, C. Graf, E. Rühl, M. F. Kling, and T. Fennel, “Field propagation-induced directionality of carrier-envelope phase-controlled photoemission from nanospheres,” *Nature Communications*, vol. 6, 2015.
53. S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, “Observation of high-order harmonic generation in a bulk crystal,” *Nature Physics*, vol. 7, pp. 138–141, Feb 2011.
54. O. Schubert, M. Hohenleutner, F. Langer, B. Urbanek, C. Lange, U. Huttner, D. Golde, T. Meier, M. Kira, S. W. Koch, and R. Huber, “Sub-cycle control of terahertz high-harmonic generation by dynamical bloch oscillations,” *Nature Photonics*, vol. 8, pp. 119–123, Feb 2014.
55. T. T. Luu, M. Garg, S. Y. Kruchinin, A. Moulet, M. T. Hassan, and E. Goulielmakis, “Extreme ultraviolet high-harmonic spectroscopy of solids,” *Nature*, vol. 521, pp. 498–502, May 2015.
56. G. Vampa, T. J. Hammond, N. Thiré, B. E. Schmidt, F. Légaré, C. R. McDonald, T. Brabec, and P. B. Corkum, “Linking high harmonics from gases and solids,” *Nature*, vol. 522, pp. 462–464, Jun 2015.
57. E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, “Real-space and real-time observation of a plasmon-induced chemical reaction of a single molecule,” *Science*, vol. 360, no. 6388, pp. 521–526, 2018.
58. S. A. Bozpolat, P. Rosenberger, M. F. Ciappina, M. F. Kling, and I. Yavuz, “Carrier-envelope-phase-controlled molecular dissociation by ultrashort chirped laser pulses,” *Phys. Rev. A*, vol. 100, p. 063409, Dec 2019.
59. W. R. Rapoport and C. P. Khatkhat, “Efficient, tunable ti:sapphire laser,” in *Tunable Solid-State Lasers II* (A. B. Budgor, L. Esterowitz, and L. G. DeShazer, eds.), (Berlin, Heidelberg), pp. 212–217, Springer Berlin Heidelberg, 1986.
60. P. Gibbon, “High-order harmonic generation in plasmas,” *IEEE Journal of Quantum Electronics*, vol. 33, no. 11, pp. 1915–1924, 1997.
61. M. F. Ciappina, T. Shaaran, and M. Lewenstein, “High order harmonic generation in noble gases using plasmonic field enhancement,” *Annalen der Physik*, vol. 525, no. 1-2, pp. 97–106, 2013.
62. P. Moreno, L. Plaja, and L. Roso, “High-order harmonic generation by electron-proton recombination,” *Europhysics Letters (EPL)*, vol. 28, pp. 629–633, dec 1994.
63. B. Fetić, K. Kalajdžić, and D. B. Milošević, “High-order harmonic generation by a spatially inhomogeneous field,” *Annalen der Physik*, vol. 525, no. 1-2, pp. 107–117, 2013.
64. J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, “Tomographic imaging of molecular orbitals,” *Nature*, vol. 432, pp. 867–871, Dec 2004.

65. S. Weiß, D. Lüftner, T. Ules, E. M. Reinisch, H. Kaser, A. Gottwald, M. Richter, S. Soubatch, G. Koller, M. G. Ramsey, F. S. Tautz, and P. Puschnig, “Exploring three-dimensional orbital imaging with energy-dependent photoemission tomography,” *Nature Communications*, vol. 6, p. 8287, Oct 2015.
66. M. Hentschel, R. Kienberger, C. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, “Attosecond metrology,” *Nature*, vol. 414, pp. 509–513, Nov 2001.
67. F. Krausz and M. I. Stockman, “Attosecond metrology: from electron capture to future signal processing,” *Nature Photonics*, vol. 8, pp. 205–213, Mar 2014.
68. M. Schultze, A. Wirth, I. Grguras, M. Uiberacker, T. Uphues, A. Verhoef, J. Gagnon, M. Hofstetter, U. Kleineberg, E. Goulielmakis, and F. Krausz, “State-of-the-art attosecond metrology,” *Journal of Electron Spectroscopy and Related Phenomena*, vol. 184, no. 3, pp. 68 – 77, 2011. Advances in Vacuum Ultraviolet and X-ray Physics.
69. R. Paschotta, *Article on 'chirp' in the RP Photonics Encyclopedia*, 2020 (accessed August 19, 2020).
70. B. Nikolaus and D. Grischkowsky, “12 pulse compression using optical fibers,” *Applied Physics Letters*, vol. 42, no. 1, pp. 1–2, 1983.
71. F. He, C. Ruiz, and A. Becker, “Control of electron excitation and localization in the dissociation of H_2^+ and its isotopes using two sequential ultrashort laser pulses,” *Phys. Rev. Lett.*, vol. 99, p. 083002, Aug 2007.
72. W. T. V. B. P. F. William H. Press, Saul A. Teukolsky, *Numerical Recipes, The Art of Scientific Computing*. Cambridge University Press, 3 ed., 2007.
73. M. Kling, C. Siedschlag, I. Znakovskaya, A. Verhoef, S. Zherebtsov, F. Krausz, M. Lezius, and M. Vrakking, “Strong-field control of electron localisation during molecular dissociation,” *Molecular Physics*, vol. 106, no. 2-4, pp. 455–465, 2008.
74. F. Kelkensberg, G. Sansone, M. Y. Ivanov, and M. Vrakking, “A semi-classical model of attosecond electron localization in dissociative ionization of hydrogen,” *Phys. Chem. Chem. Phys.*, vol. 13, pp. 8647–8652, 2011.
75. B. Abeln, J. V. Hernández, F. Anis, and B. D. Esry, “Comparison of theoretical analyses of intense-laser-induced molecular dissociation,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 43, p. 155005, jul 2010.
76. A. D. Bandrauk, S. Chelkowski, and H. S. Nguyen, “Attosecond localization of electrons in molecules,” *International Journal of Quantum Chemistry*, vol. 100, no. 6, pp. 834–844, 2004.
77. M. Fischer, F. Grossmann, R. Schmidt, J. Handt, S. M. Krause, and J.-M. Rost, “Mixed quantum-classical approach to multiphoton dissociation of the hydrogen molecular ion,” *New Journal of Physics*, vol. 13, p. 053019, may 2011.
78. C. C. Marston and G. G. Balint-Kurti, “The fourier grid hamiltonian method for bound state eigenvalues and eigenfunctions,” *The Journal of Chemical Physics*, vol. 91, no. 6, pp. 3571–3576, 1989.

79. G. G. Balint-Kurti, R. N. Dixon, and C. C. Marston, "Grid methods for solving the schrödinger equation and time dependent quantum dynamics of molecular photofragmentation and reactive scattering processes," *International Reviews in Physical Chemistry*, vol. 11, no. 2, pp. 317–344, 1992.
80. D. Pavicic, *Coulomb Explosion and Intense-Field Photodissociation of Ion-Beam H_2^+ and D_2^+* . PhD thesis, Ludwig–Maximilians–Universität, 2004.
81. A. D. e. Bandrauk, *Molecules in Laser Fields*. Marcel Dekker, Inc., 1994.
82. L. D. Landau and E. M. Lifshits, *Quantum Mechanics: Non-Relativistic Theory*. Pergamon Press, Oxford, 1977.
83. M. H. Mittleman, *Introduction to the Theory of Laser-Atom Interactions*. Plenum Press, 1993.
84. H. Yao, Z. Sun, X. Jiang, and C. Cao, "The dissociation pathways and isotope effects in intense field dissociation of h_2^+ and hd ," *Laser Physics Letters*, vol. 16, p. 105201, aug 2019.
85. A. Kondorskiy and H. Nakamura, "Photodissociation of h_2^+ and hd^+ in an intense laser field," *Phys. Rev. A*, vol. 66, p. 053412, Nov 2002.
86. M. V. Ammosov, N. B. Delone, and V. P. Krainov, "Tunnel ionization of complex atoms and of atomic ions in an alternating electromagnetic field," *Journal of Experimental and Theoretical Physics*, vol. 64, p. 1191, 1986.
87. X. M. Tong, Z. X. Zhao, and C. D. Lin, "Theory of molecular tunneling ionization," *Phys. Rev. A*, vol. 66, p. 033402, Sep 2002.
88. J. Schötz, B. Förg, M. Förster, W. A. Okell, M. I. Stockman, F. Krausz, P. Hommelhoff, and M. F. Kling, "Reconstruction of nanoscale near fields by attosecond streaking," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 23, no. 3, pp. 77–87, 2017.
89. L. Novotny and B. Hecht, *Principles of Nano-Optics*. Cambridge University Press, 2006.
90. S. Thomas, G. Wachter, C. Lemell, J. Burgdörfer, and P. Hommelhoff, "Large optical field enhancement for nanotips with large opening angles," *New Journal of Physics*, vol. 17, p. 063010, jun 2015.
91. M. Yamaguchi and K. Nobusada, "Photodissociation path in H_2^+ induced by nonuniform optical near fields: Two-step excitation via vibrationally excited states," *Phys. Rev. A*, vol. 93, p. 023416, Feb 2016.
92. B. Feuerstein and U. Thumm, "On the computation of momentum distributions within wavepacket propagation calculations," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 36, pp. 707–716, feb 2003.
93. B. Feuerstein and U. Thumm, "Fragmentation of h_2^+ in strong 800-nm laser pulses: Initial-vibrational-state dependence," *Phys. Rev. A*, vol. 67, p. 043405, Apr 2003.
94. P. Q. Wang, A. M. Saylor, K. D. Carnes, J. F. Xia, M. A. Smith, B. D. Esry, and I. Ben-Itzhak, "Dissociation of H_2^+ in intense femtosecond laser fields studied by coincidence three-dimensional momentum imaging," *Phys. Rev. A*, vol. 74, p. 043411, Oct 2006.

95. V. Roudnev and B. D. Esry, “ hd^+ in a short strong laser pulse: Practical consideration of the observability of carrier-envelope phase effects,” *Phys. Rev. A*, vol. 76, p. 023403, Aug 2007.
96. F. Anis and B. D. Esry, “Enhancing the intense field control of molecular fragmentation,” *Phys. Rev. Lett.*, vol. 109, p. 133001, Sep 2012.
97. V. S. Prabhudesai, U. Lev, A. Natan, B. D. Bruner, A. Diner, O. Heber, D. Strasser, D. Schwalm, I. Ben-Itzhak, J. J. Hua, B. D. Esry, Y. Silberberg, and D. Zajfman, “Tracing the photodissociation probability of h_2^+ in intense fields using chirped laser pulses,” *Phys. Rev. A*, vol. 81, p. 023401, Feb 2010.
98. A. Natan, U. Lev, V. S. Prabhudesai, B. D. Bruner, D. Strasser, D. Schwalm, I. Ben-Itzhak, O. Heber, D. Zajfman, and Y. Silberberg, “Quantum control of photodissociation by manipulation of bond softening,” *Phys. Rev. A*, vol. 86, p. 043418, Oct 2012.
99. S. Skruszewicz, J. Tiggesbäumker, K.-H. Meiwes-Broer, M. Arbeiter, T. Fennel, and D. Bauer, “Two-color strong-field photoelectron spectroscopy and the phase of the phase,” *Phys. Rev. Lett.*, vol. 115, p. 043001, Jul 2015.
100. J. J. Hua and B. D. Esry, “The role of mass in the carrier-envelope phase effect for h_2 dissociation,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 42, p. 085601, mar 2009.

Appendices

A Vibrational Energy Levels and KER Values of H_2^+

Vibrational energy levels and KER energy values for hydrogen for different processes are given in **Table A.1**. The KER values in **Table A.1** are calculated for 800 nm photon.

Table A.1 Vibrational level energies and contributions to KER from vibrational levels for 1-photon and net 2-photon dissociation channels for hydrogen induced by two-cycle at FWHM laser pulse with wavelength of 800 nm.

vibrational level	vibrational level energy (eV)	KER (1-photon) (eV)	KER (2-photon) (eV)
0	-2.647	-	0.453
1	-2.373	-	0.727
2	-2.114	-	0.986
3	-1.870	-	1.230
4	-1.641	-	1.459
5	-1.427	0.123	1.673
6	-1.227	0.323	1.873
7	-1.043	0.507	2.057
8	-0.873	0.677	2.227
9	-0.718	0.832	2.382
10	-0.578	0.972	2.522
11	-0.453	1.097	2.647
12	-0.343	1.207	2.757
13	-0.247	1.303	2.853
14	-0.167	1.383	2.933
15	-0.101	1.449	2.999
16	-0.050	1.500	3.050
17	-0.014	1.536	3.086
18	0.007	1.543	3.093
19	0.014	1.536	3.086

B Vibrational Energy Levels and KER Values of D_2^+

Vibrational energy levels and KER energy values of deuterium for different processes are given in **Table B.1**. The KER values in **Table B.1** are calculated for 800 nm photon.

Table B.1 Vibrational level energies and contributions to KER from vibrational levels for 1-photon and net 2-photon dissociation channels for deuterium induced by two-cycle at FWHM laser pulse with wavelength of 800 nm.

vibrational level	vibrational level energy (eV)	KER (1-photon) (eV)	KER (2-photon) (eV)
0	-2.688	-	0.412
1	-2.491	-	0.609
2	-2.302	-	0.798
3	-2.114	-	0.980
4	-1.946	-	1.154
5	-1.427	-	1.321
6	-1.227	-	1.480
7	-1.468	0.082	1.632
8	-1.323	0.227	1.777
9	-1.186	0.364	1.914
10	-1.056	0.494	2.044
11	-0.934	0.616	2.166
12	-0.819	0.731	2.281
13	-0.711	0.839	2.389
14	-0.611	0.939	2.489
15	-0.519	1.031	2.581
16	-0.434	1.116	2.666
17	-0.356	1.194	2.744
18	-0.285	1.265	2.815
19	-0.222	1.328	2.878

C Vibrational Energy Levels and KER Values of T_2^+

Vibrational energy levels and KER energy values for tritium for different processes are given in **Table C.1**. The KER values in **Table C.1** are calculated for 800 nm photon.

Table C.1 Vibrational level energies and contributions to KER from vibrational levels for 1-photon and net 2-photon dissociation channels for tritium induced by two-cycle at FWHM laser pulse with wavelength of 800 nm.

vibrational level	vibrational level energy (eV)	KER (1-photon) (eV)	KER (2-photon) (eV)
0	-2.706	-	0.394
1	-2.545	-	0.555
2	-2.388	-	0.712
3	-2.236	-	0.864
4	-2.090	-	1.010
5	-1.948	-	1.152
6	-1.811	-	1.289
7	-1.679	-	1.421
8	-1.552	-	1.548
9	-1.430	0.120	1.670
10	-1.313	0.237	1.787
11	-1.201	0.349	1.899
12	-1.094	0.456	2.006
13	-0.991	0.559	2.109
14	-0.894	0.656	2.206
15	-0.802	0.748	2.298
16	-0.714	0.836	2.386
17	-0.632	0.918	2.468
18	-0.554	0.996	2.546
19	-0.482	1.068	2.618

D KER-CEP Maps of H_2^+

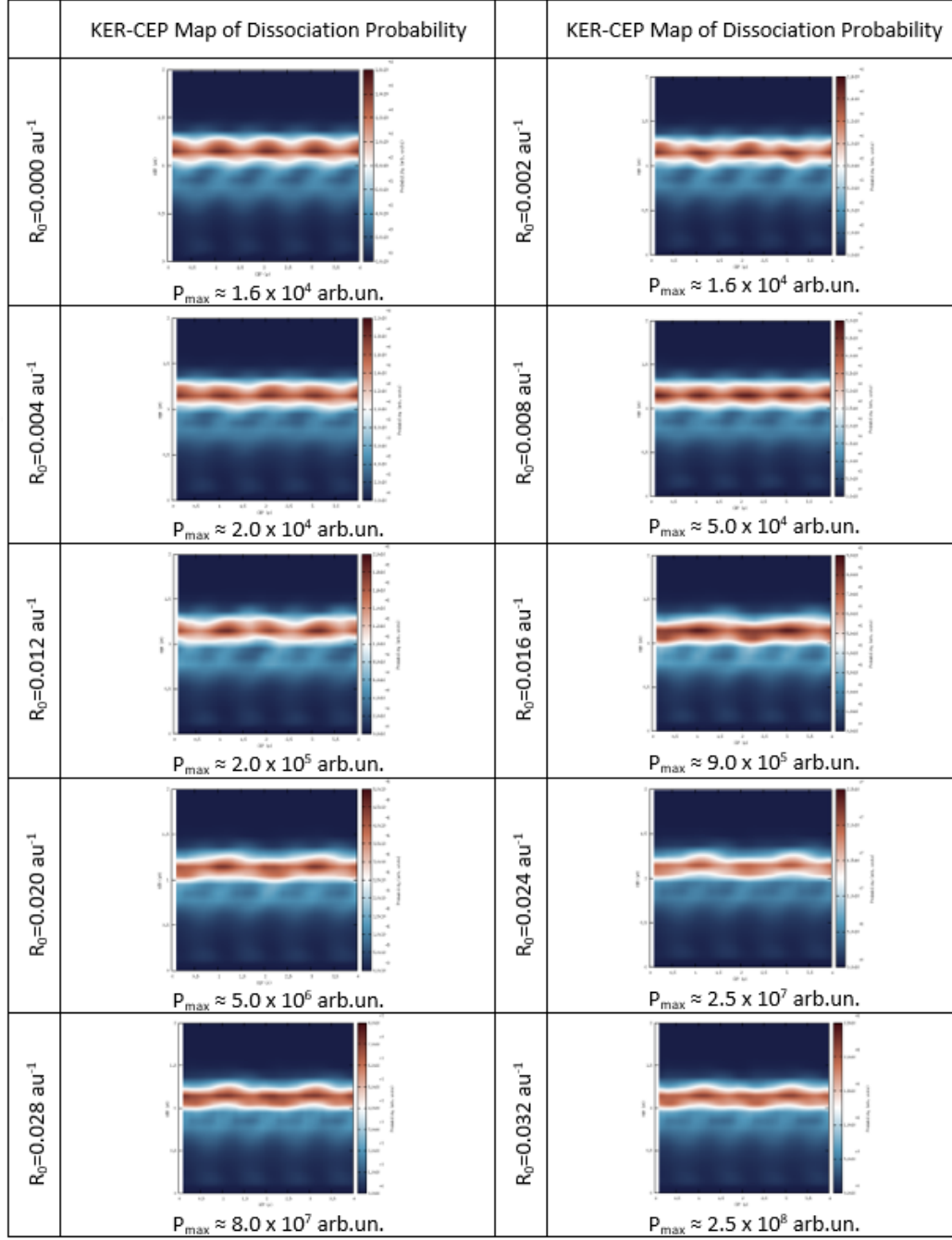


Figure D.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for H_2^+ .

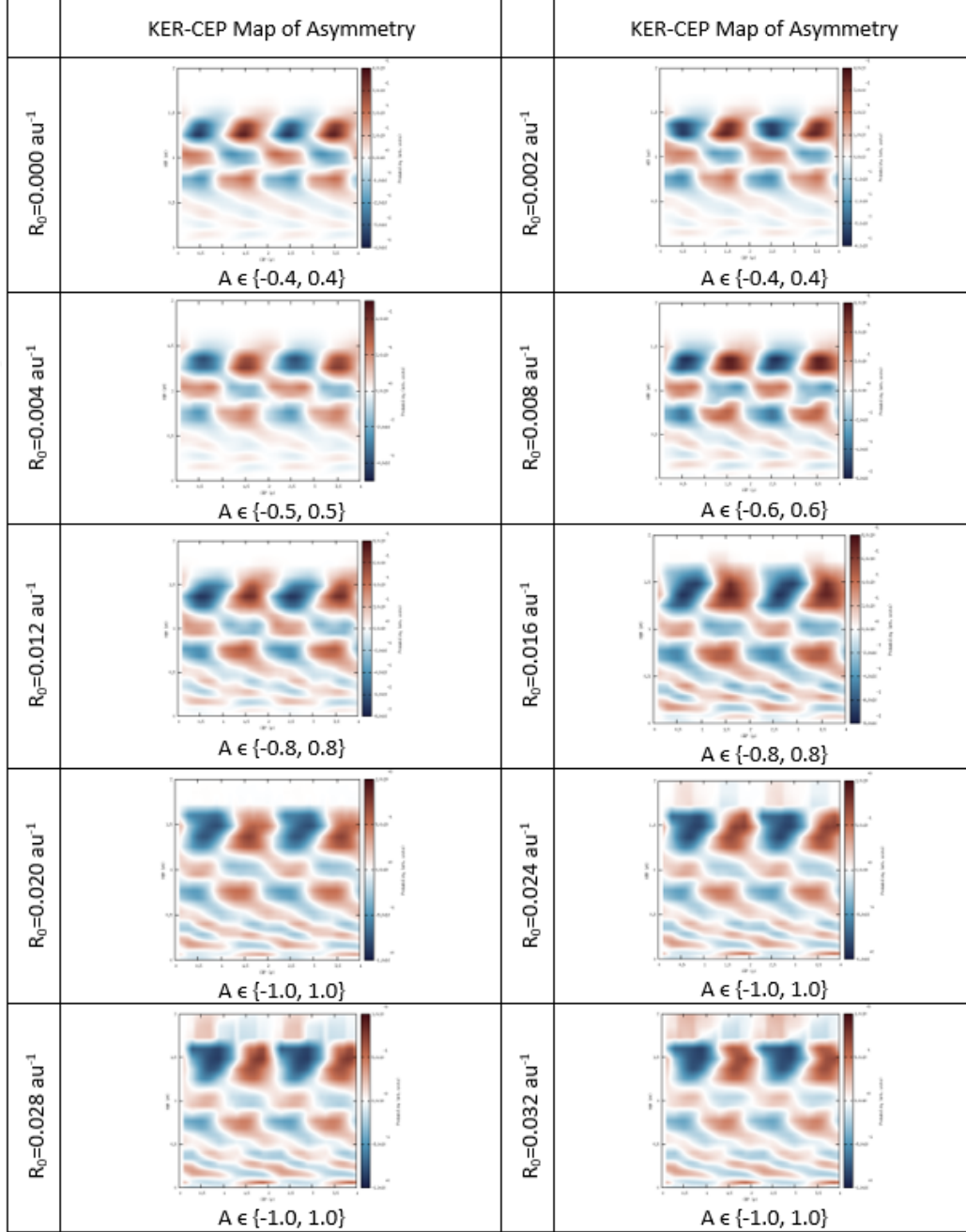


Figure D.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for H_2^+ .

E KER-CEP Maps of Left-Oriented HD^+

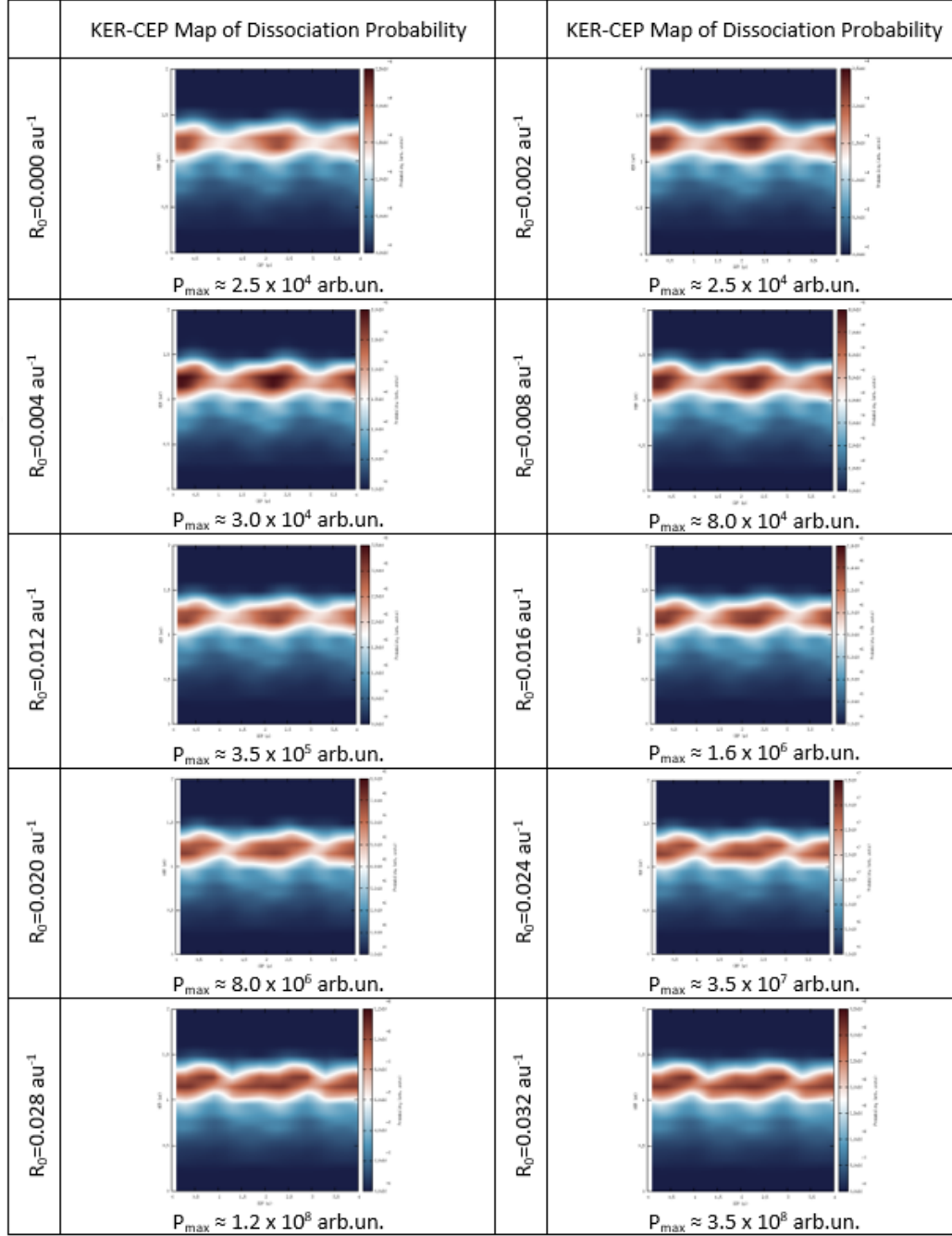


Figure E.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented HD^+ .

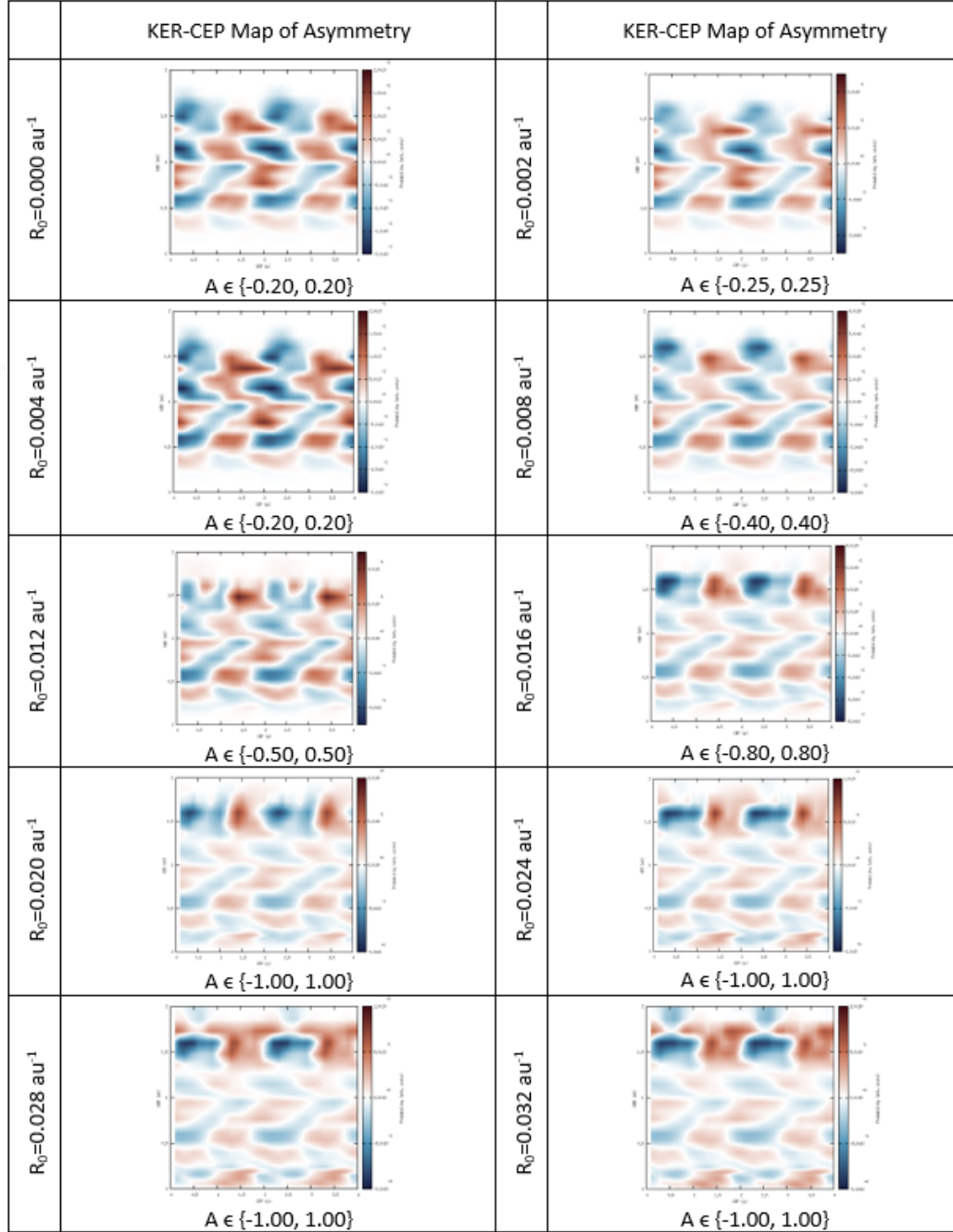


Figure E.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented HD^+ .

F KER-CEP Maps of Right-Oriented HD^+

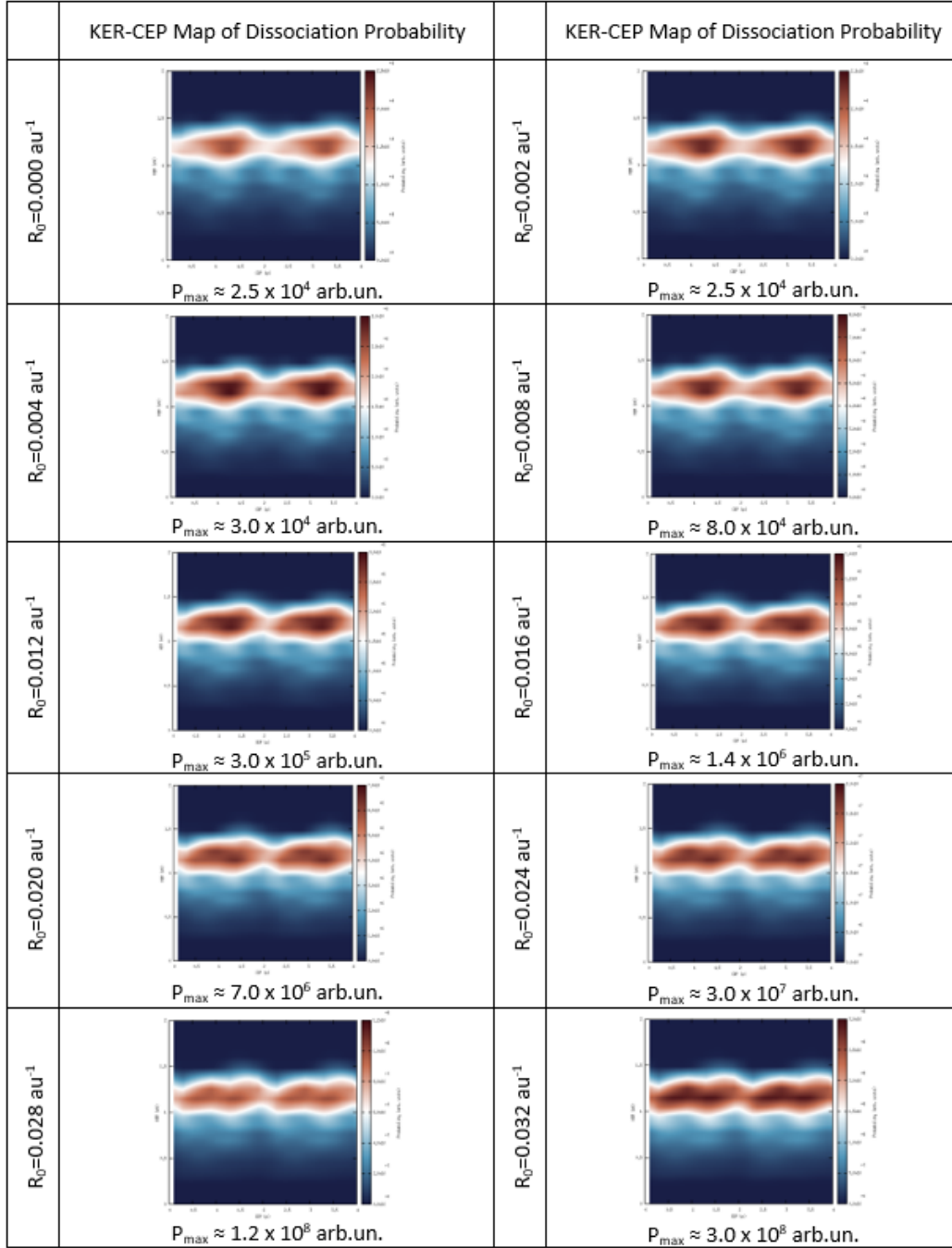


Figure F.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented HD^+ .

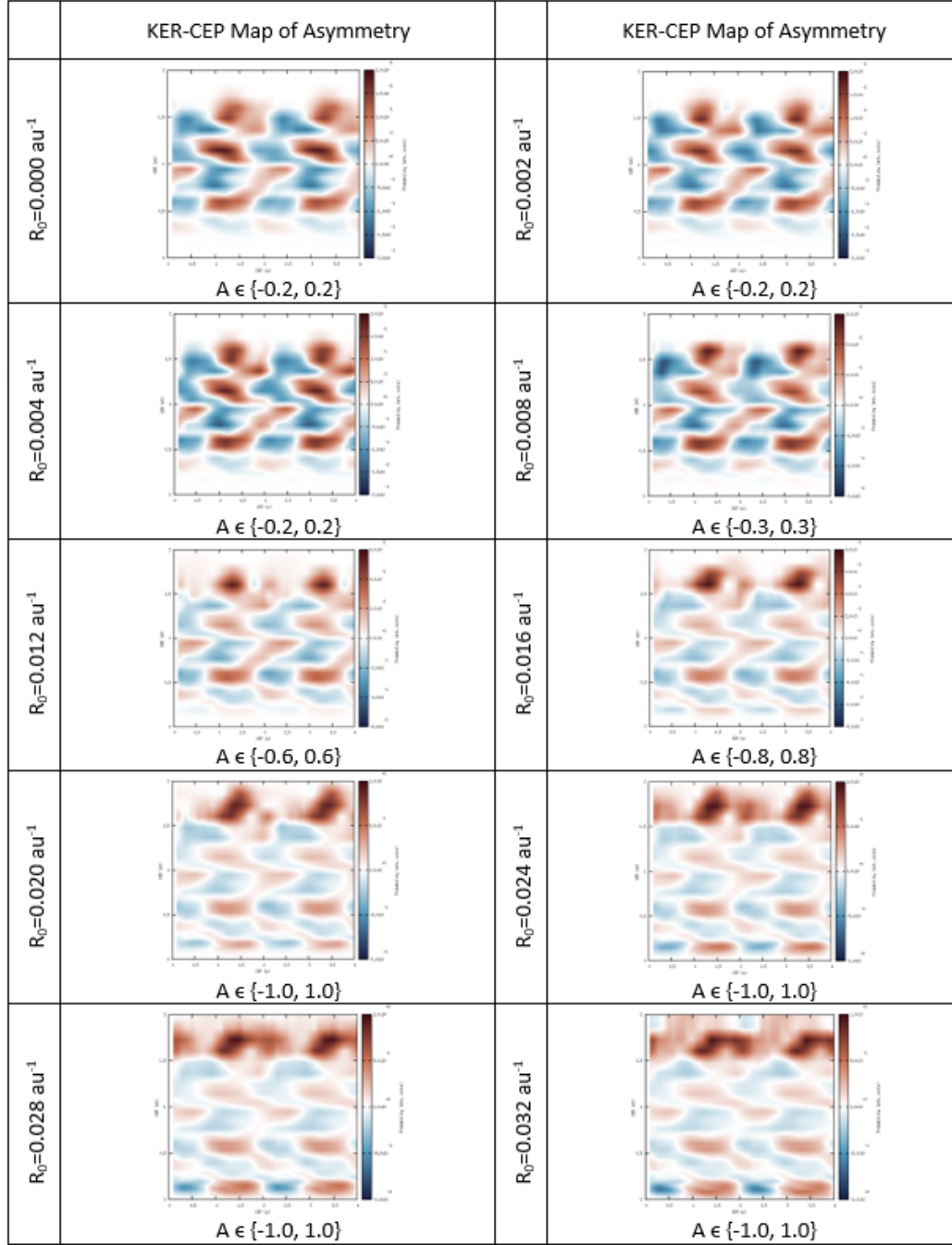


Figure F.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented HD^+ .

G KER-CEP Maps of Left-Oriented HT^+

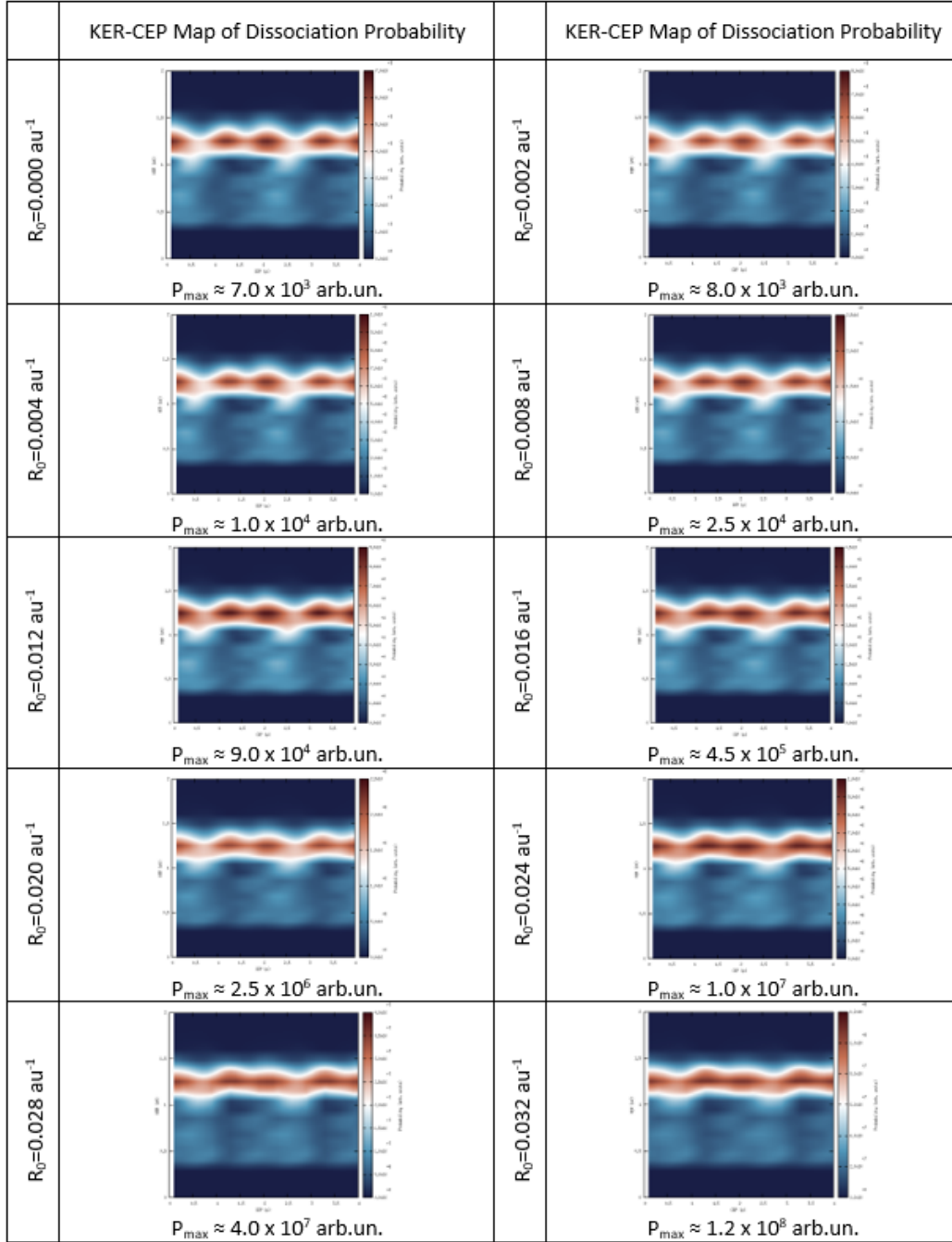


Figure G.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented HT^+ .

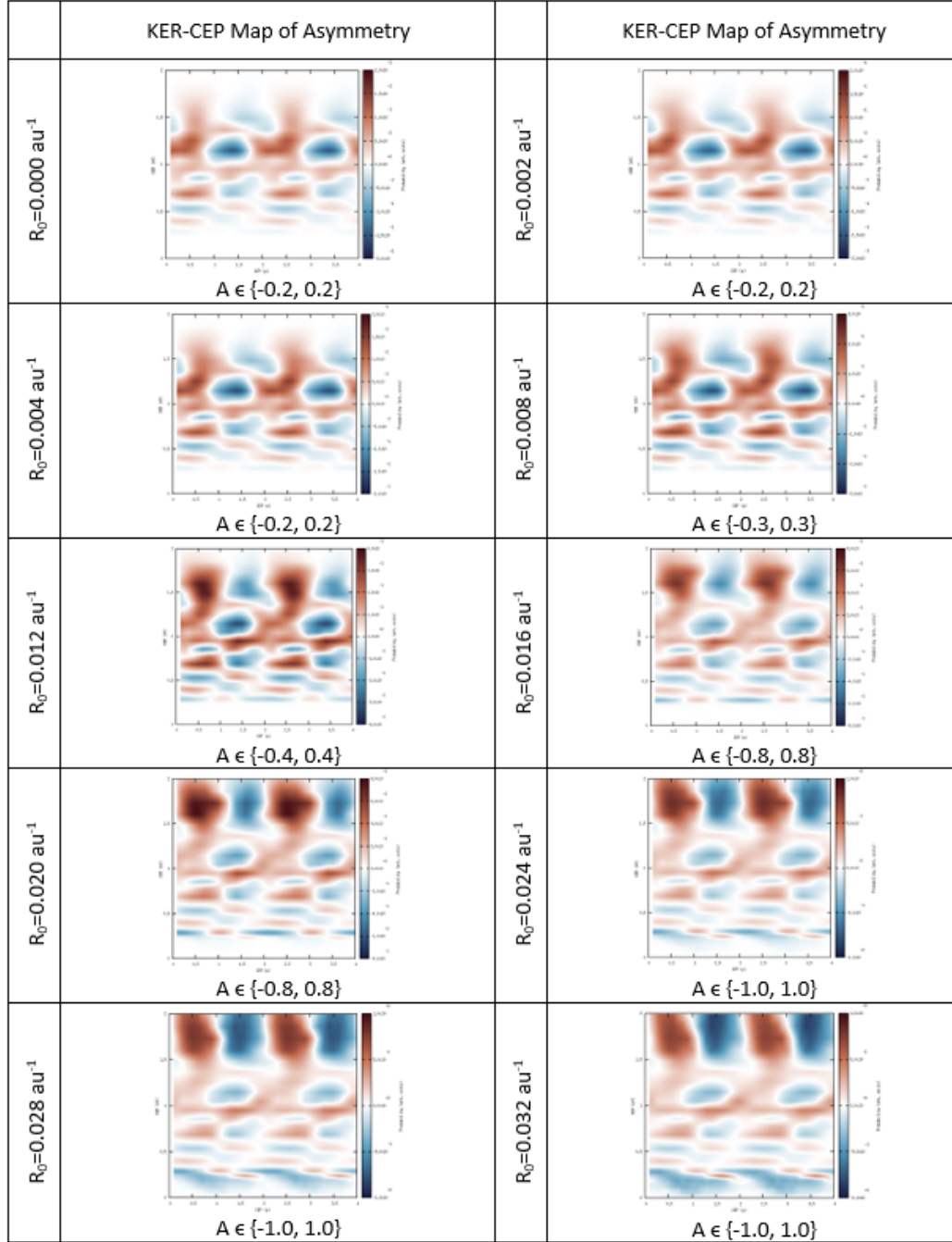


Figure G.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented HT^+ .

H KER-CEP Maps of Right-Oriented HT⁺

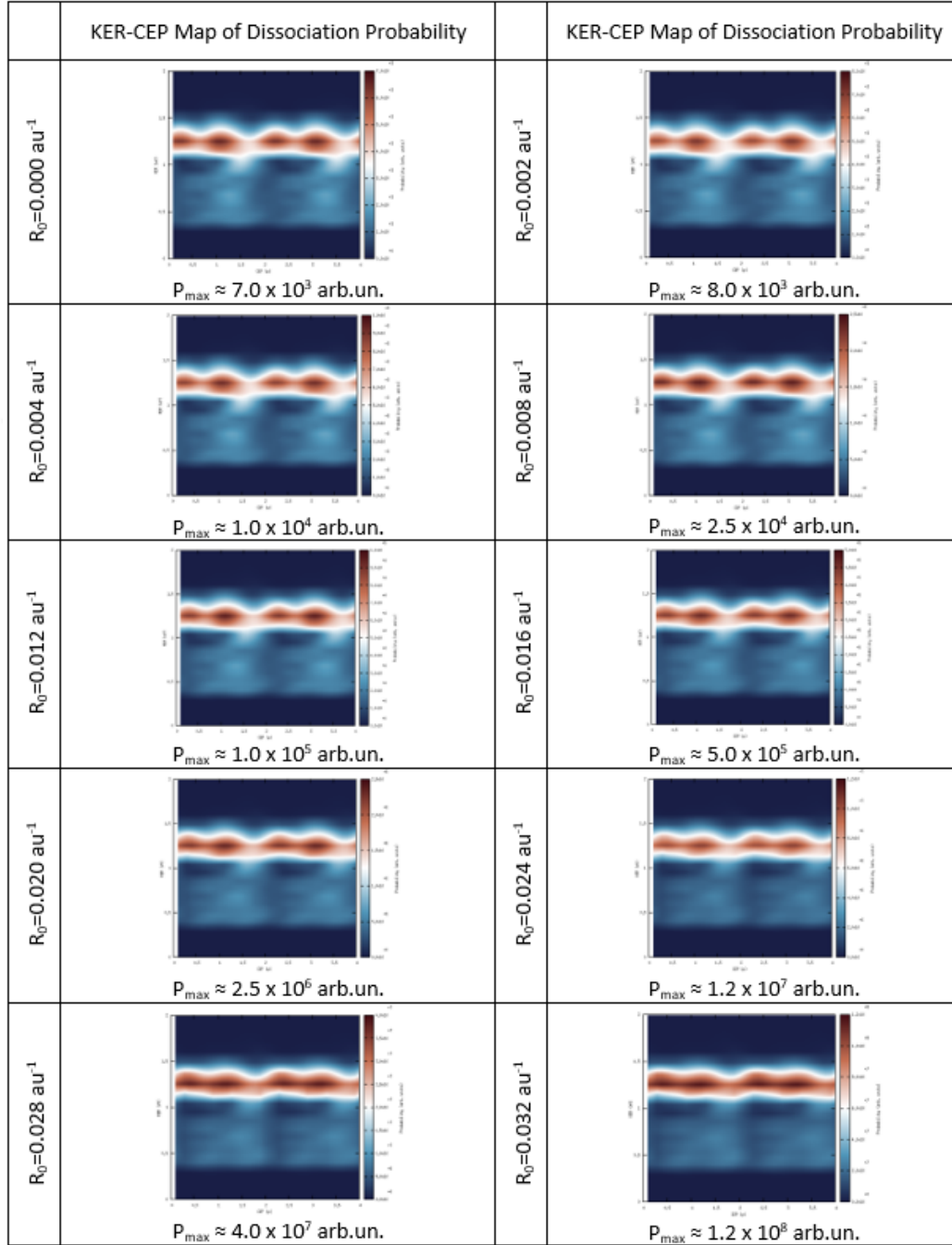


Figure H.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented HT⁺.

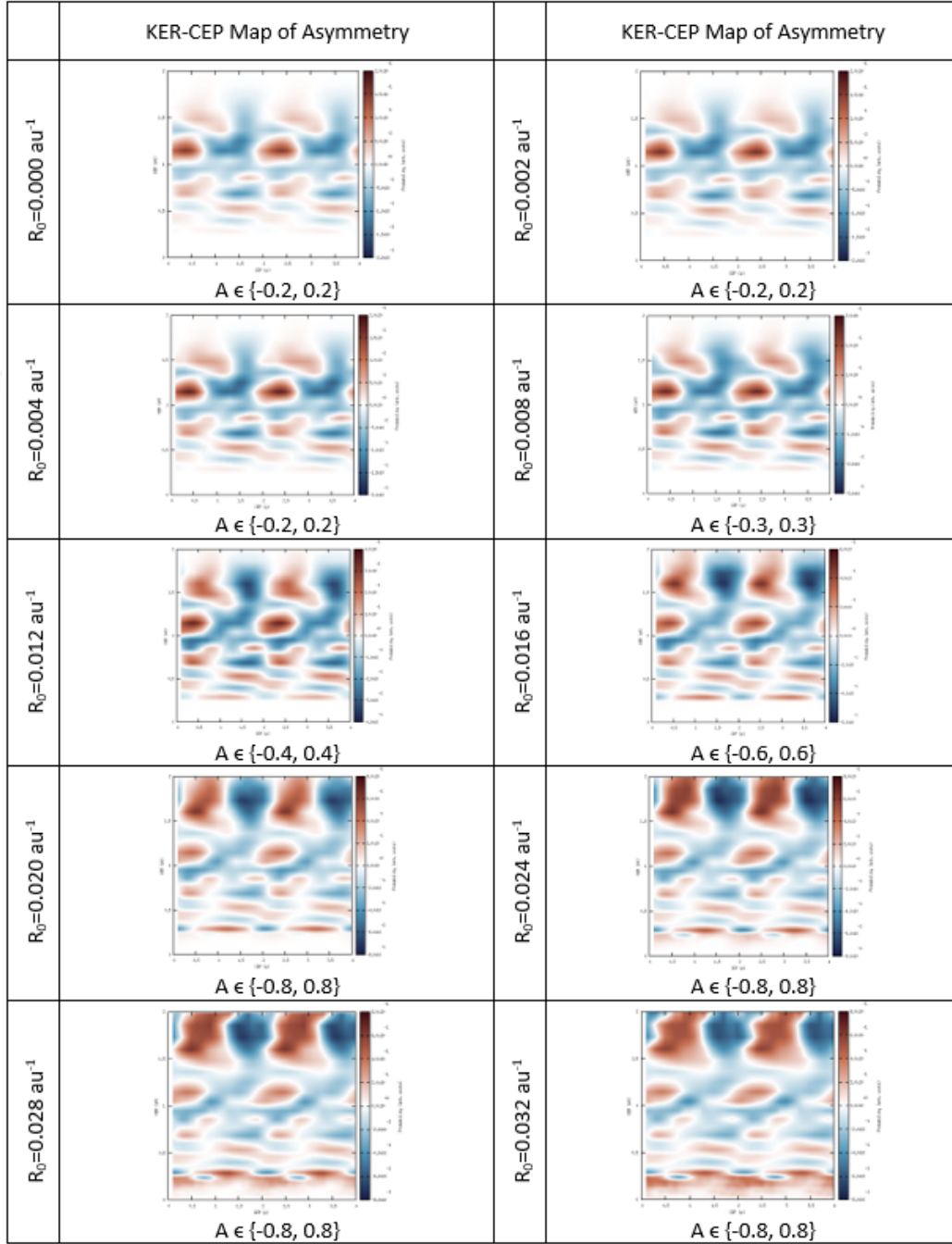


Figure H.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented HT^+ .

I KER-CEP Maps of D_2^+

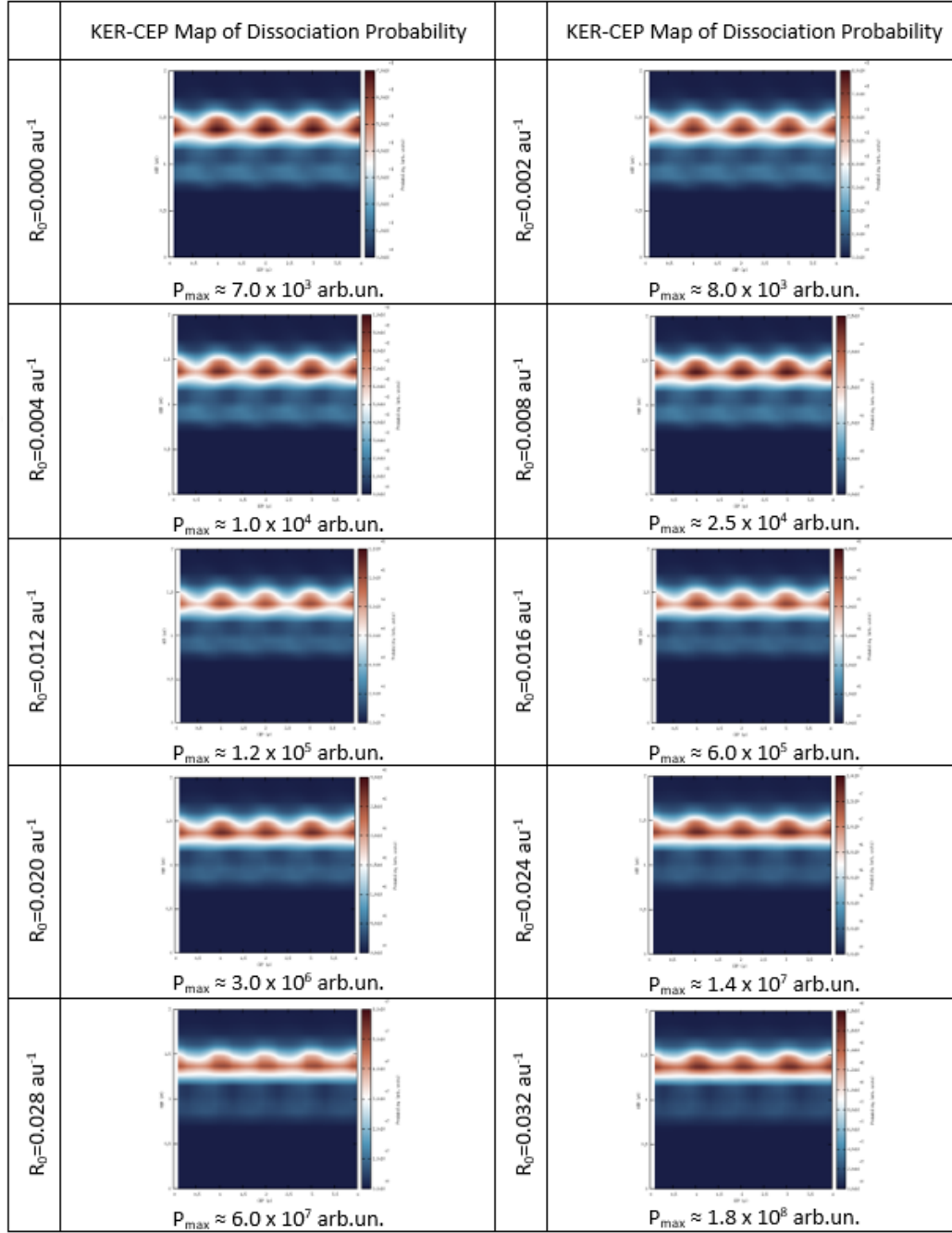


Figure I.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for D_2^+ .

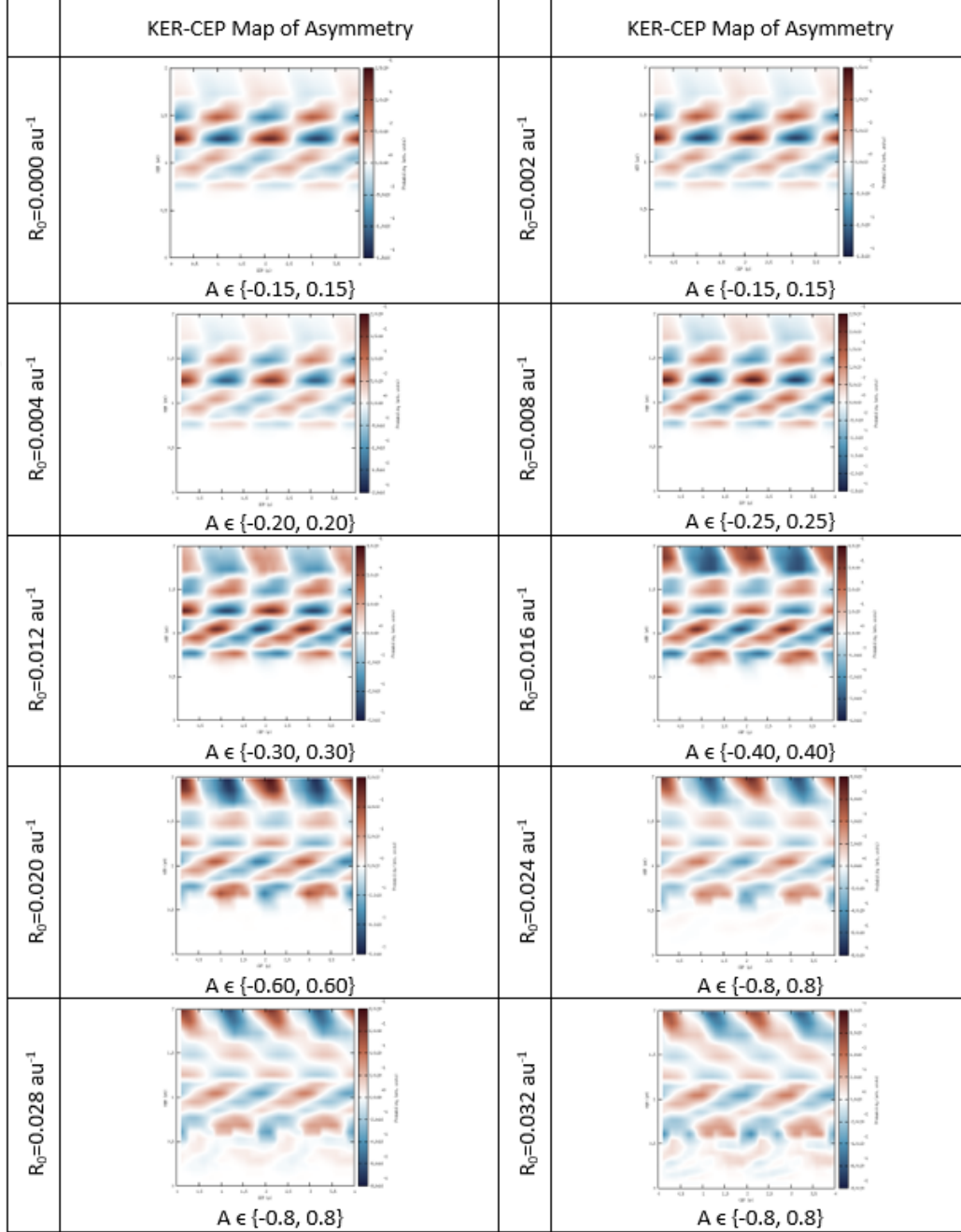


Figure I.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for D_2^+ .

J KER-CEP Maps of Left-Oriented DT⁺

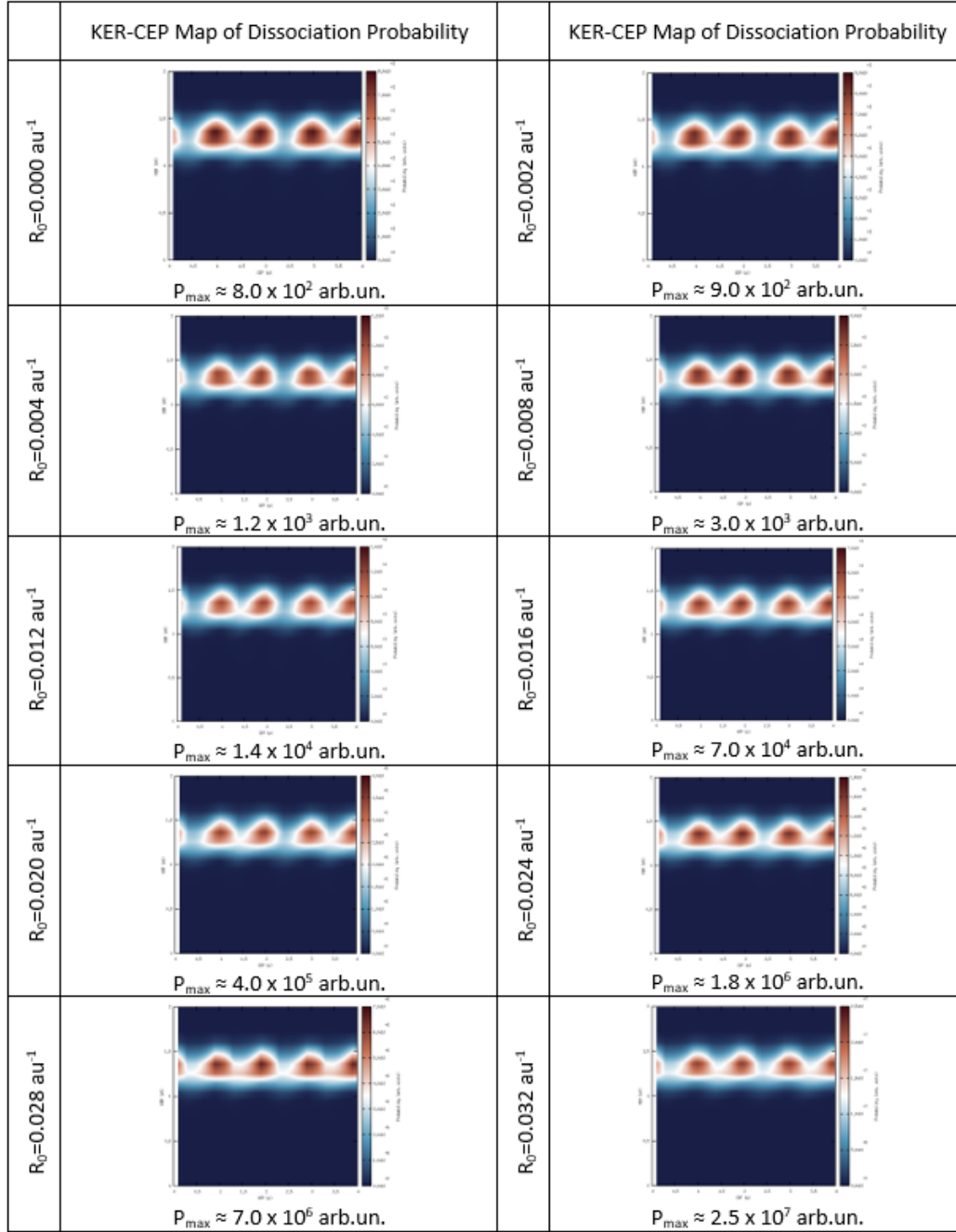


Figure J.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented DT⁺.

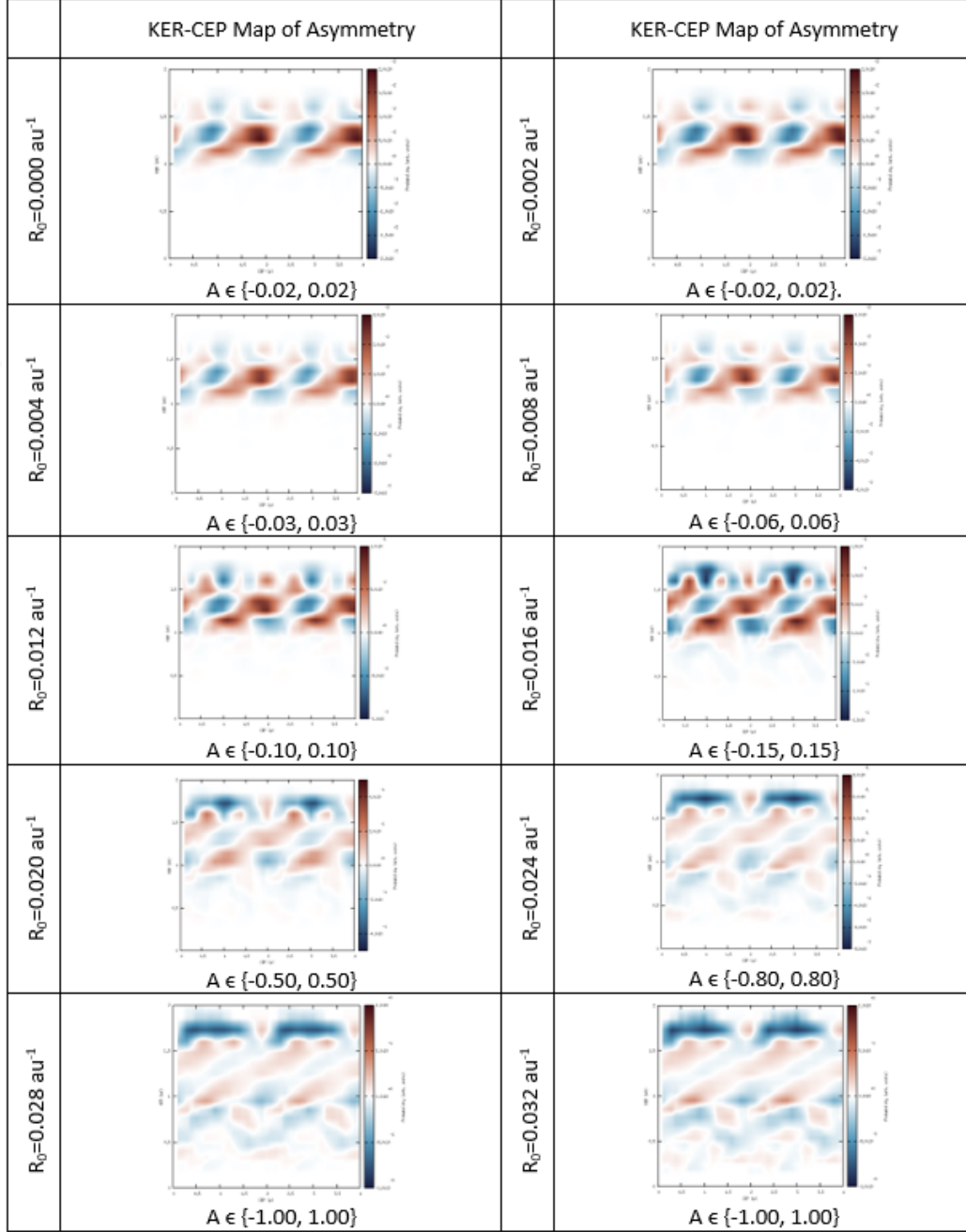


Figure J.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for left-oriented DT^+ .

K KER-CEP Maps of Right-Oriented DT⁺

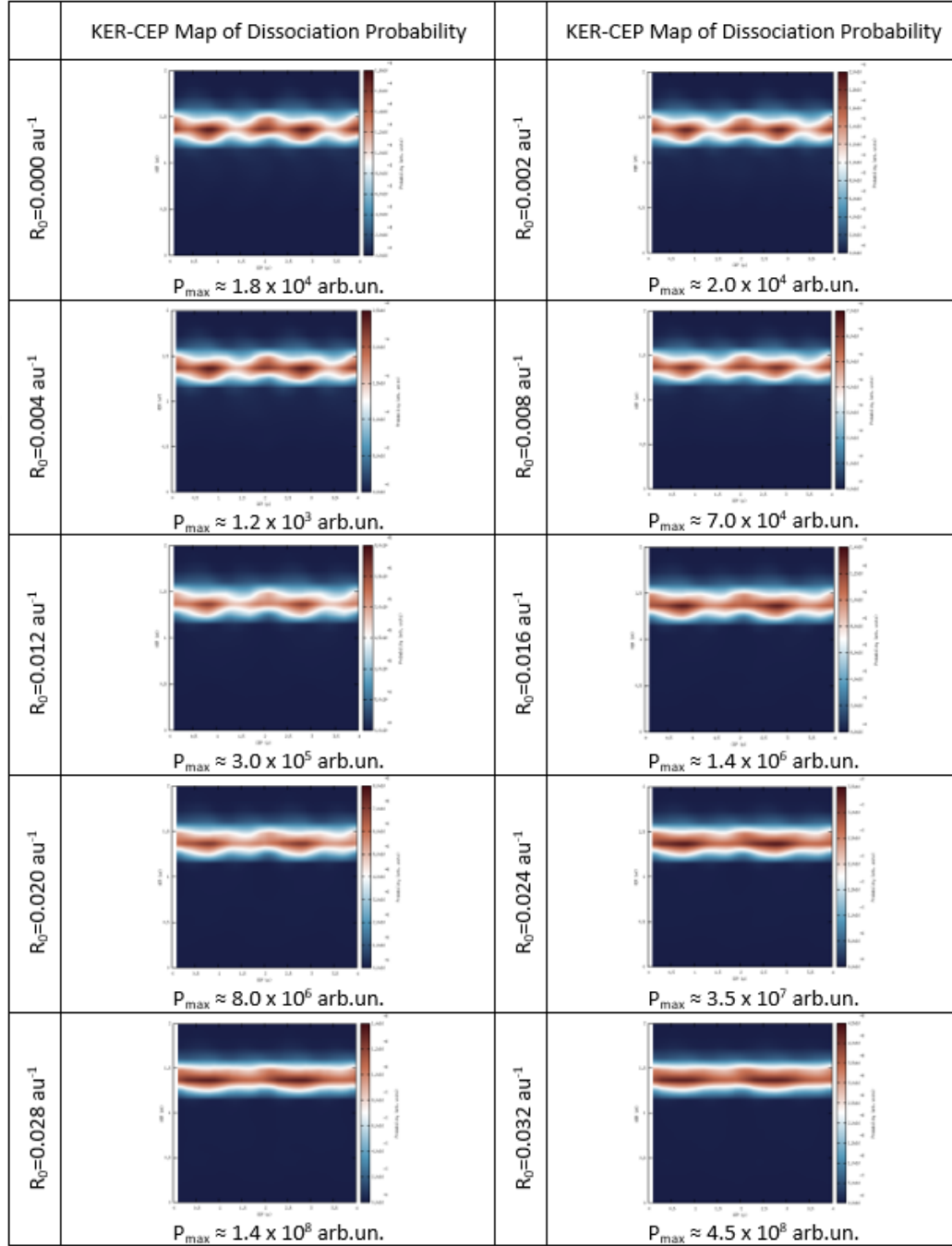


Figure K.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented DT⁺.

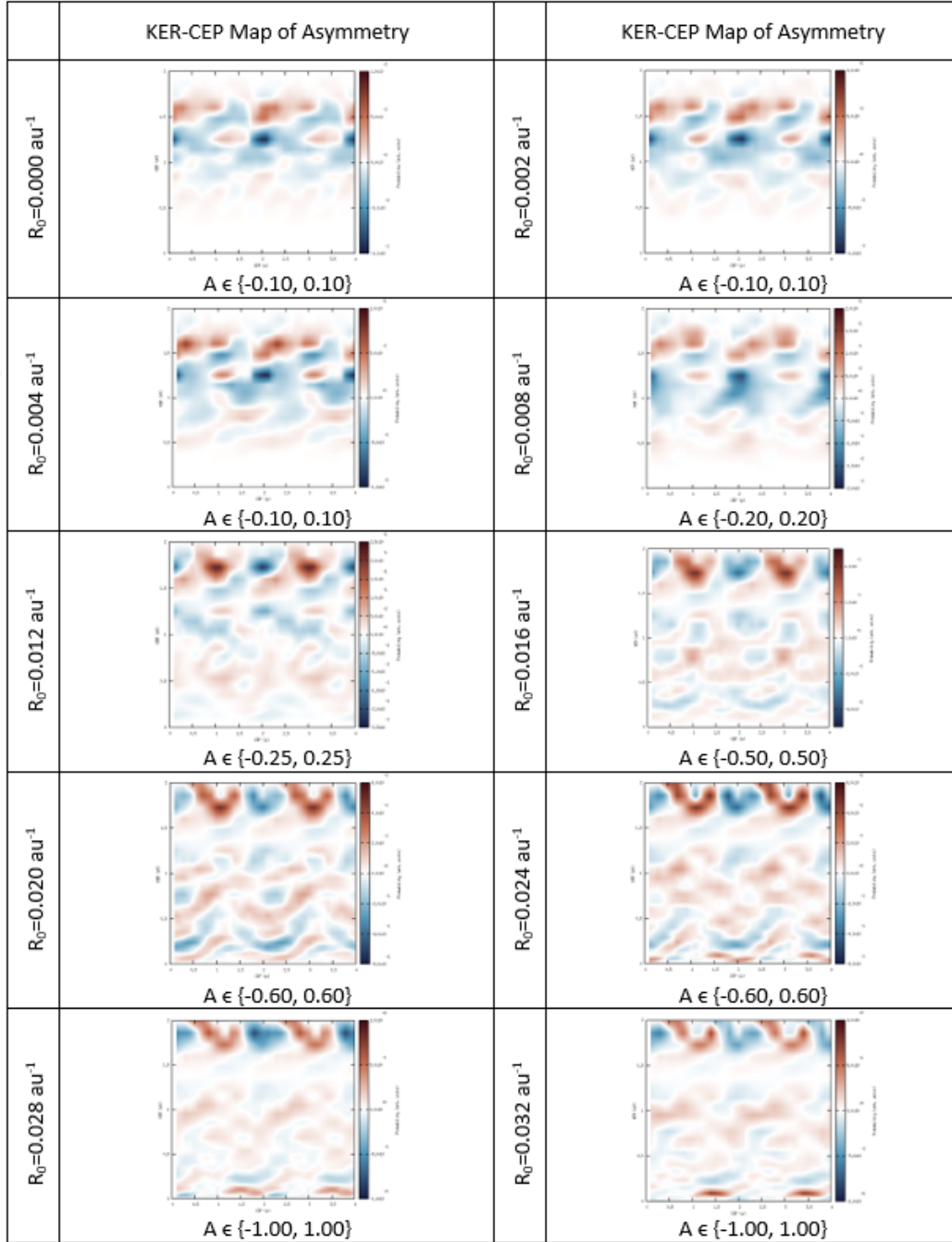


Figure K.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for right-oriented DT^+ .

L KER-CEP Maps of T_2^+

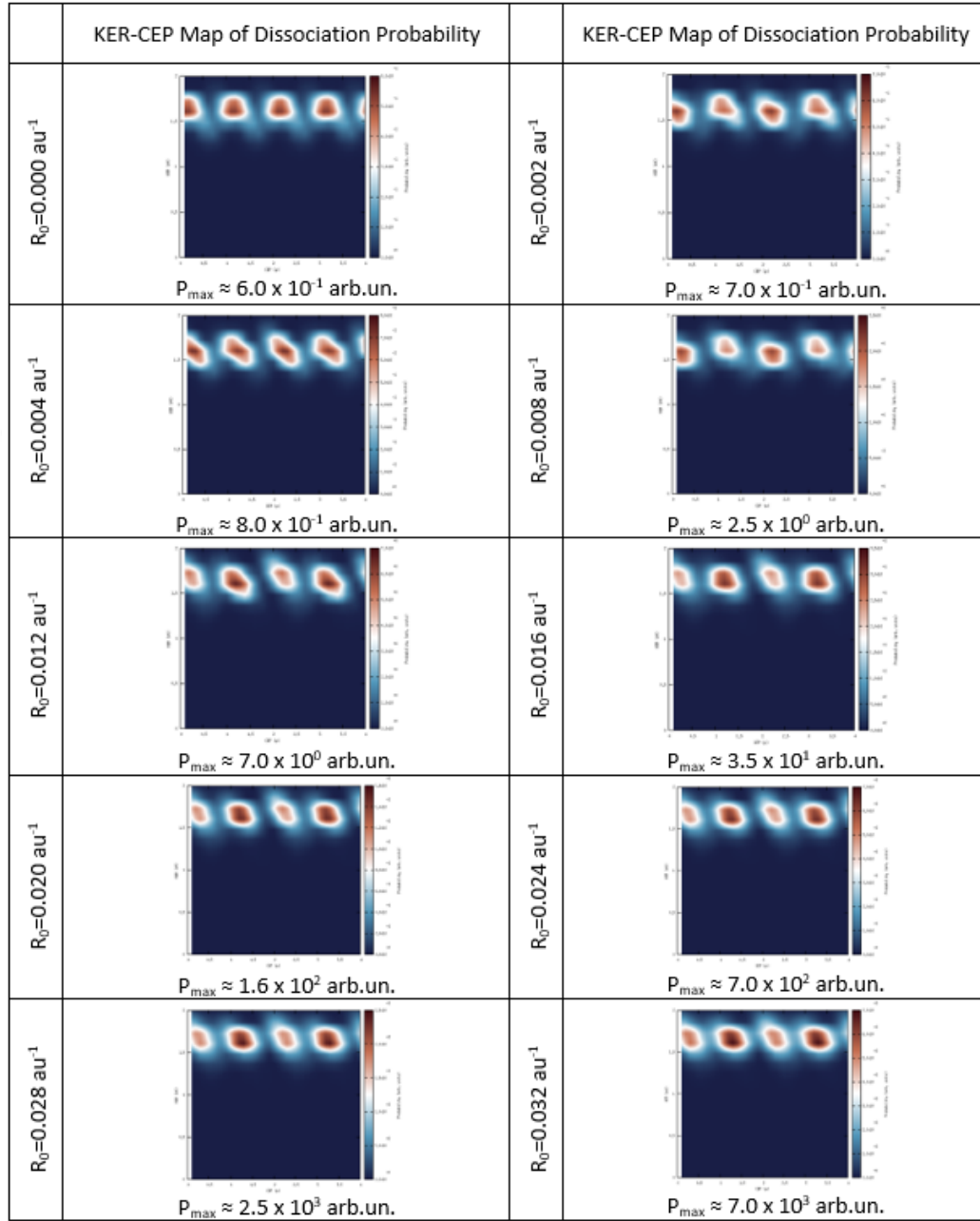


Figure L.1 KER-CEP maps of dissociation induced by two-cycle, 800 nm laser pulse with nanotip for T_2^+ .

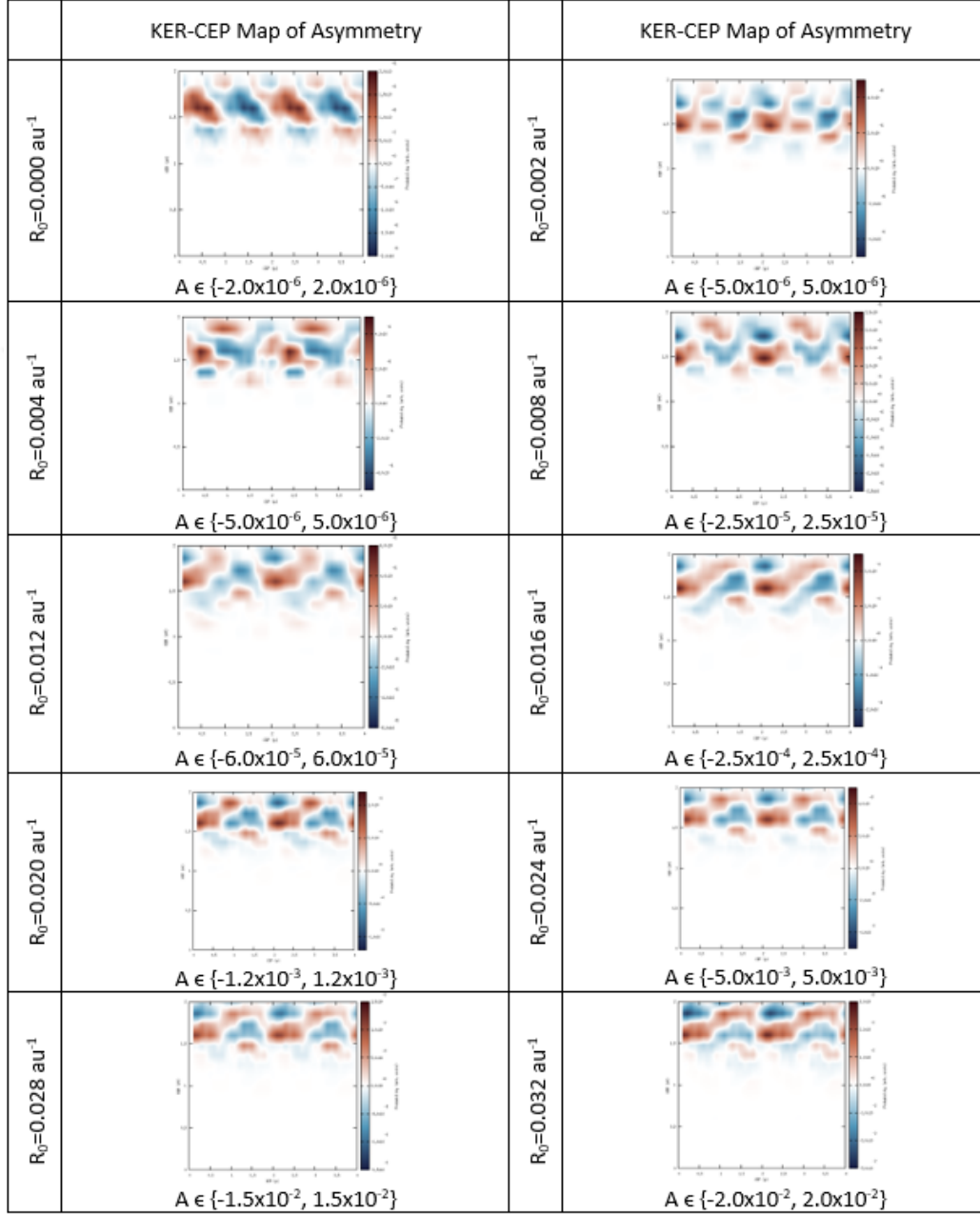


Figure L.2 KER-CEP maps of asymmetry in dissociation induced by two-cycle, 800 nm laser pulse with nanotip for T_2^+ .

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Projects and Publications from the Thesis Study

Projects:

- Metalik Nanotip Civarında Cep-Kontrollü Moleküler Ayrışma Üzerine İzotop Ve Kütlesel Asimetri Etkisi, TÜBİTAK 1002, 119F250 (Coordinatorship)
- Metalik Nanotiplerin Civarında Moleküler Ayrışmanın ve Ayrışmalı-İyonlaşmanın Yönlü Kontrolü, Marmara University, BAPKO, FEN-C-DRP-230119-0005 (Bursary Studentship)

Publication:

- Carrier-envelope-phase-controlled molecular dissociation by ultrashort chirped laser pulses, S. A. Bozpolat, P. Rosenberger, M. Ciappina, M. F. Kling and İ. Yavuz, Phys Rev A, 100 063409, 2019