Scaled Strong Field Interactions at Long Wavelengths

DISSERTATION

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By

Emily Frances Sistrunk

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The Ohio State University

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Dissertation Committee:

Dr. Louis F. DiMauro, Advisor

Dr. Pierre Agostini

Dr. Robert Perry

Dr. Ezekiel Johnston-Halperin
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Abstract

The strong field regime describes interactions between light and matter where the electric field of the laser is a significant fraction of the binding field of the atom. Short pulsed lasers are capable of producing local fields on the order of the atomic unit of electric field. Under the influence of such strong fields, the ionization regime and electron dynamics are highly dependent on the wavelength used to drive the interaction. Few studies have been performed in the mid-infrared (MIR) spectral range. Using MIR wavelengths, the ponderomotive energy, $U_p$, imposed on the electrons can be a factor of 20 greater than in the visible and near-infrared. Experiments on above threshold ionization (ATI) of cesium, nonsequential ionization (NSI) of noble gases, and high harmonic generation (HHG) in condensed phase media highlight the benefits of performing strong field investigations in the MIR.

The photoelectron energy spectrum from above threshold ionization (ATI) of atoms provides details about the strong field interaction. Cesium atoms driven by a 3.6 µm laser indicate that excited states can play a large role in ionization from the ground state. Previous experiments on argon in the near-infrared can be compared to cesium at 3.6 µm due to their similar Keldysh-scaling. Unlike argon, the measured ionization yield in cesium saturates at a higher intensity than predicted due to the Stark shift of the ground state. Such shifts have not been detected in argon. The low-lying 6P excited states of cesium produce a strong effect on the photoelectron energy spectrum, resulting in a
splitting of each ATI peak. Enhancements in the photoelectron energy spectrum similar

to those found in argon are observed in cesium. These enhancements are relatively

insensitive to ellipticity of the drive laser.

To take advantage of the large ponderomotive energy associated with Mid-IR

lasers, ionization of argon, krypton and xenon is studied at 3.6 µm. The factor of 20

increase in $U_p$ between the near-infrared and MIR experiments allows electrons to return

with up to ~300eV in energy. Inelastic scattering of returning electrons impinging on

their parent ion results in impact ionization, producing up to the 6th charge state in xenon.

The large increase in the ionization yield produced by impact ionization is understood by

scaling the impact ionization cross section by the electron return energy distribution and

the calculated wavepacket spread. Elastic scattering of the returning electrons provides

information about the structure of the parent ion, as the differential cross section can be

extracted from the experimental photoelectron angular distribution.

High harmonic generation (HHG) in atomic gases occurs with notoriously low

conversion efficiency. The advantages of a MIR laser system are used to study HHG in

liquid and solid samples. The long wavelength makes possible the first demonstration of

high order harmonics from the bulk of a crystalline solid. Harmonics generated in liquids

appear perturbative in nature, while those generated in a crystal are highly

nonperturbative. The high order harmonics yield information about the strong field

response of the crystal’s band structure.

The use of MIR wavelengths allows the observation of new strong field

phenomena. As all of the above methods are applicable to molecules as well as atoms,
MIR studies have a strong impact on understanding the interaction between light and matter.
This document is dedicated to my family and Tony.
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Vita

June 2001 .................................................. Mission Viejo High

2005 .......................................................... B.S. Physics, University of California, Santa Barbara

2008 .......................................................... M.S. Physics, The Ohio State University

2005 to present ........................................... Graduate Research Associate, Department of Physics, The Ohio State University

Publications


8. “Redshift in the optical absorption of ZnO single crystals in the presence of an intense mid-infrared laser field,” S. Ghimire, A. D. DiChiara, E. Sistrunk, U. B. Szafruga,


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Chapter 1: Introduction

1-1: Motivation

Since the development of the first optical laser in 1960 [1], the laser has become a valuable tool for the study of atomic and molecular systems. As a research tool, the laser has become one of the most diverse and customizable pieces of equipment used in the laboratory. The development of the laser was particularly critical for investigating the interaction of light and matter, as it provided access to a wide range of experimental parameters and extreme conditions to aid in understanding the mechanisms and dynamics of atoms and molecules. Achievable sources of coherent radiation today span the electromagnetic spectrum from THz [2] to x-rays [3] and intensities up to $10^{22}$ W/cm$^2$ [4], pulse durations down to a single optical cycle [5] and the capability of producing pulses less than 100 attoseconds (1 as $= 1 \times 10^{-18}$ s) in duration via Fourier synthesis of frequency combs generated by a strong-field laser-matter interaction [6]. In Strong Field Physics this customizability is critical to provide electric field strengths close to and well above that of the Coulomb binding field of the atomic or molecular system.

There is much interest in devising experiments capable of producing both the fine spatial and temporal resolution required to study the dynamics of electrons over atomic time scales. The techniques developed for femtochemistry [7] have produced time-resolved measurements of molecular dynamics, but have been limited to tracking the motion of ions and molecular fragments. Techniques such as electron momentum...
spectroscopy [8] and ultrafast electron diffraction [9] have also been utilized to study atomic and molecular structure with high spatial resolution, but often without the desired temporal resolution. Of major interest in strong field physics is to bring these techniques to the study of atomic and molecular structure and dynamics on a sub-femtosecond (1fs = 1x10^{-15}s) timescale. To put this timescale in perspective, the time for an electron to orbit a hydrogen nucleus (proton) is 0.15fs or approximately 6.3 atomic units of time. Time resolved studies on the attosecond scale should allow scientists to study the motion of electrons. Many researchers worldwide [6] have begun working towards the development of attosecond techniques. To interpret the results of ultra-fast high harmonic or electron pump-probe experiments it is necessary to understand the mechanisms that occur when an atom or molecule is subjected to the strong fields necessary for attosecond science.

1-2: The AC Stark Effect and Strong-Field Ionization

To develop an understanding of strong field ionization it is important to discuss ionization mechanisms at high intensity. In the limit of high frequency and low intensity, ionization occurs via the photoelectric effect, the explanation of which earned Albert Einstein the Nobel Prize in 1921, well before the development of coherent radiation sources. Ionization of an atomic system by a single photon can be treated purely quantum mechanically and is described in any basic quantum mechanics textbook [10]: an atom with ionization potential, \( I_p \), can be ionized by a photon with energy, \( E \), provided that \( I_p \leq E = \hbar \omega \), where \( \hbar \) is Planck’s constant and \( \omega \) is light’s angular frequency.
The absorption of multiple photons, was predicted by Maria Göppert-Mayer in 1931 [11], but was not observed until higher intensity radiation sources became available. The first demonstration of multiphoton absorption by an atomic system was performed with a radio-frequency source in 1950 [12]. Within the first few years of the laser’s development multiphoton absorption by an atomic system was verified in the optical regime [13]. The development of Q-switching [14] produced pulsed lasers with shorter, nanosecond (ns), pulse durations and higher intensities up to around $10^{13}$ W/cm$^2$. This provided experimentalists with the intensities necessary to observe multiphoton ionization (MPI) in atomic gases [15, 16]. The energy conservation law for MPI amounts to a simple modification to the familiar Einstein photoelectric effect law: $I_p \leq E = n\hbar\omega$, where $n$ is the number of photons required for ionization. Early theoretical descriptions of MPI were based on time-dependent perturbation theory, consistent with the assumption that the electric field strength of the laser is small compared to the atomic binding potential and amounts to only a small perturbation to the Coulomb interaction. Surprisingly, in early experiments the ionization yields seemed to increase exponentially with intensity instead of fitting the power law dependence expected from perturbation theory [17].

At high intensities ($10^9$-$10^{15}$ W/cm$^2$) more photons are available to excite each atom and the electric field can become significant when compared to the Coulomb field binding the valence electrons to the atom. When the laser’s electric field is large enough additional considerations must be taken into account and under certain conditions the perturbative description can break down.
The effect of an intense laser’s electric field on an atomic potential can be understood in terms of the AC Stark Effect [18]. We know that an atom in an electric field will experience a shift in its energy levels. The Stark Effect is typically discussed in terms of perturbation theory [19]. While it is a more general effect, still present when perturbation theory is invalid, the perturbative result yields some important numbers.

The shift of the nth atomic level with field-free energy $E_n$ is given by:

$$\Delta E_n = -\frac{1}{4} \chi_n(\omega) F^2,$$

(1.1)

where $\chi_n(\omega)$ is the dynamical polarizability of the nth level for the driving frequency, $\omega$, and $F$ is the instantaneous field strength of the laser. In the limit of highly excited states ($n\gg1$) (or high frequency, such that $\hbar \omega \gg E_n - E_{n'}$) $\chi_n$ trends to $-1/\omega^2$. In this limit equation 1.1 becomes

$$\Delta E_{\infty} = \frac{e^2 F^2}{4 \omega^2} = U_p,$$

(1.2)

where $e$ is the electron’s charge. Of note is the interesting result that the energy shift of the continuum is equal to the ponderomotive energy, or the cycle averaged kinetic energy of a free electron in an oscillating electric field. For a peak intensity, $I$, in $\text{W/cm}^2$ and wavelength, $\lambda$, in $\mu\text{m}$, $U_p$ can be estimated in electron volts (eV) by:

$$U_p = 9.33 \times 10^{-14} I \lambda^2.$$

(1.3)

In terms of ionization this means that the effect of the field is to change the energy required for ionization to include not only the field-free ionization energy, $I_p$, but also the “quiver” energy of the electron. The familiar energy conservation relation used for the photoelectric effect can be re-written to include the energy shift and electrons reach the detector with energy:
For the continuum and Rydberg levels this Stark Shift can be quite large as a function of laser intensity. The effect on the ground state and lower energy levels is smaller, so it is often neglected. A qualitative understanding of the effect of the AC Stark Shift on ionization can be achieved without considering the shift of the ground state and lower levels.

The ionization mechanisms we will discuss fall into three categories, determined by the relative values of the energies associated with the field-dressed atomic system, $I_p$, $U_p$ and $\hbar\omega$ [20]:

\begin{align}
I_p &> \hbar\omega \gg U_p \quad (1.5a) \\
I_p &> U_p > \hbar\omega \quad (1.5b) \\
U_p &> I_p \gg \hbar\omega. \quad (1.5c)
\end{align}

In the regime described by Eq. 1.5a ionization occurs as described by nonlinear optics, where multiple-order perturbation theory is valid. The other two regimes, described by equations 1.5b and 1.5c describe the conditions for Above Threshold Ionization (ATI) and Tunneling Ionization, respectively. The following sections will describe these two regimes in more detail.

**Above Threshold Ionization**

After the advent of pulsed lasers and the demonstration of MPI many experiments were performed by observing ionization yields [21]. The first observation of Above Threshold Ionization (ATI) was made when researchers began to investigate the
photoelectron energy spectra produced during MPI [22]. The characteristic energy spectrum recorded for ATI consists of well-defined peaks separated by the photon energy, $\hbar \omega$. It was determined that because of the large Stark Shift experienced by the atom as a function of laser intensity the effective ionization energy can shift through resonance with multiple integer numbers of photons as demonstrated in Figure 1.1. In principle all energy levels of the atomic system should experience a periodic shift, including bound and ground states. The magnitude and sign of the induced Stark Shift is dependent on the coupling between bound states [20]. For high-lying states, such as Rydberg levels, the full shift of $U_p$ is felt; however for more tightly bound states the effective ponderomotive energy felt is decreased to

$$U_p' = U_p (\omega / \omega_0)^2,$$  \hspace{1cm} (1.6)

where $\omega_0$ is the characteristic frequency of the wiggle motion of a bound state. For ground states $\omega_0 \gg \omega$ [23], so this shift is very small and neglecting the shift of the ground state is often a reasonable simplification.

After the development of mode-locking, when pulse durations in the picosecond (ps) and sub-picosecond range became available, ATI was revisited. For pulses shorter than 1ps the resulting photoelectron energy spectra are remarkably different than those achieved with longer pulses. Since the laser pulse is shorter than the time required for electrons to leave the focal volume of the laser the energy conservation relation given in Eq. 1.4 is no longer valid. The ATI peaks are observed to shift to low energy, broaden and split into fine structure separated by the energies of the high-lying bound states [24]. These structures are another consequence of the substantial AC Stark Shift imposed on
the atomic levels by the laser field. They appear when the instantaneous laser intensity
shifts each level through resonance with an integer number of photons, producing an
enhancement to the ionization yield. The Rydberg series in these so-called Freeman
Resonances [24] end between each two successive ATI peaks at an energy equal to $s\hbar\omega$, where $s$ is the number of photons above the minimum number required to ionize the
unperturbed atom. Each enhanced peak is attributed to a different laser intensity. When
longer pulses are used the same sweeping of the energy levels through resonance occurs,
but as the electrons gain energy leaving the focal volume, the effect is masked.

Figure 1.1: Cartoon demonstrates the Stark shift of atomic energy levels as a function of
the laser’s instantaneous intensity. The field-free ionization potential $I_{p0}$ is included with
a dashed line to illustrate the shift. A few Rydberg Levels are included to demonstrate
the large shift of the continuum and Rydberg states. Here $n=10$ corresponds closely to
the ionization of argon ($I_p=15.76\text{eV}$) by $0.8\mu\text{m}$ ($1.55\text{eV}$).
**Tunneling Ionization**

When the electric field is a significant fraction of the Coulomb binding field for the atomic/molecular species being studied it produces a significant effect on the atom’s binding potential. In the DC case, as shown in Fig. 1.2(b) a strong field perturbs the Coulomb potential, creating a potential barrier with approximately finite width:

\[ l = \frac{I_p}{eF}. \]  \hspace{1cm} (1.7)

Under these conditions there is a significant probability that the electron(s) will tunnel through the barrier. If it is assumed that the oscillation period of the laser is slow compared to the tunneling frequency it is acceptable to treat the interaction as quasi-static and apply the DC tunneling theory at each time interval. The validity of this approximation and some of its limitations will be discussed in the following section.

---

**Figure 1.2:** Illustration of the difference between multiphoton and tunneling ionization. In (a) the Coulomb field remains largely unperturbed and the energy necessary for ionization is achieved from absorbing multiple photons. In (b) the perturbation to the potential is large and the electron can tunnel ionize through the resulting barrier. In (c) the barrier is suppressed below the energy of the bound electron, allowing Over the Barrier Ionization to occur.
The tunneling probability for atoms in a strong alternating electric field was first described by Keldysh in 1965 [25]. Keldysh described the multiphoton picture presented in Figure 1.2(a) and the tunneling description in Figure 1.2(b) as being the result of the same general expression for the ionization probability. He demonstrated that as the ratio of intensity to photon energy, $I_0/\hbar \omega$, increases the term responsible for the discrete number of absorbed photons becomes a constant proportional to $1/\gamma^2$, where $\gamma$ is the ratio of the tunneling time to the laser period, and the rate simplifies to that of tunneling. This indicates that in the tunneling picture the effect of absorbing individual photons becomes washed out.

Soon after Keldysh’s result was published, Perelomov, Popov and Terent’ev (PPT) [26] improved the derivation to achieve an ionization rate that agreed with the solution for the hydrogen atom in the low-frequency limit. They determined that a solution was only possible provided that $F \ll F_0$ and $\omega \ll \omega_0$, where $F_0$ and $\omega_0$ are characteristic of the atom. The formalism described by PPT was later generalized to describe the ionization of more complex atoms by Ammosov, Delone and Krainov (ADK) in 1986 [27-29]. The potential used to calculate the rate is the sum of a Coulomb potential and a linear term from the laser field:

$$V = -\frac{Q}{r} + Fz,$$

(1.8)

where $Q$ is the charge of the nucleus, $r$ is the distance from the center of the atomic potential and $z$ is distance along the laser propagation direction. This potential is valid as long as we can assume that the electron is at a large enough value of $r$ to see the Coulomb potential from the nucleus screened by the inner-shell electrons. A complete description
of the calculation is included in Ref. [28, 29]. To calculate the ionization rate we consider the effect of a slowly varying strong field, \( F(t) \), on the Coulomb potential and describe the interaction as tunneling through a time dependent barrier. As long as the field can be approximated as adiabatic (not changing rapidly) then the total rate is treated as the sum of the static rate at each time interval. The transition amplitude from an initial state, \( i \), to a final state, \( f \), can be expressed using the Landau-Dykhne adiabatic approximation to be:

\[
A_{if} = \exp \left\{ \left( \frac{i}{\hbar} \right) \int_{t_0}^{t_f} [E_f(t) - E_i(t)] dt \right\},
\]

(1.9)

where \( E_i \) and \( E_f \) are the adiabatic energies of the initial and final states in the electric field \( F(t) \), and \( t_0 \) is the classical turning point determined from the relation \( E_f(t_0) = E_i(t_0) \).

Therefore the rate can be determined by:

\[
w_{if} = \exp \left\{ \left( \frac{2}{\hbar} \right) \int_{t_0}^{t_f} [E_f(t) - E_i(t)] dt \right\} \quad (1.10a)
\]

\[
= \exp (-2 \text{Im}(S)), \quad (1.10b)
\]

where \( S \) is the classical action. This is valid as long as the amplitude of the wavefunction does not change rapidly (is adiabatic) during the ionization process. The electron’s initial energy is approximated to be \( E_i(t) = -l_p \) and its final energy can be expressed as:

\[
E_f(t) = \frac{(|\vec{p} - \vec{A}|^2}{2} + V_C,
\]

(1.11)

where \( \vec{p} \) is the generalized momentum, \( \vec{A} \) is the vector potential of the laser field and \( V_C \) is the Coulomb potential of the atom. As a good starting point, the momentum can be assumed, \( \vec{p} = 0 \) since \( w_{if} \) is maximum under these conditions when \( V_C \) is zero, and after
calculating the classical action we arrive at the final result for the observed ionization rate in a linearly polarized field:

\[ W_{i_f}^0 = \left( \frac{4e^2 Z^2}{\hbar n^4} \right)^{2 n^* - m - 1} \exp \left( \frac{-2 Z^3}{3 \hbar n^3} \right), \]

(1.12)

where \( Z \) is the ion charge, \( n^* \) and \( m \) are the effective principal quantum number and the magnetic quantum numbers of the initial state, \( i \). This result is effective in predicting the ionization rate of the first charge state. The overall validity of ADK theory is determined by our ability to express the important energy levels in Eq. 1.9. The AC Stark shift induced in the ground state energy, affecting \( E_i \) for the initial state of the electron, is unavoidable, but can be neglected when the ground state is particularly tightly bound and experiences a smaller shift. The shift can be accounted for in deriving the ionization rate, however since the shift is dependent on the polarizability of the ground state, which is atom-dependent. The above result is generalized for any atomic system, provided the AC Stark shift of the ground state can be neglected. The approximations made to achieve the result in Eq. 1.12 determine the validity of this solution. The assumption that \( V_C = 0 \) is valid far from saturation (the over-the-barrier case illustrated in figure 1 - 2c) because under these conditions the barrier is wide and the Coulomb potential decreases like \( 1/r \). This is known as the short-range formulation of tunneling theory. The authors of Ref. [29] provide a correction for the case where \( \vec{p} \neq 0 \), for electrons ejected parallel and perpendicular to the polarization direction:

\[ W_{i_f}^{p_1} = W_{i_f}^0 \exp \left( -p_1^2 \omega^2 (2E_i)^{3/2} / 3 \hbar^3 \right). \]

(1.13a)
The results above for the short-range formulation of ADK theory can be extended to be valid when used with longer-range potentials by including a correction in calculating the outer turning point [30], given by:

\[
W_{CADK} = \frac{1}{\sqrt{2i}} \left[ 1 + \frac{1}{\left( \frac{p^2 + ZE_i}{Z^2 E_i^2} \right)^{2n^* - 1}} \right].
\] (1.14)

The results in Eq. 1.12-1.14 assume a static field. Another important result to note is that for an oscillating field of the form:

\[
F(t) = F \cos(\omega t) \dot{\hat{a}}
\] (1.15)

the observed tunneling rate can be calculated from the above results as:

\[
W_{obs} = \left( \frac{3F}{\pi(2E_i)^3} \right)^{1/2} W_{stat},
\] (1.16)

where \( W_{stat} \) is the rate for the static case.

**Over The Barrier Ionization**

It is important to note the special case of tunneling ionization, when the field strength is strong enough that the energy required for ionization becomes zero. Ionization under these conditions is considered to be “over the barrier” (OTB) as the coulomb barrier is completely suppressed by the laser field as demonstrated in Figure 1.2(c). The intensity at which this occurs is (in atomic units):

\[
l_{OTB} = F_{OTB}^2 = \left( \frac{l^4}{16} \right).
\] (1.17)
$I_{\text{OTB}}$ can be used as an estimate for the maximum intensity that will be “felt” by the electron as it undergoes tunneling ionization. Beyond $I_{\text{OTB}}$ the ionization rate should not increase with intensity. Often $I_{\text{OTB}}$ is used interchangeably with the saturation intensity, $I_{\text{SAT}}$, as it is a reasonable estimate of this value. In most tunneling ionization experiments, the ion yield as a function of intensity is seen to increase as the DC tunneling rate (typically close to $I^9$) until an intensity close to $I_{\text{OTB}}$ is reached, where the rate decreases to approximately $I^{3/2}$. This slower rate is consistent with the increase in the size of the Gaussian focal volume as the intensity is increased.

Short pulses are a requirement for witnessing over the barrier ionization. A long pulse with a peak intensity of $I_{\text{OTB}}$ would result in depletion of the ground state via MPI and tunneling ionization before the field reaches its peak value. Over the barrier ionization will not be discussed further in this document, but will be used as a tool for evaluating the saturation intensity.

1-3: The Keldysh Picture

In 1965 L. V. Keldysh defined an adiabaticity parameter, $\gamma$, as the ratio of the laser frequency to the tunneling frequency [25]:

$$\gamma = \frac{\omega}{\omega_c} = \sqrt{\frac{I_p}{2\mu_p}}. \tag{1.18}$$

The Keldysh parameter provides a useful metric for predicting the likelihood that ionization will occur via tunneling. The ratio of the perturbation to the unperturbed Hamiltonian is given by: $H_I/H_0 = 1/\gamma^2$. In the high frequency limit, where $\gamma \gg 1$, the effective binding potential oscillates too quickly for tunneling to occur at the peak of the
field and the electron “feels” the time average of the oscillating field. Under these conditions no tunneling can occur and ionization only occurs via multiphoton ionization. In the low frequency limit, where $\gamma \ll 1$, the adiabatic approximation can be made, where the oscillating effective field is treated as quasi-static and the tunneling rate is identical to that for the DC tunneling case.

Many experiments on tunneling ionization have been performed in the noble gases with approximately 0.8\,\mu m light [31]. This corresponds to the regime where $\gamma$ is very close to one. Ionization dynamics are often taken to be approximately like tunneling in this regime where the boundaries between MPI and tunneling are not so well defined.

*Invariance and Keldysh-Scaled Systems*

The concept of Keldysh Invariance is illustrated in Figure 1.3. When a dressed atomic system with a given value of $\gamma$ is compared to a different dressed atom (different ionization potential, laser intensity and wavelength) with the same value of $\gamma$ the two systems are said to be Keldysh-scaled systems. For two systems with the same value of $\gamma$ the ionization dynamics are typically taken to be identical. Under these conditions qualitative similarities in the photoelectron energy spectrum (PES) are can be interpreted as illustrating similarities in the ionization dynamics, while different features in the spectra must give some insight into the differences between the atomic species.
Figure 1.3: Demonstration of the Keldysh Invariance. Two atomic systems with different ionization potentials $I_{p1}$ and $I_{p2}$ are ionized by two different lasers with frequencies $\omega_1$ and $\omega_2$ such that the two Keldysh parameters $\gamma_1 = \gamma_2$ are equal. The two dressed-atomic systems are considered to be Keldysh-scaled equivalents.

The experiments presented here and those in the literature span a large range of Keldysh parameter values. For comparison, typical values for $\gamma$ are presented in Table 1.1 for relevant atoms and laser parameters. For each atomic system the Keldysh parameter is calculated at $I_{\text{OTB}}$ for that particular species and using wavelengths close to the experimental values.

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>$I_p$ (eV)</th>
<th>$I_{\text{OTB}}$ (W/cm²)</th>
<th>Keldysh Parameter $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.8\mu$m</td>
</tr>
<tr>
<td>Argon</td>
<td>15.74</td>
<td>$2.46\times10^{14}$</td>
<td>0.73</td>
</tr>
<tr>
<td>Krypton</td>
<td>13.99</td>
<td>$1.54\times10^{14}$</td>
<td>0.87</td>
</tr>
<tr>
<td>Xenon</td>
<td>12.13</td>
<td>$8.66\times10^{13}$</td>
<td>1.08</td>
</tr>
<tr>
<td>Cesium</td>
<td>3.89</td>
<td>$9.20\times10^{11}$</td>
<td>5.95</td>
</tr>
</tbody>
</table>

Table 1.1: Keldysh parameter values supplied for experimentally relevant atomic species and ionizing laser field wavelengths. All values are calculated at the relevant value of $I_{\text{OTB}}$ for the given atomic species.
"After" Ionization

It is often instructive to separate ionization and the dynamics of the electron wavepacket in the field into multiple steps. Although the separation is merely a construct, the results of these stepwise descriptions agree well with experiment. After the tunneling ionization event occurs, the influence of the atomic potential is often assumed to be negligible; the free electron(s) are left in a strong oscillating electric field, which produces some interesting dynamics of its own. A free electron in an oscillating electric field experiences the ponderomotive force of the laser field, $U_p$. An electron in this oscillating field will gain momentum until the sign of the field changes. The Simpleman model [32, 33] describes the maximum kinetic energy gained by a free electron during a half cycle of the laser field. If we assume the field to be of the same form as Eq. 1.15, the electron emerges with zero initial velocity and the peak field strength does not change significantly over a half cycle, we can calculate classically the velocity and average kinetic energy of the system from the equation of motion:

\[
\ddot{x} = eF_0 \cos(\omega t) \quad (1.19a)
\]

\[
v = \frac{eF_0}{m \omega} (\sin(\omega t) - \sin(\omega t_0)) \quad (1.19b)
\]

\[
\langle \frac{1}{2} m v^2 \rangle = U_p (1 + 2 \sin^2 \omega t_0). \quad (1.19c)
\]

The first term of Eq. 1.19c corresponds to the oscillatory motion of the electron in the alternating field and can be neglected, while the second term corresponds to the translational motion gained by the electron. This yields the familiar value of $2U_p$. Soon after the first observation of above threshold ionization evidence was found in photoelectron angular distributions that the dynamics must be more complicated than
what was originally suspected [34]. A plateau at high energy (well above the expected value of $2U_p$) was observed in high intensity photoelectron experiments [35]. This plateau has been attributed to electrons that do not escape the field after the first half cycle and instead return to their parent ion [35]. This explanation is derived from what is known as the rescattering or 3-Step Model [36, 37]. The rescattering model takes over where the Simpleman model leaves off. When the field changes sign the electrons that do not escape (as described by Simpleman) are accelerated back towards their parent ion. They arrive with a maximum energy of $3.17U_p$ and can interact with the core.

The exact energy of each returning electron is dependent on the phase at which the electron was born [38]. By using the equations of motion described in equations 1.19 the relationship between the phase at which the electron was born and the return energy when the electron revisits the core can be determined and is shown in Figure 1.4. Here we see

![Figure 1.4](image)

Figure 1.4: The electron return energy calculated classically in units of $U_p$ as a function of the phase at which the electron was born. Phase in radians is labeled on the right-hand side and phase in time for a 3.6 µm driving field is included on the left-hand side.
the maximum return energy of $3.17U_p$ illustrated. The earlier (later) birth times correspond to the long (short) trajectories. An important consequence of this classical propagation is that each electron can be mapped to a specific return time based on its return energy, allowing access to some important effects on sub-cycle timescales.

Once a returning electron reaches the core it can interact in one of two ways. The electron wavepacket can recombine with the core, producing High Harmonic Generation (HHG), or it can scatter from the core, a process known as rescattering, and continue its oscillation with the field to gain more energy up to a maximum value of $10U_p$. When rescattering occurs further ionization can take place, leading to Nonsequential Ionization (NSI) [39]. The rescattering model is illustrated in Figure 1.5.

![Figure 1.5: Illustration of the rescattering model. Step 1: Near the peak of the field an electron wavepacket tunnels from the atom. Step 2: As the field strength decreases and changes sign the wavepacket travels in the continuum, gaining energy and spreading transverse to the field direction. Step 3: After returning to the core, the wavepacket recombines or scatters.](image)
In both the Simpleman and rescattering models it is assumed for the second (propagation/acceleration) step that the Coulomb field’s interaction with the free electron is negligible. This is typically a reasonable approximation since the laser field can be very strong with respect to the coulomb, particularly over the course of the wavepacket’s excursion, which can be quite large. At 3.6 µm with an intensity of $8 \times 10^{13}$ W/cm$^2$ (saturation intensity of xenon), this excursion length can be on the order of ~7 nm.

During its excursion the wavepacket spreads in the direction transverse to the laser field [40]. The width of the wavepacket, R, is determined by:

$$R^2(t) = \Delta r_0^2 + \frac{t^2}{\Delta r_0^2}$$

(1.20a)

$$\Delta r_0^2 = \sqrt{2I_p/F},$$

(1.20b)

where $\Delta r_0$ is the initial width of the wavepacket and $t$ is the time since birth. These semiclassical theories reproduce the main signatures of HHG and tunneling photoelectron energy spectra with good qualitative agreement [38].

In Figure 1.6 spectra collected at around the same peak intensity with the same species, but different wavelengths are compared to demonstrate the near-classical behavior of the spectral features at small $\gamma$ [41]. The change in wavelength produces a significant effect on the values of $U_p$ and $\gamma$ from the MPI regime at shorter wavelengths, where $\gamma \gg 1$, to the tunneling regime at longer wavelengths, where $\gamma \ll 1$. The spectra, reproduced from Ref [41], demonstrate the dominant features in the two regimes. At wavelengths where the interaction is predominantly MPI, significant photon effects, such as ATI, are visible. These photon effects are not visible where the interaction is well-
described by tunneling; instead the dominant features are a distinct change in slope at $2U_p$ and a cutoff at $10U_p$. For the experimental data $U_p$ (and $\gamma$) are 5 (1.26), 13 (0.78), 30 (0.51), and 100 eV (0.28) for 0.8, 1.3, 2.0 and 3.6 $\mu$m, respectively.

Figure 1.6: Photoelectron spectra from argon at $8 \times 10^{13}$ W/cm$^2$ collected at four wavelengths: 0.8$\mu$m (black, solid), 1.3$\mu$m (green, dash-dot), 2$\mu$m (red, dash), and 3.6$\mu$m (blue, dot). Yield is plotted against energy in eV in (a) and energy scaled to the ponderomotive energy ($U_p$) in (b) to make scaling more apparent. Grey spectra in (b) are the results of a simulation. Reproduced from [41].

In addition to the semiclassical models addressed above, a series of quantum mechanical theories also produce good agreement with experimental results. Solution of the time-dependent Schrödinger equation (TDSE) or time-independent Floquet equations [42] produces theoretical results that match the experiment well. In addition to requiring a lot of computing time, these methods, unfortunately, are rather opaque and do not yield information about where the interesting physics occurs. In these cases the strong field approximation (SFA) [43] is typically used to approximate the interaction. The SFA is a
purely quantum-mechanical approach, centered around calculating the transition amplitude between an initial state $|\psi_0\rangle$ and final state $|\psi_p\rangle$:

$$M_p = \lim_{t \to \infty, t' \to \infty} \langle \psi_p(t) | V(t, t') | \psi_0(t') \rangle. \quad (1.21)$$

$V(t, t')$ is the time evolution operator in the presence of both the binding potential and the laser field. In principle this should yield the exact result for the interactions considered here, however the wavefunctions themselves are not well known. Many approximations exist under the name of SFA, each in a different gauge. All SFA theories feature the same main three assumptions that 1) all bound states except for the ground state can be neglected, 2) the depletion of the ground state can be neglected, and 3) in the continuum the electron can be treated as a free particle moving in the laser’s electric field without the effect of the binding potential. A recent review of SFA theory is given in Ref. [44].

One of the most well-known SFA formulation is the Keldysh-Faisal-Reiss approximation (KFR). Here the length gauge is used, so $V(t, t') = \bar{r} \cdot \vec{F}(t)$, $|\psi_0(t)\rangle$ is the atomic ground state with energy $-I_p$, and the final state is the (field free) Volkov state with drift momentum $\vec{p}$:

$$|\psi_p(t)\rangle = |\vec{p} + \vec{A}(t)\rangle \exp[-iS_p(t)], \quad (1.22)$$

where $\vec{A}(t)$ is the vector potential of the laser field and $S_p(t)$ is given by:

$$S_p(t) = \frac{1}{2} \int_0^t dt' [\vec{p} + \vec{A}(t')]^2. \quad (1.23)$$

If we combine the actions for the initial and final states into: $S_{t_p}(t) = I_p t + S_p(t)$, we reach the final result for the transition amplitude:

$$M_p = -i \int_{-\infty}^{\infty} dt \ e^{iS_{t_p}(t)} \langle \vec{p} + \vec{A}(t) | \bar{r} \cdot \vec{F}(t) | \psi_0 \rangle. \quad (1.24)$$
The KFR-SFA is one of many approaches to a quantum solution of the interaction between a strong light field and an atomic potential. Each has its benefits and drawbacks, however this class of solutions is successful in reproducing the experimental data.

*High Harmonic Generation*

In the late 1980’s HHG was first demonstrated up to the 17th harmonic of a 0.248µm KrF laser in neon [45] and up to the 33rd (21st) harmonic of a 1.053nm Nd:YAG laser in argon (xenon) [46]. All HHG experiments demonstrate the same global features, namely odd harmonics of the driving laser frequency with a rapid decrease in efficiency for the first few orders followed by a long plateau of nearly constant intensity leading to a sharp cutoff at a maximum energy given by [47]:

$$E_{\text{max}} = I_p + 3.17U_p. \quad (1.25)$$

These harmonics were later determined to be the result of high energy photoelectrons returning to the core after ionization and recombining with their parent ion, causing stimulated emission of the energy gained by the electron in propagation.

*Nonsequential Ionization*

As the achievable intensities of visible and near-infrared short-pulsed lasers increased it became possible to witness multiple ionization effects in the multiphoton regime in rare gases. It quickly became clear from the first observation [48] that the process involved was not the direct stepwise ionization of a single electron from the ion. The observation determined that for intermediate intensities the yields of ions of up to the 4th charge state
in krypton were many orders of magnitude higher than predicted by tunneling theory for sequential multiple ionization. At higher intensities the ionization was observed to revert back to the sequential process [49]. Non-sequential ionization (NSI) spectra are easy to identify from their dominant feature, a so-called “knee”-structure where the enhancement of the nonsequential process causes an increase from the expected sequential (tunneling) process, as shown in Figure 1.7, reproduced from ref. [39]. Later it became clear that an indirect method was a more likely cause of NSI [50] and many experiments were performed in the rare gases to determine the exact mechanism [39, 50-52]. We now

![Figure 1.7: Ionization rate in helium ions (He$^+$ and He$^{2+}$) as a function of laser intensity for linearly polarized, 100fs, 0.78µm light displaying the characteristic knee-structure attributed to nonsequential (NS) ionization. Solid and dashed lines depict calculations of SAE and ac-tunneling theory predictions. Reproduced from Ref. [50].](image)
know NSI to be the result of impact excitation from the energetic (up to $3.2U_p$) electrons accelerated by the field as they return to scatter inelastically from the core [52]. As with HHG, NSI is very sensitive to ellipticity in the laser’s polarization. If the transverse momentum induced by an elliptical pulse is larger than the transverse spread of the wavepacket, no electrons will be able to return to the core. Both HHG and NSI are effectively “turned off” by increasing the ellipticity of the driving laser.

In both the HHG and ATI processes information can be gained about the state of the atomic system when the electron returns. Many experiments have been done to attempt a reconstruction of structural information from the HHG spectrum [53]. Others have used angular distributions of the photoelectron energy spectrum to try to glean structural information from the elastically scattered electrons in the plateau [54, 55]. Although both methods (tomographic imaging from HHG data and laser-induced electron diffraction (LIED) from photoelectron angular distributions) seem to produce information about structure, the diffraction is a much more straightforward method, since it does not involve any macroscopic effects, such as phase matching. Recent experiments [56] indicate that moving towards longer wavelengths to take advantage of the quadratic wavelength scaling of $U_p$ will greatly improve the capabilities of LIED. This will be discussed in more detail in Chapter 5.
1-5: This Thesis

This first chapter provides a theoretical framework for interpreting the experiments presented in the following chapters. As a general theme we will consider the effect of the quadratic scaling of $U_p$ with wavelength on the ionization and rescattering dynamics of atomic systems driven by mid-infrared lasers. As established by the rescattering model, that the values of $U_p$ and $\gamma$ have a large effect on electron dynamics as well as on the ionization dynamics. The Keldysh scaling will be tested in light of this wavelength dependence to determine the similarities between Keldysh-scaled systems comprised of very different atoms.

In order to exploit the Keldysh scaling a long wavelength source in the mid-infrared spectral region ($3-5 \text{ \mu m}$) is needed. An increase in wavelength from 0.8 \text{ \mu m} to 3.6 \text{ \mu m} increases $U_p$ by a factor of 20 and decreases $\gamma$ by more than a factor of 4. A description of this laser system and a full characterization is presented in Chapter 2. The experimental apparatuses needed to record high harmonic, photoelectron and ionization data are described in Chapter 3.

To address the Keldysh scaling, experimental ionization data of cesium driven by the 3.6 \text{ \mu m} laser system will be compared to its Keldysh-scaled equivalent of xenon driven by a 0.8 \text{ \mu m} laser. Global similarities between the two systems will be discussed in light of their similar ionization dynamics. The electronic characteristics of cesium and xenon are very different. Addressing differences between the strong-field behavior of the two species under similar ionization dynamics provided by the Keldysh scaling will allow us to evaluate the effect of electronic structure. The effect of the AC Stark Shift of the
ground state and coupling between the ground and first excited states will be discussed for these two scaled systems in Chapter 4.

Many experiments since the discovery of NSI have been performed in the noble gases around 0.8 \( \mu \text{m} \) [31]. Utilizing wavelengths in the mid-IR it is possible to see the effects of increased ponderomotive energy on rescattered electrons. When the kinetic energy of electrons returning to scatter from their parent ion are in the 100s of eV there is new potential to compare laser-driven scattering data to previous results obtained in electron-gun scattering experiments. In Chapter 5 the ionization of noble gases with the mid-IR source will be used to examine the effects of inelastically scattered electrons on the NSI behavior as well as studying the angular dependence of elastically scattered electrons in the plateau of the photoelectron energy spectrum.

A unique side-effect of moving towards longer wavelengths to exploit the Keldysh scaling is that the frequencies of the high harmonics are more closely spaced, producing high harmonics in the visible and near-infrared region of the spectrum. This is experimentally advantageous because it allows the study of harmonics near the ionization threshold. Visible and near-UV harmonics from a mid-IR source propagate in air without being absorbed, which is advantageous for simple experiments using condensed phase media. HHG experiments in liquids will be discussed in Chapter 6.
Critical developments in laser technology that led to the discovery of strong-field phenomena are all tied closely to pulse duration. For a relatively new technology, the laser has seen a remarkable amount of development since its invention in 1960. The development of Q-switching and Kerr-lens mode-locking in 1962 [14] and 1990 [57], respectively allowed the first laser developers to make rapid progress in shortening the pulse duration of their systems. Advances in new laser media allowed more bandwidth to be produced for creating shorter pulses. The relationship between spectral bandwidth and pulse duration will be addressed in Section 2-1. The first of these new media were liquid dyes, developed in the late 1960’s, followed by diode lasers in the early 1980’s and other solid-state lasers in the late 1980’s. Each medium poses advantages and limitations. The shortest pulse duration achievable with a given laser medium is plotted in Figure 2.1(a) as a function of year from 1965 until 2003 [58]. Achieving pulses shorter than approximately 10 femtoseconds (1fs = 1x10^{-15} s) requires compensation for the phase shift induced by spectral dispersion in the generation medium. This pulse compression will be discussed in the following section. Today pulses as short as approximately one optical cycle are possible [5]. Technological developments in the Fourier synthesis of attosecond pulses from high harmonic generation have made even shorter pulses possible.
in the last decade, as demonstrated in Figure 2.1(b). The shortest pulse recorded to date was 80as, produced in 2008 [60].

![Diagram of pulse duration vs. year for different gain media and the minimum achievable pulse duration including recent developments in attosecond pulses.](image)

Figure 2.1: (a) The development of short-pulsed lasers is demonstrated for a variety of gain media as a function of year. Reproduced from [58]. (b) The minimum achievable pulse duration including recent developments in attosecond pulses. Reproduced from [59].

**2-1: Creating Short, Intense, Long Wavelength Sources**

The relationship between pulse duration and bandwidth in laser pulses can be illustrated by considering the Fourier Transform of a delta function, which produces a continuum. It is clear from the Fourier Transform from the time domain to the frequency domain that to construct a short pulse in time a large bandwidth of frequencies is needed. The other requirement that must be satisfied to create a short pulse is that all these frequencies must be in phase. The electric (and magnetic) fields of each frequency
component will interfere to create a short pulse. If we define Δω as the $1/e^2$ spectral width of a Gaussian pulse and Δt as the $1/e^2$ pulse duration of the same pulse, we can generalize the conditions for a short pulse into the time-bandwidth relation: $Δt Δω ≥ \frac{1}{2}$. 

In the near infrared spectral region (0.7-1.5 µm), high pulse energies and short pulse characteristics can be achieved with a variety of gain media, including Ti:Sapphire (Ti:S, Ti:Al₂O₃) [61, 62], which can support enough bandwidth to generate pulses only a few cycles in duration.

An important development in the amplification of ultrashort pulses was the development of chirped pulse amplification (CPA) [61-63]. Even though amplification requires large pulse energies, high intensities can lead to damage in amplifier crystals. The intensity,

$$I = \frac{E}{\pi r^2 \Delta t},$$

where $I$ is the intensity in W/cm², E the pulse energy in joules, $r$ the radius of the beam in centimeters and $\Delta t$ the pulse duration in seconds. Because the duration of a short pulse is sensitive to all frequencies having the same (or nearly the same) phase, the duration can be lengthened significantly by introducing a phase difference as a function of frequency. In a CPA system, dispersion is increased to lengthen or “stretch” the pulse duration to reduce the peak intensity. This is achieved by dispersing the beam spatially with a grating and allowing the shorter wavelengths to travel a longer path than the longer wavelengths before restoring the spatial profile of the beam as shown in Figure 2.2(a). After amplification is completed the pulse is compressed and the dispersion is
compensated by reversing this path-length difference between the colors. Pulse compression is illustrated in Figure 2.2(b).

![Diagram of stretcher and compressor layouts](image)

Figure 2.2: (a) Layout of stretcher. (b) Layout of compressor. For both, G = grating, M = mirror, L = lens, input beams are given in black and dispersed beams in color.

The Need for Long Wavelength Sources

In Chapter 1 the scaling of \( U_p \) (linear with intensity and quadratic with wavelength) was discussed (Eq. 1.3). In order to exploit the principle of Keldysh scaling to the farthest extent possible it is necessary to take advantage of this wavelength scaling in addition to the intensity dependence by using wavelength sources in the mid-Infrared (MIR). This requires the development of intense, short pulse laser systems operating at longer wavelengths. Tunable MIR lasers with wavelengths greater than 3µm that produce >100µJ femtosecond laser pulses will also have applications in nonlinear MIR
pump-probe spectroscopy [64], hydrogenic vibrational spectroscopy in molecules [65],
strong-field vibrational spectroscopy [66], and nonlinear spectroscopy in anomalous
dispersion materials [67].

At wavelengths longer than 1 µm there are no known traditional solid state gain
media that support a bandwidth broad enough for pulses shorter than a few picoseconds
(ps). At around 1 µm, lasers based on Nd-doped media (Nd:YAG, Nd:glass, etc.)
routinely produce pulses as short as 10 ps [62, 68], and often shorter. Erbium-doped
fiber lasers have been developed that support femtosecond pulses at a center frequency
around 1.5 µm [68] and CO₂ lasers routinely produce pulses down to a few ps at around
10 µm [69]. This leaves a large gap in the MIR between 2-5 µm. In order to achieve
femtosecond pulses in this spectral region it is necessary to down-convert the frequency
from a short-pulsed source into the desired wavelength range utilizing Difference
Frequency Generation (DFG).

Nonlinear Light Sources: DFG

To achieve short pulses at wavelengths in the MIR it is necessary utilize
parametric down-conversion to map the spectral content of a short laser pulse onto
another spectral region. This is performed in a nonlinear medium: a medium in which the
refraction index can be expanded into a function of an applied electric field, \( \vec{F} \):

\[
n(\vec{F}) = n_0 + n_2 \vec{F}^2, \tag{2.2}
\]
where $n_0$ is the refractive index in the absence of the field and $n_2$ is the nonlinear index.

The direct result of this is that the dielectric polarization of the material, $\vec{P}$, also varies with field:

$$\vec{P}(\vec{F}) = \chi^{(1)}\vec{F} + \chi^{(2)}\vec{F}^2 + \chi^{(3)}\vec{F}^3 + \cdots = \chi^{(1)}\vec{F} + \vec{P}^{NL},$$  \hspace{1cm} (2.3)

where $\chi^{(1)}$ is the linear susceptibility and $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibilities of the material. The wave equation in a nonlinear medium can be expressed as:

$$\nabla^2 \vec{F} - n^2 \frac{\partial^2 \vec{F}}{c^2 \partial t^2} = \frac{4\pi}{c^2} \frac{\partial^{2}\vec{P}^{NL}}{\partial t^2}.$$  \hspace{1cm} (2.4)

DFG is a process that can occur in any material with strong second order susceptibility.

A schematic and an energy level diagram for DFG are illustrated in Fig 2.3: when two beams are incident on a nonlinear medium and interact such that the material absorbs one photon from the beam with the largest photon energy (pump) and is stimulated by the other beam (signal) to emit a photon at the signal frequency. The excess energy left in the nonlinear medium is released by emission of a photon (idler) at a frequency.

![Figure 2.3](image.png)

Figure 2.3: (a) An energy level diagram for DFG shows the absorption of one pump photon followed by the emission of one signal and one idler photon. (b) Schematic of DFG.
determined by conservation of energy:

\[ \omega_p = \omega_s + \omega_i \quad [70]. \quad (2.5) \]

The naming of the pump, signal and idler beams is historically related to the Optical Parametric Amplifier (OPA) which uses DFG to amplify the signal. Here we use the same mechanism, but utilize the idler in our experiments.

Also critical to nonlinear processes is the concept of phase matching, which requires that all three colors propagate through the medium in phase, or that:

\[ \vec{k}_p = \vec{k}_s + \vec{k}_i, \quad (2.6) \]

where each \( |\vec{k}_j| = k_j = \omega_j n(\omega_j)/c \) and \( n(\omega_j) \) is the frequency- and sometimes polarization-dependent (linear) index of refraction. While this can technically be performed in any nonlinear medium it is typically performed in a nonlinear crystal. In these nonlinear crystals the index of refraction is anisotropic, depending on wavelength, propagation direction, polarization and sometimes temperature. Each crystal contains a distinct optic axis. The plane containing both the optic axis and the light propagation vector, \( \vec{k} \), is defined as the principal plane. The degree of phase matching can be affected by rotating the crystal in the principal plane. Beams polarized perpendicularly to the principal plane are labeled “ordinary” and those polarized in the principal plane “extraordinary”. There are many types of phase matching, described in detail in Ref. [68], for the different combinations of ordinary and extraordinary polarizations for the three beams. However, all schemes share the common goal of making the beams propagate in phase as they traverse the crystal.
Commercial OPAs are available in the near to mid-infrared region (1-5 \( \mu \)m) [71]. Schemes used in most commercial systems contain a single input beam. This beam is spectrally broadened and split into two sections to perform DFG in a Beta Barium Borate (BBO) crystal. Utilizing both the signal and the idler they produce light between approximately 1-2.5 \( \mu \)m. Above 3 \( \mu \)m two DFG stages are typically used, drastically decreasing the conversion efficiency. These systems typically can achieve pulses around 100fs in duration, but with less than 10\( \mu \)J in energy. Even with fairly tight, \( f \# = 4 \), focusing this only produces an intensity of \( \sim 10^{12} \) W/cm\(^2\) for a 4\( \mu \)m source, far short of the mid-10\(^{13}\) to 10\(^{15}\) W/cm\(^2\) needed to produce significant ionization in the noble gases. To achieve the large pulse energies necessary for strong field experiments we utilize DFG driven by two separate, synchronized, 1 KHz repetition rate laser systems. The scheme used here converts pump photons at 0.816 \( \mu \)m generated in Ti:S into idler photons at 3.6 \( \mu \)m and signal photons at 1.053 \( \mu \)m generated in Nd:YLF (Neodymium: Yttrium Lithium Fluoride).

2-2: Overview of the MIR Laser System

In our DFG scheme the pump and signal beams are collimated to a 2.75mm diameter and sent into the crystal in a near collinear geometry, as demonstrated in Figure 2.4(a). A near-collinear (<1°) mixing geometry is used for lossless spatial separation of the idler beam while also maintaining good mode quality by alleviating the intrinsic angular dispersion in a non-collinear geometry [72, 73]. KTiOAsO\(_4\) (KTA) is used because of its high damage threshold [74] and good transparency to wavelengths from
0.3-5.0µm, Figure 2.4(b) [75]. KTA is a positive biaxial crystal and DFG is performed in the XZ plane (θ=39°, υ=0°, d_{eff}=2.0pm/V) with Type II ($\vec{k}_p^o = \vec{k}_s^e + \vec{k}_i^o$, also denoted o-eo) phase matching [74]. The crystal length was chosen as 2.5mm to optimize the peak power of the MIR while minimizing idler pulse broadening. For example, doubling the crystal length to 5mm produced nearly twice the pulse energy but with twice the pulse duration due to group velocity mismatch. The phase matching angle of the crystal, υ, is demonstrated in Figure 2.4(a). The wavelength tuning that will be discussed in Section 2-3 is controlled by changing the phase matching angle.

Figure 2.4: (a) Layout of DFG for MIR laser. The pump (blue) and signal (red) undergo DFG in 2.5mm of KTA, producing an idler (purple) and amplifying the signal. The frequency-doubled signal (green), filter (f) and monitor photodiode (PD), used in the timing stabilization are included. (b) Transmission of KTA [75].

The amplification of the signal beam provides a loss-free method of monitoring the temporal overlap of the pump and signal in the crystal. While the input signal is a 16ps pulse, the amplified portion is closer to 100fs. This shorter portion of the pulse is
able to drive significant second harmonic generation (SHG) as it propagates through the crystal. While the second harmonic (0.527 µm) does not hinder the idler production, it is tied to the DFG process and maintains the same dependence on the temporal overlap of the pump and signal, making it an excellent monitor of the DFG process. The second harmonic of the signal is spectrally filtered and recorded on a photodiode.

**The Nd:YLF System**

The Nd:YLF laser consists of a commercial oscillator (Time Bandwidth: GE-100) and a home-built regenerative amplifier. The passively mode-locked [76] oscillator produces approximately 7.5 nJ, 16 ps pulses at 1.053 µm with a repetition rate of 80 MHz. One of the cavity mirrors is mounted on a piezoelectric transducer, allowing for modulation of the cavity length [77]. Since the repetition rate is given by \( r = \frac{c}{2l} \), where \( c \) is the speed of light and \( l \) is the cavity length, the piezoelectric-mounted mirror allows the repetition rate to be locked to an external 80 MHz electronic oscillator inside the Time-Bandwidth CLX1100 which controls the piezoelectric transducer in the oscillator.

The oscillator’s output seeds a regenerative amplifier [78], producing 0.8-1.2 mJ, 16 ps pulses at 1.053 µm with a 1 KHz repetition rate.

**The Ti:Sapphire System**

As Ti:S can easily produce short, tunable pulses in the near-infrared, it is an appropriate choice for the front end of the DFG system. A commercial oscillator (Spectra Physics: Tsunami) is used to generate 8.75 nJ, 90 fs pulses with a center
wavelength of 0.816 µm and 15 nm of bandwidth at an 80 MHz repetition rate. The Tsunami is also equipped with a mirror mounted on a piezoelectric transducer and timing electronics that can lock the cavity’s repetition rate to an external reference signal. The signal from the CLX1100 is used as the 80 MHz reference for the Tsunami in addition to the GE-100, synchronizing the two oscillators to within a jitter of 3 ps (the stability of the locking electronics for the Tsunami: Spectra Physics Model 3930).

A CPA scheme is utilized to safely amplify the pulses. After being stretched to 200 ps in pulse duration, the first stage of amplification occurs in a homebuilt regenerative amplifier producing 1.7 mJ, 200 ps pulses at 0.816 µm and a 1 KHz repetition rate. This amplifier is very sensitive to amplified stimulated emission (ASE) produced in the crystal. While the ASE contributes a maximum of 0.2 mJ, it is a long (ns) pulse instead of picoseconds and does not constitute a significant contribution to the peak power. Therefore it does produce a significant effect on the MIR production, which depends nonlinearly on power. Further amplification is achieved in a home-built multipass amplifier. After two passes the Ti:S energy is increased to 4.4 mJ.

After compression and transport to the crystal the Ti:S measures 3.2 mJ, 90 fs pulses with a center wavelength at 0.816 µm and 13 nm of bandwidth. A diagram of the laser configuration is displayed in Figures 2.5.

The timing signals used in locking the repetition rates of the two lasers ultimately originate from the 80MHz oscillator in the CLX1100. The GE-100 and Tsunami oscillators (blue boxes) send pulse-train information to their respective locking electronics, the CLX1100 and Model 3930, respectively (white boxes). In turn the
locking electronics send the intra-cavity piezoelectric transducers a voltage that corresponds to a length correction. The same 80MHz signal from the CLX1100 is used to lock the repetition rates of both oscillators. A trigger or reference signal from each set of timing electronics is sent to the RF input of the Pockels Cell Driver (Medox) (grey boxes) for its respective laser. The Pockels Cell Driver contains an internal frequency converter that transforms the 80 MHz signal into 1 kHz and produces three identical outputs used to trigger the remainder of the equipment in the system, including a Delay Generator (Stanford Research Systems: DG535), which sends appropriate triggers to the pump lasers for the amplifiers and a reference signal that is sent to the detection electronics described in Chapter 3. The signal routing is shown in Figure 2.6. The signal sent to the detection electronics for the experiments is labeled “ETR”.

Figure 2.5: Layout of the 3.6 μm System.
Timing Stabilization

Since the DFG crystal is fed by two independent laser systems it is necessary to stabilize the pulse-trains of the two oscillators. The commercial electronics that lock the oscillators to the same 80 MHz reference signal achieve sufficient timing overlap over approximately 10-30 minutes, depending on vibrations, temperature and other environmental fluctuations. To extend the time scale to several hours and allow for long data accumulations, a cross-correlation technique is used to monitor the amplitude of the signal. The amplified signal pulse, Figure 2.4(a), is on the order of 100 fs long and produces significant second harmonic generation (SHG) in the KTA crystal. The amplitude of the frequency doubled signal is monitored by an amplified-integrated photodiode that is sampled with a data acquisition card and monitored with an 80 Hz LabView loop. When the photodiode signal drops by more than 5% of its maximum
value a voltage signal, interpreted as a timing shift, is sent to the timing synchronization circuitry. As the voltage is swept, the photodiode records a cross-correlation (Figure 2.7) and sends the optimal timing shift ($\tau = -15$ ps as shown) to the timing circuit. Each cross-correlation is performed in one second or less than 0.3% of a typical data acquisition.

![Graph](image.png)

Figure 2.7: Timing synchronization is monitored with a cross-correlation technique.

2-3: Tunability

In a conventional DFG or OPA scheme to change the frequency of the idler it is necessary to change the frequency of either the pump or the signal. A popular method is to use self phase modulation (SPM) or continuum generation on one of the input beams prior to the crystal [72]. Here tuning is achieved without making changes to the pump or signal prior to the DFG crystal. We employ SPM and DFG simultaneously in the same crystal to achieve expedient wavelength tuning.
Measurements

The broadening of the pump in the KTA crystal allows the laser to be tuned continuously between 3.2 and 3.9 µm by rotating the crystal around the phase matching angle, ϑ (defined in Figure 2.4(a)), over a range of approximately 80 mrad as shown in Figure 2.8. The maximum pulse energy achieved at a given center wavelength is plotted in Figure 2.9(a). The peak pulse energy is near 150 µJ between 3.4-3.6 µm and falls rapidly outside of that range. The conversion efficiency of the idler yield is also included on the right-hand side of the plot. Although 15% of the pump power is lost in reflections from the front surface of the crystal the conversion efficiency is still quite good. This 15% loss is not taken into account for the numbers included in Figure 2.9(a).

Figure 2.8: To demonstrate tuning of MIR the idler center wavelength is plotted as a function of crystal tilt with respect to laser normal, ϑ.
Spectra for the idler at a range of center wavelengths are shown in Figure 2.9(b). Each idler spectrum is recorded using an infrared spectrometer (Instruments SA, Inc., HR320) and an InGaAs linear detector array (Hamamatsu C7369) with a linear spectral response between 1.2-2.6 μm and peak response at 2.3 μm. The detector’s response to the idler occurs through two-photon absorption and each spectrum in Figure 2.9(b) is corrected for the detector’s quadratic response. The total tuning range corresponds to adjusting the phase-matching angle, \( \varphi \), by a total of 80mrad.

![Figure 2.9](image)

Figure 2.9: MIR energy and conversion efficiency are shown corresponding to each normalized spectrum in (b). The efficiency in (a) is given by the initial energy in the pump beam and does not take into account measured 15% reflection losses. Each power spectrum of the idler in (b) is corrected for the detector’s quadratic response (see text for details). The broad spectra slightly overfill the detector and clip on the red edge.

The significant tuning range observed in Fig. 2.9(b) depends on the spectral broadening of the pump. For example, considering the FWHM of the unbroadened pump, 0.810 to 0.822μm, and the corresponding maximum and minimum idler
wavelengths allowed would be 3.4 and 3.8\mu m. Moreover, idler wavelengths would be created at low energies due to the low spectral densities of unbrodened pump.

**Broadening Mechanisms**

The pump is roughly collimated to a waist radius \( (1/e^2) \) of approximately 1.375 mm. The signal beam size is adjusted to be slightly larger to ensure good overlap between the beams for propagation through the entire length of the crystal. The large pulse energy and small spot size of the pump produces an intensity of roughly \( 1 \times 10^{12} \) W/cm\(^2\). KTA has a large nonlinear refractive index, \( n_2 = 1.7 \times 10^{-15} \) cm\(^2\)/W [79]. At such large intensities the on-axis nonlinear phase shift accumulated during propagation is significant. This phase shift is quantified by the B-integral:

\[
B = k \int n_2 I(z) dz, \tag{2.7}
\]

where \( I(z) \) is the intensity and \( k \) is the wavenumber, \( 2\pi/\lambda \) [80]. For \( B > 2 \) rad SPM and continuum generation produce significant spectral broadening [80]. Assuming the intensity is constant with \( z \) we calculate for our beam parameters \( B \sim 17 \) rad. The spectral phase accrued by the pump as it travels through the KTA is measured using second harmonic frequency resolved optical gating (FROG) [81]. The spectral phase and measured broadening are displayed in Figure 2.10. In 2.10(a) the spectral phase recorded before the KTA is plotted in black and after propagation through the KTA in red. The measured phase is several radians: much larger than can be accounted for by material dispersion, but less than the simple B-integral calculation. The discrepancy indicates that
changes in intensity with propagation are important for successfully modeling the process.

Figure 2.10(b) shows the power spectra of the pump before the KTA (black), after the KTA (red long dash) and after the KTA in the presence of the signal (grey short dash). To determine spectral depletion in the Mid-IR we define:

\[
S_{\text{depletion}}(\%) = \frac{S_p - S_{p+s}}{S_p} \times 100,
\]  

(2.8)

where \( S_p \) is the broadened power spectrum of the pump after the KTA and \( S_{p+s} \) is the power spectrum of the pump after the KTA in the presence of the signal. \( S_{\text{depletion}} \) is

---

Figure 2.10: Second harmonic FROG measurement of spectral phase for pump before (black) and after propagation (red) through the 2.5 mm KTA in (a) demonstrates the nonlinear propagation of the pump. The measurement is made with 100 ms of integration per 1.5 fs time step. Shown in (b) is the pump spectrum: before KTA (black solid), after KTA without signal present (red long dash), and after KTA with signal present (grey short dash). \( S_{\text{depletion}} \), defined in Eq. (2.8), for 3.6 µm idler (grey solid) and the absorption curve through 2.5 mm KTA (blue dot) are plotted in (c).
referenced to the spectral region of the MIR by the conservation of energy relation given in Eq. 2.5: \( \omega_p = \omega_s + \omega_i \), to compare with the transmission spectra of KTA [75]. We plot \( S_{\text{depletion}} \) (grey) and the absorption spectrum of KTA, calculated from the results of Ref. [75], (blue dotted) in Figure 2.10(c).

It is clear from the spectra in Figure 2.10(b) that after the KTA crystal there is more spectral content in the wings of the pump spectrum to be converted into idler photons. The measured cutoff of idler production at 3.2 and 3.9 \( \mu \text{m} \) in Figure 2.9(a) indicate that idler production spans pump central frequencies from 0.792 to 0.829 \( \mu \text{m} \), instead of the 0.810 to 0.822 measured from the FWHM of the unbroadened pump spectrum. The peak energy conversion between 3.4-3.6 \( \mu \text{m} \) corresponds to the higher spectral density in the center of the spectrum. As the spectral density in the pump decreases on the red and blue wings of the pulse, so does the idler production. Looking at the depletion spectrum in 2.10(c) the high-frequency cutoff in the idler is apparent from the sharp drop in \( S_{\text{depletion}} \) at around 3.2 \( \mu \text{m} \). This corresponds to the spectral density of the pump being too low for successful conversion. The low-frequency cutoff is a little more unexpected. \( S_{\text{depletion}} \) shows a large amount of depletion at longer wavelengths, but this is not reflected in conversion to the idler. As the spectral density of the pump decreases the absorption (blue dotted line in Figure 2.10(c)) begins to increase. It is possible that differences in KTA fabrication methods could result in deviations of the absorption edge that couples to the low spectral density in the pump, thus limiting the tuning on the low frequency side.
The pump power was varied to study how SPM and conversion of the idler scale for lower pump energies. Broadening is present for all pump energies above 0.1 mJ; the $e^{-2}$ width of the broadened pump spectrum increases linearly with pump energy from 0.1-1.0 mJ and remains nearly constant from 1.0-3.2 mJ. With the MIR wavelength tuned to 3.6 μm, idler production increases quadratically from 0.5-2.5 mJ and is not detected below 0.5 mJ of pump. Above 2.5 mJ of pump idler production saturates and increases linearly with pump energy.

The shot-to-shot stability of the broadening process was verified by monitoring the spectral variations of the pump pulse and amplitude fluctuations of the idler. We compared the rms fluctuation of each amplitude component of the power spectrum of the pump pulse before and after the KTA crystal. The rms of the broadened pump pulse’s spectral density was consistently ≤ 2% of the rms of the unbroadened pump pulse across the entire spectrum. The rms fluctuation of the idler, measured with a fast linear photodiode is 3-5%. For comparison the signal and pump beams prior to the KTA crystal have < 2% rms variation. The stability measurements indicate that the nonlinear broadening of the pump is driven in a stable regime despite the high pump fluence, SPM and observed saturation of the DFG process.

2-4: Characterization

In order to determine the performance of the MIR system it is necessary to accurately measure the pulse duration, pulse energy, mode and overall beam quality to determine its efficacy as an intense field experimental tool. A complete characterization
of the idler beam was performed to evaluate any deleterious effect of the high pump fluence. In addition to these ‘macroscopic’ laser parameters, observations of single-atom response were used to infer details about the strong field of the laser.

The MIR pulse duration is inferred from the interferometric autocorrelation (IAC) using the two-photon response of an InGaAs photodiode described in Figure 2.11(a). Figure 2.11(b) shows a typical IAC with a pulse duration of 110-120 fs FWHM assuming a Gaussian deconvolution factor of $\sqrt{2}$. Figure 2.12 illustrates the clean spatial mode of the MIR beam recorded 20 cm after the KTA crystal using a thermal imaging camera (Electrophysics, PV320). In addition, an $M^2$ value was measured to be $1.2\pm0.1$ at 3.6µm.

![Figure 2.11: (a) The interferometric autocorrelator consists of a Michelson interferometer with a translation stage on one arm. BS denotes the beam splitter, each M are gold mirrors, and f are neutral density filters. The output can consist of either an InGaAs photodiode to record a two-photon response for the interferometric autocorrelation or an InAs photodiode to record a single photon response for a field autocorrelation. (b) IAC of MIR pulses centered at 3.6 µm measured with two photon absorption in an InGaAs detector. The FWHM is 110 fs assuming a Gaussian envelope.](image-url)
Figure 2.12: Demonstration of MIR Mode. (a) Spatial mode of MIR is measured 20 cm after KTA crystal. (b) and (c) show line-outs of the recorded spatial mode. A Gaussian fit to each is better than. (d) displays the $M^2$ measurement. The black points are the experimental width of the beam as a function of position. The red line is a fit to the far field portion, yielding $M^2 = 1.2 \pm 0.1$.

To further evaluate the beam quality and substantiate our individual beam measurements we measure the strong-field photoelectron energy spectrum (PES) of argon atoms. PES distributions in the strong-field tunneling regime have a characteristic break in slope near a scaled-energy of $2U_p$, which corresponds to the maximum classical drift energy for electrons ejected from the laser focus (Eq. 1.3). The maximum electric field
and thus the intensity can then be calculated directly from the energy of the $2U_p$ break [41]. Maximum intensities of $0.8, 1.2$ and $1.1 \times 10^{14}$ W/cm$^2$ are inferred from the PES (the total error is estimated to be within $\pm 10\%$) for center wavelengths $3.2$, $3.4$ and $3.6 \mu$m, respectively. At $3.6 \mu$m the maximum, diffraction limited, intensity achievable is $1.5 \times 10^{14}$ W/cm$^2$. The close agreement between the inferred and diffraction limited cases demonstrates that the overall beam quality is good even for strong pump fluences. The intensity measured from the PES is a complete assessment of the pulse encompassing the effects of the pulse duration, mode and focused spot size on the laser fields experienced by atomic argon. Deviations from the diffraction limited intensity can be attributed to small errors in the mode as well as aberrations from the final focusing optic.

Fine control over the laser polarization and pulse energy is necessary for use in experiments. Due to the long wavelength of the laser certain optics are difficult and/or expensive to obtain. For studies using elliptical and circular polarization we have characterized a low-order quarter waveplate (VM-TIM). This characterization was performed in two ways. First the waveplate was tested by placing a polarizer followed by a power meter downstream from the waveplate and measuring the attenuation as a function of waveplate angle. The results of this study are included in Figure 2.13(a). This calibration was verified by rotating the waveplate while measuring the xenon ionization rate at an intensity around $1 \times 10^{14}$ W/cm$^2$. When ellipticity is introduced into the polarization, the electric field of the laser is modified to become

$$E(t) = E_0(\cos(\omega t)\hat{x} + \epsilon \sin(\omega t)\hat{y})/\sqrt{1 + \epsilon^2},$$  \hspace{1cm} (2.9)
where $\varepsilon$ is the ellipticity, $\hat{x}$ denotes the polarization direction of the laser before the waveplate and $\hat{y}$ is the direction perpendicular to the original laser polarization. In Figure 2.13(b), the measured ionization yield is compared to an ADK calculation of the tunneling ionization rate for the field in Eq. 2.9.

Figure 2.13: Characterization of MIR quarter waveplate. (a) demonstrates the measurement performed with a polarizer and power meter. LP and CP denote linear and circular polarizations, respectively. (b) demonstrates the measurement of the Xenon ionization yield as a function of ellipticity. The black circles are the experimental data. ADK calculations performed at $9 \times 10^{13}$ and $1 \times 10^{14}$ W/cm$^2$ are included in the blue and red curves, respectively. In both plots the angles listed are the ticks on the mount for the waveplate.

The laser polarization and attenuation are also partially controlled via a half waveplate (CVI: QWP0-3600-10-2-R15) and two multi-plate infrared polarizers (II-VI Infrared: PAZ-20-AC-2 and PAZ-35-AC-4) with 30:1 and 200:1 extinction ratios containing two and four ZnSe plates, respectively, placed at Brewster’s angle with...
respect to the beam input. The performance of the two-plate polarizer was determined by comparing the transmission of the beam through the $\lambda/2$ waveplate-polarizer combination to the expected transmission of a plate at Brewster’s angle:

$$T = 1 - R (2 - R) \sin^2(\theta_i),$$

(2.10)

where $R$ is the reflection coefficient and $\theta_i$ is the input beam polarization angle with respect to the axis of the plate. This is the same result that can be found in any basic optics text for a ‘pile-of-plates’ polarizer [82]. Figure 2.14(a) shows the experimental data for the two-plate polarizer and a fit to Eq. 2.10 to determine the correct value of $R \approx 0.67895$. From this result it is possible to determine the leakage of the opposite polarization through the polarizer as a function of $\theta_i$ to determine the resulting polarization rotation from the leakage:

$$\tan(\theta_f) = (1 - R) \tan(\theta_i).$$

(2.11)

The calculated polarization rotation as a function of input laser polarization angle for two, four and six plates is displayed in Figure 2 - 14(b). The expected transmission for polarizers containing four and six plates are included in Figure 2.14(a). This information was both instrumental in the purchase of a new four-plate polarizer assembly to ensure polarization linearity and for early experiments was a source of error to be carefully accounted for.
Figure 2.14: Transmission through plate polarizer for two (red), four (blue) and six (green) plates are shown in (a). Red circles are the experimental data recorded with the two-plate polarizer with the 3.6 µm laser. The residual rotation for the three plate configurations is shown in (b). The color assignment is the same.
Chapter 3: Experimental Apparatus

The experiments are performed using a variety of measurement methods, depending on the data to be collected. Spectroscopic measurements were recorded using a high resolution spectrometer and intensified charge coupled device (ICCD) setup. Ionization measurements and photoelectron energy spectra were recorded using a time of flight (TOF) spectrometer capable of recording either ions or electrons.

3-1: High resolution spectrometer

Spectral density measurements were recorded using a commercial monochrometer (ISA, Triax180) and an intensified charge coupled device (ICCD) (Princeton Instruments, ICCD-1024MS-E). As displayed in Figure 3.1 the interaction region is relay imaged onto the spectrometer’s slit assembly (s) using two parabolic mirrors, labeled P1 and P2, both with an effective focal length of 152.4 mm. The commercial spectrometer is built using a Czerny-Turner design [83, 84] with three gratings on a rotating turret, labeled G. The three available gratings are displayed in Table 3.1. The ICCD spectral range is 180-900 nm, limited at high frequencies by the fused silica window on the camera. For some experiments it was desirable to use a spectrometer optimized for the near UV. This spectrometer (Acton: SP300i) is layed out identically to the Triax, but uses a different set of gratings, blazed to optimize detection in the UV, also displayed in Table 3.1. This
A spectrometer is used with a similar ICCD (Princeton Instruments, PI-MAX1024UV) with a MgF$_2$ window, extending transmission on the high-frequency end of the spectrum to approximately 115 nm. The Acton spectrometer is also designed to be purged to allow propagation of wavelengths shorter than 200 nm that would be otherwise absorbed propagating in air. Both cameras use a photocathode and a proximity-focused microchannel plate (MCP) image intensifier fiber-optically coupled to a CCD array and can be gated as fast as 2 ns. Depending on the gain setting on the intensifier the sensitivity can be increased up to a factor of 80, allowing for single-photon detection. Noise is reduced by cooling the detectors to -35°C. Both spectrometers achieve spectral resolution down to 0.2 nm using the 147 and 150 g/mm gratings used for the majority of experiments.

Figure 3.1: Layout of spectroscopic detection system. The l denotes a lens, P1 and P2 are parabolic mirrors both with an effective focal length of 152.4 mm. The green rectangle denotes the Czerny-Turner monochromator, where s is the slit assembly, G is the rotatable grating turret and ICCD is the intensified camera.
<table>
<thead>
<tr>
<th>Groove Density (1/mm)</th>
<th>Blaze Wavelength (nm)</th>
<th>Groove Density (1/mm)</th>
<th>Blaze Wavelength (nm)</th>
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<td>250</td>
<td>3600</td>
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Table 3.1: Grating groove densities and blaze wavelengths for the two spectrometers used for spectroscopic measurements.

3-2: Electron and Ion Time of Flight Spectrometer

Ion and electron spectra were recorded in a time of flight (TOF) spectrometer mounted within an Ultrahigh Vacuum System. Vacuum is maintained using two 360 liters/sec turbomolecular pumps located above the interaction region (Leybold: Turbovac TMP361) and above the flight tube (Leybold: Turbovac 360 CSVG). A base pressure of 1.2x10^-9 Torr is achieved by baking at a temperature of 100°C to increase desorption of water and other contaminants from the chamber walls. A background mass spectrum is shown in Figure 3.2. The background scan was collected at a pressure of 1x10^-9 Torr with the 3.6 µm laser system intensity of 9x10^13 W/cm² and was integrated over 600,000 laser shots. The major contaminants (water, carbon dioxide, oxygen, nitrogen and oils) are labeled in the figure.

The laser is focused into the interaction region between field plates P₁ and P₂ as illustrated in Figure 3.3. For the experiments on water molecules and noble gases described in Chapters 5 and 6, respectively, the sample gas is delivered into the chamber effusively through a Sapphire-flat leak valve, by back-filling the chamber to the desired pressure. For the alkali experiments described in Chapter 4 an oven is used to deliver a
Figure 3.2: Background mass spectrum collected at the photoelectron chamber base pressure of $1 \times 10^{-9}$ Torr using the 3.6 µm laser system at $8 \times 10^{13}$ W/cm$^2$. Major contaminants are labeled in the plot.

slow-moving beam of atoms to the interaction region (moving out of the page between plates $P_1$ and $P_2$). This oven will be described in detail in Section 3-3. When electrons are detected, the field plates are grounded and electrons travel field-free down the 55.2 cm flight tube to reach the detector. Ions can be extracted from the interaction region by applying voltages of 270 V, 100 V, and 0 V to plates $P_1$, $P_2$ and $P_3$, respectively. The flight tube region is still field-free for the time-of-flight measurement. To ensure that no external magnetic fields are present in the chamber, the flight tube is surrounded by a
Figure 3.3: Layout of Time of Flight spectrometer. The interaction region, flight tube and detector are labeled using brackets. $P_1$, $P_2$ and $P_3$ are the field plates used for detecting ions. Their set voltages are 270 V, 100 V, and 0 V, respectively. All are grounded for electron detection. For alkali experiments an oven sends a beam of atoms vertically (out of the page) between plates $P_1$ and $P_2$.

tube of Mu metal. The flight tube and detector are shielded from external electric fields by a grounded Faraday Cage. Since the smaller Mu-metal tube in the interaction region requires holes to allow the laser and gas samples to enter the interaction region it is gold plated so that it may act as a Faraday Cage to eliminate external electric fields.

The detector assembly used was built by R. M. Jordan company and consists of two image-oriented microchannel plates (MCP) (in chevron configuration to eliminate ion feedback) that amplify and accelerate electrons into the detector’s conical anode. Electrons and ions can each be detected by the same detector configuration by changing the bias across the detector. A diagram of the detector is shown in Figure 3.4. The electrons and ions travel through a grounded grid before reaching the front surface of the top MCP plate (T). The voltages applied to the top plate (T), bottom plate (B), and the
front surface of the anode, (A) are indicated in the table in Figure 3.4. Because the laser pulse (and interaction) is very fast (fs) compared to the detection electronics (ns) there is no need to pulse the detector voltages.

Figure 3.4: Layout of detector assembly is shown above. For both electron and ion detection the grid (far left) is grounded. Voltages used for Top and Bottom MCP’s and anode are indicated.

Recording spectra requires precise knowledge of how much time was required for the electrons (or ions) to reach the detector. This requires the use of fast timing electronics. The layout of the timing electronics is shown in Figure 3.5. The signal pulses leaving the detector anode are amplified using a fast preamplifier (Ortec: VT120) providing a factor of 20 gain. The pulses are then discriminated using a pico-timing discriminator (Ortec: 9307). The amplified electron (and ion) signal pulses have a FWHM of 1.5ns and a mean pulse-height of -830mV (-1.27V) and a standard deviation of $\sigma = -450\, \text{mV}$ ($\sigma = -320\, \text{mV}$). The pico-Timing Discriminator threshold is set to -300mV for electrons and -600mV for ions to ensure that noise is not counted as signal.
Timing jitter due to the pico-timing discriminator is less than 20 ps. The discriminated signal is sent into the first channel of an 8-channel Time-to-Digital Converter (TDC) (LeCroy 4208) with a time resolution of 1 ns. Because energy resolution is limited by how well the time can be determined, this 1 ns resolution is our limit. The 8 channels of the TDC are interleaved to allow detection of up to 8 pulses per trigger signal. The average count rate is limited to a few hits per laser pulse or below to ensure that no hits are missed by the electronics. Clear (CLR) and End of Window (EDW) signals are
distributed to the TDC from a Digital Delay/Pulse Generator (Stanford Research Systems: DG535), which receives a timing signal from the Nd:YLF regenerative amplifier’s Pockels Cell controller (see Chapter 2 for description). The common trigger signal for the TDC is first recorded by a fast (1ns rise time) InAs photodiode (Judson Technologies: J12) approximately two meters upstream from the chamber. Because the photodiode pulse is positive and the electronics require a negative signal, we employ an Inverting Transformer (EG&G: IT100) followed by a splitter (Mini-circuits: 15542) to provide a second signal to use as a beam monitor. The other signal leaving the splitter is used as the common trigger. Because the InAs photodiode is unbiased and produces a small, -15mV, signal it must be amplified through two stages of a fast Timing Amplifier (Ortec: 574). Each amplification stage yields a factor of 4.5 in gain and has a rise time of 1.2ns. The amplified trigger signal is discriminated using a Constant-Fraction Discriminator (CFD) (Ortec: 584). The discriminator threshold is set to -170mV to produce the most stable constant fraction signal with a timing jitter of less than 200ps. The output of the CFD is sent in to the Common input on the TDC.

*Photoelectron Energy Spectrum Detection*

The electron energy can be determined by the time required for each electron to reach the detector. The classical relationship between time and energy yields:

\[ E = \frac{1}{2} m \left( \frac{d}{t} \right)^2, \quad (3.1) \]

where E is the energy, m is the electron mass, d is the length of the flight tube, and t is the time of flight. In order to extract the time of flight from the measured time, it is necessary
to account for the amount of time required for trigger and detector signals to travel to the computer \((t_0)\) and for the propagation of the laser from the trigger photodiode to the interaction region \((t_l)\). The 100 fs duration of the laser pulse is much shorter than the time required for the electrons to travel to the detector (measured in ns), so we can treat the laser pulse as instantaneous and neglect it. The total recorded time is: \(t_r = t_0 + t_l + t\). The time delay contribution from cables and electronics, \(t_0\), is easy to measure by sending the photodiode trigger signal simultaneously through the triggering electronics and the detection electronics. The propagation of the laser from the trigger to the interaction region, \(t_l\), is somewhat trickier to determine. This requires collecting data of photoelectrons with known energy dependence. Here we utilize the fact that on an ATI spectrum the peaks are separated by the photon energy to determine the correction necessary to account for laser propagation. The single-photon spacing of the peaks results from detecting ionization in a small solid angle \((5^\circ)\) along the polarization axis. A wavepacket is launched towards the detector once per laser cycle. The Fourier Transform of this rate yields peaks in energy separated by the photon energy. A sample ATI spectrum shown in Figure 3.6, displays peaks spaced by \(1.52eV = \hbar\omega\) for an 816nm laser. After we account for \(t_0\), the values of \(t_l\) and \(d\) can be adjusted to experimentally determine the time delay and spectrometer length that produce the most accurate energy separation in the recorded spectrum. These values are 7.1ns and 55.2cm.

Energy resolution in the photoelectron spectra can be determined by looking at the Rydberg structure (Freeman Resonances) [24] on the first ATI peak. As described in Chapter 1, Freeman Resonances arise when high-lying Rydberg states are Stark-shifted.
Figure 3.6: Spectrum of argon ionized by an 816nm laser. Vertical dashed lines indicate photon spacing of $\hbar \omega = 1.52eV$.

through resonance with each integer number of photons as the laser intensity increases. When performed with an 816nm laser ($\hbar \omega = 1.52eV$) in argon gas ($I_{p,Ar} = 15.76eV$) the minimum number of photons necessary for ionization from the ground state is 11. The energy where each ATI peak is observed to end is: $E_{end} = s\hbar \omega$, where $s$ is the number of excess photons (beyond the minimum number) absorbed. Rydberg lines should be detected with an energy spacing given by:

$$\Delta E = I_p \left( \frac{1}{m^2} - \frac{1}{n^2} \right),$$  \hspace{1cm} (3.2)
where \( m \) and \( n \) are the quantum numbers of two Rydberg levels. \( E_{\text{end}} \) can be taken as the \( n = \infty \) case and we should find the Rydberg resonances separated from \( E_{\text{end}} \) by the energies listed in Table 3.2. The spectrum displayed in Figure 3.7 shows the first two ATI peaks from ionization of argon by an 816nm laser. The end energy of each peak at \( E_{\text{end}} \) corresponds to the dashed lines, and the detected Freeman Resonances are labeled with blue lines and the corresponding quantum number from Eq. 3.2. The width of the peaks indicates the time duration for which the Rydberg states remained populated before finally being ionized. For example, the Fourier transform of the \(~150\) meV width of the \( n=5 \) Freeman Resonance indicates that the level was populated for \(~4.4\) fs. The highest energy resonance resolvable is \( n=10 \), where we measure a width of \( 10 \) meV, indicating the limit of our resolution near \( 1\) eV. Below \( 0.5 \) eV the collection is poor, demonstrating the low-energy cutoff in the spectrometer’s transmission function.

<table>
<thead>
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<th>( m,n )</th>
<th>( \Delta E_{m,n} )</th>
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Table 3.2: Energy spacing between Rydberg Levels with quantum numbers \( m \) and \( n \), calculated for argon.
Time of flight data is recorded in time bins of equal width. Therefore when the transformation is made from time to energy it is necessary to account for the Jacobian of the transformation. Since \( t \propto E^{-1/2} \) we use the Jacobian \( E^{-3/2} \) and achieve the correct transformation in counts per energy bin up to a constant. Because the spectra measured are relative it is acceptable to omit the constant. Error in the energy calibration measurement can be determined simply by:

\[
\frac{\Delta E}{E} = 2 \frac{\Delta L}{d} + 2 \frac{\Delta t}{(t_f - t_0 + t_1)},
\]

(3.3)

where \( \Delta L \) is the uncertainty in length, \( \Delta t \) is the uncertainty in time.

Figure 3.7: Rydberg Peaks (Freeman Resonances [24]) are visible on the first few ATI peaks of argon generated with 816nm light. The end of each ATI peak is indicated with dashed lines. The blue lines indicate quantum numbers of Rydberg peaks identified from equation 3.2. Below approximately 0.5eV most of the signal is rejected by the spectrometer.
Ion Mass Spectrum Detection

To record ion spectra the field plates, P₁, P₂ and P₃ in Figure 3.3 are held at 270 V, 100 V, and 0 V, respectively. This accelerates the ions out of the interaction region and into the flight tube, where they travel field-free to the detector. The field plates are arranged in a Wiley-McLaren configuration [85], where the electric fields focus the electrons into bunches for higher resolution measurement. Although we operate in a regime where approximately 1 ion travels down the flight tube per laser pulse, the bunch picture, as used by Wiley and McLaren, accurately describes the interaction. The force, \( F \), on a particle with charge \( q \) in an electric field \( V \) is \( F = q \cdot V \). Therefore we can calculate the kinetic energy, \( KE \), of the accelerated ions:

\[
KE = \frac{1}{2}mv^2 = qxV,
\]

(3.4)

where \( m \) is the ion’s mass, \( v \) is the velocity and \( x \) is the distance traveled in the field. From this there is a simple relationship between the measured time, \( t \), and the ratio of mass and charge:

\[
t = \frac{d^2}{2x\sqrt{\frac{m}{q}}} \approx \frac{m}{\sqrt{q}},
\]

(3.5)

where \( d \) is the length of the flight tube as determined from photoelectron spectra. The maximum mass resolution is measured to be 0.2%

Ions are detected by biasing the detector to accelerate the ions up to the MCP front surface and amplify the resulting electrons into the conical anode. As displayed in Figure 3.4, the voltages used on the anode, bottom and top plates are 0V, 200V and 2.20kV, respectively.
3-3: Alkali Oven

For alkali metal experiments it is necessary to convert the solid alkali into an atomic beam. The source is an effusive oven with a source pinhole \( w_s = 300 \ \mu\text{m} \) and a collimating aperture \( w_c = 1\text{mm} \). The oven is heated by a coaxial inductive heater (Thermocoax: SEI 10/100) which can be operated to a maximum voltage of 65 V and supports a maximum current rating of 5 A, supplying the heater with 320 W for heating the oven. The temperature ultimately reached by the heater is dependent on the thermal contact between its walls and the heater and the amount of mass being heated. The response of the heater is shown in red circles in Figure 3.8. The measurement is performed by attaching a type-K thermocouple directly to the side of the heater in vacuum. The green squares indicate the temperature recorded for below the alkali reservoir for the same range of voltages. At high voltages the discrepancy between the heater and reservoir temperatures is up to a factor of 3. Because the silver braise that fixes the heater to the oven melts at approximately 760°C it is inadvisable to run the heater much above 42 V in its current configuration. This limits the maximum temperature of the oven reservoir to approximately 320°C.
Figure 3.8: Performance of the alkali oven. Temperature is measured on the heater (red circles) and below the alkali reservoir (green squares). A linear fit to the heater temperature gives a projection for the maximum achievable temperature of the heater.

The layout of the alkali oven is shown in Figure 3.9. The oven is mounted to the underside of the chamber and aimed using a bellows and series of three actuators, labeled A. The oven is held by a water cooled jacket, J, to keep the rest of the chamber cool. The reservoir of the oven, labeled R, is probed with a thermocouple, attached with a set screw to the lower end of the oven. The oven beam travels between field plates P₁ and P₂, through the interaction region (here the laser travels out of the page) and the escaping material is collected on a liquid nitrogen trap. The trap is angled at 45° to allow the material to be removed by a vacuum pump mounted to the side of the chamber. The location of the source and collimator apertures, wₛ and wₑ, are included as a reference. Portions of the details of the field plate assembly and the flight tube, as well as the Mu Metal shielding from Figure 3.3 are also included for reference.
Figure 3.9: Diagram of the alkali Oven setup. The oven is mounted to the underside of the chamber and aimed using bellows and a series of three actuators, A. The oven is held by a water cooled jacket, J. The reservoir of the oven, labeled R, is probed with a thermocouple. The oven beam travels between field plates $P_1$ and $P_2$, through the interaction region and the escaping material is collected on a liquid nitrogen trap. The locations of apertures $w_s$ and $w_e$ are indicated.
According to Ramsey [86], the number of atoms to leave an effusive source per second in a solid angle $d\omega$ at an angle $\theta$ relative to the normal is:

$$dQ = (d\omega/4\pi)n\bar{v}\cos\theta A_s,$$

(3.6)

where $n$ is the number of molecules per unit volume inside the source, $\bar{v}$ is the mean molecular velocity inside the source and $A_s$ is the area of the source aperture. This requires the assumption that every molecule that hits the slit does not change direction and that the spatial and velocity distributions inside the source are not affected by the effusion. In other words, we must require that $w_s \ll \lambda_{ms}$, where $w_s$ is the width of the source aperture and $\lambda_{ms}$ is the collisional mean free path inside the source, defined as:

$$\lambda_{ms} = \frac{1}{n\sigma\sqrt{2}},$$

(3.7)

where $\sigma$ is the molecular collision cross-section. The vapor pressure inside the source, $P$, can be determined as a function of temperature by:

$$\log_{10} P = -\frac{0.05225a}{T} + b$$

(3.8)

where $T$ is temperature in Celsius, $P$ is the pressure in torr and $a$ and $b$ are constants that vary by atomic species and are included in Table 3.3 [87]. The vapor pressure is converted to density using the ideal gas law. A comparison of the source aperture radius and the mean free paths for each species as a function of temperature is given in Fig. 3.10.
Table 3.3: Constants necessary for calculating the mean free path of alkali metal atoms by species. Atomic collision cross-sections, $\sigma$, are given in $10^{-15}\text{cm}^2$, and constants $a$ and $b$ are utilized for vapor pressure calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>$a$</th>
<th>$b$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>103300</td>
<td>7.553</td>
<td>1.02</td>
</tr>
<tr>
<td>K</td>
<td>84900</td>
<td>7.183</td>
<td>1.52</td>
</tr>
<tr>
<td>Rb</td>
<td>76000</td>
<td>6.976</td>
<td>1.75</td>
</tr>
<tr>
<td>Cs</td>
<td>73400</td>
<td>6.949</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Figure 3.10: Mean free paths are calculated for the four alkali metals studied (blue-sodium, green-potassium, red-rubidium, black-cesium) as a function of temperature and compared to the radius of the source aperture (thick black line).

The shape of the atomic beam can be calculated using the following:

\[2p = [w_c + (w_c - w_s)a]\]  \hspace{1cm} (3.9a)

\[2d = [w_c + (w_c + w_s)a]\]  \hspace{1cm} (3.9b)
\[ a \equiv \frac{l_{cd}}{l_{sc}}, \quad (3.9c) \]

where \( w_s \) is the diameter of the source aperture, \( w_c \) is the diameter of the collimating aperture, \( l_{sc} \) is the distance from source to detector and \( l_{cd} \) is the distance from collimator to detector, \( p \) is the half-width of the bottom of the trapezoidal beam shape and \( d \) is the half-width of the top of the trapezoidal beam shape. Experimental values for our system are included in Figure 3.11.

Figure 3.11: Geometry of oven layout and resulting beam shape are displayed with relevant measurements.
The most probable velocity within a molecular beam is given by \( v_p = \sqrt{\frac{3kT}{m}} \). The partial pressure in the interaction region can be estimated by the ratio of the pinhole radius to the distance from the pinhole: \( P_{\text{int}} = P_{\text{vap}} \frac{w_s}{l_{sc}} \frac{w_c}{l_{cd}} = 4.573 \times 10^{-4} * P_{\text{vap}} \). For the cesium experiments \( f\# = 10 \) focusing is used with a 3.6 µm laser, producing a beam with a waist radius of \( w_0 = f\# \cdot \lambda = 36 \mu m \). Because the waist of the laser focus is much smaller than the atomic beam diameter the pressure can be treated as constant.

At saturation intensity, \( I_{\text{sat}} \), 100% of the population is ionized. We can treat the intensity dependence of the Gaussian focus at a peak intensity of \( I_{\text{sat}} \) as a series of iso-intensity surfaces with volume obeying the relation:

\[
V(\eta) = \frac{\pi^2 w_0^4}{\lambda} \left\{ \frac{2}{9} \eta^3 + \frac{4}{3} \eta - \frac{4}{3} \arctan(\eta) \right\}
\]

(3.10)

\[
\eta = \sqrt{\frac{I_{\text{sat}}}{I} - 1},
\]

where \( w_0 \) is the size of the Gaussian beam’s waist, \( \lambda \) is the wavelength and \( I \) is the peak intensity [88]. The measured ionization rate in Cs varies roughly as \( I^7 \) below saturation, so we can estimate the total ionization rate as the sum of the rate from each iso-intensity volume element in 5% increments. The expected signal for Cs can be estimated at a peak intensity of \( I_{\text{sat}} \) by multiplying sum of the weighted focal volumes by the ionization rate and the density in the interaction region. This is plotted in Figure 3.12.
Figure 3.12: Estimated Cs ion signal as a function of oven temperature. Since the exact detector efficiency is unknown, the black and red lines denote 50% and 25% detection efficiency, respectively. An example of the measured signal near $I_{sat}$ is provided at 80 degrees by the green circle.

A comparison of the calculated vapor pressure to the measured cesium ionization yield as a function of oven temperature was made with all other parameters held constant. Figure 3.13 shows a comparison between the measured yield and the calculated vapor pressure as a function of temperature. Since the density of Cs atoms in the interaction region should scale linearly with vapor pressure and the detected signal should scale linearly with density, this should be a valid comparison. The vertical scale of the experimental ionization rate data is changed arbitrarily to achieve the best agreement between the two sets. The comparison allows for the determination that the temperature
measured by the thermocouple is 10% lower than the actual temperature inside the cesium reservoir.

Figure 3.13: Comparison of calculated cesium vapor pressure and Cs\(^+\) ion signal as a function of oven temperature (C). The experimental ion signal (black circles) is plotted on the left-hand axis and the calculated vapor pressure (red line) is plotted on the right-hand axis. The experimental counts are normalized to the duration of each acquisition.
Since the late 1980’s studies on Above Threshold Ionization (ATI) have produced surprising results. In the 1990’s multiple groups studying ATI in the visible and near-infrared in argon and xenon discovered a range of intensities where a portion of the photoelectron energy spectrum (PES) experiences a large (orders of magnitude) increase in yield as a function of intensity [35, 89-92]. This so-called quasi-resonant behavior indicates a mix of both multiphoton and rescattering dynamics [93]. The features of these ATI resonant-like enhancements are reproduced well by two different groups of theories. The first group reproduces the structure using the time-dependent Schrödinger equation (TDSE). Results are produced by either numerical solution [94] or using the Floquet theorem [95]. The second group of theories centers on the Strong-Field Approximation (SFA) and interprets the humps as a consequence of channel closings [91]. The kth channel closes when the energy of k photons matches the needed ionization energy: 

\[ k \hbar \omega = I_p + U_p. \]

Both theoretical predictions agree that the hump in the spectrum is the result of combining the dynamics of multiphoton resonances with dressed atoms and rescattering [93]. The electron wavepackets produced from these resonant processes can linger near the core for many cycles and experience an enhanced recollision process. There is still no consensus as to which theory correctly describes the process that creates these quasi-resonances.
It is well established that the electric field of the driving laser produces a significant effect on the states of the atom. AC Stark shifts have been observed to have a significant effect on the photoelectron energy spectrum [24]. Because the Stark Shifts are large, atomic transitions can be highly important for the spectrum [96]. The AC Stark splitting of atomic levels has been observed in the ATI photoelectron spectrum [97, 98]. Because rescattering effects take place far from the ion core, it is reasonable to expect the plateau electrons may be strongly influenced by dressed resonances [93]. Perry, et al., observed resonant enhancements in the ATI photoelectron spectrum of helium [99].

In the existing literature, most calculations of ATI are typically done with one-electron models, but most experiments are performed using the noble gases [100]. In general the agreement between theory and experiment is good, particularly in the case of TDSE predictions of photoelectron energy spectra. It is unclear if any differences between experimental and calculated spectra should be attributed to inaccuracies in modeling the atom or an incomplete understanding of the ATI process [100]. Compared to the noble gases, few experiments have been performed with hydrogen [101] or alkali-metal atoms [97, 102]. By utilizing alkali atoms, which can be approximated as single-electron systems, a more careful comparison can be made to single-electron theories. Experiments using the alkalis are problematic because the ionization potentials are so low compared to the photon energies that are easily available, producing only a few ATI peaks [97]. Other longer-wavelength studies use long (4 ns and 20 ps) pulses, producing a very low ponderomotive potential [102]. Utilizing the 3.6 \( \mu \)m system described in Chapter 2, alkali experiments become comparable to those of 0.8 \( \mu \)m and noble gases, as
described in Chapter 1. ATI in cesium driven by 3.6 \(\mu\)m can be addressed in terms of the Keldysh scaling and compared with noble gas spectra collected at 0.8 \(\mu\)m. It is possible to determine the effect of the ionization regime on the spectra from the similarities between the spectra, and likewise the dependence on electronic states from the differences between the spectra. Perhaps the study of the Keldysh-scaled system can prove instructive as to the origin of the quasi-resonant enhancements that appear in the ATI photoelectron plateau.

### 4-1: Ionization Yield and the Effective Binding Energy

Previous experiments in cesium have indicated that the AC Stark shift has an unusually strong effect on the ground state of the atom [97, 100]. The Stark shift can be the result of either a large induced dipole moment or a quasi-resonance. The AC Stark shifts described by Nicklich, \textit{et al.} [97] were caused by the large dipole induced by a strong laser field. The effect of this large shift of the ground state was observed in the discrepancy between the measured saturation intensity and the predicted value. In the tunneling regime the intensity at which saturation of the ground state occurs is typically approximated by the over-the-barrier ionization threshold intensity, \(I_{\text{OTB}}\), in Eq. 1.17. Cesium appears to be an anomaly to this rule, as \(I_{\text{OTB}}\) underestimates the saturation intensity. Nicklich, \textit{et al.} reported a saturation intensity of \(4.2 \times 10^{12}\) W/cm\(^2\), at 0.621 \(\mu\)m (this corresponds to \(\gamma=3.6\)), far above the calculated \(I_{\text{OTB}}=9 \times 10^{11}\) W/cm\(^2\) [97]. Ionization yield curves for cesium at 3.6 \(\mu\)m are included in Figure 4.1. Here we also see a small increase in the saturation intensity above the over-the-barrier estimate, however not
nearly as large a shift as that reported in Ref. [97]. At low intensity the ionization rate increases as approximately $I^6$ for almost five orders of magnitude in dynamic range.

Ionization from the ground state corresponds to the absorption of 12 photons; according to perturbation theory, $yield \propto I^n$, where $n$ is the number of photons absorbed. At high intensities saturation of the ground state is seen in the familiar $I^{3/2}$ dependence corresponding to the volume increase of the Gaussian focus.

Figure 4.1: Experimental yield of Cs$^+$ ions as a function of intensity for 3.6 µm driving laser. Black lines are included for the two power laws, $I^6$ and $I^{3/2}$. 
Under the influence of a strong field, the atomic ground state is shifted by $\Delta E_0$. This coupled with the shift of the ionization threshold by $\Delta E_{thr} \approx U_p$ yields a total change in the binding energy of the atom [19]:

$$\Delta E_{bind} = \Delta E_{thr} - \Delta E_0 = \frac{F_0^2}{4} \left[ \frac{1}{\omega^2} + \chi_0(\omega) \right],$$

(4.1)

where $\chi_0(\omega)$ is the frequency-dependent polarizability of the ground state and $F_0$ is the peak value of the field, defined in Eq. 1.15. This dynamic polarizability can be calculated from the static polarizability, $\chi_0$, using:

$$\chi_0(\omega) = \frac{\omega_0^2 \chi_0}{(\omega_0^2 - \omega^2)},$$

(4.2)

where $\omega_0$ is the (field-free) resonant frequency of the lowest-energy excited state transition, in this case the D1 line of cesium, $\omega$ is the laser frequency and $\chi_0 = \hbar \cdot 0.1001 \text{Hz} / (\text{V/cm})^2$ [103]. For $1 \times 10^{12} \text{W/cm}^2$ this yields a shift in the binding energy of 0.19eV. Calculating $I_{OTB}$ for this new binding energy (4.08eV) yields $I_{sat} = 1.3$ TW/cm$^2$, which is within the 10% intensity measurement uncertainty of the value of 1.4 TW/cm$^2$ estimated from the ionization yield plotted in Figure 4.1. In experiments performed in argon and xenon, this change in the effective binding energy is often negligible due to the lack of strongly coupled low-energy levels.

4-2: Fine Structure in the Cesium ATI Spectrum

The appearance of the Stark Shift of atomic levels has been observed in ATI spectra [20, 96, 97]. At large field strengths it is now common to see the effect of the AC Stark Effect on the spectrum of the photoelectrons. As demonstrated by Freeman, et al.,
high-lying electronic states can be resolved in the ATI spectrum [20]. Early experiments on noble gas atoms indicated a shift in the detected energy of some of the higher order (plateau) ATI peaks [104]. Later studies [89, 90] using very high resolution measurements indicated that these ATI peaks do not shift, but are composed of a series of sub-peaks that vary in relative strength as the intensity is varied. These peaks were thought to have been produced by high-lying excited states, populated by integer numbers of photons as the AC Stark effect shifts the states through resonance.

The difference in electronic structure between the alkali metals and noble gases produces a significant effect when excitation is involved. In the noble gases all excited states have energies much higher than that of the ground state, allowing them to be treated as Rydberg states. In Cesium this is not the case; in particular, the strong coupling of the 6p states can be expected to produce significantly different spectral features compared to those reported in the noble gases. The effect of resonant enhancements on the ATI spectrum has been addressed by the work of Perry, et al., [98, 99, 88].

Using a 3.6 μm laser system the ATI peak separation is expected to be \( \hbar \omega = 0.34 \) eV. As a result of the small energy range covered by each peak and the resolution limit of the spectrometer, \( \Delta E/E = 0.02 \), the high-lying Rydberg levels detected in the noble gases [24] are not observed. Although the Freeman resonances from high-lying levels are not observed, the Cs ATI spectral peaks have a very complicated structure, dominated by a splitting into two discrete peaks. Figure 4.2 shows a sample photoelectron energy spectrum for cesium ionized by 3.6 μm at an intensity of 1.4 TW/cm\(^2\). The ticks on the
energy axis correspond to integer multiples of the drive laser photon energy. The splitting is apparent in the ATI peaks until around 3 eV, when it drops below the resolution limit of the spectrometer. The relative strengths of the two peaks vary with increasing ATI order.

Figure 4.2: Splitting of above threshold ionization peaks for Cs at 3.6 µm and 1.4 TW/cm².

To address the splitting of the Cs ATI spectrum it is necessary to calculate the expected AC Stark Shift of the first two excited states of cesium. The shift in energy of the nth atomic level is given by:

\[ \delta E_n = \frac{-1}{2} \chi_n(\omega) F_0^2 \]  

where \( \chi_n(\omega) \) is the polarizability of the excited state, n, to a nearby state, n’[19]. Because the fundamental frequency of the laser is so far from any resonance the
polarizability can be adequately approximated as the DC case, where $\omega=0$ in Eq. 4.2. As a first order estimate of the shift felt by the 6P$_{1/2}$ (D1) and 6P$_{3/2}$ (D2) levels the dipole contribution from only the ground state to each level is considered. This is a reasonable estimate because of the strong coupling between the ground state and each of the 6P states. The transition dipole matrix elements for the levels considered are 3.1822 and 4.4786 atomic units for the D1 and D2 transitions, respectively [103]. In Figure 4.3, the results of equation 4.3 as a function of intensity are compared for the ground state and 6P levels. The shift of all three levels is significant at an intensity of $10^{12}$ W/cm$^2$. The ground state, 6P$_{1/2}$ and 6P$_{3/2}$ excited states are plotted in solid, long dashed, and short dashed lines, respectively.

Figure 4.3: Calculated energy levels resulting from the AC Stark Shift of the ground state (6S$_{1/2}$) in solid lines and first two excited states (6P$_{1/2}$ and 6P$_{3/2}$) in long dash and short dash lines, respectively. The full intensity range of the calculation is shown in (a) and the intensity range used in the experiments is shown in a linear scale in (b).
As the intensity is increased the energy required to excite each excited state increases. This excitation energy is plotted in Figure 4.4 for the intensity range used in the experiment for the $6P_{1/2}$ (long dash) and $6P_{3/2}$ (short dash). As the intensity increases each of the excited states moves through 5-photon multiphoton resonance each wavelength used in the experiment, 3.4, 3.6, and 3.9 µm. The $5\hbar\omega$ energy for each wavelength is included in Figure 4.4 in black (3.4 µm), red (3.6 µm) and green (3.9 µm).

![Graph](image)

**Figure 4.4:** Energy of 5 photons for 3.4, 3.6 and 3.9 µm is indicated by solid horizontal lines in black, red and green, respectively. The energy needed to excite population to each the $6P_{1/2}$ and $6P_{3/2}$ excited states, accounting for the AC Stark shifts of both the levels and the ground state, is plotted in long dashes and short dashes, respectively.
It can be expected that as the intensity increases the excited states should be more likely to become populated. This should cause a quasi-resonant contribution to the Stark Shift. The effect of populating the excited states is corroborated by the splitting of each ATI peak in two. Nicklich, et al., observed a very similar ATI peak splitting due to excitation of the 6P excited states [97]. Ionization of the 6P excited states corresponds to 7 photons in the MIR.

Figure 4.5 demonstrates the intensity dependence of the individual ATI peaks; the ATI peaks appear to shift as a function of intensity and the shape of each peak is different from its neighbors. The ATI peaks detected in cesium at 3.6 µm display very complicated structure. Once the 6P levels have been excited, population can also become coupled to higher excited states before ionization occurs [96, 97, 104]. A contribution from other excited states is likely, but complicated to calculate. Compared to similar studies [90, 97] very fine intensity resolution, ~1%, is needed to successfully resolve the substructure within the ATI peaks. The 5% intensity stability of the 3.6 µm laser system smears the fine structures, causing the apparent shift of the ATI peaks. The effect of the AC Stark Shift on the individual ATI peaks could be addressed more quantitatively if the intensity resolution were improved to a few percent.

Ionization from excited states is a possible explanation for the ionization rate measured from the ionization yield curve plotted in Figure 4.1. According to perturbation theory the I^6 power law is much slower than the rate expected from 12-photon ionization. However, ionization from either of the 6P excited levels requires only
seven photons, much closer to the observed rate. A contribution from higher excited levels would be expected to decrease the exponent for the yield power law further.

Figure 4.5: ATI peak fine structure detected for the first few ATI peaks of Cesium. The ticks on the energy axis indicate the photon spacing for 3.6 µm. The complex structure in the ATI peaks is visible for 1.22 (blue), 1.12 (green) and 1.05 TW/cm^2 (magenta) in (a) and 1.05 (magenta), 0.96 (cyan) and 0.86 TW/cm^2 (orange) in (b).

4-3: Quasi-Resonant Enhancements in the Cesium Spectrum

Many experiments performed in argon and xenon in the Near-IR have produced a quasi-resonant enhancement structure in the plateau of the ATI spectrum. These quasi-resonant enhancements have been studied by many researchers [89-94, 105], detailing the features appearing in the plateau. A representative picture of these features in the photoelectron energy spectrum, reproduced from Ref. [35], is displayed in Figure 4.6. A prominent hump between 20-40 eV is apparent in all spectra above 1x10^{14} W/cm^2, becoming more noticeable and then disappearing as the intensity is decreased.
Theoretical predictions made by two distinct groups of theories are successful in reproducing the features observed in the noble gases [91-94]. Both theories propose that the enhancements arise from electrons that scatter with very small drift velocity and become trapped near the core. These electrons become “bunched” near the core, on oscillating electron trajectories that revisit the origin multiple times per laser cycle [93, 105, 106]. The electron bunches from each half laser cycle are in phase for certain intensities and interfere constructively, producing the enhanced hump feature in the envelope of the ATI spectrum [93]. These electron bunches also become focused along the laser polarization direction [93].

Figure 4.6: ATI spectra from argon at 630nm are reproduced from Ref. [35]. The curves are separated vertically to make them easier to distinguish and represent intensities: $6 \times 10^{13}$ (a), $1.2 \times 10^{14}$ (b), $2.4 \times 10^{14}$ (c), and $4.4 \times 10^{14}$ W/cm$^2$ (d).
The two competing theories describing the origin of the hump differ in the theoretical methods used and in their description of the origin of these electron bunches. The theories that utilize solving the TDSE [93, 94] predict that the electron bunches are created by a multiphoton resonance with a high-lying excited state. Those that utilize the strong field approximation (SFA) predict that the electron bunches responsible for the enhancement result from a multiphoton quasi-resonance due to channel closing [91]. The main difference between the two proposed mechanisms for the enhancement lies in the fact that Stark-shift induced resonances depend on an interaction between the initial state and a specific resonant excited state, while channel closings do not [94].

In cesium, photoelectron energy spectra produce a similar enhancement of regions of the ATI plateau to experiments performed in argon and xenon at shorter wavelengths. Enhanced humps appear in the plateau, indicating they could have a similar origin to those observed in argon. It has been suggested that if channel closings are indeed responsible for these resonant-like enhancements, that low-lying electronic states may disrupt the appearance of channel-closings because of the multiple ionization pathways available [92]. If this were the case we would expect to see a significant disruption of the channel-closing dynamics due to the very strong coupling of the low-lying 6P states in cesium. The intensity dependence of cesium spectra is shown in Figure 4.7 for 3.4, 3.6 and 3.9 µm.
Figure 4.7: Cesium ATI spectra. (a) and (b) 3.4 nm, (c) and (d) 3.6 nm, (e) and (f) 3.9 nm. Energy axis in eV for (a), (c) and (e), scaled to \( U_p \) for (b), (d) and (f). See text for details. All spectra shifted vertically arbitrarily to make them easier to see.
Photoelectron energy spectra at 3.4 µm were collected at intensities of 1.4, 1.3, 1.21, 1.01 and 0.99 TW/cm² (black, red, blue, green and magenta, respectively). When plotted with respect to detected electron energy (Figure 4.7(a)) a very prominent hump feature is recorded between 2-4 eV. The central energy of the enhancement shifts toward lower energy as the intensity is decreased. Figure 4.7(b) indicates that the feature seems to maintain a constant value of roughly 2Uₚ for all intensities. At 3.6 µm, as shown in Figures 4.7(c) and (d), the enhancement is also present, but seems to behave differently in intensity. For intensities of 1.75, 1.39, 1.22, 1.12, 1.05, 0.96 and 0.86 TW/cm² (black, red, blue, green, magenta, aqua and orange, respectively), the feature between 2-4 eV remains roughly constant in energy. Like the 3.6 µm data, the 3.9 µm results (Figures 4.7(e) and (f)) at intensities of 1.55, 1.48, 1.24, 1.17 and 1.05 TW/cm² (black, red, blue, green and magenta, respectively) consists of features constant in energy. The hump feature below 4 eV is present in all spectra, but is less pronounced with increasing wavelength. All three wavelengths also yield a second spectral feature between roughly 4-7 eV in the plateau, where the height of the ATI peaks becomes larger. This higher-energy feature is reminiscent of the features observed in Ref.’s [24, 35]. Both broad features within the ATI spectrum of cesium appear to be constant in Uₚ at 3.4 µm and constant in energy at 3.6 and 3.9 µm.

Channel closure requires the condition nhω = Iₚ+Uₚ be satisfied. For each n above the minimum number of photons required for ionization any electrons ionized during channel closure are expected to be detected at energies between 5Uₚⁿ and 8Uₚⁿ, where Uₚⁿ = nhω-Iₚ [90, 91]. This means that for the case of channel closure the energies
at which the electrons are detected after rescattering are independent of the laser intensity. This is a plausible explanation for the 3.6 and 3.9 µm data sets, but not at 3.4 µm. In Figure 4.8 photoelectron spectra for 3.6 and 3.9 µm are compared with the expected energy ranges for enhancements caused by channel closure. The expected energies for enhancements produced by channel closure fall close to, but not exactly on the observed enhancements in the spectra. At 3.4 µm the enhancements are almost certainly not due to channel closing, as their detected energies change with intensity.

Figure 4.8: Photoelectron spectra are compared to the expected energy range for enhancements due to channel closure. (a) 3.6 µm spectra are compared to channel closure for n = 12, 13 and 14 in red, orange and green, respectively. (b) 3.9 µm spectra are compared to channel closure for n = 13, 14 and 15 in orange, green and blue, respectively.

To more accurately address the wavelength dependence of these features it is necessary to understand the effect of the low-lying energy levels on the dressed atomic
system. The Rabi frequency for the fundamental field is expected to be very large in cesium at large intensity [96] and large detuning. Higher energy excited states must also be taken into account. The simple two-level atom approach is insufficient. More population is expected to reach the excited states as the 6P levels pass through a multiphoton resonance with five photons for each wavelength used in the intensity range studied. A multiphoton contribution to the atomic polarizability is to be expected to have a contribution to the Rabi frequency [107]. This should have an additional influence on the AC Stark shifts and the excited state population as a function of drive laser intensity. In order to make a more quantitative prediction of the system a more complete theoretical model is required.

4-4: Angular and Ellipticity Dependence of Cesium Photoelectrons

Information about the rescattering dynamics at play can be obtained by studying the angular distributions and ellipticity dependence of the photoelectron energy spectrum. Many studies have been performed on the angular dependence of strong field photoionization in the near-infrared [34, 108]. The maximum detected energy at each angle of detection can be estimated by solving the equation of motion for a free electron in an oscillating electric field, given in Eq. 1.19. A full description of the classical theory and its predictions can be found in Ref. [108]. Building from Eq. 1.19, if the electron is born into the field at time \( t_0 \) with zero velocity, the first time at which it revisits the core, \( t_1 \), can be determined from:

\[
\sin(\omega t_1) - \sin(\omega t_0) = \omega (t_1 - t_0) \cos(\omega t_0). \tag{4.4}
\]
Assuming that the returning electrons scatter elastically at an angle $\theta_0$, the motion after scattering can be described by two new coupled equations of motion:

\[ m\ddot{x}(t) = -\frac{eF}{\omega} (\cos(\omega t) - \cos(\omega t_1) + \cos(\theta) \cdot (\cos(\omega t_1) - \cos(\omega t_0))), \quad (4.5a) \]
\[ m\ddot{y}(t) = -\frac{eF}{\omega} \sin(\theta) (\cos(\omega t_1) - \cos(\omega t_0)). \quad (4.5b) \]

The measured kinetic energy outside of the field is equal to the time average of the kinetic energy inside the field, yielding a relationship for the detected energy:

\[ \frac{E}{U_p} = 2(\cos^2(\omega t_0) + 2(1 - \cos(\theta_0)) \cos(\omega t_1) (\cos(\omega t_1) - \cos(\omega t_0))), \quad (4.6) \]

and a relation for the detected angle of the electron, $\theta$:

\[ \cot \theta = \frac{p_x}{p_y} = \cot \theta_0 - \frac{\cos(\omega t_1)}{\cos(\omega t_1) - \cos(\omega t_0) \sin(\theta_0)} \cdot \frac{1}{\sin(\theta_0)}. \quad (4.7) \]

Equations 4.6 and 4.7 can be solved numerically to determine the maximum energy predicted by classical mechanics for each detected angle, $\theta$.

The results of the classical calculation for maximum detected energy at each angle for 3.6 $\mu$m at 1.4 TW/cm$^2$ are overlaid with the experimental data collected in cesium at 3.6 $\mu$m and the same intensity in Figure 4.9. The close agreement between the classical calculation and the experimental cutoff energy indicate that the cutoff in the spectra is likely only a result of the motion of the electrons in the oscillating field.

The momentum distribution of the photoelectron spectra can be illustrative of the electron dynamics. The momentum angular distribution of the detected electron spectrum in cesium at 1.4 TW/cm$^2$ and 3.6 $\mu$m is displayed in Figure 4.10. Individual ATI peaks are apparent in the photoelectron spectrum as vertical lines in energy or as rings centered on the origin in the momentum distribution. There are a number of local
Figure 4.9: Detected electron signal for Cs at 3.6 μm at 1.4 TW/cm² as a function of energy and angle. Dashed line shows results of classical calculation for the maximum detected energy.

maxima beginning near the origin and radiating outward. These are believed to be the result of interference of the electron trajectories [109]. The interferences are more prominent in the Cs angular distribution than they are in Kr at a higher intensity, as will be discussed in section 5-3.
Figure 4.10: Momentum representation of the photoelectron angular distribution of cesium ionized by 1.4 TW/cm$^2$ at 3.6 µm.

The ellipticity dependence of the strong field ionization can also be very instructive as to the dynamics occurring during the interaction. The ellipticity dependence of strong field processes, such as NSI and HHG has been well-documented [110-112]. Rescattering is known to be very sensitive to the ellipticity of the laser field. As the free electrons travel in the field they are subject to the transverse component of the field, causing them to miss the core on their return trajectory. Even small amounts of ellipticity can effectively “turn off” the plateau.
As described in Ref. [110, 111], for an elliptical field with ellipticity, $\varepsilon$, described by Eq. 2.9, the field can be treated as two separate fields, one in the x-direction: $F_x = F_{0x} \cos \omega t$, and one in the y-direction: $F_y = F_{0y} \sin \omega t$, where $F_{0x} = F_0 / \sqrt{1 + \varepsilon^2}$ and $F_{0y} = F_0 \varepsilon / \sqrt{1 + \varepsilon^2}$. Assuming that $\varepsilon$ is small and that the electron tunnels close to the peak of the field, the lateral displacement along the y-direction when the electron returns to the core can be calculated as:

$$\Delta y = \frac{\varepsilon e F_{0x}}{m \omega^2} [-\sin(\omega t_1) + \sin(\omega t_0) + \omega(t_1 - t_0) \cos(\omega t_0)].$$  (4.8)

The size of the returning electron wavepacket must also be taken into account [40]. The relations in Eq. 1.20 for the spread of the wavepacket can be used to evaluate the size of the returning wavepacket at time $t_1$. The values of these two quantities are compared as a function of ellipticity in Figure 4.11. The lateral displacement of the returning wavepacket is expected to be larger than the $1/e^2$ width of the wavepacket at ellipticities as small as $\sim 0.05$.

The ellipticity dependence of photoelectron spectra is determined using a half-waveplate followed by a quarter-waveplate. The $\lambda/4$ waveplate is set for zero retardance if the input beam is polarized along the spectrometer axis, and is kept stationary while the $\lambda/2$ waveplate is rotated to change the ellipticity. This ensures that the major axis of the polarization ellipse is always maintained along the spectrometer axis instead of rotating the ellipse as the ellipticity is adjusted. Experimental spectra and the ellipticity dependence are shown in Figure 4.12. All experimental data on the ellipticity dependence for cesium was collected at 3.6 $\mu$m, and all spectra are shifted vertically to
allow for easier viewing. A comparison of linear ($\varepsilon \approx 0$) and circular ($\varepsilon \approx 1$) polarization is shown in Figure 4.12(a) for 1.4 TW/cm$^2$. For circular polarization the total laser pulse energy is increased to maintain the same value of the field for both spectra. The peak of the circular polarization spectrum is located approximately at the expected value of $U_p$. In Figure 4.12(b) a few representative energy spectra collected at 1.0 TW/cm$^2$ are shown for ellipticities of $\varepsilon \approx 0$, 0.21 and 0.45. As ellipticity is increased both the plateau and the quasi-resonant enhancement hump in the spectrum drop rapidly. To quantify this rapid decrease, the relevant portions of the photoelectron spectra are integrated. In 4.12(c) the spectra collected at 1.4 TW/cm$^2$ are integrated for energies above 5 eV to evaluate the dependence of the plateau, plotted in black circles, and between 2.5-5 eV to evaluate the dependence of the hump, plotted in red squares. The same procedure is performed for
spectra collected at 1.0 TW/cm² in Figure 4.12(d). Error bars on the two data sets reflect the statistical counting noise from the data collection.

The ellipticity dependence measured for cesium at 3.6 µm is unexpected at first glance. Both intensities share the same anomalous behavior. At low ellipticities between
0 and 0.2, the quasi-resonant hump decreases much like the plateau. Between ellipticities of 0.2-0.45 the feature seems to reach a plateau, remaining almost constant. At large ellipticities, 0.5 and above, the hump decreases almost as rapidly as the plateau. In the 1.0 TW/cm² data, the plateau count rate is low at large ellipticities. Due to a lack of statistics, corroborated by the large error bars, the signal appears depleted at such low count rates. Comparing these ellipticity ranges to the spectra shown in Figure 4.12(b) it is clear that the quasi-resonant hump is still apparent at 0.2 eV, where the integrated signal reaches a plateau. By an ellipticity of 0.45 the enhancement feature is not present and the signal drops rapidly.

Compared to other phenomena driven by rescattering this quasi-resonant hump feature is relatively insensitive to ellipticity. Since both groups of theories used to describe the feature require the effect of rescattering, this insensitivity is highly instructive in thinking about the dynamics involved. As discussed in section 4-3, the theoretical work of Muller, et al. [94, 105] indicates that a portion of the wavepacket is allowed to linger near the core. These electron wavepackets form compact bunches and are focused on axis. Less sensitivity to ellipticity is strong evidence for the on-axis focusing of the electron trajectories. This focusing effect would help to counteract the transverse momentum gained by the electron in the elliptical field.
The ponderomotive energy changes quadratically with driving field wavelength \[113\] and produces a significant effect in the strong field regime. The factor of approximately 20 increase in \(U_p\) when the wavelength is changed from 0.8\(\mu\)m to 3.6\(\mu\)m causes a substantial change in the rescattering dynamics of the returning electrons. At the peak intensity of the MIR source, \(1 \times 10^{14} \text{ W/cm}^2\), we expect the electrons to return with energies up to around 390eV. Electrons in this energy range are routinely used to do crossed-beam impact ionization \[114\] and scattering experiments \[115\] used to determine electronic structure. This is a regime where results from synchrotron experiments are abundantly available for comparison to results found using short-pulse, long wavelength lasers. In the visible and near-infrared, where returning electron energies are lower, nonsequential ionization (NSI) in neon, argon and xenon has been attributed to impact excitation and subsequent field ionization from the excited state \[116\].

5-1: Impact Ionization in the Noble Gases from Rescattered Electrons

In the mid-infrared ionization yields reproduce some of the same characteristic features found in the visible and near-infrared. Namely, the so-called knee structure attributed to NSI is still present; however the nonsequential (NS) yield is considerably larger than those reported in the same species using shorter wavelength sources. A very
representative study of NSI in the noble gases driven in the NIR by 0.8µm lasers was presented by Larochelle, Talebpour and Chin [116]. A good example of a typical NSI ion yield curve is the neon data represented from [116] in Figure 5.1. The authors calculated the ADK tunneling prediction for the first and second charge states of Ne for comparison. The Ne\(^+\) experimental data (circles) matches relatively well to the ADK theory in curve 1. The Ne\(^{2+}\) experimental data (squares) deviates from the tunneling prediction in curve 3 for all except the highest intensities. It was noticed that the enhanced knee-structure (classic feature of the NSI regime) has the same intensity dependence as the first charge state. To illustrate this dependence the Ne\(^+\) ADK prediction is shifted down to overlap with the knee in curve 2. The interpretation of this dependence is that the Ne\(^{2+}\) data can be described as a superposition of the tunneling prediction and a factor proportional to the number of free electrons produced by single ionization. This superposition for the expected signal for the n\(^{th}\) charge state of a species, A, is represented as:

\[
S(A^{n+}) = \sum_{i=1}^{n} a_{in} S_{ADK}(A^{i+}) \quad (n \geq 2),
\]

(5.1)

where \(S_{ADK}\) is the signal expected from ADK theory and \(a_{in}\) are coefficients that can be determined experimentally for each set of experimental parameters. Since the knee evolves like the first charge state it was determined that it must be dependent on rescattering of the electrons produced in the first ionization event. By comparing the ratio of doubly charged to singly charged ions (\(S(\text{Ne}^{2+})/S(\text{Ne}^+)\)) it was determined that the inelastic rescattering proposed by Kuchiev [117] produced a solution dependent on the inelastic cross section for electron impact. The results determine that in the NIR the
nonsequential contribution arises from impact excitation of the ion, followed by field ionization.

Figure 5.1: NSI data from neon at 0.8 µm reproduced from [116]. The circles and squares represent the experimental ion signal for Ne$^+$ and Ne$^{2+}$, respectively. The three theoretical curves are all the predictions of ADK theory. Curve 1 is the ADK tunneling rate for the first charge state, curve 3 is the ADK tunneling rate for the second charge state and curve 2 is the same as curve 1, multiplied by a constant to match the knee of the Ne$^{2+}$ data.
The experiments performed in the MIR correspond to a much lower value of the
Keldysh parameter than the experiments performed in the NIR. In xenon, krypton and
argon ionization with $1 \times 10^{14}$ W/cm$^2$ of 3.6µm light, the Keldysh parameters are $\gamma = 0.22,$
0.30 and 0.38, respectively. In contrast, for studies performed at the same intensity in
argon with 0.8µm light the Keldysh parameter is $\gamma = 1.15$. This illustrates that the
ionization regimes are quite different in the near infrared (NIR).

The photoelectron energy spectrum in Figure 5.2(a) confirms that the ionization
mechanism is dominated by tunneling in the MIR. The dominant features are the
exponential decay at $2U_p = 133$ eV and the plateau out to $10U_p$. Ionization rates and
photoelectron energy spectra were recorded using the ion time of flight spectrometer
described in Chapter 3. Intensity is determined from the change of slope at $2U_p$ in the
photoelectron energy spectrum and calculated using Eq. 1.3. The intensity estimate is
expected to have an error of approximately 10%. In Figure 5.2(b) we see the ionization
yields of the first six charge-states of xenon. The raw data is binned in 2% intensity bins.
The first striking feature of the Xe$^+$ data (red) is its excellent agreement with the ADK
calculation. The yields of the other five charge states are greatly increased from the
predictions of ADK for Xe$^{2+}$ and Xe$^{3+}$ indicated in the plot. Two blue bars are indicated
on the Xe$^+$ curve to demonstrate which intensities correspond to the indicated Keldysh
parameter values of 0.22 and 0.50.
Figure 5.2: MIR ionization of xenon at 3.6 µm. (a) Photoelectron energy spectrum for xenon and 3.6 µm at 5.5x10^{13} W/cm². (b) Ionization yields are presented for Xe⁺ (red), Xe²⁺ (blue), Xe³⁺ (green), Xe⁴⁺ (yellow), Xe⁵⁺ (pink) and Xe⁶⁺ (black). The calculated ADK rates are included in dashed lines for Xe⁺ (red), Xe²⁺ (blue) and Xe³⁺ (green). The blue vertical bars indicated on the single ionization curve indicate the intensities matching the values of the Keldysh parameter γ = 0.22 and γ = 0.50.

The results of Larochelle, et al. for the ionization of xenon are presented in Figure 5.3. The intensity range studied is significantly larger than that available with the MIR source, however comparison can still be made with the shorter-wavelength data set. Both the recent MIR data and the Larochelle, et al. NIR data presented in Figures 5.2(b) and 5.3 have been marked with orange, dashed boxes, indicating a common range that can be examined for both experiments. In the NIR for the intensity range of 10^{13}-10^{14} W/cm² and the roughly 6.5 orders of magnitude dynamic range shown, xenon experiences
ionization up to the third charge state. For the analogous ranges for the MIR experiment the xenon atoms experience ionization up to the sixth charge state. This indicates a drastic change in the ionization dynamics involved in the MIR experiment.

Figure 5.3: Results for NSI in xenon are reproduced from [116]. The blue vertical bars indicate the intensities at which the values of $\gamma=1$ and 2.3 are calculated. These are the same as in Figure 5.2(b). The orange dashed box indicates the region of the plot to be compared to the orange box in Figure 5.2(b).

The experimental data in the MIR for krypton and argon (shown in Figure 5.4) is similar in its characteristics to that in xenon. In Figure 5.4(a), ionization up to the fourth charge state in argon is demonstrated at around $1 \times 10^{14}$ W/cm$^2$ at 3.6 µm. Krypton, Figure 5.4(b), experiences ionization up to the fifth charge state for a similar range of intensity.
As in xenon, the agreement of the first charge state to the calculated ADK tunneling rate is almost as remarkable as the discrepancy from the calculated tunneling rate for the higher charge states. These species also show a higher degree of discrepancy from the ADK prediction when compared to the NIR data, indicating the extreme wavelength and factor of 20 increase in $U_p$ may require a different interpretation.

Figure 5.4: Ionization yield as a function of intensity for argon and krypton. (a) $\text{Ar}^+$ (red), $\text{Ar}^{2+}$ (blue), $\text{Ar}^{3+}$ (green) and $\text{Ar}^{4+}$ (yellow). (b) $\text{Kr}^+$ (red), $\text{Kr}^{2+}$ (blue), $\text{Kr}^{3+}$ (green), $\text{Kr}^{4+}$ (yellow) and $\text{Kr}^{5+}$ (pink). The calculated ADK rates for the first three charge states of each species are plotted in dashed lines (red, blue and green, respectively).
We understand the traditional cross-section for impact ionization as described by Lotz [118]. The multi-parameter empirical formula for the impact ionization cross-section presented in Lotz’ first publication was:

\[ \sigma = \sum_{i=1}^{N} a_i q_i \frac{\ln(E/IP_i)}{EIP_i} \{1 - b_i \exp[-c_i(E/IP_i - 1)]\}, \]  

(5.2)

where \( E \) is the energy of the colliding electron, \( IP_i \) is the ionization energy of the \( i^{th} \) charge state and \( a_i, b_i \) and \( c_i \) are coefficients for each electron configuration of the atom or ion. The coefficients \( a, b, \) and \( c \) were determined for atoms with atomic number up to \( Z=108 \) [119]. The single-parameter form of Eq. 5.1 is used in the high-energy limit, where \( E \gg IP_i \) and the exponential is taken to be zero. The formulas introduced by Lotz show decent agreement with experimental results collected in crossed-beam impact ionization experiments. Calculated Lotz cross-sections are plotted in Figure 5.5.

![Graph showing impact ionization cross-section as a function of energy according to the Lotz Formula (Eq. 5.1) for xenon (red), krypton (blue) and argon (green).](image)
The most efficient way to check for a dependence on impact ionization is to find a way to compare the collected ionization yields to the impact ionization cross-section for each ion charge state. At any given intensity the number of electrons that return to their parent ion to scatter is proportional to the total number of singly charged ions. Therefore we can calculate the ratio of doubly to singly charged ions, which should be proportional to the cross-section for creating doubly charged ions. Likewise the ratio of triply to singly charged ions should be proportional to the cross-section for creating triply charged ions, and so on. These ratios (multiplied by an arbitrary constant) show a dependence that is very similar to the Lotz impact ionization cross-section. Unfortunately we now have a cross-section-like parameter as a function of intensity, but we would really like to know the associated return energy. It is known from the Simpleman model that we expect a certain distribution of return energies, shown in Figure 1.4. This is unfortunately too complicated for a direct comparison to the impact ionization cross-section without taking into account the returning wavepacket’s energy distribution. For now we can take the naïve approximation of the average value of the return energy distribution, which should be close to 1.6$U_p$. Transforming the intensity axis into units of 1.6$U_p$, we can make a direct comparison between the ionization ratios and the associated impact ionization cross-sections. To account for any error in the calculated cross-section the comparisons are done with published impact ionization measurements for argon [120-122], krypton [123-125] and xenon [125-127]. The results in argon, krypton and xenon are shown in Figure 5.6.
Figure 5.6: Ionization ratios recorded at 3.6µm. For all plots, symbols are experimental ionization ratios and lines are cross-sections. (a) Ar data with cross-sections from Ref’s [120-122]. (b) Kr data with cross-sections from Ref’s [123-125]. (c) Xe data with cross-sections from Ref’s [125-127].
The ionization ratio data shows that the naïve interpretation of the energy as the average of the intensity axis is flawed, more noticeably in the higher charge states of krypton and xenon. In order to achieve a better interpretation we must account for the return distributions of the electrons. Data sets were also collected at a center wavelength of 3.2 µm and showed similar results to those at 3.6 µm.

5-2: Interpretation of Impact Ionization Results

In order to successfully compare the ionization ratio results to an impact ionization cross section it is necessary to account for all of the experimental differences between electron gun experiments and laser-driven ionization experiments. To simplify the analysis we will focus on the xenon data as it provides more charge states to use in the comparison. The electron beam scattering cross-section experiments used in Ref’s [125-127] have a narrow energy distribution. The width of the beam used is approximately one angstrom. The broad energy distribution due to the distribution of ionization times (presented in Figure 1.4) and wavepacket spread inherent in laser-driven rescattering experiments are well established phenomena [38, 40]. It is therefore necessary to scale cross-section data accordingly to make a comparison with the ratio data.

First it is necessary to define the branching ratio: \( Xe^{n+}/Xe^+, \ n > 1 \). It can be assumed that the yield of the nth charge state is proportional to the photoionization yield of the neutral. This means that the contributions from field ionization of the n>1 charge states are ignored, which is reasonable since the expected tunneling ionization yields in
this intensity range are very low. It is also assumed that impact ionization occurs only for the first return event. If the returning electron flux is proportional to the ionization rate, then the branching ratios must be energy averaged cross-sections of the laser-driven case. To calculate the probability of encountering a series of (e, 2e) scattering events a full description of the dynamics of every electron must be taken into account. Instead of the total scattering cross-section the differential cross section would be needed. We know from semiclassical models of the strong field interaction, discussed in Section 1-4, that only the electrons that appear in the field with zero initial velocity are able to return to the core. Without knowing the energy and angle of each scattered and impact-ionized electron it is impossible to determine the effect of multiple (e, 2e) scattering events. Therefore we treat only the direct (e, ne) case.

Impact ionization cross-section data from electron beam experiments was only available up to quadruple ionization of the Xe$^+$ ion. Therefore it was necessary to determine an estimated cross-section for the (e, 6e) cross-section by scaling the Lotz formula (Eq. 5.2) based on the cross-sections for the first four ionization cross-sections. The error on the Lotz fit for the (e, 6e) cross-section is assumed to be 25%. For the second charge state, Xe$^{2+}$, the largest impact excitation cross-section is also included to determine if this is a contributing factor. Since Xe$^{+*}$ has a 9.9 eV ionization potential, the field ionization probability at the experimental laser intensity can be taken to be unity. The impact excitation and impact ionization cross-sections used in the calculation are included in Figure 5.7(a).
As discussed above the energy width of the returning photoelectron-distribution is broad due to the distribution of electron birth phases (ionization times). Due to the nature of laser ionization experiments the recorded experimental results are integrated over spatial and temporal intensity distributions of the laser focus. The experimental scattering cross-section, $\sigma(E)$, and the net return energy distribution as a function of the intensity distribution, $W_p(E(I))$, can be combined as an effective energy-averaged [128] cross-section:

$$\bar{\sigma}(I) = \frac{\int dE' \sigma(E') W_p(E'(I))}{\int dE' W_p(E'(I))}. \tag{5.3}$$

This yields a new cross-section that is weighted over the return energy distribution.

Figure 5.7: Collisional excitation (5s5p$^6$) and ionization cross-sections used in the calculation of the effective cross-section are shown in (a). See text for details. The energy-distribution of returning photoelectrons is shown for intensities: 100 (red), 80 (green), 64 (blue) and 51 (black) TW/cm$^2$ in (b).
The first important component to calculate for the effective cross-section is the return distribution, $W_p$. In order to determine the return distribution the 1-D electron trajectory discussed in Chapter 1 is calculated by solving $\ddot{x} = -F(t)$ in time increments of 1 atomic unit (au). The initial conditions are chosen to be consistent with the treatment in Ref. [129-130]. All trajectories that do not return to the core are rejected and each trajectory is weighted by the calculated ADK yield to account for tunneling ionization of the neutral and ground state depletion. To account for averaging over the temporal and spatial intensity distribution of the laser focus the energy distribution is summed for individual volume elements of a Gaussian focus (as described in Eq. 3.10) [88]. The resulting distribution is plotted in Figure 5.7(b).

The final factor that must be accounted for is the expansion of the wavepacket before the time of rescattering [28]. It is important to ensure the correct area is used for the recollision since the average colliding wavepacket has a $1/e^2$ width greater than 1nm. The dependence of the ionization probability on impact parameter [129, 131] must be included to obtain:

$$P(b, I) = \tilde{\sigma}(I) \frac{\exp (b^2/a_0^2)}{\pi a_0^2},$$

(5.4)

where $b$ is the impact parameter and $a_0 = \sqrt{2/\Delta E}$, where $\Delta E$ is the spread of the wavepacket. The results of the calculation are plotted in Figure 5.8(a) and (b) alongside the experimental ratio data collected at 3.6 and 3.2 $\mu$m, respectively. Xe$^{6+}$ data was not available at 3.2 $\mu$m. The experimental branching ratio data points and calculated impact ionization curves are shown in blue (e,2e), green (e,3e), black (e,4e), lavender (e,5e) and orange, (e,6e). The impact excitation calculation for the 5s5p$^6$ level is also included in
light blue. Both plots feature a cross-section axis to the left and a ratio axis to the right. The vertical overlap of the data is adjusted to achieve the best overlap over the entire set of branching ratios.

The agreement for (e,3e) and above is very good to within the experimental measurement error and a 10% error in the intensity estimate. At 3.2 µm the data samples a lower-energy portion of the effective ionization cross-section, as demonstrated in the figure. A dashed line at 100 TW/cm² is an aid to demonstrate how the intensity axis lines up with the calculated electron return energy axis. The (e,2e) experimental branching ratio data falls between the impact excitation and impact ionization, indicating the interaction is likely a mix of the two mechanisms. It is also possible that the excitation

Figure 5.8: Effective ionization cross-sections calculated for (e,ne) impact ionization and impact excitation to the 5s5p6 state followed by field ionization and the corresponding experimental ratio data are shown for 3.6 µm (a) and 3.2 µm (b). See text for details.
ionization of Xe\textsuperscript{+} is beyond the simple semi-classical interpretation presented here. This could be due, in part, to the fact that excitation cross-sections are typically inferred from a fit to the actual data and could have large errors \cite{131} or that high-lying excited states are coupled to the field and might not be accurately described by the field-free cross-sections \cite{132}. The excellent agreement between the experimental data and the threshold response of the (e, ne) cross-sections implies that this is an accurate picture of the dynamics and that a succession of (e, 2e) processes is unlikely.

As a result of the high ponderomotive energies available for the returning electrons, more complicated ionization pathways are accessible and perhaps apparent in the experimental data. Ref. \cite{133} determined that (e,3e) ionization of Xe\textsuperscript{+} could involve ionization from the 4d shell, through an Auger (NOO) channel \cite{127,133}. They support this conclusion by comparing impact ionization data to synchrotron photoionization experiments \cite{134}. The contribution of the Auger channel is apparent in their results through a large enhancement in the impact ionization yield around 100-150 eV. The results from Ref. \cite{133} are displayed in Figure 5.9. The filled circles indicate the Xe\textsuperscript{+} σ\textsubscript{1,3} data. Open circles are a different ionic species and can be disregarded for this discussion. The solid curves are a fit to the Lotz formula given in Eq. 5.2.
Figure 5.9: Experimental electron gun impact ionization (e,3e) cross-section data for Xe\(^+\) ion is shown in filled circles. Open circles are for a different ionic species and can be omitted for this discussion. Reproduced from Ref. [133].

In laser-driven rescattering impact ionization, sharp features are expected to be averaged over by the broad return-energy distribution. This is apparent in the experimental results on a linear scale, displayed in Figure 5.10. The impact ionization (e,3e) cross-section from [133] is included as red-dash. The effective cross-section calculated above is included in black. The experimental branching ratio data at 3.6 µm (green up triangle) and 3.2 µm (blue down triangle) are fit to a green line to guide the eye. The photoionization cross-section associated with the ionization of the 4d electron is
highlighted by a purple shaded region. The enhancement from the Auger channel is visible in the branching ratio data, but is smeared over a larger range of return energies by the broad return distribution.

Figure 5.10: Comparison of branching ratio data and experimental $\sigma_{1,3}$ impact ionization cross-section including the 4d Auger (NOO) ionization channel from Ref. [133] (red long dash). Branching ratios at 3.6 $\mu$m (green up triangle) and 3.2 $\mu$m (blue down triangle) are fit to a line (green) to guide the eye. The effective cross-section for impact ionization by rescattered electrons is included for reference (black). The cross-section associated with the 4d Auger channel is illustrated in purple.

5-3: Reconstruction of Scattering Cross-Section from Plateau Photoelectrons

Recently there has been much interest in utilizing the interaction of electrons with their parent ion to learn about the structure and dynamics of the parent ion. Various groups have attempted to perform tomographic imaging of molecules with structural data extracted from High Harmonic (HH) spectra [53]. Recently much interest has developed
in using the rescattered electrons in the plateau region of the photoelectron energy spectrum to attain the same structural information [54, 55]. The electrons that scatter elastically from their parent ion carry the same structural information as the HH emission. This structural information may be achieved by collecting the angular distribution of the photoelectron energy spectrum.

A photoelectron angular distribution is collected by inserting a $\lambda/2$ waveplate into the beam prior to the experiment chamber. The laser polarization is then rotated with respect to the spectrometer axis, with an angle of $0^\circ$ corresponding to the laser being polarized along the spectrometer axis. Data is collected in discrete steps in angle. Since each raw data point corresponds to an angle and a time, it is necessary to transform the time axis into momentum to construct the angular distribution. The necessary Jacobian ($J = p^2$) must be applied to account for the discrete time bins. An angular distribution collected for krypton with a 3.6 μm driving field is displayed in Figure 5.11. Angles were recorded in random order to rule out any influence from systematic fluctuations in the laser intensity. Each angle was collected for at least $6 \times 10^5$ laser shots and normalized to account for the length and number of scans and the pressure at which they were collected.

As indicated by a number of groups, the experimental differential elastic scattering cross-section can be extracted from the angular distribution by considering a simple geometric argument displayed in Figure 5.12. Electrons are detected
Figure 5.11: Photoelectron angular distribution collected in krypton at 3.6 µm and an intensity of 1x10^{14} W/cm². Detected electron momentum shown in atomic units on a logarithmic false color scale. See text for details.
Figure 5.12: Law of sines argument for extracting the differential scattering cross-section from the detected momentum is overlaid over a segment of the Krypton 3.6 µm angular distribution displayed in Figure 5.11.  \( \mathbf{A}_r, \mathbf{p}_r, \) and \( \mathbf{p} \) are the vector potential at the time of collision, collision momentum and detected momentum, respectively.

corresponding to a momentum \( \mathbf{p} \) and angle \( \theta \).  The vector describing the electron’s momentum at detection is the sum of the momentum at recollision, \( \mathbf{p}_r \), and the vector potential, \( \mathbf{A}_r \), at the time of collision: \( \mathbf{p} = \mathbf{A}_r + \mathbf{p}_r \).  The scattering angle, \( \phi \), between \( \mathbf{p}_r \) and \( \mathbf{A}_r \) can be determined from the law of sines:

\[
\frac{p}{\sin(\phi)} = \frac{A_r}{\sin(\pi - \theta - \phi)} = \frac{p_r}{\sin(\theta)}. \tag{5.5}
\]
The circle traced out by rotating $p_r$ through values of $\varphi$ produces the differential cross-section for collision momentum $p_r$.

As demonstrated in Figure 1.4, the return energy (or momentum) of a given electron can be determined from the time at which the electron experienced ionization. This yields a phase relationship between the return momentum and the vector potential of the field. Unfortunately the problem is complicated by the presence of the two trajectories discussed in Chapter 1. Electrons that travel the long trajectory are born closer to the maximum of the field, while the short trajectories are born when the field is smaller. Since the tunneling ionization rate increases exponentially with field, the plateau signal should be dominated by electrons born at larger field, or the long trajectories. This yields a one-to-one correspondence between each return momentum, $p_r$, and the detected momentum, $p$.

For a desired electron return momentum, $p_r$, and experimental value of $\theta$, we determine $\varphi$ and the necessary detected momentum, $p$. The detected signal at a given detected angle, $\theta$, is then integrated over the range of detected momenta that correspond to $\pm 10\%$ of the desired return momentum, $p_r$. This integrated signal is proportional to the differential scattering cross-section measured for the returning electron wavepacket impinging on its parent ion. To within a multiplicative scaling constant, this experimental cross-section can be compared to the differential scattering cross-section measured from electron gun experiments. The results of the experiment at 3.6 $\mu$m and krypton at $1 \times 10^{14}$ W/cm$^2$ are displayed in Figure 5.13(a).
This data is reminiscent of that reported by the authors of Ref [135, 136]. However, there are two major advantages to performing the above experiment in the Mid-IR (3.6 µm) spectral region as opposed to using a Near-IR source (0.8 µm). The first advantage is derived directly from the quadratic scaling of $U_p$ with wavelength. At $1 \times 10^{14}$ W/cm$^2$ the values of $U_p$ obtained for 3.6 µm and 0.8 µm are ~120 and ~6 eV, respectively. As electrons return to the core they gain up to $3.2U_p$ in energy; at 3.6 µm, these returning electrons have energies in the 100’s of eV, which matches much closer to the energies used in electron gun experiments. Therefore, using a Mid-IR source yields

Figure 5.13: Differential elastic scattering cross-sections reconstructed from laser-induced electron diffraction in (a) and reproduced from Ref. [137] in (b). Both cross-sections are for elastic electron impact scattering from krypton with a scattering energy of 100eV. See text for details.
the ability to compare the data to experimental results from crossed-beam scattering experiments. The differential cross-sections for elastic scattering of 100eV electrons from Kr from crossed-beam scattering studies are reproduced from Ref. [137] in Figure 5.13(b). The lines indicate the theoretical predictions of the authors and the data points represent experimental data from electron gun experiments. The other advantage to performing LIED in the Mid-IR is the larger vector potential ensures that for a given return energy, fewer detected momenta overlap with the direct electrons (those that do not rescatter, but escape the field in the first half cycle). As a result the LIED data collected at Mid-IR wavelengths yields more accurate results at small recollision angles. Small scattering angles are difficult to measure in electron-gun experiments and Near-IR LIED experiments.

Recent results by the authors of Ref. [56] make use of the relationship between electron return energy and return time to map the bond relaxation of molecules after ionization. A genetic algorithm is utilized to determine the ionic bond length for each experimental cross-section. By recording the differential cross-section at the same return energy for a variety of wavelengths it is demonstrated that the bond relaxation of O₂ molecules can be tracked with sub-cycle precision. The ability to probe molecular dynamics during chemical processes has very important implications for future experiments.
Chapter 6: High Harmonic Generation in Condensed Phase Systems

While a large fraction of high harmonic generation (HHG) experiments are carried out in noble gas vapors, other media have attracted researchers. For instance, harmonic generation up to the 9th harmonic order (H9) of the fundamental was observed from a 1060 nm laser in sodium vapors [138] and up to H7 of a MIR laser was observed in semiconductor ZnSe [139] as well as liquid chloroform [140]. Recent results from the 3.6 µm laser system described in Chapter 2 produced up to the 31st harmonic in cesium vapor [141]. Experimental results show that the proximity of an electronic resonance can enhance HG in atomic vapors [142] and suggest that vibrational resonances in liquids may also offer significant enhancement [140]. In the last decade, gas-phase experiments have been extended to molecules. With more sites at which recombination can take place, molecules have been found to offer richer dynamics allowing imaging of molecular orbitals [143, 53], higher conversion efficiency [144] and the possibility of extending the high-energy cutoff [145].

The major drawback to HHG is its low conversion efficiency, typically $10^{-5}$ at best [146], which falls far short of the efficiency of frequency combs generated by Stimulated Raman Scattering [147, 148]. Condensed phase media are attractive for use in Harmonic Generation (HG) and HHG because the increased density is promising for enhanced efficiency as there are more sites at which ionization and recombination can
Harmonic generation from the surface of solids and plasmas is readily performed [149], but few attempts have been made to achieve HHG in the bulk of condensed phase media. Until very recently the generation of harmonics in crystals has been below the ionization limit of the medium and limited to low intensities, where the perturbative description of HG is still valid.

When working with driving laser fields in the mid-infrared, in addition to the advantages of the quadratic scaling of the cutoff with wavelength, harmonics occur at visible and near UV wavelengths transmitted in air, simplifying both signal detection and propagation. This makes a new range of simple initial experiments possible.

6-1: Harmonics Generated in Liquid Water

An interesting candidate for HHG in condensed phases is liquids. A flowing sample can decrease the effect of a damage threshold, since the sample refreshes itself. The peak intensity for these studies is estimated to be 40-80 TW/cm² from similar focusing conditions performed to collect photoelectron spectra from xenon gas. The estimated intensities listed are the vacuum intensities since the dynamics of the condensed phase response are complex and a variety of mechanisms may alter the actual peak intensity from the vacuum intensity. It is the extreme nature of the intense laser field that distinguishes this experiment. Few studies have been performed with fluids in a regime where the material can suffer ionization induced by an ultrafast laser pulse.

In condensed phase media, the average atomic separation (0.1-1.0nm) is smaller than the quiver amplitude, making the rescattering model problematic. In typical liquids,
the electron excursion driven by a MIR laser far exceeds the molecular separation. For the experimental parameters described below, the quiver amplitude can be on the order of 3nm, therefore the electron could be perturbed on its return path to the molecule required for HHG. The concept of quiver motion with significant excursion and large kinetic energy may give rise to interesting phenomena not observed at shorter wavelengths or less dense media. How such situations modify HHG is a question initially best explored experimentally.

**Flowing Liquid Sample**

Because a flowing liquid source is advantageous, we built a version of the apparatus created by Tauber et al. [150] consisting of a 27 cm fluid column constructed from stainless steel tubing, chromatography fittings, custom glassware, and a peristaltic pump to recycle the fluid after the interaction region. At the end of the column is a narrow aperture, 2.7 mm × 0.3 mm, that holds a thin wire loop to provide enough capillarity for the fluid to form a film. Using a fluid source has the advantage of self regeneration and as described in [150] is well suited for kHz spectroscopy. A diagram of the fluid jet design used from Ref. [150] and a picture of the completed jet are shown in Figure 6.1. Absorption measurements were performed to determine the thickness of the film at the interaction region. The thickness of the sample was 150 μm and roughly matched the Rayleigh range of the laser focus used here. The average linear velocity of the fluid was 900 μm/ms and corresponds to a Reynold’s number of Re = 500. This is
well within range of laminar flow (Re<2000) [151]. The fluid source remained stable over acquisitions of several hours.

Figure 6.1: Fluid jet used for liquid HHG experiments. (a) Diagram reproduced from Ref. [148]. UR and LR = upper and lower reservoirs, PP = peristaltic pump, V = vent, VT = Viton tubing, SST = stainless steel tubing, BU = bulkhead union, WG = wire guide. (b) Picture of working fluid jet’s wire guide.

H₂O and D₂O were chosen because of their well documented and widely accessible chemical properties and also to allow a direct comparison of near resonant OH stretches ~2.9 µm and OD stretches ~3.9 µm in the two samples [152]. The absorption data for water and heavy water from reference [153] is shown in Figure 6.2(a) along with the power spectrum of the MIR laser in Figure 6.2(c). Because of the MIR pulse’s
proximity to resonance, absorption shifts the pulse slightly red in H₂O and strongly blue in D₂O. The calculated absorption loss for propagation through the liquid source is 94.7% and 98% for H₂O and D₂O, respectively.

Another useful group of samples to try for a liquid HHG experiment are alcohols. Larger molecules, like isopropanol (C₃H₈O), were also studied. Here the absorption of the fundamental is significantly less than in water. Absorption coefficients are included

![Graphs showing absorption profiles and power spectrum](image)

Figure 6.2: (a) Absorption profile of H₂O (solid blue line) and D₂O (dash red line). α is the linear absorption coefficient that obeys \( I = I₀ exp[-αz] \), here \( z \) is the propagation length through the material. (b) Absorption profile of isopropanol (dash black line) and hexane (solid green line). (c) The MIR power spectrum measured by field autocorrelation using the apparatus in Figure 2.11(b).
in Figure 6.2 (b) [154]. Since the other samples are all polar molecules a study was performed in hexane (C₆H₁₄) to determine if the polarity of the molecule has a significant effect on the HG. Compared to the values for water in Figure 6.2(a) for H₂O and D₂O the absorption by alcohols is approximately two to four orders of magnitude lower, respectively, over the bandwidth of the MIR pulse. In C₃H₆O absorption is affected by vibrational modes from the CH as well as the OH stretching vibrations, and C₆H₁₄ only affected by the CH stretch.

Selected Results

Figure 6.3(a) illustrates typical HG spectra in H₂O and D₂O near the maximum pulse power. The highest order harmonic observed (H13 in H₂O and H9 in D₂O) as well as the slow decrease in harmonic intensity with increasing harmonic order in the spectra, suggest a nonperturbative process. However, the intensity scaling, which will be discussed later, demonstrates that this is unlikely. The conversion efficiency of all harmonics is 4 × 10⁻⁶ for H₂O and 1 × 10⁻⁶ for D₂O. At first glance, the difference in yield between HG in water and heavy water is unexpected.

As Fig. 6.3(a) shows, the individual harmonic peaks in the HG spectra in H₂O and D₂O do not coincide and are slightly shifted from the values of λ₀/q where λ₀ is the laser driving wavelength and q is the order of the harmonic, demonstrated by the vertical bars along the wavelength axis. The other striking observation from Fig. 6.3(a) is that even though the electronic structure of H₂O and D₂O are identical their efficiency for
Figure 6.3: (a) Heavy water (dash-red) and water (solid-blue) harmonic spectra at approximately 600 MW of MIR. The vertical bars along the wavelength axis are odd multiples, $\lambda_0/q$ of the fundamental field shown in Fig. 6.2(c). (b) Efficiencies of water and heavy water considering collinear propagation with phase matching and resonant absorption. The vertical bars are the $\text{Imax}/10$ points within the thickness of the fluid. Shown on top is $\text{H}_2\text{O}$ (solid lines-blue) and bottom $\text{D}_2\text{O}$ (dashed lines-red). In both cases $\text{H}5$ is dark, $\text{H}7$ is medium, and $\text{H}9$ is light.

producing harmonics is not. At least two distinct physical mechanisms contribute to the difference in harmonic generation yield. First, there is strong spectral modulation induced on the pulse by resonant absorption from vibrational modes that manifests as strong absorption of short wavelengths of the laser pulse in water and long wavelengths in heavy water. Phase matching can additionally skew the harmonics. It has been demonstrated that self-phase modulation (SPM) can aid phase matching by adding spectral content to the fundamental laser pulse [139]. Consider the total bandwidth (180 nm FWHM) of the MIR pulse, Fig. 6.2(c). Although SPM is not substantial in our experiment the initial bandwidth is, providing an opportunity for phase matching effects
to significantly affect the harmonic spectrum. The phase mismatch in collinear geometry is

\[ \Delta k_q = k_q - qk_0 = \frac{2\pi q}{\lambda_0} \left( n(\lambda_q) - n(\lambda_0) \right) \]  

(6.1)

and the coherence length is \( L_c \equiv \pi / \Delta k_q \) [155]. Large values of \( L_c \) will result in increased conversion efficiency since destructive interference is minimal. For example, the coherence length for H9 at \( \lambda_0 = 3.66 \mu m \) in H\(_2\)O is 9.5 \( \mu m \) i.e. short compared to the sample thickness. If we consider the wavelengths corresponding to the FWHM ends of the spectrum, \( \lambda = 3.57 \mu m \) and \( \lambda = 3.75 \mu m \), the coherence lengths are \( L_c = 6.1 \mu m \) and \( L_c = 15.3 \mu m \) respectively. Clearly, the long wavelength side of the laser will phase-match more efficiently in H\(_2\)O because of the larger coherence length. In D\(_2\)O the corresponding values are \( L_c = 0.98 \mu m \), 1.4 \( \mu m \) and \( L_c = 0.90 \mu m \) for the fundamental (3.66 \( \mu m \)), 3.57 and 3.75 \( \mu m \), respectively. Although the coherence length is much shorter in D\(_2\)O it is clear that the short wavelength side of the laser is preferred. Thus, absorption of the fundamental will introduce a spectral shift that aids phase matching in both samples yielding a long wavelength shifted spectrum in water and a short wavelength shifted spectrum in heavy water. The decreased efficiency in D\(_2\)O is easily explained by the increased absorption of the fundamental and shorter coherence length.

The difference in yield can be addressed more quantitatively by considering only collinear phase matching and resonant absorption. Averaging \( \alpha \) over the entire spectrum of the fundamental and taking \( \Delta k_q \) at \( \lambda_0 \), the HG efficiency parameter, \( \varepsilon(L) \), is [140, 156]

\[ \varepsilon(L) = \left( \frac{2 \exp\left( -\frac{q\alpha}{2} \right)}{\left( \left( \frac{q\alpha}{2} \right)^2 + \Delta k_q^2 \right)} \right) \left( \cosh\left( -\frac{q\alpha}{2} L \right) - \cos(\Delta k_q L) \right), \]  

(6.2)
where \( L \) is the length in the material. Since absorption of the fundamental is different in each sample, \( L \) is estimated to be the propagation length for which the Gaussian focusing geometry and absorption reduce the peak intensity of the field by one order of magnitude. These lengths are indicated in Figure 6.3(b) by black vertical bars. It is assumed the surface of the fluid experiences the peak of the laser focus. The calculated efficiency ratios of \( H_2O/D_2O \) for \( H_5 \), \( H_7 \) and \( H_9 \) are 160, 230 and 440, respectively. As displayed in Figure 6.3(b), the measured ratios are 4, 1.33 and 92. The best agreement is observed for \( H_9 \), however, in all three cases this simple calculation largely overestimates the yield ratio between the two samples.

The total harmonic yield is determined by Eq. (6.2) and the response of the medium. According to Ref. [140] a nuclear contribution to the nonlinear material polarizability from stretching resonances is responsible for the efficiency enhancement. This may be corroborated by our results since \( \lambda_0 = 3.66 \mu m \) is much closer to the OD stretches than the OH stretches. Nuclear enhancements would be expected to decrease with increasing harmonic order, according to perturbation theory, which may explain why the simple calculation agrees best with \( H_9 \). This simplified approach is necessary since knowledge of how the laser propagates in the medium is limited. More rigorous and accurate approaches, such as coherence mapping [157] exist, and may provide better agreement, but are unlikely to describe a discrepancy of one to two orders of magnitude, as measured. Therefore, the simple treatment presented here is preferred to other methods.
The spectra collected in the alcohols vary greatly from those collected in the water isotopes. As shown in Figure 6.4(a) the spectra of isopropanol and hexane do not produce as many harmonic orders as H\textsubscript{2}O. At the highest intensities achievable (around \(1 \times 10^{14}\) W/cm\(^2\) vacuum intensity) Hexane only produces a very small amount of H11, while Isopropanol produces nothing beyond H9.

![Figure 6.4](image)

Figure 6.4: (a) Harmonic spectrum generated in alcohols isopropanol (orange) and hexane (blue) from 3.6\(\mu\)m light at approximately \(1 \times 10^{14}\) W/cm\(^2\). (b) Conversion efficiency as a function of laser energy for harmonics generated in a variety of sources are compared: H\textsubscript{2}O (●-red), D\textsubscript{2}O (■-green), isopropanol(▼-orange) and hexane (□-blue). For each point the yield of H5 and higher are summed to determine the total yield.

Although the harmonics produced by the alcohols are lower in order they do have the distinct advantage of being brighter. The conversion efficiency seen in the alcohols is approximately a factor of 100 greater than in water. Figure 6.4(b) shows the scaling of the HHG conversion efficiency with intensity. For comparison to H\textsubscript{2}O and D\textsubscript{2}O the
yields in isopropanol and hexane are included at $1 \times 10^{14}$ W/cm$^2$. They exhibit close to the same power law scaling with intensity as the waters. The increase in efficiency for hexane and isopropanol is an interesting effect, however the lack of harmonics above the ionization threshold is less than desirable. The significantly decreased level of absorption in isopropanol and hexane is expected to have a contribution to the increase in efficiency. The longer effective propagation length of the Mid-IR laser in the sample also indicates that the efficiency should be higher.

Figure 6.5 illustrates how the experimentally determined harmonic intensity scales with laser power. It is found that the harmonic intensity scales as $I_{q\omega_0} \propto I_\omega^q$ [155]. The results for D$_2$O (not shown) are comparable. In the perturbative limit, the nonlinear polarization of the material

$$P^{(q)}(t) = \sum_q \chi^q E^q(t)$$

is the source for the radiated field at frequency $q\omega_0$. Each data point is the average of several data points in 10% energy increments. H5, H7, and H9 scale in the perturbative limit as described above with power laws of $I^{1.5}$, $I^{7.1}$, and $I^{8.8}$ respectively. These scaling laws hold over an order of magnitude change in intensity and seven orders in signal, down to the single photon-per-event level. In fact, the yield rates do not change until approximately 270 MW where ionization is assumed to become significant. The presence of ionization is corroborated by white light plasma emission. The dominant contribution to H11 no longer appears to be a direct 11 photon process as is the case for the lower harmonics observed. Here the power law decreases to a value of $I^{8.1}$ indicating a clear break in the direct perturbative scaling. One possibility is that lower order indirect
N-wave mixing process(es) is/are contributing to the total yield. For example, consider fifth harmonic generation from a direct process $\chi^5(5\omega; \omega, \omega, \omega, \omega, \omega)$ and an indirect wave mixing process $\chi^3(5\omega; 3\omega, \omega, \omega)$. The observed rate would then scale as a weighted average from all contributing orders and processes; here we measure $I^{8.1}$ for H11. Again the rate holds over the entire measurement up to saturation at approximately 270 MW.

![Graph showing harmonic yield intensity vs laser power](image)

Figure 6.5: The intensity of the harmonic yield is given by the peak of the harmonic field averaged to a single laser shot. The harmonic yields measured were the fifth (■-red), seventh (●-green), ninth (○-blue) and eleventh (▼-orange).

A change in the power law scaling for all harmonic orders at approximately 300MW indicates saturation of the harmonic generation. As the intensity imposed on the fluid is difficult to determine, the exact cause of the saturation is tricky to determine. Heating of the sample is corroborated by a large plume of material emanating from
surfaces of the interaction region. Despite nearly complete absorption of the fundamental during propagation through the sample plumes are observed on both faces of the jet.

Surprisingly, no evidence of significant spectral broadening of the fundamental or supercontinuum generation (SCG) in the near IR or visible portion of the spectrum is observed. A simple argument explains why no significant broadening occurs. Broadening of the fundamental 3.66 μm laser to the visible would require a spectrum that spans more than two octaves. Therefore, an argument can be constructed by considering how the efficiency of SCG will scale with wavelength and focusing conditions in the simple limit where self-phase modulation (SPM) is largely responsible for spectral broadening. First, for a medium with an intensity dependent refractive index, \( n = n_0 + n_2E^2 \), the applied electric field strength, \( E \), determines a critical power:

\[
P_{\text{crit}} = \pi (0.61)^2 \lambda_0^2 / (8n_0n_2)
\]

below which self-focusing and significant SPM do not occur [142]. Since the critical power scales as \( \lambda_0^2 \), we observe that at \( \lambda_0 = 3.66 \) μm, \( P_{\text{crit}} \) is 20 times larger, \( \sim 40 \) MW, than at the Ti:sapphire wavelength of \( \lambda_0 = 0.8 \) μm (neglecting changes in \( n_2 \)). Second, spectral broadening occurs with the accrual of nonlinear phase given by

\[
\phi = 2\pi n_2 P_0 L / (\lambda_0 (\text{Area}))
\]

for a pulse with peak power \( P_0 \), and propagation length \( L \) [158]. If the focusing conditions are such that the Rayleigh range is much larger than \( L \), \( \phi \propto \lambda_0^{-3} \), and spectral broadening decreases accordingly. Combining these two arguments with the fact that, even at 800 nm, experiments show minimal spectral broadening in the wings of the pulse
representing only a few percent of the total power spectral density, we assert that SPM and SCG are strongly suppressed in the experiments performed here.

Another interesting feature observed in HG from liquid water is a clean spatial mode, displayed in Figure 6.6(a). Measurements of the mode of the 5th harmonic of 3.66 µm were made as a function of intensity using a CCD camera (Genwac: GW-525EX) positioned 0.9 and 2.0 inches from the interaction region to determine the divergence angle of the harmonics. The other harmonic orders were considerably weaker and more difficult to spectrally filter, so these were not recorded. The results of the divergence study are presented in Figure 6.6(b). The half angle of the divergence remains approximately constant for low laser powers and decreases rapidly above approximately 35 µJ, which corresponds to the saturation intensity of 270 MW observed in the harmonic yield in Figure 6.5. This sudden change in the divergence and the saturation of the yield are thought to be a result of ionization in the sample.

![Figure 6.6: Spatial mode of the 5th harmonic of 3.66 µm generated in liquid water in (a). The divergence (half-angle) measured for the 5th harmonic as a function of laser energy is included in (b).](image)
In order to better understand the role played by the proximity of the OH/OD and CH/CD stretching vibrational resonances it is instructive to compare isopropanol (C\textsubscript{3}H\textsubscript{8}O) to its deuterated counterpart (C\textsubscript{3}D\textsubscript{8}O). Since C\textsubscript{3}D\textsubscript{8}O is very expensive, and the liquid jet described in Figure 6.1 requires a large amount of a sample, studying its liquid response is cost-prohibitive. In vapor the stretching vibration resonance is expected to be narrower than in the liquid, however the resonance is still strong near the MIR laser wavelength. The vapor should also exhibit a much longer propagation length due to the lower density.

\textit{Vapor Cell}

Instead a vapor cell was used to introduce each C\textsubscript{3}H\textsubscript{8}O and C\textsubscript{3}D\textsubscript{8}O to the interaction region for a comparative study. A room-temperature vapor cell design using parts from the heat pipe used in Ref. [141] produces vapor pressures up to \(~\text{30 torr}\). The general design is shown in Figure 6.7.
Isopropanol liquid and vapor harmonic spectra are shown in Figure 6.8. The spectra were recorded at different gain settings and are not corrected for the factor of $2 \times 10^4$ increase in gain used for the vapor spectra so that they are easily comparable with the same scale. The harmonics produced in the gas phase are reminiscent of the liquid phase spectra; however they lack the bandwidth of their liquid counterparts. Hints of $H_{11}$ and even $H_{13}$ seem to be evident in the vapor spectrum, near the single photon limit of the detection system, while the liquid produces up to $H_{11}$ and an unidentified feature between where we expect $H_{13}$ and $H_{15}$ to appear.
Figure 6.8: Isopropanol harmonics generated at comparable laser energy in a liquid film with a gain of 1 (red) and in a 30 Torr vapor with a gain of 9 (green). The difference in gain setting from 1 to 9 yields approximately a factor of $2 \times 10^4$ in signal.

In Figure 6.9, HG spectra of the vapors of $\text{C}_3\text{H}_8\text{O}$ and $\text{C}_3\text{D}_8\text{O}$ are compared. The two spectra are almost identical with a small increase in harmonic efficiency in $\text{C}_3\text{D}_8\text{O}$ and hints of $\text{H}11$. Unlike the water harmonics the $\text{C}_3\text{H}_8\text{O}$ and $\text{C}_3\text{D}_8\text{O}$ harmonics are not shifted spectrally from their expected $\lambda_0/q$ center wavelengths. Since the absorption coefficient is relatively flat and a factor of 100 lower across the bandwidth of the MIR the lack of spectral shift is to be expected. HG in alcohols seems to behave similarly to HG in water, as the highest harmonic order produced and the scaling of the harmonic yield with intensity appears to be perturbative.
Strong Field Response in Gas Phase Water Molecules

As a measure of the strong field response of water molecules we studied photoelectron energy spectra from H$_2$O and D$_2$O. Due to the complexity of condensed phase dynamics, it is difficult to determine the effect of processes like ionization on harmonic generation and the effective intensity experienced by the sample. Ionization must be present in the liquid sample since a significant amount of white light plasma emission is visible by eye. The most straightforward way to measure ionization is in the gas phase, utilizing the time of flight (TOF) ion and electron spectrometer described in Chapter 3.

Photoelectron energy spectra and ionization yield curves for H$_2$O and D$_2$O are displayed in Figure 6.10(a) and (b), respectively. The ionization potential for the ground
state of both water samples is 12.6 eV. Using a 3.6 µm laser, the high intensity used, 8x10^{13} \text{ W/cm}^2, corresponds to the tunneling regime. The spectra exhibit the features expected from semiclassical theories for rescattering, namely an exponential decay to 2U_p and a long plateau out to approximately 10U_p. A spectrum of xenon at

![Graph](image)

**Figure 6.10:** (a) Photoelectron energy spectra from H_2O (red), D_2O (green) collected at an intensity of 8x10^{13} \text{ W/cm}^2 and xenon (blue) collected at 7x10^{13} \text{ W/cm}^2. (b) Ionization yields collected for H_2O (○-red), D_2O (□-green) and xenon (◊-blue).

similar laser intensity is included for comparison since the value of I_p = 12.1 eV is very close to that of water. H_2O and D_2O spectra are almost identical and are distinguished from xenon by the drop in the plateau height by almost a factor of five.
The ionization yield curves in Figure 6.10(b) indicate that the ionization response of H\textsubscript{2}O and D\textsubscript{2}O is the same. This is to be expected since the tunneling ionization rate is the same for two systems with the same ionization potential. The xenon ion yield is approximately a factor of three higher than that of water, as expected from a species with a smaller value of I\textsubscript{p}. Both molecules experience a yield that scales as \sim I^{0.5}. The PES indicates that the ionization is in the strong field regime, so the perturbative scaling of the harmonics in liquid water must be a result of the condensed phase dynamics.

6-3: Harmonics Generated in Crystals

While HHG studies in liquids do not produce high enough order harmonics to be a candidate for the production of attosecond pulses, they yield some interesting results as to the strong field response of condensed media. In flowing samples of water, heavy water, isopropanol, and hexane, we were able to observe the role of vibrational resonances on high harmonic yields. In a recent experiment on ZnO crystals using the MIR laser system with the central frequency tuned to 3.25 \( \mu \)m, we were able to make the first observation of high order harmonics in the bulk of a crystalline solid, as well as study the strong field effects on the band structure of the crystal [159]. A major difficulty to generating high harmonics in bulk material is overcoming the damage threshold of the material. Using 70 fs pulses at 0.8 \( \mu \)m the measured single-shot ablation threshold of ZnO is 0.6 V/ \( \text{Å} \). With a 3.25 \( \mu \)m laser it was possible to impose a field of 0.6 V/ \( \text{Å} \) on the sample at a 1kHz repetition rate without damage. At 3.25 \( \mu \)m nine photons are required to promote electrons from the valence to the conduction band, compared to two
photons of 0.8 µm light, indicating that the lower photoabsorption cross-section for the higher-order process plays a role in the increase of the damage threshold.

Using a 3.25 µm laser and a 500 µm-thick sample of ZnO, harmonics up to the $17^{\text{th}}$ and $25^{\text{th}}$ order were recorded using 0.52 and 2.63 µJ, respectively, as shown in Figure 6.11. Harmonics extend well beyond the 3.2 eV band edge of the crystal, producing significant non-perturbative behavior, under conditions where the laser’s electric field (~0.6V/Å) across a lattice constant is comparable to the band gap (3.2 eV). In addition to the odd-order harmonics, fluorescence at 3.2 eV from electron-hole recombination is evident in the spectra. As shown in Figure 6.11(b), the cutoff of the harmonic spectrum scales linearly with the field strength of the drive laser in contrast to those generated in the gas phase, which scale quadratically with field strength.

The ZnO harmonics differ from those generated in liquids because of the periodic nature of the bulk material. The yield of all harmonic orders is very steep below saturation at an estimated intensity of 1 TW/cm$^2$. An $I^{15}$ power law is plotted with the data to illustrate the non-perturbative scaling recorded for even the lowest order harmonics. The excursion amplitude is still larger than the lattice constant of a typical crystal, indicating that ionization from one site and recombination at another is likely, however unlike the liquid case the crystal periodicity allows the process to remain coherent [159]. Before this experimental data non-perturbative HHG from a bulk crystal has been predicted [160-162], but never observed.
Figure 6.11: Measured high-order harmonic spectra and field dependence of the cutoff. (a) Spectra from a 500µm-thick ZnO crystal where the optic axis is perpendicular to the surface. The wavelength of the driving field is centered at 3.25 µm. The spectra correspond to driving pulse energies (estimated vacuum field strengths) of 0.52 µJ (0.27V/Å) – green and 2.63 µJ (0.6V/Å) – blue. The inset shows an expanded view of the 2.63 µJ spectrum on a linear scale. The dotted vertical line marks the approximate band edge of the crystal as indicated by the residual fluorescence signal. (b) The high-energy cutoff scales linearly with drive-laser field.
Further description of HHG in a bulk solid is included in Ref. [161]. A simple model is used to describe the harmonic generation process in terms of Bloch oscillations. The harmonics are identified as the result of a combination of Bragg scattering near the peaks of the electric field and the anharmonic oscillation of the band edge [161]. As this repeats every half cycle of the laser field only odd order harmonics are expected. For a cosine band the cutoff of the harmonic spectrum is expected to extend to:
where $n$ is the order of the last harmonic produced, $\omega_B$ is the Bloch frequency, and $a$ is the lattice spacing. This explains the linear scaling of the harmonic cutoff with drive laser field shown in Figure 6.11(b). The HHG spectrum itself is expected to carry information about not only the electron dynamics, but also the dressed band structure in the strong-field limit [159, 163].

The above experiments performed in condensed phase media constitute the first successful attempt to generate high-order harmonics in the bulk of liquid or solid media. Although the total harmonic yield is still quite low, the results are instructive into the nature of the strong-field response of condensed-phase media. Future studies on HHG in crystalline solids could potentially yield a solution to the low conversion efficiency of high harmonic generation.
Chapter 7: Conclusions

In the regime where the electric field of the interrogating laser is comparable to the binding field of the atom, the system is subjected to some very interesting dynamics. These dynamics are described in the literature with respect to light in the visible and near-infrared. In this document evidence has been presented that similarly complex dynamics occur in the mid-infrared. By increasing the laser wavelength and combining Keldysh theory and the quadratic scaling of the ponderomotive energy, $U_p$, with $\lambda$, it is possible to explore new regimes of the strong-field interaction.

In chapters 4 and 6 the effect of a strong mid-IR field on the electronic and vibrational structure of atomic and molecular systems was considered. Above threshold ionization of cesium atoms indicates a very strong dependence on the atom’s electronic structure. The strong coupling between the ground state and the low-lying first excited state has a significant effect on the photoelectron energy spectrum. Individual ATI peaks are split by the fine structure of the 6P state. When high harmonic generation is driven in molecular liquids, resonant vibrational levels play an important role in the harmonic production. The combined effects of absorption and phase matching produce spectrally shifted harmonics as a function of the driving laser’s proximity to the vibrational resonance. These resonant effects illustrate the influence of electronic structure on the strong-field processes.
An in-depth study of the photoionization of cesium atoms by an intense, mid-infrared laser indicate that the complex mechanisms behind strong field ionization give rise to some very interesting dynamics. Understanding the role of ionization dynamics versus electronic structure in strong-field processes is very important to the interpretation of strong field phenomena and the development of attosecond techniques. The application of Keldysh-scaled systems addresses the similarities (and differences) in the above quantities by changing the atomic system and wavelength used, but maintaining similar ionization dynamics, described by the Keldysh parameter, \( \gamma \). Over the last few decades surprising results have been obtained in argon and xenon in the visible and near-IR. The Keldysh-scaled equivalent system of cesium in the mid-IR presented in Chapter 4 yields qualitatively similar results. Quasi-resonant enhancements of the ATI spectrum appear as a result of a coupling between ionization from excited states and rescattering. These enhancements are particularly strong in cesium. The strong coupling of cesium to its excited states could be evidence that the excited state picture is accurate. The insensitivity of the enhancements in cesium to ellipticity is evidence that the interpretation of bunching and focusing of electron wavepackets that become trapped near the core proposed by Muller, et al., is accurate.

When wavelength is increased the ponderomotive energy gained by the free electron becomes significant, changing the dynamics of electron rescattering. As discussed in Chapter 5, the strong effect of rescattering is important for both the inelastically and the elastically scattered electrons. The factor of 20 increase in ponderomotive potential between 0.8 and 3.6 \( \mu \)m experiments causes the electrons to
gain sufficient energy for comparison with electron gun experiments. The extreme effect of this wavelength dependence produces up to the 6th charge state in xenon at a moderate intensity of $1 \times 10^{14}$ W/cm$^2$. In contrast to near-IR experiments the higher charge states are produced at a much higher rate due to impact ionization. The elastically scattered electrons carry away information about the structure of their parent ion. Structural information can be retrieved from the angular distribution of the photoelectron angular distribution. Utilizing the scattering of electrons off of their parent ion could become a valuable tool for understanding molecular dynamics with sub-laser-cycle time resolution.

The method behind laser-induced electron diffraction is of great interest in the strong-field physics community, as it allows for both fine temporal and spatial resolution. The mid-IR spectral range is very promising for further investigation of the strong-field response of condensed phase media, as discussed in Chapter 6. The first description of high harmonic generation in the bulk of a crystal has recently been reported utilizing mid-IR fields. Future results will increase the understanding of the response of the band edge to a strong field. In addition to producing high harmonics the oscillation of the band structure is likely to produce interesting dynamics of its own. This is analogous to the effect of the AC Stark effect in atomic and molecular systems.

The mid-IR spectral range has a lot of potential for addressing the dynamics of atomic and molecular systems in strong fields. The effect of the first excited state fine structure on the ATI spectrum of cesium could be addressed by increasing the intensity resolution. The other alkalis can be expected to produce similar dynamics and have a
similarly large contribution from the low-lying excited states. A study of another alkali species could solve some of the unanswered questions pertaining to cesium.
References


[113] In atomic units: $U_p = F^2/4\omega^2$, where $F$ and $\omega$ are the amplitude and frequency of the laser field, respectively.


