Molecular Ionization from the Ground and Excited States of I₂ by Intense Laser Fields

Hui Chen

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Molecular Ionization from the Ground and Excited States of I$_2$ by Intense Laser Fields

Hui Chen, Ph.D.
University of Connecticut, 2014

ABSTRACT

Exposing molecules to strong laser fields produces a variety of effects, which has led to considerable work in many areas, such as enhanced ionization, high harmonic generation, nonsequential double ionization, and coherent control. However, these strong-field experiments start with neutral ground-state molecules at their equilibrium internuclear separation. In this dissertation, we experimentally investigate the internuclear-separation-dependent ionization of different molecular orbitals in neutral I$_2$. With a pump-probe scheme, a vibrational wavepacket is launched in the B$^3\Pi_u$ (B state) of I$_2$ by promoting an electron from the highest occupied molecular orbital (HOMO) $\pi_g$ to the lowest unoccupied molecular orbital (LUMO) $\sigma_u$, and then the ionization rate as a function of internuclear separation $R$ is measured through detection of the I$_2^+$ signals as the wavepacket evolves in the B state. Moreover, since the ground X$^1\Sigma_g^+$ to B$^3\Pi_u$ state optical transition dipole moment is parallel to the internuclear axis, the B-state sub-population of the I$_2$ thermal ensemble will have a high degree of alignment, allowing for angular measurements. In this way, both the angle-resolved and $R$-resolved measurements of the ionization rate of the LUMO $\sigma_u$ state
are obtained, and enhanced ionization is found at $\sim 8.67$ a.u.. Based on the above idea, a wavepacket is generated in the ground state of I$_2$ by adding a dump pulse at a certain delay when the B-state wavepacket reaches the one-photon resonant crossing to return the wavepacket in the ground state. Using this returning wavepacket and Fourier-transform spectroscopy, we study the R-dependent ionization of the ground state on different molecular orbitals, HOMO $\pi_g$, HOMO-1 $\pi_u$ and HOMO-2 $\sigma_g$. We find that HOMO $\pi_g$ and HOMO-1 $\pi_u$ do not have a strong R-dependent ionization, however, HOMO-2 $\sigma_g$ does. Further, HOMO-2 $\sigma_g$ provides the dominant ionization pathway, which is unusual in small molecules. With the wavepacket in the B state, we discuss the enhanced ionization in HOMO-2 $\sigma_g$ through detection of dissociative fragment ions, and find that enhanced ionization also happens in this inner orbital. For heavy molecules, like I$_2$, 50-fs pulses can provide good resolution in the study based on vibrational motions, however, for light molecules, like H$_2$, sub 10-fs pulses are needed. To obtain 10-fs pulses, we study white-light supercontinuum generation via filamentation in a gaseous medium SF$_6$. A filament is formed at a pressure of 1 atm with an input power as low as 350 mW. The spectrum is widely broadened which is capable of producing sub 10-fs pulses.
Molecular Ionization from the Ground and Excited States of I$_2$ by Intense Laser Fields

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A Dissertation
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at the
University of Connecticut

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Molecular Ionization from the Ground and Excited States of I$_2$ by Intense Laser Fields

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2014
Dedicated to my parents and little sister

In memory of my beloved grandfather
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## Contents

Ch. 1. **Introduction** .................................................. 1

1.1 What is a strong field? .............................................. 1
1.2 Behavior of molecules in strong fields ......................... 2
  1.2.1 Strong-field induced vibrational motion ................. 2
  1.2.2 Molecular ionization in strong fields ................... 6
  1.2.3 Enhanced ionization .................................... 10
  1.2.4 Self-trapping of light ................................ 18
1.3 Experimental apparatus ........................................... 20
  1.3.1 Femtosecond laser system ............................ 20
  1.3.2 Pulse measurement ................................ 22
  1.3.3 Time-of-Flight Spectroscopy ......................... 23
1.4 Outline .................................................................. 28

Ch. 2. **Enhanced ionization of the B-state of I$_2$ by strong laser fields** 32

2.1 Introduction ......................................................... 32
2.2 Experiment ......................................................... 35
2.3 Results ............................................................... 38
  2.3.1 Internuclear-separation-resolved measurements .... 38
  2.3.2 Angle-resolved measurements ........................ 44
2.4 Discussion ........................................................... 50
2.5 Conclusion .......................................................... 51

Ch. 3. **Internuclear separation dependent ionization of the valence orbitals of I$_2$ by strong laser fields** 52

3.1 Introduction .......................................................... 52
3.2 Experiment ........................................................... 54
3.3 Results ................................................................. 59
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Potential curves of the X state and B state of I$_2$.</td>
<td>7</td>
</tr>
<tr>
<td>1.2</td>
<td>Simulation of vibrational wavepacket generated in the B state of I$_2$.</td>
<td>8</td>
</tr>
<tr>
<td>1.3</td>
<td>The three ionization regimes: multiphoton, tunneling, and over-the-barrier ionization.</td>
<td>11</td>
</tr>
<tr>
<td>1.4</td>
<td>Enhanced ionization found at $R \sim 8.67$ a.u. in I$_2$ B$^3\Pi_u$ state.</td>
<td>15</td>
</tr>
<tr>
<td>1.5</td>
<td>Schematic illustration of the electronic potential at three internuclear separations in the absence of the field.</td>
<td>16</td>
</tr>
<tr>
<td>1.6</td>
<td>Schematic illustration of the electronic potential at three internuclear separations in electric field.</td>
<td>17</td>
</tr>
<tr>
<td>1.7</td>
<td>Radial intensity distribution of the laser beam and the refractive index distribution of a self-trapping laser beam.</td>
<td>21</td>
</tr>
<tr>
<td>1.8</td>
<td>Autocorrelation signal in a second-order autocorrelator.</td>
<td>24</td>
</tr>
<tr>
<td>1.9</td>
<td>Schematic illustration of the third-order autocorrelator.</td>
<td>25</td>
</tr>
<tr>
<td>1.10</td>
<td>Schematic illustration of the time-of-flight spectrometer.</td>
<td>29</td>
</tr>
<tr>
<td>1.11</td>
<td>Typical time-of-flight signals of iodine ions.</td>
<td>30</td>
</tr>
<tr>
<td>1.12</td>
<td>Vibrational wavepacket of the ground state of I$_2$ seen in the TOF spectrum of I$^{2+}$ ion fragments.</td>
<td>31</td>
</tr>
<tr>
<td>2.1</td>
<td>Potential curves and pump-probe experimental scheme.</td>
<td>36</td>
</tr>
<tr>
<td>2.2</td>
<td>Angular dependence of the B state.</td>
<td>39</td>
</tr>
<tr>
<td>2.3</td>
<td>Ionization signal of I$_2^+$ as a second-order autocorrelator.</td>
<td>40</td>
</tr>
<tr>
<td>2.4</td>
<td>$R_c$ found at $\sim 8.67$ a.u.</td>
<td>42</td>
</tr>
<tr>
<td>2.5</td>
<td>Simulation of $R(t)$ of the WP in the B state.</td>
<td>43</td>
</tr>
<tr>
<td>2.6</td>
<td>Ionization rates as a function of pump-probe delay and internuclear separation $R$ at two different pump wavelengths</td>
<td>45</td>
</tr>
<tr>
<td>2.7</td>
<td>Angular dependence of ionization rates at $R_c$, $R_i$, and 6.45 a.u.</td>
<td>46</td>
</tr>
<tr>
<td>2.8</td>
<td>Angular averaging effect.</td>
<td>48</td>
</tr>
<tr>
<td>2.9</td>
<td>Angular averaging calculation and the comparison with data.</td>
<td>49</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic potential energy curves, showing the physical scenario of the pump-dump-probe experiments.</td>
<td>55</td>
</tr>
<tr>
<td>3.2</td>
<td>Depletion of the B state.</td>
<td>57</td>
</tr>
<tr>
<td>3.3</td>
<td>X-state vibrational wavepacket in the (2,0) channel.</td>
<td>58</td>
</tr>
<tr>
<td>3.4</td>
<td>FFT spectra of the (1,0) signal and the bound $I_2^+$ signal.</td>
<td>61</td>
</tr>
<tr>
<td>3.5</td>
<td>Branching ratio of the (1,0) channel.</td>
<td>63</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic potential energy curves, showing the physical scenario of the pump-probe experiments.</td>
<td>68</td>
</tr>
<tr>
<td>4.2</td>
<td>The ionization signals of $I_2^+$ and the (1,0) channel as functions of pump-probe delay.</td>
<td>70</td>
</tr>
<tr>
<td>4.3</td>
<td>The ionization signal of the (1,0) channel as a function of internuclear separation $R$ with two different pump wavelengths.</td>
<td>72</td>
</tr>
<tr>
<td>4.4</td>
<td>Calculation of the ionization probability as a function of internuclear separation $R$ with two electrons initially in the ground state.</td>
<td>76</td>
</tr>
<tr>
<td>5.1</td>
<td>The experimental layout of filamentation.</td>
<td>81</td>
</tr>
<tr>
<td>5.2</td>
<td>Spectra for various laser input energies when the pressure of the SF$_6$ is 735 torr.</td>
<td>83</td>
</tr>
<tr>
<td>5.3</td>
<td>Spectra for various SF$_6$ pressures when the input energy is 0.75 mJ.</td>
<td>85</td>
</tr>
<tr>
<td>5.4</td>
<td>Spectra for various laser repetition rates when the SF$_6$ pressure is 1 atm and the input energy is 0.35 mJ.</td>
<td>86</td>
</tr>
<tr>
<td>5.5</td>
<td>Spectra for various positions in the beam.</td>
<td>88</td>
</tr>
<tr>
<td>5.6</td>
<td>Discussion of pointing stability of the filament.</td>
<td>91</td>
</tr>
<tr>
<td>5.7</td>
<td>Pulse duration measurement after recompressing the output pulses.</td>
<td>92</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.1</td>
<td>Typical values for ground X states of different molecules.</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Experimental values of $\omega_e$ for different electronic states of $I_2$ and $I_2^+$</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>A summary of studies of EI, including both 1-electron system and 2-electron system.</td>
<td>34</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 What is a strong field?

In 1980s, the generation of ultrafast femtosecond lasers opened up a new research area in physics, known as strong-field physics. A strong field refers to an external electromagnetic field which is comparable with the internal Coulomb fields in atoms or molecules which bind the electrons ($\sim 5 \times 10^9$ V/cm in H, corresponding to $\sim 3 \times 10^{16}$ W/cm$^2$ in intensity). Generally speaking, when the external field is weak and almost negligible compared with the internal field, the interaction between the external field and electrons in atoms or molecules can be described by perturbation theory. However, when the field is strong, for example, in the case when the intensity is larger than $10^{12}$ W/cm$^2$, perturbation theory does not work very well. A non-perturbation theory, such as dressed states or ADK model, is needed to explain the strong-field phenomena. Typically, a focused femtosecond laser beam can have a peak intensity spanning from $10^{12}$ W/cm$^2$ to $10^{16}$ W/cm$^2$. In these high peak inten-
sities, many strong-field phenomena have been explored experimentally, such as high
harmonic generation [1, 2], nonsequential double ionization [3, 4], Lochfrass [5, 6, 7],
bond softening [8], enhanced ionization [9, 10, 11, 12], etc. Further, femtosecond
pulses provide the time resolution to investigate short-time-scale physics and chem-
istry. With a pump-probe technique, one can produce electronic transitions, as well
as vibrational and rotational motions in molecules. Also, bond breaking in molecules
can be monitored, giving rise to a new field of research in chemistry, femtochemistry
[13], for which 1999 Nobel Prize in Chemistry was awarded.

1.2 Behavior of molecules in strong fields

1.2.1 Strong-field induced vibrational motion

In strong-field physics, with a pump-probe technique, one can prepare a target cell of
molecules in a certain intermediate state through the use of vibrational wavepackets.
A vibrational wavepacket is a superposition of different vibrational eigenwavefunc-
tions. Considering a multilevel vibrational system, a wavepacket is described as the
following:

$$\Psi(R, t) = \sum_n C_n e^{-iE_n t/\hbar} \phi_n(R)$$ (1.1)

where $\phi_n(R)$ is the $n^{th}$ vibrational eigenwavefunction, and $C_n e^{-iE_n t/\hbar}$ is the projection
of the wavepacket onto that eigenwavefunction. Here, $|C_n|^2$ gives the projection
probability, and $e^{-iE_n t/\hbar}$ is a quantum phase factor which is relative to the eigenenergy
of the $n^{th}$ vibrational level $E_n$. The energy difference between levels is $\Delta_n = E_n -$
Since $\triangle_n$ varies with $n$, the wavepacket is dephasing and spreading while traveling.

Typically, for diatomic molecules, a potential curve of a certain state can be considered as a harmonic oscillation and a small anharmonic part. In this case, the energy of vibrational levels can be written as:

$$E_\nu = \hbar \omega_e (\nu + 1/2) - \hbar \omega_e \chi_e (\nu + 1/2)^2$$

(1.2)

where $\hbar \omega_e (\nu + 1/2)$ is the approximation of harmonic oscillation, and $\hbar \omega_e \chi_e (\nu + 1/2)^2$ is due to the anharmonicity on the potential curve. Typical values of $\omega_e$ and $\omega_e \chi_e$ for the ground states of different molecules are seen in Table 1.1, and the values of $\omega_e$ for different electronic states of I$_2$ and I$_2^+$ are shown in Table 1.2.

From Tables 1.1 and 1.2, we can see that the energy difference between the first two vibrational levels for ground electronic state H$_2$ and I$_2$ are $\sim$ 0.55 eV and 0.026 eV, respectively. Since the thermal energy at room temperature is $kT = \sim$ 0.026 eV, H$_2$ molecules stay in the lowest vibrational level, while I$_2$ is vibrationally excited.

There are several ways to excite vibrational states, coherently or incoherently. For instance, room temperature thermal energy can excite I$_2$ incoherently. The excited vibrational levels will have random phase, in which case, no vibrational wavepacket is generated. Another way is to use a coherent light source, i.e., a laser. The energy spacing for different vibrational states is small, usually in the infrared or microwave frequency range, so, direct resonant excitations between vibrational levels within the same electronic state require a long wavelength. But, a femtosecond pulse, due to its high intensity, can excite or ionize multiple vibrational levels in a different electronic state through nonresonant process. For instance, the energy difference between the
**Table 1.1:** Typical values for ground X states of different molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\omega_c$ (cm$^{-1}$)</th>
<th>$\omega_c\chi_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2^+$</td>
<td>2321</td>
<td>66.2</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>4401.21</td>
<td>121.3</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>159.124</td>
<td>0.725</td>
</tr>
<tr>
<td>$\text{K}_2$</td>
<td>92.021</td>
<td>0.2829</td>
</tr>
<tr>
<td>NO</td>
<td>1904.2</td>
<td>14.1</td>
</tr>
</tbody>
</table>

**Table 1.2:** Experimental values of $\omega_c$ for different electronic states of $\text{I}_2$ and $\text{I}_2^+$ [14, 15, 16, 17, 18, 19, 20, 21].

<table>
<thead>
<tr>
<th>States</th>
<th>$\omega_c$ (cm$^{-1}$)</th>
<th>configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{I}_2$ $X^1\Sigma_g^+$</td>
<td>214.5</td>
<td>$\sigma_g^2\pi_u^4\pi_g^4\pi_u^0$</td>
</tr>
<tr>
<td>$\text{I}_2$ $B^3\Pi_u$</td>
<td>125.7</td>
<td>$\sigma_g^2\pi_u^4\pi_g^3\pi_u^1$</td>
</tr>
<tr>
<td>$\text{I}_2^+$ $X^2\Pi_g, 3/2$</td>
<td>240±1</td>
<td>$\sigma_g^2\pi_u^4\pi_g^3\pi_u^0$</td>
</tr>
<tr>
<td>$\text{I}_2^+$ $X^2\Pi_g, 1/2$</td>
<td>229±2</td>
<td>$\sigma_g^2\pi_u^4\pi_g^3\pi_u^0$</td>
</tr>
<tr>
<td>$\text{I}_2^+$ $A^2\Pi_u, 3/2$</td>
<td>138±2</td>
<td>$\sigma_g^2\pi_u^3\pi_g^3\pi_u^0$</td>
</tr>
</tbody>
</table>
B and X states of neutral I\(_2\) is about one 513 nm photon energy, so one can excite multiple vibrational levels to the B state using 513 nm femtosecond pulses with fairly low laser intensity. One can also ionize the X state to produce a wavepacket in the A state of I\(_2^+\) via non-resonant ionization. These scenarios can be considered as a direct projection of the initial wavefunction onto the upper-level electronic state. Due to the coherence of the light, vibrational states in the upper level electronic state will have a well-defined relative initial phase, and thus a vibrational wavepacket is generated.

At room temperature, for I\(_2\) in the ground electronic state (X state), the first vibrational state \(\nu=0\) contains only \(\sim 60\%\) of the initial population, and up to 5 vibrational states have significant population (for \(\nu=1-4\), population is \(\sim 22\%, \sim 8\%, \sim 3\%, \sim 1\%, \) respectively). However, different states have random phases, so the vibrations in different states average out and leave only an increase in the average vibrational energy. Unlike the incoherent thermal excitation, a femtosecond pulse centered at 513 nm can generate a vibrational wavepacket in the excited B\(^3\Pi_u\) state (B state) via one-photon resonant excitation, as seen in Fig. 1.1. We simulate the evolution of the vibrational wavepacket generated in the B state, when the temperature is 300 K and the peak intensity is \(1.4 \times 10^{11} \text{ W/cm}^2\), as shown in Fig. 1.2. In the simulation, the first nine vibrational states are populated initially in the X state according to a Boltzmann distribution. The vibrational wavepacket launched in the B state is obtained by solving the time-dependent nuclear one-dimensional Schrödinger equation for the X and B states coupled by a 50-fs 513 nm pulse. We calculate incoherent sums of the wavepacket in the B state obtained with each of the nine lowest vibrational states as the initial state weighted by the Boltzmann factors. From the simulation, the wavepacket is narrow in the first half period, but getting broader and broader after 0.4 ps, due to the dephasing of different vibrational states.
Nevertheless, the first half cycle can be used to study the strong-field interaction as a function of internuclear separation with fairly high resolution.

1.2.2 Molecular ionization in strong fields

In strong laser fields, there are three different mechanisms for molecular ionization [22]: multiphoton ionization, tunneling ionization and over-the-barrier ionization. The three mechanisms can be classified according to the Keldysh parameter \( \gamma \), defined as the ratio of the bound energy of an electron in an atom or molecule (ionization potential energy) to the energy of a free electron gained in the laser field (ponderomotive energy). Equivalently, it is also the ratio of the tunneling time of ionization (\( T_{\text{tunneling}} \)) to the laser period (\( T_{\text{laser}} \)). The Keldysh parameter can be written as [23]:

\[
\gamma = \frac{\sqrt{I_p}}{2U_p} \propto \frac{T_{\text{tunneling}}}{T_{\text{laser}}} \tag{1.3}
\]

where \( I_p \) is the ionization potential energy, and \( U_p \) is the ponderomotive energy, the average quiver energy of a free electron gained in a laser field. \( U_p \) can be written as the following:

\[
U_p = \frac{e^2 E_0^2}{4m_e \omega^2} \tag{1.4}
\]

where \( e \) and \( m_e \) are the charge and mass of the electron, \( E_0 \) is the amplitude of the electric field, and \( \omega \) is the laser angular frequency. Practically, \( U_p \) (in eV) is usually written in another way based on the laser intensity \( I \) (in W/cm\(^2\)) and laser wavelength \( \lambda \) (in \( \mu \)m):
Figure 1.1: Potential curves of the X state and B state of I$_2$, showing that 513 nm femtosecond pulses launch a vibrational wavepacket in the B state through one-photon resonant excitation.
Figure 1.2: Simulation of the evolution of the vibrational wavepacket generated in the $I_2$ $B^3Π_u$ state (B state). The y axis R is the internuclear separation of $I_2$. In the simulation, the first nine vibrational states of the X state are included as the initial state. The temperature is 300K, the peak intensity is $1.4 \times 10^{11}$ W/cm$^2$, $λ_{XB}=513$ nm, and the pulse duration is 50 fs.
\[ U_p = (9.3 \times 10^{-14})I\lambda^2 \] (1.5)

thus Keldysh parameter \( \gamma \) becomes:

\[ \gamma = 2.32 \times 10^6 \sqrt{\frac{I_p}{I\lambda^2}} \] (1.6)

Three ionization regimes are classified by evaluating the Keldysh parameter \( \gamma \), as seen in Fig. 1.3, for the simple case of an atom. When \( \gamma \gg 1 \), multiphoton ionization is more likely to happen. In this case, the ionization potential energy is high, but the laser intensity is relatively low or the laser wavelength is short. The laser field is too weak to distort the potential well, and the electron needs to absorb many photons to escape from the atom or molecule. The ionization rate is \( \Gamma \propto I^n \), where \( n \) is the number of photons absorbed by the electron. When \( \gamma \approx 1 \), tunneling ionization is more likely to happen. In this case, the external laser field is strong enough to distort the potential well, and the electron has a certain probability to tunnel out from the low side of the potential barrier, as seen in Fig. 1.3. The tunneling ionization rate can be described by the ADK model [24], as seen in the following:

\[ \Gamma = |C_{n,l}|^2 \frac{(2l + 1)(l + |m|)!}{2^{|m|}(|m|)!(l - |m|)!} I_p \left( \frac{3E_0}{\pi F_0} \right)^{1/2} \left( \frac{2F_0}{E_0} \right)^{2n-|m|-1} \exp \left( \frac{-2F_0}{3E_0} \right) \] (1.7)

where \( F_0 = \sqrt{2I_p} \), \( n, m, l \) are the principal quantum number, the orbital quantum number and the magnetic quantum number, respectively, and \( C_{n,l} \) is a constant. As the laser intensity increases, making \( \gamma \ll 1 \), the potential barrier on the low side is completely suppressed, and the electron can escape without tunneling. In this case, over-the-barrier ionization happens.
For the three ionization regimes, Keldysh parameter $\gamma$ provides an intuitive guide, rather than a strict classification. Especially, when $\gamma \approx 1$, there is a significant interplay between multiphoton and tunneling ionization. In this case, the ionization process needs to be carefully discussed.

1.2.3 Enhanced ionization

In Fig. 1.3, the three ionization regimes were illustrated for the simple case of an atomic potential well. However, ionization of a diatomic molecule is much more complicated due to the double potential well structure. In intense laser fields, the tunneling ionization of a diatomic molecule can be enhanced dramatically as the two atoms are pulled apart, and reaches a peak at a certain internuclear separation, as seen in Fig. 1.4. This phenomenon is known as enhanced ionization, and has been invoked in many experiments in different molecular systems, such as $\text{H}_2^+$ [9], $\text{I}_2^+$ [11], and $\text{I}_2$ [25, 26].

Since enhanced ionization is a specific phenomenon depending on the double-well structure, it happens when the external electric field is polarized parallel to the molecular axis, but disappears when the field is perpendicular to the molecular axis [27]. In a one-electron system, such as $\text{H}_2^+$, enhanced ionization can be explained by electron localization [28, 29]. We consider a generic diatomic molecular ion $\text{A}_2^+$ aligned along the electric field vector of the linearly polarized light, with a single active electron moving in a one-dimensional potential [29]

$$V(z, R) = -\frac{Q}{|z + R/2|} - \frac{Q}{|z - R/2|} - Fz$$

(1.8)

where $Q$ is the charge on each well, $R$ is the internuclear separation, $z$ is the distance
Figure 1.3: The three ionization regimes defined by Keldysh parameter $\gamma$: multiphoton ($\gamma \gg 1$), tunneling ($\gamma \approx 1$), and over-the-barrier ionization ($\gamma \ll 1$), illustrated for an atomic potential well.
along the internuclear axis, and $F$ is the electric field. In the absence of the field, the electronic potential at three internuclear separations is seen in Fig. 1.5. In (a), at small $R$, the inner barrier is much lower than the electron energy $E_{\text{electron}}$, so the electron can move freely in the double well. As $R$ increases, the inner barrier rises and touches $E_{\text{electron}}$ at a certain and critical $R$, and the electron is localized. Then in (c), when $R$ is large enough, the inner barrier is much higher than $E_{\text{electron}}$, so the electron only stays in one well. At very small or large $R$, the tunneling ionization of the double well is quite similar to that of an atomic potential well. While at the critical $R$ ($R_c$) where the electron is localized, the ionization is determined by the double-well structure, and is enhanced dramatically. The electron energy $E_{\text{electron}}$ in the double well can be approximated as [29]

$$E_{\text{electron}} = -Q I_p - \frac{Q}{R}$$  \hspace{1cm} (1.9)

In equation 1.9, $Q I_p$ is the ionization potential of an ion with a charge $Q - 1$, using an empirical formula [28], where $I_p$ is the ionization potential of a neutral atom, and the electron energy is lowered by the Coulomb potential of a neighbouring ion by $Q/R_c$. Equation 1.8 gives the inner barrier at $z = 0$ in the absence of the field

$$V(0, R_c) = -\frac{Q}{R_c/2} - \frac{Q}{R_c/2} = -\frac{4Q}{R_c}$$  \hspace{1cm} (1.10)

Electron localization happens when the inner barrier touches the electron energy, so letting $E_{\text{electron}} = V(0, R_c)$, we have

$$R_c = \frac{3}{I_p}$$  \hspace{1cm} (1.11)
This is the prediction of $R_c$ from the simple model of electron localization, which is hardly affected by the external electric field, and this prediction is consistent with our experimental result for the B state of $I_2$ [25] (see chapter 2).

There is another mechanism of the enhanced ionization in the one-electron system, called charge resonance enhanced ionization (CREI), to explain the anomalously high ionization rate at $R_c$ [30, 31]. Based on the discussion of the $R$-dependent ionization of $H_2^+$, it is believed that the ionization enhancement is due to two factors [31]: (1) there exists a pair of charge-resonant states that are strongly coupled to the electric field at large $R$ which guarantees a sufficient population in the upper state by nonadiabatic excitations; and (2) there is a field-induced barrier suppression which allows for fast ionization from the upper state. For $H_2^+$, the ground state, $1\sigma_g$, and the first excited state, $1\sigma_u$, have been characterized as charge-resonant states [32].

Using equation 1.8, we can illustrate the potential in a static electric field ($F = 2$) at three internuclear separations with the charge on each well $Q = 1$, as seen in Fig. 1.6. The units are arbitrary and merely represent the form of the $H_2^+$ potential. At $R = 0.5$, the inner barrier is lower than the electronic potential, however, the outer barrier is hard to penetrate, resulting in a slow ionization from either of the two states. At $R = 1$, the upper level state just lies above the inner barrier and also above the outer barrier, and thus ionizes very quickly. Furthermore, the strong coupling of the charge-resonant states guarantees the population of the upper-level state. At $R = 2$, the inner barrier rises and become hard to penetrate again, so the ionization is suppressed.

If the electric field $F$ is included, the electron’s energy $E_{\text{electron}}$ becomes:
\[ E_{\text{electron}} = -QI_p - \frac{Q}{R_c} + FR/2 \] (1.12)

An analytic expression for the critical \( R \) at which CREI occurs was derived by Bandrauk [30], following the condition that the electron energy exceeds the inner and outer potential barriers:

\[ R_c \approx \frac{4}{I_p} \] (1.13)

For two-electron systems, such as \( \text{H}_2 \), the mechanism of enhanced ionization is believed to differ from that of the one-electron system. The potential of the two-electron system is more complicated, as seen in the following:

\[
H_s(x_1, x_2, t) = \frac{-Z}{\sqrt{(x_1 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_1 + d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 + d)^2 + a^2}} + \frac{1}{\sqrt{(x_1 - x_2)^2 + a^2}} - (x_1 + x_2)F(t) \] (1.14)

where \( Z \) is the charge on each well, \( x_1 \) and \( x_2 \) are the coordinates of the two electrons, \( d = R/2 \) is half of the internuclear separation, \( a \) is the smoothing parameter of the Coulomb potential [28] and \( F(t) \) is the electric field strength. In \( \text{H}_2 \), it is believed that enhanced ionization is due to the role of ionic states [33, 34]. As the separation \( R \) increases, the population of the ionic state \( \text{H}^-\text{H}^+ \) created decreases, but the ionization rate from the state \( \text{H}^-\text{H}^+ \) increases owing to the weaker attraction by the distant nucleus. As a result, the ionization rate has a peak at a certain critical \( R \).
Figure 1.4: Tunneling ionization rates as a function of internuclear separation $R$ in $\text{I}_2$ $\text{B}^3\Pi_u$ state [25] in a pump-probe experiment. The two different pump wavelengths $\lambda_{\text{pump}}=500$ nm and 513 nm provide different ranges of $R$. The enhancement between 5.0 a.u. and 6.5 a.u. is due to the temporal overlap of the pump and probe pulses.
Figure 1.5: Schematic illustration of the electronic potential at three internuclear separations in the absence of the applied electric field. In (a), at small $R$, the inner barrier is much lower than the electron energy $E_{\text{electron}}$, so the electron can move freely in the double well. In (b), as $R$ increases, the inner barrier rises and touches $E_{\text{electron}}$ at a certain and critical $R$, and the electron is localized. Then in (c), when $R$ is large enough, the inner barrier is much higher than $E_{\text{electron}}$, so the electron stays in one well.
Figure 1.6: Schematic illustration of the electronic potential at three internuclear separations in an electric field.
1.2.4 Self-trapping of light

Self-trapping of light is a process in which a strong beam of light modifies the optical properties of a material medium so that the beam keeps the same size for a long distance (compared with Rayleigh length) without diverging. This phenomenon is mainly due to the balance of self-focusing and diffraction. For a material medium with positive nonlinear refractive index \( n_2 \) (true for most materials), the refractive index is the largest at the center of an Gaussian beam and decreases with \( r \), the distance from the center. Usually, \( n_2 \) is small compared to the linear refractive index \( n_0 \). For instance, \( n_2 \) of typical glasses is in the range \( 5 \times 10^{-16} \text{ cm}^2/\text{W} \) to \( 5 \times 10^{-15} \text{ cm}^2/\text{W} \), and \( n_2 \) of a gaseous medium is much smaller, \( \sim 5 \times 10^{-19} \text{ cm}^2/\text{W} \) for air at 1 atm. However, for an laser beam with intensity \( I \sim 10^{13} \text{ W/cm}^2 \), the nonlinear index can not be neglected. The total refractive index becomes:

\[
n = n_0 + n_2 \times I
\]  

\hspace{2cm} (1.15)

The process of laser beam self trapping can be described in terms of an argument presented by Chiao [35]. We can make a simplying assumption that the laser beam has a flat-top intensity distribution [36], as seen in Fig. 1.7 (a). Then the refractive index distribution in the medium is shown in Fig. 1.7 (b). Here \( n = n_0 \) is the linear refractive index of the medium outside the self-trapping beam, and \( n = n_0 + \delta n = n_0 + n_2 I \) is the refractive index inside the self-trapping beam. We consider a ray of light incident on the boundary of the two regions. Since it is one ray of the bundle that makes up the self-trapping laser beam, a total internal reflection should occur for the ray to be trapped. The critical angle \( \theta_0 \) for total internal reflection is given by the equation:
\[ \cos(\theta_0) = \frac{n_0}{n_0 + \delta n} \]  

(1.16)

Since \( \delta n \) is very small compared with \( n_0 \), \( \theta_0 \) should also be very small. We can make the approximation, as seen in equation 1.17, from which an expression of \( \theta_0 \) can be obtained, as seen in equation 1.18. \( \theta_0 \) is dependent on the nonlinear refractive index. Any incident ray with angle smaller than \( \theta_0 \) will have total internal reflection.

\[ 1 - \frac{1}{2}\theta_0^2 = 1 - \frac{\delta n}{n_0} \]  

(1.17)

\[ \theta_0 = \sqrt{2\delta n/n_0} \]  

(1.18)

For the laser beam, the diffraction angle is given by \( \theta_{df} = 0.61\lambda_0/n_0d \), where \( \lambda_0 \) is the wavelength of the light in vacuum. When self trapping occurs, all of the rays are trapped within the laser beam, so we have \( \theta_{df} = \theta_0 \). In this way, an expression for \( \delta n \) is obtained:

\[ \delta n = \frac{1}{2}n_0(0.61\lambda_0/n_0d)^2 \]  

(1.19)

Since \( \delta n = n_2I \), we have

\[ I = \frac{(0.61\lambda_0)^2}{2n_0n_2d^2} \]  

(1.20)

The power contained in the laser beam is then given by

\[ P_{cr} = \frac{\pi}{4}d^2I = \frac{\pi(0.61\lambda_0)^2}{8n_0n_2} \]  

(1.21)
$P_{cr}$, called the critical power, is crucial in determining whether self-focusing will occur. When the laser power exceeds the critical power greatly, self-trapping of light occurs and a filament will be formed in the medium. Different media have very different $P_{cr}$, and $P_{cr}$ of a solid medium is much smaller than a gaseous medium. For air at 1 atm pressure, $P_{cr}$ is $\sim 2$ GW when $\lambda_0 = 800$ nm, and for typical glasses, $P_{cr}$ is in the range 0.2 MW to 2 MW for 800 nm laser pulses. In the High-Intensity Laser Group at the University of Connecticut, we have a Spitfire laser system (750 $\mu$J, 50 fs, 800 nm) which produces a maximum power of 15 GW. With this laser system, we have obtained a filament in a gaseous medium SF$_6$. We will discuss this experiment in chapter 5.

1.3 Experimental apparatus

1.3.1 Femtosecond laser system

In strong-field experiments, the Ti:sapphire (Ti:Al$_2$O$_3$) femtosecond laser systems are widely used. The material Ti:sapphire has the broadest gain bandwidth (roughly from 600 to 1100 nm) of solid-state laser materials [37], and it is capable of producing laser radiation with broad spectral bandwidth. Usually, Ti:sapphire lasers are pumped by another laser centered at 514 - 532 nm, and operate most efficiently at wavelengths near 800 nm. Ti:sapphire femtosecond lasers consist of two principal components: the oscillator and the amplifier. The oscillator generates a ultrashort pulse through self mode locking via a Kerr lens effect in the Ti:sapphire crystal. The output pulses of the oscillator have a high repetition rate of around 90 MHz, dependent on the cavity length. The amplifier chooses a certain repetition rate of pulses, and then
Figure 1.7: (a) Radial intensity distribution of the laser beam. (b) A ray of light incident on the boundary formed by the edge of the laser beam. $n = n_0$ is the linear refractive index of the medium outside the self-trapping beam, and $n = n_0 + \delta n$ is the refractive index inside the self-trapping beam.
significantly increases the intensity of those pulses.

The experiments in this dissertation utilize two Ti:sapphire femtosecond laser systems: one is home-built, and the other is commercial from Spectra-Physics. The home-built system produces linearly-polarized pulses centered at 800 nm with a transform-limited pulse duration of ~ 35 fs, a repetition rate of 1 kHz, and a pulse energy up to 800 µJ. The details can be seen in Refs. [38, 39]. The commercial system produces similar pulses, with linear polarization, 1 kHz, 800 nm and pulse energy up to 750 µJ, but a longer transform-limited pulse duration of ~ 50 fs.

1.3.2 Pulse measurement

The pulse duration is measured with two home-built autocorrelators. One is based on the second-order nonlinear effect, and the other is based on the third-order nonlinear effect. Both of them are single-shot, real-time autocorrelators. The complete details of the second-order autocorrelator are given in Ref. [39], and those of the third-order one are given in Ref. [40].

In the second-order autocorrelator, a single laser beam is split into two beams with equal intensity which then cross at a small angle in a nonlinear crystal to produce second harmonic signals, as seen in Fig. 1.8 (a). An 800 nm filter is placed right after the nonlinear crystal to block the fundamental signals, and a CCD camera is used to record the spatial profile of the generated second harmonic signals. The FWHM (full width of half maximum) of the spatial profile, as seen in Fig. 1.8 (b), is linearly proportional to the duration of the pulse.

\[ \tau_{\text{pulse}} = \frac{B}{\sqrt{2}} \times \tau_{\text{trace}} \]  

(1.22)
where $\tau_{\text{pulse}}$ and $\tau_{\text{trace}}$ are the FWHM of the pulse (in fs) and the spatial trace (in pixels), $B$ is the calibration factor (in fs/pixel), and $\sqrt{2}$ in the denominator is due to the Gaussian shape of the measured pulse. In Fig. 1.8 (b), $\tau_{\text{trace}}$ is 16 pixels, and $B$ is 2.99 fs/pixel, so the measured $\tau_{\text{pulse}}$ is 34 fs.

In the third-order autocorrelator, the pulse to be measured is split into two pulses by a beam splitter. The two pulses have different linear polarizations. As seen in Fig. 1.9, the polarization of beam 2 is still horizontal, but that of beam 1 is rotated by $45^\circ$. The two beams are focused by a cylindrical lens to two thin lines which are spatially and temporally overlapped in a thin piece of glass acting as the nonlinear optical medium. The intensity of beam 2 is high, so the nonlinear refractive index of the glass can not be neglected. It induces birefringence which rotates the polarization of beam 1. Then a lens projects the signal and background of beam 1 onto a CCD camera. By carefully rotating the polarizer between the lens and the CCD camera, the background is minimized, but the autocorrelation signal goes through. By inserting filters, the signal-to-noise ratio can be optimized. The spatial profile of the autocorrelation signal is recorded by the CCD camera, and then the FWHM is calculated which is proportional to the pulse duration.

### 1.3.3 Time-of-Flight Spectroscopy

In the experiments, we investigate the internuclear separation dependence of molecular ionization. Molecules are ionized to a dissociative channel, and then ion fragments are collected by a Time-of-Flight (TOF) Mass Spectrometer. The TOF system is a standard two-region Wiley-McLaren mass spectrometer [41, 42], as seen in Fig. 1.10. The laser beam sent into the vacuum chamber is focused by an on-axis spherical silver
Figure 1.8: (a) Schematic illustration of the two beams crossing in the nonlinear crystal, producing second harmonic signals. (b) The autocorrelation trace obtained by the CCD camera.
Figure 1.9: Schematic illustration of the third-order autocorrelator.
mirror with 3-inch focal length to a small focus with a diameter $\sim 20 \, \mu \text{m}$. With 3 $\mu \text{J}$, 30 fs, 800 nm pulses, the intensity at the focus will be $\sim 3 \times 10^{14} \, \text{W/cm}^2$. The vacuum chamber is pumped by a turbo pump to a base pressure $\sim 8 \times 10^{-10} \, \text{torr}$. Molecular gas is then introduced by a leak valve to a pressure $\sim 8 \times 10^{-7} \, \text{torr}$. At the beam focus, molecules are ionized to some dissociative channels and ion fragments will be collected by microchannel plates (MCPs) at the end of the TOF spectrometer. There are three grids in the TOF system: far grid, near grid and ground grid. A high positive voltage (usually 1000 V) is applied on the far grid, and a lower positive voltage (usually 675 V) is applied on the near grid. For a positive ion with zero kinetic energy, the time it takes to reach the MCP is shown in equation 1.23

$$T = T_0 + A \times \sqrt{\frac{m}{q}}$$

(1.23)

where $m$ and $q$ are the mass and charge of the ion, respectively. $T_0$ and $A$ are constants of the TOF system.

However, dissociating ion fragments have initial kinetic energy due to the kinetic energy release (KER) of the molecular ions. The molecular ion dissociates into one forward-going ion fragment and one backward-going ion fragment. For diatomic homonuclear molecules, like $\text{H}_2$, $\text{I}_2$ and $\text{N}_2$, the two ion fragments have the same magnitude but opposite direction of momentum. The fragment moving toward the MCP is accelerated directly, while the one moving backward will turn around, and then move toward the MCP, as seen in Fig. 1.10. The time difference between the two fragments when they strike the MCP is dependent on the KER of the molecular ion, as seen in equation 1.24
\[
KER = \frac{(V_f - V_n)^2 q^2}{4md^2} \times (\Delta t)^2
\]  

(1.24)

where \(V_f\) and \(V_n\) are the voltages applied on the far and near grids, respectively, \(d\) is the distance between the two grids, and \(\Delta t\) is the time difference between the two fragments when they strike the MCP. The momentum \(P\) of either ion fragment is linearly proportional to \(\Delta t\):

\[
P = \frac{(V_f - V_n)q}{2d} \times (\Delta t)
\]  

(1.25)

In the TOF system, pinholes in front of the MCP help define the TOF axis. Ion fragments moving along the TOF axis or with small angle and large velocity will be allowed to strike the MCP. A discriminator amplifies and filters the analog signal from the MCP and a time-to-digital converter (TDC) sends a digital signal to a computer for recording and processing. Typical TOF signals of \(I_2\) ions are shown in Fig. 1.11 (a), and the forward-going and backward-going \(I^{2+}\) signals are shown in Fig. 1.11 (b). From Fig. 1.11 (a), the TOF of \(I^{2+}\), \(I^+\) and \(I_2^+\) are 3730 ns, 5229 ns and 7352 ns, respectively. For the three ions, \(\sqrt{m/q}\) are \(\sqrt{127/2}\), \(\sqrt{127/1}\) and \(\sqrt{254/1}\), respectively. Using equation 1.23, we linearly fit the three data points and obtain the values of \(T_0\) and \(A\): \(T_0 = 107.4 \pm 2.2\) ns, \(A = 454.5 \pm 0.2\). Since \(T_0\) and \(A\) are constant for the same system, we can predict the TOF of other ions with known \(m\) (in standard atomic weight) and \(q\) (in electron charge) using equation 1.23. In Fig. 1.11 (b), forward-going and backward-going \(I^{2+}\) fragments from different dissociative channels have different \(\Delta t\), due to the different KER between dissociative channels.

If we generate a vibrational wavepacket in a certain state and then ionize the wavepacket as it vibrates, we can have different KER and thus different \(\Delta t\) between
the forward-going and backward-going ion fragments due to the structure of potential curves. In this way, the wavepacket motion can be obtained via plotting TOF as a function of delay time, as seen in Fig. 1.12. These data were obtained in a pump-dump-probe experiment, with pump and dump pulses generating a wavepacket in the ground state of $I_2$, and a probe pulse ionizing the wavepacket at different dump-probe delay. Details of the experiments can be found in chapter 3.

1.4 Outline

In the dissertation, we experimentally investigate the internuclear-separation-dependent and angle-dependent ionization of the B state of neutral $I_2$, as seen in chapter 2. The enhanced ionization is studied on the lowest unoccupied molecular orbital (LUMO) $\sigma_u$ state. In chapter 3, we generate a vibrational wavepacket on the ground electronic state of $I_2$, whose valence orbitals are $\sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^0$, using a pump-dump-probe technique. With the wavepacket, internuclear-separation-dependent ionization of different molecular orbitals, HOMO $\pi_g$, HOMO-1 $\pi_u$ and HOMO-2 $\sigma_g$, is discussed. In chapter 4, enhanced ionization of an inner orbital, HOMO-2 $\sigma_g$ is studied. Then in chapter 5, a pulse compression experiment using filamentation in SF$_6$ is described. We study the pressure dependence and energy dependence of the spectral broadening with a filament in SF$_6$. Finally, we summarize the dissertation in chapter 6.
Figure 1.10: Schematic illustration of the time-of-flight spectrometer.
Figure 1.11: (a) Time of flight of different iodine ions, showing that TOF is dependent on $\sqrt{m/q}$; (b) Time of flight of $I^{2+}$, showing the forward-going and backward-going fragments (the (m,n) channel refers to the dissociating channel $I^{(m+n)+} \rightarrow I^{m+} + I^{n+}$).
Figure 1.12: Vibrational wavepacket of the ground state of I$_2$ seen in the TOF of I$_2^+$ ion fragments. The data were obtained in a pump-dump-probe experiment, with pump and dump pulses generating a wavepacket in the ground state of I$_2$, and a probe pulse ionizing the wavepacket at different dump-probe delay. Details of the experiments can be found in chapter 3.
Chapter 2

Enhanced ionization of the B-state of I\textsubscript{2} by strong laser fields

2.1 Introduction

In most cases of the interaction of diatomic molecules with intense laser fields, the tunneling ionization rate increases as a function of the internuclear distance R, reaches a significantly high peak at a certain critical internuclear separation R\textsubscript{c}, and then decreases. This very general phenomenon, known as enhanced ionization (EI), is invoked in many experiments [9, 10, 11, 12].

EI has been explored in a number of cases both experimentally and theoretically. The simplest example is 1 electron in a double well, such as H\textsubscript{2}\textsuperscript{+}. It has been shown that the effects leading to EI in this case are charge-resonance-enhanced-ionization (CREI) and electron localization, as discussed in chapter 1.2.3. CREI is a combination of the field-induced barrier suppression and the strong coupling between the charge-resonant
states. The former allows for fast ionization from the upper state at a certain critical internuclear separation, and the latter guarantees a sufficient population in the upper-level state through nonadiabatic excitation from the lower state [31]. The calculations have been verified by experimental studies of EI in H\textsubscript{2}\textsuperscript{+} [9, 10]. In addition, EI in H\textsubscript{2}\textsuperscript{+} as a function of angle \(\theta\) between the molecular axis and the field polarization has been calculated and is found to decrease as the angle increase, finally disappearing at 90\(^\circ\) [27]. However, this has not yet been demonstrated experimentally.

EI can also occur in more complex systems. In the 1-electron case, it is shown theoretically that EI is highly dependent on the molecular symmetry and only occurs for \(\sigma\) states, not \(\pi\) or \(\delta\) states [43]. In the case of 2-electron equivalent states in neutral H\textsubscript{2}, it is believed that EI is due to the ionic states working as doorway states [33, 34]. One experiment on EI in a 2-electron system has been performed by launching a wavepacket (WP) on an excited state of I\textsubscript{2}\textsuperscript{+} correlating with the I\textsuperscript{2+} + I dissociation limit, through multiphoton ionization by an intense pump pulse. Then a temporally delayed probe pulse ionizes the WP to the I\textsubscript{2}\textsuperscript{3+} state which dissociates to I\textsuperscript{2+} and I\textsuperscript{+}, allowing the ionization rate to be measured as a function of \(R\) [11]. EI of I\textsubscript{2}\textsuperscript{3+} is found at a certain critical internuclear distance when the field is polarized along the molecular axis, and the effect disappears when the field has perpendicular polarization, just as predicted. However, in this experiment, the molecule is already in the ionic states, and so it is not clear if the mechanism is the same as for the covalent ground state. Indeed, there are actually many different molecular configurations, even just for diatomics (see Table 2.1), that may show EI and only a few have been fully studied experimentally, especially through pump-probe techniques.

In this chapter, we use a pump-probe technique and choose the excited B-state of neutral I\textsubscript{2} as an intermediate state to study EI, as shown in Fig. 2.1. By launching
Table 2.1: A summary of studies of EI, including both 1-electron system and 2-electron system.

<table>
<thead>
<tr>
<th>Electron system</th>
<th>States</th>
<th>Properties</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-electron</td>
<td>$\sigma$ states of $H_2^+$ [9, 10, 31, 27, 43]</td>
<td>EI in parallel case (both theoretical and experimental), not in perpendicular case (need experiment)</td>
<td>CREI</td>
</tr>
<tr>
<td></td>
<td>$\pi$ or $\delta$ states of $H_2^+$ [43]</td>
<td>No EI (need experiment)</td>
<td>CREI</td>
</tr>
<tr>
<td>2-electron</td>
<td>$\sigma$ states of $H_2$ [33, 34]</td>
<td>EI in parallel case, perpendicular case unknown (need experiment)</td>
<td>Ionic states as doorway states</td>
</tr>
<tr>
<td>2-electron</td>
<td>Ionic excited state of $I_2^+$ [11]</td>
<td>EI in parallel case, not in perpendicular case (only experimental)</td>
<td>Similar to CREI</td>
</tr>
<tr>
<td>2-electron</td>
<td>Covalent excited state of $I_2$, B-state ($\sigma_u$ state)</td>
<td>Similar to 1-e $\sigma_u$ case (this paper)</td>
<td>CREI (this paper)</td>
</tr>
</tbody>
</table>
a WP in the B-state with a pump pulse [44], we obtain the R-dependent ionization rates with a temporally delayed probe pulse as the WP evolves in the B-state. In addition, since the ground to B-state optical transition dipole moment is parallel to the internuclear axis, the molecules excited to the B state will be highly aligned along the field polarization of pump pulse, allowing for angle-dependent measurements of ionization rates by changing the polarization of the pump pulse with respect to the probe pulse. From this work, we find a peak in the ionization rate at $R_c$ in the parallel case, and the peak gradually goes away as the angle increases to $90^\circ$, as predicted by CREI [27]. Indeed, we find that $R_c = (3.02 \pm 0.01)/I_p$ at a wavelength of the pump pulse $\lambda_{\text{pump}}=513$ nm and $R_c = (3.03 \pm 0.03)/I_p$ at $\lambda_{\text{pump}}=500$ nm, in very good agreement with the theoretical prediction of $R_c = 3/I_p$ [28, 29], where $I_p$ is the ionization potential of the separated atom.

To the best of our knowledge, this current work is the first time EI has been studied in a neutral molecule experimentally. This is significant as virtually all strong-field experiments start with neutral molecules, in particular, HHG [45, 46, 47] from molecules, Lochfrass [5, 6, 7, 48], suppressed ionization [49] and coherent control [50, 51]. In all of these cases, ionization of the neutral molecules is the critical first step.

### 2.2 Experiment

The experiments are performed with a home-built ultrafast Ti:sapphire laser system and a TOPAS (Optical Parametric Amplifier) system. The ionization signal of $I_2^+$ is recorded with a time-of-flight (TOF) spectrometer. The ultrafast laser and the TOF
Figure 2.1: (a) Potential curves and pump-probe experimental scheme. The wavelength of the pump and probe pulses are 513 nm and 800 nm, respectively. (b) The ionization potentials of the B state and the $^1\Pi_u$ state as a function of R.
spectrometer have been described in Refs [52, 53]. The I$_2$ gas is leaked effusively into the chamber with a base pressure of $6 \times 10^{-9}$ torr. The Ti:sapphire laser produces pulses with a central wavelength of 800 nm, a pulse duration of 35 fs, and an output energy of up to 900 $\mu$J at a repetition rate of 1 kHz. The output beam is split with $\sim 90\%$ of the energy sent into the TOPAS to generate a pump beam and the rest is used as a probe beam. The pump pulses have a central wavelength of 513 nm or 500 nm, a duration of 50 fs and an energy of up to 2 $\mu$J. The pump and probe beams are parallel but offset in space and focused by a 3-inch-focal-length silver spherical mirror inside the TOF chamber. An aperture is used to reduce the energy of pump beam to 0.5 $\mu$J in order to decrease ionization by the pump pulse and also increase the focal spot size in the chamber. This creates a more uniform focal volume for the probe pulse. The beam radius and intensity of pump beam at the focus are 48 $\mu$m and $1.4 \times 10^{11}$ W/cm$^2$, respectively, while those of the probe beam are 8 $\mu$m and $1.4 \times 10^{13}$ W/cm$^2$ (to singly ionize the I$_2$). The temporal delay of the two beams is adjusted by a computer controlled translational stage and the spatial overlap is optimized by maximizing an I$^{2+}$ signal resulting from ionization of the B state.

In the experiment, we first measure the B-state alignment as it is important for measuring the angular dependence of the ionization rate. We use a linearly-polarized pump pulse to align the molecules excited to the B state, and then use a horizontally-polarized probe pulse to ionize those molecules to I$_2^{2+}$, which dissociates into I$^2+$+I$^+$, the (2,1) channel. The polarization of the pump pulse is rotated from 0$^\circ$ to 180$^\circ$ with a $\frac{1}{2}\lambda$ plate and the I$^{2+}$ signal is recorded by the TOF spectrometer at each angle at a fixed pump-probe delay (0.3 ps after $T_0$, the temporal overlap of the pump and probe pulses). Since $\frac{1}{2}\lambda$ plates are used to control the polarization angle of both beams, some residual ellipticity is introduced. However, the ellipticity was measured to be
less than 1.5%. The angular dependence of the B state is shown in Fig. 2.2, in which
the data from 180° - 360° are the inversion of the data from 0° - 180° with respect to
the origin. The data are fitted by $A \times \cos^2(\theta - \theta_0) + B$, with $A = 0.01912$, $\theta_0 = 0°$, $B = 0$.

From Fig. 2.1, the pump pulse populates not only the B state, but possibly the $^{1}\Pi_u^+$ state which can also be ionized by the probe pulse [54]. Different from the B state, the optical transition dipole moment from the ground state to the $^{1}\Pi_u^+$ state is perpendicular to the molecular axis and may contribute to the signal, especially near 90°. However, the coupling from the ground state to $^{1}\Pi_u^+$ is weak at 513 nm [20], especially compared to the wavelength used in Ref. [54]. From Fig. 2.2, the weak, almost zero $I_2^+$ signal at $\theta = 90°$ shows that the $^{1}\Pi_u^+$ state has little effect in this experiment.

2.3 Results

2.3.1 Internuclear-separation-resolved measurements

The ion signals of $I_2^+$ as a function of pump-probe delay $S(\tau)$ at different $\theta$ are measured with a step size of 0.030 ps, as shown in Fig. 2.3, for $\theta = 0°$, 40° and 90°. At each angle, the ionization peaks at a delay of around 0.33 ps.

There are two possible explanations for the peaks at $\sim 0.33$ ps in Fig. 2.3: (1) as the WP evolves in the B state (see Fig. 2.1 (a)), the ionization rate increases as R increases and finally it reaches a maximum at the outer turning point; (2) there is a critical internuclear separation $R_c$. The rise in ionization rate as R increases cannot be attributed to simple tunneling, because the tunneling rate is a strong inverse function.
Figure 2.2: Angular dependence of the B state. The solid square data points are the experimental results, obtained by integrating $I^{2+}$ signals in the (2,1) channel from ionization of the B-state. The intensities of pump and probe beams are $1.4 \times 10^{11}$ W/cm$^2$ and $5.6 \times 10^{13}$ W/cm$^2$, respectively. The red curves are the fit of the data points by $A \times \cos^2(\theta - \theta_0) + B$, with $A = 0.01912$, $\theta_0 = 0^\circ$, $B = 0$. 
Figure 2.3: Ionization signals $S$ of $I_2^+$ versus pump-probe delay $\tau$ at three different angles: $\theta = 0^\circ$, $40^\circ$ and $90^\circ$. The step size is 0.030 ps. The pump pulse has an energy of 0.5 $\mu$J giving an estimated intensity of $1.4 \times 10^{11}$ W/cm$^2$, and the probe pulse has an energy of 1 $\mu$J giving an estimated intensity of $1.4 \times 10^{13}$ W/cm$^2$. The delay of 0 ps represents $T_0$. 
of the ionization potential and the ionization potential of the B-state is an increasing function of R (see Fig. 2.1 (b)), resulting in a decreasing tunneling ionization rate with R. To determine whether the peak occurs at or before the outer turning point, we obtain \(<R>(t)\) of the WP in the B state from theoretical simulations and compare it with the measurements of the momentum time evolution \(P(t)\) of the WP in the (2,1) channel, as shown in Fig. 2.4 (a). The outer turning point is reached at 0.40 ps which is consistent with the minimum momentum from the data, while the peak is at 0.33 ps in Fig. 2.3. Since the peak is 0.07 ps before the outer turning point, this corresponds to a critical separation \(R_c\). However, if the peak is due to EI at \(R_c\), one would expect there to be another peak of the ionization rate as the WP returns, approximately at 0.47 ps, 0.07 ps after the outer turning point. None of the three curves in Fig. 2.3 show the expected double-peak structure. However, numerical simulation shows that the disappearance of the second peak is due to the dephasing and spreading of the wavepacket. From the simulation of the WP in the B state in Fig. 2.5, we can see that the wavepacket is narrow during the first half period, but starting from 0.40 ps, it spreads quickly. Thus at 0.47 ps, the wavepacket is too broad to show the ionization peak.

Nevertheless, to confirm our interpretation, we repeated the experiment with a pump pulse centered at 500 nm. This will start the WP higher up in the B state potential and allow the WP to reach a larger R. If the ionization peak found at 513 nm was somehow related to the outer turning point, the peak with the 500 nm pump should move to longer delays. As it turns out, the peak occurs at a shorter delay, as shown in Fig. 2.6 (a). The WP moves a bit faster with the 500 nm pump and reaches \(R_c\) sooner. We obtain the corresponding R at each pump-probe delay according to the simulation results of \(<R>(t)\) in Fig. 2.4 (b). Plotting both data sets as functions
Figure 2.4: (a) The simulation of \( <R>(t) \) of the WP in the B state and the momentum \( P(t) \) of I\(^{2+}\) in the (2,1) channel ionizing from the B state; (b) The simulation of \( <R>(t) \) of the WP in the B-state and the ionization signal \( S \) of I\(^{+}\) versus pump-probe delay \( \tau \) at \( \theta = 0^\circ \). In the simulation, the first nine vibrational states of the X state are included as the initial state. The temperature is 300 K, the peak intensity is \( 1.4 \times 10^{11} \text{ W/cm}^2 \), \( \lambda_{XB} = 513 \text{ nm} \), and the pulse duration is 50 fs.
Figure 2.5: Simulation of $R(t)$ of the WP in the B state. The condition is the same as in Fig. 2.4.
of R (as shown in Fig. 2.6 (b)) gives the same value (within the error bars) for \( R_c \):

\[ R_c = 8.67 \pm 0.03 \text{ a.u. (513 nm)} \text{ and } 8.71 \pm 0.09 \text{ a.u. (500 nm)} \].

In addition, we find that the ionization rate is enhanced by a factor of 22 at \( R_c \) compared to the minimum rate.

### 2.3.2 Angle-resolved measurements

Having established that the peak in each curve in Fig. 2.3 is due to enhanced ionization at \( R_c \), we compare the angular dependence of the ionization rates (see Fig. 2.7) at three time delays, 0.33 ps (\( R_c \)), 0.26 ps (\( R_i \), intermediate R) and 0.07 ps, corresponding to R values of 8.67 a.u., 8.42 a.u. and 6.45 a.u., respectively. The latter value is the smallest delay (i.e. closest to \( R_e \), the equilibrium internuclear separation) that could be measured without significant temporal overlap of the pump and probe pulses. The probe pulse is horizontal, and the pump pulse is rotated from 0° to 180° with respect to the probe pulse. The data from 180° - 360° are from the inversion of the data from 0° - 180° with respect to the origin.

As seen in Fig. 2.7, the ionization rate at \( R_c \) at 90° is nonzero, and it corresponds to the peak at 90° in Fig. 2.3. Since the B state has a \( \cos^2(\theta) \) distribution, even if the probe pulse is polarized perpendicularly to the pump pulse, there are still molecules in the direction at which the field of probe pulse has a nonzero component and thus those molecules are singly ionized and detected, as well. As shown in Fig. 2.8 (a), in the lab frame, we suppose that the pump pulse is polarized in the \( z \) direction, and the probe pulse is polarized in the \( yz \) plane, in the direction \( \hat{e} \), rotated by an angle \( \Psi \) from the \( z \) direction. The molecules in the direction \( \hat{n} \) have a population probability of \( \cos^2(\theta) \). To understand whether the peak at 90° is just an angular
Figure 2.6: Ionization rates as a function of (a) pump-probe delay and (b) internuclear separation $R$ at $\lambda_{\text{pump}}=500$ nm and 513 nm. In (b), the enhancement between 5.0 a.u. and 6.5 a.u. is due to the temporal overlap of the pump and probe pulses.
Figure 2.7: Angular dependence of ionization rates at $R_c$, $R_i$, and 6.45 a.u. The intensities of pump and probe beams are $1.4 \times 10^{11}$ W/cm$^2$ and $1.4 \times 10^{13}$ W/cm$^2$, respectively, and $\lambda_{pump}=513$ nm.
averaging effect of the peaks at other angles or is really EI in the perpendicular case, we calculate the angular averaging. We project the probe field onto the direction \( \hat{n} \), apply a multiphoton ionization model (Ionization rate \( \propto (E_0 \hat{e} \cdot \hat{n})^n \)), and then integrate over \( \theta \) and \( \phi \), to calculate the angular averaging effect at angle \( \Psi \), \( S(\Psi) \):

\[
S(\Psi) = \int_0^\pi \int_0^{2\pi} (E_0 \hat{e} \cdot \hat{n})^n \cos^2(\theta) \sin(\theta) d\theta d\phi
\]  

(2.1)

where \( \hat{n} = (\sin \theta \sin \phi, \sin \theta \cos \phi, \cos \theta) \) and \( \hat{e} = (0, \sin \Psi, \cos \Psi) \).

While the effect of averaging does not depend strongly on \( n \), we obtained a rough value by measuring the intensity-dependent ionization rate at \( R_c \), as shown in Fig. 2.8 (b). The slope of the ion-yield curve in the immediate vicinity of the intensity where the angular-dependence data were taken gives a value for \( n \). The slopes at \( 1.4 \times 10^{13} \) W/cm\(^2\) and \( 5.6 \times 10^{12} \) W/cm\(^2\) are 1.2 and 1.8, respectively, which means \( n = 2.4 \) at \( 1.4 \times 10^{13} \) W/cm\(^2\) and 3.6 at \( 5.6 \times 10^{12} \) W/cm\(^2\). Then, we calculate \( S(\Psi) \) at each angle \( \Psi \) between 0° and 360° for \( n = 2 \) and then compare with the angular dependence measurements, as shown in Fig. 2.9 (a). From Fig. 2.9 (a), the measurements are consistent with the angular averaging calculation. To further confirm this result, we decrease the intensity of the probe beam to \( 5.6 \times 10^{12} \) W/cm\(^2\), and repeat the measurements at \( R_c \) and calculations with \( n = 4 \), as shown in Fig. 2.9 (b). They are still in good agreement. Therefore, we conclude that the peak at \( \theta = 90^\circ \) is just an angular averaging effect of the peaks at other angles, and by itself does not show enhanced ionization.
Figure 2.8:  (a) The configuration of molecules in the B state and the field polarizations of pump and probe pulses. (b) Measured $I^+_2$ ion signals as a function of the intensity of probe pulse.
Figure 2.9: The data points are the angular dependence measurements at $R_c$ at intensities of (a) $1.4 \times 10^{13}$ W/cm$^2$ and (b) $5.6 \times 10^{12}$ W/cm$^2$, and the red smooth curves are the angular averaging calculations with (a) $n=2$ (b) $n=4$. 
2.4 Discussion

EI has been rigorously studied theoretically in only a few relatively simple cases: the 1-electron molecules such as H$_2^+$, and the 2-electron molecule H$_2$. However, further work suggests the predictions from the above studies are much more general. Nevertheless, ionization from the B state of I$_2$ would appear to be much more complex, having features of both the 1-e and 2-e models. The B state could be considered to be a 1-e system, as the lone electron in the $\sigma_u$ orbital would be the most active electron. However, neutral I$_2$ has ionic states (I$^+$+I$^-$) which play a critical role in even charged molecules [33, 34]. In either case, the electronic structure of the excited states of I$_2$ is far more complex than anything previously considered.

The most basic consideration for EI in a 1-e molecule is electron localization, as, without this, EI is not possible. The prediction of $R_c$ from electron localization has been discussed in chapter 1, as seen in equation 1.11. Since we have the experimental measurement of $R_c$, we want to test whether it is consistent with the prediction. In this work, $I_p$ for the B-state of I$_2$ is 9.5 eV (0.35 a.u.), and $R_c = 8.67 \pm 0.03$ a.u. (513 nm) and 8.71 \pm 0.09 a.u. (500 nm), which give $I_p \times R_c = 3.03 \pm 0.01$ (513 nm), 3.05 \pm 0.03 (500 nm), respectively, remarkably close to the prediction of 3. From this, we must conclude that electron localization is the over-riding requirement for EI at $R_c$ and that the conditions for localization can be deduced from very simple considerations, despite the specific complexities of particular molecules.

Interestingly, the simple model of electron localization was extended to include field-induced changes in the energy levels. This gives the result $R_c = 4/I_p$, as seen in chapter 1, which is definitely inconsistent with our results. Clearly, more experimental and theoretical work is required to fully understand the phenomenon of $R_c$. 
2.5 Conclusion

For the first time, we obtain fully R- and $\theta$- resolved measurements of $R_c$ in a homonuclear neutral diatomic molecule. The angular distribution of the B state of $I_2$ is obtained, and it shows the expected $\cos^2(\theta)$ distribution. When the laser field is parallel to the molecular axis, the B state shows enhanced ionization at a certain critical separation $R_c$ with an enhancement factor of 22, and as the angle between the two increases, the ionization peak at $R_c$ decreases and finally disappears in the perpendicular case. The enhanced ionization of the B state of $I_2$ can be explained by CREI, and the determination of $R_c$ shows that $R_c$ can be precisely predicted by a simple model of electron localization. EI is a very general phenomenon which has yet to be fully explored.
Chapter 3

Internuclear separation dependent ionization of the valence orbitals of I$_2$ by strong laser fields

3.1 Introduction

Exposing molecules to strong laser fields produces a variety of effects, which has led to considerable work in many areas, such as high harmonic generation [1, 46, 2, 47], nonsequential double ionization [3, 4], and coherent control [50, 51]. In virtually all of these phenomena, single-electron ionization of the neutral ground-state molecule is the critical first step. However, single-electron ionization is still not well-understood, given the many degrees of freedom in a molecule (rotational, vibrational, and electronic).

In particular, the ionization rate as a function of internuclear separation $R$, $\Gamma(R)$, has become a topic of much research, leading to the phenomena of enhanced ionization
(EI) (discussed in chapter 1 and 2) in which $\Gamma(R)$ peaks at a certain critical separation $R_c$, and Lochfrass [6, 5, 7, 48] in which a vibrational wavepacket (VWP) in the ground electronic state (GES) of neutral molecules is formed due to a large slope of $\Gamma(R)$ at the equilibrium separation $R_e$. However, the VWP generated through Lochfrass only vibrates within a very small range of $R$ around $R_e$, prohibiting extended measurements of $\Gamma(R)$. For I$_2$, there is even disagreement between the experimental results and the theoretical predictions on whether the slope of $\Gamma(R)$ is positive or negative at $R_e$. The experiment implies $d\Gamma/dR > 0$ at $R_e$ [7], while the dependence of ionization potential on $R$ implies just the opposite [14, 55, 56]. To fully understand $\Gamma(R)$ of the GES, a VWP vibrating over a large range of $R$ is needed.

While most experiments consider ionization from the highest occupied molecular orbital (HOMO), it has been known for some time that inner-orbital ionization occurs in strong laser fields [57]. Recently, ionization from inner orbitals is attracting more attention [2, 58, 73, 60]. However, for small light-atom molecules, like N$_2$, O$_2$, CO$_2$ and HCl, the ionization branching ratio of inner orbitals is usually rather small, given the large differences in ionization potentials, compared with the HOMO. To better understand the role of inner-orbital ionization in strong fields, these studies must be extended to both large light-atom molecules, like uracil [61], and small heavy-atom molecules, like I$_2$.

To study the ionization of a ground-state neutral molecule, we use a pump-dump-probe scheme to create a coherent VWP in the GES of I$_2$, whose valence orbitals are $\sigma^2_g\pi^4_u\pi^4_g\sigma^0_u$. The VWP vibrates between 4.4 a.u. and 6.2 a.u., over which $\Gamma(R)$ is measured. The single ionization from different orbitals is determined from analyzing the final states and using Fourier-transform spectroscopy. We will show that $\Gamma(R)$ actually increases with $R$, consistent with the experimental results of Lochfrass.
However, the increased ionization comes from the HOMO-2 ($\sigma_g$), but not from the HOMO ($\pi_g$) or HOMO-1 ($\pi_u$). In fact, the ionization rate of the HOMO-2 exceeds that of the combined rate of the less bound orbitals and this branching ratio increases with $R$. To our knowledge, this has never been seen in small light-atom molecules.

### 3.2 Experiment

The pump-dump-probe scheme is shown in Fig.3.1. The VWP is first launched to the B state of I$_2$ by a weak 525 nm pump pulse through a one-photon resonant transition, brought back to the GES by a weak 800 nm dump pulse through resonant deexcitation, and finally singly ionized by a delay-controllable 800 nm probe pulse. All pulses are linearly polarized along the time-of-flight (TOF) axis, except where noted. Since the X-B transition is a parallel transition [62], the molecules excited to the B state will be aligned with the pump laser polarization with a $\cos^2(\theta)$ distribution [25], and the ones deexcited back to the X state will have a higher degree of alignment, $\cos^4(\theta)$.

The experiments are performed with one of two ultrafast Ti:sapphire laser systems (home-built or Spectra-Physics) and a TOPAS (Optical Parametric Amplifier) system. The ionization signals of I$_2^+$, I$^+$ and I$_2^{2+}$ are recorded with a TOF spectrometer. Room-temperature (295 K) I$_2$ gas is leaked effusively into the chamber with a base pressure of $2 \times 10^{-9}$ torr. The Ti:sapphire laser produces linearly-polarized pulses (800 nm, 37 fs (home-built) or 50 fs (Spectra-Physics), 1 kHz, up to 800 $\mu$J) and the output beam is split with $\sim$ 80% of the energy sent into the TOPAS to generate a pump beam (525 nm, 50 fs, up to 2 $\mu$J) while the rest is sent to another beamsplitter to generate the dump and probe beams. An aperture is used in either of the first two
Figure 3.1: Schematic potential energy curves, showing the physical scenario of the pump-dump-probe experiments.
beams in order to decrease ionization by the pump and dump pulses, while creating a more uniform focal volume for the probe pulse. The pump-dump delay $\tau_{p-d}$, and the dump-probe delay $\tau_{d-pr}$ are adjusted by two computer controlled translational stages. From the separation of the peaks in the TOF spectrum, one can determine the momentum and kinetic energy release (KER) of a pair of dissociating fragments. More details can be found in Refs [25, 52].

To find the best $\tau_{p-d}$, we fix the delay between the pump and probe pulses at 0.3 ps and scan the dump pulse. The depletion of the B state can be found by looking at the variation of the $I^{2+}$ signal in the (2,1) channel (the (m,n) channel refers to the dissociating channel $I_2^{(m+n)+} \rightarrow I^m+ + I^n+$) which results from ionizing the B state, as seen in Fig.3.2(a). The maximum depletion is around 75% and occurs at $\tau_{p-d} = 0.045 \text{ ps}$, as shown in Fig.3.2(b), consistent with simulations.

The simulation for the depletion of the B state is performed as follows: the first nine vibrational states are populated initially according to a Boltzmann distribution. The WP launched in the B state and then returned to the X state is obtained by solving the time-dependent nuclear one-dimensional Schrödinger equation for the X and B states coupled by a 50-fs 525 nm pump pulse and a delayed 50-fs 800 nm dump pulse. We calculate incoherent sums of the WPs in the X and B states obtained with each of the nine lowest vibrational states as the initial state weighted by the Boltzmann factors. Then, we calculate the population left in the B state at each $\tau_{p-d}$, as seen in Fig. 3.2 (b), and find that the best delay for depleting the B state is 0.045 ps.
Figure 3.2: (a) The TOF of I$^{2+}$ as a function of $\tau_{p-d}$ (background subtracted) with a step size of 0.005 ps with the pump-probe delay fixed at 0.3 ps. (b) The depletion of the B state as a function of $\tau_{p-d}$ from the simulation (red line, normalized), and experiment (black line with data points, normalized). The experimental data correspond to the integrated signal in the range of 3670 ns - 3700 ns in (a). In the experiment, the intensities of the pump, dump and probe pulses are estimated to be $\sim 1.2 \times 10^{11}$ W/cm$^2$, $\sim 1.3 \times 10^{12}$ W/cm$^2$ and $\sim 2.4 \times 10^{13}$ W/cm$^2$, respectively, and the I$_2$ pressure is $\sim 7.0 \times 10^{-7}$ torr.
Figure 3.3: (a) The TOF plot of the (2,0) and (2,1) channels as a function of $\tau_{d-pr}$ with a step size of 0.020 ps with $\tau_{p-d}$ fixed at 0.045 ps, showing the returning VWP in both channels. The background has been subtracted, and the experimental parameters are the same as in Fig. 3.2. (b) The FFT plot of the delay variable of (a).
3.3 Results

We fix $\tau_{pr-d}$ for maximum depletion and scan $\tau_{d-pr}$ to obtain the ionization signals of I$^{2+}$ as a function of $R$ to characterize the X-state VWP. In Fig.3.3(a), we see the expected VWP motion in the (2,0) channel [52]. We further analyze the data by taking a Fourier transform of the delay variable $\tau_{d-pr}$. The FFT of the signal in the (2,0) channel in Fig.3.3(b) gives not only the frequency of the vibration, but also the KER of the VWP in the X state projected onto the (2,0) state. There are two frequencies, 6.3 THz at large KER associated with an $R$ near $R_e$ which is created through Lochfrass or bond-softening from the dump pulse (see below) [7], and 5 THz at lower KER associated with large $R$ which corresponds to the returning VWP. The variation of the KER of the returning VWP in the (2,0) channel directly maps the motion of the VWP as a function of $R$, with the largest and smallest KER corresponding to the smallest and largest $R$, respectively. Simulations confirm the vibrational frequency of 5 THz, which corresponds to an average vibrational quantum number of 33 and a VWP motion between 4.4 a.u. and 6.2 a.u..

Since we see both the 5 THz and 6.3 THz modulations in the (2,0) channel, we expect to see them in the I$^{2+}$ signal, as well, allowing us to measure $\Gamma(R)$ over a large range of $R$. If we found a strong 5 THz component in the FFT of the I$^{2+}$ signal, its phase would give us a new measurement of the slope of $\Gamma(R)$. Surprisingly, the FFT shows no 5 THz modulation, but only a 6.3 THz modulation in the I$^{2+}$ signal, as seen in Fig.3.4(a). However, there is a strong 5 THz component in the (1,0) channel (Fig.3.4(a)) which shows that the VWP is actually ionized to this dissociating channel. The ionization rate of the (1,0) channel is out of phase with the momentum of the VWP in the (2,0) channel (Fig.3.4(b)), showing that $\Gamma(R)$ of the X state increases
with $R$, in good agreement with our previous study of Lochfrass [7]. Moreover, from Fig.3(a), we only see the VWP vibrating within the normal range of the (2,0) channel, showing that $\Gamma(R)$ at $R < R_e$ is vanishingly small. If not, we would see an abnormally high KER in the (2,0) channel associated with ionization at $R < R_e$.

In order to check that these results are from the excited X-state VWP and not residual population in the B state, we ran the experiment with the pump and probe pulses polarized as before, but with a perpendicularly polarized dump pulse. Because the B state is aligned horizontally with the pump pulse, the vertical dump pulse will not deplete it. As seen in Fig.3.4(a), both the 5 THz and 6.3 THz modulation disappear, showing that the dump pulse, indeed, generates the 6.3 THz signal and that the 5 THz signal does not come from the B-state VWP.

Having established that the 5 THz signal comes from the large amplitude VWP in the X-state of $I_2$, we need to understand why it occurs in the (1,0) and not the $I_2^+$ channel. Single ionization of the HOMO, HOMO-1 and HOMO-2 of $I_2$ will leave the molecule in the $X^2\Pi_{1/2,3/2g}$ ($\sigma^2g^4\pi^3g^0$, $\Lambda^2\Pi_{1/2,3/2g}$ ($\sigma^2g^3\pi^4g^0$) and $B^2\Sigma^+_g$ ($\sigma^1g^4\pi^4g^0$) states of $I_2^+$, respectively. These five states are clearly seen in XUV photoelectron spectroscopy [63]. The X and A states are bound and both contribute to the $I_2^+$ signal, while the B state dissociates, leading to the (1,0) channel [63, 14]. Thus, ionization of the HOMO-2 will produce a (1,0) signal, although we must consider the other source of (1,0): resonant population transfer in the molecular ion.

As the molecule vibrates, electronic states will go in and out of resonance. At a resonance, population can be transferred from the bound X and A states to the dissociating B state and vice versa. Thus, the (1,0) channel could arise from a two-step process involving ionization of the HOMO or HOMO-1 and subsequent resonant excitation. Moreover, this process would be modulated at 5 THz. However, population
Figure 3.4: (a) The FFT spectra of the (1,0) signal and the bound $I_2^+$ signal (normalized). The data were taken with a step size of 0.020 ps, and the FFT curves were obtained by integrating the forward-going (1,0) signals or the total $I_2^+$ signals and then performing an FFT. (b) Variation of the signal in the (1,0) channel and the momentum of the returning VWP in the (2,0) channel as a function of $\tau_{d-pr}$. The intensities of the pump, dump and probe pulses are estimated to be $\sim 7.5 \times 10^{11}$ W/cm$^2$, $\sim 1.4 \times 10^{12}$ W/cm$^2$ and $\sim 6.2 \times 10^{12}$ W/cm$^2$, respectively. The $I_2$ pressure is $\sim 7.2 \times 10^{-7}$ torr.
transfer would simultaneously increase one signal while decreasing another, so both
would be modulated at 5 THz with the same amplitude and opposite phase. As a
5 THz modulation is not seen in the $I_2^+$ signal, resonant population transfer in the
molecular ion can be ruled out. Hence, the (1,0) channel must be associated with the
B state of $I_2^+$ through single ionization of the HOMO-2 $\sigma_g$ orbital.

3.4 Discussion

Based on this assignment, we can write the single ionization rate of the GES of $I_2$
as $\Gamma_X(R) = \Gamma_{XX}(R) + \Gamma_{XA}(R) + \Gamma_{XB}(R)$, where $\Gamma_{XX}(R)$, $\Gamma_{XA}(R)$ and $\Gamma_{XB}(R)$ are
the ionization rates of the HOMO $\pi_g$ electron, HOMO-1 $\pi_u$ electron and HOMO-2 $\sigma_g$
electron, respectively. The first two combined give the rate to $I_2^+$, and the last one
 gives the rate to the (1,0) channel. Since we find the 5 THz modulation in the (1,0)
channel and not the $I_2^+$, ionization of the HOMO and HOMO-1 does not have a strong
dependence on $R$, while the ionization of the HOMO-2 does. We have previously seen
that the ionization of the B state of $I_2$ also has a strong dependence on $R$ [25]. We
attributed this strong dependence to EI as the outer orbital in the B state is $\sigma_u$ and EI
is expected for $\sigma$ orbitals [43]. Similarly, the HOMO-2 is $\sigma_g$ and should also experience
EI, giving rise to a strong modulation in our experiment. It is also predicted that
$\pi$ orbitals will not have EI [43] and, as a result, their ionization rate does not have
nearly as strong a dependence on $R$ - explaining the lack of modulation of our $I_2^+$
signal. Moreover, our pump-dump-probe technique produces target molecules well
aligned along the TOF axis providing the best comparison of EI in $\sigma$ and $\pi$ orbitals.

One final observation corroborates our conclusion that the observed $R$ dependence
Figure 3.5: The branching ratio of the (1,0) signal ionizing from the B state as a function of $R$ (branching ratio: (1,0) signals/total single ionization signals). Inset: the TOF signal of the (1,0) and bound $I^+_2$ with a single red pulse with an intensity of $\sim 6.2 \times 10^{12}$ W/cm$^2$, and the branching ratio of the (1,0) signal is 65.2%.
of the ionization rate of the valence orbitals of I\textsubscript{2} is due to their $\sigma$ or $\pi$ character. In light molecules, such as N\textsubscript{2}, O\textsubscript{2}, or CO\textsubscript{2}, the contribution of the inner-orbitals is small compared to the HOMO as a result of their larger binding energies. However, in I\textsubscript{2}, we find that the single-pulse branching ratio at $R_e$ is 65\% for ionization of the HOMO-2, as shown in the inset of Fig.3.5, indicating that the orbital geometry is more important in determining the ionization rate than the relative ionization potential of the orbitals. In a related experiment \cite{25}, we determined this branching ratio as a function of $R$ by launching a VWP on the B state of I\textsubscript{2}. We find that the branching ratio of the (1,0) channel increases with $R$, reaches a peak at around 6.85 a.u. and then drops again, as shown in Fig.3.5. While this experiment uses the B state of I\textsubscript{2} ($\sigma_g^2\pi_u^4\pi_g^3\sigma_u^1$) as the initial state, the ionization from the X state VWP will likely have the same property. Indeed, the branching ratio should be higher, because ionization to the bound I\textsubscript{2}+ state from the B state is easier than from the X state, with the former requiring the removal of one electron from the LUMO and the latter requiring ionization from the HOMO. For instance, the branching ratio of the (1,0) signal ionizing from the X state (65.2\%) is higher than that from the B state (52.7\%) at the same $R$ of 5.03 a.u.. The increasing branching ratio as a function of $R$ is consistent with the strong dependence of the ionization rate for $\sigma$ orbitals and the weak dependence for $\pi$ orbitals.

3.5 Conclusion

In conclusion, we generate a coherent VWP in the GES of neutral I\textsubscript{2} and the target molecules are highly aligned with the laser polarization. This is a new way to study
the behavior of the GES of molecules in strong laser fields. The $R$ dependence and relative strength of the ionization rates of different orbitals of I$_2$ have been discussed. The ionization rates of the HOMO ($\pi_g$) and HOMO-1 ($\pi_u$) initially increase with $R$ but level off, however, the ionization rate of the HOMO-2 ($\sigma_g$) keeps increasing with $R$, presumably until $R_c$ where EI is reached. Finally, the HOMO-2 provides the dominant ionization pathway, which is highly unusual for strong-field ionization.
Chapter 4

Enhanced ionization of an inner orbital of I$_2$ by strong laser fields

4.1 Introduction

For diatomic molecules driven by intense laser fields linearly polarized along the molecular axis, their tunneling ionization rate increases with the internuclear separation $R$ and peaks at a critical separation $R_c$. This very general phenomenon, known as enhanced ionization (EI), has been discussed in chapter 1 and 2.

In chapter 2, we investigated EI in the $B$ state ($\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u^1$) of I$_2$ by using a pump-probe technique. The pump pulse promoted one electron from the highest occupied molecular orbital (HOMO) $\pi_g$ state to the lowest unoccupied molecular orbital (LUMO) $\sigma_u$ state, and the probe pulse removed the electron in the $\sigma_u$ state leaving the molecular ions in the deeply bound I$_2^+$ $X^2\Pi_{3/2g}$ state. The vibrational wavepacket (VWP) motion in the $B$ state provided a large range of $R$, and $R_c$ was found to be at
∼ 8.7 a.u.. Then, in chapter 3, we produced a VWP moving between 4.4 and 6.2 a.u. in the ground electronic state (GES) \((\sigma^2 \pi_u \pi_u \sigma_u)\) of I\(_2\), and discussed the \(R\)-dependent single ionization of different orbitals. We found that the HOMO-2 \(\sigma_g\) orbital showed a strong \(R\)-dependence, while the HOMO \(\pi_g\) and HOMO-1 \(\pi_u\) orbitals did not, and the HOMO-2 \(\sigma_g\) orbital provided the dominant single ionization pathway. We even predicted that the \(\sigma_g\) orbital would also show an \(R_c\) if the VWP moved to a sufficiently large \(R\).

In this chapter, using the pump-probe technique described in chapter 2, we obtain a large range of VWP motion in the \(B\) state of I\(_2\) over which the \(R\)-dependent single ionization of the HOMO-2 \(\sigma_g\) orbital is observed by analyzing the final state of the (1,0) dissociation channel \([(1,0) \text{ refers to the dissociating channel } I_2^+ \rightarrow I^+ + I]\), and we find an \(R_c\) at \(\sim 7.3\) a.u.. Furthermore, the HOMO-2 \(\sigma_g\) orbital again provides the dominant ionization pathway. However, another peak at \(\sim 8.7\) a.u. in the (1,0) channel reveals that different molecular orbitals might be strongly mixed at large \(R\) since the (1,0) channel shows the ionization feature of the LUMO \(\sigma_u\) orbital.

### 4.2 Experiment

The pump-probe scheme is shown in Fig. 4.1. A VWP is launched in the \(B\) state by a weak green pump pulse through one-photon resonant excitation, and then singly ionized by a delay-controllable 800 nm probe pulse. With a 513 or 500 nm pump pulse, the VWP reaches \(R \sim 8.72\) a.u. or \(\sim 9.38\) a.u., respectively, and the VWP motion is well understood [25]. Both of the pulses are linearly polarized along the time-of-flight (TOF) axis. Since the \(X-B\) transition is a parallel transition [62], the
Figure 4.1: Schematic potential energy curves, showing the physical scenario of the pump-probe experiments.
molecules excited in the $B$ state will be aligned with the pump laser polarization with a $\cos^2(\theta)$ distribution [25] in which the $\sigma$ orbitals will be preferentially ionized. In the molecular orbital picture, the molecules end up in the $I_2^+ \ X^2\Pi_{g3/2}$ state by removing the electron from the LUMO $\sigma_u$ orbital, but in the (1,0) channel by removing one electron in the HOMO-2 $\sigma_g$ orbital [63].

The experiments are performed with our home-built ultrafast Ti:sapphire laser system and a TOPAS (traveling-wave optical parametric amplifier of superfluorescence) system. The ionization signals of $I_2^+$ and $I^+$ are recorded with a TOF spectrometer. The ultrafast laser and the TOF spectrometer have been described in Refs [25, 52]. Room-temperature (295 K) $I_2$ gas is leaked effusively into the chamber with a base pressure of $2 \times 10^{-9}$ torr. The Ti:sapphire laser produces linearly-polarized pulses with a central wavelength of 800 nm, a transform-limited pulse duration of 37 fs, and an output energy of up to 800 $\mu$J at a repetition rate of 1 kHz. The output beam is split with $\sim 80\%$ of the energy sent into the TOPAS to generate a pump beam while the rest serves as a probe beam. The pump pulses have a central wavelength of 513 or 500 nm, a duration of 50 fs and an energy of up to 2 $\mu$J. The pump and probe beams are focused by a 3-in.-focal-length silver spherical mirror inside the TOF chamber. An aperture is used in the pump beam in order to decrease ionization and also increase the focal spot size in the chamber. This creates a more uniform focal volume for the probe beam. The pump-probe delay $\tau$ is adjusted by a computer-controlled translational stage. In the experiments, the probe pulse just singly ionizes the $B$ state to avoid double ionization [44].
Figure 4.2: The ionization signals of $I_2^+$ and and (1,0) channel as functions of $\tau$ (background subtracted) with a step size of 0.030 ps with two different pump wavelengths. The delay of 0 ps is the temporal overlap of the pump and probe pulses. In the experiments, the intensities of the pump and probe pulses are estimated to be $\sim 1.4 \times 10^{11}$ and $\sim 1.4 \times 10^{13}$ W/cm$^2$, respectively, and the $I_2$ pressure is $\sim 7.0 \times 10^{-7}$ torr.
4.3 Results

The ionization signals of $I_2^+$ and the (1,0) channel as functions of $\tau$ with different pump wavelengths are shown in Fig. 4.2. With either wavelength, the $I_2^+$ signal shows one peak, while the (1,0) channel shows two peaks. The peaks with 500 nm pump wavelength appear earlier than those with 513 nm, since the 500 nm pump wavelength starts the VWP higher up in the potential curve of the $B$ state of $I_2$ and the VWP moves faster. The ionization signals of the (1,0) channel are much stronger than those of $I_2^+$ with either wavelength which is consistent with our previous study [66]. The corresponding signal from $I_2^+$ or the (1,0) channel with 513 nm is stronger than those with 500 nm, due to the stronger $X$-$B$ coupling at 513 nm [67]. There is only one peak in either of the $I_2^+$ curves, which shows the EI of the LUMO $\sigma_u$ orbital [25], and there are two peaks in both the (1,0) channel curves, with the inner one not seen in $I_2^+$ and the outer one occurring at the same delay as in $I_2^+$.

Since the VWP motion in the $B$ state of $I_2$ is fully understood [25], $\tau$ will determine the expectation value of $R$ for the VWP. From this, we obtain the $R$-dependent ionization signal of the (1,0) channel, as shown in Fig. 4.3. The two different pump wavelengths give almost the same inner $R_c$: $R_c = 7.29 \pm 0.18$ a.u. (513 nm) and $R_c = 7.28 \pm 0.16$ a.u. (500 nm), and also the same outer $R_c$ at $\sim 8.7$ a.u. (within the error bars). The peaks at $\sim 5.9$ a.u. (500 nm) and $\sim 5.2$ a.u. (513 nm) are due to the temporal overlap between the pump and probe pulses.

Having established the inner $R_c$ in the ionization signal of the (1,0) channel, we need to understand its origin. There are two possibilities: one is from ionization of an inner orbital, and the other is from resonant population transfer from the bound $I_2^+$ to the (1,0) channel. However, population transfer would simultaneously increase
Figure 4.3: The ionization signal (normalized) of the (1,0) channel as a function of $R$ with two different pump wavelengths: 500 and 513 nm. There are two $R_c$'s: the inner one at $\sim 7.3$ a.u. and the outer one at $\sim 8.7$ a.u. The peaks at $\sim 5.9$ a.u. (500 nm) and $\sim 5.2$ a.u. (513 nm) are due to the temporal overlap between the pump and probe pulses.
the (1,0) signal while decreasing the I\textsuperscript+ signal. As this is not seen in Fig. 4.2, population transfer can be ruled out. Therefore, the inner peak should be associated with ionization of an inner orbital.

The \(B\) state of \(I_2\) has valence orbitals of \(\sigma_g^2\pi_u^4\pi_g^3\sigma_u^1\). The ionization of the LUMO \(\sigma_u\) electron will leave the molecule in the bound \(I_2^+\ X^2\Pi_{g3/2}\ ((\sigma_g^2\pi_u^4\pi_g^3\sigma_u^0)\) state, and this was fully discussed in our previous work [25] in which only one \(R_c\) at \(\sim 8.7\) a.u. was found. On the one hand, the (1,0) channel must be from the ionization of an inner orbital, HOMO \(\pi_g\), HOMO-1 \(\pi_u\), or HOMO-2 \(\sigma_g\); on the other hand, the \(R_c\) implies that the target orbital should show a strong \(R\)-dependent ionization. In this case, the HOMO \(\pi_g\) should be ruled out first, because the final state of \(\sigma_g^2\pi_u^4\pi_g^3\sigma_u^1\) is also bound [14]. The removal of one electron from the HOMO-1 \(\pi_u\) orbital could leave the molecule in a dissociating channel. Normally, removal of the HOMO-1 would leave the molecule in the bound \(A\) state, but since the HOMO is excited to the LUMO, the \(\sigma_g^2\pi_u^3\pi_g^3\sigma_u^1\) configuration may not be bound. However, our previous work shows that the HOMO-1 \(\pi_u\) orbital does not have a strong \(R\)-dependent ionization feature [66]. Moreover, it is predicted that \(\pi\) states do not show EI [43]. So, the HOMO-1 \(\pi_u\) orbital is also ruled out. Therefore, the \(R_c\) \(\sim 7.3\) a.u. must be associated with the HOMO-2 \(\sigma_g\) orbital. In our previous work [66], we did see a strong \(R\)-dependent ionization of the \(\sigma_g\) orbital when the VWP vibrated between 4.4 and 6.2 a.u. in the ground electronic state, and we predicted that there would be an \(R_c\) if the VWP moved to larger \(R\) [66]. Now, we find this \(R_c\).

In order to determine if this value of \(R_c\) makes physical sense, we note that \(R_c \times I_p\) appears to be a useful way to characterize enhanced ionization, independent of the details of the system under study (see above and [28, 30]). Since \(I_p\) of the HOMO-2 \(\sigma_g\) orbital is \(\sim 15.07\) eV (0.554 a.u.) [68, 14], we find the product of \(R_c\) and \(I_p\).
to be 4.04. The product is different from that of the LUMO $\sigma_u$ orbital in which $R_c \times I_p \sim 3$ [25]. The LUMO $\sigma_u$ orbital has only one active electron, and it is more like a one-electron system with its $R_c$ well predicted by EL. However, the HOMO-2 $\sigma_g$ orbital has two equivalent electrons in which the ionic states should play an important role in the ionization. As we do not know of any predictions of this product for enhanced ionization in two-electron systems, we need to answer two questions: is the magnitude of the product similar to that in one-electron systems, and do $R_c$ and $I_p$ scale inversely?

4.4 Discussion

In order to learn more about $R_c \times I_p$ in a two-electron system, we consider a one-dimensional model of a generic diatomic molecule $A_2$ with two equivalent electrons moving in a double-well potential [69, 70]:

$$
H_s(x_1, x_2, t) = \frac{-Z}{\sqrt{(x_1 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_1 + d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 + d)^2 + a^2}} + \frac{1}{\sqrt{(x_1 - x_2)^2 + a^2}} - (x_1 + x_2)F(t)
$$

(4.1)

where $Z = 1$ is the charge on each well, $x_1$ and $x_2$ are the coordinates of the two electrons, $R = 2d$ is the internuclear separation, $a$ is the smoothing parameter of the Coulomb potential and $F(t)$ is the electric field strength. Throughout the calculation, atomic units are used.
In this one-dimensional (1D) model, the parameter $a$ affects the ionization potential $I_p$: the smaller the $a$, the deeper the ground state. $a = 0.700$ or $0.742$ corresponds to $I_p = 0.90$ or $0.86$ a.u., respectively. The ionization probability at different $R$ is obtained after solving the Schrödinger equation. As it turns out (Fig. 4.4), $R_c$ becomes smaller as the initial target state becomes more deeply bound. Moreover, this model gives $R_c \times I_p \sim 3.15 \ (a = 0.700)$, and $R_c \times I_p \sim 3.44 \ (a = 0.742)$, verifying the inverse relationship between $R_c$ and $I_p$ and showing that the magnitude of this quantity is between 3 and 4, as is true for one-electron systems. Thus, this corroborates our identification of the peak at 7.3 a.u. with enhanced ionization of an inner orbital.

The outer $R_c$ in the $(1,0)$ channel is at $\sim 8.7$ a.u., and this is the same as that in the $I_2^+$ signal since the peaks occur at the same delay. In Ref. [25], we fully studied the EI of the LUMO $\sigma_u$ state in which the bound $I_2^+ \ X^2\Pi_{g3/2}$ state was the final state and the $R_c$ was found at $\sim 8.7$ a.u.. The peak at $\sim 8.7$ a.u. can be considered as a signature of ionizing from the LUMO $\sigma_u$ state. However, from the molecular orbital picture, the ionization of the LUMO leaves the molecule only in the bound $I_2^+ \ X^2\Pi_{g3/2}$ state, not the $(1,0)$ channel. An interesting question is why the $(1,0)$ channel shows the ionization characteristics of the LUMO $\sigma_u$ state. One possibility is resonant population transfer between molecular ions. However, population transfer should be weak, if there is any, since the resonant crossing is far away from $8.7$ a.u., although this cannot be completely ruled out.

Another possible explanation is the mixture of different molecular orbitals [71] in $I_2$ when the two I atoms are pulled apart. The molecular orbital picture works well for light molecules, like $N_2$, $O_2$ [72], $CO_2$ [73], and $HCl$ [60]; however, whether it still works properly for heavy molecules, like $I_2$, especially when the two atoms are far away from each other, is still an open question. The heavy molecule $I_2$ shows
Figure 4.4: Calculation of the ionization probability as a function of internuclear separation $R$ with two electrons initially in the ground state. The two different values of $a$ correspond to different ionization potentials.
different ionization characteristics from the light molecules, as seen from the ionization branching ratios of different orbitals. For light molecules, the branching ratio of inner orbitals is usually rather small [60], compared with the HOMO. However, for I$_2$, the HOMO-2 provides the dominant single-ionization pathway [66]. At large $R$, the $\sigma_u$ and $\sigma_g$ orbitals are probably mixed and the electron transfer can occur as the LUMO $\sigma_u$ electron is ionized. In this case, the ionization feature of the LUMO also appears in the (1,0) channel.

4.5 Conclusion

In conclusion, with a pump-probe technique, we generate a VWP in the $B$ state of I$_2$ and study the single ionization of the HOMO-2 $\sigma_g$ orbital. As predicted by previous work, an $R_c$ is found at $\sim 7.3$ a.u.. This implies that the enhanced ionization also occurs in lower lying orbitals, not just the HOMO or LUMO. Another $R_c$ at $\sim 8.7$ a.u. implies that there might be a mixture of molecular orbitals in I$_2$ at large $R$, since the (1,0) channel shows the ionization feature of the LUMO $\sigma_u$ orbital.
Chapter 5

White-light supercontinuum generation via filamentation in SF₆ with low threshold and stable pointing

5.1 Introduction

In recent years, the generation of few-cycle intense femtosecond pulses has attracted much attention. The generation of few-cycle pulses requires extremely broad spectral bandwidth which can be obtained mainly via two mechanisms: nonlinear self-phase modulation (SPM) and filamentation. Typically, spectral broadening via SPM can be achieved when a pulse is propagating through an optical fiber [74, 75] or a gas-filled hollow-core optical waveguide [76, 77, 78]. Sub-5-fs pulses were obtained based on the SPM mechanism [77]. However, fibers only support low energy, and hollow-core fibers are lossy. Both of them are sensitive to alignment and damage at the input.
Unlike SPM, spectral broadening through filamentation requires a relatively simple setup since no fiber is needed and the energy loss is lower. The formation of filaments is believed to be from the dynamic balance between linear and nonlinear effects in the medium, as discussed in chapter 1.2.4. Filamentation has been studied for years both theoretically [79, 80, 81] and experimentally in different media, such as air [82], noble gases [84, 85, 83], water [86], and fused silica [87]. In addition, different types of laser beams have been used in the formation of filaments including Gaussian [82], flat-top [88], Bessel beams [89] and Airy beams [90, 91]. The main disadvantages to filamentation are a high energy threshold [82, 92] and relatively low pointing stability [84].

Filamentation in SF$_6$ has been discussed before [93]. It was found that a filament in SF$_6$ was easier to form than in argon, though the two had similar values of self-focusing critical power $P_{cr} \sim 6$ GW. Compared with argon, SF$_6$ molecules are easier to be multiply ionized and higher electron density is achieved to contribute to the defocusing [93, 94]. In this case, a filament could be formed in SF$_6$ at a low input power threshold.

In this work, we produce white-light supercontinuum with a simple experimental setup through filamentation in SF$_6$, with an input laser energy as low as 0.35 mJ and a transform-limited pulse duration (TLPD) of 50 fs. The spectra at different input laser powers, SF$_6$ pressures, and different laser repetition rates are investigated. In addition, the spatial chirp of the output beam with spectral broadening below or above the filamentation threshold is discussed. Broadening below the filamentation threshold does not have a spatial chirp, however, the spectrum above the threshold does. With 0.75 mJ, 50 fs input pulses and 1 atm SF$_6$, a TLPD of less than 3 fs is obtained. Furthermore, the pointing stability of the filament is investigated and is
found to be similar to that of the input laser beam. Finally, with 0.35 mJ, 50 fs input pulses, the output pulses are recompressed by a pair of chirped mirrors and a pulse duration of 14.6 fs is obtained, limited by the bandwidth of the mirrors.

5.2 Experiment

The experimental setup for spectral broadening through filamentation and pulse compression is shown in Fig. 5.1. The experiments are performed with one of two ultrafast Ti:sapphire laser systems (home-built or Spectra-Physics). The commercial one produces linearly-polarized pulses with a central wavelength of 800 nm, a pulse duration of 50 fs (1.1× TLPD), and an output energy of up to 0.75 mJ at an adjustable repetition rate up to 1 kHz. The home-built laser produces 35 fs (1.1× TLPD) and an output energy of up to 1.2 mJ. A transparent plastic tube is filled with SF$_6$ with a pressure up to 1 atm. The beam is focused by a f=1.5 m focal length lens located on the input end of the tube. There is a 1-mm-thick fused silica window on the output end. The beam is collimated by another f=1.5 m lens and then sent into a pair of chirped mirrors (Venteon DCM7 mirrors, -120 fs$^2$/pair at 800 nm) to compensate the positive dispersion. The dispersion is finely adjusted by several small pieces of fused silica glass. The recompressed pulse duration is measured by a home-built third-order autocorrelator. A small aperture on a translational stage selects certain parts of the beam to investigate the spatial chirp of the output beam with or without a filament. The spectra are measured with one of two spectrometers (Ocean Optics). Finally, there is a card sitting at $\sim$ 1.7 m after the focus of the beam and a camera to measure the intensity centroid of the beam in order to investigate the pointing stability. The
Figure 5.1: The experimental layout. L1: focusing lens with f=1.5 m and antireflection coating for 800 nm; L2: collimating lens with f=1.5 m; M1 and M2: silver mirrors with reflectivity $\geq 95\%$ for 450 nm - 12 $\mu$m; M2: flip mirror; CM: chirped mirror (Venteon DCM7, -120 fs$^2$/ pair at 800 nm); C: card. The aperture is on a translational stage. The card C is sitting at $\sim 1.7$ m after the focus of the beam so that the intensity centroid of the beam is measured by the camera (PixeLINK PL-B953U).
experimental setup is simple and easy to build, as seen in Fig. 5.1.

5.3 Results

First, we fill the tube with SF$_6$ to a pressure of 735 torr, and increase the input laser energy to see whether we can produce a filament. When the energy reaches 0.35 mJ, a stable bright white spot is seen at the output of the tube due to a white-light supercontinuum generation. With 0.35 mJ input, the laser energy at the output of the tube is $\sim 0.3$ mJ which gives an efficiency of $\sim 86\%$. Further, through the transparent tube, one can see the formation of the filament roughly starting from the focus of the beam and the color changing from red to blue along the length of the filament. By inserting M2, we align the output beam into a spectrometer to measure the spectra. The spectra as a function of the input laser energy are shown in Fig. 5.2 (a). As seen in the figure, higher input energy extends the spectrum to shorter wavelengths, with 0.35 mJ input having a cutoff at $\sim 550$ nm and 0.69 mJ at $\sim 350$ nm. We believe that the long-wavelength part would show the same trend but is limited by the measuring range of the spectrometer which has a cutoff at 890 nm. The original spectrum is narrow, corresponding to the original pulse duration of 50 fs ($1.1 \times$ TLPD), while the spectral range with 0.69 mJ input pulse energy is from 350 nm to 890 nm. We calculate the TLPD based on the spectra with 0.69 mJ input pulse energy, as seen in Fig.5.2 (b), and obtain a TLPD of 2.7 fs. This demonstrates that we can produce a spectrum wide enough to produce few-cycle laser pulses.

Next, we fix the input laser energy at 0.75 mJ, and increase the pressure of SF$_6$ in the tube to investigate the change in the spectra with the pressure and the pressure
Figure 5.2: (a) Spectra for various laser input energies when the pressure of the SF$_6$ is 735 torr. (b) The TLPD calculated with 0.69 mJ input energy.
threshold at which the filament starts to appear. When the pressure is lower than 370 torr, there is some spectral broadening but no filament or white-light supercontinuum generated. At 370 torr, the beam color becomes yellow, and when the pressure reaches 420 torr, a bright white spot is seen together with a bright filament in the tube. The pulse spectrum as a function of the pressure is shown in Fig.5.3. As the pressure increases from 230 torr, the cutoff at short wavelength extends to shorter wavelengths. However, after the pressure reaches 460 torr, the cutoff stays the same, at $\sim 350$ nm, probably because the spectral broadening reaches the upper limit.

As far as we know, SF$_6$ has never been used as a medium to generate filamentation. It is a relatively complicated molecule, compared to the commonly used gaseous media such as air [82] and noble gases [84], with a sulfur atom in the center and six fluoride atoms attached to it with an octahedral geometry. SF$_6$ is relatively easy to ionize, generating some SF$_4$ and F$_2$, raising the question of whether molecular dissociation dynamics is an integral part of filamentation in SF$_6$. To prove that the molecules in which the filament is formed are really SF$_6$, we ran continuously for more than 5 hours and found that there is almost no change to the output spectra. Further, we change the laser repetition rate with the energy per pulse fixed, and obtain the output spectra at different repetition rates, as shown in Fig.5.4. The spectra are nearly the same at 100, 200 or 250 Hz, while slightly broadened at 500 Hz or 1 KHz. The slight broadening could be due to residual changes in the molecules or a slight change in the laser conditions when the repetition reaches 500 Hz. However, there is no significant change in the spectrum with laser repetition rate.

An important question is whether the spatial chirp [84] of the output beam changes below or above the filamentation threshold. In the experimental layout, when M2 is inserted, the small aperture selects different parts of the output beam for spectral
Figure 5.3: Spectra for various SF$_6$ pressures when the input energy is 0.75 mJ.
Figure 5.4: Spectra for various laser repetition rates when the SF$_6$ pressure is 1 atm and the input energy is 0.35 mJ.
measurements, as seen in Fig. 5.1. At 300 torr, below the filamentation threshold, the spectra look uniform, as seen in Fig.5.5 (a), and the TLPD calculated at different locations in the beam is close to that of the center of the beam, as seen in Fig.5.5 (c). However, at 495 torr, above the filamentation threshold, the spectra at the center are much broader than at the edge, as seen in Fig.5.5 (b). It is easy to see from Fig.5.5 (c) that the TLPD is roughly 4.2 fs only within a radius of 1.5 mm. Beyond this region, the left part (negative on the x axis of Fig.5.5 (c)) has TLPD’s between 7 and 8 fs, while the right part has values between 9 and 12 fs. Therefore, the broadening below the filamentation threshold does not have a spatial chirp, however, the one above threshold does.

The pointing stability is a main concern for filamentation as it can be worse than for broadening methods using a fiber [84]. Although the pointing stability of a filament can be similar to that of the original beam [95], it is necessary to test this in our system since we use a new medium SF₆. In this experiment, we perform a pointing stability measurement for the following three cases: original laser beam, and spectral broadening below and above the filamentation threshold. The tube is filled with 1 atm SF₆ and the experiment is performed with our home-built laser system which produces 35 fs, up to 1.2 mJ pulses at 1 kHz. We place a card at ~ 1.7 m after the focus of the beam and record the beam’s intensity profile on the card and then determine the (x,y) coordinates of the intensity centroid for every 50 consecutive laser shots. By increasing the input laser energy, we go through the three cases: 0.06 mJ input giving the original beam, 0.26 mJ giving spectral broadening below the filamentation threshold and 0.35 mJ giving broadening above the filamentation threshold. The data are obtained by filtering out the long-term drifting of the original beam using a FFT high pass filter, as shown in Fig.5.6. The original beam has a pointing variation of
Figure 5.5: Spectra for various positions in the horizontal direction in the beam when the SF$_6$ pressure is (a) 300 torr (below filamentation threshold) and (b) 495 torr (above filamentation threshold). Negative readings correspond to the positions left of the center of the beam. The input energy is 0.75 mJ and the pulse duration is 50 fs. (c) The TLPD calculated as a function of position in the beam.
0.35 % rms in the horizontal direction (X) and 0.51 % rms in the vertical direction (Y), the broadening below threshold has 0.33 % rms (X) and 0.57 % rms (Y), and the broadening above threshold has 0.25 % rms (X) and 0.49 % rms (Y), relative to the beam diameter. The results indicate that the spectral broadening process with or without filamentation does not introduce significant pointing fluctuations.

After optimizing the spectral broadening as a function of pressure, input laser energy and laser repetition rate, we need to investigate whether the pulse is recompressible. We use a pair of chirped mirrors to compensate the positive dispersion and several small pieces of fused silica glass to finely adjust the dispersion. With 0.35 mJ, 50 fs input pulses and a pressure of 1 atm, we obtain spectral broadening, as seen in Fig.5.4. The output beam is collimated by a f=1.5 m lens, aligned into the chirped mirrors and then to a home-built third-order autocorrelator for the pulse duration measurement. To compensate the positive dispersion introduced by the SF$_6$ gas cell, the collimating lens, the glass at the output end of the tube, and the glass and lens in the autocorrelator, 9 pairs of bounces on the chirped mirrors are applied. Limited by the bandwidth of the chirped mirrors and optics in the autocorrelator, the spectra are narrowed, as seen in Fig.5.7 (a). A TLPD of 12 fs is calculated based on this spectra, as seen in the inset of Fig.5.7 (a). The pulse duration measurements are shown in Fig.5.7 (b). With 9 pairs of bounces on the chirped mirrors, the net dispersion is slightly negative, $\sim$ -48 fs$^2$. The negative dispersion is then compensated by a small piece of glass and a shortest pulse duration of 14.6 fs (1.2 $\times$ TLPD) is obtained. Furthermore, the pulse duration as a function of positive dispersion added by different pieces of glass is obtained (see the data points in Fig.5.7 (b)). The data points are fit well by theoretical calculations.
5.4 Conclusion

We discuss filament formation in SF$_6$ with an input laser energy as low as 0.35 mJ with 50 fs pulse duration, under which conditions, no filaments are formed in N$_2$ or CO$_2$ even up to 0.75 mJ under the same gas pressure. This shows that SF$_6$ requires much lower laser energy to form a filament. This will allow for greater flexibility in typical mJ-level laser systems to use filamentation in pump-probe experiments, as the entire beam need not be devoted to the continuum generation. The spectral broadening increases with pressure or input laser energy until the broadening upper limit is reached. At 736 torr, the spectrum obtained with a 0.69 mJ input pulse is capable of producing sub-3 fs pulses. In addition, the spatial chirp in the presence of filament is discussed and the spectra are uniform only within a radius of 1.5 mm. Further, the pointing stability of the beam with spectral broadening below or above filamentation threshold is found to be similar to that of the original beam. Finally, with 0.35 mJ input, the pulse is recompressed by a pair of chirped mirrors and a pulse duration of 14.6 fs is obtained.
Figure 5.6: The intensity centroid movement of the laser beam at \( \sim 1.7 \) m after the focus for every 50 consecutive laser shots for (a) original beam; (b) spectral broadening below filamentation threshold; (c) above filamentation threshold. The data are recorded with a PixeLINK CCD camera (PL-B953U).
Figure 5.7: (a) Spectra measured in the autocorrelator with 0.35 mJ, 50 fs input pulses and 1 atm of SF$_6$ pressure. Inset: the calculated TLPD which is 12 fs based on the spectra; (b) The pulse duration measured as a function of the dispersion introduced by several small pieces of glass with 9 pairs of bounces on the chirped mirrors.
In this dissertation, we present the experimental study of the internuclear-separation-dependent ionization of electrons in different molecular orbitals in neutral I$_2$ through the use of nuclear vibrational motion. With a pump-probe scheme, a vibrational wavepacket is generated in the B state of I$_2$ which can reach up to $\sim$ 9.3 a.u., allowing for the study of enhanced ionization on the LUMO $\sigma_u$ and HOMO-2 $\sigma_g$ orbitals. With a pump-dump-probe scheme, a vibrational wavepacket is generated in the ground electronic state of I$_2$ which vibrates between 4.4 a.u. and 6.2 a.u., allowing for R-dependent ionization measurements on valence orbitals of the ground state. For the heavy molecule I$_2$, the nuclear vibrational motion is relatively slow, and thus 50-fs pulses provide a good resolution.

For the electron in the LUMO $\sigma_u$ state, we obtain fully R- and $\theta$- resolved measurements of R$_c$ through detection of I$_2^+$ signals. The angular distribution of the B state of I$_2$ is obtained, and it shows the expected $cos^2(\theta)$ distribution. When the laser field is parallel to the molecular axis, the B state shows enhanced ionization at R$_c$ $\sim$
8.7 a.u. with an enhancement factor of 22, and as the angle between the two increases, the ionization peak at $R_c$ decreases and finally disappears in the perpendicular case. The enhanced ionization of the $\sigma_u$ electron can be explained by CREI, and $R_c$ can be precisely predicted by a simple model of electron localization. With the wavepacket in the ground state of $I_2$, we investigate the R-dependent ionization of electrons in the HOMO $\pi_g$, HOMO-1 $\pi_u$ and HOMO-2 $\sigma_g$ orbitals. We find that HOMO and HOMO-1 do not have a strong R-dependent ionization, while HOMO-2 does. This result is consistent with theoretical predictions by Bandrauk. Further, HOMO-2 provides the dominant single-ionization pathway which is highly unusual for strong-field ionization. With the wavepacket in the B state, single ionization of the HOMO-2 $\sigma_g$ orbital is investigated through detection of (1,0) signal, and an $R_c$ is found at $\sim 7.3$ a.u.. This implies that the enhanced ionization also occurs in lower-lying orbitals. Another $R_c$ at $\sim 8.7$ a.u. implies that there might be a mixture of molecular orbitals in $I_2$ at large $R$, since the (1,0) channel shows the ionization feature of the LUMO $\sigma_u$ orbital.

Finally, we discuss filament formation in SF$_6$ with an input laser energy as low as 0.35 mJ with 50 fs pulse duration, under which conditions, no filaments are formed in N$_2$ or CO$_2$ even up to 0.75 mJ under the same gas pressure. This shows that SF$_6$ requires much lower laser energy to form a filament. The spectral broadening increases with pressure or input laser energy until the broadening upper limit is reached. In addition, spatial chirp in the presence of a filament is discussed and the spectra are uniform only within a radius of 1.5 mm. Further, the pointing stability of the beam with spectral broadening is found to be similar to that of the original beam. Finally, with 0.35 mJ input, the pulse is recompressed by a pair of chirped mirrors and a pulse duration of 14.6 fs is obtained.
Bibliography


