Velocity Map Imaging of the Single Ionization of Molecular Iodine

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Dale L. Smith, Ph.D.
University of Connecticut, 2018

ABSTRACT

Single ionization in molecules is a critical first step in many higher order processes such as high harmonic generation, however it remains poorly understood even in simple diatomic systems. Ultrafast laser systems with pulse durations in the femtosecond (1 fs = 10^{-15} s) range allow for the study of molecular systems while freezing out the vibrational and rotational degrees of freedom. Velocity map imaging of the ion fragments produced from dissociation after single ionization provide access to the kinetic energy released (KER) during the dissociation over the entire fragment distribution. In this thesis, I will present two experimental studies of the single ionization of diatomic iodine. From a long wavelength scan spanning 400-800 nm the single ionization of I\(_2\) is found to have a contribution from deeply bound 5s electrons. In the I\(^+\) + I\(^-\) dissociation channel much of the measured KER is found to be inconsistent with ionization from the X, A, and B states of I\(_2^+\) which implies ionization from deeper orbitals. A pump-probe Fourier transform technique shows that X and A state modulation is only seen for low KER dissociation through the B state. In a narrow wavelength scan of the single ionization of I\(_2\) around the 530 nm one-photon B state resonance a strong enhancement of up to 98% in the branching ratio is found for inner orbital ionization while a weaker peak in the outer orbital ionization is found to occur at a
slightly different wavelength. The branching ratio from double ionization into an excited state of $I_2^{2+}$ as a function of wavelength closely matches the branching ratio of single ionization of deep orbitals, implying that excitation of molecular ions generally comes about through inner orbital ionization. Current molecular ionization theory, such as tunneling ionization theory, suggests that the least bound outer electrons will play a significant role in the single ionization of molecules. These findings are inconsistent with such ionization theories.
Velocity Map Imaging of the Single Ionization of Molecular Iodine

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B.S. Bridgewater State University, 2011
M.S. University of Connecticut, 2014

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Requirements for the Degree of
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at the
University of Connecticut

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Velocity Map Imaging of the Single Ionization of Molecular Iodine

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My path in physics started as an undergraduate at Bridgewater State University where I met my advisor and friend Dr. Edward Deveney. He has encouraged me and helped me in so many ways that I can never thank him enough. Through his guidance I made it to the University of Connecticut as a Ph. D. candidate and he continues to mentor me as I move on beyond graduate school. Upon entering graduate school I was given an advisor, Dr. Richard Jones. Dr. Jones helped me to understand how to teach upper level undergraduate courses and expertly guided me to find my major advisors with whom I would finish my Ph. D.

Dr. George Gibson has not only been an excellent research advisor helping me to understand how to look at experimental data and find new meaning in it, but he has also maintained my interest in many varied things from music to electronics. He is always willing to have a discussion about how to present at a conference or how to build a list of key words for journal writing but in addition to those things he is also very willing to discuss how to move a piano or the finer points of raising my son. Dr. Gibson has been not only an outstanding advisor he has also been a good friend over the course of this thesis.

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Chapter 1

Introduction

For many decades atoms and molecules have been intensively studied by various means. Many of these investigations have involved one form of spectroscopy or another and the contents of this thesis is no different. Perhaps it is not apparent why atoms and molecules have garnered so much attention. While made of still smaller constituents, protons, neutron, and electrons, it is the atom and the molecule, in their particular configuration of these more basic building blocks, which define the world we live in and understanding their make-up and the interactions between different species helps us to understand and manipulate our world.

Recently, high intensity short pulse lasers have been developed which allow us to probe atoms and molecules in new and interesting ways. Although it is true that such high intensity light with ultrashort pulse duration does not exist in the world around us, it does give us access to the structure and dynamics of atoms and molecules on their time scale. For example, molecular vibrations occur on the time scale of tens to hundreds of femtoseconds (1fs = $10^{-15}s$). Since the pulse duration of the laser can be made shorter than this time
interval we can study the dynamics of the system as the system evolves.

1.1 Time Scales

The study of fast phenomena can be dated back to the experiments of Eadweard Muybridge in the late nineteenth century. Muybridge used a series of photographs of a horse trotting to investigate the motion. This allowed him to slow down the motion of the horse enough to prove that, in gallop, all four of the horses’ legs completely leave the ground. For many years a debate over the galloping horse lacked a convincing argument since the motion was too fast for the human eye to see. The invention of the camera allowed for such photos to be taken. Further evolution of the camera allowed for even faster shutter times and shorter exposures. In the twentieth century, Harold E. Edgerton used cameras with a fast shutter time and a strobe light to slow down the action of fast everyday objects, such as a bullet or a drop of milk, to expose the dynamics of events which are much too fast for the eye to perceive. Edgerton’s rapatronic camera was used to slow down the motion of explosions and the detonation of atomic bombs. These cameras could capture motion which takes place on the order of tens of nanoseconds ($1\text{ns} = 10^{-9}\text{s}$).

More recently femtosecond pulse lasers have been used to slow down the motion of atoms and molecules so that we may study the processes of ionization and dissociation. Since molecular vibrations of heavy molecules, such as diatomic iodine, occur on the order of hundreds of femtoseconds we can use the laser to take snap shots of the molecular vibrations with the duration of the pulse acting as the shutter. As with Muybridge’s photographs of the moving horse, these molecular images may be strung together at different time delays throughout the molecular motion to allow us to analyze the kinematics and dynamics
of the motion. Fig. 1.1.1 presents an overview of the time scales used in this thesis and those mentioned in the paragraph above.

1.2 Fast Pulse Lasers

The generation of ultrashort, ultrahigh-intensity laser pulses began with the development of the saturable absorber using a bleachable dye in a regenerative oscillator [1]. The generation of short pulses was then dramatically improved with the self-mode-locked Ti:Sapphire oscillator [2]. This laser oscillator takes advantage of the large gain bandwidth, approximately 400 nm, of the Ti:Sapphire crystal to generate short pulse gain around 800 nm. The crystal is generally pumped with 532 nm light from a Nd:YVO$_4$ laser. The crystal is cut at Brewster’s angle and a pair of off–axis concave mirrors are used to compensate for astigmatism introduced by the crystal. In the cavity, a prism pair is used to compensate for dispersion introduced by the crystal. The Kerr effect, introduced by the crystal, results in self-focusing which leads to passive mode-locking. Mode locking is achieved through a fast saturable absorber which is generated from an aperture placed in the cavity such that, as the intensity is increased, the self-focusing results in a narrow beam waist. In Kerr lens mode-locking a perturbation in the cavity is required to start the mode-locking. This is sometimes referred to as magic mode-locking. In this configuration, pulses as short as 5.5 fs are possible. However the energy per pulse is low, on the order of nanojoules [3]. To achieve high intensity the laser pulse must be amplified.

Direct amplification of the short pulse is not possible since nonlinear effects in the optics of an amplifier would result in damage to the optics. To prevent optical damage the beam is stretched in time by adding a chirp. See Sec. 1.4. An example of a stretcher
Figure 1.1.1: (Color online) Scale showing the timing of the blink of an eye, a galloping horse, a recreation of Edgerton’s famous “milk drop” photograph, the beginning of an atomic explosion, and a femtosecond VMI image. The milk drop photograph was taken with a modern cell phone camera with a 1000 frames per second frame rate. Edgerton’s original photograph used a faster shutter speed.
Figure 1.2.1: (Color online) A pulse stretcher consisting of two gratings and two lenses with a mirror. (a) The stretcher schematically laid out. (b) The input short pulse. (c) A representation of the time stretched pulse.
is shown in Fig. 1.2.1. In this stretcher two anti-parallel gratings in combination with a telescope are used to add negative chirp to the pulse. The group delay introduced by the stretcher is given by:

\[
\phi''(\omega) = \frac{2\omega l_g}{c} \left[ 1 - \left( \frac{2\pi c}{\omega d} - \sin \gamma \right)^2 \right]^{1/2},
\]

(1.2.1)

where \(\omega\) is the angular frequency, \(l_g\) is the distance between the gratings, \(d\) is the groove density, \(c\) is the speed of light, and \(\gamma\) is the angle of incidence [3]. The B-integral, Eq. 1.2.2, gives the nonlinear contribution to the stretching. For an amplifier, the value of the B-integral should be kept below one. This requirement implies for Ti:sapphire laser amplifiers that the pulse must be stretched to at least 300 ps. The B-integral is given by:

\[
B = \frac{2\pi n}{\lambda} \int_0^z I(t,z) \, dz,
\]

(1.2.2)

where \(n\) is the refractive index and \(I(t,z)\) is the intensity of the laser pulse [3].

After the pulse is sufficiently stretched it can be amplified without damage to the optics.

As in the oscillator, Ti:sapphire is used as the gain medium due to its large saturation fluence, \(J_{SAT}\). For example, Ti:sapphire has a \(J_{SAT} = 0.88 J\) cm\(^{-2}\) while an organic dye laser has a \(J_{SAT} \approx 0.001 J\) cm\(^{-2}\). The larger fluence results in more energy per pulse after amplification. Ti:sapphire is also more desirable to use for short pulse generation since it has a longer storage time compared with dye lasers. Ti:sapphire has a storage time of \(3 \times 10^{-6}\) s while dyes have storage times of \(10^{-8}\) s to \(10^{-12}\) s. And even though dyes have a larger cross section then Ti:sapphire, greater then \(10^{-6}\) cm\(^{-2}\) for dyes compared to \(3 \times 10^{-19}\) cm\(^{-2}\) for Ti:sapphire, it turns out that the storage time and fluence have greater influence on the pulse duration [3]. There are two types of amplifiers configurations in common use; the regenerative amplifier and the multipass amplifier.
Figure 1.2.2: (Color online) A short pulse amplifier in the multipass configuration. Each pass is color coded.

The regenerative amplifier uses a cavity layout which is reminiscent of the oscillator. The low energy pulse from the oscillator is injected using a polarizer and it is then trapped in the cavity using a Pockel cell. The regenerative amplifier makes use of a low gain per pass configuration to lower the buildup of amplified spontaneous emission (ASE). After amplification another Pockel cell is switched such that the pulse exits the amplifier. Since the amplification is low, there are more passes through the gain medium required than in the multipass amplifier [3].

In the multipass amplifier, the beam makes several non-collinear passes through the gain medium. Without the cavity configuration of the regenerative amplifier, the multipass amplifier can afford much higher gain per pass with less buildup of ASE. A typical multipass amplifier is shown in Fig. 1.2.2. Both regenerative and multipass amplifiers are typically pumped by either a Nd:YAG or a Nd:YLF laser. These configurations generally run at a 1 kHz pulse rate due to switching time limitations in the Pockel cell.

The compressor essentially reverses the operation of the stretcher and recovers the short pulse duration of the input oscillator which is now greatly amplified.
1.3 Nonlinear Optics

Wavelength conversion of the 800 nm pulses provided by the Spitfire system in this thesis is accomplished using two methods; (1) Frequency doubling using second harmonic generation (SHG), (2) conversion with an Optical Parametric Amplifier (OPA).

1.3.1 Second Harmonic Generation

SHG is brought about through a nonlinear interaction in a Beta Barium Borate (BBO) crystal. SHG is an example of the nonlinearity in the expansion of the polarization

\[ P(t) = \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \cdots \]  

where \( \chi \) is the susceptibility [4]. The superscript describes the order of the susceptibility where the linear term is labeled (1), the second-order term is labeled (2), the third order term is labeled (3), etc. The first term in Eq. 1.3.1 is referred to as the linear polarization, the second term is referred to as the second-order polarization, and the third term is referred to as the third-order polarization. It is the second term which is responsible for SHG. Second-order nonlinear effects can only be achieved in a crystal which does not have an inversion symmetry, a noncentrosymmetric crystal [4]. BBO is noncentrosymmetric and therefore the second-order term does not vanish under optical interactions with BBO.

We can express the laser's electric field as

\[ E(t) = E e^{-i\omega t} + c.c. \]  

with the second term from Eq. 1.3.1 we have that
Figure 1.3.1: SHG generation and energy diagram. (a) shows the geometry of photons of frequency $\omega$ interacting with a $\chi^{(2)}$ material and producing second harmonic photons with frequency $2\omega$. (b) The energy level diagram for SHG where two photons of frequency $\omega$ are absorbed to produce a photon of frequency of $2\omega$. Adapted from [4].

\[
P^{(2)}(t) = 2\chi^{(2)} EE^* + \left( \chi^{(2)} E^2 e^{-2i\omega t} + c.c. \right)
\]

(1.3.3)

The first term does not produce an electromagnetic field. We see from the second term that indeed light of frequency $2\omega$ is produced. See Fig 1.3.1. Fig. 1.3.1 (b) shows the energy level diagram and the exchange of photons. In the process two photons of frequency $\omega$ are converted to one photon of frequency $2\omega$. The states in the diagram which are shown as dashed lines are not energy eigenstates of the system and therefore represent virtual states formed from the energy levels of the atom and the radiation field [4].

The efficiency of the SHG signal is dependent upon phase matching. The BBO must be critically phased matched between the $\omega$ and $2\omega$ signals otherwise the electric fields of the two signals will destructively interfere resulting in a loss of the SHG. Phase matching occurs when light of the two wavelengths $\omega$ and $2\omega$ travel through a medium with refractive index $n$ at the same velocity. The phase matching condition for SHG is given by [4],
\[ n(\omega_1) = n(2\omega_2) \] (1.3.4)

### 1.3.2 Optical Parametric Amplification

The second method, OPA, is used for wavelengths which are not simple multiples of the laser frequency. A single photon of frequency \( \omega_p \), where \( p \) stands for pump, along with a photon of frequency \( \omega_s \), where \( s \) stands for signal, can be split into two photons of wavelength \( \omega_s \) and \( \omega_i \), where the \( i \) stands for idler, by stimulated emission. Stimulated emission generates a photon of frequency \( \omega_s \) and an idler photon, frequency \( \omega_i \), so that energy is conserved. For parametric amplification the phase matching condition in Eq. 1.3.5 must be met.

\[ k_3 = k_1 + k_2 \] (1.3.5)

where \( k_3 \) is the \( k \)-vector for the pump, \( k_1 \) is the \( k \)-vector for the signal, and \( k_2 \) is the \( k \)-vector for the idler. Wavelength conversion of the OPA can be calculated with Eq. 1.3.6.

\[ \frac{1}{\lambda_p} = \frac{1}{\lambda_s} + \frac{1}{\lambda_i} \] (1.3.6)

where \( \lambda_j \) is the wavelength of the pump, signal and idler for \( j = p, s, \) or \( i \) respectively. Fig. 1.3.2 shows the conversion through a nonlinear medium and the energy level diagram for the process.
Figure 1.3.2: Optical parametric amplification generation and energy diagram. (a) shows the geometry of photons of frequency $\omega_p$ and $\omega_i$ interacting with the nonlinear material and producing $\omega_s$ photons through stimulated emission along with the idler photon, $\omega_i$, which conserves energy. (b) The energy level diagram for SHG where a photon of frequency $\omega_p$ is absorbed and then de-excited through stimulated emission from a photon of frequency $\omega_s$ to produce two photons of frequencies $\omega_s$ and $\omega_i$. Adapted from [4].

1.3.3 Self Diffraction

Self diffraction is brought about by high intensity laser pulses which generate a transient grating in a medium. For a strong field the effective index of refraction is given by,

$$n_{eff} = n_0 + n_2 I + \cdots.$$  \hspace{1cm} (1.3.7)

When two high intensity coherent beams overlap at an angle they form a periodic $n_{eff}$ which is a time dependent diffraction grating, a transient grating. The self diffracted beam is generated by three beams and the $k$-vector is given by,

$$k = 2k_1 - k_2 - \delta k$$ \hspace{1cm} (1.3.8)

where $k$ is the self diffraction $k$-vector, $k_1$ and $k_2$ are the two input beams, and $\delta k$ is the
phase mismatch. See Fig. 1.3.3. As the angle between the input $k$-vectors increases so does the phase mismatch. In addition, $\delta k$ is a function of the interaction length implying that the nonlinear medium must be thin, otherwise complete destructive interference may cancel the self diffracted signal [5].

### 1.4 Pulse Duration and Pulse Characterization

It is important to maintain a short pulse which is transform limited. As the temporal extent of a laser pulse is shortened the spectral component must necessarily spread. However, the spectral components must not spread out in time. A transform limited pulse is one in which all of the spectral components of the pulse are in phase with each other. See Fig. 1.4.1. A pulse which is not transform limited is said to have a chirp, see Fig. 1.4.2.

Chirp introduces a time dependence to the frequency of a laser pulse. A chirp can be brought about when light interacts with a dispersive medium such as glass. To compensate for the dispersion a pair of prisms is used. Alternatively chirped mirrors or a grating pair may be used. The material of the prism, such as BK7, adds a small amount of normal dispersion to the chirped pulse, however by separating the two prisms anomalous dispersion is also introduced. By balancing the two types of dispersion, in reference to the chirped pulse, a transform limited pulse can be reconstructed, see Fig. 1.4.3.

To characterize the pulse width of the beam an autocorrelator is used. Two types of autocorrelators were used in the work leading to this thesis: (1) a real-time autocorrelator (RTA) using SHG; and (2) a self-diffraction (SD) autocorrelator. An RTA has the advantage that the pulse duration is displayed in real time. However, since the technique relies on SHG and a CCD camera to image the signal it is only useful for wavelengths in the region from
Figure 1.3.3: $k$-vectors for Eq. 1.3.8. $k$ and $k'$ are the self diffracted beams and $k_1$ and $k_2$ are the input beams. $\delta k$ is the phase mismatch. Adapted from [5].
Figure 1.4.1: (Color online) Transform limited pulses with the axis in fs. (a) A set of pulses which are transform limited. The line (black) shows the envelope of the pulses. (b) A set of pulses which are not phase matched and are not transform limited. The dashed line (blue) shows the envelope of the pulses. (c) The envelope of the two pulses super imposed over each other. The transform limited pulse (solid black curve) has a shorter pulse duration than the pulse which is not transform limited (blue dashed curve). Adapted from [5].
Figure 1.4.2: (Color online) A chirped pulse which show how the wavelength is compressed in time.
Figure 1.4.3:  (Color online) Pulse dispersion can be compensated for by using a prism pair. The input beam is on the left. For normally dispersive compensation (a) When the prisms are close together there is more normal dispersion than anomalous so that the pulse is still chirped. (b) At the critical point where both normal and anomalous dispersion are balanced. (c) With the prisms too far apart anomalous dispersion takes over and the pulse remains chirped. Note that the prism on the right is usually on a translation stage so that it can be inserted to or removed from the beam to adjust the compensation without having to change the prism locations. It is generally more difficult to move the prism positions along the prisms axis.
about 750 to 2000 nm. The self-diffraction autocorrelator does not have this limitation since
the signal is at the same wavelength as the beam although one of the beams must be scanned
in time. The signal is then detected using a photo diode which are available in a wide range
of bandwidths. The RTA is an improvement over a scanning SHG autocorrelator.

In the second order autocorrelator configuration the delay must be scanned over and
this scanning takes time and therefore the signal is not presented in real time. The 2nd
order autocorrelation signal is given by [6],

\[ I(t) \propto \int_{-\infty}^{\infty} \left| [E(t) + E(t - \tau)]^2 \right|^2 dt \]  

(1.4.1)

where \( E(t) \) is the electric field of the fixed laser and \( E(t - \tau) \) is the electric field of the time
delayed laser. Since the two electric fields are short pulses there will be little signal from
the SHG crystal until the two fields begin to overlap, with the peak in the signal occurring
at \( \tau = 0 \) [5]. The full width half maximum of the autocorrelation signal for a Gaussian
pulse is given by \( \tau_{FWHM} = \tau_{ac}/1.414 \).

An RTA uses the overlap function in a SHG crystal to generate the autocorrelation
signal [7]. The RTA is schematically shown in Fig. 1.4.4. Here the overlap is produced
by using a split mirror to separate the input beam and the amount of overlap depends on
the pulse duration of the beam. The second harmonic signal is then recorded with a CCD
camera. The CCD camera is calibrated using a known time delay between pulses so that
the width of the pulse can be extracted.

In an SD autocorrelator the overlap is produced from the mixing of split beams in a
nonlinear medium, see Sec. 1.3.3. The autocorrelation signal is given by,

\[ I(\omega, t) \propto \left| \int_{-\infty}^{\infty} \left| (E(t))^2 + E(t - \tau) \right| e^{-i\omega t} \right|^2 dt \]  

(1.4.2)
Figure 1.4.4: (Color online) Geometry to produce a real time autocorrelation signal in SHG. A split mirror separates the beam into two. The autocorrelation signal is convoluted into the SHG signal due to the temporal overlap of the two pulses in the BBO crystal.

where the electric fields phase remains intact. Time delay is introduced using a delay stage as in the second order autocorrelator [5]. A schematic an SD autocorrelator is shown in Fig. 1.4.5.

1.5 Molecular Physics

For a description of molecules it is important to first discuss atoms since they are the building blocks of molecules. In atoms, electrons are bound in shells which are states of quantized energy such that the outermost electrons having the lowest binding energy. For each of these energy levels, labeled by the principal quantum number \( n \), the electron is described by a wavefunction. The wavefunction gives the probability distribution of the electrons location around the nuclei. In addition to the quantum number \( n \), the wave function is also
Figure 1.4.5: (Color online) Schematic of a self diffraction autocorrelator. The mask separates the beam into two. One mirror is fixed while the other is on a delay stage to introduce the time delay. The beam is focused into a piece of glass where the self diffraction occurs. An aperture selects the self diffracted signal before it is detected by a photodiode.
described by two additional quantum numbers \( l \) and \( s \). The quantum number \( l \) describes the intrinsic angular momentum of the electron and quantum number \( s \) describes the spin angular momentum of the electron. Degeneracy in these last two quantum numbers is removed in the presence of a magnetic field. For the purposes of this discussion the quantum numbers \( n, l, \) and \( m_l \), where \( m_l \) is the magnetic quantum number and represents the projection of angular momentum, are sufficient [8].

The electron type in an atom is described by the angular momentum of the electron. Azimuthal quantum numbers \( l=1-4 \) are defined as; \( s \) for \( l=0 \), \( p \) for \( l=1 \), \( d \) for \( l=2 \), and \( f \) for \( l=3 \). Therefore, an electron with \( l=0 \) is referred to as an \( s \)-electron and an electron with \( l=1 \) is referred to as a \( p \)-electron. In each quantum state \( n \) there are \( 0 \leq l \leq n - 1 \) momentum states. The lower the angular momentum quantum number, the more tightly bound the electron. For example a \( 2s \) electron, where this notation stands for \( nl \) such that \( n=2 \) and \( l=0=s \), is more tightly bound in an atom than a \( 2p \) electron. The magnetic quantum number \( m_l \) removes the degeneracy in the state \( l \). In each state \( l \) there are \( -l \leq m_l \leq l \) states. Due to the Pauli exclusion principle there are two spin states allowed in each level \( n,l,m_l \).

This notation allows us to write down a unique electron configuration for an atom. For example the electron configuration for nitrogen, which has 7 electrons, is \( 1s^22s^22p^3 \) where the superscript notation identifies the number of electrons in each shell. An individual orbital in an atom is simply written as one of the configuration terms for the atom. For the nitrogen example used previously the second orbital is described as the \( 2s^2 \) orbital. The shape of the orbitals are defined by the azimuthal quantum number and its magnetic projection [8]. The shape of orbitals for \( n = 1 \) and \( n = 2 \) are shown in Fig. 1.5.1.

In molecules the electrons are shared between nuclei in a configuration know as a molecular orbital (MO) [9–11]. The term MO is appropriate in that the absolute square of the wave function represents the spatial probability density distribution of the electron
Figure 1.5.1: (Color online) Atomic orbitals for $n = 1, 2$. The notation in the figure is $|n, l, m_l >$. 
and this is in turn related to the classical orbit of the electron. MOs are formed from combinations of atomic electrons which make up the parent molecule. When the atoms are far from one another there is no overlap in the wave functions and thus no interaction, such that no bond is formed. This is called the separated atom limit. The most common mathematical approximation of the MO is a linear combination of the atomic orbitals (LCAO) [12]. The number of MOs formed in the molecule is the same as the number of atomic orbitals of the constituent atoms. In a diatomic, the simplest molecule which is made up of two atoms, the wave function is given by LCAO as,

\[ \psi = c_a \psi_a + c_b \psi_b \]

(1.5.1)

\[ \psi^* = c_a \psi_a - c_b \psi_b \]

where \( \psi \) is the wave function for a bonding MO and \( \psi^* \) is the wave function for an antibonding MO, \( \psi_i \) is the wave function corresponding to the wave function for atom \( a \) or \( b \), and \( c \) is a coefficient which is calculated such that the energy for the MO wave function is a minimum. MOs which are bonding have a lower energy than the atomic orbitals from which they are formed and antibonding MOs have a higher energy than the atomic orbitals from which they are derived [13, 14].

MOs share a similar notation to that used for atoms orbitals. The orbitals in a molecule are characterized by the particular symmetry of the orbital. The symmetry of an orbital is related to the number of nodal planes intersecting the internuclear axis. For a MO the lowercase Greek alphabet symbol corresponding to the Latin counterpart for an atomic orbital with the same digit is used. In homodiatomic, a diatomic molecule made from one element, a bonding MO with no nodal plane is labeled a \( \sigma \) orbital while the antibonding MO with one nodal plane perpendicular to the internuclear axis is labeled a \( \sigma^* \). For a bonding
MO with one nodal plane containing the internuclear axis the orbital is labeled a $\pi$ orbital and for an antibonding MO with two nodal planes, one plane containing the internuclear axis and another between the nuclei, is labeled a $\pi^*$ orbital. A bonding MO with two nodal planes is labeled a $\delta$ orbital and an antibonding MO with three nodal planes is labeled a $\delta^*$. Further nodal symmetries following this pattern. MOs arise from the combination of atomic orbitals. For example, $\sigma$ symmetry results from the combination of two $s$ orbitals or from the combination of two $p_x$ or $p_y$ orbitals. $\sigma$ symmetry is symmetric with respect to a rotation about the internuclear axis while $\pi$ orbitals are asymmetric. Since homonuclear diatomics also have a center of inversion, referred to as a centrosymmetric molecule, a further symmetry is defined. For inversion through the center in which there is no phase change in the MOs then the molecule is said to have gerade (for even) symmetry such that under inversion $I(\psi_g(r)) = \psi_g(-r) = \psi_g(r)$. While MOs which have a phase change under inversion are said to have ungerade (for odd) symmetry $I(\psi_u(r)) = +\psi_u(-r) = -\psi_u(r)$. Bonding $\sigma$ and $\pi$ orbitals have gerade symmetry while antibonding $\sigma^*$ and $\pi^*$ orbitals have ungerade symmetry [13, 15].

MO’s are also identified by their distance in energy space from the outer most MO containing an electron. This outer most MO is called the highest occupied molecular orbital (HOMO). Inner MOs are then numbered in decreasing order from the HOMO; HOMO-1, HOMO-2, etc. The next outermost MO after the HOMO which does not contain an electron is referred to as the lowest unoccupied molecular orbital (LUMO). Fig. 1.5.2 shows the MOs of nitrogen, $N_2$.

For an allowed transition between states the dipole moment must not be zero,

$$\langle \psi_f | \mu | \psi_i \rangle \neq 0 \quad (1.5.2)$$
Figure 1.5.2: The molecular orbitals of nitrogen, \( \text{N}_2 \).
where $\psi$ is the electronic wave function of the $f$ final or $i$ initial state in the Born-Oppenheimer approximation (See Sec. 1.5.1) and $\mu$ is the electron dipole operator $\mu = -e\mathbf{r}$. Since the dipole operator is odd, only transitions to states of opposite parity will be allowed.

Electronic states are labeled in the order in which they were discovered and according to their energy. Generally the ground state is called the $X$ state and then higher lying states are labeled in alphabetical order; $A, B, C$, etc. However, not all state are found in this chronological ordering and therefore these missing states are generally labeled with a prime; $A', B', C'$, etc. as they are found. Triplet states are named with lowercase letters $a, b, c$, etc. in increasing energy.

In addition to the electronic state labels, states in molecules are also labeled by the fine structure components. This labeling has the form

$$^{2S+1}A\Omega$$

(1.5.3)

where the terms are defined as follows. $\Lambda$ is the projection of the total angular momentum about the internuclear axis. Each electron from which the state is derived comes from an orbital with a component of angular momentum $\lambda$. To find the total angular momentum $\Lambda$, we sum the individual components of angular momentum $\lambda$: $\Lambda = \lambda_1 + \lambda_2$. $\Lambda$ follows the same naming convention as $\sigma$ for molecular orbital except a capital Greek letter is used. For $\Lambda = 0$ the state is labeled a $\Sigma$, for $\Lambda = 1$ the state is called a $\Pi$, and for $\Lambda = 2$ the state is called a $\Delta$. $\Omega$ is the parity and describes the combination of the parity of the atomic orbitals from which the electrons come from. Gerade and ungerade are used again to describe even and odd parity of the state. $S$ in the superscript term is the total spin of the electrons in the state. The term $2S + 1$ is called the multiplicity of the state. From Hund’s rule the state with lowest multiplicity will have the lowest energy. Therefore a full description of the state of
1.5.1 Born–Oppenheimer Approximation

In molecules, the nucleus is much heavier than the electrons, $m_e << m_N$, and therefore the electron motion can be considered to happen instantaneously during nuclear motion. This allows us to fix the nuclear coordinates and solve the Schrödinger equation for the electron in a static electric potential. This is the Born–Oppenheimer approximation. If the nuclei are moved to a different arrangement, then we must resolve the Schrödinger equation. The solution allows for potential energy curves to be constructed.

Consider a hydrogen cation, $H_2^+$, with all particle located along the $z$-axis as shown in Fig. 1.5.3. The Hamiltonian for this arrangement is,

$$ H = T_e + T_N + V $$

(1.5.4)

where $T_e$ is the kinetic energy of the electron, $T_N$ is the kinetic energy of the nuclei, and $V$ is the Coulomb repulsion of the nuclei and the Coulomb attraction of the electrons to the
nuclei. The Schrödinger equation is,

\[ H \psi(z, Z_1, Z_2) = E(z, Z_1, Z_2) \psi \]  \hspace{1cm} (1.5.5)

where \( \psi \) is the wavefunction of the atom. Since the motion of the nucleus is frozen we can separate variables,

\[ \psi(z, Z_1, Z_2) = \psi_e(z; Z_1, Z_2) \psi_N(Z_1, Z_2) \]  \hspace{1cm} (1.5.6)

where \( \psi_e \) is the electrons wave function and \( \psi_N \) is the nuclear wavefunction. Substituting Eq. 1.5.6 into Eq. 1.5.5 we have,

\[ H \psi\psi_N = \psi_N T_e \psi + \psi T_N \psi_N + V \psi \psi_N + W = E \psi \psi_N \]  \hspace{1cm} (1.5.7)

where,

\[ W = - \sum_{\ell=1}^{2} \frac{\hbar^2}{2m_\ell} \left( 2 \frac{\partial \psi}{\partial Z_\ell} \frac{\partial \psi_N}{\partial Z_\ell} + \frac{\partial^2 \psi}{\partial Z_\ell^2} \psi_N \right) \]  \hspace{1cm} (1.5.8)

Since \( m_N \) is small in Eq. 1.5.8 we may neglect it. We can rewrite Eq. 1.5.7 as,

\[ \psi T_N \psi_N + (\psi T_N \psi_N + V \psi) \psi_N = E \psi \psi_N \]  \hspace{1cm} (1.5.9)

Letting,

\[ \psi T_N \psi_N + V \psi = E_e(Z_1, Z_2) \psi \]  \hspace{1cm} (1.5.10)

for fixed nuclear coordinates. The solutions to Eq. 1.5.10, \( \psi \) and \( E_e(Z_1, Z_2) \) allow us to solve for potential energy curves for the molecule. The Born–Oppenheimer approximation works best for ground electronics states [8].
Figure 1.6.1: (Color online) Atomic potentials showing distortion due to a strong laser field. $V_B$ is the binding potential of the atom and $V_L$ is the laser field. $I_p$ is the ionization potential. The arrows (red) show multiple photons are required to ionize the state.

1.6 Ultrafast Physics

In a strong field, the potential of a molecule becomes distorted. This distortion allows the electron to escape. For simplicity we will consider an atomic potential since the physics of ionization is roughly the same for atoms and molecules. The way in which an electron can escape the potential of the atom depends on the intensity of the laser field and the distortion it introduces to the atomic potential. See Fig. 1.6.1. There are three regions of strong field ionization: (1) Multiphoton ionization; (2) Tunneling ionization; and (3) Over the barrier ionization. See Fig. 1.6.2. If the field of the laser is not strong enough to lower the barrier to allow tunneling ionization to occur then ionization occurs through multiphoton ionization in which multiple photons are absorbed so that the electron gains the energy required
Figure 1.6.2: (Color online) Distortion of the potential due to a strong laser field. Tunneling can occur when the potential is lowered enough as in the dashed curve (yellow). For stronger intensities the barrier is lowered enough, dotted (green) curve, that the electron escapes to the continuum without tunneling.
to reach the continuum. If the intensity is strong enough to sufficiently lower the barrier then the electron can tunnel through the barrier and reach the continuum. Separation between multiphoton ionization and tunneling ionization may be quantified using the Keldysh parameter [16]. The Keldysh parameter is given by,

$$\gamma = \sqrt{\frac{|I_p|}{2U_p}} \quad (1.6.1)$$

where $I_p$ is the ionization potential and $U_p$ is the pondermotive energy. The pondermotive energy is the kinetic energy of a free electron in the laser field and is given by,

$$U_p = \left( \frac{F_0}{2\omega} \right)^2 \quad (1.6.2)$$

where $F_0$ is the amplitude of the laser electric field and $\omega$ is the angular frequency of the laser field. In atomic units the laser field is approximately given by,

$$F_0 \approx \sqrt{\frac{I}{3.51 \times 10^{16} \text{ W/cm}^2}} \quad (1.6.3)$$

If $\gamma >> 1$ then the ionization occurs through multiphoton ionization. For $\gamma << 1$ then the ionization is through tunneling ionization. The crossover point between multiphoton and tunneling ionization is not well defined. Over the barrier ionization occurs when the intensity of the laser field is strong enough to launch the electron into the continuum, in other words the barrier is sufficiently lowered that the electron does not need to tunnel through the barrier [3].

Dissociation of molecules may also be distorted by strong laser fields. If two potential curves cross under the influence of an intense laser field at integer multiple of the photon energy then a bound state may cross to an unbound state and dissociate in a process called
bond softening (BS). This process is highly intensity dependent and is shown schematically in Fig. 1.6.3 for hydrogen. This strong intensity dependence can be used to identify dissociation through bond softening.
Chapter 2

Velocity Map Imaging

Velocity mapping is an extension of time of flight (TOF) and ion imaging and it is therefore essential to understand these techniques before undertaking an analysis of velocity map imaging (VMI).

2.1 Time of Flight

TOF is essentially a mass spectrometer in which various charged species, atomic and molecular, are separated in time during a free drift region due to the acceleration imparted to the particles by an electric field. This field is created by ion optics such as that developed by Wiley and McLaren, an example is shown in Fig. 2.1.1 [19]. The pinhole after the lens selects particles only with momentum in the $x$-direction, particles with no transverse momentum. A typical TOF spectrum is shown in Fig. 2.1.2. In the focus in Fig. 2.1.1 particles with a KER in the $x$-direction are accelerated directly toward the detector while particles with a KER in the negative $x$-direction are accelerated to a stop and then accelerated in the
positive $x$–direction toward the detector. This accounts for the two sets of peaks for each ionization channel $A + B \rightarrow A^{n+} + B^{m+}$ where $n = m = 0, 1, 2, \ldots$ For $n = m = 0$ there is no charge and the particles are not accelerated toward the detector. The two peaks can be clearly seen in a TOF spectrum for $I^{2+}$ as shown in Fig. 2.1.3.

The KER of the photodissociation of two particles $A$ and $B$,

$$AB + h\nu \rightarrow AB^* \rightarrow A + B$$

(2.1.1)
Figure 2.1.2: (Color online) TOF spectrum of $I_2$ showing the atomic cation $I^+$, the atomic double cation $I^{2+}$ and the molecular cation $I_2^+$. 
Figure 2.1.3: (Color online) Enlarged TOF spectrum of $I^{2+}$ clearly showing forward and backward going KER.
where \( h\nu \) is the photon energy is described by the conservation of energy by

\[
E_{AB^*} \rightarrow E_A + E_B + KER_T
\]

(2.1.2)

where \( E_{AB^*} \) is the energy of the excited complex, \( E_A \) and \( E_B \) are the internal energies of the dissociated products, and \( KER_T \) is the total KER. The total energy of the products is the photon energy minus the dissociation energy such that,

\[
KER_T = h\nu - D_0 - E_{int}.
\]

(2.1.3)

where \( D_0 \) is the dissociation energy and \( E_{int} \) is the internal energies of fragments \( A \) and \( B \).

Fig. 2.1.4 shows the KER for a photodissociation process and defines \( D_0 \). The KER for the photofragments is partitioned based on the masses of the particles,

\[
KER_A = \left( \frac{M_B}{M_{AB}} \right) KER_T
\]

(2.1.4)

\[
KER_B = \left( \frac{M_A}{M_{AB}} \right) KER_T
\]

For photoionization, where \( M_e \ll M_A \), Eq. 2.1.4 shows that the electron will receive most of the energy. Therefore in the case of photoionization \( \leftrightarrow \) photodissociation experiments the KER imparted to the molecular or atomic fragments can be neglected [20, 21]. For homodiatomtic molecules, where the molecule is composed of two of the same atoms with the same mass \( M_A \), the energy is shared equally between the two products,

\[
KER_A = KER_B = \frac{1}{2} KER_T.
\]

(2.1.5)

In the center of mass frame the photodissociation process is seen as two products trav-
Figure 2.1.4: (Color online) Potential energy curves showing the dissociation of complex \( AB \) to \( A + B \). The dissociation energy, \( D_0 \), is defined in the figure along with the KER.
Figure 2.1.5: Center of mass dissociation of product fragments. (a) Depicts the recoil KER of two fragments. (b) Time average of many dissociation events. In this case the Newtonian sphere has a $\cos^2 \theta$ distribution.

eling in opposite directions, see Fig. 2.1.5. For many such photodissociation events a distribution will emerge which is referred to as a Newtonian Sphere. For photodissociation of a diatomic molecule from a $\Sigma$ initial state to a $\Sigma$ final state the transition will be a parallel transition and will have a $\cos^2 \theta$ distribution. $\theta$ is the angle formed between the photolysis laser polarization and the internuclear axis, see Fig. 2.1.5. For a $\Sigma$ initial state to a $\Pi$ final state the transition will be a perpendicular transition and will have a $\sin^2 \theta$ distribution [20, 22, 23].

In TOF, the time it takes a particular particle to hit the detector is proportional to the particles mass and inversely proportional to its charge. The strength of the electric field in the ion lens also contributes to the TOF. In particular, from energy conservation, the time it takes a particle to reach the detector is given by,
Figure 2.1.6: (Color online) Time of flight for the VMI with $V_R = 1250V$ and timing from the Spitfire. The iodine fragments TOF are experimentally determined and the remaining product TOF are calculated from a fit to the iodine data.

$$t_{TOF} = A \sqrt{\frac{m}{2qV}} + C \quad (2.1.6)$$

where $m$ is the mass of the particle, $q$ is the charge of the particle, $V$ is the voltage on the ion optics, $A$ is a constant which depends upon the experimental setup, and $C$ is a constant which scales the TOF due to an offset introduced in a particular experimental configuration which comes from delays in detector gate timing. Fig. 2.1.6 show the TOF of several species and the constants from Eq. 2.1.6, where the voltage $V$ and the constant 2 have been absorbed into the constant $A$, for the current VMI configuration with $V = 1250V$. 

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2.2 Ion Imaging

Ion (or product) imaging is a combination of TOF spectrometry with a 2D visual detector. Chandler and Houston came upon the idea of using a microchannel plate (MCP) with a phosphor screen to directly image the product in a TOF photodissociation event [24]. Initially the images were recorded with a film camera although this was quickly replaced with a CCD camera so that images could be combined to average the results and improve statistics. Two conclusions were made about the usefulness of the imaging technique: 1. The image provides both angular as well as velocity distributions. 2. If the products are produced using resonantly enhanced multiphoton ionization (REMPI) then the products may be state selected. REMPI is an excitation process as described by Eq. 2.2.1

\[ A + nh\nu \rightarrow A^+ + e^- + KER_T \]  

(2.2.1)

where \( n \) is the number of photons and the condition \( n > 2 \) satisfies the REMPI condition [20]. Since this 2D image is a projection of the flattened 3D distribution it must be deconvoluted to regain the velocity distribution. Several reconstruction techniques will be discussed in Sec. 2.5. An alternative method is to slice the 3D distribution such that inversion is not required. This will be discussed in Sec. 2.6. Since the distribution in the focus is spread out in the plane of the detector there is a blurring of the image. This reduces the energy resolution of the detector. Another use of ion imaging is to detect photoelectrons. By reversing the voltages on the plates the electrons will be observed on the detector. However the speed at which the electrons move along with the blurring due to the distribution in the focus make the electron images less useful.
2.3 Velocity Map Imaging

If the particles at different locations in the focus could be mapped to the detector at the same location then the blurring seen in ion imaging would be removed and the energy resolution would be greatly improved. Eppink and Parker realized the TOF electrostatic lens could be reconfigured such that this condition of velocity mapping would be met [25]. In addition to velocity mapping the resolution could also be improved due to the removal of the grids in the TOF lens, see Fig. 2.1.1, which are not required for a velocity mapping lens. Eppink and Parker coined the term *velocity map imaging* for this improvement to the ion imaging experiment. A typical VMI image is shown in Fig. 2.3.1. In a TOF lens the electric field is flat and no magnification is formed. This is due to the grounded grids in the lens plates. This potential surface can be seen in Fig. 2.3.2 (a) and (b). The figure also shows the trajectory of a distribution of several particles in the $z$–direction. These particles all have the same KER and show that the lens is not velocity mapping since the particles do not intersect the detector at the same position. When the VMI condition is met, then a flat field is not produced and all particles will arrive at the same location on the detector if they have the same initial KER. This can be seen in the SIMION simulation shown in Fig. 2.3.2 (c) and (d). The VMI condition can be met by the use of an appropriate set of lens optics and then adjusting the ratio of the voltages on the repeller and the extractor. A product with no KER, such as an atomic cation, can be used to experimentally set the ratio. There are two methods which can be used to adjust the voltage depending on the setup. If a molecular beam is used then the cation should be imaged at the detector. By adjusting the voltage ratio for the smallest image on the detector this condition can be met. If no molecular beam is used then the position of the focus can be moved using the focusing mirror in the $xz$–plane. If velocity mapping is achieved then there will be no movement in
Figure 2.3.1: (Color online) Typical VMI images of \( I^+ \) after the single ionization and dissociation using 488 nm photolysis. (a) Gray scale image with a linear intensity scale. (b) A hot nonlinear image scale to show detail in the VMI image.

Eq. 2.1.6 shows that the TOF will scale with voltage. This scaling will result in a magnification of the image on the VMI detector. If the voltage is low then it will take longer for the fragments to reach the detector and this will in turn give the fragments more time to expand. The opposite condition will exist for higher voltages. See Fig. 2.3.3. From Eq. 2.1.6 we see that the images scale as \( \sqrt{V_R} \). Fig. 2.3.4 shows the scaling for the three images in Fig. 2.3.4.

Two VMI images which have been taken at different repeller voltages can be scaled so that they can be directly compared. The scaling goes as \( \sqrt{V_{R1}/V_{R2}} \). An example of axis scaling of unequal repeller voltage images is shown in Fig. 2.3.5.
Figure 2.3.2: (Color online) Potential surfaces for the VMI lens configuration shown in Fig. 2.3.6. (a) VMI with no velocity mapping where the particles arrive at the detector at different locations. (b) Expanded view of (a) to show detail at the lens location with no lens formed. (c) VMI in velocity mapping mode where all particles arrive at the same detector location regardless of the spread in the y direction. (d) Expanded view of (c) to show detail at the lens location with the formation of a lens in the field.
Figure 2.3.3: (Color online) Three VMI images of $I^{2+}$ at three different repeller voltages: (a) 1000V, (b) 2000V, (c) 3000V. As the voltage on the repeller is increased more dissociation channels appear in the image.

The VMI apparatus used in this thesis is a three element lens design similar to that used by Eppink and Parker. For the current setup a voltage ratio of $V_E = 0.7V_R$ was experimentally determined to achieve velocity mapping. The voltages on the MCP and the phosphor, 1900V and 4500V respectively, were chosen to deliver excellent image characteristics while minimizing wear and damage to the MCP or phosphor. Figs. 2.3.6 and 2.3.7 depict the lens inside of the high vacuum chamber and define the axis as well as the dimensions and voltages of the electrostatic lens and TOF drift region.

### 2.4 VMI Pump-probe

Molecular dynamics can be studied with VMI by introducing a second laser pulse which can be offset in time relative to the other pulse which remains fixed in time. This technique is referred to as pump-probe since in the general experimental procedure the fixed pulse is
Figure 2.3.4: (Color online) Lineouts of VMI images from Fig 2.3.3 of \( I_2^+ \) for different repeller voltage with the same repeller to extractor ratio. (a) Raw lineouts with no scaling. (b) The same lineouts in (a) which have been scaled by \( \sqrt{V_R} \).
Figure 2.3.5: (Color online) The blue (square) and circle (orange) points show VMI line out data at repeller voltages of 1250 V and 500 V respectively. The diamond (red) points have the pixel value, the abscissa axis, scaled by $\sqrt{V_{500}/V_{1250}}$ to account for the difference in TOF which reduces the energy range of the 500 V image.
Figure 2.3.6: (Color online) Diagrammatic views of the VMI lens and chamber generated by the SIMION program. (a) shows a 3D cutaway and labels the axis. (b) a cutaway in the xy-axis which defines the three lens plates; R is the repeller, E is the extractor, and G is the grounded grid.
Figure 2.3.7: (Color online) A schematic of the VMI apparatus (not to scale). Voltages on the VMI lens plates are given in the figure along with the pulsed high voltage on the MCP and the phosphor voltage. $\tau$ is the duration of the pulse on the MCP. Distances between the plates in the grid and the distance from the focus to the MCP are also shown.
Figure 2.4.1: (Color online) A pump-probe delay stage configured as a Michelson type interferometer. Careful choice of the beam splitter orientation must be made such that each path in the interferometer has the same amount of dispersion.

Weaker in intensity such that it acts as a stimulus, inducing molecular dynamics, while the second stronger pulse, which is delayed, probes the action induced by the first pulse. Delay between the two pulses can be achieved by introducing a delay line in one of the beam paths. In this thesis a computer controlled delay stage in a Michelson interferometer is used. See Fig. 2.4.1. To balance the dispersion in the two beam paths in the interferometer the beam splitters must be configured as they are shown in Fig. 2.4.1 such that each beam see the same amount of glass.

Analysis of VMI pump-probe data is accomplished by performing a Fast Fourier Transform (FFT) on the complete data set. A simple 1D FFT performed on an integrated lineout
Figure 2.4.2: (Color online) Steps involved in performing a 2D FFT on a VMI image. (a) All lineouts from a region of interest (ROI) selected from an original VMI image as seen in (d). (b) The integral of the lineouts in (a). (c) 1D FFT performed on the integral data in (b) Two frequencies of interest are noted. 3.8 THz and 7.0 THz which correspond to the A- and X-states of \( I^+ \). (d) An unprocessed \( I^+ \) VMI image showing a ROI window. (e) 2D FFT image performed at the A-state frequency of 3.8 THz. (f) 2D FFT image performed at the X-state frequency of 7.0 THz. Note that the peak in (c) at 0.5 THz is due to a slight offset in the data and does not correspond to a vibrational state.

of all the VMI images will show frequency dependent dynamics such as molecular vibrations. After a molecular vibration is identified it can then be studied in a 2D FFT. The 2D FFT is carried out by taking the same pixel \((i, j)\) in each image \(k\) and then performing a 1D FFT on the data which results in a value \(S_{i,j}\) at a frequency of interest determined from the 1D FFT. This is done for all pixels in the image. Each value \(S_{i,j}\) is then assigned to pixel \((i, j)\) in a new 2D FFT image. This 2D image represents the amount of vibration at a particular frequency at each pixel location. See Fig. 2.4.2
Figure 2.5.1: As the velocity distribution of fragments moves out of the focus toward the detector the distribution is flattened in the $x$–direction while the distribution expands in the $y$–direction. The flattening, or crush, is due to the longer time the backward going fragments see the accelerating field compared to the forward going fragments. The axis are also defined in this image. The $z$–axis is out of the page.

2.5 VMI Image Deconvolution

To extract the most data from a VMI image it must be deconvoluted to reconstruct the central slice of the 3D distribution. As mentioned in Sec. 2.2 the image is a projection of the full 3D image onto a 2D surface. See Fig. 2.5.1. We will discuss two deconvolution methods: Abel inversion and onion peeling. Both of these methods require that the distribution which is to be inverted has cylindrical symmetry. This is the case for many molecular dissociation events.
2.5.1 Abel Inversion

Abel inversion requires that the entire ion cloud distribution, Newtonian sphere, arrives at the detector during the period in which the gate on the detector is open. If this the case then the distribution is defined as,

\[ p(z,y) = \int_{-\infty}^{\infty} i(x,y,z) \, dx \] (2.5.1)

where the coordinates are defined in Fig. 2.5.1 and \( i(x,y,z) \) is the velocity distribution of photoframents and is centered on the focus. For one row of and image along the \( z \)–axis at \( y = y_0 \) then,

\[ f(z) = p(z,y_0) = \int_{-\infty}^{\infty} s(z,x) \, dx = 2 \int_{0}^{\infty} s(z,x) \, dx \] (2.5.2)

where \( s(z,x) = i(z,x;y_0) \) is a slice in the distribution in the \( zx \)–plane. The original velocity distribution is now encoded in the function \( s(z,x) \). Due to cylindrical symmetry Eq. 2.5.2 can be rewritten as,

\[ f(z) = 2 \int_{z}^{\infty} \frac{s(r)r}{\sqrt{r^2-z^2}} \, dr \] (2.5.3)

where we have change variables \( r^2 = x^2 + z^2 \). This is the Abel transform [20, 26]. Applying the convoluted Fourier transform will recover the function \( s(r) \). This is then given by [20, 27],

\[ s(r) = \frac{1}{\pi} \int_{r}^{\infty} \frac{df/dz}{\sqrt{z^2-r^2}} \, dz. \] (2.5.4)

A package for the Python programming language, called PyAbel, is capable of performing
the inversion on VMI images if the image has not been sliced by the MCP gating. Fig. 2.5.2 shows an example of an Abel inverted image.

### 2.5.2 Onion Peeling

The other reconstruction method to be discussed in this thesis is the onion peeling method. We consider a charged particle created at the origin of the axis defined in Fig. 2.5.3 which has velocity components given by,
Figure 2.5.3: Definition of the axis for the velocity distribution for onion peeling.
\[ v_x = v_0 \sin(\theta) \cos(\varphi) \]
\[ v_y = v_0 \cos(\theta) \]
\[ v_z = v_0 \sin(\theta) \sin(\varphi) \quad (2.5.5) \]

For a homogenous electric field, \( F \), which accelerates the particle towards a detector along the \( x \)-axis and is located at \( x = 0 \) the particle will be located at the detector at the position given by,

\[ z = \frac{2l \sin(\theta) \cos(\varphi)}{\rho} \left( \sqrt{\sin^2(\theta) \sin^2(\varphi) + \rho - \sin(\theta) \sin(\varphi)} \right) \quad (2.5.6) \]
\[ y = \frac{2l \cos(\theta)}{\rho} \left( \sqrt{\sin^2(\theta) \sin^2(\varphi) + \rho - \sin(\theta) \sin(\varphi)} \right) \]

where,

\[ \rho = \frac{qFl}{KER} \quad (2.5.7) \]

The field is not a uniform accelerating field all the way to the detector, there is a field free region in the TOF section. However this only adds a magnification factor of \( t \sqrt{2KER/m} \) and does not affect the following calculations. Since \( \rho \) is large for small KER particles, of a few eV, we may re-write Eq. 2.5.6 as,

\[ z = \frac{2l \sin(\theta) \cos(\varphi)}{\sqrt{\rho}} \quad (2.5.8) \]
\[ y = \frac{2l \cos(\theta)}{\sqrt{\rho}} \]

as \( \rho \) goes to infinity. Inverting Eq. 2.5.8 we have,
\[ \theta = \cos^{-1} \left( \frac{y \sqrt{\rho}}{2l} \right) \]

\[ \varphi = \cos^{-1} \left( \frac{z \sqrt{\rho}}{2l \sin(\theta)} \right) = \cos^{-1} \left( \frac{z \sqrt{\rho}}{2l \sqrt{4 - \rho y^2 l^2}} \right) \]  (2.5.9)

at the detector position \((y, z)\) for a fixed value of \(\rho\) [20]. Since there is always some spread in the initial velocity distribution, due to thermal broadening for example, we cannot easily transform the image to its initial velocity distribution. However, we can use a so called onion peeling method where we consider the particle with the highest KER, the particle at the outer edge of the VMI image, remove the value of \(\rho\) from the image and then work backwards in KER to the center of the image [20]. As with the Abel inversion the Python package PyAbel can perform an onion peeling VMI image inversion. An example of an onion peeled image is shown in Fig. 2.5.4. An onion peeling algorithm developed to deal with partially sliced VMI data will be discussed in Sec. 4.3.

### 2.6 VMI Slicing

To avoid the need for using an inversion algorithm, which adds distortion to the VMI image data, it is possible to slice the VMI image using the MCP gate. If the gate is short enough, then only the center of the Newtonian sphere will be imaged on the phosphor. See Fig. 2.6.1. However, if the gate time is too long, then a thick slice will be produced. In this case the image cannot be inverted by standard inversion algorithms which require the image to be cylindrically symmetric. In Sec. 4.3 we introduce a modification to the onion peeling method to invert VMI images with a thick slice. For heavy fragments, such as iodine, simply gating the MCP may be all that is required to slice the Newtonian sphere. In the
Figure 2.5.4: (Color online) An image which has been inverted using the onion peeling method. (a) The original 485 nm $I^+$ image. The laser polarization is vertical. (b) The onion peeled image. Note the distortion along the vertical axis.
Figure 2.6.1: By narrowing the MCP gate the fragment distribution can be sliced avoiding the need to invert the VMI image. On the left is the fragment distribution for a particular KER, the center shows the effect of the MCP pulse, and on the right is a computer generated example of a VMI image created by image slicing.

Case of light molecules additional experimental methods are required to improve the slicing method. One method increase the length of time the fragments see the accelerating field. After the particles are accelerated they become flattened in the TOF drift region as the backward KER particles catch up to the forward KER particle. See Fig. 2.5.1. If we delay the application of the accelerating field then the particle will spread out more in the region of the focus. After the time delay, the backward going particles will see the acceleration field for longer than if there had been no delay. This allows the backward going particle to catch up with and overtake the forward going particles. By increasing the delay we can stretch out the particle distribution in the x-direction. This will greatly improve the slicing resolution. See Fig. 2.6.2. For this thesis, in combination with the improved onion peeling method, it was not necessary to delay the field in part because iodine is heavy and therefore takes longer to reach the detector.
Figure 2.6.2: Delayed acceleration allows for thinner sliced images. 1. The Newtonian sphere is created by the photolysis laser. 2. Delaying the application of the accelerating electric field to the fragments allows them to see the field for longer. This results in the backward going particles to catch up to and overtake the forward going particles. 3. If the delay is long enough then the distribution will be inverted and stretched out allowing for a much thinner slice. 4. The application of the MCP gating catches most of the particle distribution if no delay is used, however with the delay a thin slice is captured.
Chapter 3

Single Ionization of Molecular Iodine

3.1 Introduction

While the single-electron ionization rates of atoms in strong fields are relatively well understood [28, 29] molecules have attracted attention over the years due to their additional degrees of freedom (vibrational, rotational, and electronic). These degrees of freedom allow for the study of the dependence of ionization on angle and internuclear separation [30, 31]. Bond softening and enhanced ionization are two such prominent effects that have been predicted and observed [32–36]. More recently, the electronic degrees of freedom have attracted more attention. For example, in molecules, inner-valence orbitals can play an important role, as they lie less deeply bound than the corresponding inner-shells in atoms [37–39]. Ionization of an inner-orbital will leave the molecular ion in an excited state affecting all subsequent strong-field phenomena, such as rescattering, high-harmonic generation (HHG) and multiple-ionization. Moreover, given the highly nonlinear nature of these interactions, the possibility arises that understanding these strong-field effects may,
in turn, provide information about the structure of the MOs, using techniques such as quan-
tum tomography [40] and electron diffraction [41]. Given the likelihood that ionization
will not be selective from a particular orbital, but, rather, produce a hole involving multiple
orbitals, ultrafast dynamics may be introduced and measured [42, 43]. Nevertheless, all
of these questions and opportunities rely on knowing which orbitals are involved in the
interaction.

As mentioned above, inner-orbital ionization (IOI) will lead to a molecular ion in an
excited state. As it turns out, ample evidence has accumulated over the years showing
excitation of the molecules through strong-field ionization. Experiments include the ob-
servation of charge asymmetric dissociation of even-charged molecular ions [44–46], ob-
servation of molecular fluorescence in the vacuum ultraviolet (VUV) spectral region [38],
electron spectroscopy directly showing ionization of the HOMO-2 in $N_2$ [37], and the dra-
matic manifestation of excitation through lasing in the atmosphere on a transition from
a state possibly produced through ionization of the HOMO-2 orbital [47, 48]. While the
excitation of molecules could be produced through IOI, it does not prove that this is the
mechanism. Another experiment provides a closer link [49]. VUV radiation from atomic
fragments following strong-field ionization revealed a clear pattern: radiation from plasma
excitations could all be identified with Rydberg-type excitations of the atomic ions, while
radiation from the direct laser-molecule interaction was uniquely identified with atomic ion
states involving one or two holes in the 2$s$ shell. This implies a coupling with the molecular
orbitals formed from the 2$s$, not just the 2$p$ electrons. This also sets the energy scale of the
excitation of at least 10–20 eV and, indeed, VUV fluorescence from strong-field ionization
was observed in this energy range [50]. Why these deep inner orbitals couple strong to the
laser field remains to be explored and understood.

While light simple molecules, such as $N_2$, $O_2$, $CO_2$, $SO_2$ have been extensively studied
[46, 51–54], it is important to expand the range of molecules studied to gain a deeper understanding of the strong field interaction. One extension is to more complex light molecules, such as \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_6\text{H}_6 \), etc. In these molecules there are numerous low-lying orbitals that can readily interact with the laser field [55, 56]. However, in light molecules, the ionization and dissociation generally happen at the same time during the laser pulse, because the light nuclei move fast. In this thesis, we take a different approach and look at a heavy diatomic molecule – iodine. Like the light polyatomic molecules, \( \text{I}_2 \) has low-lying accessible molecular orbitals [57, 58]. However, its nuclear motion is very slow, due to its large mass and we can cleanly decouple ionization from dissociation. In this case, the kinetic energy of the atomic fragments following ionization should be easily interpreted through energy conservation with the known potential energy curves at the equilibrium internuclear separation and the atomic dissociation limits. \( \text{I}_2 \) is interesting as the orbitals are much harder to calculate [57] and insight from strong-field experiments may be useful. In addition, \( \text{I}_2 \) immediately stands out compared to light diatomic molecules, as it is more likely to dissociate after ionization than remain as a molecular ion, unlike light molecules, which tend to remain intact [59].

In this thesis, we measure the KER of the \( \text{I}_2^+ + \text{I}(1,0) \) dissociation channel [throughout this thesis \((n,m)\) designates the \( \text{I}_2^+(n+m)^+ \rightarrow n^+ + m^+ \) dissociation channel] of \( \text{I}_2^+ \) over a wide range of wavelengths (800 nm – 400 nm) with ultrashort (40 fs) laser pulses. The vibrational period of the \( \text{I}_2^+ \) ground state is 139 fs [60]. Given the fact that most ionization will occur at the peak of the pulse, very little internuclear motion will occur during ionization. This means that bond-softening should not play a role. In this case, the KER will depend only on the energy of the initial state of \( \text{I}_2^+ \) and the dissociation limits. Ionization of the HOMO populates the \( X_{1/2,3/2} \) states and the HOMO-1 the \( A_{1/2,3/2} \) states [60, 61]. All of these states remain bound when populated at the equilibrium internuclear separation.
$R_e$ of the $I_2$ ground state, resulting in no dissociation. Ionization of the HOMO-2 populates the B state that will dissociate in the range of 0-0.15 eV, which is easily seen in the data. However, our attention will be focused on the majority of the ionization signal, which produces fragments with KERs above 0.5 eV. These channels cannot be associated with the three least bound orbitals based on the KER data and a pump-probe technique described below. For this reason, we conclude that the bulk of the ionization involves the deeper orbitals built on the $5s$ electrons, reminiscent of the ionization of the $2s$ electrons in $N_2$, discussed above. The $5s$ electrons in atomic iodine lie about 10 eV below the $5p$ electrons and so it remains an open question as to why there is such a strong coupling to the deeply bound inner-orbitals in both the light and heavy homonuclear diatomics.

### 3.2 Experiment

The experimental configuration is shown schematically in Fig 3.2.1. To produce photoionization and photodissociation a Spectra Physics Spitfire, 800 nm, 40 fs, 800 μJ, 1 kHz, Ti:Sapphire laser is used [39]. This pumps a dispersion compensated Light Conversion TOPAS Optical Parametric Amplifier to produce 450 to 750 nm photons with a pulse duration of 45 fs. The pulse duration, spectrum, and beam profile out of the OPA is checked for each wavelength. 400 nm photons are generated through second harmonic generation in a type-I 500 μm thick BBO crystal. A broadband beam splitter splits the beam path into a pump-probe configuration for certain experiments. The higher transmission from the beam splitter is sent to the BBO or the OPA. A motorized stage is used to introduce temporal delay between the pump and probe. After the OPA and delay stage the pump and probe are recombined collinearly and sent into the vacuum chamber. Pump-probe experiments
Figure 3.2.1: (Color online) Experimental setup. BS: Beam splitter, $\lambda/2$: half-wave plate, $\lambda/4$: quarter-wave plate, BBO: Barium borate crystal, Delay: delay stage, OPA: Optical parametric amplifier, IL: ion lens, FM: focusing mirror, MCP: microchannel plates and phosphor screen. The mirror after the OPA is removed when using the BBO crystal. An example VMI image is shown at the top.
were only run at 800 nm with a delay of 25 fs per image and a total scan time of 1300 fs. In this configuration a 800 nm beamsplitter was used for the recombining mirror. For single pulses from the OPA a silver mirror was used and for single pulses from the BBO the mirror was removed. In the chamber the beam is focused using a spherical mirror with a focal length of 7.6 cm. The focus intensity ranges from $6 \times 10^{13}$ to $1 \times 10^{15}$ W/cm$^2$ depending on wavelength and energy. Room temperature iodine is diffused into the chamber through a leak valve. The chamber is pumped by a turbo molecular pump with a typical background pressure of $5 \times 10^{-9}$ Torr. The I$_2$ pressure is set between $10^{-8}$ to $10^{-7}$ Torr, depending on the experiment. A three element VMI ion lens configuration similar to the one used by Eppink and Parker [25] is used to accelerate the cations. A MCP and phosphor screen, Beam Imaging Solutions BOS-40, are used to detect the cations which are imaged by a PixeLink PL-B953U CCD camera at 20 fps. The MCP is gated using a DEI PVX-4140 pulse generator. In order to record the data in ion-counting mode each image is thresholded to remove noise and the remaining pixel values are set to one to remove MCP fluctuations. A single frame contains 50 laser shots, however since we maintain a relatively low iodine pressure and low intensities we rarely see more than 2 ion counts per 50 laser shots. Anywhere from 100 to 50,000 images are summed depending on the experiment. Since iodine is heavy, and therefore slow in TOF, we are able to slice the VMI images using DC gating [62, 63].

The momentum space image is transformed to energy space using the known following conversion

$$y_E = A y_p^2$$

(3.2.1)

where $y_E$ is the total KER of the ion and its dissociation partner in eV, $y_p$ is the momentum
in units of pixels in the image, and $A$ is a scale factor. Using 5 block averaged images
we find $A = 1/700 \text{ eV/pixel}^2$, based on the known total KER of the (1,1) channel, 4.7 eV
[45, 64]. Figure 3.2.2 shows a sample of typical VMI images for four wavelengths and
identifies the $I^+$ channels as well as the $I_2^{2+}$.

### 3.3 Data Analysis

To identify the KER of the various channels in the VMI images we employ the following
fitting algorithm. First, to improve statistics, we five block averaged and folded the images
in quadrature. We then fit each image using an in house Matlab program. For the angular
dependence the fit uses the sum of the first four even Legendre polynomials. A Gaussian
function of the radius $r$ and the polar angle $\theta$, is used for the radial dependence:

$$S(r, \theta) = \sum_{i=1}^{N} \left\{ \exp \left( -\frac{1}{2} \left[ \frac{r - r_i}{w} \right]^2 \right) \times (a_{1,i}L_0(\theta)_i + a_{2,i}L_2(\theta)_i + a_{3,i}L_4(\theta)_i + a_{4,i}L_6(\theta)_i) \right\}$$

(3.3.1)

$i$ runs from 1 to the number of fit curves needed $N$, $r_i$ is the radius of the fit curve, $w$ is the
width, $L_n$ is the $n^{th}$ Legendre polynomial and $a_{j,i}$ is the amplitude which scales each of the
$j = 1, 2, 3, 4$ Legendre polynomials for $i$ fit curves. A $\chi^2$ test is used to find the best fit.
The fitting algorithm is capable of finding fits which are not physical. Since we are in ion
counting mode we expect that all of the fit will be positive definite. To ensure this, each fit
function is plotted radially and examined for a positive going curve. For this experiment
we found 6 fit functions are needed to achieve the best fit. Example fit images are shown in

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1 A polar onion peeling program, G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede, and J. R. R. Verlet,
Rev Sci Instrum 80, 053104 (2009), is used to do the folding however it is not used to deconvolute the images
since the images are sliced.
Figure 3.2.2: Typical single ionization images at various wavelengths. (a) 487 nm, (b) 520 nm, the arrow shows the polarization axis used for all images, (c) 691 nm, and (d) 800 nm. All images are 5 block averaged. The $I^+$ channels and $I_2^{2+}$ are identified in (a). The amplitude of the signal is displayed in arbitrary units.
Figure 3.3.1: (Color online) Typical fit images showing single ionization at 485 nm with vertically polarized light. The x–axis is in intensity with arbitrary units. (a) The original image five block averaged and folded in quadrature. The white arrow shows the polarization axis. (b) The fit image. (c) The original image subtracted from the fit image. (a) and (b) have the same intensity scale while in (c) the scale is magnified by 10 to show the residuals.

Fig. 3.3.1. We required 6 functions for the following reasons: The $I_2^{2+}$ peak at the center of the image has a fixed thermal width for constant repeller voltage. Since the width is dependent on charge and independent of the cation mass we experimentally determined the width of the $I_2^{2+}$ using $Ne^{2+}$ and $Ar^{2+}$. We find the width of the thermal peak to be 0.0275 eV.\(^2\) This width agrees with calculations and simulations in SimIon. For each image fit the thermal peak is fixed at zero radius and its width is fixed to the previously mentioned value. Also, for the thermal peak, the amplitude of the $L_0$ function is allowed to vary while the amplitudes for $L_2, L_4,$ and $L_6$ are set to zero. A second function was used for the (1,1) channel present in all the images. A third function accounted for the low energy peak with a relatively constant KER which is described in the next section. The remaining structure in the (1,0) dissociation channel required 3 functions to fit well, as shown in Fig. 3.3.2. It is not at all clear from the 1D lineouts that 3 functions are needed. However, the 3 channels differentiated themselves in the 2-D fits and were consistently needed for all wavelengths.

\(^2\)The energy scale we have used is based on the (1,1) KER. Since this is the total energy of two particles we must double the thermal width to match the single particle $I_2^{2+}$ width in the fit.
Figure 3.3.2:  (a) and (c) show a representative 3D image and lineout at 485 nm. In this image the B state peak is clearly visible at low energy. (b) and (d) show a representative 3D image and lineout at 590 nm. In this image the outer second high energy peak is just emerging around the bottom of the larger inner high energy peak. In the 3D image the central $I_2^{2+}$ peak is removed as described in the text and the lineouts are along the $\theta = 0$ direction. In figures (c) and (d) a labels the thermal $I_2^{2+}$ fit curve and b labels the low KER fit curve which we will associate with the B state.
To attempt to understand the dissociation pathways in the (1,0) channels 2D FFT spectroscopy is performed on pump-probe VMI data. The idea is that the higher energy KER channels may come from a two-step process through the X or A states of the ion. Thus the X or A states may dissociate through the absorption of one or more photons. If this were the case, then these dissociation channels would be modulated at the vibrational frequency of the X or A state. To perform the 2D FFT each pixel \( i \) in image \( j \) is converted into a time series running from 1 to \( j \). A 1D FFT is performed on this series and the value of the FFT corresponding to the frequency of the state of interest is used for the pixel value \( i \). This is done for all pixels in the original image forming a new 2D FFT image. This allows us to clearly identify X or A state modulation in the 2D FFT VMI image. A typical 2D-FFT image is shown in Fig. 3.3.3.

We considered three sources of error in the KER measurements. First, there is the quality of the fits. We used the standard method of using the curvature of \( \chi^2 \) in parameter space to estimate the errors in the fit parameters [65]. This gave a relative uncertainty in the KER of \( 10^{-4} \), which only sets a lower bound on the error. Second, we used the repeatability of the KERs for datasets taken at the same wavelength but at different intensities and gas pressures, and on different days. This gave an error of 0.125 eV for the (1,1) channel. This agrees nicely with the standard deviation of the measurement of the (1,1) for different wavelengths (again, 0.125 eV), as we do not expect a strong wavelength dependence to the (1,1) KER. Third, there may be a systematic error from the use of Gaussian functions to fit the KER spectrum, as that may not reflect the true KER distribution of a single dissociation channel. However, this error will be independent of the other experimental parameters, such as wavelength, intensity, and pressure. Since the fitting was done in momentum space, we scaled the KER uncertainty of 0.125 at 4.7 eV according to \( dE = 2\sqrt{2}Apdp \), where \( E \) is the energy in eV, \( A \) is the same constant as in Eq. 3.2.1, and \( p \) is the momentum in the
Figure 3.3.3: (Color online) Example 2D FFT VMI analysis images showing (a) X state modulation and (b) A state modulation. The pump and probe are vertically polarized 800 nm light. In addition to 5 block averaging these images have also been smoothed to enhance the modulation signal. Also shown is the 0.2 eV radial distance consistent with dissociation through the $B$ state. Note: Since a slightly lower repeller voltage was used to magnify the (1,0) channel these images have been scaled to the same image size as the single pulse images used in this thesis.

3.4 Results

In this thesis, we are mainly concerned with the KER of the various (1,0) dissociation channels of $I_2^+$. In fitting the data, we needed to include the angular distribution and the magnitude of the signal, but we will not consider them further, in this thesis. Fig. 3.4.1 shows the main results of the wavelength dependent study of the dissociation channels. In addition to the dissociation, there is, of course, an $I_2^+$ signal not seen in these images. At
the top of Fig. 3.4.1, there is the (1,1) channel. This is relatively constant as a function of wavelength and has been measured by several different groups, producing a total KER of 4.7 eV. There is some deviation around photon energies of 2.3 eV, but this is where the OPA crosses over from one mixing scheme to another and will be the studied in Chapter 4. The rest of the data points in Fig. 3.4.1 correspond to individual (1,0) channels.

As mentioned above, to first order, the $X$ and $A$ states of $I_2^+$ are bound and will not produce a (1,0) signal. The $B$-state has a binding potential, but if populated at the equilibrium internuclear separation $R_e$, the wavepacket will dissociate, although with very low energy in the range of 0.05-0.15 eV. This can be seen in Fig. 3.4.1 at the very bottom of the graph and is produced at every wavelength. So, our goal is to understand the rest of the data. Simple ionization of the HOMO, HOMO-1, and HOMO-2 will not give rise to the observed KERs. There are several possible explanations. The first is the simplest and is the one we believe to be correct: ionization occurs from deeper orbitals, HOMO-3 and HOMO-4, which involve orbitals built on the 5s electrons. However, before we can make this conclusion, we must consider other possibilities. Rescattering is well known to occur in strong fields and leads to HHG [28], non-sequential double ionization [46, 51, 66], and hot electrons [67]. It may well lead to excitation. For example, if an electron is ionized from the HOMO, the $X$ state would be populated, but the rescattered electron may excited the molecular ion to a higher state producing a large KER. However, this can be ruled out by using circular polarization, as shown in Fig. 3.4.2. While there are slight differences in the VMI images comparing linear and circular polarization, the number of channels and corresponding KERs are clearly the same. Thus, the multiplicity of (1,0) channels and their KERs cannot be attributed to rescattering.

The other scenario that does not invoke direct IOI is some post-ionization interaction with the laser field. This can occur in two limits: first the cation starts to dissociation while
Figure 3.4.1: (Color online) Plot of fit KER versus 32 photon energies. Fit data is plotted in black. The horizontal blue box shows the B state dissociation energy range from 0 to 0.15 eV. The slanted lines show the 1 photon mediated KER calculated for the X state (3/2 is the solid red line and 1/2 is the dotted blue line) and the A state (3/2 is the dashed green line and 1/2 is the dash-dotted purple line) to the $^2P_{3/2} + ^3P_2$ dissociated $I^+ + I$ state. The data points at 0 eV corresponding to the thermal $I_2^{2+}$ are not shown.
Figure 3.4.2: (Color online) Example VMI images for the polarization dependence at 661 nm. (a) VMI image with circular polarization. (b) Two VMI images, one with vertical polarization and one with horizontal polarization, summed together.

the field is on, or the cation is essentially stationary in the field. In the former case, the
cation can encounter laser induced curve crossings, generally known as bond-softening.
This is not likely, as iodine is quite heavy and will not move during the laser pulse. More-
over, one would expect an intensity dependence to the KER mediated by bond-softening as
the magnitude of the laser induced gap would be intensity dependent. We found no such
intensity dependence and Fig. 3.4.3 shows an example of this.

Finally, we must consider one other possibility: if, for example, the $A$ state is populated
through ionization of the HOMO-1, the cation may be able to absorb an additional photon
and reach a dissociating curve which produces a large KER. However, since the $X$ and $A$
state curves are known, one can predict the resulting KER. Furthermore, there should be a
linear dependence of the KER on the wavelength. Fig. 3.4.1 includes these possible KER
curves resulting from one-photon absorption from the $X$ or $A$ states. There does seem to be
Figure 3.4.3: (Color online) Fit for one wavelength showing the KER dependence of the peaks for five intensities.
a signal consistent with ionization to the $X_{1/2}$ state plus one photon and perhaps to the $A_{1/2}$ plus one photon. However, this is just a consistency check and there are several issues: 1) this assumes that there are states available to absorb the photon, which may not be the case: 2) the $A_{3/2} + \gamma$ line is clearly offset from the data; 3) the $A_{1/2} + \gamma$ line goes roughly through the data points, but a horizontal line at about 1.6 eV would do equally as well.

Because it is important to make a definitive conclusion on this possibility, we also performed a more involved experiment. When the $X$ or $A$ states of the cation are populated, they will start to vibrate at their characteristic vibrational frequencies. In order to test whether there is a post-ionization interaction, we applied a second probe pulse which we scanned in time. Presumably, there will be some R dependence to the post-ionization interaction, in which case, the signal produced by the absorption of an additional photon will be modulated at the field-free vibration frequency of the intermediate state. To look for this, we performed an FFT of the time-series for each pixel in the VMI image. We could then select the frequency of any of the low lying states of $I_2^+$ and create an image of the dissociation mediated by that particular state. Indeed, this was the original goal of this series of experiments. We assumed the higher KER channels were the result of such post-ionization absorption and the FFT VMI images would tell us something about the intermediate state. However, as it turns out, we saw modulation at the $X$ and $A$ state frequencies, but only in the very low KER region, see Fig. 3.3.3. The (1,0) channels with a KER above 0.2 eV showed no modulation, implying that they came from dissociating potential curves populated directly by the laser field.
Figure 3.5.1: (Color online) Potential energy curves for the X, A and B states of I$_2^+$. The I$_2$ ground state is shown in the inset as well as the KER definitions used in Eq. 3.5.2. The known Frank-Condon transition energy from the I$_2$ ground state to I$_2^+$ are shown as blue dots and labeled as in [58]. Plotted on the right hand side of the figure are the possible dissociation energies as described in Sec. 3.4 and labeled as in [57]. The dashed lines show two possible dissociation pathways from Table 3.5.1.
3.5 Discussion

Iodine has 106 electrons in the following MO structure [58],

\[
(\text{core})^92 (10\sigma_g)^2 (10\sigma_u)^2 (11\pi_u)^4 (6\sigma_g)^4 (11\sigma_u)^0
\]  

Ionization from an outer valence MO places the molecule in a particular state of \(I_2^+\): The HOMO ionizes to the \(X\) state, the HOMO-1 ionizes to the \(A\) state and the HOMO-2 ionizes to the \(B\) state [60, 61]. Figure 3.5.1 shows the potential energy curves for the low–lying states of \(I_2\) and \(I_2^+\). As can be seen a vertical transition from the ground state of \(I_2\) at the equilibrium internuclear separation will only lead to an unbound state in the \(I_2^+\) \(B\) state. The \(X\) and \(A\) states of \(I_2^+\) will remain bound. Wavepacket simulations show that population in the \(X\) and \(A\) states can be promoted to the \(B\) state and dissociate. This is consistent with the data in Fig. 3.3.3.

The number of states to which \(I_2^+\) can dissociate is surprisingly limited due to energy conservation restrictions. These states are even further limited by the known KER of the (1,0) channel in which we are interested in. This puts a limit on the KER that we expect to see. Through energy conservation we can identify the KER of the direct ionization and dissociation states:

\[
\text{KER} = I_V - [E_1 + E_2 + I_p + D_e]
\]  

where \(I_V\) is the vertical excitation energy of \(I_2\) to various states of \(I_2^+\), \(E_1\) and \(E_2\) are the internal energies of the two atomic iodine fragments, \(I_p\) is the ionization potential of atomic iodine, and \(D_e\) is the dissociation energy of the \(I_2\) ground state. See the inset in Fig. 3.5.1. \(I_2\) has an ionization potential of 10.45 eV. The dissociation energy of \(I_2\) is 1.57 eV.
Using Eq. 3.5.2 and the ionization potentials and dissociation limits of iodine, we can put limits on the KER we expect to see. The ionization potentials of $I_2$ have been measured using electron–momentum spectroscopy (EMS) and photo–electron spectroscopy (PES) [58, 68]. These values are plotted in Fig. 3.5.1. The dissociation limits are set by the known atomic energy levels [69]. As an example we look at the $B$ state KER. The $B$ state dissociates to the D2 manifold [57]. The D2 limit has 3 atomic configurations, giving three possible dissociation energies. The $B$ states ionization potential is 12.95 eV as given by PES. This gives the following KER values: 0.14 eV for $^2P_{3/2} + ^3P_0$, 0.05 eV for $^2P_{3/2} + ^3P_1$, and 0.00 eV for $^2P_{1/2} + ^3P_2$. As can be seen in Fig. 3.4.1 we find the KER to be within this range. 3 We can also see that there is a flat response versus the photon energy only for the low energy $B$ state dissociation and the (1,1). Allowing for the possibility of photon assisted dissociation, which adds $n\hbar\omega$ where $n = 1, 2, \ldots$, to Eq. 3.5.2, we can attempt to identify some of the channels with the $X$ or $A$ state of $I_2^+$ as discussed above. It can be seen in Fig. 3.4.1 that these channels do not fit well with the possible KER of the photon mediated $X$ or $A$ state except possibly the $X_{1/2}$ state. The pump-probe data, as shown in Fig. 3.3.3, confirm this result since they only show $X$ and $A$ state modulation in the low energy $B$ state dissociation channel. There is no modulation of the high KER (1,0) in the 2D FFT spectrum.

Nuclear wavefunction simulations of $I_2^+$ show that the $X$ and $A$ state do impress modulation on to the $B$ state dissociation and that the $B$ state dissociates at low energy around 0.2 eV. The simulations do not produce any high KER dissociation which is consistent with the investigation results above, see Fig. 3.5.2. Thus, in order to understand the high-energy dissociation channels, we must consider additional initial states (blue dots in Fig. 3.5.1)

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3EMS and PES show slightly different values for the $B$ state ionization potential [58]. However the EMS values would not allow for the $B$ state to dissociate. The PES data only covers the first five ionization levels. We have therefore used the EMS values to expand the range of ionization potentials of $I_2$.  

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Table 3.5.1: Some possible combinations of the dissociation of $I_2$ to atomic fragments. DL is the dissociation limit as labeled in [57] and $I_p$ is the atomic ionization potential level as labeled in [58] where level 5 corresponds to the $B$ state of $I_2^+$. We have average the D2, D3, and D7 manifolds. D2 and D3 have 3 possible dissociation limits while D7 has 2 possible dissociation limits. We only show possible KER which fall in the (1,0) range of 0.0 to 3.0 eV. Atomic levels are from Ref. [69].

<table>
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<tr>
<th></th>
<th>Ip</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
<th>D7</th>
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<tr>
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<td>1.01</td>
<td>0.12</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.21</td>
<td>1.2</td>
<td>0.26</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.35</td>
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<td>D</td>
<td></td>
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<td>2.67</td>
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and dissociation limits (D3, D4, ...). Table I summarizes possible KERs from the known initial and final states that fall within the measured range. We are not claiming a precise identification. Rather, we are showing that dissociation pathways exist that fit the data.

### 3.6 Conclusion

We have completed an exhaustive study of the dissociation of $I_2^+$. In this study we have ruled out electron rescattering and BS since there was no polarization or intensity dependence. We have found that single ionization in a strong field to high KER (1,0) channels is not consistent with dissociation through the $X$, $A$ or $B$ states. However, low energy KER does occur through the $B$ state. This implies that single ionization to the high KER (1,0) does not appear to come about through ionization of the HOMO, HOMO-1, or the HOMO-2, but is consistent with ionization coming from a deeper HOMO-3 or HOMO-4 MO formed from the $5s$ electrons. Further work is needed to identify the exact dissociation
Figure 3.5.2: (Color online) Example of a wavepacket pump-probe simulation at 800 nm showing only low energy $B$ state dissociation. The inset shows there is no dissociation from 0.25 to 6 eV.
pathways and the orbitals involved.
Chapter 4

Resonantly Enhanced Inner Orbital Ionization in Molecular Iodine

4.1 Introduction

Most strong field interactions with atoms and molecules, such as HHG, start with single electron ionization [28]. In atoms and light molecules, most of the ionization comes from the least bound electron in either the outer shell for atoms or the HOMO for molecules [70]. The influence of inner orbitals can be seen in the strong-field molecular interaction, but the angularly averaged ionization rate from the inner orbitals is small (< 10%) [71]. We have shown in previous experiments that this is not the case for iodine. In fact, the branching ratio for ionization of the inner orbitals can exceed 90% [72]. We have also recently observed an interesting wavelength dependence to the ionization rates of the different orbitals as described in Chapter 3. Both of these results run counter to a simple tunneling model of strong field ionization, in that tunneling ionization strongly prefers the least bound electron
and predicts no wavelength dependence [73].

In this thesis, we present a detailed study of the single ionization of $I_2$ in the vicinity of the $X$ to $B$ state resonance in the neutral molecule, where we previously saw a large wavelength effect on ionization. Since the $X$–$B$ transitions involves driving an electron from the HOMO to the LUMO, one might expect that ionizing $I_2$ at this resonance would simply enhance the ionization rate of the HOMO, as that electron would be promoted to the LUMO where it should easily ionize. However, it turns out the results are significantly more complicated and counter-intuitive. We divide the ionization signal into two parts: one corresponding to ionization of the HOMO, the HOMO-1 and HOMO-2, leading to the population of the $X$, $A$, and $B$ states of the molecular ion, respectively [60, 61]. We refer to this part as outer-orbital ionization (OOI). The other part of the ionization signal corresponds to ionization of deeply bound inner orbitals through IOI. Both signals show a strong resonant behavior around the $X$ to $B$ transition, but the peaks in the two signals as a function of wavelength are slightly different. As a result, the branching ratio into the IOI channel shows a dispersion type profile with the peak of the branching ratio exceeding 98%. At this point, the resonant interaction does not increase the ionization rate of the HOMO, but rather enhances the ionization rate of the inner orbital electrons. We speculate that driving the neutral molecule on a one photon resonance creates a strong dipole that couples to the inner orbitals, leading to their large ionization rates, compared to the outer orbitals.
4.2 Experiment

We use a Spectra Physics Ti:sapphire laser (800 µJ, 40 fs, 800 nm, 1 kHz) and send 450 µJ of the beam to a TOPAS OPA. The OPA generates short pulses from 489 nm to 680 nm with a pulse duration of 45 fs. For this experiment we were unable to cover the ranges of 525-550 nm and 590-626 nm with sufficient energy for ionization. We use the same experimental configuration as described in 3 and as shown in Fig. 3.2.1. In addition we have introduced a pickoff mirror and photodiode after the OPA’s prism compressor to monitor the beam energy. We use the signal from the photodiode, which is sent to a Stanford Research Systems Boxcar, to remove energy variations which are longer than 30 ms. We hold the energy to 1 µJ which leads to a $1/\lambda^2$ scaling in the intensity and corresponds to an intensity of $5.13 \times 10^{12}$ to $2.7 \times 10^{12}$ W/cm² for 489 to 680 nm. The pulse duration out of the OPA was measured with an achromatic self-diffraction scanning autocorrelator. Room-temperature (295K) I₂ gas is diffused into a high-vacuum chamber to achieve a pressure of $7 \times 10^{-7}$ Torr with a background pressure of $7 \times 10^{-9}$ Torr. To achieve velocity mapping of ion fragments we use a 3 element ion lens in conjunction with a MCP and phosphor screen which is imaged by a CCD camera at a rate of 20 frames/s, see Sec.3.2. [25]. The MCP is gated to slice the data and produces a temporal width of 15 ns. The camera rate corresponds to the boxcar averaging of the energy signal as described above. A typical ion image is shown in Fig. 4.2.1 with the laser polarized along the y-axis as it is for all images in this section. Data is take in ion-counting mode where a threshold is applied to each camera pixel to determine if an ion was detected. This removes noise and fluctuations in the MCP response. For each wavelength data was taken sequentially in the order $I^+$, $I^2+$ and $I_2^+$ with 10,000 frames for $I^+$ and $I^2+$ and 1,000 frames for $I_2^+$.

Data were taken at 16 wavelengths around the neutral X to B state transition at 530 nm
Figure 4.2.1: Two de-convoluted VMI images which define the ionization channels. (a) The $I^+$ image has the $I^+_2$ at the center and is shown as a black circle. The OOI (1,0) channel is shown as a dark grey region outside of the $I^+_2$. The IOI channel is shown as a light grey region and the remaining region to the outer black circle is the (1,1) channel. (b) The $I^{2+}$ image shows the (2,0) channel as a light grey region. The rest of the image contained in the outer black circle shows the (2,1) which is not analyzed in this thesis. The three axis are labeled in the image with the $x$–axis being the time of flight axis. All data was taken with the laser polarization lying along the $y$–axis.
[74]. The bounds of the wavelength range were set by the unusual enhancement in the IOI $I^+ (1,0)$ channel. This channel deviates from its characteristic signal at 489 nm which sets the lower bound and returns to its normal pattern at the upper bound of 680 nm.

### 4.3 Data Analysis

To analyze the VMI data we begin by block averaging and folding the images in quadrature to improve statistics. Since we are interested in branching ratios we must have completely de-convolved images. However the temporal detector gate leaves us with a thick slice and the resulting data can not be de-convoluted with standard methods. To de-convolute the VMI data we have modified the onion-peeling algorithm which allows us to transform partially sliced 2D data [75, 76]. However, this method requires knowledge of the slice thickness. Since the ion distribution has cylindrical symmetry we can compare a slice at the center of the $I^+$ signal in the $zy$–plane to a slice in the $xy$–plane [22]. The $xy$–slice is reconstructed from 29 sliced VMI images in which the gate delay is varied by 5 ns such that the entire $I^+$ signal is captured, see Fig. 4.3.1. Using this method we find a 15 ns width for sliced VMI images. The modified onion-peeling algorithm allows us to back-project the higher energy contributions which occur in the thick sliced region to the lower energy pixels to invert the image, see Fig. 4.3.2. This is accomplished by calculating the contributions to inner pixels, $i$, from the value of the next outermost pixel, $i + 1$. The image is processed starting at the $n – 1$ pixel, where the number of pixels in the image is $n$, and then continues inward toward the center of the image. From the area of the annular rings located behind the pixel of interest the value of the $i + 1$ pixel is scaled and subtracted for each region of overlap. The images are then angularly integrated to restore the full information for each
Figure 4.3.1: (Color online) 3D reconstruction of the \( I^+ (1,0) \) channels from sliced 490 nm VMI images \([77]\). The reconstructed image is comprised of 29 sliced VMI images taken at consecutive gate delays which are 5ns apart. (a) shows the central slice VMI image in the \( zy \)-plane, (b) show the reconstructed 3D image, and (c) shows the reconstructed slice in the \( xy \)-plane. The central slice in the \( zy \)-plane is compared to a central slice taken from the \( xy \)-axis to determine the temporal width of the VMI gate.

channel \([20]\). This allows us to determine branching ratios for the various channels which we define below.

The \( I^+_2 \) signal corresponds to ionization of the HOMO and HOMO-1 resulting in the \( X \) and \( A \) state of the ion. However, some of the \( X \) and \( A \) state population can be excited to the dissociating \( B \) state. Direct ionization of the HOMO-2 can also populate the \( B \) state, see Section \(3.5\). Thus, \( I^+_2 \) and low energy \((1,0)\) constitutes the OOI signal. The \( B \) state dissociates with a KER of 0.025 to 0.21 eV. The IOI signal comes from high KER \((1,0)\) dissociation. In Chapter 3 we have shown that the high KER \((1,0)\) signal cannot come from 1) direction ionization of an outer-orbital, using energy conservation, as the energy levels at the equilibrium internuclear separation and the separated atom limit are known; and
Figure 4.3.2: (Color online) A diagrammatic view of the slice inversion technique described in the text. The image shows a section of the Newtonian sphere as it approaches the MCP (the flattening of the sphere toward the MCP has been neglected). The $I_2^{2+}$ is shown as the central circle, in blue. The rectangle, in green, on the central axis labeled 1 to 19 depicts the width, in time, of the MCP gate. The circle surrounding the $I_2^{2+}$ circle shows the region in which the gate is long enough to catch all ions. The two rings represent ions which lie outside the full gate region. This is the slice region. However as can be seen ions which correspond to pixel 15 will also overlap with pixels from 0 to 14. The overlap for pixel 14 is shown with black hash lines.
2) a two-step process through the $X$ or $A$ states, using pump-probe and Fourier transform spectroscopy. For double ionization into the low lying levels of the dication we include $I_2^{2+}$, which has a known thermal width of 0.025 eV, and the (1,1) channel. The (2,0) channel corresponds to electronically excited dications.

We measure the thermal width of the $I_2^{2+}$ as described in Section 3.2 and find that it has a half-width half maximum of 0.019 eV. We therefore integrate the signal below 0.023 eV in the $I_2^{2+}$ sum. For the (1,0) channel we start with the $B$ state which has a known energy as described above. Therefore for the OOI we sum over all energies from 0.035 to 0.21 eV. We determine the region for the IOI channel from the images and sum the energies from 0.24 to 3.43 eV. All of the signal above 3.49 eV is taken in the (1,1) sum. In the $I_2^{2+}$ images the (2,0) and the (2,1) channels are well separated. We find that the (2,0) channel lies below 3.8 eV and the (2,1) is everything above 3.8 eV. This is shown in Fig. 4.2.1.

The uncertainty in the signals come from three sources. 1) The uncertainties due to counting statistics are negligible. 2) Changes in the $I_2$ pressure during data taking are monitored and contribute to the uncertainty. 3) Signals from images with intensities larger and small than the desired intensity range provide an upper bound to the uncertainty from intensity fluctuations within the specified range.

In Fig. 4.3.3 we show the total integrated sum of the IOI and the OOI channels as a function of wavelength. At short wavelengths, between 489 nm to 508 nm the two channels track well and at longer wavelengths, from 626 nm to 690 nm, the two channels have nearly the same wavelength dependence. However, in the region from 508 nm to 626 nm we find that there is a difference in where the two channels peak with the IOI peaking at a slightly shorter wavelength than the OOI. The branching ratios for these two channels, shown in Fig. 4.3.4, also show wavelength dependent peaks for the two channels. The IOI channel has a branching ratio peak which coincides with the peak signal. Interestingly, the OOI
branching ratio has a peak at 580 nm while the signal has a peak at 558 nm. Fig. 4.3.5 shows that the VMI data clearly exhibits a dramatic change in the channel structure for this wavelength region which only spans 200 nm. In particular Figs. 4.3.5b and c only differ in wavelength by \( \sim 60 \) nm. As a check we also performed all of the analysis on the raw slice image. The only major difference in the raw data was an increase in the intensity as can be expected since we have removed data in the deconvolution process outlined above. Since the data was analyzed using branching ratios and normalized data there was little impact due to the intensity changes. The branching ratios and integrated signals only show slight changes which are well inside the error bars on the presented data. This shows that the slice we have for iodine is thin enough that it does not require deconvolution. However, for this thesis we have maintained the fully deconvoluted data analysis.

We also find that the double ionization (2,0) channel has a wavelength dependence (Fig. 4.3.6). Interestingly this dependence tracks well with the branching ratio of the IOI channel. There is an additional dip in the (2,0) channel which does not track with the IOI. This dip occurs at 508 nm and is on the same order as the dip in the branching ratio at 590 nm. This may be indicative of some other resonance effect.

### 4.4 Discussion

Iodine has 106 electrons with the MO structure as defined in Eq. 4.4.1 which also shows the IOI and OOI orbitals.

\[
\text{(core)}^9\underbrace{(10\sigma_g)^2 (10\sigma_u)^2 (11\sigma_g)^2 (6\pi_u)^4 (6\pi_g)^4 (11\sigma_u)^0}_{\text{inner valence IOI}}\underbrace{}}_{\text{outer valence OOI}}\]  

(4.4.1)
Figure 4.3.3: (Color online) The normalized integrated signals of the IOI and OOI as a function of wavelength. The peaks in the signals occur at different wavelengths. The dashed line show the region we are unable to cover. Error bars are calculated from uncertainty in the counting statistics and the pressure and intensity variation.
Figure 4.3.4: (Color online) Branching ratios of the IOI (IOI/(IOI + OOI)) and OOI (OOI/(IOI + OOI)) as a function of wavelength. The peaks in the ratios occur at different wavelengths and the IOI is strongly enhanced at 519 nm. The dashed line show the region we are unable to cover. Error bars are calculated from uncertainty in the counting statistics and the pressure and intensity variation.
Figure 4.3.5: Four $I^+$ VMI images corresponding to (a) the beginning of the data set at 489 nm, (b) the peak in the IOI branching ratio at 519 nm, (c) the peak in the OOI branching ratio at 580 nm, and (d) the end of the data set at 670 nm.
Figure 4.3.6: (Color online) Branching ratios of the OOI (OOI/(IOI + OOI)) and the \((2,0)\) channel \([(2,0)/((2,0)+(1,1)+I_m^2)]\) as a function of wavelength. The two ratios track well above 519 nm. There is an unexplained dip in the \((2,0)\) channel at 508 nm. The dashed line show the region we are unable to cover. Error bars are calculated from uncertainty in the counting statistics and the pressure and intensity variation.
Our previous work shows that the IOI electrons play a role in ionization of iodine which is contrary to strong field ionization theory as described in Chapter 3. In this work we have found that there is also a strong wavelength dependence to this ionization. As shown in Figs. 4.3.3 and 4.3.4 the ionization depends on the MO from which the electron is removed. Also, we see that there is a strong preference for the IOI as there is a 98% branching ratio at the peak at 519 nm. Such a strong wavelength dependence is likely to play a key role in higher order processes such as HHG. Since tunneling ionization theory does not directly predict inner orbital ionization the data suggests the presence of an additional interaction. The work presented in Chapter 3 suggests that static (induced or permanent) dipoles influence the tunneling rate of different orbitals. In our experiment, we strongly drive a one-photon resonant dipole between the $X$ and $B$ states in the neutral molecule. This additional field appears to have a profound influence on the ionization rates of the inner orbitals. This effect can either enhance or suppress the IOI branching ratio, depending sensitively on the exact driving frequency.

For double ionization we also see the influence of the IOI channels. Fig. 4.3.6 shows that there is a similar wavelength dependence to the branching ratios of the IOI and the (2,0) channels. This implies that double ionization takes place through the IOI and leaves the double cation in an excited state.

Finally, these result may be connected to prior work in which the branching ratio of the (1,0) was seen to rise to nearly 95% as a function of internuclear separation ($R$) [59]. The $X$–$B$ transition in neutral iodine shifts to lower frequency as $R$ increases, bringing it into resonance with the 800 nm beam used in Ref. [59] at a distance of 5.71 a.u.. The peak was seen in the data at a value of $<R> = 6.85$ a.u. where the $X$–$B$ transition is longer than 800 nm. However, the vibrational wavepacket is moving in this experiment, affecting the phase. Moreover, the phenomenon of enhanced ionization starts to play a role
at large $R$ [78]. Nevertheless, it is remarkable that in these rather different experiments (the wavelength dependence at fixed $R$ and the $R$ dependence at fixed wavelength) both show an enhanced branching ratio for IOI, indicating that the strength of IOI depends on many factors and can dominate the ionization.

### 4.5 Conclusion

In conclusion, we find that there is an unexpectedly strong wavelength dependence in a narrow 200 nm region for the strong field single electron ionization of molecular iodine. This wavelength dependence does not occur at the same wavelength for the two single ionization (IOI and OOI) channels. We speculate that the resonant enhancement of the IOI channel is brought about through a coupling between molecular orbitals brought on by a strong dipole. The double ionization (2,0) channel has a wavelength dependence which correlates well with the single ionization IOI channel which suggests that double ionization takes place through excited states and deeply bound molecular orbitals.
Chapter 5

Outlook and Conclusion

5.1 VMI Reconstruction of TOF Data

TOF pump-probe data for iodine shows interesting features in the $I^+$ and $I^{2+}$ channels. Over very short time scales, tens of femtoseconds, the KER of the channels shift dramatically in the (2,0) channel and it shows a sharp peak which drops in KER very close to zero delay between the pump and the probe. This data has been reproduced using VMI images. For each image in the VMI pump-probe scan a line out was taken down the vertical axis to reproduce the conditions of the TOF data. This set of lineouts was combined into a single data set and then processed using the same software which processed the TOF data. Fig. 5.1.1 show an example of the comparison of TOF data to the VMI data.

In addition to the lineout data which recreates the TOF analysis, VMI also records angular information as well as the entire velocity distribution. In the VMI images it may be possible to isolate state specific changes to the KER as a function of pump-probe delay. However, the VMI data taken so far does not have enough statistic or resolution to make
Figure 5.1.1: (Color online) Comparison of TOF data with data reconstructed using VMI images. (a) and (b) show the (1,0) channel in $I^+$ from TOF and VMI data respectively. (c) and (d) show the (2,0) and (2,1) channels in $I^{2+}$ from TOF and VMI data respectively. In the $I^{2+}$ there are large changes in the KER throughout the time delay scan.
Figure 5.1.2: (Color online) VMI analysis of the TOF KER structure in the (2,0) channel of $I^2+$. (a) Shows the points of interest to be studied with full VMI images. (b) Show the VMI images where the numbering corresponds to the numbering shown in (a).

Fig. 5.1.2 shows an example of a VMI image analysis for several points of interest in the $I^2+$ TOF. The addition of a molecular beam and alignment will lead to an improvement in the energy resolution of the current VMI apparatus and may shed light on the sharp changes in KER noticed in the TOF data.
5.2 Ion Pairs

Ion pair production, in which both the cation and the anion are produced, is possible during dissociation. However, this process is highly wavelength dependent since direct excitation to the ion pair dissociating state is required. Recently Bogomolov et al. investigated an ion pair channel in iodine using the two-photon excitation of $I_2$ using 270.486 nm photolysis laser light [79]. This is interesting for the work in Ch. 4 since the two-photon energy is equivalent to a 4-photon transition at 540.972 nm. With short pulses the spectrum is broadened and therefore it may be possible to excite this transition near the 530 nm resonance we have observed. The KER for this channel is low at only $\approx 0.3$ eV which is coincident with the $B$ state KER so the ion pairs may play no role in the unusual resonance we have observed. It is a simple matter of reversing the potential on the ion lens to see anions produced from 530 nm photolysis and therefore relatively easy to measure the KER of the anions if they are present to determine their impact if any.

5.3 Conclusions

This thesis focused on the single ionization of molecular iodine with strong laser fields. In Ch. 3 a VMI wavelength study was performed to investigate the process of ionization through the KER of the (1,0) fragments. Unexpectedly we found that the single ionization has a contribution from inner orbital $5s$ electrons. The KER of the majority of the fragments in the (1,0) channel was inconsistent with ionization to the $X$, $A$, and $B$ states of $I_2^+$. Pump-probe Fourier analysis showed that modulation from the $X$ and $A$ states was only present in low KER below 0.2 eV. In addition, we ruled out bond softening and electron rescattering as possible ionization pathways. This implies that ionization in $I_2$ in a strong field does not
come about through the HOMO, HOMO-1, or the HOMO-2, but through the HOMO-3 and HOMO-4 formed from 5s electrons. Interestingly, the HOMO-3 and HOMO-4 are more tightly bound than the outer valance electrons and thus these findings are inconsistent with the current tunneling ionization models.

In Ch. 4 we focused on a narrow 200 nm wavelength portion of the spectrum surrounding a one-photon B state resonance at 530 nm. We found that the single ionization branching ratio of high-lying MOs and the inner MOs both show a resonance enhancement and that the two peaks in the branching ratios occur at slightly different wavelengths. For the IOI we see a strong peak in the branching ratio which reaches more than 98% at 519 nm. We have speculated that this resonance enhancement comes about through a coupling between MO’s brought about through a strong dipole. Along with the single ionization results we also find that the branching ratio for double ionization into an excited state of I$_2^+$ as a function of wavelength closely matches that of the branching ratio of the IOI. This implies that excitation of molecules generally comes about through IOI.
Bibliography


