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Mapping Ultrafast Dynamics of Highly Excited D2+ by Attosecond XUV Radiation

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Mapping Ultrafast Dynamics of Highly Excited D$_2^+$ by Attosecond XUV Radiation

Leigh S. Martin

April 16, 2012

A thesis directed by Dr. Margaret Murnane and Dr. Henry Kapteyn and submitted to the Honors Committee of the University of Colorado in partial fulfillment of the requirements for honors designation for the degree of Bachelor of Arts, Department of Physics
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Abstract

Using high harmonic generation in a pump-probe geometry, we populate and measure the $2p\pi_u$ potential in $D_2^+$. Cold target recoil ion momentum spectroscopy (COLTRIMS) provides the ability to measure full three-dimensional momenta of ion coincidence pairs, enabling full reconstruction of nuclear dynamics. Identification of single ion, ion pair and electron-ion detections confirms the observed state and shows mechanisms through which the nuclear wave packet may be redistributed among other molecular states in a controlled fashion. We quantify the observation via simulation of the time independent Schrödinger equation. Excellent agreement between theory and experiment enables practical implementation of the calculations to further study dynamics. This complete characterization of the potential curve and the dynamics it produces demonstrate a powerful tool poised to study crossings in the $2p\pi_u$ state, as well as coherent control mechanisms.

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1 Introduction

Despite its title as the simplest molecule in nature, hydrogen still receives widespread attention from the physics community. The reasons are twofold. Firstly, its simplicity enables a deep understanding and even control of much of its dynamics. Starting from the foundations of quantum mechanics, theorists can calculate a plethora of measurable parameters with excellent accuracy. Furthermore, familiar dynamics can also present manageable routes of manipulation, paving the way for coherent control of quantum systems. A well understood molecule like $\text{H}_2$ serves as a testing ground for both theoretical models and experimental methods, which can then be confidently applied to more complex systems.

The second reason that, despite over a century of study, such a simple molecule still demands the attention of so many physicists is that, in reality, it is still an incredibly intricate system. Full analytic solutions remain intractable, and many effects it exhibits break down the approximation methods employed to study almost all real molecular systems. The study of many of these effects is in a nascent stage, and sundry opportunities for novel physics remain. For example, a whole series of doubly excited states eluded prediction[1] and observation[2] until the last decade. Bond softening, bond hardening, charge resonance enhanced ionization and above-threshold ionization, all actively studied phenomena, occur in $\text{H}_2^+$ [3]. These effects not only emerge in more sophisticated molecules, but also play a vital role in the dynamics of foundational systems. For instance, curve crossings play an important role in biological vision and the photostability of DNA[4]. Arguably, such processes will not be adequately understood until they are comprehended in a few-body molecule like hydrogen.

Among the above listed anomalies of molecular hydrogen, curve crossings (or more
generally, avoided crossings, of which curve crossings are the one-dimensional case) present a frontier in modern quantum chemistry. As will be described below, the dynamics of a polyatomic system are well approximated with a potential surface model. This model is based on the Born-Oppenheimer approximation, which currently underlies most molecular physics. The approximation allows theorists to treat nuclei and electrons separately, which has been a necessary simplification in rendering chemical dynamics tractable to solve. Even the Hamiltonians of large, complex molecules have been successfully solved in this approximation. However, when potential surfaces approach each other or intersect, the Born Oppenheimer approximation breaks down, and the correlated motion of nuclei and electrons play a non-negligible role. These crossings provide a channel by which molecules may rapidly change state or configuration without radiating[5]. In this situation, even $\text{H}_2^+$ may display effects that surpass current understanding. Furthermore, the crossing of potential energy curves presents a region in which the final molecular state could be manipulated, opening new prospects for control of chemical reactions. Dihydrogen’s simplicity makes it the ideal platform for studying such dynamics, which occur widely in fields as far ranging as biology and atmospheric science.

In this work, I present the first steps toward directly observing and controlling avoided crossing dynamics in $\text{H}_2^+$. In demonstrating the necessary experimental capabilities, I also measure the potential curve of a highly excited molecular state called the $2p\pi_u$ state and confirm the observation using simulation of the one dimensional time-independent Schrödinger equation (TISE). Although, from a theoretical standpoint, the excited states are well known, and can even be solved analytically, they have never been directly observed. This measurement not only confirms a fundamental quantum mechanical calculation, but also demonstrates a powerful technique called Coulomb ex-
plosion imaging, at higher energies than have so far been demonstrated in H$_2$. I also derive a correction to the method that creates a modest improvement in resolution by removing systematic error. Implementation of the technique used here could measure unknown states in more complicated molecules.

Work is conducted using D$_2$, which has the same number of electrons and nuclear charge as H$_2$ but a larger mass due to the addition of a neutron in each nucleus. This heavier version of dihydrogen slows down nuclear motion, enabling easier interrogation of its dynamics without changing any salient features. The experiment as a whole relies on several experimental techniques, each of which has been used independently to study H$_2$. Coulomb explosion imaging (described in detail in section 3), first demonstrated in 1998 with I$_2$[8], enabled the direct measurement of nuclear dynamics using multiple ionization. Several studies have implemented the technique in H$_2$[3, 9, 10]. However, the states that exhibit curve crossings lie above 35 eV, requiring correspondingly high energy photons to excite the molecule, which have not been present in previous studies. Here, we use 43 eV photons created through high harmonic generation to excite the desired state.

The 2$p\pi_u$ state has been observed in other experiments, though none resolve the state in the way demonstrated below. The first experiment to use 43 eV photons was conducted by Hoshina et. al. in 2006. They found above threshold ionization into the 2$p\pi_u$ state, but did not have sufficient intensity to observe Coulomb explosion. Jiang et. al. used a limited form of Coulomb explosion imaging in which they observed a signal from the 2$p\pi_u$ state. However, their method did not include time resolved measurements required for full Coulomb explosion imaging. Furthermore, they only used 38 eV photons, and consequently the 2$p\pi_u$ did not constitute the main signal.

I discuss several important prerequisites before describing the experiment itself. The
following section reviews the Born-Oppenheimer approximation, which forms the foundation for modern quantum chemistry. Next, I review the basics physics of ultrafast lasers, without which the transient molecular states explored here would remain invisible to modern experiment. I then describe the detection scheme, called cold target recoil ion momentum spectroscopy (COLTRIMS). Several classical calculations explore the experimental details of a Coulomb explosion experiment. After this general background, I present the data in the context of the Born-Oppenheimer approximation. Section 5 succinctly describes the numerical methods employed to solve the TISE before presenting a comparison between theory and experiment. I conclude with a discussion of the prospects of further experiments and anticipated applications.

1.1 The Born-Oppenheimer Approximation

As $D_3^+$ is a three body system, it cannot be studied analytically even with classical calculations. However, as nuclei are several orders of magnitude heavier than electrons, their motions are correspondingly slower. The difference in time scale suggests that nuclear motion and electronic motion could be treated separately, with the electronic state adapting instantaneously to every nuclear motion.

To implement this approximation, consider the Hamiltonian of a general molecule:

\[
\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{A,i} Z_A \left| R_A - r_i \right| + \sum_{A>B} Z_A Z_B \left| R_A - R_B \right| + \sum_{i>j} \frac{1}{\left| r_i - r_j \right|}
\]

\[\text{Electron KE} \quad \text{Nuclear KE} \quad \text{Electron-Nuclear Attraction} \quad \text{Internuclear Repulsion} \quad \text{Electron Repulsion} \quad (1.1) \]

$Z_A$ and $M_A$ are the nuclear charge and mass respectively, and $r$ and $R$ are the electronic and nuclear coordinates. This Hamiltonian neglects energies due to spin in-
teractions, relativistic terms and corrections due to quantum electrodynamics, as these effects are small perturbations in comparison to the main interactions studied. Throughout this work, I use atomic units, in which all quantities are determined by defining the mass of the electron \( m_e \), the reduced Planck’s constant \( \hbar \), the Coulomb force constant \( 1/4\pi\epsilon_0 \) and the elementary charge \( e \) as unity. See Appendix A for a discussion and a conversion table. If we treat the electrons as adapting instantaneously to nuclear motion, the form of the electronic wave function only depends on the instantaneous position of the nuclear wave function. Similarly, the nuclear wave function is only affected by the electronic wave function, which is completely determined by the nuclear state. The assumed behavior of the two classes of particles suggests separating the total molecular eigenstate:

\[
\Psi(r,R) = \psi_e(r;R)X_N(R) \tag{1.2}
\]

The semicolon signifies that \( \psi_e \) depends on the functional form of \( X_N \). Substitution of 1.2 into 1.1 yields[11]:

\[
\hat{H}_e\psi_e = \left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{|R_A - r_i|} + \sum_{i>j} \frac{1}{|r_i - r_j|} \right] \psi_e = E_e(R_A)\psi_e(R_A) \tag{1.3}
\]

\[
\hat{H}_N X_N = \left[ -\sum_A \frac{1}{2M_A} \nabla_A^2 + \frac{E_e(R_A)}{\text{Electronic Energy}} + \sum_{A>B} \frac{Z_A Z_B}{|R_A - R_B|} \text{Intermolecular Repulsion} \right] X_N = E_{\text{tot}}X_N \tag{1.4}
\]
Thus solving equation 1.3 gives a series of energy eigenvalues $E_e$ that only depend on the instantaneous position of the nuclei. In equation 1.4, this energy contributes a static potential term to the Hamiltonian. The equation shows that we can model nuclear dynamics as nuclei propagating in static potentials determined by the electronic state of the molecule. This separation is called the Born-Oppenheimer approximation, and enables theorists to compute with the Hamiltonians of intricate, many-atom molecules. For a diatomic molecule, we can write 1.4 as:

$$\hat{H}_N X_N = -\frac{1}{2M} \frac{\partial^2 X_N(R)}{\partial x^2} + V_{\text{ElectronicState}}(x) X_N(x) = E_{\text{tot}} X_N \quad (1.5)$$

For $\text{H}_2^+$, these potentials can be calculated analytically using generalized Lambert W function in prolate spheroidal coordinates. Figure 1.1 shows many of the excited states of $\text{H}_2^+$. As nuclear mass does not appear in equation 1.3, the curves are the same for $\text{D}_2^+$. The separation neglects the correlated motion of electrons and nuclei, assuming any nuclear motion will not couple electronic states. This is an example of quantum adiabatic theorem, which states that if a particle starts out in an eigenstate of some initial potential, which is then gradually deformed into another potential, then the particle will be found in the corresponding eigenstate of the final Hamiltonian. Intuitively, this is akin to changing the potential so slowly that the work done at any step only suffices to continuously change the energy from the initial eigenvalue to the final eigenvalue, but not to make a discrete transition to another level. When energy levels approach one another, as exhibited in curve crossings and conical intersections, such a transition becomes possible and orthogonal electronic states may couple via nuclear motion. Once it becomes necessary to consider multiple electronic states, the concept of a potential
curve ceases to apply. Mathematically, it is meaningless for $E_e(R_A)$ in equation 1.4 to be multivalued.

The Von Neumann-Wigner non crossing rules determine when curves or surfaces may intersect and how they may do so. In systems with three degrees of freedom such as linear triatomics, they may intersect only at a point, creating the characteristic shape in the potential energy surfaces called a conical intersection. In these systems, a molecule may transition between electronic states without radiating. In diatomics, curves may not cross at all unless they are avoided in symmetry of the electronic state. Parity conservation prevents transition in the absence of external influence, but an external light field can induce coupling. Excitation between these states could lead to novel dynamics. Moreover, careful choice of the driving field could potentially manipulate the molecule’s final state, giving a route to coherent control of chemical dynamics.

This work focuses on the $2p\pi_u$ state, which has a crossing near 5.5 au. In order to image it, we employ time resolved COLTRIMS, which involves dissociating the molecule and detecting the electrons and ionized fragments. A pump-probe geometry using ultrafast laser technology enables time resolution on the order of femtoseconds ($10^{-15}$ s). A great deal of energy is necessary to both ionize $D_2$ and leave the remaining ion in an excited state where significant non Born-Oppenheimer dynamics could occur. High harmonic generation using an ultrafast laser pulse generates the required 43 eV photons, and a subsequent laser pulse induces the subsequent ionization necessary for Coulomb explosion imaging. The physics behind each of these experimental systems is described in the following section.
Figure 1.1: Dissociating potential curves of $\text{H}_2^+$. The Franck-Condon region marks the location where the nuclear ground state resides in unexcited $\text{H}_2$. Figure edited from Aoto et. al.[2]
2 Ultrafast Lasers

2.1 Titanium Sapphire Lasers and Mode-Locking

Using lasers to study time dependent processes requires cavities that produce a pulsed output, a design challenge that continues to this day. The original lasers operated either in continuous wave (cw) mode or in relatively long bursts. In normal cw operation, lasers typically emit a narrow spectrum, a property that made the laser immensely useful in spectroscopy. However, light obeys time-energy Fourier uncertainty relation, so spectrally narrow beams cannot be confined to brief pulses. A more familiar example of this limitation is the Heisenberg uncertainty relation, which states that a particle cannot simultaneously have a definite position and momentum. Analogously, a light wave cannot be simultaneously localized in time and spectrum. A sinusoidal plane wave, which is infinitely delocalized, has a definite energy but infinite spatiotemporal extent. Figure 2.1 shows the converse, which is a superposition of plane waves of many frequencies constructively adding at several discrete positions to create a series of temporally localized pulses.

A broad spectrum is therefore a necessary, but by no means sufficient condition for a pulsed laser. If the spectral components displayed in figure 2.1 did not precisely align, the output would resemble a noisy cw beam. Furthermore, in a realistic laser cavity, certain wavelengths extract more energy from the gain medium than others, and consequently several select modes win out over the rest. In order to maintain a pulsed beam, a laser must be mode-locked. Mode-locking refers to the forced correlation between phases of individual spectral components. When a laser is mode-locked, then it not only maintains a phase relationship across its spectrum, but also stably amplifies all components of the pulse.
The development of mode-locked lasers has spanned many decades and continues to this day. The field was not unfamiliar to spinning mirrors, toxic chemicals and other unwieldy methods of creating fast lasers. Of the many breakthroughs achieved in the field, few parallel the development of the Ti:sapphire laser[14]. Ti:sapphire, or titanium doped sapphire, refers to the gain medium, which has exceptional energy capacity, a high damage threshold and a wide amplification bandwidth. However, it lacks many of the properties that were used to mode-lock when the field was young. As a result, although it had the bandwidth to support femtosecond pulses (a pulse duration shorter than any other laser could produce at the time), theoreticians predicted that such a short duration was not experimentally achievable. It therefore came as a great surprise in 1990 when, for no apparent reason, a research group studying the laser found it outputting a 45 femtosecond pulse[15]. The phenomenon went unexplained for some time, for it was unclear what could be causing the huge number of modes required to line up so precisely within the cavity.

Nonlinear optics eventually explained the strange but incredibly useful behavior of
the Ti:sapphire laser. In conventional optics, the electrical polarization in a medium can be treated as varying linearly with the applied electric field. This approximation sets the context in which many standard results of optics are derived. In this regime, the index of refraction of a material does not depend on the intensity of light transmitted through it[16]. Linear polarization is only an approximation however, and when electric field strength becomes large, the electrical polarization of a material takes the more general form:

$$P_i = \sum_j X_{ij}E_j + \sum_{j,k} X^{(2)}_{ijk}E_jE_k + \sum_{j,k,l} X^{(3)}_{ijkl}E_jE_kE_l + ... \quad (2.1)$$

Where $X^{(n)}$ is the nth order electrical susceptibility of the medium and summations are over the Cartesian coordinates $x, y, z$. Such indexing is superfluous in an isotropic medium or in an instance when the electric field is oriented along a crystal axis. In such a situation, the polarization takes the simpler form:

$$P = X|E| + X^{(2)}|E|^2 + X^{(3)}|E|^3 + ... \quad (2.2)$$

Each term in the above expansion gives rise to novel effects. In particular, it turns out that the $X^{(3)}$ term changes the index of refraction of a material by adding an intensity dependent term[17]:

$$n = n_0 + n_2 I \quad (2.3)$$

where $n_0$ is the linear index and $n_2$ is a coefficient proportional to $X^{(3)}$. The intensities generated in a Ti:sapphire laser operating in cw mode are not sufficient to create significant nonlinear effects in the gain medium. However, if random changes are intro-
duced into the relative phase of the cavity modes, small pulses may briefly appear. The intensity of the pulse varies across the profile of the beam, so the resulting nonlinear index of refraction is also spatially non-uniform.

As a Gaussian beam (the natural spatial intensity profile at which a laser cavity resonates), is quadratic to first order, a sufficiently intense pulse will induce an index of refraction that is largest at the center and weaker at the edges. As Gaussian modes have an approximately quadratic intensity profile, the result is an effective optical path length that decays quadratically from the center of the beam. A more familiar optical element with the same property is a lens, with varying glass thickness replacing varying index of refraction. Therefore, a pulse travelling through a Ti:sapphire crystal creates a lens with focal length[17]:

\[ f_{NL} = \frac{\pi \omega^4}{4n_2 P_0 d} \]  

(2.4)

Where \( d \) is the thickness of the crystal and \( P_0 \) is the peak power of the pulse. The cavity that ‘magically mode-locked’ (as the phenomenon was called until this more scientific explanation surfaced) had been misaligned in such a way that inserting a lens of focal length \( f_{NL} \) into the cavity would optimize the system. Simply bumping a mirror or physically shifting one of the prisms was enough to stochastically create a pulse. Once a pulse existed, it traveled optimally through the cavity and was amplified more than the randomly aligned modes. Once the pulse is created, the temporal center of the pulse, being the most intense, is amplified more than the front and tail. This non-uniform amplification tends to remove the front and tail of the pulse, gradually shortening it. Thus, with an accidental bump, a properly aligned Ti:sapphire laser can start producing extremely short pulses of its own accord.
In order to achieve the intensities necessary to perform our experiments, we amplify the output of our Ti:sapphire laser using a technique called chirped pulse amplification (CPA). CPA allows one to work with intensities that would destroy most materials by first spreading the pulse out in time. As a pulse is made of precisely aligned modes, any misalignment of these modes may easily widen the pulse. In CPA, different spectral components are separated with a diffraction grating and then sent along different path lengths. This significantly reduces the peak intensity of the pulse, so it can be safely sent through further gain media. Another diffraction grating then realigns the modes, creating a much more powerful pulse. The resulting peak intensity is on the order of $10^{13}$ W/cm$^2$. If such an energy output lasted for a single second instead of a few femtoseconds, it would rival the energy liberated in an atomic bomb blast.

2.2 Nonlinear Upconversion and High Harmonic Generation

When a material is exposed to low intensity light, its electrons respond approximately linearly to the incident field. The fact that they respond harmonically means they can only radiate at the driving frequency, as is exhibited in every day phenomenon. However, the immense intensities present in amplified Ti:Sapphire laser pulses drive the electrons into a regime in which they no longer respond harmonically. In this case, they may emit photons at different colors. Substituting an oscillatory electric field $E(t) = |E_0|e^{i\omega t}$ into equation 2.2 yields

$$P = X|E_0|e^{i\omega t} + X^{(2)}|E_0|^2e^{i2\omega t} + X^{(3)}|E_0|^3e^{i3\omega t} + ...$$  \hspace{1cm} (2.5)

As can be seen, the dipole radiation now occurs at integer multiples of the initial laser frequency. In a quantum picture, this spectrum corresponds to multi-photon absorption.
The first application of nonlinearity demonstrated second harmonic generation\cite{12}, and
the above expansion formed the basis of nonlinear optics for many years.

The effect used in this work, high harmonic generation (HHG), occurs in a regime in
which the perturbative expansion of equation 2.2 breaks down. This failure arises when
intensities are large enough to ionize atoms in the material, and as a result, polarization
depends on the complicated dynamics of free electrons in the laser field. Although the
full dynamics of HHG require intricate quantum mechanical calculations, it turns out
that a simple, semi-classical model accurately explains many salient features. Figure 2.2
shows such a model of the process. First, the laser ionizes a bound electron. The ejected
electron accelerates in the laser field, and when the light field reverses direction, it pushes
the free electron back toward its parent atom. Once the electron resides near the nucleus
again, there is a probability that it will make a transition back into a bound state. At
this point, it has gained a large amount of kinetic energy from its unbound motion in
the laser field, and therefore the energy of the emitted photon will be greater than the
ionization potential of the bound state. This energy gain yields harmonics that are
vastly more powerful than are possible in conventional nonlinear optics, and currently
the record photon energy corresponds to a single electron absorbing more than 5000
photons\cite{18}. The kinetic energy depends on the time at which the electron initially
entered the continuum. Classical calculations of its energy reveal several important
details. First, there is an upper limit to the energy of the emitted photon, which is
given by\cite{19}:

\[
E_{\text{max}} = I_p + 3.2 \left( \frac{e^2 E^2}{4m_e \omega^2} \right) \tag{2.6}
\]

The first term is the ionization potential of the atom or molecule, and the second
The classical model of high harmonic generation. Figure taken from Popmintchev et al., Nature Photonics 2010[13]

term is the ponderomotive energy, which corresponds to the kinetic energy of the electron at the time of rescattering. High laser intensity will produce high energy harmonics. Furthermore, lower frequency light gives the electron more time to accelerate before recombining, and therefore raises the cut-off energy.

The simple classical model can also elucidate the structure of the harmonics in time[20]. Equation 2.6 gives the maximum energy possible, which corresponds to ionization occurring at an electric field phase angle of 17 degrees after the peak. Figure 2.3 shows several possible trajectories, which correspond to the electron entering the continuum at different times relative to the laser field oscillation. Only a narrow range of possible trajectories contribute the full possible energy, and many do not recombine at all. Consequently, the medium emits harmonics in sub-optical cycle bursts that occur every half period. In the simplest configuration, the result is an attosecond pulse train of energies anywhere from tens to thousands of eV.
The above models seem to present a coherent x-ray source that is quite simple from an experimental standpoint. Given a sufficiently intense laser beam, harmonics should emerge from any medium. However, several difficulties immediately arise if one attempts to implement things so simply. Firstly, many materials absorb strongly in the extreme ultraviolet regime that HHG accesses. Problem materials include most solids, thus restricting HHG to gas-phase media. Secondly, if the driving light and harmonics do not travel at the same velocity, the generated light from different parts of the generating medium will eventually destructively interfere, limiting the generated flux.

The second difficulty finds its solution in a method called phase matching, whereby the phase velocities of the driving and converted light are made to match. In solids, birefringence of the nonlinear medium can accomplish this. In gas phase, where molecules are randomly oriented, another method is necessary. Several solutions exist. In this work, we use the fact that the phase velocity of a TEM00 mode in a hollow fiber may exceed the speed of light. Harmonics have a much greater frequency than the fundamental light, so they travel near the speed of light in the gas. By tuning the pressure of the gas in a hollow core fiber, the fundamental light can be slowed down to the speed of the harmonics, resulting in coherent addition of harmonic light generated at different points on the beam path.

Using this tool, we employ a pump-probe experiment to time resolve the dynamics of molecules. The geometry, shown in figure 2.4, creates two laser pulses spaced in time by a controlled amount. The high harmonic light excites the sample into the state we wish to study. In the following experiment, the pump pulse ionizes D$_2$ molecules and leaves the remaining electron in the 2p$\pi_u$ state. This potential is not bound, and rapidly dissociates. After a set delay, the probe pulse (an intense IR pulse) will sometimes eject the remaining electron. This occurrence is called a Coulomb explosion as the two
Figure 2.3: Classically calculated electron trajectories in a strong IR field (period of 2.6 fs). X axes are time in seconds and y axes are electron position or electric field strength in arbitrary units. The large sin wave depicts the driving field, which is assumed to be spatially uniform over the path of the electron. A: An electron ionized at 0° phase angle past the peak electric field point. Electron rescatters but with no kinetic energy. B: An electron ionized at 170° phase angle. The electron does not return to the parent atom. C: An electron ionized at 17° phase angle. Electron rescatters with a large kinetic energy, emitting harmonics. D: The time sensitivity of the process ensures that harmonics are only generated every half optical cycle in short, intense bursts. D is for illustrative purposes only, and is not quantitatively accurate.
positively charged nuclei strongly repel each other. The repulsive force, the well known \(1/r^2\) force, captures the nuclear motion and orientation at the instant of ionization. By measuring the momenta of both ejected deuterons, we can infer the molecular orientation and the nuclear dynamics at the moment the probe pulse arrived. By scanning the pump-probe delay, we can almost directly observe the intermediate potential curve. In populating this state and applying a strong field while the molecule lies near a curve crossing, I will explore the possibility of observing novel dynamics in this region. Before presenting the data, I review the apparatus used that enables the measurements of ionized fragments: COLTRIMS.

3 COLTRIMS

Historically, optical absorption spectroscopy elucidated the quantum mechanical nature of chemistry. Lasers, and more recently, optical frequency combs gave spectroscopists ever more precise, robust tools for probing molecular transitions. However, many fundamental processes prove difficult, if not impossible, to isolate and study using conventional methods. For example, molecular events with low cross sections are easily washed out by prominent resonances. Furthermore, such spectroscopy only measures the energy levels between states, while ignoring the energy of possible fragmentation events and directional dependence. Unlike many conventional forms of spectroscopy, COLTRIMS offers full characterization of single chemical events. Furthermore, it provides a full three-dimensional view of the momenta of all particles released in the reaction. This relatively new technology, coupled with ultrafast lasers, is providing a completely new class of experiments in quantum chemistry.

A COLTRIMS device is essentially a vacuum chamber with a gas jet to inject the
Figure 2.4: The geometry of our pump-probe experiment. A laser pulse from a Ti:sapphire laser enters a beam splitter and travels along two different paths. Along the first path, we focus it into an argon filled fiber, which generates high order photons. Two multilayer mirrors (not shown), one of which is parabolic, filter out most light save the 43 eV photons and focus it onto the gas sample. The second pulse is delayed in time by introducing a variable path length difference using a delay stage. This pulse is focused onto the sample without any nonlinear upconversion.
molecule of interest. A series of electrodes at different potentials set up an electric field in the interaction region to accelerate electrons and charged fragments towards position sensitive, time resolved detectors. For a typical experiment, the chamber is kept at $10^{-5}$ Torr, so that the mean free path is on the order of hundreds of meters. In this absence of intermolecular interactions, a single ionized particle can travel unimpeded to the detectors. The electric field forces negatively charged particles one way and positively charged particles the other. At the ends of the chamber, two detectors measure and record the time and position at which particles arrive. As the location where particles are ionized (the intersection between the gas jet and laser) and the times at which they are created (the laser pulse arrival time) are known, the full three-dimensional velocity vector of each can be measured.

The disparity in mass between the electron and nucleon leads to an interesting experimental challenge. As particles tend to leave the interaction region with equal momenta, electrons travel several orders of magnitude faster than nuclei. In order to collect particles emitted in any direction, the geometry of the apparatus must collide all electrons into the detector before any of them travel radially out to the edge of the chamber. Furthermore, in order to optimize resolution, one wishes to focus particles as little as possible, so that a change in velocity maps to as large a change in detected position as possible. Consequently, the most energetic particles should hit the edge of the detector, so that we use the full area. With only the electric field as a free parameter, such an optimization may not be simultaneously achieved for electrons and ions. In order to optimize the system for a given experiment, an applied magnetic field parallel to the electric field adds the additional control necessary. Nuclei, being both massive and slow, experience negligible acceleration due to the field. However, light and swiftly moving electrons may execute one or more cyclotron periods before reaching the detector. Thus,
Figure 3.1: Inside a model COLTRIMS apparatus. Image taken from http://www.atom.uni-frankfurt.de/research/coltrims/.
after optimizing the electric field for ion momentum resolution, application of a magnetic field may bend high energy electron trajectories to focus them onto the detector edge.

Detecting single ions and electrons is a significant experimental challenge, and demanding spatial and temporal resolution further complicates the task. Like all COLTRIMS setups, we use microchannel plates (MCPs) and several delay lines to accomplish the feat. MCPs consist of millions of micron-sized channels, with each behaving as a minuscule photomultiplier tube. A high voltage across the plates accelerates any secondary electrons generated by the initial collision. These electrons pick up enough kinetic energy to cause further ionization when they hit the channel walls. The result is a cascade of electrons out the other side of the plate. Figure 3.2 shows a zoom in of an MCP and the effect that occurs within. Behind the plate, two or three arrays of wires measure the x and y position of each event, as well as the timing.

The electron-ion and ion-ion coincidences provide a massive amount of information.
Considering the huge number of ways in which we can create ions using our laser pulses, the amount of data can appear overwhelming. Post-experiment processing to filter out the signal of interest is therefore non-trivial and typically takes much longer than the data acquisition itself. In this experiment, we primarily seek D$_2^{++}$ counts in which the probe pulse initiated the first ionization event and the pump pulse initiated the second. As the HHG photon energy, 43 eV, is below the double-ionization threshold, seeking coincidence D$^{+}$ counts is sufficient. However, in detecting ion coincidences, it turns out to be more likely to detect two D$^{+}$ ions that came from two different molecules. These constitute false coincidences, and wash out the signal of interest. In order to observe true coincidence pairs, we employ a momentum conservation filter, which true coincidences must satisfy but false coincidences will only satisfy by chance. This filter is described below.

3.1 The Momentum Conservation Filter

Consider a molecule that explodes into two singly-ionized fragments of mass $m_1$ and $m_2$ respectively. After the initial Coulomb interactions between molecules, each experiences a force $E_x e$, where $E = E \hat{z}$ is the electric field in the chamber. As the nuclei experience little acceleration due to the magnetic field, its effect can be neglected. In this case, motions along $\hat{x}$, $\hat{y}$ and $\hat{z}$ directions are decoupled, and we can assume for now that the molecule dissociates along the $\hat{z}$ direction. Finally, conservation of momentum requires that $p_0$ is equal and opposite between fragments 1 and 2. The equations of motion are then given by the familiar Newtonian expressions:

$$\frac{1}{2} E e t_1^2 + p_0 t_1 - d_a m_1 = 0$$

(3.1)
\[
\frac{1}{2} Ee t_2^2 - p_0 t_2 - d_a m_2 = 0 \quad (3.2)
\]

Where \(d_a\) is the distance from the interaction region to the MCP detectors and \(p_0\) is the initial momentum. Throughout, the subscript 1 signifies a parameter of the first detected particle and 2 marks the second detected particle. Using the quadratic formula, equation 3.2 becomes:

\[
t_2 = \frac{p_0 + \sqrt{p_0^2 + 2Ee d_a}}{Ee} \quad (3.3)
\]

As the radical term is strictly greater than \(p_0\), the positive root has been selected to ensure that \(t_2\) is greater than zero. To find how this fragment will show up in the time-of-flight spectrum, we must eliminate \(p_0\), so instead of solving for \(t\) in equation 3.1, solving for \(p_0\) yields:

\[
p_0 = \frac{d_a m_1 - Ee t_1}{2} \quad (3.4)
\]

The final result may be obtained by substituting 3.4 into equation 3.3:

\[
t_2 = \frac{d_a m_1 - Ee t_1^2/2 + t_1\sqrt{(d_a m_1 t_1)^2 + (Ee t_1/2)^2 + Ee(2m_2 - m_1)}}{t_1 Ee} \quad (3.5)
\]

The above expression indicates that fragments that satisfy momentum conservation will show up along a curve in a time-of-flight 1 versus time-of-flight 2 plot. This characteristic curve is called a photoion-photoion coincidence (PIPICO) curve. Such a curve is shown in figure 3.3. By filtering on this line and requiring that \(p_x\) and \(p_y\) are conserved as well, data can be filtered just on doubly-ionized Coulomb exploding states.

An immediate use of equation 3.5 is the extraction of experimental parameters the
PIPICO curve depends on. Fitting the curve can place constraints on the possible electric field and ion acceleration region, which in turn removes uncertainty in these parameters. One approach would be to use a least squares fit, allowing all constants in the equation to vary. However, this neglects any correlations between parameters. For instance, if the ion masses double and the electric field strength halves, the same dynamics should occur. To elucidate such structure from the formula, I non-dimensionalize the expression by introducing a characteristic time $t_0 = \sqrt{2d_a m_1/Ee}$, which corresponds to the time it would take ion 1 to reach the detector if it started with no kinetic energy. I then define two unitless times $\tau_1 = t_1/t_0$ and $\tau_2 = t_2/t_0$. With these parameters, equation 3.5 simplifies to:

$$\tau_2 = \frac{1 - \tau_1^2 + \sqrt{1 + \tau_1^4 + 2\tau_1^2 \frac{2m_2-m_1}{m_1}}}{2\tau_1}$$

(3.6)

and for the case $m_1 = m_2$, the term in the radical factors, giving the simple expression:

$$\tau_2 = \frac{1}{\tau_1}$$

(3.7)

Thus, the appearance of the PIPICO curve only depends on the ratios $(2m_2-m_1)/m_1$ and $d_a m_1/Ee$. As ion masses and charges are usually known (or can be determined in other ways), the second quantity allows one to compute the ratio of the electric field to the ion acceleration region to high accuracy. As both parameters may change between experiments and are vital for calculating energy and momentum spectra, knowing it well by employing a least squares fit should prove useful for experiments beyond the one presented here.
Figure 3.3: The PIPICO curve from the D$_2$ dataset. Color represents the number of counts in a logarithmic scale increasing from blue to red. Equation 3.5 describes the black curve. Note that only one line appears because the fragments D$^+$ and D$^+$ have equal mass.
4 The D$_2$ Molecule: Experimental Results

4.1 Experimental Design

In order to image the $2p\pi_u$ state, the molecule must first be ionized by a 43 eV photon. Assuming the Ti:sapphire output lies around 780 nm (≈1.6 eV), Coulomb explosion might require up to 8 photon absorptions. Furthermore, as MCP detectors have about a 50% active area, there is at most a 25% chance that both fragments of a Coulomb explosion will generate a signal. Moreover, in a given laser shot, many other processes may occur, and in doing so cover up the main coincidence signal. All of these factors mean that a great deal of laser power and time are required for significant statistics.

In practice, laser instability limits the duration of an experiment$^1$. In this experiment, each pump-probe time step lasted approximately one hour.

We took several steps to maximize count rate in the experiment. First, we used an effusive jet instead of the usual supersonic jet, which outputs higher density gas and spreads it out more in the chamber. Although these differences can increase count rate, the uncertainty in initial position of the molecules tends to systematically increase the measured kinetic energy and decrease resolution. In addition, we omitted the thin aluminum filter normally used to filter out the unconverted 800 nm light used to drive high harmonic generation. Lastly, we took two large ($\approx$100 fs) time steps at 130 fs and 230 fs in order to observe the long delay behavior of D$_2$ in the same data set. This non-uniform step size will be visible in all data as two large gaps, and are simply an artifact from the way we ran the experiment.

$^1$I developed a laser stabilization system in concurrence with this project. Using a CCD detector and piezo-electric mirror mount, I control the laser pointing on the order of microradians, which ameliorates problems associated with thermal drift. Currently undergoing testing on another laser, I hope to implement it on the COLTRIMS setup soon.
Even with long integration times and high intensity, only careful data analysis can hope to extract a clean signal. Much of the data analysis is already coded using CoboldPC software. Cobold takes the raw timing signals from the delay line detectors, converts them to detector coordinates, and then to particle momenta. The software comes with its own scripting language, in which the user may define histograms to be plotted. This code also provides the input for various physical and experimental parameters such as electric field, magnetic field, ion mass and spectrometer geometry. In order to implement some of the filters and corrections, I also modified the CoboldPC software on a lower level using Visual C++.

Before analyzing the data, the experimental parameters must be carefully calculated or measured. We change the electric field often in order to make sure all ions are collected. Here, the electric field was set to a relatively large value, as Coulomb explosions generate high kinetic energies. The electric field is roughly estimated from the applied voltage within the chamber. To refine the approximate value, I plot the z momentum of electrons and ions, and adjust the electric field to center both of these histograms around $p = 0$. As the interaction region moves slightly when the laser is realigned, I also adjust the electron and ion acceleration region lengths in conjunction with the electric field. As the distance between electrodes remains fixed, the sum of electron and ion acceleration lengths remains constant. Once these histograms are symmetric, I fit the PIPICO line using the method described in section 3 to refine the value. The final electric field value was 11.8 V/cm. We occasionally calculate the magnetic field by turning down the electric field, so that the electron time of flight increases to the point where several cyclotron periods are visible in the data set. The magnetic field strength may be directly extracted from the cyclotron period. The magnetic field was determined to be 7.621 Gauss from a previous experiment.
4.2 Data Analysis

Before analyzing the main signal, I identified the other spurious signals that could contribute noise. Figure 4.1 shows measured y and z momentum of the first detected ion assuming a mass of 2.0 amu. A small amount of HD is present in the gas jet. It is heavier than D, so it has a longer time of flight, and consequently appears to have had a large initial momentum away from the ion detector. The time of flight determines the z axis momentum, so HD is consistent with peak 1. Peak 2 appears through the following mechanism. The 43 eV mirrors ‘leak’ some of the lower harmonics[22]. These may excite the $1\sigma_g$ state (see figure 1.1). This state is bound, but as the ground state nuclear eigenfunction of D$_2$ is not an eigenstate of this potential, it begins to oscillate. At approximately 4.12 au internuclear distance, the difference between the $1\sigma_g$ and the excited $2\rho\sigma_a$ state is 1.6 eV, which is resonant with the probe pulse (no electron is ejected, so unlike ionizing transitions, the energy difference must be exact). Once the molecule is in this state, it dissociates into a neutral hydrogen atom in the $n=1$ state and a deuteron, releasing 1.14 eV. As only the charged deuteron is detected, a $1.14/2 = 0.57$ eV channel should appear. Peak 2 occurs at approximately 12 au (momentum), or 0.53 eV. The channel also appears to select molecules that are oriented along the laser polarization axis (z axis), indicating $\sigma$ symmetry. This is also consistent with the described mechanism.

Peak 3 appears as a channel with an extremely low KER (kinetic energy release). It may be part of the nuclear wave packet that dissociates when projected into the $2\rho\sigma_a$ state. However, viewing x and y momentum shows another strong contributing factor. The laser propagates along the x axis, and as it has a finite Rayleigh range$^2$, it remains

$^2$The Rayleigh range is the distance from the focal point at which the beam profile area doubles.
Figure 4.1: Momentum histograms in the y,z plane and the x,y plane. The z axis is perpendicular to the MCP plates, and thus momentum in this direction is determined by the time-of-flight measurement. The laser propagates in the x direction, creating the horizontal streak in the x,y plot. Numerically labeled peaks are described in the text. Note that the x,y histogram lacks much of detail visible in the y,z histogram because it is a projection down the time-of-flight axis. In this view, $D_{2}^{+}$ and all other ions are visible, so the total number of counts is greater and the finer details lose prominence.
intense along this axis. Thus, ionization occurs along a significant portion of the x axis. When viewing y and z momentum, (looking down the x axis), these counts all project to the same region. This is also a contributing factor to peak 3, and illustrates an important detail; the finite size of the interaction region blurs out the signal and adds extraneous false signals. Later, I will discuss ways to remove this artifact.

Peak 4, extending out to roughly 37 au, or 5.1 eV, clearly favors molecules that are perpendicular to the laser polarization (see figure 4.5 for a clearer graphic of the angular distribution). This suggests \( \pi \) symmetry of the electronic state. Also, the high kinetic energy suggests that these ions are due to the 43 eV photons and not leaking lower harmonics. The \( 2p\pi_u \) state lies near 43 eV, and no other nearby state has the required symmetry. Checking the expected dissociation energy at the equilibrium internuclear separation of 1.4 au, we find an expected KER of 10.4 eV, or 5.2 eV. Thus, peak 4 consists of ions that were projected into the intermediate \( 2p\pi_u \) state but did not undergo Coulomb explosion. Although these counts do not contribute to coincidence measurements (as the neutral D eludes detection), they still provide a valuable signal that shall prove interesting in analysis.

With these background counts in mind, I turn now to the first main signal. Coincidences that came from the same molecule may be filtered out from false coincidences by requiring momentum conservation using the method described in section 3. I filtered on this channel using a combination of Cobold scripting and C++ modification of Cobold’s data analysis routines. The PIPICO channel is also shown in this section in figure 4.2. Although there is a small chance that two ions from separate molecules will show up in such a way that they appear to satisfy momentum conservation, this type of event is uncorrelated to any particular energy or orientation and thus will show up as white noise. In order to further reduce the number of false coincidences, count rate is kept to
Figure 4.2: **A**: The PIPICO line gated using a momentum conservation filter for D$^+$ + D$^+$. **B**: Kinetic energy of pairs of D$^+$ fragments coming from the same molecule.

well under one event per shot.

Figure 4.2 shows the total ionic kinetic energy of these coincidences plotted against pump-probe time delay. Pump-probe overlap, called time zero, is assumed to be where the KER reaches a maximum. As the probe pulse duration is 30 fs, counts occurring before this time are likely created by the leading edge of this pulse. The salient feature is the total energy as a function of time. The black circles follow the mean energy at each delay. Any bins with fewer than 3 counts were set to zero so that background noise was not included in the mean. Also, as this channel is known to come from a Coulomb explosion, which cannot generate low KER counts, any bins with KER<6 eV have been set to zero as well.

Observation of the angular distribution, shown in figure 4.3 indicates that the 2p$\pi_u$ state contributes most to the coincidence spectra, as ionization clearly favors molecules oriented perpendicular to the laser polarization axis. The time delay dependence of the KER channel also shows a characteristic structure. At short delays, the probe pulse
projects $D_2^+$ into the highly repulsive $1/r$ curve almost instantaneously, generating a high KER. At longer delays, the presence of the electron mediates the internuclear repulsion, slowing the nuclear motion. Thus, figure 4.2 shows the qualitatively expected distribution.

The KER measurement is spread out over several eV, but it is important to consider the source of this width. Although it may look like the result of finite energy resolution, the most significant contributing factor is much more fundamental. In its ground state, $D_2$ is spread out in internuclear distance. The nuclear wave packet is spread out over a finite region called the Franck-Condon region. A simple way to imagine this spread is to
consider a measurement of internuclear distance; while the most likely single value is 1.4 au, a range of values around 1.4 au are highly likely as well. Exciting neutral D$_2$ into a dissociating state measures this internuclear separation, because we can extract $r$ from the KER and the potential curve along which it fragments. As there is a fundamental spread in $r$, there is a large uncertainty in the KER as well. In section 5.2, I address this aspect quantitatively using TISE simulations.

Although the width of the Frank-Condon region contributes largely to the spread in KER, other confounding experimental factors introduce further uncertainty. First, molecules in the gas target have a thermal velocity distribution that contributes an extra energy $3/2k_bT$. At room temperature, the mean kinetic energy is $3/2k_b \times (300 \text{ Kelvin}) \approx 0.039 \text{ eV}$, which randomly changes the true momenta. More important is the spatial spread of the gas in the chamber. Figure 4.1 shows that counts come from a large region in the chamber, as evidenced by the visibility of the laser propagation length. Using a strict momentum conservation filter prevents any molecules that were ionized outside origin from appearing in the data, but the low statistics of the experiment prevent the use of such a strict filter. In order to maximize the number of counts, I used the condition that momentum must be conserved to within 6 au in the $z$ direction, 5.5 au in the $y$ direction and 20 au in the $x$ direction where the laser propagation introduces substantial spread. In a single ion experiment, this spread also adds a fundamental limit to resolution, but in a coincidence experiment, enough information should be present to reconstruct the initial position of each molecule. As most experiments use a supersonic jet, we have not before corrected for the finite size of the interaction region.
4.3 Correction Terms for the Momentum Spectra

In the interest of brevity, I present the equations with limited derivation. The formulas come from the relations between directly measured quantities like detector coordinate and time-of-flight and physical quantities such as momentum and initial position. If particle \( i \) starts with an initial momentum \( \mathbf{p}_i \) and an initial position \( \mathbf{r} \), Colbold will calculate the following incorrect momenta \( \tilde{\mathbf{p}}_i \):

\[
\tilde{p}_{xi} = p_{xi} + \frac{mr_x}{t_i} \quad (4.1)
\]

\[
\tilde{p}_{yi} = p_{yi} + \frac{mr_y}{t_i} \quad (4.2)
\]

\[
\tilde{p}_{zi} = \frac{d_a m}{t_i} - \frac{E Et_i}{2} = p_{zi} \frac{d_a}{d_a + r_z} - \frac{r_z E E t_i}{2(d_a + r_z) t_i} \quad (4.3)
\]

The second half of equation 4.3 can be obtained from the first by substituting equation 3.3 for \( t_i \) and then eliminating as many radical terms as possible. Notice that as \( d_a, m, t_i \) and \( E \) are all known, these formulas may be easily inverted to find the true momenta once \( \mathbf{r} \) is known. To find the initial position of the molecule \( \mathbf{r} \), add expressions for \( \tilde{\mathbf{p}}_1 \) and \( \tilde{\mathbf{p}}_2 \). As we can then use \( \mathbf{p}_1 + \mathbf{p}_2 = 0 \) (up to a small thermal kinetic energy), the sums yield \( \mathbf{r} \):

\[
r_x = \frac{(\tilde{p}_{x1} + \tilde{p}_{x2}) t_1 t_2}{m(t_1 + t_2)} \quad (4.4)
\]

\[
r_y = \frac{(\tilde{p}_{y1} + \tilde{p}_{y2}) t_1 t_2}{m(t_1 + t_2)} \quad (4.5)
\]
These give \( r \) in terms of known quantities, enabling reconstruction of the position of each coincidence count. The actual momenta can then be given as a function of measured quantities and \( \tilde{p}_i \) (which is also a function of measured quantities):

\[
p_{xi} = \tilde{p}_{zi} - \frac{mr_x}{t_i}
\]

(4.7)

\[
p_{yi} = \tilde{p}_{yi} - \frac{mr_y}{t_i}
\]

(4.8)

\[
p_{zi} = \tilde{p}_{zi} \left( \frac{d_a + r_z}{d_a} \right) + \frac{r_z E e}{2d_a t_i}
\]

(4.9)

By modifying the Cobold data analysis software in Visual C++, I added these parameters into the analysis routine. Although visual inspection scarcely presents any significant difference between corrected and uncorrected spectra, the mean changes noticeably. Figure 4.4 shows the mean KER calculated both with and without the correction. As shall be seen in section 5.2, the correction brings data into closer agreement with theory.

I employed several diagnostics to make sure the correction worked properly and improved analysis quality. First, I plotted the momentum sum \( p_1 + p_2 \) to ensure that it was indeed zero. This not only verifies correctness of the above formulas, but also checks consistency with the iterative algorithm Cobold uses to calculate \( p_z \) from the ion time-of-flight. An algorithm is used instead of an analytic expression because, if a drift region is present in the ion path (a region void of an accelerating electric field),
Figure 4.4: Mean kinetic energy release versus time delay from unprocessed data and from the position-corrected KER.
the calculation becomes more difficult. Next, I calculated the standard deviation in energy for the corrected and raw data. As the KER is convolved with a spatial spread of the gas, reconstructing initial position of the molecules should narrow the KER. However, the width clearly grows slightly in the processed data. The standard deviation increases by 11% on average. Such a change has eluded explanation, and more analysis will be necessary to confirm the method. However, the correction changes the mean in the correct direction, as shown in figure 4.4. As this method produces the expected correction, it will be used for further analysis.

4.4 Further Study of Angular Distributions

So far, analysis has shown that the 43 eV harmonics couple mostly to the $2p\pi_u$ state. Many other states reside nearby, and hence we should expect them to appear in the data as well. Disregarding doubly-excited states, which have very low cross sections, the $2s\sigma_g$ lies closest to the $2p\pi_u$ in the Franck-Condon region. Although a state with sigma symmetry is not discernible behind the main channel, time resolution helps to bring out more detail. Presence of a strong IR field on top of the XUV could enhance coupling into other states, and in particular, XUV + IR absorption may transition into the $2s\sigma_g$ potential. This phenomenon would manifest itself as a change in the angular distribution near zero delay. Figure 4.5 shows polar plots at several delays. A subtle but clear change in the shape of the angular distribution occurs near time zero. This shows that an IR field can enhance coupling into other states. The data thus show that we can create a coherent superposition of multiple states in a controlled way.

Next, I turn to measurement of electronic spectra. Perhaps the most interesting counts are the electron-D$^+$ coincidences, which are shown in figure 4.6. Here, the ionic kinetic energy has been doubled to account for the other half of the molecule. Many
Figure 4.5: Polar plots of all ions for several time delays. The left plot shows angular distribution away from time zero and the right shows the same near time zero. The radial direction gives the number of counts and zero degrees is parallel to the laser polarization axis (red arrow). To remove counts from HD and the $2p\sigma_u$ (peaks 1 and 2 in figure 4.1), data have been projected down the x-axis and the positive $p_z$ side has been mirrored to replace the negative $p_z$ region. Counts are then only taken in a ring from 24.5 au to 50 au. For clarity, error bars are omitted. They are approximately ±50 counts in the radial direction.
of the peaks displayed can be identified as false coincidences or artificial counts. False
electron-ion coincidences prove more difficult to remove because unlike ions, electron
time-of-flight filtering provides no information about the parent molecule. As a result,
many of the electrons displayed originate from $\text{D}_2^+$ or even other common atmospheric
gases. Among the many details visible, peak 5 shows strong correlation that would not
arise from a false coincidence. The downward slope is indicative of energy conservation;
if the electron leaves with a large kinetic energy, it does so at the expense of some nuclear
kinetic energy and vice versa.

To further identify the peak, I placed a diagonal filter on the line and observed the
ionic momentum distribution (which again required lower-level modification of Cobold).
The spectra (not pictured) shows the same characteristic orthogonal dissociation
depicted in figure 4.1. There is also a large contribution from background counts. The
peak itself matches quite well with the form expected from 43 eV ionization into the 2pπ_u potential. To see this correspondence, consider the total energy along the line in figure 4.6, which remains constant and is approximately equal to 13.9 eV. This value can be reproduced theoretically by considering the energy levels of deuterium. The dissociation energy of D_2 is 4.71 eV \[21\] and the ionization potential of D is 13.61 eV. The sum, 18.32 eV, is required to create dissociated D_2^+, or a D and D^+. In the dissociation limit, D_2^+ in the 2pπ_u state becomes a bare deuteron and an n = 2 excited D. Excitation to the n = 2 level takes 13.61 \times (1 − 1/2^2) = 10.21 eV. These three binding energies do not show up in detected KER, but any energy in excess of their sum goes into electronic and ionic KER. Assuming 43 eV excitation, the expected total KER is 43 − 4.71 − 13.61 − 10.21 = 14.47 eV. This is in good agreement with the observed value of 13.9 eV, but suggests that the harmonics may have been slightly below 43 eV. This is wholly possible, as the phase matching condition is highly sensitive to the exact argon pressure used\[22\].

The length of peak 5 is indicative of the width in the Franck-Condon region and the coupling into the 2pπ_u state. The ion and electron KER range over a roughly 6 eV wide range. To estimate this width from prior knowledge, consider the 2pπ_u state at the edges of the Franck-Condon region. Using the width depicted in figure 1.1, the upper energy on the curve is 42 eV and the lower energy on the 35 eV. The difference 42 − 35 = 7 eV, is, roughly speaking, the span of possible energies at which the nuclear wave packet may start, and also corresponds to the range of possible nuclear kinetic energies. These calculations demonstrate that peak 5 also comes from the 2pπ_u curve, and provide example on the usefulness of electron-ion coincidences.

Finally, I searched for indications that the 2pπ_u-3dσ_g crossing created observable effects. At roughly 5.5 au internuclear distance, the 2pπ_u and 3dσ_g curves cross. These
curves should be accessible to each other through one-photon absorption, as they change in parity and angular momentum. The probe pulse and the residual IR light in the XUV line could potentially excite this transition. The angular distribution of the counts is determined by the first event only, so this facet is unlikely to show crossing dynamics. However, the absorption of a single IR photon should manifest itself in a 1.6 eV higher KER (or a 0.8 eV higher kinetic energy of the ionized fragment detected). Study of the single ion kinetic energy spectra as a function of time delay has not yet shown any additional features or shifting of peaks at zero pump-probe delay. In coincidence spectra, where the full 1.6 eV difference could be seen, data can be carefully filtered and the spatial spread correction can be applied, I will revisit this possibility.

5 Theoretical Analysis and Simulation

5.1 The Leapfrog Integration Method

The exponentially increasing power of modern computers often ameliorates the difficulty of working with analytically intractable problems. Very sophisticated methods exist for both finding eigenstates of the TISE and propagating arbitrary states in any given potential. Below, I describe a relatively simple second order, symplectic split-step method called the leapfrog integration method[23]. To avoid computing with small numbers that can lead to rounding errors, consider the time dependent Schrödinger equation in atomic units:

\[
\frac{i}{\mu} \frac{\partial \psi(t, x)}{\partial t} = -\frac{1}{2\mu} \frac{\partial^2 \psi(t, x)}{\partial x^2} + V(x)\psi(t, x)
\]

(5.1)

Where \( \mu \approx 1835 \) au is the reduced mass of D$_2$ and \( V(x) \) is the Born-Oppenheimer
potential we wish to simulate. Notice that, in terms of operators, the equation gives an 
operator for time evolution as a function of a kinetic energy operator and a potential 
energy operator. As a second order differential equation, the time evolution operator is 
non-trivial. However, treating these operators in pairs greatly simplifies the form of the 
time evolution operator. To do so, first neglect the kinetic energy term:

\[
\frac{i}{\hbar} \frac{\partial \psi(t, x)}{\partial t} = V(x) \psi(t, x) 
\]  

(5.2)

As \( V \) does not depend on time, the solution takes the form of a simple exponential:

\[
\psi(x, t + \Delta t) = \psi(x, t) e^{-iV(x)\Delta t} 
\]  

(5.3)

The kinetic energy term written below remains a second order differential equation:

\[
\frac{i}{\hbar} \frac{\partial \psi}{\partial t} = -\frac{1}{2\mu} \frac{\partial^2 \psi}{\partial x^2} 
\]  

(5.4)

Despite the apparent complexity, the absence of a potential term enables significant 
simplification. The Fourier transform, defined below, helps make this important step:

\[
\hat{F}[f(t, x)] \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t, x) e^{-ikx} dx 
\]  

(5.5)

Using the product rule of differentiation\(^3\), it is not difficult to show that equation 
5.5 converts spatial derivatives to powers of \( ik \). The Fourier transform also commutes 
with time derivatives, enabling equation 5.4 to take the form:

\(^3\)The proof requires that \( f(t, x) \) is a square-integrable function that vanishes at \(-\infty\) and \( \infty \), which 
is always the case for a physical wave function. In practical computation, one must use a finite grid, so 
this constraint requires that the magnitude of \( \psi \) is small at the end points. I monitor all simulations to 
make sure the requirement stays satisfied throughout each run.
Once again, the equation reduces to an eigenvalue equation of the time derivative operator, which has the familiar solution:

\[ \hat{F}[\psi](k, t + \Delta t) = \hat{F}[\psi](k, t)e^{-ik^2\Delta t/2\mu} \]  

or

\[ \psi \rightarrow \hat{F}^{-1}[\hat{F}[\psi](k, t)e^{-ik^2\Delta t/2\mu}] \]  

Equations 5.3 and 5.8 give two simple time step operators, one that acts in real space and one that acts in reciprocal space. Although the integral 5.5 may be difficult to solve in general, the fast Fourier transform takes a discreet grid of N values and returns the Fourier components in \( O(N \text{Log}N) \) computations. Thus, we can propagate any wave function in a static potential by discretizing \( \psi \) onto a grid and iteratively acting the potential and kinetic energy operators. It turns out that this technique is a first order algorithm, and can be made into a second order algorithm by splitting the potential operator into two steps[24], so that the full algorithm runs by cyclically acting the following three operators:

\[ \psi \rightarrow e^{-iV(x)\Delta t/2} \psi \]  

\[ \psi \rightarrow \hat{F}^{-1}[\hat{F}[\psi](k, t)e^{-ik^2\Delta t/2\mu}] \]
\[ \psi(t + \Delta t, x) = e^{-iV(x)\Delta t/2}\psi \] (5.11)

The modification is an instance of the leapfrog integration method, which is symplectic. The details of this technique are given in [25], as well as the Feynman Lectures in Physics, Volume I section 9.6.

I checked the validity of this method several ways. First, eigenstates propagated in their potentials remained constant up to a complex multiplicative factor, as expected from separation of variables in solving the time dependent Schrödinger equation. Next, using the correspondence principle equation:

\[ m \frac{\partial^2 \langle x \rangle}{\partial t^2} = -\frac{\partial V}{\partial x} \] (5.12)

I compared several classical calculations to the quantum trajectories of the expectation value of the particle’s position. These also yielded excellent agreement.

Simulations require potential curves and an initial nuclear wave packet. Potential curves were provided by Alicia Palacios of the research group of Fernando Martín in the Department of Chemistry at the Autonomous University of Madrid. These analytic calculations are unevenly spaced in the internuclear coordinate, as the curves are nearly flat at large internuclear distance but highly curved near the Franck-Condon region. I use cubic spline interpolation to fill in the missing values. I chose the spatial spacing of the computation grid by considering the KER. A Coulomb explosion in D₂ can release as much as 20 eV. In order to avoid aliasing of the nuclear wave function, the grid should oversample a plane wave with this energy. The wavelength of a single deuteron travelling

\text{meaning that the algorithm conserves area in phase space. This conservation is exact in classical and quantum mechanics, as demonstrated in Liouville’s theorem}
with a kinetic energy of 19.58 eV (the KER from equilibrium internuclear separation along the 1/r curve) has a wavelength of 0.12 au. Consequently, I used a grid spacing of 0.01 au, which maintained adequate sampling of simulated wave functions while keeping computational costs to a reasonable level (about 1 hour per simulation).

In order to estimate the nuclear eigenfunction of ground state D$_2$, I used the vibration frequency of D$_2$, $\omega = 3115.50$ cm$^{-1}$ given in the table for constants of diatomic molecules compiled by the National Institute of Science and Technology$^5$. I approximated the ground state as an eigenfunction of the simple harmonic oscillator potential:

$$\psi_0(x) = \left(\frac{m\omega}{\pi}\right)^{1/4} e^{-m\omega x^2/2} \quad (5.13)$$

The value for $\omega_e$, along with a small anharmonic term $\omega_e X_e$ gives the frequency in terms of parameters in the Morse potential. The Morse potential is a common function used to approximate a diatomic potential. $\omega_e X_e$ accounts for the asymmetry of this potential, which deviates from a parabolic well far away from equilibrium. As $\omega_e X_e$ is two orders of magnitude smaller than $\omega_e$ and I only use the ground state eigenfunction, I treat it as a negligible perturbation.

5.2 Theoretical Results

I simulate the experiment by propagating the ground state eigenfunction of D$_2$ in the 2$p\pi_u$ potential in 12 fs increments (the experimental time step), and then propagating it on the 1/r curve. To limit computational time and grid size, the simulation stops along the 1/r curve at 190 au (distance), and then adds a correction of about 100 meV to account for the additional energy it would gain from 190 au to $\infty$. In order to visualize

the kinetic energy, I use the momentum space analog of the probability density equation:

\[ P_{k_1<k<k_2} = \frac{1}{k_2} \int_{k_1}^{k_2} |\tilde{\psi}(k)|^2 \, dk \quad (5.14) \]

\[ P_{k_1<k<k_2} \] gives the probability of measuring the momentum to be between \( k_1 \) and \( k_2 \), which can easily be converted to the probability of measuring a given KER.

The nearest curve below 43 eV is actually the \( 2sσ_g \). Although this state would not exhibit the angular distribution observed in figure 4.3, I simulated it as well for comparison. It provides both a confirmation that the \( 2pπ_u \) state contributes most to the signal and a measure of how well these Coulomb explosion data can image and distinguish potential curves.

Figures 5.1 through 5.8 show a comparison between numerical calculations and experiment. Figures 5.1 and 5.5 show the KER as a function of time delay as plotted in figure 4.2. The mean KER is plotted at every time step that was measured. The remaining plots show one-dimensional slices of theory and experiment. As calculations do not attempt to estimate the transition probabilities from the intermediate state to the doubly-ionized state, I normalized each theoretical curve to the measured total count at each time step.

Data show excellent agreement with the \( 2pπ_u \) potential, and poor agreement with the \( 2sσ_g \) potential. Other curves in the vicinity of 43 eV such as the \( 3dσ_g \) and the \( 3pσ_u \) diverge even more from experiment, as they have much higher energies in the Franck-Condon region and also go to the \( n = 2 \) dissociation limit.

Several discrepancies are notable for the information they contain. First, notice that simulation completely fails to predict the KER at time zero. This comes from the fact that simulation neglect transition probabilities. At time zero, where the nuclear
Figure 5.1: Measured and simulated KER, numerically propagated along the $2p\pi_u$ curve. Color axis represents the probability as calculated using equation 5.14.
Figure 5.2: Measured and simulated KER, numerically propagated along the $2p\pi_u$ curve. Error bars only account for statistical counting error in the histogram.
Figure 5.3: Measured and simulated KER, numerically propagated along the $2p\pi_u$ curve. Error bars only account for statistical counting error in the histogram.
Figure 5.4: Measured and simulated KER, numerically propagated along the $2p\pi_u$ curve. Error bars only account for statistical counting error in the histogram.
Figure 5.5: Measured and simulated KER, numerically propagated along the $2s\sigma_g$ curve. Color axis represents the probability as calculated using equation 5.14.
Figure 5.6: Measured and simulated KER, numerically propagated along the $2s\sigma_g$ curve. Error bars only account for statistical counting error in the histogram.
Figure 5.7: Measured and simulated KER, numerically propagated along the $2s\sigma_g$ curve. Error bars only account for statistical counting error in the histogram.
Figure 5.8: Measured and simulated KER, numerically propagated along the $2s\sigma_g$ curve. Error bars only account for statistical counting error in the histogram.
wave function still resides in the Franck-Condon region, it takes 8 photons to span the gap between the $2p\pi_u$ and the double-continuum. This makes double ionization at this coordinate highly unlikely. Instead, the signal most likely arises from the tail end of the probe pulse ionizing the molecule at a later time when double ionization requires fewer IR photons. A tail end ionization also explains the lower number of counts observed at time zero.

The second consistent deviation has several possible explanations. Figure 5.1 displays measured KER residing above the peak calculated probability. In the one dimensional plots of figures 5.2, 5.3 and 5.4, the bias is clearly due to unpredicted extra counts on the high KER side of the distribution. Too see this source, notice that at most delays, the left-hand side of the curve matches quite well, but more counts consistently appear on the right-hand side. The first possible explanation is that the spatial spread of gas inside the chamber is spreading the energies out. This factor would tend to artificially increase the calculated KER of counts originating far from the origin, and if the correction has not been implemented properly, the spread would persist.

If we accept that the observed KER corresponds to the actual dissociation energy, a physical explanation is necessary to explain the current theory’s discrepancy. Consideration of the electron energy spectrum in figure 4.6 rules out excess energy due to the ion recoil during ionization, as this energy is expected to be on the order of $10^{-3}$ eV. Stark shifts due to the laser pulse could potentially broaden the $2p\pi_u$ level, allowing absorption of more energy into the nuclear eigenstate. The extreme ultraviolet light used will not cause such issues[27], but the absence of the aluminum filter means enough collinear IR light remains to potentially induce broadening[28]. This shift can be estimated by considering the stark shift of a single hydrogen atom in the n=2 excited state. From degenerate perturbation theory, this energy can be calculated to find $E^{(1)} = 3eEa_0$. 
At a laser intensity of $4 \times 10^{11}$ W/cm$^2$, this energy level shift comes out to 280 meV, which could be visible in the KER but does not quite predict the offset seen at many delays. Nevertheless, the order of magnitude of $E^{(1)}$ suggests that more careful analysis is necessary to conclusively rule out the effect.

Three anticipated effects also reproduce the observed upward shift in the KER spectrum. Firstly, analysis previously suggested that the $2s\sigma_g$ state contributed to the single ion kinetic energy. This state should therefore appear in the Coulomb explosion counts as well. Simulation of the $2s\sigma_g$ shows that, although the overall structure does not agree with experiment, optimal theory might include contributions from both states, which could shift up the KER. Secondly, at larger internuclear distances, it is possible to couple into the $2s\sigma_g$ state from the $2p\pi_u$ state with one IR photon, which would have a similar affect. Lastly, in the $2p\pi_u$ state, D$_2$ dissociates very rapidly, so that by 20 fs, the nuclear wave packet is well past the crossing between the $2p\pi_u$ and the $3d\sigma_g$. This means that when it travels through the crossing, the IR is still present. If a single IR photon couples the molecules into the $3d\sigma_g$, the event would manifest itself as an additional 1.6 eV KER, and would broaden the distribution to higher energies, just as observed. This transition would be the first step toward coherent control through a crossing. A statistical analysis would also be needed to surmise the significance of the feature under consideration. I discuss future ways to study the possibility in section 6.

6 Discussion and Conclusion

Since its quite recent invention, COLTRIMS has spawned a whole new type of measurement in atomic, molecular and optical physics. The ability to measure three dimensional dynamics of single chemical events opens an unprecedented view into the chemical
world. Coupled with ultrafast lasers capable of imaging some of the most ephemeral events nature has to offer, these technologies are poised to make many more important discoveries. In this work, these advances have enabled observation and measurement of the $2p\pi_u$ state, which had until now remained unmeasured. Through careful analysis and precise filtering of the huge amount of data COLTRIMS generates, many single ion, ion pair coincidence and electron-ion coincidence detections have been both identified and theoretically explained.

Although scientists have used Coulomb explosion imaging for several decades, the full capabilities of the technique have yet to be tapped. This is due to the extreme demands it places on the experimentalist. After exciting the state of interest, which may itself have a low cross section, a second pulse must project into at least the double continuum. Depending on the number of electrons involved in the molecular bonds, three or more ionizations may be required to create a true Coulomb explosion free from distortion[8]. After these rare events have been created, only a coincidence measurement capable of recording three-dimensional momenta can hope to extract the signal. Even in the double ionization regime, experiments remain a significant challenge. This work is one of the first to implement time resolved Coulomb explosion imaging with high harmonic generation in COLTRIMS. Here, the ability to detect electrons in coincidence adds depth to the measurement. Furthermore, the wide range of energies, the fine tuning phase matching provides and the transient pulse duration of high harmonic generation lends itself well to Coulomb explosion imaging of unknown molecular potentials. In some ways, the technique scales well with larger molecules, as heavier nuclei tend to have a narrower width in the Franck-Condon region (see equation 5.13), and thus a narrower KER band.

As for D$_2$, the measured Coulomb explosion energy agrees well with the analytically
calculated $2p\pi_u$ curve, as evidenced by TISE simulation of the nuclear wave packet. Inspection of the ionic angular distribution and electron-ion coincidences confirm population of the $2p\pi_u$ state. As discussed in section 1.1, coherent population of the $2p\pi_u$ state opens the door for many more experiments involving curve crossings and coherent control. The former has great importance in modern chemistry, and being able to explore it in a simple system like D$_2$ provides a stepping stone to more complicated and chemically interesting systems. On our experimental apparatus, ozone is an area of active study. The dynamic high energies that drive creation of ozone in the upper atmosphere can be studied using XUV pump-probe spectroscopy and Coulomb explosion imaging. Many techniques developed here could have applications in these experiments. Furthermore, ozone exhibits conical intersections, which parallel curve crossings in D$_2$. The concurrence of these experiments provides a good opportunity for shared insight between the two projects. Finally, I have been involved in study of the argon dimer, an experiment that also relies on Coulomb explosion for investigation of certain theoretical models. Returning to these data with the tools developed here could shed new light on observation. In particular, it may be relatively straightforward to image the Van der Waals forces within the dimer.

Coherent control also has interesting implications. The ability to control a molecular state during its evolution using ultrafast lasers opens the possibility of controlling chemical reactions in unprecedented ways. Pulse shaping, harmonic light, polarization states and multiple-pulse experiments all provide a host of laser parameters that could be manipulated and optimized to control molecular states. This work shows that D$_2$ provides a useful and accessible platform for exploring methods of molecular control. 43 eV high harmonic light populates the $2p\pi_u$ state, and an additional IR field can simultaneously couple into other states. A possibility remains that such control has already
been observed via coupling between the $2p\pi_u$ and $3d\sigma_g$ states. In the Born-Oppenheimer approximation, it should be relatively straightforward to simulate this mechanism and compare it to experiment. Careful analysis of the data to remove systematic error and focus in on the counts of interest enabled a glimpse this possibility, but more work will be necessary to determine the true source of the signal and its statistical significance.

$D_2$ provides an elegant but nevertheless intricate testing ground for exploring and controlling molecular dynamics. The coherently controlled population of its highly excited states lays the foundation for many possible further investigations. Simultaneously sending two nuclear wave packets through a curve crossing and coupling the two states optically could reveal novel and even non Born-Oppenheimer dynamics. Further experiments could use an aluminum filter to remove IR from the XUV line, allowing even more control over the 800 nm field as well as offering test of several hypotheses put forward thus far. Another experimental parameter that could make following experiments fruitful is laser polarization; adding an IR field rotated $90^\circ$ with respect to the XUV should suppress transition from the $2p\pi_u$ to the $3d\sigma_g$, as molecules in the $2p\pi_u$ state have already been preferentially selected with orthogonal orientation. Studying polarization dependence could offer an interesting follow-up experiment for both distinguishing various mechanisms and inducing the desired excitations. Careful development of the theoretical simulation not only imaged the $2p\pi_u$ state, but also gave a careful measure of what other effects could be playing a role. As a result, simulation becomes a powerful tool in imaging final states of the molecule and discerning novel effects.
A Atomic Units: A Brief Summary

Ubiquitous in AMO physics, atomic units not only simplify the form of many fundamental equations, but also reduce numerical values to quantities that are within a few orders of magnitude of unity. By defining the mass of the electron $m_e$, the reduced Planck’s constant $\hbar$, the Coulomb force constant $1/4\pi\epsilon_0$ and the elementary charge $e$ as unity, all other physical quantities are determined. While atomic units produce more manageable numbers in molecular calculations, one convention introduces ambiguity and can sometimes lead to confusion; instead of labeling different quantities with different letters (such as ‘m’ for meters, ‘C’ for Coulombs etc.), all values receive the labeling ’au’. Therefore, the number must be assigned its meaning by context. In order to eliminate this potential source of confusion, I accompany some values with their physical meaning in parentheses. For example, the equilibrium internuclear distance in D$_2$ would be given as 1.401 au (distance).

The following table shows the important quantities in atomic units and in a more familiar system.
The approximate size of a hydrogen atom

Hartree energy \( E_H = \frac{2}{e^2} \hbar / c \alpha \) * 27.21 eV

Potential energy of ground state hydrogen

\( \hbar / E_H \) ~ orbital period of an electron in hydrogen

\( \alpha c \) ** ~ velocity of an electron in hydrogen

Momentum of a ground state electron in H

** \( \alpha = e^2 / 4\pi \epsilon_0 \hbar c \approx 1/137 \). The fine structure constant, a unitless constant which describes the strength of the electromagnetic interaction in quantum electrodynamics.

References


