WAVELENGTH DEPENDENT STRONG FIELD INTERACTIONS WITH ATOMS AND MOLECULES

DISSERTATION

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Abstract

In the regime of strong-field physics the electric field of a laser begins to strongly rival the binding potential of an atomic or molecular species. During these interactions an ionized electron can be driven away and then back towards its parent ion by the strong laser field and undergo rescattering before being detected. The amount of energy an electron can acquire during propagation is proportional to the laser intensity and the square of the wavelength. Recent improvements in laser technology have allowed us to push strong-field studies from visible/near-infrared wavelengths to the mid-infrared regime and thereby greatly increase the electron’s maximum recollision energy. These high energy scattering events imprint target dependent structural information on the electron angular distribution from which we can extract atomic and molecular specific properties. Further, Keldysh invariance suggests that we can control the dominant ionization mechanism (multiphoton absorption versus tunneling through the field modified potential) by choosing an appropriate laser wavelength, laser intensity and target atom. Exploratory investigations in strong-field physics have produced many fascinating results which have led to production of attosecond duration laser pulses and atomic/molecular imaging techniques. As technological improvements continue we are able to gain further insights into these interesting physical phenomena.

In this work we examine photoelectron spectra and ion yields in order to gain a deeper understanding of the fundamental processes that underlie atomic and molecular strong field interactions. Alkali metal atoms at mid-infrared wavelengths possess similar Keldysh parameter values as noble gas atoms at near-infrared wavelengths, which have received much more investigative attention. Therefore, by examining alkali metal atoms at longer wavelengths we hope to expand on our understanding of the global, Keldysh invariant, and atom specific ionization features. We also examine photoelectron spectra of the noble gases at visible/near-infrared wavelengths in order to further explore the origins of the, as of yet, not completely understood enhancement features related to rescattered electrons. Finally, by using the mid-infrared laser source, which allows for high return energies of the rescattering electrons, we experimentally extract atomic elastic scattering differential cross-sections as well as bond lengths in the C\textsubscript{60} molecule.
Dedicated to my family
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Table of Contents

<table>
<thead>
<tr>
<th>Chapters</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> Introduction to Strong Field Interactions</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Ponderomotive Energy and the AC Stark Shift</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Keldysh Scaling</td>
<td>5</td>
</tr>
<tr>
<td>1.2.1 Multiphoton Ionization ($\gamma &gt; 1$)</td>
<td>6</td>
</tr>
<tr>
<td>1.2.2 Tunneling Ionization, $\gamma &lt; 1$</td>
<td>11</td>
</tr>
<tr>
<td>1.2.3 Over-The-Barrier Ionization</td>
<td>11</td>
</tr>
<tr>
<td>1.3 Semiclassical Description</td>
<td>12</td>
</tr>
<tr>
<td>1.3.1 Simpleman Model</td>
<td>12</td>
</tr>
<tr>
<td>1.3.2 Rescattering</td>
<td>13</td>
</tr>
<tr>
<td>1.4 Quantum Mechanical Models</td>
<td>20</td>
</tr>
<tr>
<td>1.4.1 Ammosov-Delone-Krainov (ADK) Theory</td>
<td>20</td>
</tr>
<tr>
<td>1.4.2 Strong-Field Approximation (SFA)</td>
<td>25</td>
</tr>
<tr>
<td>1.4.3 Single Active Electron Time Dependent Schrödinger Equation (SAE-TDSE)</td>
<td>27</td>
</tr>
<tr>
<td><strong>2</strong> Experimental Setup</td>
<td>28</td>
</tr>
<tr>
<td>2.1 Generating Short, Intense Laser Pulses</td>
<td>28</td>
</tr>
<tr>
<td>2.2 MIR Laser System</td>
<td>31</td>
</tr>
<tr>
<td>2.2.1 Ti:sapphire/CPA</td>
<td>32</td>
</tr>
<tr>
<td>2.2.2 OPA</td>
<td>35</td>
</tr>
<tr>
<td>2.3 $2\mu m$ OPA System</td>
<td>41</td>
</tr>
<tr>
<td>2.3.1 Application for Noble Gas Experiments</td>
<td>41</td>
</tr>
<tr>
<td>2.4 Time-of-Flight Spectrometer</td>
<td>42</td>
</tr>
<tr>
<td>2.4.1 Photoelectron Energy Spectrum Detection</td>
<td>48</td>
</tr>
<tr>
<td>2.4.2 Ion Mass Spectrum Detection</td>
<td>48</td>
</tr>
</tbody>
</table>
3 Alkali Metal Atoms in Wavelength Scaled Systems
3.1 Ion Yield Analysis .............................................. 64
3.2 Photoelectron Energy Spectra ................................ 73
3.3 Photoelectron Angular Distributions ....................... 85
  3.3.1 Quantitative Rescattering Scattering Theory (QRS) .... 86
  3.3.2 Experimental Results ..................................... 87

4 Wavelength Dependence of Photoelectron Emission ......... 96
4.1 Experimental Setup ............................................ 99
  4.2 Experimental Results and Analysis ......................... 101
    4.2.1 Intensity Dependence .................................. 101
    4.2.2 Wavelength Dependence ................................ 106
    4.2.3 Species Dependence .................................... 109
    4.2.4 Trajectory Analysis ..................................... 110

5 Laser Induced Electron Diffraction in C_{60} ................. 117
  5.1 Experimental Setup ......................................... 120
  5.2 Ionization and Fragmentation ............................... 121
  5.3 Laser Induced Electron Diffraction (LIED) in C_{60} ....... 123
  5.4 Discussion and Outlook ..................................... 128

6 Conclusions .................................................. 131

Bibliography .................................................. 133
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic diagram of the AC Stark effect on the bound and continuum states of an atom. The Rydberg and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>continuum states shift by approximately $U_p$ while the ground state experiences a relatively weaker</td>
<td></td>
</tr>
<tr>
<td></td>
<td>shift dependent on its polarizability. The orange arrows indicate single photon energies. Figure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>reproduced from [10].</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Ionization mechanisms as described through the Keldysh picture. From top-down: the perturbative limit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>where ionization can occur through single photon absorption; multiphoton ionization ($\gamma &gt; 1$);</td>
<td></td>
</tr>
<tr>
<td></td>
<td>tunneling ionization ($\gamma &lt; 1$); and over-the-barrier ionization ($\gamma \ll 1$) where the barrier</td>
<td></td>
</tr>
<tr>
<td></td>
<td>is completely suppressed. The field free atomic potential is shown in black, the laser field in red,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and the combined potential in blue. The electron wave packet is shown in green. GS denotes the ‘ground</td>
<td></td>
</tr>
<tr>
<td></td>
<td>state’ and IP the ‘ionization potential’. Read text for more details. Figure reproduced from [10].</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>Limits of perturbation theory as a function of wavelength. The horizontal dashed-black line corresponds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>to an atomic unit of intensity, $3.5 \times 10^{16}$ W/cm$^2$. The red, blue and green dashed lines</td>
<td></td>
</tr>
<tr>
<td></td>
<td>correspond to $z_1 = 1$, $z = 1$, $z = 0.1$ respectively. The continuum state intensity parameter, $z$,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>is usually viewed as the better indicator of perturbation theory break down. The two vertical lines at</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800nm and 4000nm correspond approximately to the wavelengths used in the experiments discussed in this</td>
<td></td>
</tr>
<tr>
<td></td>
<td>thesis. All experiments were performed at intensities above the perturbative domain.</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Photoelectron spectra showing ATI in xenon with 135ps pulses at a wavelength of 1064nm. Laser intensity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>is highest in the lowest panel. As intensity increases the maximum ATI order increases and the low order</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATI begin to be suppressed due to channel closure. Image reproduced from Yergeau et al [14].</td>
<td>9</td>
</tr>
</tbody>
</table>
1.5 The 3-Step-Model. In the lower images the dashed-blue line is the shape of the field free potential, the dashed-red line is the effect of the applied field, and the black-solid line represents the effective potential. Step 1: near the peak of the field the potential is maximally suppressed and the electron is the most likely to tunnel into the continuum. Step 2: the electron propagates in the continuum under the influence of the applied field. Step 3: the electron is driven back towards the nucleus and rescatters or recombines (releasing a high energy photon).

1.6 Calculation of an electron’s return energy in unit of $U_p$ as a function of its birth phase. The ‘long’ and ‘short’ distinction is made because there are two classical trajectories an electron can take that result in the same return energy.

1.7 Argon photoelectron spectra at $8 \times 10^{13} W/cm^2$ taken at four different wavelengths: 0.8$\mu$m (solid), 1.3$\mu$m (dash-dot), 2$\mu$m (dash), and 3.6$\mu$m (dot). When plotted in absolute energy units the spectra look very different (a). However, when plotted in units of the ponderomotive energy, $U_p$, the scaling is much more obvious (b). The inset in (a) shows the ratio of electrons detected with $>2U_p$ energy to those with $<2U_p$ energy as a function of wavelength. Figure reproduced from Colosimo et al [27].

1.8 Argon photoelectron spectra taken with 630nm, 40fs pulses at $2.4 \times 10^{14} W/cm^2$. Linearly polarized (a) and circularly polarized (b) light was used. Notice the suppression of the plateau when rescattering is suppressed. Figure reproduced from Paulus et al [22].

1.9 Ion yield as a function of intensity in helium. Taken with 780nm, 160fs laser pulses. The solid lines correspond to theoretical calculations that neglect the nonsequential double ionization process. The symbols indicate experimental results. Figure reproduced from [31].

1.10 High-harmonic spectra taken in argon at $1.8 \times 10^{14} W/cm^2$ with 0.8$\mu$m (dashed, gray fill) and 2$\mu$m (solid, yellow fill). The later spectra is cut off by the edge of the aluminum filter. The real cutoff occurs $\sim$ 220eV. Figure reproduced from [27].

1.11 ADK calculation for the fractional ionization (blue line) of argon under the influence of a 3.6$\mu$m, 100fs laser pulse at a peak intensity of $3 \times 10^{14} W/cm^2$. Notice how the ionization rate increases near the peaks of the electric field of the applied pulse (red line).

2.1 A grating based stretcher. The outgoing pulse will have a longer temporal duration and lower peak power. The stretcher produces a positive chirp since the ‘red’ portion of the spectrum (longer wavelengths) will travel a shorter net distance than the ‘blue’ portion. G1 and G2 are diffraction gratings, L1 and L2 are lenses with focal length f, RR is a retro-reflector, M is a mirror for the outgoing pulse and d represents a length which determines the stretching factor.

2.2 The compressor. After amplification the compressor returns the stretched pulse to its original temporal length, basically undoing what the stretcher did. G1 and G2 are gratings and M is a mirror that diverts the compressed pulse.
2.3 The CPA based Ti:sapphire laser system layout. The important pulse duration and energy values have been labeled. The pump powers have also been included. See text for more details. .......................... 33

2.4 A schematic of the Ti:sapphire system timing electronics which synchronize the temporal overlap of ‘pump’ and ‘signal’ pulses, and provide a trigger to the detection electronics (discussed in Sec. 2.4). See text for more details. 34

2.5 Performance of the 792nm beam immediately preceding the OPA. Left panel: the autocorrelation trace. This corresponds to 95fs for a Gaussian beam. Right panel: a FROG trace of the beam. A rounder shape signifies a closer to transform limited pulse. The side lobes signify a contribution from higher order dispersion. .......................... 34

2.6 MIR OPA layout. The input pump is split into four arms by beam splitters BS1-3. The weakest arm drives the broadband white light continuum generation (WLCG) stage. The resulting seed pulses are amplified in three KTA crystals, generating tunable 150µJ MIR pulses. The optical elements are: half wave plate (HWP), lenses (L1-2), telescopes (T1-3), dichroic mirrors (DM1-5), mirrors (M1-2) and beam dumps (BD) .......................... 38

2.7 White light continuum generation spectrum and the double pass signal. The WLCG spectrum (blue) was measured after the preamplifier stage with the pump arms blocked. After two amplification stages, the WLCG spectrum is narrowed by the acceptance angle of the KTA crystal to produce a 30nm FWHM signal pulse (red). .......................... 39

2.8 OPA tunability. Tunability of signal spectra after the preamplifier. The gap-free tunability allow generation of tunable 2.7-4µm pulses. .......................... 39

2.9 OPA Performance. Measured photoelectron spectra in xenon at 3.6µm. The vertical green dash line marks the so-called 2Up break, the maximum energy for direct electrons. This method allows us to infer an intensity of 80TW/cm². In the inset, the profile of the MIR beam before the vacuum chamber. .......................... 40

2.10 Light Conversion’s HE-TOPAS-Prime output beam characterization. The pulse energy as a function of wavelength for the signal and idler beams is plotted. .......................... 41

2.11 The % transmission and reflection curves for the DMSP1000, 45° AOI. The fundamental is p-polarized and has a wavelength range of 1100–1600nm. The BBO doubled signal is s-polarized with a wavelength range of 550 – 800nm. Characterization provided by Thorlabs. .......................... 42

2.12 Side view of the Time-of-Flight spectrometer. The listed dimensions correspond to the ‘Oven Chamber’ design. .......................... 44

2.13 Side view of the multichannel plate (MCP) based detector. The two MCP plates are arranged in a Chevron configuration. The exiting cascade of electrons are collected onto a gold coated Kapton foil. The output signal is capacitively coupled through the conical anode and further processed before detection. Applied voltages in electron and ion mode are shown in red and blue respectively. .......................... 45

2.14 Schematic layout of the detection electronics. See text for detailed description. 46
2.15 Photoelectron spectra for argon with 100fs pulses at 792nm. The clear ATI peaks allow for calibration of the TOF spectrometer energy axis. The blue vertical dashed lines are shown at increments of 1.57eV, corresponding to one-792nm photon. ................................................................. 49
2.16 Ion lens voltages are optimized by using xenon since it has multiple close lying isotopes. The mass spectrum above corresponds to 295V on $P_1$, 45V on $P_2$ and 0V on $P_3$. ................................................................. 50
2.17 Alkali metal oven layout (side view) and positioning within the chamber. The oven is mounted below the interaction region and the atomic beam travels upward. The atomic beam, laser propagation direction (out of the page) and the flight tube axis are all perpendicular to each other. $P_1$, $P_2$ and $P_3$ is the ion lens field plate assembly, S and C are the source and collimator apertures respectively, R is the alkali metal reservoir and J is the water cooled jacket. Figure reproduced with minor modification from the thesis of Dr. Emily Sistrunk [59]. ................................................................. 52
2.18 Alkali oven temperature versus voltage calibration. The two curves represent the response of a type-K thermocouple attached directly to the heater wire and to the bottom of the copper cup insert. ................................................................. 53
2.19 Calculated vapor pressure as a function of temperature in the oven reservoir. 54
2.20 Calculated mean free path of the alkali atoms as a function of temperature. The collisional cross-section is approximated by treating the atoms as hard spheres. Also included is the radius of the source aperture, $r_s = 0.15$mm. ..... 55
2.21 Zoomed in view of the atomic beam portion of the alkali oven; $w_s$ and $w_c$ are the widths of the source and collimator apertures respectively, $l_{sc}$ and $l_{cd}$ are the source to collimator and collimator to interaction region distances. The size of the atomic beam at the point where it intersects the laser beam path is sufficiently large to approximate a constant density across the focal volume. 56
2.22 Density of the alkali atoms in the interaction region as a function of the oven temperature. ................................................................. 57
2.23 Layout of the C$_{60}$ oven. ................................................................. 59
2.24 Calibration of the oven temperature as a function of applied voltage. .... 59
2.25 The black and red circles correspond to measured ion yields of C$_{60}^+$ and C$_{60}^{++}$ at a laser intensity of $2 \times 10^{13}$W/cm$^2$. These ion yields are plotted as a function of oven temperature and benchmarked to published vapor pressure measurements [72]. ................................................................. 60

3.1 Ion yield vs intensity curves for Na$^+$ performed at three different wavelengths. The two lines are $I^N$ fits to the below and above saturation data points (N is the number of photons; this corresponds to the slope on a log-log plot). The intersection of these lines corresponds to the experimentally determined saturation intensity. ................................................................. 65
3.2 Ion yield vs intensity curves for K$^+$ performed at three different wavelengths. The two lines are $I^N$ fits to the below and above saturation data points (N is the number of photons; this corresponds to the slope on a log-log plot). The intersection of these lines corresponds to the experimentally determined saturation intensity. ................................................................. 66
3.3 Na\(^+\) ion yield at 4\(\mu\)m. Black squares correspond to the experimentally measured values; this is the same data as presented in Fig. 3.1. The solid lines correspond to the ADK model calculations for ionization from the 3s ground state (blue), ionization from the 3p excited state (green) and the total ionization using our model (red). See text for more details. .......................... 69

3.4 Na\(^+\) ion yield comparison between experiment (black squares) and the calculated best fit ionization rate (red line). The model considers two ionization pathways; direct ionization from the ground state and ionization through the intermediate 3p excited state (see text). The final parameters for the plotted curves are: \(n=7, \sigma_n=7.61\times10^{25}\) a.u. (atomic units) for 3.2\(\mu\)m; \(n=7, \sigma_n=7.75\times10^{25}\) a.u. for 3.7\(\mu\)m; \(n=7, \sigma_n=7.52\times10^{25}\) a.u. for 4.0\(\mu\)m. ............. 71

3.5 K\(^+\) ion yield comparison between experiment (black squares) and the calculated best fit ionization rate (red line). The model considers two ionization pathways; direct ionization from the ground state and ionization through the intermediate 4p excited state (see text). The final parameters for the plotted curves are: \(n=7, \sigma_n=3.53\times10^{27}\) a.u. (atomic units) for 3.2\(\mu\)m; \(n=5, \sigma_n=1.63\times10^{17}\) a.u. for 3.6\(\mu\)m; \(n=5, \sigma_n=6.46\times10^{17}\) a.u. for 4.0\(\mu\)m. ............. 71

3.6 Sodium at 3.3\(\mu\)m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 5.8TW/cm\(^2\) (\(\gamma = 0.65\)), 4.8TW/cm\(^2\) (\(\gamma = 0.72\)), 4.2TW/cm\(^2\) (\(\gamma = 0.76\)) and 3.5TW/cm\(^2\) (\(\gamma = 0.84\)). ............. 75

3.7 Sodium at 3.6\(\mu\)m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 6.4TW/cm\(^2\) (\(\gamma = 0.57\)), 5.3TW/cm\(^2\) (\(\gamma = 0.63\)), 4.3TW/cm\(^2\) (\(\gamma = 0.70\)), 3.6TW/cm\(^2\) (\(\gamma = 0.76\)) and 2.9TW/cm\(^2\) (\(\gamma = 0.84\))....................... 75

3.8 Sodium at 3.7\(\mu\)m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 7.2TW/cm\(^2\) (\(\gamma = 0.53\)), 6.2TW/cm\(^2\) (\(\gamma = 0.57\)), 5.2TW/cm\(^2\) (\(\gamma = 0.62\)), 3.8TW/cm\(^2\) (\(\gamma = 0.72\)) and 3.3TW/cm\(^2\) (\(\gamma = 0.78\))....................... 76

3.9 Sodium at 3.8\(\mu\)m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 6.0TW/cm\(^2\) (\(\gamma = 0.56\)), 5.5TW/cm\(^2\) (\(\gamma = 0.59\)), 4.9TW/cm\(^2\) (\(\gamma = 0.63\)), 4.2TW/cm\(^2\) (\(\gamma = 0.68\)) and 3.5TW/cm\(^2\) (\(\gamma = 0.73\))....................... 76

3.10 Potassium at 3.4\(\mu\)m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 1.6TW/cm\(^2\) (\(\gamma = 1.24\)), 1.4TW/cm\(^2\) (\(\gamma = 1.31\)), 1.2TW/cm\(^2\) (\(\gamma = 1.40\)) and 1.0TW/cm\(^2\) (\(\gamma = 1.51\)). ............. 77
3.11 Potassium at 3.7µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 2.3TW/cm² ($\gamma = 0.93$), 2.1TW/cm² ($\gamma = 0.97$), 2.0TW/cm² ($\gamma = 0.99$), 1.8TW/cm² ($\gamma = 1.05$) and 1.5TW/cm² ($\gamma = 1.13$).

3.12 Potassium at 3.9µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 2.3TW/cm² ($\gamma = 0.89$), 2.1TW/cm² ($\gamma = 0.94$), 1.8TW/cm² ($\gamma = 1.00$), 1.6TW/cm² ($\gamma = 1.06$) and 1.4TW/cm² ($\gamma = 1.16$).

3.13 The elastic differential backscattering ($\theta = \pi$) cross-sections for potassium (short-dashed line), sodium (solid line), and the modified potassium atom (long-dashed line). The cross-section for hydrogen (circles) is shown for comparison.

3.14 SFA calculations for sodium at 3.65µm at four intensities (top curve corresponds to the highest intensity). The calculation used a 5-cycle trapezoidal pulse and includes focal volume averaging. Calculations were performed by Dr. Junliang Xu.

3.15 Two examples of the overlap between SFA calculations and the 3.6µm sodium data. The two examples shown are at the lowest and highest experimentally collected intensities. The best fit between data and experiment was chosen by matching at the 2$U_p$ break.

3.16 Photoelectron energy spectra for Br$^-$ at 1.3µm and 6.5×10¹³W/cm². Spectra was taken along the laser polarization with linearly polarized light. The experimental results (circles); SFA calculation which includes rescattering (solid line); and an SFA calculation which only accounts for direct electrons (dashed line) are shown. Figure reproduced from [92].

3.17 Panel (a) is reproduced from [91]. The two birth times that contribute to the trajectories that produce the ‘bump’ in negative ions are labeled as $t^+_1$ and $t^+_2$, they are symmetric with respect to the zero crossing of the field. Panel (b) shows physically the behavior of the atomic/negative-ion potential and ionizing electron. The laser field at the moment of ionization is displayed by the red-dashed lines. Also shown are the two trajectories (after ionization) that contribute to this interference.

3.18 Potassium photoelectron spectra at 3.4µm and 3.7µm. The shaded areas correspond to the predicted enhancement regions for the 15-photon (purple) and 17-photon (green) channel closures.
3.19 Calculated results for sodium and potassium interacting with a $3.2\mu m$, 5-cycle pulse with a peak intensity of $1.0TW/cm^2$. Panel (a) and (b) are 2D photoelectron momentum distributions calculated using TDSE and the QRS model for the two species. These are only compared in the rescattering region of $>4U_p$. Panels (c) and (d) show the calculated DCS for large scattering angles at three different electron return momenta, $p_r$. Panel (e) shows the angle-integrated photoelectron spectra vs detected energy. The TDSE (solid lines) and QRS (dotted lines above $4U_p$) results are plotted together. Panel (f) is a comparison to experimental data; potassium was performed at $1.5TW/cm^2$ and sodium at $1.8TW/cm^2$.

3.20 Sodium 2D electron momentum distribution. Taken at $3.6\mu m$ and $5.5TW/cm^2$. The momentum is expressed in terms of atomic units.

3.21 Potassium 2D electron momentum distribution. Taken at $3.6\mu m$ and $2.2TW/cm^2$. The momentum is expressed in terms of atomic units.

3.22 An example of a 2D electron momentum distribution of nitrogen ($N_2$). The black-dashed circle corresponds to the region of direct electrons which have energies $<2U_p$. The offset magenta-dashed circle represents the final momenta an electron may have when it elastically scatters from its parent ion with a return momenta of $p_r$. The detected momentum is: $p = p_r - A_r$ where $A_r$ is the field vector potential at the moment of rescattering. See text for more details. Figure reproduced from [96].

3.23 DCS versus scattering angle, $\theta_r$. Left panel shows sodium at $3.6\mu m$ and $5.5TW/cm^2$. Right panel shows the results for argon at $2.0\mu m$ and $234TW/cm^2$. The experimentally extracted values are represented by the points connected by a dashed-line. The calculated DCS is plotted as a solid-line. The results at three different electron return energies are shown. Both systems were in the tunneling regime: $\gamma \sim 0.6$ for sodium and $\gamma \sim 0.3$ for argon.

3.24 DCS versus scattering angle, $\theta_r$, for potassium. The experimentally extracted values are in blue and the theory is shown in red. The three panels correspond to electron return energies of 3eV, 5eV, and 7eV. Better agreement is observed at larger return energies. The potassium data was taken near the multiphoton regime, $\gamma \sim 0.9$.

4.1 Experiments performed on the inert gas atoms with a 40fs, 630nm laser source. The left panel shows that the enhancement in the plateau exists for all of the inert gas atoms to various extents. The right panel shows how the enhancement ($20-40eV$) behaves in argon as a function of intensity. The plotted intensities are: (a) $6\times10^{13}$ W/cm², (b) $1.2\times10^{14}$ W/cm², (c) $2.4\times10^{14}$ W/cm² and (d) $4.4\times10^{14}$ W/cm². Figure reproduced from [22].

4.2 The effect of pulse duration on the ATI spectra in argon. All spectra were taken at 800nm and an intensity near $0.8\times10^{14}$ W/cm². The observed enhancement ($15-30eV$) vanishes as pulse duration decreases. Figure reproduced from [100].
4.3 Comparison of experimental and TDSE calculated photoelectron energy spectra at a wavelength of 620nm. Experimental results for argon (green) and neon (blue) are plotted along with TDSE results for argon (black) and neon (red). TDSE calculations used a 5-cycle trapezoidal pulse (one-cycle turn-on and turn-off), $2.5 \times 10^{14} \text{W/cm}^2$ and incorporated focal volume intensity averaging.

4.4 Neon photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

4.5 Argon photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

4.6 Argon photoelectron spectra dependence on wavelength and intensity (continued). The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

4.7 Krypton photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

4.8 Krypton photoelectron spectra dependence on wavelength and intensity (continued). The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

4.9 Argon photoelectron spectra at various wavelengths and a nearly constant intensity of $2.2 \times 10^{14} \text{W/cm}^2$. From top to bottom the wavelengths correspond to 744nm (green), 710nm (orange), 695nm (red), 680nm (purple), 650nm (blue), 620nm (gold) and 583nm (black). For a constant intensity the plateau enhancements shift to higher energy as wavelength decreases.

4.10 Argon photoelectron spectra at various wavelengths and a nearly constant ponderomotive energy, $U_p = 7.5 \text{eV} (\gamma \approx 1)$. From top to bottom the wavelengths correspond to 744nm (green), 710nm (orange), 695nm (red), 680nm (purple), 650nm (blue), 620nm (gold) and 583nm (black). For a constant ponderomotive energy/Keldysh parameter the plateau enhancements shift to higher energy as wavelength decreases.

4.11 Argon photoelectron spectra plotted as detected energy versus wavelength. Experimental results are shown in (a) and the TDSE calculations are shown in (b). The color scale is on a log gradient and indicates the strength of the signal where red (orange) indicate high yields and blue (black) indicate low yields in the experiment (TDSE calculation). The arrows indicate the approximate locations of the N-photon channel-closures at an intensity of $1.3 \times 10^{14} \text{W/cm}^2$ for N=10 (608nm), N=11 (648nm), N=12 (689nm) and N=13 (725nm).

4.12 Comparison of argon and neon photoelectron spectra with the same laser parameters; wavelength of 620nm and pulse energy of 58µJ. A clear species dependence is observed.
4.13 SFA calculations for argon and neon using a 620nm, 5-cycle flat-top pulse at an intensity of $1.65 \times 10^{14}$ W/cm$^2$. ($\psi_{Ar} V_{Ar}$) indicates using the argon ground state wavefunction with the $e^- - Ar^+$ rescattering potential. ($\psi_{Ar} V_{Ne}$) indicates using the argon ground state wavefunction with the $e^- - Ne^+$ rescattering potential. ($\psi_{Ne} V_{Ne}$) indicates using the neon ground state wavefunction with the $e^- - Ne^+$ rescattering potential. ($\psi_{Ne} V_{Ar}$) indicates using the neon ground state wavefunction with the $e^- - Ar^+$ rescattering potential. The photoelectron spectrum is much more sensitive to the form of the ground state wavefunction.

4.14 SFA calculations for the interaction between a single-intensity 2-cycle trapezoidal pulse and an argon atom. The electric field and vector potential are shown in (a) along with the long-trajectory (purple) and short-trajectory (orange) time windows. The 2D photoelectron momentum distribution when the long and short trajectories were included are shown in (b). Panels (c) and (d) correspond to separating the regions where ionization was allowed to the long- or short-trajectories respectively. The origin of the observed plateau enhancements are attributed to intra-cycle long trajectories. Atomic units are used in panels (b)–(d).

4.15 Panel (a) shows the photoelectron spectra for argon at 620nm; experiment is shown in green and TDSE calculation in red. The three regions correspond to: low energy, direct, electrons (0–20eV; red), the enhancement region (20–46eV; green) and the remainder of the plateau (46–100eV; blue). Panel (b) shows the electron yield as a function of the intensity distribution within the focal volume in panel (a). The colors of the lines (red, blue, and green) correspond to the respective regions in (a). The black curve is the total yield.

4.16 2D momentum angular distribution in argon at 793nm and an intensity of 190TW/cm$^2$ for a linearly polarized field (along x-axis). The axes are in atomic units. The black-dashed arcs are bounding one of the rescattering rings.

5.1 Structure of the C$_{60}$ molecule. Image taken from [114].

5.2 A comparison of the C$_{60}$ mass spectra from the interaction with 800nm (40fs) and 1500nm (70fs) laser fields. Notice the suppression of fragmentation at longer wavelengths. Figure reproduced from [121].

5.3 Mass spectra from the interaction of 3.6$\mu$m light with C$_{60}$ molecules. The inset is zoomed in on the high charge states. We observe contributions from up to C$_{60}^{5+}$. 

5.4 Photoelectron momentum angular distribution for the strong-field interaction between C$_{60}$ and 3.6$\mu$m light at an intensity of 80TW/cm$^2$. The laser polarization is along the horizontal axis. The axes are expressed in terms of atomic units.
5.5 Our experimentally extracted DCS (red squares) obtained from field driven electrons rescattering with the C\textsubscript{60} cage with 100eV kinetic energies. Our results are compared to experimental CED measurements (black circles) and a theoretical model (blue line) provided in Hargreaves et al [122] for the same electron scattering energy. The observed oscillations are associated with diffraction from the molecular structure.

5.6 The experimental molecular contrast factor (MCF) for C\textsubscript{60} is extracted from the DCS (red squares). The theoretical calculation (blue line) is performed through the IAM for a 100eV electron rescattering energy. For determining bond lengths the position of the peaks is more important than their amplitude.

5.7 Extracted bond distances in Å in C\textsubscript{60}. Panel (a) shows our experimental (red) and calculated (blue) results. Panel (b) was measured through CED, image reproduced from [117]. The colors indicated the families of bond distances we observed.

5.8 The families of bond lengths we extracted. The colors correspond to those in Fig. 5.7. Figure reproduced from [117].

5.9 The DCS as a function of scattering angle. Experimental data is shown by the green squares. The IAM calculation using the known C\textsubscript{60} bond lengths is in black. These are the same results as were shown in Fig. 5.5. The red and blue lines are the IAM calculations for a hypothetical C\textsubscript{60} molecule which is 5% smaller or larger respectively.
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Table of relevant values for the analysis of an alkali metal atomic beam. Values a and b are used to calculate the vapor pressure (Eq. 2.9) which is accurate within the temperature range listed for each species [70].</td>
</tr>
<tr>
<td>3.1</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Useful alkali metal atom parameters. The columns in order are: the atomic species; atomic polarizability of the neutral atom; field-free ionization potential for the ground state atom; approximate number of photons necessary to ionize the atom, from the ground state (s) to the continuum (C), using 3–4µm light; energy gap between the ground state (G.S.) and lowest excited state (p) – the specific state is included in parentheses; and finally the number of photons necessary to transition from the ground state to the excited state.</td>
</tr>
<tr>
<td>3.2</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Useful inert gas atom parameters. The columns in order are: the atomic species; atomic polarizability of the neutral atom; field-free ionization potential for the ground state atom; approximate number of photons necessary to ionize the atom, from the ground state (p) to the continuum (C), using 550–800nm light; energy gap between the ground state (G.S.) and lowest excited state (s) – the specific state is included in parentheses; and finally the number of photons necessary to transition from the ground state to the excited state.</td>
</tr>
<tr>
<td>3.3</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Ion yield summary for sodium. Ion yields were done at the three wavelengths listed. The second and third column provide the calculated number of photons necessary for the field free ground state to continuum transition (3s → C) and the ground state to excited state transition (3s → 3p). In the approximation of perturbation theory the ionization rate is proportional to $I^N$, where N is the number of photons; the N values found experimentally are listed in the fourth column. The experimentally determined saturation intensity is listed in the last column. The over-the-barrier intensity for sodium is $I_{OTB} = 2.8TW/cm^2$.</td>
</tr>
</tbody>
</table>
3.4 Ion yield summary for potassium. Ion yields were done at the three wavelengths listed. The second and third column provide the calculated number of photons necessary for the field free ground state to continuum transition (4s → C) and the ground state to excited state transition (4s → 4p). In the approximation of perturbation theory the ionization rate is proportional to $I^N$, where $N$ is the number of photons; the $N$ values found experimentally are listed in the fourth column. The experimentally determined saturation intensity is listed in the last column. The over-the-barrier intensity for potassium is $I_{OTB} = 1.4 \text{TW/cm}^2$.

5.1 Relevant physical properties of the $\text{C}_{60}$ molecule. The bond distances and dimensions were taken from [117]. This reference also contains much more extensive bond length data. The ionization potentials were taken from [114].
Chapter 1

INTRODUCTION TO STRONG FIELD INTERACTIONS

The purpose of this chapter is to supply the reader with the necessary theoretical foundation for understanding the interactions which occur between an isolated atom or molecule and an intense laser pulse. Extensive progress has been made in this field over recent decades and this thesis will not attempt to provide a comprehensive literature summary. Instead, we will focus on introducing some of the key experimental and theoretical steps which helped illuminate our understanding of strong field phenomena. An emphasis will be made on the topics which will play an essential role in the discussions in the subsequent chapters. It is important to keep in mind that at the core of the work presented here is the desire to more completely understand and test the overarching scaling phenomena that underlie strong field interactions.

1.1 Ponderomotive Energy and the AC Stark Shift

Unless otherwise stated we will be restricting our attention to linearly polarized fields but the following results can easily be generalized to circular or elliptical polarizations. Let’s begin by considering the effect of an oscillating electric field, \( E(t) = E \cos \omega t \hat{z} \), on a free electron where \( E \) is the field amplitude, \( \omega \) is the field angular frequency and \( t \) is time. If we treat this in the nonrelativistic limit we can express the force on this electron as:

\[
m \frac{d^2 x}{dt^2} = e E \cos \omega t
\]  

(1.1)

where \( e = -|e| \) is the charge of an electron and \( m \) is the electron mass. If we integrate this expression and average over a cycle of the applied field we arrive at the definition of the ponderomotive energy [1, 2]:

\[
U_p = \frac{e^2}{2m} \left\langle A(t)^2 \right\rangle = \frac{e^2 E^2}{4m\omega^2}
\]

(1.2)
where $A(t) = -\int dt E(t)$ is the vector potential of the laser field. The word ‘ponderomotive’ refers to the oscillatory or wiggle motion that a charged particle will undergo when it is in an alternating electric field. Therefore, the ponderomotive energy is the cycle averaged quiver energy that a free charged particle, an electron in this case, will undergo when it is in an alternating electric field. This effect plays a crucial role in understanding strong field interactions and will be mentioned throughout this thesis. We can re-express this in a form more useful for the typically known experimental parameters, namely wavelength and intensity. The laser intensity, $I$, and electric field amplitude are related by:

$$I = \frac{1}{2} \varepsilon_0 c |E|^2$$

(1.3)

where $\varepsilon_0$ is the permittivity of free space and $c$ is the speed of light in vacuum. Thus we arrive at the following form for the ponderomotive energy [3]:

$$U_p = \frac{e^2}{8\pi^2 m \varepsilon_0 c^3} I \lambda^2$$

(1.4)

$$U_p [eV] = 9.33 \times 10^{-14} I [W/cm^2] \times \lambda^2 [\mu m]$$

(1.5)

where $\lambda$ is the wavelength.

Now let’s consider the effect that an oscillating electric field can have on the electronic states of an atom. Specifically, we will focus on the AC Stark shift which is an effect that arises from second order perturbation theory [4]. Before continuing it is important to clearly describe all of the approximations that are involved. First, the single active electron (SAE) approximation considers that in an atomic/molecular species only a single valence electron is affected by the field and all others remain in their ground states (this is a frequently used assumption in theoretical analysis). Further, we drop any magnetic field contributions since the velocities, which depend on wavelength and intensity, and field strengths discussed in this document make relativistic effects negligible. Finally, if the wavelength of the applied laser field is significantly larger than the atomic size, $\sim 1\text{Å}$, we can neglect the spatial component of the interaction, $kx + \omega t \rightarrow \omega t$. This simplification is known as the dipole approximation. Using these approximations we can express the electric field of a linearly polarized, pulsed laser source as $E(t) = E f(t) \cos \omega t \hat{z}$ where $f(t)$ is the pulse envelope.

We continue by considering the Hamiltonian for an electron in an applied field which is under the influence of an atomic potential, $U(r)$:

$$H = \frac{[p - eA]^2}{2m} + U(r)$$

(1.6)

where $p$ and $r$ are the momentum and position vectors of the electron and $A$ is the vector potential of the laser field. There is another form of this interaction Hamiltonian which is frequently used in strong field physics. The Hamiltonian in the Kramers-Hennenberger
(KH) picture moves the coordinate system to a noninertial frame where the ionized electron is at rest and the remaining parent ion is moving in the field [4, 5]:

$$H_{KH} = \frac{p^2}{2m} + U(r - \alpha_0 \cos(\omega t))$$  

where $\alpha_0 = E/\omega^2$ is the quiver motion amplitude.

Typically we cannot directly solve the Schrödinger equation with this Hamiltonian. The most common approach is to apply perturbation theory and treat the laser interaction as the ‘perturbing’ quantity. We can then express the total atom-laser wavefunction, $\Psi$, as a superposition of the isolated atom’s wavefunctions, $\psi_n$. Second order perturbation theory effects correspond to two photon transitions. For the AC Stark shift the initial and final states are the same; therefore we have an absorption (emission) and then an emission (absorption) of a photon through a virtual state [4].

In order to get an expression for the energy shift of an arbitrary atomic state, $n$, due to the ‘perturbing’ effect of a laser pulse we consider the form of the total wavefunction in the second order perturbation theory approach:

$$\Psi = \left[1 + C_n^{(2)}(t)\right] \exp\left(-\frac{i}{\hbar}E_n t\right) \psi_n$$  \hspace{1cm} (1.8)

where the adiabatic limit, $f(t) \to 1$, was assumed. $C_n^{(2)}(t)$ is the second-order probability amplitude arising from perturbation theory and $E_n$ are the energies corresponding to the unperturbed atom. Next, we express the total wavefunction, $\Psi$, in another form. Consider that the final atomic state is the unperturbed state, $E_n$, with a small shift of $\delta E_n$. We then expand the exponent in powers of $\delta E_n$ [4]:

$$\Psi = \left[1 - \frac{it}{\hbar} \delta E_n\right] \exp\left(-\frac{i}{\hbar}E_n t\right) \psi_n$$  \hspace{1cm} (1.9)

By comparing these two equations and substituting in the expression for $C_n^{(2)}(t)$ we arrive at the form of the AC Stark shift [4]:

$$\delta E_n = -\frac{1}{4} \chi_n(\omega) E^2$$  \hspace{1cm} (1.10)

where $\chi_n(\omega)$ is the dynamical polarizability of the n-th energy level:

$$\chi_n(\omega) = 4 \sum_{n'} |(d_x)_{n',n}|^2 \frac{2(E_{n'} - E_n)}{(E_{n'} - E_n)^2 - (\hbar \omega)^2}$$  \hspace{1cm} (1.11)

and $d_x$ is the projection of the atomic dipole moment along the electric field axis.

If we consider the limit of highly excited states near the continuum, also known as
Rydberg states [6], where \( n \gg 1 \) the expression for the AC Stark shift simplifies to [4, 7]:

\[
\delta E_n = \frac{e^2 E^2}{4m\omega^2}
\]  

(1.12)

Notice that this exactly matches Eq. 1.2 and so we expect states near the continuum to shift by the ponderomotive energy.

There is another instructive way of examining the electronic energy level shifts that occur in a laser field. By expanding the squared term in Eq. 1.6 we get [1]:

\[
H = \frac{p^2}{2m} - \frac{e}{2m}(p \cdot A + A \cdot p) + \frac{e^2 A^2}{2m} + U(r).
\]  

(1.13)

If we average the \( A^2 \) term over an integer number of laser cycles we recover the ponderomotive energy. This term is a constant and will affect the deeply bound and the highly excited/continuum states equally.

However, the \( p \cdot A \) cross-terms describe transitions between states and will not be constant for all levels. Let’s first consider the ground state and particularly where we can make the low frequency approximation, \( |E_g - E_n| \gg \hbar \omega \), where \( n \) represents the complete set of states of the unperturbed atom and \( E_g \) is the energy of the ground state. In the case of single ionization the cross terms in the above Hamiltonian can be shown to be [8]:

\[
\Delta E_g = -\frac{e^2 E^2}{4m\omega^2} - \frac{1}{2} \alpha E^2.
\]  

(1.14)

The first term is the negative of the ponderomotive energy and cancels with the \( A^2 \) term in Eq. 1.13. The second term above is effectively the DC Stark shift where \( \alpha \) is the ground state polarizability [9]. Therefore we find that for the ground state the net energy shift is only due to the second term above.

A similar approach can be applied to the high-lying (Rydberg levels) or continuum states but with a high-frequency approximation, \( |E_n - E_R| \ll \hbar \omega \). In this limit the \( p \cdot A \) cross-terms go to zero [8] and the net shift of these levels is equal to the ponderomotive energy. The effect of the laser field on the energy states of an atom are shown schematically in Fig. 1.1.

The net influence of the AC Stark shift is to increase the ionization potential of the atom. If we vary the field intensity we may shift certain energy states through resonances where the energy difference between levels is equal to an integer number of photons. We now return briefly to the idea of a pulsed laser field. In this case it is possible to observe dynamical resonances which occur at the leading and falling edges of a pulse where energy levels can be shifted through k-photon resonances [9].
1.2 Keldysh Scaling

In 1965 L. V. Keldysh published a theoretical paper which provided a fundamental basis for predicting the expected ionization mechanism for an atom or molecule in a strong laser field [11]. Though relatively simple this theory is widely used and will be referenced throughout this thesis.

Keldysh defined a dimensionless adiabaticity parameter, $\gamma$, as the ratio between the laser field frequency, $\omega$, and the electron’s tunneling frequency [11]:

$$\gamma = \frac{\text{field frequency}}{\text{tunneling frequency}} = \frac{\omega \sqrt{2mI_p}}{eE}$$  \hspace{1cm} (1.15)

The tunneling frequency is approximated by defining a barrier width $l = I_p/eE$, where $I_p$ is the ionization potential of the atom. The average velocity of the bound electron is proportional to $\sqrt{I_p/m}$. Combining these he estimated the tunneling frequency as $\omega_t = eE/\sqrt{2mI_p}$.

We can express this in the more common form by using our definition of the ponderomotive energy, Eq. 1.2 [1]:

$$\gamma = \sqrt{\frac{I_p}{2U_p}}$$  \hspace{1cm} (1.16)
The Keldysh parameter allows us to place an actual value on the competing effects of the frequency of the applied laser field and the tunneling frequency of a bound electron in an atom or molecule. The limiting cases are shown in Fig. 1.2 and are discussed in more detail in the following sections.

Before proceeding it may be worth noting the possibly glaring discrepancy in the theory discussed so far. We are working in the strong field regime, but the majority of the discussion thus far is built out of perturbation theory. To gain a deeper understanding for the relation between the strong field and perturbative regimes we consider two dimensionless parameters [5]. These parameters are introduced not so much to define a clear line where perturbation theory is valid or invalid but more to place an approximate upper bound above which we can agree that perturbation theory is expected to break down. The parameter $z_1$, called the bound-state intensity parameter, approximates the limit of perturbation theory to be when the magnitude of the interaction Hamiltonian is equal to the magnitude of the unperturbed Hamiltonian, $|H_I|/|H_0| = 1$. For this scenario we compare the applied field perturbation to the field-free atomic system and then square the result to get an expression in terms of intensity [5].

$$z_1 = \frac{2U_p}{I_p} = \frac{e^2 \langle E^2 \rangle}{m\omega^2 I_p}$$  \hspace{1cm} (1.17)

The second parameter is known as the continuum-state intensity parameter [5]:

$$z = \frac{U_p}{\hbar\omega} = \frac{e^2 \langle E^2 \rangle}{2m\hbar\omega^3}$$  \hspace{1cm} (1.18)

This parameter relates the quiver energy to the photon energy. If the energy of a single photon is small in comparison to the oscillatory motion in the field then a nonperturbative amount of these photons will be required to place an ionized electron into this motion. The wavelength versus intensity dependence of these parameters are shown in Fig. 1.3. At the wavelengths which will be relevant for experiments discussed in this thesis the continuum-state intensity parameter is the better indicator of perturbation theory break down.

However, even with this in mind, the perturbation theory approximation can still be useful and has shown some success, at least qualitatively, in describing the physics in these ionization processes. More in-depth quantum mechanical models will be described in later sections. These models can produce more quantitatively accurate results but with the increased complexity we loose the clearer physical picture of the mechanics involved.

1.2.1 Multiphoton Ionization ($\gamma > 1$)

First, let’s consider the regime of multiphoton ionization, where the Keldysh parameter is greater than one (see Fig. 1.2). In this limit the frequency of the applied laser field is larger than the tunneling frequency of the bound electron [11, 3]. A useful mental picture for this
Figure 1.1: Ionization regimes as a function of electric field strength. From top to bottom: single ionization (low field strength), multiphoton ionization (moderate strength), tunnel ionization (high field strength) and over the barrier ionization (very high field strength). The atomic potential is in black, the laser field in red, the total potential in blue and the electron wave packet in green. IP denotes the ionization potential and GS the ground state.

Figure 1.2: Ionization mechanisms as described through the Keldysh picture. From top-down: the perturbative limit where ionization can occur through single photon absorption; multiphoton ionization ($\gamma > 1$); tunneling ionization ($\gamma < 1$); and over-the-barrier ionization ($\gamma \ll 1$) where the barrier is completely suppressed. The field free atomic potential is shown in black, the laser field in red, and the combined potential in blue. The electron wave packet is shown in green. GS denotes the ‘ground state’ and IP the ‘ionization potential’. Read text for more details. Figure reproduced from [10].
mode of ionization is that the applied oscillating field is flipping the atomic potential back and forth much faster than the ground state electron can sample the potential. Therefore, on average, the atomic potential does not appear to be deformed by the applied field. In this regime an electron is ionized by transitioning from a bound (usually ground) state to a continuum state by absorbing n photons, where $n\hbar \omega$ is greater than the ionization potential of the atom ($I_p$). Since $U_p \propto I\lambda^2$ then the Keldysh parameter is proportional to $1/\sqrt{I\lambda}$. Therefore the multiphoton regime occurs at somewhat shorter wavelengths and moderate field intensities (which still allow for the absorption of many photons through real or virtual intermediate states).

Above-threshold-ionization (ATI) [12, 13] occurs when s more photons are absorbed than the minimum, n, needed for ionization which leads to a final electron energy of [3]:

$$E_f = (n + s)\hbar \omega - I_p.$$  

(1.19)

Experimentally, one of the clearest displays of being in the multiphoton regime is the visibility of ATI structure.

Figure 1.4 is reproduced from [14] and shows the photoionized electron signal as a function of the electron’s detected energy in a xenon gas phase target. Moving from the top to the bottom panel the laser intensity is increasing along with the number of observed ATI peaks. The fact that there is a point where higher-order ATI peaks contribute as much, if not more than, some of the lower energy peaks clearly demonstrates that we are moving into
Figure 1.4: Photoelectron spectra showing ATI in xenon with 135ps pulses at a wavelength of 1064nm. Laser intensity is highest in the lowest panel. As intensity increases the maximum ATI order increases and the low order ATI begin to be suppressed due to channel closure. Image reproduced from Yergeau et al [14].
the non-perturbative regime. Further, notice that as intensity is increased the low order
ATI peaks start to become suppressed. As was mentioned earlier, when we enter the strong
field regime the effect of the AC Stark shift on the bound atomic states begins to have a
non-negligible contribution. In particular, it was shown that the continuum shifts by the
ponderomotive energy, $I_p \to I_p + U_p$, and therefore the ionized electron’s final energy is \[3\]:

$$E_f = (n + s)\hbar\omega - (I_p + U_p) \quad (1.20)$$

If n photons are needed to ionize the unperturbed atom, then increasing the laser intensity,
and thereby the effective ionization potential $(I_p + U_p)$, will eventually make the n-photon
ionization impossible. This effect is often referred to as channel closure. If this occurs
then we expect the lowest ATI peak to disappear and by further increasing the intensity
consecutively higher order ATI peaks would be suppressed. However, these peaks do not
completely disappear as can be seen in Fig. 1.4. This is because laser pulses have a smooth
turn on and turn off so the n-photon ionization channel is still open during the rise and fall
of the laser pulse \[3\]. Though it is usually neglected, due to its much smaller size, there are
times when it may be important to include the shift of the ground state as well.

At this point it is worth noting a somewhat subtle effect. Since intensity is a continuous
parameter and $U_p \propto I$, then we could expect an ATI peak of a particular order to shift to
a lower detected energy as the laser intensity is increased. This is true as long as we have
short pulses, where ‘short’ is determined by comparing the temporal length of a laser pulse
to the amount of time it takes an ionized electron to exit the laser focus. In the long pulse
regime the electron will have time to exit the laser focus before the pulse ends and as it does
so it will experience a force of $-\nabla U_p$, thereby regaining the energy it lost from the shift in
the ionization potential, $U_p$. The ATI peaks will then appear at the same detected energy
for all laser intensities \[1, 13\]. This is the case for the experimental results in the ‘long’ pulse
regime shown in Fig. 1.4. In the case of short pulses we expect to see a shifting of the ATI
peaks with changing intensity since the electron will not have time to regain this energy as
it ‘slides’ down the potential during its path out of the laser focus. One of the benefits of
working in the short pulse regime is that the detected electron energies correspond to their
actual energy at the moment of ionization \[1, 13\]. From a simple calculation the switch from
the long to short pulse regime occurs when pulse durations are on the order of picoseconds,
$10^{-12}$ seconds. All of the work discussed in this thesis will be in the short pulse regime.

We now briefly return to the approach of perturbation theory where the ionization rate
for an N-photon transition, $R_N$, can be expressed as \[3\]:

$$R_N = \sigma_N I^N \quad (1.21)$$

where $\sigma_N$ is the N-photon generalized cross-section, I is the intensity, and N is the number
of absorbed photons. The slope, on a log-log plot of ionization rate versus intensity, for an N-photon transition will be N. In the strong field limit perturbation theory becomes a severe approximation but nonetheless this sort of analysis has shown some success in explaining experimental results [3].

1.2.2 Tunneling Ionization, $\gamma < 1$

As the intensity is further increased the field will begin to significantly distort the atomic potential, as shown in Fig 1.2. Eventually this reaches a point where the electron’s dominant mechanism for ionization is tunneling through the atomic barrier. Similarly, if the wavelength is increased then the rate at which this oscillating external field ‘flips’ the atomic potential back and forth will decrease and thereby increase the probability that the bound electron will tunnel through the distorted potential. In this regime the ionization rate can no longer be accurately described by an intensity dependent power law and the picture of absorbing individual photons begins to wash out. Instead, the tunneling rate scales as [11, 3]:

$$R \propto \exp[-I_p^{3/2}/E]$$

(1.22)

In this case ionization is a maximized at the peaks of the applied field where the atomic potential is maximally suppressed. The Keldysh parameter, $\gamma$, decreases as we move further into the tunneling regime. By convention, if $\gamma > 1$ the regime is referred to as multiphoton and when $\gamma < 1$ it is tunneling. However, physically this distinction is not so clear cut and both effects may have a significant contribution in the intermediate range close to $\gamma = 1$.

1.2.3 Over-The-Barrier Ionization

If we continue to increase the field strength we will eventually reach the point where the field induced suppression of the atomic potential is equal to the electron’s ground state ionization energy. This is referred to as Over-The-Barrier (OTB) ionization [11, 3] and is shown schematically in the bottom image of Fig. 1.2. The intensity at which OTB ionization occurs is [3]:

$$I_{OTB} = \frac{\pi \epsilon_0^3 I_p^4}{2Z^2 e^6}$$

(1.23)

or expressed in more typically used units:

$$I_{OTB}[W/cm^2] = 4 \times 10^9 (I_p[eV])^4/Z^2$$

(1.24)

where $Z$ is the charge of the remaining ion after the ionization process.

Another important quantity is the saturation intensity, $I_{sat}$, which may not necessarily be equal to $I_{OTB}$. $I_{sat}$ is defined as the intensity at which all of the atoms in the interaction volume become ionized during the pulse, therefore accounting for the integrated ionization
rate. Most frequently, at the wavelengths and pulse durations used in our experiments, $I_{OTB}$ can be viewed as the upper limit for $I_{sat}$ since at $I_{OTB}$ the atomic ground state potential for the valence electron will be completely suppressed.

In experimental measurements we observe a clear change in ionization rate at the saturation intensity. Above $I_{sat}$ the rate will continue to increase but at a different slope. Even though ionization in the center of the laser focus is saturated the intensity in the wings of the pulse can further increase and therefore so can the total ionization yield. For a perfect Gaussian beam this volume effect gives a rate proportional to $I^{3/2}$ [15]. This behavior may be further complicated by atomic or molecular intermediate resonant states.

### 1.3 Semiclassical Description

High laser intensities are necessary to drive transitions through virtual states (multiphoton ionization), transitions within the continuum (ATI), or reaching the limit where tunneling is the dominant ionization mechanism. Exact comparisons between theory and experiment are challenging if not impossible. Difficulties arise in developing sufficiently accurate theoretical descriptions of target atoms and their interactions. Further, experimentally a laser focus averages over many intensities and since we are studying highly nonlinear interactions slight intensity variations can have a large effect on the outcome.

The discrepancies due to these difficulties become most apparent when we attempt to make quantitative comparisons between experimental and theoretical results. The details associated with this will be discussed more thoroughly in the following chapters. At this point let’s continue to focus our attention on the more general description of an electron’s behavior when it is influenced by an atomic potential and an external strong electric field. In the previous section we discussed ways that an electron can be ionized. Now, let’s consider what happens to this electron once it has been freed.

We approach this problem by considering a semiclassical picture where the ionized electron is treated as a charged point particle which follows a classical trajectory in an alternating electric field. Neglecting the quantized nature of the electric field is a valid approximation in the strong field limit. It will only restrict us by not allowing for spontaneous emission but this is a negligible effect in our experiments [16].

#### 1.3.1 Simpleman Model

As an initial approximation we treat the influence of the parent ion’s Coulomb potential tail as negligible compared to the applied field strength. Therefore, once the electron is ionized the kinetics of its motion will be purely determined by the phase of the field at the time of ‘birth’ (the point in the laser pulse that the electron reaches the continuum), as well as its initial velocity and position [3, 16, 17].
In the first step, the electron ionizes and enters the continuum at a rate determined by the Ammosov-Delone-Krainov (ADK) theory (the details associated with this model will be discussed in Sec. 1.4.1). At this point the only important feature to note is that ADK assumes tunnel ionization and therefore the electron enters the continuum with zero initial velocity. Since barrier suppression is the greatest near the peaks of the field then this is where we expect to see the highest rate of ionization. For the typical intensities used we can neglect any relativistic effects and the magnetic component is negligible.

The second step involves determining the electron’s trajectory once it enters the continuum. If we treat this as a one-dimensional system then the equation of motion for a free electron in an applied linear monochromatic laser field, \( E(t) = E \cos \omega t \), is given by Eq. 1.1. Further we consider that the electron tunnels out at a time, \( t = t_0 \), with zero initial velocity, \( v_i = 0 \). Solving the classical equation of motion we find that at a later time, \( t \), the electron’s velocity is:

\[
v = \frac{eE}{m\omega} \left[ \sin \omega t - \sin \omega t_0 \right]
\]

and therefore has a cycle-averaged kinetic energy of:

\[
\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{e^2E^2}{4m\omega^2} \left( 1 + 2\sin^2 \omega t_0 \right)
\]

The first term on the right describes the energy associated with the oscillatory or quiver motion, which does not contribute in the short pulse regime. The second term is the translational or drift energy which, as mentioned earlier, depends on the phase of the field when the electron is born. Therefore we arrive at the well-known result that the maximum detected electron energy in short pulse experiments is \( 2U_p \), where \( U_p \) is the ponderomotive energy (see Eq. 1.2) [16, 17, 3, 18].

### 1.3.2 Rescattering

However, the Simpleman model did not appear to describe the laser-atom interaction process completely. This conclusion was reached because experimental results would detect electrons with more energy than this predicted \( 2U_p \) limit. An explanation for this behavior came in a series of papers in the early 1990s which attributed this result to the ionized electron rescattering with its parent ion [19, 20, 21, 22]. This model is typically referred to as the ‘3-Step-Model’ and is outlined below (also see Fig. 1.5).

The first two steps are the same as in the Simpleman model. First, the electron tunnel ionizes into the continuum under the influence of the applied laser field. In step two we apply classical mechanics to determine the electron’s trajectory under the influence of the field while neglecting the Coulomb potential tail [18, 20]. Next we integrate Eq. 1.25 and use the initial condition that at time, \( t = t_0 \), the electron is located at \( x_i = 0 \) (the position
Figure 1.5: The 3-Step-Model. In the lower images the dashed-blue line is the shape of the field free potential, the dashed-red line is the effect of the applied field, and the black-solid line represents the effective potential. Step 1: near the peak of the field the potential is maximally suppressed and the electron is the most likely to tunnel into the continuum. Step 2: the electron propagates in the continuum under the influence of the applied field. Step 3: the electron is driven back towards the nucleus and rescatters or recombines (releasing a high energy photon).
Figure 1.6: Calculation of an electron’s return energy in unit of \( U_p \) as a function of its birth phase. The ‘long’ and ‘short’ distinction is made because there are two classical trajectories an electron can take that result in the same return energy.

of the nucleus). Therefore the electron’s time dependent position is:

\[
x = -\frac{eE}{m\omega^2} \left[ \cos\omega t + \omega \sin \omega t_0 - \cos \omega t_0 - \omega t_0 \sin \omega t_0 \right]
\]  

(1.27)

Since the nucleus is significantly more massive we consider the approximation that it will remain stationary during a half cycle of the field. From the above expression we see that an electron in its trajectory may follow a path where it reapproaches the vicinity of its parent ion. This will occur if the electron returns to the position \( x = 0 \) at any point after ionization. The electron’s kinetic energy when it reencounters the ion as a function of the birth phase, \( \omega t_0 \), is plotted in Fig. 1.6. This shows that there are two trajectories that an electron can follow to achieve the same kinetic energy upon recollision; these are known as the ‘long’ and ‘short’ trajectories. Further, it shows that the maximum return energy is 3.17\( U_p \) which will occur at a birth phase of \( \omega t_0 = 17^\circ \) or \( 197^\circ \) [19, 20, 22].

Step three of the model is this point of interaction and upon recollision several things can happen. The electron can scatter elastically or inelastically and then be detected. The electron can also recombine with the ion and release a high energy photon (known as High Harmonic Generation) [19, 20]. Each of these scenarios is briefly introduced in the following sections. However, a thorough discussion would take much more space than is available in this thesis and is the subject of numerous review articles [13, 23, 3, 24]. The strength of the three step model is that it helped unify and explain the experimental photon, electron and ion measurements into a single theory.
Figure 1.7: Argon photoelectron spectra at $8 \times 10^{13} W/cm^2$ taken at four different wavelengths: 0.8$\mu$m (solid), 1.3$\mu$m (dash-dot), 2$\mu$m (dash), and 3.6$\mu$m (dot). When plotted in absolute energy units the spectra look very different (a). However, when plotted in units of the ponderomotive energy, $U_p$, the scaling is much more obvious (b). The inset in (a) shows the ratio of electrons detected with $>2U_p$ energy to those with $<2U_p$ energy as a function of wavelength. Figure reproduced from Colosimo et al [27].

Elastic Scattering

The first scenario we consider is the electron undergoing an elastic collision when it is driven back into its parent ion by the laser field. Quantum calculations of the photoelectron spectra using the Schrödinger equation with the approximation of a single-active-electron were able to reproduce experimental findings well [21]. This result gives justification for continuing to neglect any multi-electron effects when describing the scattering process. However, in an attempt to develop a model which provided a clearer physical description of the electron’s motion, Paulus et al [25] proceeded to build on the semiclassical picture. Using the 3-Step-Model they calculated the distribution of kinetic energies an electron has upon return to the core as a function of ‘birth’ time and ionization rate. Then, assuming elastic scattering and the subsequent influence of the laser field on the electron’s trajectory, they showed that the maximum detected kinetic energy was $10U_p$ and occurred for exact backscattering ($180^\circ$) [25, 26]. Therefore photoelectrons with energies greater than $2U_p$ are produced from trajectories that undergo scattering from the ion core at large deflection angles.

This result agrees well with experimental findings (an example of which is shown in Fig. 1.7). The total yield in the region between 0 and $2U_p$ is dominated by the ‘direct’ electron trajectories (which do not rescatter before detection) and exhibits a decaying behavior.
with energy. This is followed by a ‘plateau’ starting near $2U_p$ and a ‘cutoff’ near $10U_p$ after which the electron signal ends. Rescattered electrons posses energies between 0 and $10U_p$ but their contribution is only really visible after $2U_p$ (notice the log scale on the y-axis).

Figure 1.7 has been reproduced from [27] and shows argon photoelectron spectra at the same intensity, $8 \times 10^{13} \text{W/cm}^2$, but at four different wavelengths (0.8 µm, 1.3 µm, 2 µm, and 3.6 µm) which correspond to Keldysh parameters of 1.3, 0.8, 0.5 and 0.3 respectively. Therefore these results span the range from multiphoton to tunneling ionization. In Fig. 1.7(a) it is clear that the spectra exhibit very different energy distributions. However, in terms of $U_p$, Fig. 1.7(b), their general behavior is quite similar. Notice that the further we move into the tunneling regime the closer the spectra agrees with the smooth classical prediction; a break at $2U_p$ followed by a relatively flat distribution until the cutoff at $10U_p$. This makes sense because the semiclassical theory assumes tunneling as the mechanism for the initial ionization event.

The inclusion of rescattering, even in this simplified semiclassical model, was able to explain many experimentally observed features. For example, if circular instead of linear polarized light is used the plateau in the photoelectron spectra is suppressed, see Fig. 1.8 reproduced from [22]. With circularly polarized light the returning electron will experience a transverse displacement in its trajectory and will therefore miss the ionic core, inhibiting rescattering. Even better agreement was achieved between theory and experiment when the semiclassical calculations accounted for multiple returns and rescattering events with the ionic core [25].

Figure 1.8: Argon photoelectron spectra taken with 630nm, 40fs pulses at $2.4 \times 10^{14} \text{W/cm}^2$. Linearly polarized (a) and circularly polarized (b) light was used. Notice the suppression of the plateau when rescattering is suppressed. Figure reproduced from Paulus et al [22].
At this point we have only focused on the general behavior of the photoelectron spectra though obviously the plateau electrons exhibit significantly different features whether we are in the multiphoton or tunneling ionization regimes, see Fig. 1.7. It is important to note the differences between these modes of ionization. In the multiphoton regime electron population enters the continuum continuously and close to the nucleus. In tunneling ionization the electron wavepackets emerge in bursts near the maxima of the electric field and appear in the continuum a distance away from the nucleus, particularly at the outer turning point of the potential barrier [26, 24]. More extensive discussions on the origin and behavior of the observed structures in the photoelectron spectra will occur in the following chapters and is a key focus of this thesis.

Inelastic Scattering/Multiple Ionization

Thus far we have focused our attention on the simplified atomic picture with a single active electron. However, when we treat interactions between complex atoms and strong-fields there is the possibility of higher order ionization. A major step in understanding inelastic rescattering processes occurred by experimentally measuring ion yields of multiply ionized atoms (double ionization in He and Ne [28, 29]; in He and Xe [30, 31]; and He [32]). Theoretical calculations would predict the rate for the first ionization step quite accurately but would drastically overestimate the intensity for the onset of the second ionization step. A clear example of this is shown in Fig. 1.9 for the ionization of helium with 160fs pulses at 780nm [31]. The calculated rate for \( \text{He}^{2+} \) (solid black line) shows a dramatic difference from the experimental result.

The reason for the discrepancy was due to omission of rescattering in the models. If rescattering is neglected then multiple ionization can only be achieved through the sequential removal of electrons from the atom by the laser field. Previously we showed that a returning electron can be driven back towards its parent ion with a maximum kinetic energy of \( 3.17U_p \) and if it undergoes an inelastic collision it may deposit some of this energy before scattering away. If this energy is high enough to overcome the ionization potential of the second electron then the atom will be double ionized. However, if the deposited energy is not sufficient then the second electron can still be promoted to an excited state from which it can be field ionized [19]. In Fig. 1.9 the kink or knee-like structure in the \( \text{He}^{2+} \) ion yield is a signature of this nonsequential ionization process. Notice that when the \( \text{He}^+ \) yield begins to saturate we also observe the \( \text{He}^{2+} \) process saturate until the sequential ionization mechanism (where the field directly ionizes the second electron) kicks in.

There have now been many experimental results which can be, at least qualitatively, explained through the inelastic scattering process in the 3-Step-Model. Here I briefly discuss two of the early findings which supported this description. First, since the electron’s maximum return energy is \( 3.17U_p \) and \( U_p \propto \lambda^2 \) then the multiple ionization mechanism
should be controllable by varying the laser wavelength. This is exactly what Kondo et al [32] did by exposing helium to intense 745nm and 248nm laser light. The ionization potential for removing the second electron from helium is 54.4eV. They observed the knee-like enhancement in the ion yield of He$^{2+}$ at 745nm but not at 248nm where the 3.17$U_p$ energy is not sufficient to overcome the ionization potential. In a different experiment Fittinghoff et al [29] showed that they could suppress this enhancement in helium and neon by using circularly instead of linearly polarized light. Therefore by suppressing the rescattering process they could suppress the nonsequential mechanism for double ionization at lower intensities. Double ionization can still occur with circularly polarized light but only through the sequential ionization process.

There was one discrepancy that arose early on. The rescattering picture predicts that there should be a sharp turn on for the nonsequential He$^{2+}$ process; specifically when the returning electron’s kinetic energy is equal to the ionization potential of the second electron. However, experimentally the e-2e process was also observed at lower intensities [31, 33]. A complete discussion of the proposed mechanisms underlying this observation is beyond the scope of this brief introductory chapter. Various models have been put forward which account for higher level quantum mechanical effects [33], 2-electron correlation effects [34], or transitions through intermediate excited states [35]. In most cases the simple rescattering
picture of an inelastic collision provides a good understanding of the mechanics involved in multiple ionization.

**High Harmonic Generation**

Finally, for completeness, I briefly introduce the mechanism underlying High Harmonic Generation (HHG). However, all the work presented in this thesis is based on analysis of electron and ion measurements in strong field interactions for which the discussions in the previous sections will be much more relevant.

The mechanism for HHG has a similar starting point as ATI (above-threshold ionization, discussed earlier) namely the absorption of more photons than is necessary simply to ionize. For ATI the electron will leave the laser focus with the extra energy it has absorbed (possibly rescattering along its path) while for HHG the returning electron recombines with the atom and emits a photon [20]. Upon recombination the electron typically returns to the ground state and in order to satisfy dipole selection rules the observed photons must be at odd harmonics of the fundamental frequency [24].

The semiclassical model predicts an electron will have a maximum return kinetic energy of \(3.17U_p\) and therefore the maximum emitted photon energy will be \(3.17U_p + I_p\) [20, 19]. This prediction agrees with experimental results. The general shape of the harmonic spectrum consists of 3 regions: (1) the low-order harmonics decrease rapidly following perturbation theory; (2) a ‘plateau’ region where the harmonic intensity decreases slowly; (3) a cutoff after which no more harmonics are observed [20, 36, 37]. Since the HHG cutoff energy scales with \(U_p \propto \lambda^2\) we expect that this can be increased by moving to longer wavelengths. Figure 1.10, reproduced from Colosimo et al [27], shows the harmonic spectra in argon at the same intensity but different wavelengths; 0.8\(\mu m\) (gray) and 2\(\mu m\) (yellow). However, experimentally other factors need to be considered since not only the cutoff energy but also the total detected harmonic yields are important. Effects like the increased spread in the returning electron’s wavepacket at longer wavelengths, the recombination cross-section decreasing with increasing electron return energy, as well as phase matching and propagation conditions must be accounted for. This topic has been extensively discussed and there are numerous review articles available to the interested reader [24, 38, 39].

1.4 Quantum Mechanical Models

1.4.1 Ammosov-Delone-Krainov (ADK) Theory

In the preceding section we described the effect of a strong field on an atomic or molecular system from the semiclassical trajectory perspective. However, the ability of this model to provide quantitatively accurate results is limited and eventually quantum mechanical formulations become necessary. One of the important theoretical problems in strong field
Figure 1.10: High-harmonic spectra taken in argon at $1.8 \times 10^{14} W/cm^2$ with $0.8 \mu m$ (dashed, gray fill) and $2 \mu m$ (solid, yellow fill). The later spectra is cut off by the edge of the aluminum filter. The real cutoff occurs $\sim 220eV$. Figure reproduced from [27].

physics is accurately predicting the atomic/molecular ionization rate as a function of experimentally controllable laser parameters (wavelength, intensity, pulse duration, geometry of focal volume). Modern day numerical methods for solving the time-dependent-Schrödinger-equation have become quite accessible but frequently a simpler approach, which is more accessible to experimentalists, is desired [40].

In his original publication which introduced the Keldysh parameter, $\gamma$, L. V. Keldysh also derived a general expression for the ionization probability which was valid in the multiphoton and tunneling limits [11]. His derivation included the effect of the ponderomotive shift on the continuum states but neglected the shift of the ground state. This is a frequently used approximation since these energy shifts tend to be small in comparison with the atom’s ionization potential. Further, the model maintains more generality by neglecting the ground state shift which is dependent on an atom’s specific polarizability. Keldysh also treated the remaining ion as having a short range potential, thereby neglecting its effect on the outgoing electron’s motion [15, 41].

Though the final expression Keldysh derived was quite general it is not the most common method for calculating the ionization rate. The more standard approach was initially proposed in a 1986 paper by Ammosov, Delone and Krainov and is therefore usually referred to as the ADK model [42, 43]. The ADK model was motivated by an interest in describing the ionization rate in an alternating field for complex atoms in arbitrary initial states (with specific n, l and m quantum numbers) and allowing for higher order ionization, Z. They further considered the limit of intense, low-frequency fields. More specifically they required that $\hbar \omega \ll I_p$ and the applied field strength is much smaller than the atomic field strength.
In this limit the quantum mechanical adiabatic approximation is applicable and we can assume the potential barrier width does not change during the electron’s tunneling process [42, 7, 43]. The Keldysh model in the limit of \( \gamma < 1 \) (the tunneling regime) reproduces the ADK formalism.

One of the key limitations of ADK is that it neglects rescattering. In our earlier discussion of the semiclassical model this issue arose when we compared theory to the results of multiple ionization experiments. The ADK theory only accounts for sequential ionization and cannot reproduce the knee-like structure visible in higher charge states. As was briefly mentioned, the ADK model is frequently used to calculate the tunneling rate for ‘Step 1’ in the semiclassical 3-Step-Model.

As in the previous approaches ADK assumes the dipole approximation so the spatial dependence is neglected, \( kx + \omega t \rightarrow \omega t \). Further, in the tunneling limit, only the initial and final states are important so the theory neglects any transitions through excited states. In the following discussion we will be using atomic units unless otherwise stated. The model considers an electron influenced by a Coulomb potential and an applied laser field [43]:

\[
V = -\frac{Z}{r} + Ez
\]

where \( Z \) is the charge of the remaining ion, \( r \) is the distance from the nucleus, and \( E \) is the external field amplitude which we assume to be pointing along the \( z \)-direction. One of the key approximations in the ADK theory is that in the asymptotic limit the atomic potential appears Coulombic [7, 43]. With these approximations and considering a static electric field the ionization rate is given by:

\[
W_{\text{static}} = \frac{|B|^2}{2^{m|m|}m!} \frac{1}{\kappa^{2Z/\kappa - 1}} \left( \frac{2\kappa^3}{E} \right)^{2Z/\kappa - |m|-1} e^{-2\kappa^3/3E} \tag{1.29}
\]

where \( \kappa = \sqrt{2I_p} \) and \( m \) is the magnetic quantum number. The constant coefficient ‘\( B \)’ is given by [42, 43]:

\[
B = Q(l, m) \kappa^{Z/\kappa + 1/2} C_{n^*l^*} \tag{1.30}
\]

where \( n^* \) and \( l^* \) are the effective principal and orbital quantum numbers defined as \( n^* = Z/\sqrt{2I_p} \) and \( l^* = n_0^* - 1 \). In the latter expression \( n_0^* \) is the effective principle quantum number of the ground state and

\[
Q(l, m) = (-1)^{(m+|m|)/2} \sqrt{\frac{2l + 1}{2}} \frac{(l + |m|)!}{(l - |m|)!} \tag{1.31}
\]

The probability for ionizing from the \( m = 0 \) state is substantially greater than for \( m \geq 1 \), therefore taking \( m = 0 \) is usually a safe approximation.

In general \( C_{n^*l^*} \) needs to be calculated numerically by matching the atomic wavefunction
to the asymptotic form of the Coulomb functions. An approximate form for these constants was also derived by applying a quasi-classical approximation which achieved fairly accurate agreement with the numerical results. By treating the electron as free in the asymptotic region they showed that [42]:

$$C_{n^*l^*}^2 = \frac{2^{2n^*}}{n^* \Gamma(n^* + l^* + 1) \Gamma(n^* - l^*)}$$

The behavior of the rate equation, Eq. 1.29, is dominated by the exponential term which depends on the electric field amplitude. Therefore, we expect an increased ionization rate near the peaks of the field [43]. This relationship is shown in Fig. 1.11 where the blue line corresponds to the integrated ionization yield as a function of time for the interaction between argon and a 3.6\(\mu\)m, 100fs laser pulse with a peak intensity of \(3 \times 10^{14}\)\(W/cm^2\). The electric field of the laser pulse is shown in red and it is clear that the ionization rate increases near the peaks of the field.

Through Eq. 1.29 we can calculate the ionization rate for a single (static) electric field value. If we now consider a linearly polarized monochromatic field then the cycle-averaged rate is given by [43]:

$$W_{avg} = \left(\frac{3E}{\pi \kappa^3}\right)^{1/2} W_{static}$$

This expression is equivalent to the form in the original ADK paper [42]. A similar approach can be made for elliptically and circularly polarized light [43]. The most typical method
for calculating the ADK ionization rate in modern short-pulsed, low-frequency, strong-field experiments is to use the static rate expression, Eq. 1.29. Then the total yield is determined by integrating over the spatial and temporal profile of a focused laser pulse [43].

Various groups have tried to improve on this theory by taking into account some of the neglected effects or improving on approximations. The later work by Delone and Krainov [7] took into account the motion of the electron during the tunneling process. This approach removed the constraint that the electron has zero momentum immediately after tunneling. By considering linearly polarized light they derived the ionization rate contribution for electron momenta parallel to the field polarization:

\[ W(p_{||}) = W_{\text{static}}(p = 0) \exp \left[ -\frac{p_{||}^2 \omega^2 (2I_p)^{3/2}}{3E^3} \right] \] (1.34)

where \( p_{||} \) is the momentum of the electron along the field polarization and \( W_{\text{static}}(p = 0) \) is the previously derived result, Eq. 1.29 [7]. The ionization rate for the electron with momentum perpendicular to the field axis, \( p_{\perp} \), is:

\[ W(p_{\perp}) = W_{\text{static}}(p = 0) \exp \left[ \frac{(2I_p)^{1/2} p_{\perp}^2}{E} \right] \] (1.35)

The work by Tong and Lin [40] further extended the validity of the static field ADK model to the regime of over-the-barrier ionization. One of the key assumptions we stated in the original ADK theory was that the applied field strength had to be much smaller than the atomic field strength. Their model introduced an exponential correction factor in terms of a scaled field strength and scaled ionization potential:

\[ W_{\text{TBI}}(E) = W_{\text{static}} \times \exp \left[ -\frac{\alpha Z^2 E}{I_p k^3} \right] \] (1.36)

where \( \alpha \) is a constant dependent on the orbital quantum number from which the electron ionizes. The agreement with numerical solutions of the Schrödinger equation were significantly improved when this correction factor was included. The extent of this improvement increased at longer wavelengths and larger target ionization energies.

The ADK theory has also been extended to molecules, referred to as MO-ADK by Tong et al [44]. In general molecular systems increase the level of complication due to the electronic cloud not being spherically symmetric, accounting for the molecular alignment with the field polarization, as well as rotational and vibrational motion. The approach taken in this situation was to express the asymptotic molecular wavefunction by a summation of spherical harmonics in a single center expansion [44]. They determined that the rate was more strongly dependent on the properties of the outgoing wavefunction than specific atomic/molecular structures. This led to the prediction that species with similar ionization
potentials will exhibit similar ionization rates as a function of intensity. However, even this result was further complicated by needing to consider the type of bonding orbitals present in the molecular species [44, 15].

1.4.2 Strong-Field Approximation (SFA)

Another frequently used quantum mechanics based theory is the semi-analytical strong-field approximation (SFA). This approach focuses on calculating the transition amplitude, $M_p$, between an atomic ground state, $|\psi_0\rangle$, and a continuum state, $|\chi_p\rangle$ (where $p$ is the asymptotic momentum), due to the influence of a time-evolution operator $U(t, t')$ [45]:

$$M_p = \lim_{t\to+\infty; t'\to-\infty} \langle \chi_p | U(t, t') | \psi_0 \rangle$$  \hspace{1cm} (1.37)

As its name indicates, SFA adopts the short range potential approximation and therefore assumes that the motion of the ionized electron is only influenced by its interaction with the laser field. The exact solutions for the wavefunctions of a charged particle in an electromagnetic field have been solved and are known as the Volkov states [13, 46]. These solutions are used in the SFA model for the form of the electron’s final (ionized) state wavefunctions. Multiple approaches of using SFA exist and primarily differ in the choice of gauge and therefore the results are, in general, not gauge invariant [45, 5]. The specific approach shown here is commonly referred to as Keldysh-Faisal-Reiss (KFR) which adopts the length gauge. Further, note that KFR neglects bound excited states and level shifts due to interaction with the field [13]. Atomic units continue to be used in the following discussion.

The ionization process is described by the electron’s interaction with the applied laser field, $E(t)$. Therefore the transition amplitude for ionization is expressed as [45]:

$$M_p^{(0)} = -i \int_0^{T_p} dt \langle \chi_p(t) | r \cdot E(t) | \psi_0(t) \rangle$$  \hspace{1cm} (1.38)

where $T_p$ is the length of the pulse. The atomic ground state has an energy $-I_p < 0$. The continuum state is a Volkov state with a drift momentum of $p$:

$$|\chi_p(t)\rangle = |p + A(t)\rangle exp[-iS_p(t)]$$  \hspace{1cm} (1.39)

where the action of the continuum state is:

$$S_p(t) = \frac{1}{2} \int dt' [p + A(t')]^2$$  \hspace{1cm} (1.40)

and the vector potential is $A(t) = \int_{-\infty}^{t} d\tau E(\tau)$. Therefore the total action of the initial
(ground) and final (continuum) states is:

\[ S_{Total}(t) = I_p t + S_p(t) \]  \hspace{1cm} (1.41)

Combining these results the transition amplitude in the KFR formalism is:

\[ M_p^{(0)} = -i \int_0^{T_p} dt \, e^{i S_{Total}(t)} (p + A(t) \cdot r \cdot E(t)) \langle \psi_0 \rangle \]  \hspace{1cm} (1.42)

Notice that the KFR transition amplitude, \( M_p^{(0)} \), does not account for rescattering and can be viewed as the quantum-mechanical equivalent to the semiclassical Simpleman model discussed earlier. Therefore \( M_p^{(0)} \) only describes the direct ionization (up to \( 2U_p \)) portion of the photoelectron spectrum. The SFA model has been extended to include rescattering in which case the total transition amplitude is \([45, 47]\):

\[ M_p^{SFA} = M_p^{(0)} + M_p^{(1)} \]  \hspace{1cm} (1.43)

where the first term corresponds to the direct trajectories, given by Eq. 1.38. The second term (which is occasionally referred to as SFA2 [47]) accounts for rescattering and can be viewed as equivalent to the semiclassical 3-Step-Model. It is expressed as [45]:

\[ M_p^{(1)} = - \int_0^{T_p} dt_0 \int_{t_0}^{\infty} dt_1 \int d^3k \, \langle \chi_p(t_1) | V | \chi_k(t_1) \rangle \times \langle \chi_k(t_0) | r \cdot E(t_0) | \psi_0 \rangle \]  \hspace{1cm} (1.44)

and includes the ‘three steps’ of the electron trajectory. First, we integrate over all possible ionization times, \( t_0 \), which occur when the electric field of the laser pulse is present, \( 0 \leq t_0 \leq T_p \). Then we integrate over the possible electron momenta, \( k \), in the intermediate time interval before rescattering occurs at time \( t_1 \) (where \( t_1 > t_0 \)). In the expression above \( V \) is the parent ion’s potential with which the ionized electron interacts when it elastically rescatters (recall that SFA adopts a short range potential approximation). However, as a word of warning, in cases where a short range potential approximation is not physical, or for the case of slow electrons, this theory no longer produces very reliable results [45].

Like any other theoretical approach SFA has its strengths and weaknesses. One of its primary strengths is the ability to follow and control the ionized electron’s available quantum orbits (in the classical picture these correspond to the possible electron trajectories). This provides the ability to gain valuable insight into the dynamics of the ionization and rescattering processes.
1.4.3 Single Active Electron Time Dependent Schrödinger Equation (SAE-TDSE)

The other commonly used quantum mechanical approach is directly through the Time Dependent Schrödinger Equation (TDSE). This method requires numerical analysis and is very computationally intensive. A supercomputer is usually a necessity if one wants to model realistic conditions that include the atomic potential and the spatial and temporal profile of the interaction pulse. A common approximation is to assume that the system has a single-active electron (SAE). In this case one assumes that besides the one ionized electron the nucleus and the remaining electrons are frozen in their states. Further expansions from 1D to 3D calculations also drastically increase computational time.

SAE-TDSE calculations also become more time intensive and difficult when longer wavelength light is used. The numerical approach breaks up space and time into a grid. When you have longer wavelengths the electron’s excursion distance, travel time and maximum achievable velocity also increase. These force a much larger spatial and temporal grid than is required at shorter wavelengths. This especially is a difficulty for our data taken at 3 – 4µm which will be discussed in Chapters 3 and 5. For example, at a laser wavelength of 3.6µm a cycle of the field is approximately 12fs while for a laser wavelength of 800nm a cycle of the field is only 2.7fs. Further, the maximum excursion distance scales linearly with the field and quadratically with the wavelength. Therefore, at a constant intensity the electron’s excursion distance in a 3.6µm wavelength laser will be about 20 times larger than at 800nm. The other major disadvantage is the lack of insight into the actual dynamics that occur during the ionization and rescattering processes. In general the initial parameters are plugged in and then one gets a result out. Due to the long computational times it is difficult, if not impossible, to tweak all of the parameters to get a better understanding. Therefore, when more insight into the dynamics is desired the SFA method is usually implemented.

Despite all of these difficulties the SAE-TDSE also has important advantages. Most importantly, it produces accurate results which are great for comparison directly to experiment or as a benchmark to determine the accuracy of another model. This is because the calculation includes all of the physical features which are either ignored or approximated in other models. On the atomic side it includes the ground and excited states, the long range potential and the ionized electron’s wavepacket dynamics when it is in the continuum. It also takes into account realistic temporal and spatial pulse profiles. A beautiful example of the capabilities of the SEA-TDSE calculations can be seen in the work of Nandor et al [48].
Chapter 2

Experimental Setup

This chapter is a summary and introduction to the experimental apparatus that was used in the various studies that will be discussed in the subsequent chapters. An effort is made to concisely but thoroughly treat the important aspects so the reader may better understand the capabilities and limitations of each design. I begin by discussing the two laser systems that were used. Much more emphasis is placed on the mid-infrared (MIR) system since I was primarily responsible for its day-to-day operation and maintenance. Also, the MIR system underwent a major rebuild and therefore should be introduced more thoroughly. This laser system was used on all of the alkali metal (Chapter 3) and C$_{60}$ (Chapter 5) experiments. A more succinct discussion will be made of the 2$\mu$m system. This laser system was maintained and operated by other members in the group and has been thoroughly discussed in the thesis of Dr. Cosmin Blaga [10]. The 2$\mu$m laser system was used for the noble gas experiments (Chapter 4).

Section 2.4 will introduce the Time-of-Flight spectrometer which is our primary method for ion and electron detection during strong-field interactions. Finally, the two heating sources/ovens that were used in the alkali metal and C$_{60}$ experiments will be introduced in section 2.5.

2.1 Generating Short, Intense Laser Pulses

Since the invention of the first laser system by Maiman in 1960 which utilized ruby as the gain medium [49] there has been a consistent push towards creating lasers with shorter pulse durations and higher peak powers. The invention of the Q-switch by McClung and Hellwarth [50] just a year later decreased pulse durations from several hundred microseconds to approximately 10ns [3, 38]. The Q refers to the ‘quality’ factor in a cavity where a high Q-value refers to a low loss cavity and a low Q indicates a highly lossy cavity. In this method of pulse generation the gain medium is pumped while the cavity is maintained in a highly lossy state (low Q-value) therefore reducing the likelihood of stimulated emission
or lasing. Then abruptly the Q value is increased, energy is quickly removed from the gain medium and a short, intense pulse is generated [51]. Though this method helped greatly reduce pulse durations these lasers typically exhibited poor temporal behavior and suffered from unpredictable intensity spikes [3].

The next major technological step, mode-locking, was introduced in the mid-1960s and allowed for the generation of more stable and shorter pulses (less than 1ps) [52]. This approach gets its name because short pulses are generated by ‘locking’ the phases of many laser cavity longitudinal modes. The overlap of many modes locked in phase leads to a destructive interference for most of the cavity length except for temporally short regions where all the phases add constructively and an ultrashort laser pulse is generated. This can be achieved through active (ex. opto-acoustic modulators) or passive (ex. saturable absorber) mode-locking [3, 53, 51].

One of the fundamentally important features for a laser gain medium that can produce temporally short pulses is the ability to support a large bandwidth. This is based on the time-bandwidth relation which, for a Gaussian pulse, states $\Delta t \Delta \nu \geq 0.44$ where $\Delta t$ and $\Delta \nu$ are the full-width-at-half-maximum (FWHM) temporal and spectral pulse widths respectively [51]. This equation determines the minimum necessary spectral width in order to create a pulse with a certain duration in the time-domain. Therefore, broad bandwidth sources have been highly sought out [53].

In 1990 Spence, Kean and Sibbet [54] demonstrated a new method of mode-locking. Specifically, it was shown that the nonlinear refractive index in a Ti:sapphire crystal created its own mode-locking, known as Kerr lens mode-locking (KLM), which helped reduce the complexity of a laser cavity. Ti:sapphire has become one of the most commonly used solid-state laser crystals due to its high gain bandwidth (700-1100nm) which is centered at 800nm, high thermal conductivity and a high energy storage density. Other important broad-bandwidth solid-state laser media include Cr:LiSAF centered at 850nm [55, 3, 53] and ytterbium (Yb) doped fibers and crystals centered near 1$\mu$m [56].

Solid-state based systems have shown a lot of promise due to their relatively long upper level lifetimes, high saturation fluence, broad bandwidths and high damage thresholds. As an example, the saturation fluence for broadband dye or gas lasers is around $1 - 2mJ/cm^2$ while for solid state systems this is typically around $1J/cm^2$ [55]. However, eventually even in solid-state systems the intra-cavity peak laser intensities began approaching the damage threshold of the gain media. The strong non-linear refractive index which helped in mode-locking could also lead to damage by self-focusing [3].

The invention of Chirped Pulse Amplification (CPA) by Strickland and Mourou in 1985 [57] helped alleviate some of these issues. This process reduces the peak power of a pulse by sending it through a grating or prism pair and thereby stretching it temporally, also known as ‘chirping’. An example of a grating based stretcher is shown in Fig. 2.1. Since the red
end of the spectrum will travel a shorter net distance than the blue end the pulse duration is increased, defined as a positive chirp. A double pass mechanism is used to remove spatial dispersion [53]. This pulse can now undergo one or more stages of amplification to increase its peak power without damaging the gain media. Finally, the pulse is brought back to its original duration through the use of a compressor, shown in Fig. 2.2. The compressor is designed to compensate as much as possible for the dispersion introduced by the stretcher as well as any extra dispersion that accumulated during the amplification stages.

In order to get a better feeling for the numbers involved in a fairly standard CPA setup let’s consider an example of a Ti:sapphire based laser system. Usually the front end of the laser is an oscillator which will produce femtosecond pulses with nanojoule energies at MHz level repetition rates. The pulse is then stretched from around 100fs to 100ps which decreases the peak power by 3 orders of magnitude. This stretched pulse undergoes one or more stages of amplification which increases the energy per pulse by 6 – 9 orders of magnitude. Finally, the pulse is compressed back to femtosecond durations [55].

The combination of CPA technology and broad bandwidth gain media has made creating short, intense pulses possible. Other methods of reducing pulse duration even further have been developed but are beyond the scope of discussion for this thesis. However, for the interested reader several useful review articles include [38, 39, 55]. In any laser system design eventually one has to balance the many trade-offs; such as pulse energy, pulse duration, spatial quality, pulse contrast, repetition rate and wavelength.
The progress in reducing pulse duration and increasing intensity can be directly seen in the major experimental observations in strong-field physics. In the 1960s the first multiphoton transitions were observed. Then, in the late 1970s and 1980s, resonances were observed since lasers could finally reach intensities that would sufficiently perturb atomic states. This further opened up the non-perturbative regime with the observation of continuum-continuum transitions like ATI and harmonic generation. Finally, more recent laser systems are capable of producing fields that are comparable to or exceed the Coulomb binding potential which has opened up the tunneling and over-the-barrier regimes [3].

2.2 MIR Laser System

The majority of experiments carried out with ultra-fast strong-field sources have been done in the near-infrared (NIR) regime which is a limitation imposed by available gain media. Commercial solid-state MIR (2–5\(\mu\)m) sources [58] have began to emerge in recent years but the technology is still not mature. We have an interest in performing experiments at longer (MIR) wavelengths since this will allow us to further test the validity of the Keldysh theory. By increasing the laser wavelength we can increase the ponderomotive energy, \(U_p\), which in turn means a higher maximum rescattering energy for the freed electron and a higher maximum detected energy. Therefore, further examination of the MIR spectral region is interesting from a fundamental strong-field physics point of view. From a more applied perspective, MIR wavelengths correspond to the frequency regime of molecular bond vibrations. Therefore, ultra-short pulses at these wavelengths can allow us to investigate bond breaking, forming and relaxation on the time scales that these events occur. A more
accurate physical understanding of these processes can be very useful.

Due to the solid-state material difficulties mentioned earlier we cannot directly produce pulses at MIR wavelengths. However, with sufficiently high intensity light we can take advantage of nonlinear optical phenomena to convert light to other wavelengths. In this section I discuss our method of generating 3 - 4µm wavelengths with 100fs pulse durations. We use a CPA based Ti:sapphire system to produce intense ultra-short pulses at 792nm. Then we employ a two-stage system using Optical Parametric Amplification (OPA) and Difference Frequency Generation (DFG) to down convert the wavelength to the MIR regime. Before the laser rebuild we generated MIR wavelengths by performing DFG between a Ti:sapphire beam centered at 816nm and an Nd:YLF beam centered at 1.053µm. The details of this system are discussed in the thesis of Dr. Emily Sistrunk [59].

2.2.1 Ti:sapphire/CPA

A block diagram of the laser layout is shown in Fig. 2.3. The initial Ti:sapphire signal is produced by a Spectra Physics Tsunami mode-locked oscillator tunable in the range of 770 – 910nm. The central wavelength and bandwidth are selected through an intra-cavity slit and two sets of prisms used for dispersion control. We operate at a central wavelength of approximately 792nm with a bandwidth of 10 – 11nm which, for a Gaussian distribution, corresponds to a transform limited pulse duration of 85fs. This agrees well with our most recent measurement of approximately 80fs using the frequency-resolved-optical-gating (FROG) technique [60]. The Tsunami average output power is 700mW at 80MHz which corresponds to 8.75nJ/pulse. The Ti:sapphire gain medium is water cooled for temperature control.

A small portion of the output beam is sent onto a photodiode (see Fig. 2.4). This signal is sent to the Tsunami’s control electronics; specifically the Model 3955 (AOM driver electronics) and the Model 3930 (Lok-to-Clock electronics). The Model 3930 maintains the laser’s repetition rate by adjusting the piezo-stage of one of the cavity mirrors. It receives a timing input from the Model 3955 which monitors the strength of the photodiode signal. The Model 3955 is also the AOM (acousto-optic modulator) driver which enables mode-locking and therefore pulsed operation of the Tsunami. We continuously monitor the Tsunami’s central wavelength and bandwidth with an Ocean Optics USB 2000 spectrometer connected to a computer. The pulse train stability is monitored with a fast photodiode (Thorlabs DET 10A) connected to a Tektronix TDS2012 100MHz oscilloscope.

The Tsunami Ti:sapphire crystal is pumped by a Spectra-Physics Millennia Pro s-Series. The Millenia generates 1064nm light in a Nd:YVO₄ (neodymium yttrium vanadate) crystal which is doubled to 532nm in an LBO (lithium triborate) crystal. The Nd:YVO₄ gain medium is end-pumped by a diode module at 809nm. A small portion of the output beam is directed towards a photo-detector to help maintain the system’s power stability to within
±1% by adjusting the diode pump current. The Millenia output is continuous wave (CW) with an average power of 5W.

The output of the Tsunami is sent into a homebuilt stretcher; a modified version of the one shown in Fig. 2.1. We employ a folded, single grating design using a spherical mirror instead of lenses to avoid chromatic aberrations. The stretched output pulses have a 230ps duration at a repetition rate of 80MHz.

The stretched pulses undergo two stages of amplification. The first stage is a regenerative amplifier (also called a regen). The chirped pulse is injected into the cavity using a fast switching Pockels Cell (PC) where it undergoes multiple passes through the Ti:sapphire gain medium. The PC is rotated by another quarter wave (for a total of a half-wave rotation) to eject the amplified pulse. The Ti:sapphire crystal in the regen cavity is water cooled and pumped by a Quantronix Darwin - 527 Series. The Darwin is a diode-pumped, acousto-optical Q-switched, Nd:YLF (neodymium-doped yttrium lithium fluoride) based laser. The 1053nm light is intra-cavity doubled to 527nm in an LBO crystal. The Darwin output is multi-mode with a 1kHz repetition rate, 11W of power, <200ns pulse duration and a 1% pulse stability. The regen cuts the repetition rate from 80MHz to 1kHz. The output power is approximately 1.4W with ≤ 0.2W of ASE (amplified spontaneous emission). ASE may exhibit fairly good spatial coherence (comparable to the laser) but tends to lack temporal coherence [51] producing nanosecond length pulses. We attempt to minimize the effects of ASE while not sacrificing too much total output power. This regen design is a replica of the design discussed in the thesis of Dr. Barry Walker [61].

The second stage of amplification is a multipass power amplifier. The complete design
Figure 2.4: A schematic of the Ti:sapphire system timing electronics which synchronize the temporal overlap of ‘pump’ and ‘signal’ pulses, and provide a trigger to the detection electronics (discussed in Sec. 2.4). See text for more details.

details can be found in the thesis of Dr. Anne Marie March [62]. The multipass crystal is liquid nitrogen cooled and pumped by an acousto-optically Q-switched Positive Light Evolution-30. The Evolution is an Nd:YLF based laser with a fundamental wavelength of 1053nm which is intra-cavity doubled to 527nm using an LBO crystal. The laser rod and diodes are water cooled and the LBO temperature is maintained at 321.1°F. The Evolution produces a multi-mode beam, at a 1kHz repetition rate, 100 – 350ns pulse duration, 17W of power and an energy stability of <1%. The power after the multipass amplifier is in the range of 5 – 5.5W. This beam is then sent into a homebuilt compressor (see Fig. 2.2) which brings the pulse duration down to approximately 100fs (see Fig. 2.5). After the compressor the 792nm beam is transported from the main laser room to the target room. At this point, before entering the next phase of the laser system, the power is typically ∼ 3.5W.

Figure 2.5: Performance of the 792nm beam immediately preceding the OPA. Left panel: the autocorrelation trace. This corresponds to 95fs for a Gaussian beam. Right panel: a FROG trace of the beam. A rounder shape signifies a closer to transform limited pulse. The side lobes signify a contribution from higher order dispersion.
2.2.2 OPA

In order to generate short, MIR wavelength pulses in the 3−4µm range we use a home-built optical parametric amplifier (OPA). Our system is a modified version of the design of Cussat-Blanc et al [63]. A tunable MIR wavelength source is achieved by taking advantage of several nonlinear optical phenomena which occur in crystals when they interact with high intensity fields. The subject of nonlinear optics is very broad and a topic that can easily fill a text book [64] so in the current discussion we focus on Difference Frequency Generation (DFG) and White-Light Continuum Generation (WLCG) which are essential for the functionality of our OPA system.

In nonlinear optical media the polarization no longer has a simple linear dependence on the electric field, instead it is expressed as a power series [64]:

\[ P(t) = \epsilon_0[\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + ...] \]  \hspace{1cm} (2.1)

where \( \chi^{(1)} \) is the linear susceptibility, and \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second- and third-order nonlinear susceptibilities respectively. The first term is the one known from conventional optics where the induced polarization is linear with the field. DFG is a second order interaction, a \( \chi^{(2)} \) process, and can only occur in non-centrosymmetric crystals (in our case we use potassium titanyl arsenate or commonly referred to as KTA). KTA is a desirable medium for short pulse (large bandwidth) nonlinear interactions due to its high transparency range (0.35−5.3µm) and high effective nonlinearity (\( d_{eff} = 3.1\text{pm/V} \)) [63].

A DFG scheme corresponds to a three photon process. The beam with the highest photon energy (shortest wavelength) is known as the ‘pump’ and it is spatially and temporally overlapped in a nonlinear medium with a second beam referred to as the ‘signal’. Photons in the ‘signal’ beam have a lower energy or equivalently a longer wavelength. When these two beams interact a third beam is produced and is commonly referred to as the ‘idler’. By energy conservation the frequency of the ‘idler’ photons is:

\[ \omega_{idler} = \omega_{pump} - \omega_{signal}. \]  \hspace{1cm} (2.2)

Therefore, in order to create a single ‘idler’ photon, one ‘pump’ photon must be destroyed and one ‘signal’ photon will be created. Therefore the DFG process is not only a method for creating a new frequency, \( \omega_{idler} \), but also a means of amplifying the signal, \( \omega_{signal} \). Due to this property DFG is sometimes referred to as Parametric Amplification. In our laser scheme we take advantage of both of these mechanisms.

In addition to crystal choice, several parameters like crystal orientation, polarizations and fluences of input beams are critical for efficient amplification. Specifically, we want to optimize the process in a way that ‘idler’ photons generated throughout the length of the crystal add coherently. This process, known as phase-matching, is in fact an explicit
momentum conservation law expressed as [64]:

\[ \vec{k}_{\text{pump}} = \vec{k}_{\text{signal}} + \vec{k}_{\text{idler}}, \]  

where \( \vec{k}_{\text{pump}} \), \( \vec{k}_{\text{signal}} \), and \( \vec{k}_{\text{idler}} \) correspond to the wave-vectors of the pump, signal and idler beams respectively. The wave-vector depends on the frequency of the incident beam and the index of refraction of the material, which is also frequency dependent; \(|\vec{k}| = k = n(\omega) \omega/c\).

Since in a typical DFG scheme we are dealing with three different frequencies, the difficulty of achieving phase-matching is clear and requires a careful choice of crystal alignment and beam polarizations. A uniaxial crystal [64] has a unique optic-axis which is a property intrinsic to the crystal. Its linear optical properties have rotational symmetry about this axis. ‘Ordinary’ polarization corresponds to a polarization that is perpendicular to the plane containing the optic-axis and the wave vector, \( \vec{k} \); this plane is known as the principal plane. ‘Extraordinary’ polarization corresponds to a polarization parallel to the principal plane.

The \( \text{Al}_2\text{O}_3 \) (sapphire) crystal we use for WLCG (discussed later) is a uniaxial crystal, whereas KTA is a biaxial crystal. In general, there are several schemes for combining beams with different polarizations, propagation directions, and crystal alignments in order to maximize the nonlinear conversion efficiencies.

If we now consider our initial goal again, producing a tunable MIR wavelength source, then at least one of the frequencies, \( \omega_{\text{pump}} \) or \( \omega_{\text{signal}} \), will also need to be continuously tunable. In the previous section I discussed how we generate and amplify a short-pulsed beam at 792nm which serves as the pump beam for the OPA. Although in principle Ti:sapphire systems can operate at other wavelengths in the 700−1000nm range, in order to vary the central wavelength we would need to reoptimize and align the majority of the CPA laser system and to my knowledge no such system exist. Instead, tunability will be accomplished via the signal beam. So far I have not discussed anything related to the production of the signal beam so let’s address this now.

We produce a tunable signal beam via WLCG driven by taking a small fraction of the 792nm pump and focusing it in a sapphire window. WLCG makes use of the nonlinear refractive index [64]:

\[ n(I) = n_0 + n_2 I, \]  

where \( n_0 \) is the normal linear refractive index and \( n_2 \) is the nonlinear refractive index. The nonlinear component tends to be significantly smaller than the linear and therefore only becomes non-negligible during high intensity interactions. For sapphire \( n_0=1.7555 \) and \( n_2=3.1 \times 10^{-16} \text{cm}^2/\text{W} \) [65].

WLCG is a highly complex process which produces significant spectral broadening, along with spatial and temporal changes in the beam during high intensity interactions [66]. Self-phase modulation is often viewed as the dominant, or at least starting, mechanism in
continuum generation. If we consider a general laser pulse with an electric field, \( E(t) \cos(\omega t - kx) \), propagating in a linear media of length \( L \) then this pulse would acquire an optical phase shift of \( \phi_0 = \omega L n_0 / c \) [53]. However, in a situation where the nonlinear component cannot be neglected the medium will cause the pulse to accrue an additional phase of \( \phi_{NL} = n_2 I(t) \omega L / c \). Therefore, as the pulse traverses the nonlinear medium it exhibits a time-varying phase which depends on the intensity profile of the beam and leads to an effective broadening of the spectrum [64]. Other nonlinear processes, like self-focusing and filamentation, are also closely linked to continuum generation and arise due to the intensity dependent refractive index [65].

One frequently used method for quantifying the nonlinear phase shift accumulated during propagation is through the B-integral [51]:

\[
B = \frac{2\pi}{\lambda} \int n_2 I dz,
\]

where \( z \) is the direction of propagation of the incident beam in the material. When \( B > 1 \) nonlinear effects are considered to be significant.

At this point it may be clear how a tunable MIR laser source based on WLCG and parametric amplification works. The optical layout of our setup is shown schematically in Fig. 2.6. First, using three beamsplitters the 3.5mJ pump beam is split into four arms. The weakest arm, containing only 30\( \mu \)J drives the WLCG stage. The polarization of the WLCG-driving beam is rotated 90\( ^\circ \) using a zero-order half wave plate. This is necessary in order to produce the extraordinary-wave signal. Next, the lens L1 focuses the beam in a 3mm thick uncoated sapphire window, where the spectrum is broadened via WLCG and recollimated by lens L2. An iris inserted before L1 controls the intensity of the pump in the sapphire window to prevent multiple filament formation, an unstable regime leading to permanent damage. After L2, the beam encounters a dichroic mirror (DM) that reflects 950–1200nm light and transmits the remaining 792nm.

The WLCG seed signal reflected by DM1 is too weak to drive a single DFG stage. Therefore, two preamplification stages are necessary in order to generate a strong signal beam for the third and final DFG stage. All DFG stages use KTA crystals (Redoptronics, cut at \( \theta = 39^\circ \), uncoated). The maximum group velocity mismatch in KTA for the generation of the idler wavelength of 3.3\( \mu \)m is 75fs/mm [63]. Since our pulses are approximately 100fs in duration, 2-2.5mm crystal lengths are ideal. In our experiment we have a 5mm thick crystal for the first stage and two 2.5mm thick crystals for the last two stages. The first one is longer than we would ideally desire but this was a limitation of what we had available in the lab during construction of the system. Crystal angles and mixing geometry were modeled using SNLO, a free software developed by Dr. Arlee Smith of AS-Photonics. The chosen geometry is ordinary for pump and idler and extraordinary for signal (Type IIa). Phase matching is optimized by angle tuning the crystals, rotating the plane containing
Figure 2.6: MIR OPA layout. The input pump is split into four arms by beam splitters BS1-3. The weakest arm drives the broadband white light continuum generation (WLCG) stage. The resulting seed pulses are amplified in three KTA crystals, generating tunable 150µJ MIR pulses. The optical elements are: half wave plate (HWP), lenses (L1-2), telescopes (T1-3), dichroic mirrors (DM1-5), mirrors (M1-2) and beam dumps (BD).

the wave-vectors and the extraordinary wave’s polarization along the axis defined by the ordinary wave’s polarization.

The first two stages are driven by 170µJ and 300µJ pump beams. The diameter of each beam at the KTA crystals were controlled via telescopes T1 and T2 in order to deliver an intensity of approximately 200GW/cm², half of the damage threshold reported by Cussat-Blanc et al [63]. At the beginning of this section I mentioned that we are using a modified version of the OPA design of Cussat-Blanc et al [63]. Their design used a double-pass scheme where two stages of amplification were performed in the same crystal. After the first pass, the pump beam was reused in the second pass. In our setup we decided not to reuse the pump. The nonlinear refractive index for KTA is quite large, n₂=1.7×10⁻¹⁵cm²/W [67] and the B-integral is approximately 2.7/mm at an intensity of 200GW/cm². This B-integral accumulation is too severe as it introduces significant nonlinear instabilities that translate directly into poor beam quality. After two amplification stages, the WLCG weak seed has been amplified to approximately 30µJ, as exemplified in Fig. 2.7. The FWHM of the resulting signal was approximately 30nm, supporting a transform-limit signal of approximately 50fs. The reduction in bandwidth from the broad WLCG spectrum to that of the resulting signal was due to the acceptance bandwidth of KTA. To demonstrate the tunability of the OPA, in Fig. 2.8 we plot several signal spectra, obtained by tuning the preamplifier’s KTA crystals. Although we lack a suitable MIR spectrometer to produce a similar plot for the accompanying idler beams, using the phase matching relation above we estimate gap-free idler tunability in the 2.7-4µm range.
Figure 2.7: White light continuum generation spectrum and the double pass signal. The WLCG spectrum (blue) was measured after the preamplifier stage with the pump arms blocked. After two amplification stages, the WLCG spectrum is narrowed by the acceptance angle of the KTA crystal to produce a 30nm FWHM signal pulse (red).

Figure 2.8: OPA tunability. Tunability of signal spectra after the preamplifier. The gap-free tunability allow generation of tunable 2.7-4\(\mu\)m pulses.
Figure 2.9: OPA Performance. Measured photoelectron spectra in xenon at 3.6µm. The vertical green dash line marks the so-called 2U_p break, the maximum energy for direct electrons. This method allows us to infer an intensity of 80TW/cm^2. In the inset, the profile of the MIR beam before the vacuum chamber.

After the preamplifier, the resulting 30µJ signal beam is noncollinearly mixed with the remaining 3.0mJ pump arm in a final DFG stage in order to produce the desired MIR idler beam. The noncollinear geometry was chosen in order to separate the idler beam spatially after the KTA crystal, thus avoiding the use of expensive ultra-broadband MIR dichroic mirrors. The mixing angle was only a few degrees, kept as small as possible in order to minimize pulse phase front tilts. After mixing, we were able to generate approximately 450µJ of signal and 150µJ of idler, for a total conversion efficiency of ~20%. After the OPA, the MIR beam was collimated and transported for experiments to our ultrahigh vacuum chamber using one gold and five silver coated mirrors. The beam also passed through an anti-reflection coated silicon window, and a four-Brewster plate polarizer and half-wave plate acting as a power attenuator. At this point, using a thermal camera, the beam had a nearly round profile, measuring 11.4mm 1/e^2 diameter (see insert of Fig. 2.9). The 85µJ of MIR beam remaining after transport was focused using a CaF_2 uncoated lens with 100mm focal length into the experimental chamber. Using xenon as a calibration gas, we estimated an intensity of 80TW/cm^2 at 3.6µm. From this measurement we estimate that the MIR beam has a M^2 value approaching 1 and a time duration of ~80fs.
2.3 $2\mu m$ OPA System

The other laser system that was used is referred to as the ‘$2\mu m$’ system even though it is also a tunable source. The method of generation is actually quite similar to that of the MIR system but the laser parameters are a bit different. It is a Ti:sapphire based CPA scheme where the output of an oscillator (Nanolayers GmbH Venteon) enters a homebuilt stretcher followed by two stages of amplification (a regenerative and multipass amplifier) and then the pulse is compressed. This beam is the pump for a commercial, tunable OPA (Light Conversion’s HE-TOPAS-Prime). The pump beam before the OPA has a wavelength of 790nm, a power of 6.1W, 55fs (FWHM) pulse duration, 20nm (FWHM) of bandwidth and a repetition rate of 1kHz. The ‘signal’ or ‘idler’ beams of the TOPAS output can be used, allowing for almost complete tunability over 1100 – 2700nm. The signal beam is tunable in the range of 1100 – 1600nm with pulse energies around 0.7 – 1.4mJ. The idler beam can be tuned in the range of 1600 – 2700nm with energies of 0.4 – 1.2mJ per pulse. Figure 2.10 is reproduced from the installation service report and shows the measured pulse energy as a function of wavelength for the signal and idler beams.

Figure 2.10: Light Conversion’s HE-TOPAS-Prime output beam characterization. The pulse energy as a function of wavelength for the signal and idler beams is plotted.

2.3.1 Application for Noble Gas Experiments

The experiments on the noble gases (discussed in Chapter 4) were performed at multiple wavelengths in the range of 560 – 750nm. We take several steps to convert and clean up the output of the TOPAS to achieve this desired wavelength range. First, we block the idler
and only use the signal output which is vertically polarized upon exiting the TOPAS. Then the frequency is doubled in a BBO (beta barium borate) crystal with a second harmonic generation (SHG) conversion efficiency of $\sim 30\%$. After the BBO crystal the beam is a mix of the remaining fundamental (vertically polarized) and doubled (horizontally polarized) wavelengths. In order to remove the contamination from the fundamental beam we use two shortpass dichroic mirrors (Thorlabs DMSP1000, $45^\circ$ AOI). The transmission and reflection curves for the s-polarized doubled signal and p-polarized fundamental are shown in Fig. 2.11. If we consider an average reflectivity of $92\%$ in the range of $1100 - 1600\text{nm}$ then after two passes through the DMSP1000 we will have $< 1\%$ of the remaining fundamental beam. The ability for these optics to remove the fundamental wavelength contamination was double checked by placing a power meter after the two mirrors and detuning the BBO crystal (effectively using the full power of the signal beam at the fundamental wavelength). No transmitted leak through was detected within the sensitivity of the power meter.

### 2.4 Time-of-Flight Spectrometer

All of the experimental data which will be discussed in this thesis relates to measuring the photoelectrons or ions produced during a strong field interaction between a focused laser

![Figure 2.11: The % transmission and reflection curves for the DMSP1000, 45° AOI. The fundamental is p-polarized and has a wavelength range of 1100–1600nm. The BBO doubled signal is s-polarized with a wavelength range of 550–800nm. Characterization provided by Thorlabs.](image)
beam and a gas phase atomic or molecular target. These experiments were performed inside two different ultrahigh vacuum chambers. Alkali metal atoms and C\textsubscript{60} are a solid/powder at room temperature and therefore require heating (an oven source) to convert them to a gas phase atomic/molecular beam. Experiments on these species were performed in the same chamber so I will refer to this as the ‘Oven Chamber’. The experiments on the inert gases were performed in the second chamber and I will refer to this as the ‘Inert Gas Chamber’. The basic theory for the Time-of-Flight (TOF) measurements in these two chambers is the same. The primary difference is in the length of the two flight tubes. Therefore, I will focus on describing the details of the chamber where the majority of the experiments were performed (the Oven Chamber) and it is straightforward to change a few of the experimental parameters for application in the Inert Gas Chamber. For the interested reader, the thesis of Dr. Cosmin Blaga [10] contains more detailed information about the Inert Gas Chamber.

The ‘Oven Chamber’ pressure is maintained by pumping with two turbomolecular pumps. A 345 liter/sec pump (Leybold Turbvac TMP361) is located above the interaction region and next to the liquid nitrogen trap (see Fig. 2.17) and a 360 liter/sec pump (Leybold Turbvac 360 CSVG) is located over the flight tube. Both of these turbos are backed by a pressure in the range of $1 - 3 \times 10^{-2}$ Torr produced by a rotary vane vacuum pump (Varian SD-200). In order to further decrease the base pressure we bake the chamber near 100 $^\circ$C for 1−3 days to speed up desorption of contaminants in the chamber walls. This is performed after any major work which required opening the chamber to atmosphere for an extended period of time or between experimental runs with different species. Further, we periodically bake after long data runs since the atomic beam experiments (especially the alkalis metal atoms) deposit on the walls and may begin to create patch effects in the chamber. Typically after a bake out we reach base pressures around $1 - 5 \times 10^{-9}$ Torr and the dominant contaminant is H\textsubscript{2}O.

The side-view of the TOF spectrometer layout can be seen in Fig. 2.12. The interaction region is located between plate 1 (P1) and plate 2 (P2). The laser is focused at this point by a lens external to the vacuum chamber. The laser beam enters the chamber horizontally to the optics table so in the layout of Fig. 2.12 the beam would be perpendicular to the page. The alkali metal and C\textsubscript{60} ovens were mounted beneath the chamber so that the atomic/molecular beam would intersect the laser beam perpendicularly. These two ovens will be discussed in detail in Sec. 2.5. For species that are gases at room temperature we would backfill the chamber to the desired pressure by controlling the gas flow using a sapphire flat leak valve. This method was used on the noble gas experiments as well as for delivering argon, xenon, butane and isobutane into the chamber for various calibration measurements.

Stray magnetic fields are a major source of concern for experiments using TOF measurements of charged particles. Magnetic fields cause moving charged particles to curve
Figure 2.12: Side view of the Time-of-Flight spectrometer. The listed dimensions correspond to the ‘Oven Chamber’ design.

during their travel path and since the magnitude of this influence is velocity dependent then the effect on a spectrum is nonuniform. TOF data relies on being able to accurately convert a detected signal measured in the time domain to an energy spectrum for electrons and a mass/charge ratio for ions. Stray magnetic fields can cause electrons or ions to completely miss the detector or at the minimum affect their flight times and therefore negatively influence the accuracy of the converted spectra.

The three plates (P1, P2, and P3) make up the ion lens assembly in a Wiley-McLaren geometry [68]. These plates are made of molybdenum and are coated with Aerodag-G (a graphite spray) to reduce magnetic field effects. During experiments involving electron detection all of these plates are grounded and the electrons are allowed to propagate in free flight. In ion detection mode different potentials are applied to the plates. The method for choosing these potentials will be discussed in Section 2.4.2. The ion lens/interaction region is surrounded by a grounded, gold-coated MuMetal tube which acts as a Faraday cage to reduce the effect of stray magnetic fields penetrating the interaction region. This tube has four holes, 90° apart, to allow a laser beam and an atomic beam to pass through perpendicularly. The electrons or ions are detected after traveling down the 53cm long flight tube. In order to minimize stray magnetic field interactions during this travel path the flight tube is surrounded by a grounded Faraday cage which has been coated with Aerodag-G graphite spray. The surrounding MuMetal shield is also grounded. Whenever possible all other mounting components are chosen to be made of non-magnetic materials (typically ceramic, copper or brass).

A schematic of the multichannel plate (MCP) detector is shown in Fig. 2.13. The voltages applied in electron and ion mode are labeled in the figure. The two MCPs are impedance matched and aligned in a Chevron configuration to avoid ion feedback. When a charged particle enters one of the channels and impacts the channel walls, secondary
electrons are created. This leads to a cascade effect of electrons which are then accelerated onto the collector (a gold coated Kapton foil). In electron detection mode this foil is held at 2260V, a voltage significantly too high to be sent directly into the detection electronics for signal processing. Therefore, in order to protect the equipment the signal on the collector is capacitively coupled out of the detector through the conical anode. If two pulses arrive in coincidence the detector will not be able to distinguish them and will treat them as one. Therefore, we maintain low enough count rates during experiments to treat this as a negligible effect. For more detailed information about MCP detectors see the article by Wiza [69].

![Diagram of the multichannel plate (MCP) based detector. The two MCP plates are arranged in a Chevron configuration. The exiting cascade of electrons are collected onto a gold coated Kapton foil. The output signal is capacitively coupled through the conical anode and further processed before detection. Applied voltages in electron and ion mode are shown in red and blue respectively.]

Directly in front of the detector we have a grounded molybdenum slit which has been coated with Aerodag-G. The purpose of this slit is two-fold. First, the grounded plate helps ensure that the electric field of the detector does not penetrate the field-free flight tube. Second, it is used as an aperture for electron angular distribution studies which will be discussed in the subsequent chapters. The slit is 0.75" wide providing an angular resolution of 2.2°.

The layout of the detection electronics are shown in Fig. 2.14. We use a LeCroy Time-to-Digital Converter (TDC 4208) to record the signal as a function of time. This 8-channel TDC has been set up to run in multi-hit operation allowing a detection of up to 8 hits per laser shot. We do not exceed count rates of 2 – 3 hits/shot during data acquisition to guarantee all hit events are accurately registered. In multi-hit mode the channels are
cascaded so each consecutive channel is activated once the previous channel has detected an event. There is a 3ns dead time between an event being detected and the next channel being activated. The TDC 4208 has a time resolution of 1ns and accepts NIM type inputs. A NIM input is ‘off’ when the voltage is 0V and ‘on’ for -0.8V with a typical rise and fall time of 2 – 3ns. The time values for all hit events are communicated to the computer after every shot.

![Schematic layout of the detection electronics](image)

Figure 2.14: Schematic layout of the detection electronics. See text for detailed description.

We provide 4 inputs to the TDC 4208. The ‘Clear’ (CLR) signal clears all of the data from the previous pulse, resets the logic and places the system back in a ready to operate mode. Performing this function causes all inputs to be disabled for the duration of the CLR signal plus an additional 50ns. We make certain that this trigger is set sufficiently ahead of the laser pulse that no data is missed. The ‘End-of-Window’ (EOW) signal disables all of the inputs and places the TDC in a ready to read-out mode so that the data can be transferred to the computer. Any electron/ion event that occurs within 10ns before this signal may not be recorded properly, therefore the trigger is placed well after all electrons/ions have
reached the detector. Both of these signals are provided through a Stanford Research Systems DG535 Delay/Pulse Generator which is capable of producing NIM-type signals that satisfy the TDC 4208 input requirements. The DG535 is triggered by the ‘T0’ output of another Stanford DG535 which is synchronized with the laser system (see Fig. 2.4). The TDC 4208 ‘CLR’ and ‘EOW’ inputs require NIM-signals longer than 50ns so the DG535 is set to produce 70ns pulses to guarantee properly registered triggers. The DG535 has a channel-to-channel jitter of around 50ps. The active time for the TDC is between the ‘CLR’ and ‘EOW’ signals.

The other two signals the TDC 4208 receives correspond to data acquisition. The position of time = 0 is set by a trigger to the ‘COMMON’ input. Any detected hits before this time are handled as negative time and all signals after correspond to positive time. The TDC 4208 has a 1ns resolution and produces a 24-bit output thereby allowing for a maximum of ±8.3μs of data recording. Since the laser operates at a kHz this is plenty of time to detect all electron/ion hits during every pulse. The signal for the ‘COMMON’ input begins with an InAs photodiode located near the interaction chamber. It is triggered by a back reflection from a coated silicon window (Lambda IBAR2-R4.0-0-WI-500SSi) which filters out the pump and signal light before sending the MIR (idler beam) into the chamber. The photodiode signal is inverted with an EG&G IT100 inverter and split in a mini-circuits 15542. We monitor the stability of this signal by displaying one of the outputs on an oscilloscope. The photodiode signal is kept at ~ |15 – 20| mV. The other output is sent through 2 stages of an Ortec 574 Timing Amplifier. Each stage amplifies the signal by a factor of 4.5. A rise and fall time of 1.2ns make this unit specifically designed for amplifying high speed signals. By undergoing 2 amplification stages the −|15–20| mV signal is amplified to approximately −|300 – 400| mV and remains within the linear response region of the 574. This is sent into an Ortec 584 Constant-Fraction Discriminator which accepts negative signals between 0V and -5V, has a pulse-pair resolving time ≤ 20ns and a time walk of ≤ ±100ps. The discriminator threshold is set to 220mV to trigger on the amplified signal. The output (a NIM-standard fast negative pulse with a width of 5ns) is sent into the ‘COMMON’ input of the TDC 4208 and arrives before any electron/ion events are registered.

The final input signal delivered to the TDC 4208 corresponds to the actual electrons or ions we are measuring. The signal out of the MCP detector is sent into a Fast PreAmplifier (Ortec VT120C). This preamp is designed to amplify pulses with fast rise times of ≤ 1ns and provides a noninverting gain of 20. The amplified pulses have a FWHM of 1.5ns. The electron (ion) signal has a mean pulse height distribution of -500mV (-650mV) with a standard deviation of $\sigma = 320mV$ ($\sigma = 460mV$). The output is sent into an Ortec Model 9307 (pico-Timing discriminator). The detected pulses are discriminated by setting the threshold at 200mV. The 9307 accepts analog pulses and has a time walk of ≤ ±20ps when
the input pulses are in the range of -150mV to -1.5V. The output (a fast NIM signal with a pulse width of 2.5ns) is sent into Channel 1 of the TDC 4208. After each pulse the spectra is read off using a LabVIEW program.

### 2.4.1 Photoelectron Energy Spectrum Detection

The raw data recorded by the LeCroy TDC 4208 is a signal as a function of detection time. We want to convert this to a signal as a function of electron energy at detection since this is more useful for analysis. The classical conversion between time and energy is:

$$E = \frac{1}{2}mv^2 = \frac{1}{2} m \left( \frac{\Delta x}{\Delta t} \right)^2$$

where \(E\) is the kinetic energy and \(m\) the mass of the electron. In order to accurately determine the values of \(\Delta x\) and \(\Delta t\) we need to consider what we have actually measured. \(\Delta x\) is the distance between the interaction region and the MCP detector. The retrieval of \(\Delta t\) is a bit more complicated. The total time delay taken from the data includes: (1) the time it takes the trigger and detector signals to get to the computer (the electronic delay), \(t_e\); (2) the time the laser pulse needs to propagate from the trigger photodiode to the interaction region in the chamber, \(t_p\); and (3) the time the ionized electrons need to travel from the interaction region to the detector, \(\Delta t\). This last time increment is what we want to extract in order to determine the correct conversion in the equation above. The total time recorded in the raw data files is \(t_{measured} = t_0 + \Delta t\) where \(t_0 = t_e + t_p\).

The electronic time delay, \(t_e\), is fairly straightforward to measure. A signal is simultaneously sent through the triggering and detection electronics and the time delay between the arrival of the two signals gives us \(t_e\). In order to extract the time lag between the photodiode being triggered and the pulse reaching the interaction region we use a spectral feature that was introduced in Chapter 1, specifically, ATI (where the peaks are separated by the photon energy). Figure 2.15 shows an example of such a spectra in argon at 792nm which corresponds to photons of 1.57eV (indicated by the vertical dashed lines). We optimize the values of \(\Delta x\) and \(t_0\) for a best fit with the ATI spacing. Typical values are \(\Delta x = 0.53m\) and \(t_0 = 43ns\). Using these values we can convert time to energy. We also need to convert the signal, \(S_t\), which is initially a function of time, into a signal as a function of energy, \(S_E\). Since \(t \propto 1/\sqrt{E}\) then the conversion Jacobian will be \(E^{-3/2}\). Therefore, neglecting the constant factors, we find \(S_E \propto E^{-3/2} S_t\).

### 2.4.2 Ion Mass Spectrum Detection

The three plates (\(P_1, P_2, P_3\)), shown in Fig. 2.12, which make up the ion lens assembly are arranged in a Wiley-McLaren geometry [68]. Spatial resolution is limited by the spread of the starting positions (point of ionization) of the ions. The resolution is further influenced
Figure 2.15: Photoelectron spectra for argon with 100fs pulses at 792nm. The clear ATI peaks allow for calibration of the TOF spectrometer energy axis. The blue vertical dashed lines are shown at increments of 1.57eV, corresponding to one-792nm photon.

by the initial kinetic energy distribution of the charged particles. The goal of the ion lens is to balance these resolution limiting factors through different combinations of voltage on $P_1$ and $P_2$. $P_3$ is grounded so that the ions can undergo field-free travel down the flight tube. Ideally the ion lens will temporally spread the different charge and mass species so that when they reach the MCP detector they will be separated into bunches corresponding to differing m/q values.

In the Oven Chamber the ion lens voltages are 295V on $P_1$, 45V on $P_2$ and 0V on $P_3$. The acceleration occurs in the initial region between the point of ionization and $P_3$. These voltages are selected in order to maximize resolution. We typically optimize these by examining xenon since it is a known species and has multiple close lying isotopes. The isotopes with the most dominant abundances are: 1.91% of $^{128}$Xe, 26.44% of $^{129}$Xe, 4.07% of $^{130}$Xe, 21.18% of $^{131}$Xe, 26.89% of $^{132}$Xe, 10.44% of $^{134}$Xe and 8.87% of $^{136}$Xe. An example ion mass spectrum after optimization of the voltages is shown in Fig. 2.16. The operational resolution is $\Delta m/m = 4 \times 10^{-3}$ and therefore we expect to be able to resolve single mass differences.

The initially collected raw data, like in the electron data, comes in a form of signal versus time. We want to convert this to a form that is more useful for analysis. Consider $F = qE_p$ where $F$ is the force on a charged particle, $q$, in an electric field, $E_p$, which is supplied by the ion lens plates. We can further express this in terms of the kinetic energy.
Figure 2.16: Ion lens voltages are optimized by using xenon since it has multiple close lying isotopes. The mass spectrum above corresponds to 295V on $P_1$, 45V on $P_2$ and 0V on $P_3$.

of the ion at detection:

$$E_{ion} = \frac{1}{2} m \left( \frac{\Delta x}{\Delta t} \right)^2 = q d E_p$$  \hspace{1cm} (2.7)

where $m$ is the mass of the ion and $d$ is the distance over which it was accelerated in the potential of the ion lens plates. We solve this for the time increment, $\Delta t$:

$$\Delta t = \sqrt{\frac{(\Delta x)^2}{2 d E_p}} \sqrt{\frac{m}{q}} \propto \sqrt{\frac{m}{q}}$$  \hspace{1cm} (2.8)

All of the values in the first square root in the center expression above are constant. Therefore we can extract the mass to charge ratio by determining a constant that calibrates the time values to the m/q values. We do this by putting known species in the chamber, like xenon and argon.

2.5 Ovens

Two different oven/heating sources were used in the experiments which will be discussed in the following chapters. Both of the oven designs and specifications are included in the following sections.
2.5.1 Alkali Metal Oven

All alkali metals are solid at room temperature and need to be heated to perform gas phase experiments for which we use an effusive source oven. Small modifications were made to the initial oven design by G. G. Paulus to improve functionality for our experiments. The layout of the oven is shown in Fig. 2.17. The main body of the oven is composed of two stainless steel sections which bolt together through a 1.33” copper gasket.

The top portion is wrapped with a coaxial resistance based heater wire (Thermocoax: SEI 10/100) with the primary mode of heat transfer being conduction. This heater wire has a 1mm diameter, can support a maximum of 65V (corresponding to approximately 350W of power), has a line resistance of 12 – 14Ω (depending on the voltage applied) and reaches a maximum of 1000°C. It is compatible with ultra-high vacuum and has cold-ends which allows us to safely connect it to chamber feed-throughs.

In the initial configuration the coaxial heater wire was brazed onto the upper section which provided good thermal contact. However, during high temperature operation we approach the melting point of the braze. This led to a visible discoloration and distortion of the braze material and could have further led to chamber contamination if the braze began to significantly out-gas. Specifically, we used Braze 560 which has a melting point of 620°C and flows at 650°C. Other brazes with higher melting points are available but need to be heated to much higher temperatures (∼1400°C) during the brazing process. This would not work for us since this is equal to or exceeds the melting temperature of the heater wire components. Therefore, we wrapped a thin stainless steel wire around the heater wire in order to secure it to the main oven body. This method is worse for heat transfer but it removes the possibility of damaging the braze/heater and reduces the possible sources of chamber contamination.

The alkali metal reservoir (labeled R in Fig. 2.17) makes up the lower section of the oven. Since the oven is made of thick stainless steel there is a large temperature gradient between the heater and reservoir sections. To reduce this effect we designed a small copper-cup insert which fits into the main reservoir section and doubles as a copper gasket. Copper does not react with alkali metals and has a higher thermal conductivity allowing for more efficient heat transfer.

The purpose of maintaining the heater and reservoir sections separate is to avoid clogging the oven nozzle when the alkali metal vapor cools. By maintaining the nozzle section at a higher temperature we can usually avoid this situation. The outer water cooled jacket (labeled J in Fig. 2.17) helps thermally isolate the oven from the rest of the chamber. A thermocouple is secured to the outside of the copper-cup to monitor oven temperature. The atomic beam pointing can be controlled through the use of a bellows and a set of three actuators (labeled A in Fig. 2.17). The atomic beam travels upward through the interaction region and the liquid nitrogen trap above helps condense the remaining atoms to reduce
Figure 2.17: Alkali metal oven layout (side view) and positioning within the chamber. The oven is mounted below the interaction region and the atomic beam travels upward. The atomic beam, laser propagation direction (out of the page) and the flight tube axis are all perpendicular to each other. $P_1$, $P_2$ and $P_3$ is the ion lens field plate assembly, S and C are the source and collimator apertures respectively, R is the alkali metal reservoir and J is the water cooled jacket. Figure reproduced with minor modification from the thesis of Dr. Emily Sistrunk [59].
chamber contamination. From the side view perspective the laser propagation direction is out of the page and is perpendicular to the atomic beam and flight tube/detector axis.

During high-temperature operation we observed high levels of dark counts, up to $\sim 1000 - 3000$ counts per second. We believe this is linked to thermal emissions from the oven since the signal was present even when the laser was blocked. The dark count signal could be reduced by about 2 orders of magnitude, to $\sim 10$ hits per second, by wrapping the outer jacket with aluminum foil. A small hole was poked in the top to allow the atomic beam to exit.

The coaxial heater wire is connected to an Agilent U8032A DC Power Supply which has a maximum output of 60V and 6A. Figure 2.18 shows the calibration between voltage and temperature. The response at the heater and on the copper-cup insert were measured by direct contact with a type-K thermocouple. By using the copper-cup, instead of the original stainless steel reservoir, we decreased the effective temperature drop between heater and the alkali metal reservoir from 65% to 30%.

![Figure 2.18: Alkali oven temperature versus voltage calibration. The two curves represent the response of a type-K thermocouple attached directly to the heater wire and to the bottom of the copper cup insert.](image)

The vapor pressure as a function of temperature within the reservoir can be calculated

\[ \log_{10} p = -\frac{0.05223 a}{T} + b \]  

(2.9)

where $p$ is the pressure in Torr and $T$ is the temperature in Kelvin. Table 2.1 provides the values of $a$ and $b$ which are species dependent constants. Figure 2.19 shows the vapor
pressure as a function of temperature for the alkali metal atoms listed in the table.

<table>
<thead>
<tr>
<th>Element</th>
<th>a</th>
<th>b</th>
<th>Temp. Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>103300</td>
<td>7.553</td>
<td>180-883</td>
</tr>
<tr>
<td>K</td>
<td>84900</td>
<td>7.183</td>
<td>260-760</td>
</tr>
<tr>
<td>Rb</td>
<td>76000</td>
<td>6.976</td>
<td>250-370</td>
</tr>
<tr>
<td>Cs</td>
<td>73400</td>
<td>6.949</td>
<td>200-350</td>
</tr>
</tbody>
</table>

Table 2.1: Table of relevant values for the analysis of an alkali metal atomic beam. Values a and b are used to calculate the vapor pressure (Eq. 2.9) which is accurate within the temperature range listed for each species [70].

Figure 2.19: Calculated vapor pressure as a function of temperature in the oven reservoir.

In order to relate the vapor pressure in the reservoir to the density in the interaction region I follow the derivation by Ramsey [71]. We start by considering the number of atoms per unit time that will emerge from the source aperture:

\[
dQ = \frac{1}{4\pi} n\bar{v}\cos\theta A_s d\Omega
\]

(2.10)

where \( n \) is the number of atoms per unit volume in the source, \( \bar{v} \) is the mean molecular velocity within the oven reservoir, \( A_s \) is the cross-sectional area of the source aperture, \( \theta \) is the angle from the normal to the plane of the source aperture and \( d\Omega \) is the solid angle. The
atomic number density, $n$, can be determined by combining the ideal gas law, $p = nk_BT$, and Eq. 2.9.

The integration to determine the total number of atoms exiting the reservoir assumes that the process of effusion does not significantly affect the atom’s spatial and velocity distribution. To satisfy this condition the mean free collision path should be greater than, or at least similar in size to, the radius of the source aperture, $\lambda_{Ms} \geq r_s$. If this condition is not satisfied then atomic collisions with the oven walls will be probable and we will approach hydrodynamic flow conditions. The atomic mean free path is [71]:

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

(2.11)

where $\sigma$ is the atomic collision cross-section. This cross-section is estimated by treating the atoms as hard spheres undergoing elastic collisions. The source aperture radius and mean free path lengths for the alkali atoms as a function of temperature are shown in Fig. 2.20. During our experiments we tried to remain below this threshold temperature as much as possible but occasionally, due to low count rates, we were forced to run at somewhat higher temperatures. According to Ramsey [71] in this regime atom-atom collisions will increase which will cause a ‘cloud’ of atoms to form near the source aperture. The size of this ‘cloud’ (which is larger than the source aperture) will act as the new effective aperture width and therefore decrease the oven effectiveness. As the oven temperature is further increased the density in the interaction region will also increase but at a less efficient rate.

![Figure 2.20: Calculated mean free path of the alkali atoms as a function of temperature. The collisional cross-section is approximated by treating the atoms as hard spheres. Also included is the radius of the source aperture, $r_s = 0.15mm$.](image)

Once the atoms exit the main oven source aperture (labeled ‘S’ in Fig. 2.17) they pass through a secondary collimating aperture (labeled ‘C’). This collimator blocks the sides of
Figure 2.21: Zoomed in view of the atomic beam portion of the alkali oven; \(w_s\) and \(w_c\) are the widths of the source and collimator apertures respectively, \(l_{sc}\) and \(l_{cd}\) are the source to collimator and collimator to interaction region distances. The size of the atomic beam at the point where it intersects the laser beam path is sufficiently large to approximate a constant density across the focal volume.

The atomic beam and helps reduce chamber contamination. However, it is important that this collimator does not negatively impact the atomic density in the interaction region. Figure 2.21 provides a zoomed in view of the atomic beam path as well as the important length scales. Continuing with the approach discussed in Ramsey [71] we apply purely geometrical considerations to calculate the effect of the source and collimator apertures on the atomic density distribution at the point of detection (where the laser intersects the atomic beam). The variables are defined as: \(w_s\) is the source aperture width, \(w_c\) is the collimator aperture width, \(l_{sc}\) is the distance between the source and collimator apertures and \(l_{cd}\) is the distance between the collimator aperture and the detection point. The atomic beam dimensions in the interaction region are given by [71]:

\[
p = \frac{1}{2} |w_c + (w_c - w_s)a| \tag{2.12}
\]

\[
d = \frac{1}{2} [w_c + (w_c + w_s)a] \tag{2.13}
\]

\[a \equiv l_{cd}/l_{sc} \tag{2.14}\]

The full atomic beam intensity is present between points B and C since the collimator does not obscure any of the atoms which travel along that path. The atomic beam is
partially obscured in the regions A to B and C to D. Beyond points A or D the atomic beam is completely blocked. However, the region between B and C, which is equal to 2p, is significantly larger than our laser beam focus. In our experiments we use a 100mm focal length lens which has a beam waist at the focal point of approximately 15\mu m. Therefore, for all experimentally relevant considerations the collimator aperture has no effect on the density of the atomic beam in the interaction region.

Finally, let’s return to our initial task of calculating the atomic density in the interaction region. The number of atoms which will pass across the interaction region per second is [71]:

\[ I = \frac{1}{4\pi} \frac{A_d}{l_{sd}^2} n_s v_A \]  

(2.15)

where \( A_d \) is the cross sectional area of the detector perpendicular to the atomic beam. We can convert this atomic beam ‘intensity’ to a density and get an expression:

\[ n_{int} = \frac{1}{4\pi l_{sd}^2} v_A n_s \]  

(2.16)

The density in the interaction region for the four alkali metal atoms shown earlier is plotted in Fig. 2.22 as a function of the source temperature. Using this result we can also determine the pressure by applying the ideal gas law, \( p_{int} = n_{int} k_B T \).

Figure 2.22: Density of the alkali atoms in the interaction region as a function of the oven temperature.

As a final comment I would like to bring the reader’s attention to the choice of focusing lens that was used in the sodium and potassium data (discussed in Chapter 3). Specifically, we used a lens with a 100mm focal length even though a longer focal length lens would have still allowed us to achieve sufficiently high intensities to ionize the alkali atoms. A longer focus would have increased our interaction volume thereby increasing our count rates and
allowing us to run at lower temperatures (which would have allowed us to remain further in the effusive flow regime). However, before each data run we needed to calibrate the MIR beam intensity. The calibration gases available to us (xenon, butane and isobutane) require higher peak intensities and therefore were the defining factor for our choice of lens.

2.5.2 C\textsubscript{60} Oven

The C\textsubscript{60} oven was designed by Hui Li in the group of Dr. Matthias Kling at Kansas State University. The group has now moved to the Max-Planck Institute for Quantum Optics in Germany.

Figure 2.23 shows a layout of the oven which provides an effusive beam of C\textsubscript{60} molecules (fullerenes). The two main components of this heating source include the lower reservoir/heater section and the upper shield. The two sections are separated by a ceramic insulator to reduce heat transfer from the oven to the rest of the apparatus. The cylindrical reservoir is made of stainless steel and is wrapped with a 30" high-vacuum compatible cable heater (Watlow Part 125PS30A46A). This heater supports a maximum voltage of 240V, a maximum power of 450W and can reach temperatures of 650°C. It has 1.5" long cold ends to allow for electrical attachment to a power supply. The heater cable contains an internal type-J thermocouple to monitor the temperature. A separate thermocouple was also attached to the bottom of the reservoir to monitor the temperature during experiments. The voltage supplied to the cable heater is adjusted through the use of a variac. The C\textsubscript{60} crystalline powder is placed in the reservoir during operation.

The dependence of the oven temperature on the applied voltage is shown in Fig. 2.24. Figure 2.25 shows the calibrated C\textsubscript{60} vapor pressure as a function of this temperature. The measured ion yields for C\textsuperscript{+}\textsubscript{60} and C\textsuperscript{++}\textsubscript{60} are benchmarked to previously published results [72]. For typical operating conditions we need to maintain a temperature in the range of 450 – 600°C to obtain sufficient count rates. When sufficient vapor pressures are achieved the C\textsubscript{60} effusively passes into the upper section through the 2mm source aperture.

The upper section is a shield which further collimates the C\textsubscript{60} molecular beam. The shield is built as two concentric cylinders with off-set large holes to allow for faster pumping when the chamber is brought down to ultra-high vacuum pressures. By collimating the molecular beam we waste less of the sample and reduce chamber contamination. The aperture of the collimating shield is also 2mm wide. This oven is mounted on a 6” flange which we attach in the same location as the alkali metal oven (see Fig. 2.17).
Figure 2.23: Layout of the C_{60} oven.

Figure 2.24: Calibration of the oven temperature as a function of applied voltage.
Figure 2.25: The black and red circles correspond to measured ion yields of \( C_{60}^+ \) and \( C_{60}^{++} \) at a laser intensity of \( 2 \times 10^{13} \text{W/cm}^2 \). These ion yields are plotted as a function of oven temperature and benchmarked to published vapor pressure measurements [72].
Chapter 3

Alkali Metal Atoms in Wavelength Scaled Systems

Over the last several decades the interaction between noble gas atoms and strong-field, ultrafast laser pulses has been extensively studied both experimentally [22, 73, 74] and theoretically [48, 75, 76, 77]. The majority of these studies have been performed at visible or near-infrared (NIR) wavelengths due to the technological limitations of available laser sources. These studies have produced numerous unanticipated results that have forced us to expand on our understanding of strong-field physics. In order to further examine the accuracy or limitations of our theoretical models (both classical and quantum) it is necessary to test them against experimental results in different atomic/molecular species or different wavelength regimes. From the theoretical side the alkali metal atoms are particularly attractive due to having a single valence electron and after photo-ionization are left as closed shell ions, unlike inert gas atoms. Since the single active electron (SAE) approximation is made in the vast majority of calculations then these quasi one-electron systems seem to be an ideal testing ground.

However, from the experimental perspective, transitioning to these species was not entirely straightforward. The major issue arises in the available strong-field, short-pulsed laser sources. If we want to perform experiments that can be compared to previous noble gas results then we need to study the alkali metal atoms in a similar regime of extreme nonlinear optics. Another way of phrasing this is that we want to study these two sets of species in Keldysh equivalent processes (recall that $\gamma \propto 1/\sqrt{I\lambda^2}$). The difficulty with alkali metal atoms is that they have much smaller ionization potentials and therefore exhibit much lower saturation intensities. As an example, let’s consider an 800nm laser source for which the photon energy is approximately 1.55eV. In order to ionize argon from the ground state ($I_p = 15.75eV$) we would roughly need 10 photons but only 3 photons are necessary to ionize potassium ($I_p = 4.34eV$). Therefore, the interaction between alkali metal atoms and visible/NIR wavelength sources can be described by few-photon ionization and begins to
Approach the perturbative regime. By using our mid-infrared (MIR) laser source, photon energies are $0.3-0.4\text{eV}$ for wavelengths of $3-4\mu\text{m}$, we can examine the alkali atoms in a similar regime as the previous studies on the noble gas atoms. Tables 3.1 and 3.2 provide some useful values for the alkali metal and noble gas atoms respectively. These include the atomic polarizabilities, ionization potentials and energies necessary for transitioning from the ground state to the lowest lying excited state in each species. The approximate number of photons necessary to make these transitions (with MIR wavelengths for the alkali atoms and visible/NIR wavelengths for the noble gases) are also listed. Further, unlike the noble gas atoms, alkali metals are solid at room temperature and therefore require an oven source to produce an atomic beam for experiments.

It is important to point out that the electronic structure of alkali metal atoms differs from the noble gases in some significant ways. First of all, the dipole coupling between the ground, s-state, and the first excited, p-states, in the alkali metals is very strong. The $s\rightarrow p$ transition is actually composed of a fine-structure doublet due to the coupling between the orbital angular momentum, $L$, of the valence electron and the spin angular momentum, $S$. The total angular momentum is $J=L+S$ for which the available quantum numbers are:

$$|L - S| \leq J \leq L + S \quad (3.1)$$

The first excited state in the alkali metal atoms has $L=1$ and $S=1/2$ so $J=1/2$ or $3/2$. In sodium the oscillator strengths for the $3s\rightarrow3p$ transitions are 0.320 for $J=1/2$ and 0.641 for $J=3/2$ [79]. This is approximately two orders of magnitude higher than the next strongest.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\alpha$ [78]</th>
<th>$I_p$ [79]</th>
<th># photons $[s \rightarrow C]$</th>
<th>Exc. State [79]</th>
<th># photons $[s \rightarrow p]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>24.11</td>
<td>5.14</td>
<td>12 – 17</td>
<td>2.10 (3P$_{1/2}$)</td>
<td>5 – 7</td>
</tr>
<tr>
<td>K</td>
<td>43.40</td>
<td>4.34</td>
<td>10 – 14</td>
<td>1.61 (4P$_{1/2}$)</td>
<td>4 – 5</td>
</tr>
<tr>
<td>Rb</td>
<td>47.76</td>
<td>4.18</td>
<td>10 – 14</td>
<td>1.56 (5P$_{1/2}$)</td>
<td>4 – 5</td>
</tr>
<tr>
<td>Cs</td>
<td>59.42</td>
<td>3.89</td>
<td>9 – 13</td>
<td>1.39 (6P$_{1/2}$)</td>
<td>3 – 5</td>
</tr>
</tbody>
</table>

Table 3.1: Useful alkali metal atom parameters. The columns in order are: the atomic species; atomic polarizability of the neutral atom; field-free ionization potential for the ground state atom; approximate number of photons necessary to ionize the atom, from the ground state ($s$) to the continuum ($C$), using $3-4\mu\text{m}$ light; energy gap between the ground state (G.S.) and lowest excited state ($p$) – the specific state is included in parentheses; and finally the number of photons necessary to transition from the ground state to the excited state.
Table 3.2: Useful inert gas atom parameters. The columns in order are: the atomic species; atomic polarizability of the neutral atom; field-free ionization potential for the ground state atom; approximate number of photons necessary to ionize the atom, from the ground state (p) to the continuum (C), using 550–800nm light; energy gap between the ground state (G.S.) and lowest excited state (s) – the specific state is included in parentheses; and finally the number of photons necessary to transition from the ground state to the excited state.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \alpha ) [78]</th>
<th>( I_p ) [79]</th>
<th># photons ( p \rightarrow C )</th>
<th>Exc. State [79]</th>
<th># photons ( p \rightarrow s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.21</td>
<td>24.58</td>
<td>11 – 16</td>
<td>19.82 (2S(_1))</td>
<td>9 – 13</td>
</tr>
<tr>
<td>Ne</td>
<td>0.40</td>
<td>21.56</td>
<td>10 – 14</td>
<td>16.62 (3S(_2))</td>
<td>7 – 11</td>
</tr>
<tr>
<td>Ar</td>
<td>1.64</td>
<td>15.75</td>
<td>7 – 10</td>
<td>11.55 (4S(_2))</td>
<td>5 – 8</td>
</tr>
<tr>
<td>Kr</td>
<td>2.48</td>
<td>13.99</td>
<td>6 – 9</td>
<td>9.92 (5S(_2))</td>
<td>4 – 7</td>
</tr>
<tr>
<td>Xe</td>
<td>4.04</td>
<td>12.13</td>
<td>5 – 8</td>
<td>8.32 (6S(_2))</td>
<td>4 – 6</td>
</tr>
</tbody>
</table>
(3^2S_{1/2} \rightarrow 3^2P_{3/2})$ is 2.104eV. Potassium melts at 64°C and its main isotopes are 93.26% $^{39}$K, 0.012% $^{40}$K and 6.73% $^{41}$K [81]. The energies for the s to p transitions in potassium are: D1 line ($4^2S_{1/2} \rightarrow 4^2P_{1/2}$) is 1.609eV and the D2 line ($4^2S_{1/2} \rightarrow 4^2P_{3/2}$) is 1.617eV. This chapter is organized into three sections which discuss the ion yields, photoelectron intensity and wavelength dependence, and angular distribution results. Occasionally reference will be made to previous cesium data taken in this group. For a complete summary of that data please look in the thesis of Dr. Emily Sistrunk [59]. As a final note, this introduction was not meant to insinuate that the interaction between noble gases and visible/NIR fields is completely understood. In fact, the noble gas photoelectron spectra show very rich dynamics and enhancement structures that are still being debated. Our attempt to expand on the understanding of some of these features is the topic of Chapter 4.

3.1 Ion Yield Analysis

The ion yields as a function of peak laser intensity were measured for Na and K at three different MIR wavelengths in the range of 3–4\(\mu\)m. Pellicles, designed for MIR wavelengths, are used to make coarse steps in attenuating the laser pulse energy/peak intensity. These pellicles were calibrated during each data run since their attenuation percentage varies slightly with wavelength. Fine pulse energy adjustments were made through the use of a half-wave-plate and polarizer combination. In all cases the beam was linearly polarized along the spectrometer axis. Each data point contains at least 60,000 laser shots and typically contains 10,000 – 100,000 counts. Occasionally, on some of the lowest intensity measurements, the integrated counts are less than 1,000. The acquisition of the data points during each ion yield curve were randomized to avoid possible coupling to laser drift. The laser alignment, beam profile and maximum laser power were checked several times during each data run as methods of monitoring laser stability. The beam was focused into the interaction region with a one-inch, 100mm focal length CaF$_2$ lens. As discussed earlier, the 2$U_p$ break in xenon, butane or isobutane was used to calibrate the intensity axis. Our method for determining the error in our intensity measurements is discussed in the following section (Sec. 3.2).

The ion yield data for Na$^+$ is shown in Fig. 3.1 and the results are summarized in Table 3.3. Similarly, the ion yield data for K$^+$ is shown in Fig. 3.2 and the results are summarized in Table 3.4. All plots include error bars corresponding to Poisson statistical error, $\Delta M = \sqrt{M}$ where $M$ is the number of counts. In most cases this error bar is smaller than the data point. In the limit of perturbation theory the ionization rate is proportional to $I^N$ where $N$ is the number of photons necessary to make that transition. On a log-log plot, like Fig. 3.1 and 3.2, this corresponds to a linear fit with a slope of $N$. Notice that at a certain intensity the slope of the ion yield curve changes, this is the saturation intensity.
Figure 3.1: Ion yield vs intensity curves for Na$^+$ performed at three different wavelengths. The two lines are $I^N$ fits to the below and above saturation data points ($N$ is the number of photons; this corresponds to the slope on a log-log plot). The intersection of these lines corresponds to the experimentally determined saturation intensity.
Figure 3.2: Ion yield vs intensity curves for $K^+$ performed at three different wavelengths. The two lines are $I^N$ fits to the below and above saturation data points (N is the number of photons; this corresponds to the slope on a log-log plot). The intersection of these lines corresponds to the experimentally determined saturation intensity.
### SODIUM \((I_p = 5.14 \text{eV})\)

<table>
<thead>
<tr>
<th>(\lambda [\mu m])</th>
<th># photons (3s \rightarrow C)</th>
<th># photons (3s \rightarrow 3p)</th>
<th>Exp. Slope</th>
<th>(I_{sat} \text{ (Exp.)} )</th>
<th>[TW/cm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>13.2</td>
<td>5.4</td>
<td>5.5 ± 0.2</td>
<td>5.7 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>15.3</td>
<td>6.2</td>
<td>6.6 ± 0.3</td>
<td>5.7 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>16.5</td>
<td>6.7</td>
<td>5.6 ± 0.5</td>
<td>4.9 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Ion yield summary for sodium. Ion yields were done at the three wavelengths listed. The second and third column provide the calculated number of photons necessary for the field free ground state to continuum transition \((3s \rightarrow C)\) and the ground state to excited state transition \((3s \rightarrow 3p)\). In the approximation of perturbation theory the ionization rate is proportional to \(I^N\), where \(N\) is the number of photons; the \(N\) values found experimentally are listed in the fourth column. The experimentally determined saturation intensity is listed in the last column. The over-the-barrier intensity for sodium is \(I_{OTB} = 2.8 \text{TW/cm}^2\).

### POTASSIUM \((I_p = 4.34 \text{eV})\)

<table>
<thead>
<tr>
<th>(\lambda [\mu m])</th>
<th># photons (4s \rightarrow C)</th>
<th># photons (4s \rightarrow 4p)</th>
<th>Exp. Slope</th>
<th>(I_{sat} \text{ (Exp.)} )</th>
<th>[TW/cm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>11.2</td>
<td>4.2</td>
<td>7.5 ± 0.2</td>
<td>2.1 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>12.7</td>
<td>4.7</td>
<td>8.6 ± 0.4</td>
<td>2.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>13.9</td>
<td>5.2</td>
<td>6.8 ± 0.1</td>
<td>2.4 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Ion yield summary for potassium. Ion yields were done at the three wavelengths listed. The second and third column provide the calculated number of photons necessary for the field free ground state to continuum transition \((4s \rightarrow C)\) and the ground state to excited state transition \((4s \rightarrow 4p)\). In the approximation of perturbation theory the ionization rate is proportional to \(I^N\), where \(N\) is the number of photons; the \(N\) values found experimentally are listed in the fourth column. The experimentally determined saturation intensity is listed in the last column. The over-the-barrier intensity for potassium is \(I_{OTB} = 1.4 \text{TW/cm}^2\).
The total yield continues to increase, but at a slower rate, due to the increasing focal volume which achieves a sufficient intensity to ionize the species. For a perfectly Gaussian beam this slope is equal to $3/2$. However, our beam profiles were not perfectly Gaussian and we believe this may contribute to the deviation of this slope. Experimentally, we define the saturation intensity, $I_{sat}$, as the point where the below and above saturation fits intersect, these values are listed in Tables 3.3 and 3.4 for Na and K respectively. The $I^N$ fits are labeled in the plots and the below saturation values are also listed in the tables. Treating these strong-field interactions in the perturbative limit is a significant approximation but as a first order estimate it has demonstrated some success in describing the observed ionization dynamics. The error in the experimental slope and saturation intensity are determined from the fitting error of the lines seen in the plots. Contributions from double ionization were found to be negligible. This is expected since the ionization energy for removing a second electron from Na is 47.3eV and for K it is 31.6eV, significantly higher than the ionization potential for the first electron.

Tables 3.3 and 3.4 also include the number of photons necessary to make the nonresonant transition from the ground state to the continuum (labeled C) or the resonant transition from the ground state to the dominant excited state; an $s \rightarrow p$ transition. These numbers correspond to the field free situation where the AC Stark shift is neglected. Note that due to the selection rules the resonant transition can only occur through the absorption of an odd number of photons; the ground state is an $s$-state ($l = 0$) making a transition to a $p$-state ($l = 1$).

In sodium, the experimentally determined slope below saturation agrees fairly well with the calculated number of photons for the $s \rightarrow p$ transition, see Table 3.3. This is a clue that in sodium the initial population transfer to the excited state before subsequent ionization may be the rate limiting step. The agreement at the longest wavelength is not as good. However, in potassium we do not observe a similar behavior. Experimentally the ion yield is proportional to $I^{7-9}$ while the calculation predicts a $4-5$ photon process. This leads us to assume that the two step process, population transfer to the excited state before ionization, may not be the dominant mechanism. This simple picture does not allow us to make any quantitative predictions on the contribution of multiple ionization pathways towards the total ion yield and it neglects the AC Stark shift of the contributing energy levels.

Next, let’s consider the experimentally measured saturation intensities for Na$^+$ and K$^+$, see Tables 3.3 and 3.4 respectively. The saturation intensity is a species dependent quantity and in the strong-field limit is not expected to vary with wavelength, which agrees within the error of our findings. In sodium the over-the-barrier (OTB) intensity, see Eq. 1.24, is $2.8\text{TW/cm}^2$ while experimentally we found $5 - 6\text{TW/cm}^2$. In potassium $I_{OTB} = 1.4\text{TW/cm}^2$ but experimentally we found $2 - 2.5\text{TW/cm}^2$. This is a difference of a factor of $1.5 - 2$ and exceeds our experimental error. A similar discrepancy was found in
Figure 3.3: Na$^+$ ion yield at 4$\mu$m. Black squares correspond to the experimentally measured values; this is the same data as presented in Fig. 3.1. The solid lines correspond to the ADK model calculations for ionization from the 3s ground state (blue), ionization from the 3p excited state (green) and the total ionization using our model (red). See text for more details.

In order to analyze the ionization mechanics more quantitatively we also performed ADK calculations. The ADK model was introduced in Sec. 1.4.1 and is a commonly used method for calculating atomic and molecular ionization rates. Recall that this model assumes tunneling ionization and therefore only the initial and final states are considered; excited states as well as the AC Stark shift of the bound states are neglected. All of the following ADK calculations include focal volume averaging.

Figure 3.3 shows the result of such a calculation in comparison to our data (black squares) for sodium at 4$\mu$m. The three curves in the figure have been shifted vertically to overlap at high intensity (in the limit of saturation). The solid blue line corresponds to the ADK rate for an electron being ionized from the ground state of the atom, $\Gamma_g$. This rate underestimates the experimentally measured values by 1–3 orders of magnitude. If instead we assume that the dominant mechanism occurs by electrons first being promoted to the 3p state before subsequent ionization then we can use the ionization potential of the excited state (3.04eV) to determine the intensity dependent rate, $\Gamma_e$ (green line in Fig. 3.3). In this case we found that the calculated rate overestimates the total ion yield by approximately 1–2 orders of magnitude. A similar behavior was observed at other experimentally measured wavelengths as well as in the potassium data.
From these results we conclude that it is likely that both ionization channels contribute to the final measured rate. In order to model this behavior we defined two coupled rate equations for the time dependent ground state population, \( P_g(t) \), and excited state population, \( P_e(t) \), during the atom’s interaction with the applied laser field. The two coupled equations are given by:

\[
\frac{dP_g(t)}{dt} = -(\Gamma_g + W_{eg}) P_g(t) + W_{eg} P_e(t) \tag{3.2}
\]

\[
\frac{dP_e(t)}{dt} = -(\Gamma_e + W_{eg}) P_e(t) + W_{eg} P_g(t) \tag{3.3}
\]

where \( W_{eg} \) is the stimulated transition rate between the ground and excited states. We approximate this transition rate as a multiphoton process [64]:

\[
W_{eg} = \sigma_n I^n \tag{3.4}
\]

where \( \sigma_n \) corresponds to an \( n \)-photon absorption cross-section and \( I \) is the intensity. The above two equations were fit to the data using a genetic algorithm where the value of \( \sigma_n \) and \( n \) were allowed to vary. The value of \( n \) was restricted to odd integers in order to satisfy selection rules. The red curve in Fig. 3.3 corresponds to the result of this fitting process. When both ionization pathways are included the agreement between theory and experiment is clearly much better. The same method was applied to the experimentally measured ion yield data (Figs. 3.1 and 3.2) at each of the three wavelengths and for both species. The results for Na\(^+\) yields and K\(^+\) yields are shown in Figs. 3.4 and 3.5 respectively. The final parameters for \( n \) and \( \sigma_n \) for the best fit are included in the figure captions.

We have also considered the effect of the atom specific polarizability on the calculated ionization rates. The polarizabilities of the alkali metal atoms are significantly larger than those of the noble gases, see Tables 3.1 and 3.2, which will increase the effective atomic ionization potential when an intense field is applied. Recall that in an intense field the continuum shifts by \( U_p \) while the ground state shifts by a factor proportional to the polarizability and the field intensity. Including this effect did not significantly alter the calculated ADK curves.

Another possible concern the reader may have is the neglect of spontaneous emission in the coupled rate equations; we only accounted for ionization and stimulated transitions between the ground and excited states. The field free lifetimes for the 3p states in sodium are 16.3ns [82] and in potassium the lifetimes of the 4p states are 26.4ns [83]. The spontaneous decay rate for these states is approximately 5–8 orders of magnitude smaller than the calculate transition rate, \( W_{eg} \), within the experimentally accessible intensity range. Thus, it is justifiable to neglect spontaneous emission in our analysis.

In order to determine if this rather simple model provides us with a physically reason-
Figure 3.4: Na\(^+\) ion yield comparison between experiment (black squares) and the calculated best fit ionization rate (red line). The model considers two ionization pathways; direct ionization from the ground state and ionization through the intermediate 3p excited state (see text). The final parameters for the plotted curves are: \(n=7\), \(\sigma_n=7.61\times10^{25}\) a.u. (atomic units) for 3.2\(\mu m\); \(n=7\), \(\sigma_n=7.75\times10^{25}\) a.u. for 3.7\(\mu m\); \(n=7\), \(\sigma_n=7.52\times10^{25}\) a.u. for 4.0\(\mu m\).

Figure 3.5: K\(^+\) ion yield comparison between experiment (black squares) and the calculated best fit ionization rate (red line). The model considers two ionization pathways; direct ionization from the ground state and ionization through the intermediate 4p excited state (see text). The final parameters for the plotted curves are: \(n=7\), \(\sigma_n=3.53\times10^{27}\) a.u. (atomic units) for 3.2\(\mu m\); \(n=5\), \(\sigma_n=1.63\times10^{17}\) a.u. for 3.6\(\mu m\); \(n=5\), \(\sigma_n=6.46\times10^{17}\) a.u. for 4.0\(\mu m\).
able final result we calculated the fractional population remaining in the excited state at the end of the interaction with the laser pulse. As an example, let’s consider the previously discussed case of sodium at 4µm, Fig. 3.3, for which the remaining fractional population in the 3p state was found to be $\sim 10^{-4} - 10^{-5}$. These results are comparable to previously published calculations by Gaarde and Schafer [84]. They performed single active electron (SAE) TDSE calculations on potassium in order to better understand the effect of a strongly coupled excited state on the ionization process. The advantage of TDSE calculations is that they incorporate all bound states as well as the AC Stark shifts which occur due to the interaction with the applied field. Gaarde and Schafer [84] focused their calculations on the wavelength regime where the three photon (near 2500nm) and 5 photon (near 4000nm) resonant transition between the ground state (4s) and excited state (4p) occurs. They demonstrated that the nonresonant direct ionization from the ground state competes strongly with the resonant ionization process where the electron is promoted to the excited state before being ionized. By using model pulses (100–300fs) they determined that for the 3-photon process the fractional population in the excited state at the end of the laser-atom interaction was $\sim 10^{-3}$ while for the 5-photon transition the remaining fractional population was found to be on the order of $10^{-4}$. Therefore, our findings of $10^{-4} - 10^{-5}$ fractional population remaining in the excited state appears like a physically reasonable number.

As a final consideration we can compare the ‘best fit’ parameters to what we know about the physical system. Specifically, let’s consider the values of ‘n’ which came out of the fitting process. In sodium, see caption in Fig. 3.4, the best fit at all three wavelengths was for n=7. Table 3.3 showed that the predicted number of photons necessary for making the 3s → 3p transition in the field free limit is 5.4–6.7 in the wavelength range of 3.2–4.0µm. Therefore, our model’s prediction that the 7-photon transition process provides the dominant correction to the direct ionization mechanism makes physical sense, especially if we consider that the separation between the 3s and 3p states may increase in the applied field due to the AC Stark effect. In potassium we found that for 3.2µm the best fit occurred for n=7 while for 3.6µm and 4µm the best fit occurred for n=5 (see caption of Fig. 3.5). By calculating the number of photons necessary to make the 4s → 4p transition we found that 4.2–5.2 photons are necessary for wavelengths in the range of 3.2–4.0µm; where the least number of photons are necessary at the shortest wavelength. The 5-photon resonant transition agrees well with the best fit parameters at 3.6µm and 4µm but the 3.2µm result does not agree with our two ionization channel picture. One possible reason for this is that potassium at 3.2µm is the furthest into the multiphoton regime ($\gamma \sim 1 – 1.5$) and the ADK theory approximates the case of tunneling ionization. This could also just be a demonstration where our simple model breaks down and possibly other ionization channels, which were not included, may be contributing. In order to gain further insight into the ionization mechanics more complete calculations using TDSE may be required.
SAE models, like ADK, have shown good agreement in reproducing the first charge state ion yield curves for the noble gases in the visible and NIR regime [29, 31]. From this we conclude that the excited states in the inert gases do not contribute as strongly to the ionization dynamics as they do in the alkali metal atoms in the MIR wavelength regime.

Since there are at least two dominantly contributing ionization pathways present in the alkali metal atoms then in the future we could try to control this process in order to observe interferences between the two ionization channels. Robert Jones [85] has experimentally observed Ramsey interferences in the sodium ionization yield using 777nm light. However, his experiment used relatively low-order multiphoton ionization and coherent population transfer between the ground and excited states; a two-photon resonance with the 4s state and three-photon with the 7p. Extending this mechanism to higher photon order processes could help us further expand on our understanding of the behavior of these species in strong-field interactions. Further, extending studies to two-valence electron systems, like the alkaline earth atoms, may allow us to expand on our understanding of ionization mechanisms and possible correlation effects between the valence electrons. In this case the simple ADK rates may also be insufficient. Smits et al [86] demonstrated through studies of several transition metal atoms with 5 or 10 valence electrons in short pulse, < 90fs, long wavelength, 1.5µm, experiments that multi-electron effects can cause the measured saturation intensity to differ from the ADK results by a factor of 2–5. They attribute this deviation to the fact that ADK uses the SAE approximation while in realistic atoms all electrons will be affected by the applied field, not just the single ‘active’ one.

3.2 Photoelectron Energy Spectra

We also measured the photoelectron energy distributions in Na and K at several wavelengths with our MIR laser source. In all cases the laser was linearly polarized along the spectrometer axis and the intensity was varied by the same method as described in the ion yield discussion. At each wavelength we collected spectra at multiple laser energies to examine the intensity dependence of the observed features. We focused our studies on intensities below and slightly above the experimentally determined saturation intensities found through the ion yield curves. To cover the range of intensities shown the oven temperature was varied to change the atomic density in the interaction region. The lowest collected intensities were limited by the maximum usable oven temperature and maintaining sufficient count rates for collecting a statistically useful data set. In all cases the count rates were maintained between ~ 0.2 – 1.5hits/shot and summed over 1.2 – 2.4 × 10⁶ laser shots. The portion of the photoelectron spectra below approximately 1.5eV is not completely trustworthy. After running the alkali oven at high temperatures a noticeable peak at low energy began to contaminate our spectra. However, by checking the behavior of the spectrometer...
with other well studied species (for example argon at 800nm) we determined that the higher energy portion of the spectra were not affected.

Sodium data was collected at 3.3$\mu$m (Fig. 3.6), 3.6$\mu$m (Fig. 3.7), 3.7$\mu$m (Fig. 3.8), and 3.8$\mu$m (Fig. 3.9). The potassium photoelectron results are shown for 3.4$\mu$m (Fig. 3.10), 3.7$\mu$m (Fig. 3.11), and 3.9$\mu$m (Fig. 3.12). At each wavelength the results are plotted in terms of energy and $U_p$.

By using the ATI structure in the alkali metal photoelectron spectra we were able to double check the accuracy of our wavelength calibration. Though the contrast of these is quite weak we were able to match up series of 5 – 7 peaks to determine a photon energy and therefore a wavelength estimate. We compared these results to our typical (see Sec. 2.2.2) method of measuring the spectra of the ‘pump’ and ‘signal’ beams after the OPA and assuming collinear geometry to determine the MIR wavelength (‘idler’ beam). This placed an error estimate of $\pm 5\%$ on the wavelength measurements.

Similarly, we used the sodium and potassium photoelectron data to assist us in placing an error estimate on our intensity calibration. We did this by comparing the measurement from the 2$U_p$ break in the calibration gas (xenon, isobutane or butane) to the 10$U_p$ cutoff in the alkali data. In the alkali spectra we observe features and enhancements near 2$U_p$, so we did not use this 2$U_p$ break to assist in the error estimate. By comparing the calibrations from these two methods we place an error on our intensity measurements of $\pm 15\%$. However, in order to maintain consistency all the listed intensity values are from the calibration gas measurements. This eliminates the possibility of different calibrations based on different alkali metal atoms, especially since the plateau strengths in the two species are significantly different and therefore could substantially alter our calibration.

Let’s begin by making a few observations in relation to the data in Figs. 3.6–3.12. First of all, both sodium and potassium exhibit the characteristics predicted by the semiclassical 3-Step-Model. At low energy the spectrum is dominated by the ‘direct’ electron signal which decreases rapidly between 0 and 2$U_p$ (the maximum detected energy an electron can acquire without rescattering). The (b) panels in Figs. 3.6–3.12 are plotted in terms of the ponderomotive energy (recall that $U_p \propto I \lambda^2$, see Eq. 1.2). Also notice the log scale on the vertical axis. Near 2$U_p$ we observe a rapid change in slope, after which the signal remains relatively constant until the cutoff near 10$U_p$. The region between 2$U_p$ and 10$U_p$ is commonly referred to as the ‘plateau’ and corresponds to rescattered electron trajectories. Based on the Keldysh parameter values the sodium photoelectron energy spectra are in the tunneling regime ($\gamma = 0.53 – 0.84$) while the potassium results are in the quasi-multiphoton regime ($\gamma = 0.89 – 1.51$) though some of the spectra strictly span into the region of ‘tunneling’ ionization.

An important difference to notice between these two species is the relative strengths of the plateau electrons ($> 2U_p$). In sodium, the yield in the plateau is about 4 orders of
Figure 3.6: Sodium at 3.3µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 5.8TW/cm$^2$ ($\gamma = 0.65$), 4.8TW/cm$^2$ ($\gamma = 0.72$), 4.2TW/cm$^2$ ($\gamma = 0.76$) and 3.5TW/cm$^2$ ($\gamma = 0.84$).

Figure 3.7: Sodium at 3.6µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 6.4TW/cm$^2$ ($\gamma = 0.57$), 5.3TW/cm$^2$ ($\gamma = 0.63$), 4.3TW/cm$^2$ ($\gamma = 0.70$), 3.6TW/cm$^2$ ($\gamma = 0.76$) and 2.9TW/cm$^2$ ($\gamma = 0.84$).
Figure 3.8: Sodium at 3.7\(\mu m\). The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 7.2TW/cm\(^2\) (\(\gamma = 0.53\)), 6.2TW/cm\(^2\) (\(\gamma = 0.57\)), 5.2TW/cm\(^2\) (\(\gamma = 0.62\)), 3.8TW/cm\(^2\) (\(\gamma = 0.72\)) and 3.3TW/cm\(^2\) (\(\gamma = 0.78\)).

Figure 3.9: Sodium at 3.8\(\mu m\). The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, \(U_p\) (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, \(\gamma\), are: 6.0TW/cm\(^2\) (\(\gamma = 0.56\)), 5.5TW/cm\(^2\) (\(\gamma = 0.59\)), 4.9TW/cm\(^2\) (\(\gamma = 0.63\)), 4.2TW/cm\(^2\) (\(\gamma = 0.68\)) and 3.5TW/cm\(^2\) (\(\gamma = 0.73\)).
Figure 3.10: Potassium at 3.4µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 1.6TW/cm$^2$ ($\gamma = 1.24$), 1.4TW/cm$^2$ ($\gamma = 1.31$), 1.2TW/cm$^2$ ($\gamma = 1.40$) and 1.0TW/cm$^2$ ($\gamma = 1.51$).

Figure 3.11: Potassium at 3.7µm. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 2.3TW/cm$^2$ ($\gamma = 0.93$), 2.1TW/cm$^2$ ($\gamma = 0.97$), 2.0TW/cm$^2$ ($\gamma = 0.99$), 1.8TW/cm$^2$ ($\gamma = 1.05$) and 1.5TW/cm$^2$ ($\gamma = 1.13$).
Figure 3.12: Potassium at 3.9 $\mu$m. The spectra are plotted as a function of Energy (a), and the Ponderomotive Energy, $U_p$ (b). The data is displaced vertically to allow for easier viewing. The spectra, from highest to lowest intensity, and the respective Keldysh parameters, $\gamma$, are: 2.3TW/cm$^2$ ($\gamma = 0.89$), 2.1TW/cm$^2$ ($\gamma = 0.94$), 1.8TW/cm$^2$ ($\gamma = 1.00$), 1.6TW/cm$^2$ ($\gamma = 1.06$) and 1.4TW/cm$^2$ ($\gamma = 1.16$).

magnitude below the peak in the direct electrons. In potassium the plateau is only around 1–2 orders of magnitude lower. The species dependence of the strength of the plateau appears to be much larger than in the noble gases [22]. For example, in the NIR wavelength regime the argon plateau is about 2 orders of magnitude lower than the peak of the direct electrons while neon is approximately 3 order of magnitude lower. Previous experiments in cesium also showed a strong plateau which is only about an order of magnitude lower than the direct electrons [59].

The difference in the photoelectron plateau strengths between sodium and potassium has been observed previously by Gaarde et al [87]. Their experiment used a similar wavelength, 3.2 $\mu$m, to the work presented here but the pulse duration (1.9ps) was approximately a factor of 20 longer. Panel (f) in Fig. 3.19 shows the experimentally measured photoelectron spectra for sodium (black) and potassium (red). Their experimental curves have a similar yield dependence of direct to plateau electrons as to what we observed; approximately a 4 orders of magnitude drop for sodium and 1–2 for potassium. Further, they [87, 88] performed TDSE calculations in the SAE approximation using a ‘realistic’ atomic potential which included the alkali atom specific short range component and the Coulomb like long range contribution. These calculations reproduced the experimental photoelectron spectra well and showed that the difference between the sodium and potassium plateau strengths can be attributed to the electron–ion elastic scattering differential cross-section (DCS).
Figure 3.13 shows their calculated differential cross-sections for electrons backscattered \((\theta_r = 180^\circ)\) from sodium (solid line) and potassium (short-dashed line) ions. At an intensity of 1TW/cm\(^2\) the maximum electron rescattering energy \((\sim 3U_p)\) is 2.8eV. At this return energy the potassium cross-section is approximately 200 times larger than the sodium cross-section. This agrees well with the difference in rescattering efficiency we observed between sodium and potassium.

In further TDSE calculations Gaarde et al [87] modified the short range component of the \(e^- - K^+\) scattering potential to make it similar to the \(e^- - Na^+\) scattering potential. Through this they showed that the strong plateau in the potassium photoelectron spectra drops out and looks nearly identical to that of the sodium spectra. The differential scattering cross-section for this ‘modified’ potassium atom is shown by the long-dashed line in Fig. 3.13. Clearly the strength of the detected plateau photoelectrons are closely tied to the elastic scattering DCS the electron experiences upon return to its parent ion. Further, these calculations showed that the atom specific short-range contribution to the electron-ion scattering potential cannot be neglected when analyzing scattering dynamics. The accuracy of these TDSE results supports the validity of the SAE approximation for describing the alkali metal atoms. Similarly, experimental and theoretical studies of inert gas atoms interacting with visible or NIR wavelength laser sources have shown that the behavior of the plateau electrons can also be attributed to the atom specific elastic scattering DCS [22, 26, 87].

The sodium photoelectron results (Figs. 3.6–3.9) mostly exhibit the standard tunneling spectra characteristics. However, the nonstandard feature to notice are the kink-like
structures that we observe in the intermediate region of $U_p - 3U_p$. The arrow in Fig. 3.7(b) indicates one example of such a feature. At each wavelength these ‘kinks’ are most pronounced at the lower intensities where the Keldysh parameter is larger, $\gamma \rightarrow 1$, and begins to approach the multiphoton regime. Since these features shift in detected energy as intensity is varied we expect that they have a nonresonant origin. The count rates for the plateau electrons are very low and the observed oscillations in this region are not statistically significant.

We have performed initial SFA (see Sec. 1.4.2) calculations in sodium. Figure 3.14 shows the photoelectron spectra for a focal volume averaged 3.65$\mu m$, 5-cycle trapezoidal pulse with a one-cycle ramp-up and ramp-down. Notice that this calculation also predicts a weak plateau. Further, the oscillations/bumps near the $2U_p$ break shift with intensity and may be linked to the kink-like features we have observed in the experiment. The highest and lowest intensities plotted differ by a factor of approximately 2 which is similar to the intensity range we were able to observe experimentally. However, further studies are required to better understand if the oscillations observed in the SFA calculations are directly linked to the experimental observations and whether the calculations are actually capable of picking up such fine changes in the experimental photoelectron spectra. Figure 3.15 shows the overlap between the experimental and calculated spectra for the lowest and highest experimentally measured intensities. The spectra were shifted vertically for easier comparison and were matched up by finding the best agreement at the $2U_p$ break. The SFA calculations definitely show some discrepancies with the experimental results. It appears that the calculation either overestimates the contribution of the direct electrons or it underestimates the plateau electrons. Also, the experimentally measured plateau does not extend as far as predicted. This discrepancy may be due to the very low count rates in the plateau region; possibly better agreement would be achieved with longer data acquisition times.

In potassium (Figs. 3.10–3.12) there are two interesting spectral features that should be pointed out. First, notice the ‘bump’ that appears shortly before $2U_p$. This feature is most pronounced at the longest wavelength, 3.9$\mu m$, and diminishes as we move towards shorter wavelengths. Also, the position of this ‘bump’ appears to be constant in $U_p$ as well as coinciding with an increased contrast in the ATI structure. Since this feature moves in energy as the intensity is varied we do not expect it to be linked to a resonance like mechanism. A similar ‘bump’ was observed in cesium but in that case it was most noticeable at shorter wavelengths, 3.4$\mu m$ and 3.6$\mu m$, and less visible at 3.9$\mu m$ [59].

Experimental measurements of the photodetachment electron energy spectra of several negative ions in the wavelength range of 1.0–2.2$\mu m$ have observed a possibly related feature [89, 90, 91, 92]. An example spectra in Br$^-$ is shown in Fig. 3.16 (image reproduced from [92]) where the bump around 8eV (slightly below $2U_p$) appears similar to what we observe. Negative ions have similar ionization potentials as alkali atoms, in the few eV range.
Figure 3.14: SFA calculations for sodium at 3.65\(\mu\)m at four intensities (top curve corresponds to the highest intensity). The calculation used a 5-cycle trapezoidal pulse and includes focal volume averaging. Calculations were performed by Dr. Junliang Xu.

Figure 3.15: Two examples of the overlap between SFA calculations and the 3.6\(\mu\)m sodium data. The two examples shown are at the lowest and highest experimentally collected intensities. The best fit between data and experiment was chosen by matching at the 2\(U_p\) break.
Figure 3.16: Photoelectron energy spectra for Br$^-$ at 1.3$\mu$m and 6.5\times10^{13}$W/cm$^2$. Spectra was taken along the laser polarization with linearly polarized light. The experimental results (circles); SFA calculation which includes rescattering (solid line); and an SFA calculation which only accounts for direct electrons (dashed line) are shown. Figure reproduced from [92].

Bergues et al [91] examined the origin of this feature and its dependence on experimental parameters, like laser wavelength and intensity. They found that as intensity or wavelength is increased this features moves towards higher detected energies and its amplitude decreases. We also observed this behavior in our potassium data. Their theory employs a Keldysh-like model based off of the strong-field approximation (SFA). The assumption of a short-range potential is fairly accurate for negative ions. They attribute this ‘bump’ to an interference between two coherent trajectories that an electron can take as it is photodetached from the core. The trajectories that interfere emerge at two distinct times which are symmetric in respect to the zero crossing of the laser field (see Fig. 3.17(a)). Physically the two electron trajectories are shown in Fig. 3.17(b). Bergues et al [91] also showed that the point sources (in atomic units) for these two emissions occur at $r_{1,2} = \pm(E/\omega^2)\sqrt{1+\gamma^2}$ where E is the field amplitude, $\omega$ is the frequency of the field and $\gamma$ is the Keldysh parameter. Therefore, this interference is similar to a double-slit experiment where the constructive and destructive interference pattern depends strongly on the separation of the slits. The separation between the point sources, $\Delta r = r_1 - r_2$, is approximately 4–5 times larger for an alkali metal species at 3600nm versus a noble gas species at 800nm (when considering intensities near saturation for both species). This may be one of the reasons why this feature is more clearly observed in the alkali metal atoms (and negative ions) at MIR wavelengths than the noble gases at NIR wavelengths. While performing a pulse duration study Kübel et al [93] observed a similar feature in argon with 4fs, 790nm pulses (approximately 1.5 cycles). As pulse duration was increased towards 30fs this enhancement vanished. This gives further
Figure 3.17: Panel (a) is reproduced from [91]. The two birth times that contribute to the trajectories that produce the ‘bump’ in negative ions are labeled as $t_1$ and $t_2$, they are symmetric with respect to the zero crossing of the field. Panel (b) shows physically the behavior of the atomic/negative-ion potential and ionizing electron. The laser field at the moment of ionization is displayed by the red-dashed lines. Also shown are the two trajectories (after ionization) that contribute to this interference.

credence to the prediction that this feature is caused by an intra-cycle interference. Our preliminary SFA calculations in potassium have accurately reproduced the experimentally measured position of the ‘bump’ near $2U_p$.

The second spectral feature to notice in potassium are the enhancements/oscillations present in the plateau region of the spectrum. This enhancement is clearest at the shortest wavelength, 3.4$\mu$m, where the ATI structure appears more pronounced. These features are less noticeable when we move to longer wavelengths, corresponding to smaller Keldysh parameters, and therefore appear to be tied to the multiphoton regime. The arrows in Figs. 3.10(a) and 3.11(a) indicate the structures being discussed here. Further, as intensity is varied they seem to remain nearly constant in energy (but not $U_p$) and therefore we are inclined to associate them with a resonant like interference.

Plateau enhancements have also been experimentally observed in the noble gases at visible/near-infrared wavelengths [22, 74, 73]. These enhancement regions often exhibit an increased ATI contrast and are most pronounced in argon and xenon. However, a consensus on the physical origin of these features has not been reached. The disagreement arises because there are two theories which reproduce the experimental results but their physical explanations for the origin of the feature do not agree. The main focus in these noble gas experiments has been on the effects observed in the ATI structure. For the majority of our alkali metal data we do not observe ATI structure. However, this does not necessarily exclude the possibility that some of the spectral features in the alkali metal data could be
linked to similar physical origins. Therefore, these theories are briefly introduced here.

First, let’s discuss the points on which these two models agree. They both attribute the enhancement to a rescattering effect since the feature occurs in the plateau of the photoelectron spectra. Further, they both adopt the SAE approximation and produce reliable results; therefore multi-electron effects appear to be negligible. This accuracy is clearly observed in the SAE TDSE calculations of Nandor et al [48].

The first theory was introduced in the late 1990s and uses TDSE [75, 94, 48, 77]. They attribute the process to resonant population transfer into the Rydberg states from which the electrons can be field ionized. The enhancement occurs when the nuclear potential and laser field interact with the electron wavepacket causing a focusing or bunching mechanisms. This causes the electron to linger near the atom for long periods of time after the initial ionization step and undergo multiple rescattering events before finally escaping and being detected.

The second model was introduced in the early 2000s and used SFA with a zero-range potential which only allowed for bound-free transitions. However, even though no Rydberg levels exist in this model the experimental features were well reproduced. This model attributed the enhancements to ‘channel-closure’ induced resonances. The continuum states in an atom are shifted by the ponderomotive energy which is dependent on the laser intensity; so the n-photon transition channel becomes ‘closed’ when this ponderomotive shift exceeds the n-photon energy [22, 95]. By using this model they predict that the n-photon channel closure will produce a resonant enhancement in the photoelectron energy spectra between $5U_p^n - 8U_p^n$ where $U_p^n = n\hbar \omega - I_p$ [48, 76]. The only alkali data we have that appears to exhibit an enhancement in the plateau is potassium at 3.4$\mu$m and 3.7$\mu$m. According to this prediction at 3.4$\mu$m we observe the 15-photon (5.7–9.1eV) and 17-photon (9.3–14.9eV) channel closure enhancements and at 3.7$\mu$m we observe the 17-photon (6.8–10.8eV) channel closure enhancement, see Fig. 3.18. These appear to overlap fairly well with our data but it is difficult to draw any definite conclusions from so few, and rather weak, enhancement regions. More noticeable enhancements were observed in cesium and these are discussed in the thesis of Dr. Emily Sistrunk [59].

In order to gain further insight into these quasi-resonant enhancements observed in the plateau region of the alkali metal atoms more extensive SFA or TDSE theoretical analysis will be required. We have also performed a more thorough study of these enhancement features in the inert gases at multiple intensities and visible/NIR wavelengths. The results of this work is discussed in Chapter 4.
3.3 Photoelectron Angular Distributions

We also studied the angular distributions of the photoelectrons in sodium and potassium. Both of these were performed at 3.6μm and near their respective saturation intensities (5.5TW/cm² for sodium and 2.2TW/cm² for potassium). These were then used to extract the elastic scattering differential cross-section (DCS). This method is the strong-field equivalent to conventional electron diffraction (CED) [96, 97]. In CED an external high-energy electron beam is shot at an atomic or molecular gas target. The electrons are scattered elastically and the subsequent diffraction pattern is used to extract structural information about the species. In strong field interactions the ‘electron’ source is taken from the species itself. The ionized electron propagates in the field and upon return the coherent electron wavepacket scatters with its parent ion. The electrons in the plateau region correspond to these rescattered trajectories and it has been shown that species dependent information is contained in this portion of the spectra. For atoms we can extract the DCS by measuring the backscattered electron distribution. In more complex molecular systems the interaction between the returning electron wavepacket and its parent ion provides further structural information. An example of this is discussed in Chapter 5 where we obtained bond length measurements from the angular distributions of C_{60}. I begin this section by providing a brief theoretical background on the quantitative rescattering theory (QRS) which is the basis for extracting the DCS from experimental data. Then the experimental findings for sodium and potassium are discussed and compared with previously published results on the noble gases.
3.3.1 Quantitative Rescattering Scattering Theory (QRS)

In 2009 Chen et al [47] presented their quantitative rescattering theory (QRS) which describes the electron-ion interaction upon rescattering. The key expression for this model is:

\[ D(p, \theta) = W(p_r) \sigma(p_r, \theta_r) \] (3.5)

where \( D(p, \theta) \) is the detected photoelectron momentum distribution, \( W(p_r) \) is the spectral density of the returning wavepacket (RWP), and \( \sigma(p_r, \theta_r) \) is the field-free elastic scattering DCS. On the left hand side the value of \( p \) and \( \theta \) are the detected momenta and angle. On the right hand side \( p_r \) is the momentum of the returning electron and \( \theta_r \) is the electron’s scattering angle. The returning direction is taken to be along the laser polarization. For a clearer picture of how these quantities are related see Fig. 3.22.

The preferred method of calculating the RWP term, \( W(p_r) \), is through the second-order strong field approximation (SFA2). Chen et al [47] have shown that their SFA2 model produces accurate results when checked against “exact” TDSE calculations. Further, the computation time for SFA2 is a factor of thousands faster than TDSE. The strong-field approximation uses the electron-field interaction as the dominant mechanism and the electron-ion interaction as a perturbation. Since the ionized electron spends most of its time away from the ion (before it rescatters) it makes sense that SFA2 could produce accurate results. They have also shown that the RWP is independent of the scattering angle, or other target specific features, and can therefore be characterized purely by the laser parameters. It is important to note that SFA2 uses the first-order Born approximation (1BA) to describe the momentum distribution of the returning electron wavepacket. The 1BA has been shown to produce highly inaccurate results in short range interactions since it completely neglects the atom/ion potentials. However, since the RWP dynamics are dominated by the influence of the strong laser field, SFA2 can still be used to produce accurate results. The target dependence is embedded in the elastic scattering DCS term, \( \sigma(p_r, \theta_r) \), and therefore SFA2 cannot be used to calculate this value accurately. So QRS assumes that the extracted DCS is independent of laser parameters and only depends on species specific features. This is one of the strengths of the QRS model; the laser and atom dependent components are separated in the RWP and DCS terms respectively.

The QRS model only uses the high-energy portion of the photoelectron energy spectrum and specifically the ones that have been back scattered with final energies \( > 4U_p \). The portion of the spectrum below this energy contains contribution from the direct electron trajectories. As a final note, Chen et al [47] have compared their TDSE and SFA2 calculations to numerous experimental results and found a high level of agreement, therefore further supporting the validity of the SAE approximation.

For atomic species the accuracy of this method has been demonstrated experimentally
in several noble gases (Ne, Ar, and Xe) at 800nm [98] and (Ar, Kr, and Xe) at 2µm [97]. Further, calculations using the QRS model have shown good agreement with TDSE in sodium and potassium [99]. A demonstration of its close agreement can be seen in Fig. 3.19 which is reproduced from [99]. Figures 3.19(a) and 3.19(b) compare the TDSE and QRS results for the photoelectron angular momentum distributions in Na and K respectively. The white circle in the center represents energies below $4U_p$ which are not calculated through QRS. The agreement is very good. Figures 3.19(c) and 3.19(d) show the calculated DCS at three different electron return momenta for Na and K respectively. Notice that the DCS for K is significantly higher than that for Na, this agrees well with the much stronger plateau we observed in K. Figure 3.19(e) compares the angle-integrated spectra which is calculated through TDSE and the QRS model where the agreement is once again shown to be quite good. Figure 3.19(f) shows the experimental photoelectron spectra at 3.2µm and 1.9ps pulse duration reproduced from Gaarde et al [87]. QRS can also be applied to high-harmonic generation (HHG) and non-sequential ionization (NSI) if the elastic scattering DCS is replaced by the recombination cross-section for HHG and the inelastic scattering ionization cross-section for NSI. The QRS model has also been extended to self-imaging of molecular species and this will be discussed in more detail in Chapter 5.

### 3.3.2 Experimental Results

In the experimental setup the interaction chamber, along with the flight tube axis and detector position, are stationary and therefore the laser polarization must be rotated to collect photoelectron spectra at various angles. The fine adjustment to the laser power was made through a series of two polarizers. The first polarizer was rotated while the second was fixed to produce a horizontally polarized beam (directed along the flight tube towards the detector). A half-wave plate after the second polarizer was used to rotate the laser polarization. The half-wave plate was calibrated and its full rotation was checked to guarantee it produced symmetric results in all quadrants. The power was measured after the half-wave plate and was checked between data collection at each angle. A pellicle was placed after the power meter and used to apply a coarse adjustment to the laser pulse energy (this was also calibrated before data collection). The alkali oven temperature was monitored for stability. The order of the collected angles was randomized to assure that the observed count rate changes were not linked to laser drift. Further, two complete sets of spectra were taken back-to-back to guarantee the reproducibility of the data. In all data presented here the agreement between the two sets was very good. This shows that we can maintain fairly good laser stability over 6-8 hour intervals which are necessary to run these scans. As mentioned earlier, the slit before our MCP detector is what limits our angular resolution to 2.2°. Experimentally we took 4° steps in field therefore avoiding possible issues with double counting electrons near the boundaries between scans.
Figure 3.19: Calculated results for sodium and potassium interacting with a 3.2\(\mu\)m, 5-cycle pulse with a peak intensity of 1.0TW/cm\(^2\). Panel (a) and (b) are 2D photoelectron momentum distributions calculated using TDSE and the QRS model for the two species. These are only compared in the rescattering region of \(>4U_p\). Panels (c) and (d) show the calculated DCS for large scattering angles at three different electron return momenta, \(p_r\). Panel (e) shows the angle-integrated photoelectron spectra versus detected energy. The TDSE (solid lines) and QRS (dotted lines above \(4U_p\)) results are plotted together. Panel (f) is a comparison to experimental data; potassium was performed at 1.5TW/cm\(^2\) and sodium at 1.8TW/cm\(^2\) (figure taken from [87]). Figure reproduced from [99].

The experimental angular distributions for sodium and potassium at 3.6\(\mu\)m and near their saturation intensities are shown in Fig. 3.20 and 3.21 respectively. These results are plotted in momentum space where the horizontal axis is along the laser polarization and the vertical axis is perpendicular to the laser polarization. The detected signal is plotted on a logarithmic scale where the sodium data spans 7 orders of magnitude and the potassium data spans 6 orders of magnitude. Experimentally the angular data is gathered over a single quadrant. It is copied over to the other quadrants for ease of viewing and analysis. The low momenta region corresponds to the direct electrons which do not return to the core after ionization. As we saw in Sec. 3.2, the total detected electron yield is dominated by the
Figure 3.20: Sodium 2D electron momentum distribution. Taken at 3.6µm and 5.5TW/cm². The momentum is expressed in terms of atomic units.

Figure 3.21: Potassium 2D electron momentum distribution. Taken at 3.6µm and 2.2TW/cm². The momentum is expressed in terms of atomic units.
signal in this region. The electrons with higher momenta are associated with trajectories that undergo rescattering before detection. The rescattered electrons are the ones from which we aim to extract species specific structural information. From the two angular distributions it is clear that sodium has a much weaker plateau than potassium. Further, notice that the sodium data is more focused along the laser polarization. This is a typical feature of spectra that are further into the tunneling regime.

Once the photoelectron angular distributions have been collected we proceed to extracting the experimental elastic scattering DCS. We briefly summarize the method here but more detailed information can be found in the thesis of Dr. Cosmin Blaga [10] or in the Supplementary Information of [96]. First, consider that the detected momentum, \( p \), can be related to the momentum of the electron upon return, \( p_r \), and the vector potential of the field, \( A_r \), at the return time, \( t_r \). In atomic units this relationship is given by
\[
p = p_r - A_r.
\]

Figure 3.22 shows how these values are related to the momentum angular distribution spectra. The figure is reproduced from Blaga et al [96] for the case of \( \text{N}_2 \) but this method is equivalent when applied to atomic targets. The radius of the black-dashed circle centered on the origin corresponds to an energy of 2\( U_p \). This region is dominated by the signal from the direct electrons. As mentioned earlier, in order to extract the DCS we only want to use the signal from the rescattered electrons and therefore do not include angles which overlap with the direct electron region. The points along the dashed-magenta circle correspond to the elastically scattered electrons originating from the same returning electron momentum, \( p_r \). By sweeping around the circle we sweep through the electron scattering angles, \( \theta_r \). This corresponds to the angle \( \theta \) and momentum \( p \) in the raw data files.

One important point to recall is that for any electron return energy there are two trajectories that correspond to it, namely the ‘long’ and ‘short’ trajectory. This is true everywhere except for 3.17\( U_p \) where these converge to a single value. Therefore, in order to have the most accurate value for the time the electron wavepacket spends in the field it may theoretically seem sensible to use the return energy of 3.17\( U_p \) which, for exact backscattering, corresponds to a final detected energy of 10\( U_p \). However, experimentally the count rates near 10\( U_p \) are very low and it would be difficult to extract an accurate DCS. Lower return energies can be used if we consider the ionization probabilities relating to the birth times for the short and long trajectories. The long trajectories are ionized near the peak of the field and therefore have much higher ionization rates. The approximation of neglecting the short trajectories has been used successfully [96, 97].

In order to determine the radius of the ring (dashed-magenta circle in Fig. 3.22) one chooses a returning electron momentum, \( p_r \). By assuming that only the long trajectories contribute we can calculate the birth and return time for these trajectories. If we further approximate that the ionized electron has zero initial momentum then the rescattering momentum is given by \( p_r = A_r - A_b \). Next, by using the calculated return time we can de-
Figure 3.22: An example of a 2D electron momentum distribution of nitrogen ($N_2$). The black-dashed circle corresponds to the region of direct electrons which have energies $<2U_p$. The offset magenta-dashed circle represents the final momenta an electron may have when it elastically scatters from its parent ion with a return momenta of $p_r$. The detected momentum is: $p = p_r - A_r$ where $A_r$ is the field vector potential at the moment of rescattering. See text for more details. Figure reproduced from [96].

determine the laser field’s vector potential at the moment the electron rescatters, $A_r$. With the use of these two quantities we have now defined the origin and radius of the dashed-magenta circle in Fig. 3.22 which corresponds to a constant scattering energy. Since experimentally there is a limited number of counts at any particular position along this circle we integrate over a chosen uncertainty in the return momentum, $p_r$, and angle $\theta_r$. Choosing the range over which we integrate is a balance between a window that is small enough so that we do not wash out the features we wish to observe and a window that contains enough counts so that the uncertainty due to counting error, $\Delta N = \sqrt{N}$, is reasonable (5% is fairly typical). When summing the yield we use the raw time-of-flight data which contains the true number of collected counts.

The experimentally extracted elastic scattering DCS for sodium is shown in the left panel of Fig. 3.23 for three different return energies. Similarly, the DCS for potassium at three different return energies is shown in Fig. 3.24. These are compared to the theoretically calculated values which were performed by Dr. Junliang Xu using a standard potential scattering theory [97, 47]. In this model the total scattering amplitude is a sum of that due to the long-range Coulomb potential and the short-range contribution which is expressed in terms of a partial wave expansion. The number of terms used in this expansion is determined
by examining the convergence of the series. A clear dip in the DCS is observed at scattering angles $\sim 100^\circ - 140^\circ$ for both species. By examining the angular distributions, Figs. 3.20 and 3.21, we can clearly see the origin of this feature. The dips correspond to the regions which resemble indents in the rescattered electrons. For sodium these appear near $\pm 1.3$ au in the parallel momentum and $\pm 0.5$ au in the perpendicular momentum. In potassium these occur near $\pm 0.75$ au in the parallel momentum and $\pm 0.5$ au in the perpendicular momentum.

In sodium, the agreement between theory and experiment is quite good, see Fig. 3.23. For all three return energies which we considered (10, 15 and 20 eV) the theoretical model reproduced the location of the dip accurately and in general, overlaps well with the data for scattering angles greater than $\sim 80^\circ$. The discrepancy at small scattering angles, which we see in sodium and potassium, is an indication of the region where our experimental spectra becomes contaminated by the direct electron contribution. For potassium (Fig. 3.24), the theory and experiment both demonstrate a clear dip in the DCS but they do not agree on its exact scattering angle position. This discrepancy increases at lower electron rescattering energy; approximately a 7.5$^\circ$ difference is observed at a 3 eV rescattering energy, 6.8$^\circ$ at 5 eV, and near agreement at the highest return energy of 7 eV. However, even at this highest return energy the agreement between theory and experiment is not very good.

One contributing factor for the larger discrepancy observed in potassium is due to the lower return energies of the rescattered electrons (10–20 eV for sodium and 3–7 eV for potassium). The theoretical model treats the scattering process in the limit of high energy collisions where the short-range atomic potential dominates and the valence electrons can effectively be viewed as transparent. However, for very low energy electron-ion collisions the importance of multi-electron effects increases. Also, the better agreement in sodium appears to be correlated with the data being taken further in the tunneling regime, corresponding to a smaller Keldysh parameter. In the sodium data $\gamma = 0.6$ while in the potassium results $\gamma = 0.9$ (practically in the multiphoton regime). The classical electron trajectory picture works better in the tunneling regime where the assumption that an electron enters the continuum with zero initial momentum is more valid. A similar observation was made in the noble gases where xenon showed a larger discrepancy between the experimental and theoretical DCS than neon, argon or krypton [97, 98]. This can be attributed to the larger Keldysh parameter ($\gamma \sim 0.9$) and lower electron rescattering energies present in the xenon experiments. As an example, in the right panel of Fig. 3.23 the experimentally extracted DCS for argon at 2 $\mu$m (where the Keldysh parameter is approximately 0.3) shows very good agreement with the calculations. Therefore, we can draw the conclusion that in order to extract an accurate DCS it is important to perform the experiment in the tunneling regime and preferably when $\gamma < 0.6$. This condition appears to be more important than having very high energy recollisions, as can be seen in the sodium data where we achieved good agreement even at 10 eV return energies.
The other feature to notice is the shifting of the minima in the DCS. Here I only focus on the sodium spectra where the behavior is better understood. The electron scattering process can be viewed in analogy to an Airy disk pattern. In this picture we expect that with a larger return energy the scattering angle for the first minima becomes smaller, exactly as observed in the sodium data at 3.6$\mu m$ and the argon at 2$\mu m$. Such a simple qualitative picture is not available for the potassium data and the experimental results actually show a trend in the opposite direction.

By taking advantage of the electron rescattering process present in strong-field interactions we can extract target dependent information from the plateau electrons in the measured angular distribution spectra. This method has shown success for extracting the elastic scattering DCS in the noble gases and diatomic molecules [96, 97, 98]. To our knowledge, this is the first experimental demonstration of applying this method to extract the DCS in the alkali metal atoms.
Figure 3.23: DCS versus scattering angle, $\theta_r$. Left panel shows sodium at 3.6 $\mu$m and 5.5 TW/cm$^2$. Right panel shows the results for argon at 2.0 $\mu$m and 234 TW/cm$^2$. The experimentally extracted values are represented by the points connected by a dashed-line. The calculated DCS is plotted as a solid-line. The results at three different electron return energies are shown. Both systems were in the tunneling regime: $\gamma \sim 0.6$ for sodium and $\gamma \sim 0.3$ for argon.
Figure 3.24: DCS versus scattering angle, $\theta_r$, for potassium. The experimentally extracted values are in blue and the theory is shown in red. The three panels correspond to electron return energies of 3eV, 5eV, and 7eV. Better agreement is observed at larger return energies. The potassium data was taken near the multiphoton regime, $\gamma \sim 0.9$. 
Chapter 4

WAVELENGTH DEPENDENCE OF PHOTOELECTRON EMISSION

In the preceding chapters I already emphasized our interest in studying Keldysh scaled systems to gain insight into universal and species specific spectral features occurring in strong-field interactions. As of now, even the systems that have been studied the most extensively, namely the inert gas atoms in visible/NIR fields, are still not completely understood. Their measured photoelectron spectra demonstrate many interesting phenomena but here we focus on investigating the resonance-like enhancements in the plateau region which often correlate with an increased ATI contrast. Though I have already briefly introduced some of the relevant experimental and theoretical findings in Chapter 3, a recap and a bit more detailed introduction is warranted here.

Much of the interest began through a series of experiments in the 1990s when portions of the high-energy plateau were observed to occasionally exhibited electron yield enhancements as large as an order of magnitude. In 1994 Paulus et al [22] used 630nm, 40fs pulses to demonstrate that these enhancements were present, to various degrees, in all of the noble gases, see the left panel in Fig. 4.1. The shapes and strengths of these plateaus have been associated with the scattering cross-section [100]. Further examination of argon demonstrated that the ‘strength’ of these enhancements is sensitive to intensity but their position in detected energy remains relatively constant [22]. The feature of interest is clearly seen near 30eV in curve (b) in the right panel of Fig. 4.1. Since these features are observed in the plateau it is expected that they are linked to a rescattering process. In 1997 Hertlein et al [73] measured argon photoelectron energy spectra with a high resolution spectrometer using a 790nm, 120fs laser source. They observed that each ATI peak was actually composed of 3 sub-peaks and the strengths of the individual peaks were highly sensitive to intensity. Since the energy position of these peaks did not shift with intensity they were attributed to a resonant process. That same year Hansch et al [74] performed experiments on xenon with 800nm, 120fs pulses and also observed substructure in the ATI
Figure 4.1: Experiments performed on the inert gas atoms with a 40fs, 630nm laser source. The left panel shows that the enhancement in the plateau exists for all of the inert gas atoms to various extents. The right panel shows how the enhancement (20–40eV) behaves in argon as a function of intensity. The plotted intensities are: (a) $6 \times 10^{13}$ W/cm$^2$, (b) $1.2 \times 10^{14}$ W/cm$^2$, (c) $2.4 \times 10^{14}$ W/cm$^2$ and (d) $4.4 \times 10^{14}$ W/cm$^2$. Figure reproduced from [22].

peaks which did not shift in energy as intensity was varied. The further work by Nandor et al [48] in argon found excellent agreement between their experimental (800nm, 120fs) results and SAE-TDSE calculations.

As already discussed in Chapter 3, two theoretical models were proposed to describe the physical origin of these features. The first used SAE-TDSE with a ‘realistic’ model atomic potential. The enhancements were attributed to an initial multiphoton resonant transition of electron population to the AC Stark shifted Rydberg states. At certain intensities a constructive interference is observed between the ejected electron wavepackets from consecutive laser cycles. Ionization from these excited states, which recollide with the core multiple times, contribute to the enhancement region of the photoelectron spectra [75, 94, 77]. The second model also reproduced the experimental results but through SFA calculations with a zero-range potential, which does not allow for bound excited states. In this case, the effect was attributed to channel-closure which occurs when the laser ponderomotively shifts the continuum states, thereby closing off progressively higher n-photon channels. At the channel closing intensities many electrons are born with near zero drift momenta and linger in the vicinity of the core for many cycles, recolliding multiple times, before finally rescattering and being detected. The model shows these electron orbits exhibit a constructive interference which is physically observed as the enhancement in the plateau [95, 76].

Though these two models disagree on the physical mechanism for the initial step of promoting the electrons to the continuum they agree that the constructive interference between multiply scattered electron wavepackets is essential for the observed plateau enhancement.
Further, they both agree that the SAE approximation is sufficient and multi-electron effects can be neglected.

One of the theoretical predictions made by these models is that the plateau enhancement should demonstrate a nonlinear dependence on pulse duration [77]. Several more recent studies, which were able to produce nearly single-cycle pulses, examined this predicted dependence. Grasbon et al [100] showed that these enhancements were suppressed when short pulses were used. Figure 4.2 clearly shows that as pulse duration increases from 7fs to 40fs the region between 15eV and 30eV in argon at 800nm becomes enhanced. The spectra in the figure have been shifted vertically for visual convenience. This result agrees with the theoretical models since multiple rescattering is suppressed for nearly single-cycle pulses. A similar observation was made by Kübel et al [93] in argon with 790nm light and varying the pulse duration between 4fs and 30fs.

What currently appears to be missing in the literature is a thorough experimental exploration of the effects of varying the important adjustable parameters; like intensity, wavelength and target species. The results discussed in the preceding paragraphs tend to emphasize the effect of varying one or occasionally two adjustable parameters. However, quantitative comparison between data sets can be difficult due to the differences in the laser sources used to study the interaction. In general, a laser beam cannot be completely characterized and therefore we do not know if temporal and spatial beam profiles, focusing conditions and other laser fluctuations/instabilities may be coupling to the observed spectral differences. This chapter is a presentation of our experimental findings and analysis using a single tunable laser source to examine the wavelength, intensity and species dependence of the resonant-like plateau enhancements.
The experimental setup will be described first. Then our experimental findings are summarized and discussed in relation to theory. All of the TDSE and SFA calculations that will be presented were performed in our group by Dr. Junliang Xu. These quantum mechanical calculations have shown great success in reproducing experimental results. An example of the level of agreement we have been able to achieve between experiment and theory is shown in Fig. 4.3.

4.1 Experimental Setup

For all of the following experimental results we used the tunable 2\( \mu \)m laser system which was introduced in Sec. 2.3. We frequency double the signal out of the HE-TOPAS-Prime using a BBO crystal to produce a continuously tunable beam in the range of 560–750nm, at 1kHz, and a multi-cycle pulse duration of 60fs. These experiments were performed in the ‘Inert Gas Chamber’ using a similar Time-of-Flight apparatus as was discussed for the ‘Oven Chamber’ (see Sec. 2.4). The gas pressure is controlled through the use of a sapphire flat variable leak valve.

The wavelength was calibrated using a USB spectrometer (Ocean Optics USB2000+). The spectral content at each wavelength contains a smooth, symmetric distribution; the wavelengths listed in the following data correspond to the central peak of these measurements. The pulse energy is attenuated with neutral density (ND) filters and focused into the chamber with a 125mm focal length lens. The power measurements are made after
attenuation but before the focusing lens.

In these experiments we are specifically studying the photoelectron energy distributions of the plateau electrons. The raw data collected with the TDC is taken in constant width time bins and therefore our spectral energy resolution decreases at larger energies ($E \propto 1/t^2$). To improve our energy resolution in the plateau we used a LeCroy TDC2228A which is capable of 50ps or 100ps time bins along with the LeCroy TDC4208 which has a 1ns temporal resolution. The TDC2228A is limited to approximately 2000 time bins and therefore cuts off the low energy (long travel time to detector) photoelectrons. This issue can be alleviated by stitching together spectra with the 1ns time bins for the low energy portion where the TDC4208 provides good resolution with the 50/100ps data of the TDC2228A which has superior resolution at higher energies.

For all of the photoelectron studies present in this chapter the laser is linearly polarized along the spectrometer axis. The count rates are maintained below 3 hits/shot to avoid space-charge effects and data overflow on the TDCs, which are limited to 8 hits/shot. Pressures of $2 \times 10^{-4}$ Torr were not exceeded in order to avoid detector damage. We used the 50ps (TDC2228A) for all of the neon data and each photoelectron energy spectrum is summed over $1.2-5.4 \times 10^6$ laser shots. For the argon data each spectrum was stitched together from the 1ns (TDC4208) and 50ps (TDC2228A) time-bin results. For the 1ns binned scans we collected data from $0.3 \times 10^6$ laser shots, this spectra was only used for the low-energy (direct electron region) where the yields are high. For the fine resolution scans, 50ps, we collected data over $0.9-3.6 \times 10^6$ laser shots; longer scans were required to build up sufficient statistics in the plateau region. For the krypton data we used the 100ps (TDC2228A) binning and each spectra is summed over $0.3-2.7 \times 10^6$ laser shots. The electrons in the krypton plateau do not extend as far as for the other species and this slightly coarser temporal binning provided sufficient resolution. The method of stitching spectra together was only performed for argon and therefore the very low energy electrons in the neon and krypton were not collected.

Angular distributions were also performed on argon in a similar setup as discussed in the alkali data. The half-wave-plate was calibrated over its full rotation. However, during data acquisition we only collected spectra over a single quadrant of the photoelectron energy distribution (corresponding to a 45$^\circ$ portion of the half-wave-plate rotation) in 3$^\circ$ steps. The order of collection was randomized and the scan at each angle was summed over $0.3 \times 10^6$ laser shots.
4.2 Experimental Results and Analysis

4.2.1 Intensity Dependence

Let’s first examine the intensity dependence of the photoelectron energy spectra for a laser polarized linearly along the spectrometer axis. The neon results are shown in Fig. 4.4, the argon results in Figs. 4.5–4.6 and krypton in Figs. 4.7–4.8. For each species/wavelength combination we measured spectra at multiple intensities. The species, wavelength, peak intensity and corresponding Keldysh parameter values are included on each plot. The spectra are shifted vertically to allow for easier viewing. At each wavelength we calibrated the intensity through the $10U_p$ cutoff of the highest energy spectra and then applied this calibration to the lower energy results. Therefore, the absolute intensity uncertainty is ±15% but the relative uncertainty between spectra for the same wavelength/species is ±3%.

By examining the photoelectron spectra in Figs. 4.4–4.8 we observed rich dynamics in the plateau enhancement structures as experimental conditions were varied. The plateau region corresponds to electron energies from $2U_p$ to $10U_p$ (the high energy cutoff). A change in slope is observed between the direct (low energy) and plateau portions of the spectra. The three species differ in the steepness and strength of their respective plateaus which has been experimentally observed before [22] and physically related to the species specific scattering cross-section [100]. Notice that for each wavelength/species combination the energetic position of these enhancements remains constant as intensity is varied. The enhancement regions also tend to coincide with an increased level of contrast in the ATI structure.

Neon ($I_p=21.56\text{eV}$) photoelectron spectra were collected at wavelengths of 567nm, 600nm and 620nm which correspond to a Keldysh parameter range of $\gamma = 0.89 - 1.32$ (Fig. 4.4). Between two and three enhancement regions are visible in each spectra; for example, at 600nm these are centered near 20eV, 33eV and 60eV (only visible at $319\text{TW/cm}^2$).

The argon ($I_p=15.75\text{eV}$) photoelectron spectra were measured over a wavelength range of 566–744nm which corresponds to Keldysh parameters of $\gamma = 0.80 - 1.30$ (Figs. 4.5–4.6). In argon we typically observed 1–2 plateau enhancement regions which show dramatic spectral variation with changing wavelength. For example, at 583nm we observe a single enhancement near 40eV but in general the yield in the plateau decreases monotonically with detected energy. However, at the next longer wavelength, 620nm, there are two distinct enhancement regions near 30eV and 55eV. The argon 620nm spectra also provides one of the clear examples of the correlation between an enhancement region and an increased ATI contrast. The ATI structure is sharp between 20–40eV, then nearly vanishes between 40–47eV, and finally its visibility increases again until we begin to be limited by the resolution of our spectrometer near 65eV. Further, notice that at each wavelength the ATI contrast increases as the Keldysh parameter moves further into the multiphoton regime,
Figure 4.4: Neon photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

\( \gamma > 1 \). As an example consider argon at 566nm, at 155TW/cm\(^2\) (\( \gamma = 1.30 \)) the ATI contrast spans approximately an order of magnitude near 25eV but at 221TW/cm\(^2\) (\( \gamma = 1.09 \)) the contrast is only approximately a factor of two.

Finally, krypton (13.99eV) spectra were measured in the wavelength range of 570–741nm, corresponding to Keldysh parameters of \( \gamma = 1.09 – 1.55 \) (Figs. 4.7–4.8). At shorter wavelengths, 571nm and 581nm, we observe a single enhancement region centered near 20–30eV. As the wavelength is further increased, 620nm, the enhancement becomes less noticeable but then reappears near 700nm. At 741nm we observe two clear enhancement regions centered at 20eV and 35eV. As in the neon and argon spectra the plateau enhancements do not shift in detected energy as intensity is varied.
Figure 4.5: Argon photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.
Figure 4.6: Argon photoelectron spectra dependence on wavelength and intensity (continued). The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.

Figure 4.7: Krypton photoelectron spectra dependence on wavelength and intensity. The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.
Figure 4.8: Krypton photoelectron spectra dependence on wavelength and intensity (continued). The laser central wavelength, peak intensity and Keldysh parameter are listed on each figure. Spectra are offset vertically for easier viewing.
4.2.2 Wavelength Dependence

We can also group this data by constant intensity or constant ponderomotive energy while allowing the wavelength to vary. The intensity and ponderomotive energy values were determined by using the $10U_p$ cutoff. Figure 4.9 shows argon photoelectron energy spectra at approximately $2.2 \times 10^{14}$ W/cm$^2$ between 744nm (top curve) and 583nm (bottom curve). Notice that as wavelength decreases the plateau enhancements appear to move out to higher energy. For example, the enhancement centered near 25eV at 744nm (green curve) shifts towards higher energy while becoming more pronounced and at 680nm (purple curve) it is centered at 40eV. Also, notice the appearance of a second enhancement at 650nm (blue curve) near 25eV (it may also be said that we initially observe its appearance near 20eV at 680nm (purple curve)). This enhancement also appears to shift towards higher energy as the wavelength is further decreased. We attribute the ‘disappearance’ of these enhancements at high energy to limitations of the experimental apparatus (spectrometer resolution and count rates decrease at high detection energies). Several spectra with higher temporal resolution and statistics in the plateau region were collected to support this statement. A similar shifting and appearance of new enhancements is observed when we plot the data for a constant ponderomotive energy. Figure 4.10 shows argon spectra corresponding to $U_p = 7.5eV$; a constant $U_p$ also means a constant Keldysh parameter, in this case $U_p = 7.5eV$ corresponds to $\gamma \approx 1$.

In order to convince ourselves that these enhancements do in fact shift smoothly with wavelength we reproduced the experimental study with finer wavelength steps of 10nm over the range of 566–746nm. Fig. 4.11(a) shows the detected energy as a function of laser wavelength for argon with the logarithmic color scale indicating the strength of the signal. An attempt was made to maintain an approximately constant intensity but our attenuation precision is limited by the available ND filters which allow for steps of $\Delta$ND=0.1. This corresponds to a laser intensity uncertainty of approximately ±10%. However, as shown in the previous section we do not expect the energetic position of the enhancements to be sensitive to intensity variations. The spectra are well reproduced by TDSE calculations shown in Fig. 4.11(b). The calculation uses a realistic model potential and accounts for focal volume averaging. These results agree with our earlier findings since the enhancements shift towards higher energy with decreasing wavelength. Further, this behavior repeats with partial stripes visible at the short and long wavelength edges.

A channel-closing event occurs when an integer number of photons is equal to the atomic ionization potential plus the ponderomotive shift of the continuum induced by the applied laser field, $Nh\omega = I_p + U_p$ [76, 95] where $I_p = 15.75eV$ for argon and $U_p \propto I\lambda^2$. This neglects the shift of the ground state energy which is a valid approximation for the inert gases due to their small polarizabilities [78], also see Table 3.2. The arrows in Fig. 4.11 correspond to the expected positions of the N = 10–13 channel-closures at a peak intensity of $1.3 \times 10^{14}$ W/cm$^2$. 106
Figure 4.9: Argon photoelectron spectra at various wavelengths and a nearly constant intensity of $2.2 \times 10^{14} \text{W/cm}^2$. From top to bottom the wavelengths correspond to 744nm (green), 710nm (orange), 695nm (red), 680nm (purple), 650nm (blue), 620nm (gold) and 583nm (black). For a constant intensity the plateau enhancements shift to higher energy as wavelength decreases.

Figure 4.10: Argon photoelectron spectra at various wavelengths and a nearly constant ponderomotive energy, $U_p = 7.5 \text{eV} (\gamma \approx 1)$. From top to bottom the wavelengths correspond to 744nm (green), 710nm (orange), 695nm (red), 680nm (purple), 650nm (blue), 620nm (gold) and 583nm (black). For a constant ponderomotive energy/Keldysh parameter the plateau enhancements shift to higher energy as wavelength decreases.
Figure 4.11: Argon photoelectron spectra plotted as detected energy versus wavelength. Experimental results are shown in (a) and the TDSE calculations are shown in (b). The color scale is on a log gradient and indicates the strength of the signal where red (orange) indicate high yields and blue (black) indicate low yields in the experiment (TDSE calculation). The arrows indicate the approximate locations of the N-photon channel-closures at an intensity of $1.3 \times 10^{14}$ W/cm$^2$ for N=10 (608nm), N=11 (648nm), N=12 (689nm) and N=13 (725nm).
This intensity corresponds approximately to the average value used in the experiment. In the calculations performed by Kopold et al. [95] they found that enhancements from even-N channel-closures had a much sharper turn-on than odd-N channel-closures whose impact on the spectrum developed more gradually. By examining our experimental and calculated spectra we also observe a difference between the odd and even N channel-closures however it is still unknown if the effect discussed in [95] has any connection to our observation.

TDSE calculations also allow us to examine the distribution of electron population among the atomic bound states at the end of the laser-atom interaction. Single intensity (1.3×10^{14} W/cm^2) TDSE results show an increase in the highly excited (Rydberg) state population of approximately a factor of 10−15 when a channel-closing condition was met (at the N = 10−13 positions marked in Fig. 4.11). Physically this indicates that as the intensity increases and the N-photon ionization transition is shifted to below threshold we begin to populate the high-lying Rydberg states. As we sweep across the wavelength range of 566−746nm the integrated electron population in the Rydberg states exhibits an oscillatory behavior where population is maximized at a channel-closure. We further observed oscillations in the total ionized population as a function of wavelength which were exactly out of phase with the oscillations in the Rydberg state population. However, the modulations in the total ionized population are not as strong and only differ by a factor of 1.4 between a maximum and minimum. These results demonstrate the direct physical connection between a channel-closing event and resonant population transfer into the Rydberg states and therefore indicate why the two theories introduced in the beginning of this chapter could produce similar results [75, 76]. Li et al. [101] performed similar TDSE calculations in hydrogen while smoothly varying the peak laser intensity (instead of the wavelength like we have done here) and observed an out-of-phase oscillatory behavior between the total ionization and excitation probabilities which they also attributed to channel-closure.

### 4.2.3 Species Dependence

Figure 4.12 shows a comparison of an argon and neon photoelectron spectra at 620nm and a 58μJ pulse energy. These two spectra were taken within a few minutes of each other (the amount of time necessary to evacuate one gas from the chamber and then send in the other) and therefore all laser parameters are expected to be nearly identical. Clearly the location and strength of the plateau enhancements are species specific.

In order to better understand how the species dependent properties influence the shape of the detected photoelectron spectra we performed SFA calculations. Specifically we focused on two important atomic parameters which determine an electron’s final (detected) energy: its initial ground state wavefunction and the shape of the electron-ion rescattering potential. Figure 4.13 shows the SFA results for all combinations of the electronic wavefunctions (where \( \psi_{Ar} \) and \( \psi_{Ne} \) are the ground state wavefunctions of an electron in an argon and neon atom...
respectively) and forms of the electron–ion rescattering potentials (where \( V_{\text{Ar}} \) and \( V_{\text{Ne}} \) are the argon and neon rescattering potentials respectively). Therefore, as an example, \((\psi_{\text{Ar}}, V_{\text{Ar}})\) indicates using the argon ground state wavefunction and the electron-argon ion rescattering potential. The calculation uses a 5-cycle flat top pulse, 620nm central wavelength and an intensity of \(1.65 \times 10^{14}\) W/cm\(^2\).

The results indicate that the shape of the photoelectron spectra is significantly more sensitive to the form of the ground state wavefunction. Changing the form of the potential has nearly no effect except for some relatively minor differences in the signal amplitude. We currently do not completely understand why the shape of the enhancement is so sensitive to the form of the wavefunction. Further theoretical investigations are necessary to understand which features of the ground state wavefunction survive ionization and propagation in the field in order to influence the rescattering step so drastically.

The experimental spectra (Fig. 4.12) and the SFA calculations (Fig. 4.13) are qualitatively similar. The quantitative differences are partially a result of an approximated pulse shape (trapezoidal) and neglecting focal volume averaging in the calculation. The purpose of Fig. 4.13 was to clearly demonstrate the effect of varying the wavefunction and rescattering potential parameters.

### 4.2.4 Trajectory Analysis

Finally, in order to gain a better understanding of the physical origin of these enhancements we focus on the trajectories that electrons can follow in their interaction with the
Figure 4.13: SFA calculations for argon and neon using a 620nm, 5-cycle flat-top pulse at an intensity of $1.65 \times 10^{14}$ W/cm$^2$. \((\psi_{\text{Ar}} V_{\text{Ar}})\) indicates using the argon ground state wavefunction with the e$^- - \text{Ar}^+$ rescattering potential. \((\psi_{\text{Ar}} V_{\text{Ne}})\) indicates using the argon ground state wavefunction with the e$^- - \text{Ne}^+$ rescattering potential. \((\psi_{\text{Ne}} V_{\text{Ne}})\) indicates using the neon ground state wavefunction with the e$^- - \text{Ne}^+$ rescattering potential. \((\psi_{\text{Ne}} V_{\text{Ar}})\) indicates using the neon ground state wavefunction with the e$^- - \text{Ar}^+$ rescattering potential. The photoelectron spectrum is much more sensitive to the form of the ground state wavefunction.
laser field. SFA calculations were performed to study this and the results are shown in Fig. 4.14. For clarity the calculation uses a simplified model of a single-intensity, 2-cycle trapezoidal pulse (Fig. 4.14(a)) interacting with an argon atom. Further, we limit ionization to a quarter cycle of the laser pulse (shown by the purple and orange region in panel (a)) and then allow the ionized electron trajectories to propagate through the rest of their interaction with the laser and parent ion. Figure 4.14(b) shows the 2D photoelectron momentum distribution at the end of the pulse.

The green-dashed circle corresponds to an energy of $2U_p$ and therefore any electrons with higher energies are expected to have undergone rescattering before detection. In Fig. 4.14(b) the yellow-dashed circle overlays one of the off-center rescattering rings which correspond to the broad plateau enhancements observed in experiment. This signifies that rescattering is vital to determining the energetic location of these features. In order to determine if the long or short trajectories contribute more significantly to these structures we performed further SFA calculations using the time-windowing method. The selection of the long trajectories is indicated by the purple region in Fig. 4.14(a) and the resultant 2D momentum distribution is shown in Fig. 4.14(c). Similarly, the short trajectories are indicated by the orange time window in Fig. 4.14(a) and plotted in Fig. 4.14(d). It is clear that the long trajectories are the main contributor to the enhancements in the rescattering rings.

Our results indicate that multiple returns may not be a necessary condition for observing the enhancement features. From Fig. 4.14 we notice that they persist even when we are limited to the case where the electron returns to the core only once. Further, we note that these enhancements must be a result of intra-cycle interactions since they persist even when we windowed the allowed ionization region to a small portion of a single cycle. The fact that the trajectories that contribute to these features originate from a temporally short portion of the pulse could be expected due to their broad width in energy. This is opposite of the inter-cycle interferences that are necessary to observe the energetically thin structure of ATI.

When longer laser pulses were used in SFA calculations these plateau enhancements persisted but their energetic positions would shift. Therefore, the possibility of an electron being driven back towards its parent ion multiple times during its interaction with the applied laser field does not appear to destroy this spectral feature. This agrees with our experimental conditions since the laser pulses used were approximately 20–25 cycles (full width at half maximum) depending on the wavelength.

A valid concern should be addressed at this point. The calculations just presented are for a single-intensity pulse, but under realistic experimental conditions a focused laser beam contains a distribution of intensities. If we account for this we could expect that the enhancements observed in Fig. 4.14 would wash out, but this does not appear to be the case. In order to understand this let’s examine argon again. Figure 4.15(a) shows
Figure 4.14: SFA calculations for the interaction between a single-intensity 2-cycle trapezoidal pulse and an argon atom. The electric field and vector potential are shown in (a) along with the long-trajectory (purple) and short-trajectory (orange) time windows. The 2D photoelectron momentum distribution when the long and short trajectories were included are shown in (b). Panels (c) and (d) correspond to separating the regions where ionization was allowed to the long- or short-trajectories respectively. The origin of the observed plateau enhancements are attributed to intra-cycle long trajectories. Atomic units are used in panels (b)–(d).
Figure 4.15: Panel (a) shows the photoelectron spectra for argon at 620nm; experiment is shown in green and TDSE calculation in red. The three regions correspond to: low energy, direct, electrons (0−20eV; red), the enhancement region (20−46eV; green) and the remainder of the plateau (46−100eV; blue). Panel (b) shows the electron yield as a function of the intensity distribution within the focal volume in panel (a). The colors of the lines (red, blue, and green) correspond to the respective regions in (a). The black curve is the total yield.

argon photoelectron spectra at 620nm acquired experimentally (green line) and through TDSE calculations (red line); good agreement is observed. The spectra is broken up into three regions: the low energy, direct, electrons (0−20eV; red), the enhancement region (20−46eV; green) and the remainder of the plateau (46−100eV; blue). Figure 4.15(b) shows the weighted ionization yield which is the ionization rate scaled by the respective slice of focal volume which corresponds to that intensity. The colored lines (red, green, blue) correspond to their respective energy regions in panel (a) and the black line is the total ionization yield. Clearly, the total ionization yield is dominated by the direct electron region and remains nearly constant over the intensity range plotted. However, the green curve, which corresponds to the enhancement region, exhibits significant oscillations. Since this yield is plotted on a log scale the bump near 150TW/cm² provides a substantial contribution to the total detected electrons within the green region. Therefore, a likely reason why the observed enhancements do not wash out in a realistic focal volume is because there is a region of dominant intensities which contribute the majority of the detected signal.

We have also taken multiple angular distributions to confirm experimentally that the observed plateau enhancements correspond to the rescattering rings predicted by theory. Figure 4.16 is one example of a 2D momentum angular distribution taken in argon at 793nm where the laser polarization is along the x-axis. The two black-dashed arcs are bounding one such rescattering ring, though it is not as clear as in the single-intensity SFA calculation. A line-out along the x-axis is equivalent to the previously shown photoelectron energy spectra.
Figure 4.16: 2D momentum angular distribution in argon at 793nm and an intensity of 190TW/cm² for a linearly polarized field (along x-axis). The axes are in atomic units. The black-dashed arcs are bounding one of the rescattering rings.

in Figs. 4.4–4.8. Similar observations were made in the angular distributions taken with the TOF spectrometer in argon at 620nm and 671nm. Further angular distributions were taken in argon at each of the wavelengths shown in Figs. 4.5 and 4.6 using a velocity map imaging technique [102] also available in our laboratory.

In conclusion, we experimentally studied the dependence of the plateau enhancements on wavelength, intensity and species. The energetic position of these enhancements in the photoelectron spectra appears to be largely unaffected by intensity but shows a strong dependence on wavelength and target atom. Through SFA and TDSE calculations we have gained much insight into the physical origin and behavior of these features. We showed that these enhancements originate from intra-cycle long trajectories which rescatter with their parent ion. The shape and position of the enhancements in the photoelectron spectra depends strongly on the species specific ground state wavefunction. We further showed that the electrons which contribute to the total detected yield in the plateau enhancements predominantly come from a ‘dominant’ intensity region (which is not necessarily near the peak laser intensity). This region of dominant intensities provides a possible explanation for why these enhancements do not wash out during focal volume averaging and also why they don’t shift in energy as intensity is varied. The range of intensities which contribute dominantly
to a particular plateau enhancement remains constant as the peak laser intensity is increase. Further theoretical analysis is underway to address why the increased ATI contrast appears to correlate with these enhancement regions. However, our current hypothesis is that this is also tied to the existence of dominantly contributing intensities. The ATI structure tends to appear sharper when fewer intensities contribute to the spectra.
Chapter 5

Laser Induced Electron Diffraction in C$_{60}$

When a strong laser field ionizes an atom or molecule the freed electron can either be ejected from the interaction region immediately or be driven back towards its parent ion. The electrons which never return are known as the ‘direct’ electrons and dominate the low energy portion of the photoelectron spectra, $<2U_p$. The electrons which rescatter will return to their parent ion within a cycle of the laser field and can gain substantial energy during this time interval. For a specific return energy the electron can follow either the ‘long’ or ‘short’ trajectories, see Fig. 1.6, which converge for the highest return energy of $3.17U_p$ (corresponding to the maximum detected electron kinetic energy of $10U_p$) [20, 19]. The long trajectories are born near the peak of the field and due to the exponential dependence of the ionization rate on the field amplitude they contribute dominantly to the high energy photoelectron spectrum [96, 97]. If the electron wavepacket is scattered elastically then the detected high energy photoelectron signal can carry information about the atomic core or molecular structure. We used this to our advantage in the alkali metal experiments when we extracted the differential cross-section (DCS) of potassium and sodium (Chapter 3). In the noble gas experiments we were able to further understand the origin of the observed enhancements by linking them to intra-cycle long trajectories (Chapter 4). However, we now consider a more complex species, specifically a molecule instead of an atom. In this case the high energy, ‘plateau’, photoelectrons can also carry structural information (like bond lengths) about the species from which they have scattered.

This approach can be viewed as the strong-field equivalent of conventional electron diffraction (CED), but in this case we use the target’s own electron, instead of an electron-gun, to produce the diffraction image. The ability to probe nuclear dynamics of isolated molecules by measuring the interference structure in the plateau of photoelectron angular distributions was initially proposed theoretically for diatomic [103, 104, 105] and also larger molecular species [106]. These theoretical models predicted that near femtosecond temporal
resolution and sub-angstrom spatial resolution should be possible with the use of angle and energy-resolved electron spectra. This method is now generally referred to as laser induced electron diffraction (LIED). Gas-phase CED measurements also have the capability for sub-angstrom spatial resolution. However, due to available electron pulse durations they are typically limited to studying dynamics occurring on the picosecond time scale \[107, 108\]. It should be noted that recent progress in ultrafast electron diffraction has achieved \(\sim 100\) fs resolution in condensed phase systems \[109, 110\] but the current fluxes are inadequate for more dilute, gas-phase, molecular studies \[111\]. Therefore, the method of electron diffraction through the use of strong-field, short-pulsed laser systems has gained much interest over the last decade as a means of ultrafast molecular imaging.

Starting in the late-2000s it was experimentally shown that extracting target specific information from rescattered photoelectrons in diatomic molecules (specifically \(\text{N}_2\) and \(\text{O}_2\)) was in fact possible \[112, 96, 113, 111\]. In order to observe diffraction the returning electron’s de Broglie wavelength must be of a similar dimension as the molecule it is ‘imaging’. Blaga et al \[96\] further demonstrated that by changing the wavelength of the incident field the dynamics of the molecular species can be probed at different times after ionization. In other words, by varying the wavelength we can generate the equivalent of a pump-probe experiment but with a single pulse. The ‘pump’ is the moment of ionization and the ‘probe’ is the time at which the ionized electron resscatters with its parent molecular ion. Blaga et al \[96\] employed MIR wavelengths, \(1.7 - 2.3\) \(\mu\)m, in order to effectively ‘probe’ the relaxation of the \(\text{N}_2\) and \(\text{O}_2\) molecular bond 4–6fs after ionization. These experiments demonstrated a temporal resolution of 2–3fs and a spatial resolution of the bond lengths of \(\pm 5\) pm.

LIED has shown experimental success for extracting the DCS of atoms \[98, 97\] and imaging the nuclear positions of small molecules \[96, 111\]. However, the bond lengths of diatomic molecules are, in general, well known and therefore it is of great interest to expand this method to larger molecules. In a collaborative project with the group of Dr. Matthias Kling (Kansas State University at the start of the project; currently at the Max-Planck Institute for Quantum Optics in Germany) we specifically focused on \(\text{C}_{60}\). They designed and built the oven source which was discussed in Sec. 2.5. Our group at The Ohio State University contributed the strong-field MIR wavelength laser source and the electron spectrometer vacuum chamber. All of the measurements were performed in our laboratories at OSU.

\(\text{C}_{60}\) is an extensively studied species with important applications in nanotechnology \[114\]. Its photoinduced behavior (for example excitation, ionization, or fragmentation) has been studied through single-photon mechanisms \[115\] as well as in multi-photon interactions \[116\]. The breadth of research into \(\text{C}_{60}\) is far more extensive than can be covered here and therefore the discussion in this chapter will remain focused on the characteristics important for performing LIED experiments. We believe that the ability to image these
C\textsubscript{60} Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C distance in 5-member ring</td>
<td>1.458 Å</td>
</tr>
<tr>
<td>C-C distance in 6-member ring</td>
<td>1.401 Å</td>
</tr>
<tr>
<td>Average C-C distance</td>
<td>1.44 Å</td>
</tr>
<tr>
<td>Cage diameter</td>
<td>7.113 Å</td>
</tr>
<tr>
<td>First ionization potential</td>
<td>7.65 eV</td>
</tr>
<tr>
<td>Second ionization potential</td>
<td>12.4 eV</td>
</tr>
<tr>
<td>Center of plasmon resonance</td>
<td>~20 eV</td>
</tr>
</tbody>
</table>

Table 5.1: Relevant physical properties of the C\textsubscript{60} molecule. The bond distances and dimensions were taken from [117]. This reference also contains much more extensive bond length data. The ionization potentials were taken from [114].

molecular systems on their characteristic time-scales (femtosecond) could provide highly useful information for understanding the behavior of C\textsubscript{60}.

A summary of some important physical properties of C\textsubscript{60} is included in Table 5.1 and an image of its physical structure is shown in Fig. 5.1. The high spherical symmetry of the C\textsubscript{60} molecule makes it a good candidate for initial LIED studies in macromolecules. Further, due to the extensive experimental and theoretical studies already present in the literature we will have the ability to benchmark our results against well established values. The molecular structure is a truncated icosahedral made up of 60 carbon atoms which are located at the vertices of 12 pentagons and 20 hexagons [114]. The approximate diameter of the whole cage is 7 Å and the average C–C bond length is 1.44Å. The ground state electronic structure of a carbon atom is 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{2} and therefore each carbon atom contributes four valence electrons. In a simple model, the C\textsubscript{60} molecule can be viewed as a spherical shell with 240 valence electrons being contributed from the 60 carbon atoms. One of its particularly interesting characteristics is a giant plasmon resonance at approximately 20eV [115, 114] where the 240 valence electrons can be collectively photoexcited. A 20eV electron rescattering energy is well within our experimental capabilities and therefore we may expect this energetically broad resonance structure to play a role in the observed dynamics.

This chapter will summarize our initial investigations into the feasibility of performing LIED type experiments on macromolecules. I begin by discussing the experimental setup. Then, a brief literature summary of previous ion mass spectra results will be presented along with our findings at 792nm and 3.6\textmu m. Finally, the photoelectron momentum angular distribution results will be discussed, and the method of retrieving the DCS and bond lengths will be introduced. The chapter will conclude with an analysis of the limitations of the current experiment and future plans for improvement. Unless otherwise stated all
calculations were performed by the theorist in our group, Dr. Junliang Xu.

5.1 Experimental Setup

For all experimental results which will be presented we used the C\textsubscript{60} oven which was mounted on the ‘Oven Chamber’ beneath the interaction region (see Sec. 2.5). An effusive beam of C\textsubscript{60} molecules was generated by heating the oven to 600℃ providing an approximate vapor pressure of 10^{-7} Torr in the interaction region. The C\textsubscript{60} sample is a 99.9\% highly crystalline sublimed fullerene purchased from Sigma-Aldrich. The MIR laser source was tuned to 3.6\textmu m for all ion and electron analysis. In order to benchmark our system against previously published results we also examined ion mass spectra of C\textsubscript{60} at 792nm (the Ti:sapphire pump beam for the OPA).

When heating the oven to high temperatures we measured excessive noise on the MCP detectors, producing roughly 1000 hits per second. By applying a 3V bias potential to the oven shield we were able to reduce this to 2–3 hits per second which is well within our typical noise levels. Therefore we speculate that heating the oven to high temperatures causes emission of low energy charged particles which can be deflected by a small applied potential. In order to guarantee that applying this voltage would not be detrimental to the accuracy of our experimental results we examined its effect on the photoelectron spectra. We found no experimentally detectable influence, even at an applied potential of 5V, and feel confident in this approach.

The ion mass spectra data (Sec. 5.2) was performed with 792nm and 3.6\textmu m light. The 792nm beam was attenuated using neutral density (ND) filters and focused into the interaction region with a 250mm focal length CaF\textsubscript{2} lens. For the 3.6\textmu m results we used a polarizer to clean up the beam polarization before focusing into the interaction region with a 100mm focal length CaF\textsubscript{2} lens. The tighter focus at 3.6\textmu m is necessary to achieve sufficient intensities.
In the angular distribution study presented in Sec. 5.3 we used $80 \mu J$ of $3.6 \mu m$ light which corresponded to an intensity of $80 \text{TW/cm}^2$. The intensity was calibrated through the $2U_p$ break in the $C_{60}$ photoelectron data and benchmarked to xenon spectra. The setup for the angular distribution study is nearly identical to that used in the alkali metal analysis. The main difference here is the use of the full beam power in order to achieve the highest possible electron return energies, and therefore attenuation through the use of pellicles is not necessary. The polarization of the ingoing MIR beam was first cleaned up using a polarizer and then the angle of the linearly polarized beam was rotated using a half-wave-plate. The beam was focused into the interaction region using a 100mm focal length $\text{CaF}_2$ lens. Data was taken over one quadrant in steps of $4^\circ$. The order of angle collection was randomized to avoid coupling experimental results to laser drift. At each angle we collected data for $0.6 \times 10^6$ laser shots. Two sets of data were taken back-to-back to demonstrate reproducibility and then summed before analysis; therefore each angle corresponds to the accumulated signal from $1.2 \times 10^6$ laser shots. The count rate was maintained below 2 hits/shot for all angles. We used the TDC2228A for data collection which gave us a 285ps/bin temporal resolution. The thermocouple reading was monitored throughout the experiment to guarantee oven temperature stability.

5.2 Ionization and Fragmentation

In order to gain a better understanding of the influence our strong-field laser pulses have on the $C_{60}$ molecule we first examined the ion mass spectra. This is an essential step before attempting to extract structural information from the angular photoelectron distributions. The ionization mechanisms in $C_{60}$ have been studied with synchrotron sources which used vacuum ultraviolet single-photon interactions [115], as well as strong field sources ranging from visible to MIR wavelengths [118, 116, 119, 120]. Though the literature regarding ionization and fragmentation in $C_{60}$ is quite extensive here we focus on a few findings that are most relevant for LIED experiments.

Hohmann et al [120] studied the photoionization and fragmentation of $C_{60}$ using 15ns (193nm and 308nm) and 100fs (310nm and 620nm) pulses. When long pulses were used, 15ns, they observed significant fragmentation of the molecule but ionization was limited to the first charge state. When they used 100fs pulses the ion mass spectra showed a large contribution from doubly ionized $C_{60}$ along with fragmentation. At high laser intensities, which are necessary in LIED for high energy elastic recollisions, the species will fragment into three or more pieces. Another important distinction is that of ‘fast’ versus ‘metastable’ fragmentation. Fast fragmentation is that which occurs during the time that the field is interacting with the molecule while metastable fragmentation can occur from nanoseconds to milliseconds after the initial excitation [116]. These metastable fragments were shown to
significantly contribute to the total ion yield [120]. The most energetically favorable means of removing carbons from C\textsubscript{60} has received much theoretical interest, for further details see [120] and references therein.

Tchaplyguine et al [119] studied the ionization and fragmentation of C\textsubscript{60} using short pulses at visible/NIR wavelengths; specifically 35fs, 795nm and 45fs, 400nm pulses. The use of short pulses allowed them to attribute the initial laser-C\textsubscript{60} interaction as a purely electronic excitation since electron-phonon coupling occurs on time scales on the order of hundreds of femtoseconds. They argued that in longer pulsed experiments, nanoseconds, excitation through the molecular vibrational degrees of freedom may contribute significantly, as shown in [120]. In the work of Tchaplyguine et al [119] at 795nm and 400nm and relatively low intensities, \(\sim 10^{13}\)W/cm\(^2\), the ion spectra was dominated by singly and doubly charged C\textsubscript{60} which they attribute to sequential ionization through multiphoton absorption. However, with increasing intensity, starting \(\sim 10^{14}\)W/cm\(^2\), they observed a large contribution from fragmentation, both fast and metastable. Therefore, they concluded that the electronic excitation provided by the interaction with the short laser pulse couples strongly to the vibrational degrees of freedom. These experiments [120, 119] demonstrated that fragmentation of C\textsubscript{60} contributes significantly at visible/NIR wavelengths over a broad range of pulse durations (from nanosecond to femtosecond).

In the work of Bhardwaj et al [121] they demonstrated a significant dependence on wavelength when femtosecond duration laser pulses are used. Specifically, they showed that at longer wavelengths (1500nm, 70fs in this case) fragmentation is suppressed and the mass spectrum is dominated by highly charged cations (up to 12\(^+\)) even at intensities of \(3.5 \times 10^{14}\)W/cm\(^2\). A comparison between their spectra taken with 800nm, 40fs and 1500nm, 70fs pulses is shown in Fig. 5.2. Further, they attribute fragmentation to a rescattering process since it showed a strong dependence on the ellipticity of the laser polarization. However, the yields of the higher charge states demonstrated nearly identical behavior with linearly and circularly polarized light and are expected to be due to sequential ionization. The 800nm data in Fig. 5.2 shows a series of peaks after each primary charge state. If the molecule acquires excess internal energy during its interaction with the field the process of sequential evaporation of C\textsubscript{2} units has been identified as a primary method for de-excitation [116].

In our experimental preparations we first measured ion mass spectra using 792nm (the pump beam for the OPA). We observed a significant contributions from fragmentation, C\textsubscript{2} evaporation, and higher order ionization; in agreement with previously published results [121]. Next, we measured the ion mass spectra at 3.6\(\mu\)m and the results are shown in Fig. 5.3. The spectra is dominated by C\textsubscript{60} ionization peaks and no significant fragmentation was detected even at our peak intensity of 80TW/cm\(^2\). In Fig. 5.3 the fractional yields of the observed charge states are 0.556 for C\textsubscript{60}\(^+\), 0.376 for C\textsubscript{60}\(^{2+}\), 4.03\(\times 10^{-2}\) for C\textsubscript{60}\(^{3+}\), 2.69\(\times 10^{-2}\)
Recollision during the High Laser Intensity Ionization of C₆₀

V. R. Bhardwaj, P. B. Corkum, and D. M. Rayner

Steacie ... JULY 2004VOLUME 93, NUMBER 4

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The lateral velocity that we measure is fragmentation cross sections [10]; (iii) spherical symmetry
and then drives it back to the parent ion where it can recollide with significant energy [1]. This
and 1500nm (70fs) laser fields. Notice the suppression of fragmentation at longer wave-
lamnths, we observe recollision in C₆₀ upon rescattering.

We identify recollision in C₆₀ is an ideal molecule to study recollision in multi-
molecules, it has allowed attosecond time resolved dy-
to this information, providing a probe to interrogate the
which it has just departed. Recollision gives us access
electron retains information about the molecule from
and maximum electron recollision energies (3.2
over again is countered by Coulomb attraction of the ion
driving the electron away is countered by Coulomb attraction of the ion
of the molecule [5] or it might produce high
structure of the molecule [5] or it might produce high
harmonics more efficiently [6].

We show that the electron that emerges from
conducting sphere we show how the polarizability of the
ionization is simplified, fragmentation is one of the fundamental reasons why moving
towards long wavelengths is essential for laser induced electron diffraction experiments. In
order to extract structural information about the C₆₀ species we need it to remain intact
for the duration of the interaction process. In other words, when the ionized electron is
driven back into its parent ion it needs to scatter off of the full cage. If fragmentation
contributes significantly we expect the features to wash out. The fact that at high intensity
we observe higher charge states of C₆₀ should not pose a significant problem. The C₆₀ cage
is quite stiff and contains approximately 240 valence electrons, therefore we do not expect
the removal of two electrons instead of one to significantly affect the shape of the C₆₀ cage
upon rescattering.

5.3 Laser Induced Electron Diffraction (LIED) in C₆₀

In order to extract bond lengths in the C₆₀ molecule we follow a similar process of laser
induced electron diffraction (LIED) as outlined by Blaga et al [96] for experiments in N₂
and O₂. A significantly more detailed discussion of this method can also be found in the
Supplementary Information of [96] and the work of Xu et al [106, 107].

First, we experimentally measured the photoelectron momentum angular distribution.
Figure 5.4 shows our result in C₆₀ with a linearly polarized 3.6µm beam at an intensity

![Figure 5.2: A comparison of the C₆₀ mass spectra from the interaction with 800nm (40fs)
and 1500nm (70fs) laser fields. Notice the suppression of fragmentation at longer wave-
lengths. Figure reproduced from [121].](image-url)
Figure 5.3: Mass spectra from the interaction of 3.6\(\mu m\) light with \(C_{60}\) molecules. The inset is zoomed in on the high charge states. We observe contributions from up to \(C_{60}^{5+}\).

of 80TW/cm\(^2\). The laser polarization is along the horizontal axis and the color gradient corresponds to a logarithmic scale. The maximum detected momentum was 8.4au (atomic units) which, in energy, corresponds to the 10\(U_p\) cutoff. Therefore the ponderomotive energy, \(U_p\), is approximately 96eV and the maximum rescattering energy is \(\sim 300eV\) (3.17\(U_p\)).

As expected, we observe that the total detected electron yield is dominated by the direct electron contribution which corresponds to the low energy region of \(< 2U_p\); an energy of 2\(U_p\) (192eV) corresponds to a momentum of 3.8au. We do not observe any dips in the rescattered electron region, like we saw in the alkali metals near scattering angles of 120\(^\circ\), and therefore expect that the extracted DCS will be monotonically decreasing with increasing scattering angle.

The elastic scattering differential cross-section (DCS) is extracted from the experimental data by sweeping across scattering angles at a constant electron rescattering momentum. Recall that \(\mathbf{p} = \mathbf{p}_r - \mathbf{A}_r\) where \(\mathbf{p}\) is the detected momentum, \(\mathbf{p}_r\) is the momentum of the rescattering electron and \(\mathbf{A}_r\) the vector potential of the field at the time of rescattering. The quantitative rescattering (QRS) model provides the theoretical basis for our extraction method and was discussed in detail in our analysis of the alkali metal data, see Sec. 3.3. Most importantly, Lin and coworkers [47] demonstrated in their QRS theory that the field-free DCS can be extracted from the rescattered photoelectron portion of the momentum angular distribution. The experimentally extracted DCS for \(C_{60}\) as a function of scattering angle for an electron with a rescattering energy of 100eV (corresponding to a de Broglie wavelength of 1.2Å) is shown in Fig. 5.5 by the red squares. The error bars correspond to
the Poisson counting statistical error, $\Delta M = \sqrt{M}$ where $M$ is the total number of counts. Figure 5.5 also shows the experimental (black circles) DCS results measured by Hargreaves et al [122] through electron diffraction in a standard crossed-beam apparatus for 100eV electron collision energies. In their experimental configuration they were able to measure scattering angles between $15^\circ$ and $135^\circ$. In our experimental results we could retrieve the DCS between scattering angles $\sim 35^\circ$–$180^\circ$; the region below $35^\circ$ begins to be influenced by direct electron contributions. The ‘theoretical model’ (solid blue line) in Fig. 5.5 was also calculated in Hargreaves et al [122] using the Schwinger multichannel technique with the static-exchange approximation [123]. The static-exchange approximation neglects polarization, excitation, and ionization since the electron density in the molecule is treated as static during the collision process. Nevertheless this method is one of the more rigorous theoretical approaches used to describe elastic scattering in electron diffraction experiments [122]. Our data shows good agreement with the DCS measured through CED and their theoretical model. The good agreement provides further proof that $C_{60}$ fragmentation is not contributing during the electron diffraction process in MIR fields.

So far we have demonstrated that the $C_{60}$ DCS extracted through LIED can produce comparable results as those from electron-gun experiments. Before proceeding to bond-length retrieval it is worth emphasizing where the need for long-wavelengths arises (besides

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**Figure 5.4:** Photoelectron momentum angular distribution for the strong-field interaction between $C_{60}$ and $3.6 \mu m$ light at an intensity of $80TW/cm^2$. The laser polarization is along the horizontal axis. The axes are expressed in terms of atomic units.
reducing fragmentation in $C_{60}$). Typically, in CED, an electron gun will direct high-energy electrons ($\sim$10–100keV) at a molecular gas and the detected diffraction pattern in the forward direction is analyzed to retrieve structural information. In these hard collisions the electron beam will scatter from the atomic cores which make up the molecule and the valence electrons will be effectively ‘transparent’ [106, 96]. One may notice that in our LIED experiments the electron returns to its parent molecule with energies on the order of several hundred electron volts; nowhere near $\sim$10–100keV used in CED. However, the true measure of a hard collision is a large momentum transfer which is expressed as

$$q = 2p_r \sin(\theta_r/2)$$

where $p_r$ is the electron rescattering momentum and $\theta_r$ is the rescattering angle [106, 96] (also see Fig. 3.22). Therefore, a similar range of $q$ can be achieved with MIR laser fields and large scattering angles. In strong-field experiments the maximum energy an electron can posses upon returning to its parent molecular ion is $3.17U_p$ where $U_p \propto I \lambda^2$ and therefore by using longer wavelength sources we can further increase the momentum transfer during the collision process. Previous studies with 800nm wavelength sources were not able to accurately extract bond-lengths in diatomic molecules ($N_2$ and $O_2$) [112, 113]. However, at this wavelength the electron return energies are on the order of a few tens of eV which is not sufficient for clearly resolving the atomic core positions in a molecule [97].

In the limit of high energy scattering a common method for structural analysis is the independent atom model (IAM) [122, 96]. In the case of $C_{60}$ the IAM will treat the molecule as
60 independent carbon scattering centers and the properties of the inter-atomic binding orbitals are neglected. In hard collisions, where the short range component of the rescattering potential dominates, the electron–ion potential is nearly identical to the electron–neutral potential and therefore we can neglect the fact that we are scattering from an ionized instead of a neutral molecule [97]. The agreement we observe in Fig. 5.5 between the DCS extracted through LIED versus that of CED is further proof that in high momentum transfer collisions the scattering of an electron with an ionized or neutral molecule is similar.

The carbon atom cross-section monotonically decreases with an increasing scattering angle, $\theta_r$ [122]. Therefore, the oscillatory structure we observe in the $C_{60}$ DCS, Fig. 5.5, is attributed to the electron wavepacket diffracting from the 60 scattering centers contributing to the $C_{60}$ molecular cage. For extracting bond lengths the amplitudes of these oscillations are not as important as their angular position. In order to more clearly observe this oscillatory component we performed a polynomial fit to subtract out the smooth atomic DCS background. The method of subtracting off the smooth background to improve the visibility of the oscillatory behavior has been used successfully in previous CED experiments [117]. The isolated molecular interference term is often referred to as the molecular contrast factor (MCF) from which we can further extract structural information. Our experimentally extracted MCF as a function of the momentum transfer, $q$, is shown in Fig. 5.6 (red squares). Figure 5.6 also shows the theoretical MCF calculated through the IAM (blue line) for a constant rescattering energy of 100eV. The calculations were performed using the known dimensions of $C_{60}$ [117] and spanning the same $q$ range as we achieved experimentally. Since we do not align the molecules in our experiment the calculation averages over a random distribution of molecular alignment with respect to the laser polarization [124]. Overall the agreement between theory and experiment is quite good where the positions of the oscillations as a function of momentum transfer are well reproduced. Previous work in diatomic molecules ($N_2$ and $O_2$) where only one bond length contributes demonstrated a simple sine function dependence of the MCF on the momentum transfer [96]. Therefore, by comparing this result to our findings in Fig. 5.6 we expect to be able to extract a larger number of different bond lengths.

Finally, we retrieve the radial distribution as a function of the internuclear distance, $R$, by performing a Fourier transform on the MCF($q$). The experimental (red) and theoretical (blue) results are shown in Fig. 5.7(a). Though the amplitudes are not identical, the positions of the peaks corresponding to extracted bond lengths are quite good. Figure 5.7(b) is a comparison to a measurement performed through CED by Hedberg et al [117]. Due to the limitation of the available range of $q$ values we were able to achieve experimentally our resolution for distinguishing bond lengths was not as good as in [117]. However, we were able to extract similar families of bond lengths. In Fig. 5.8 the four classes of bonds that we were able to observe are shown by the colored lines which correspond to the same colors
Figure 5.6: The experimental molecular contrast factor (MCF) for C\textsubscript{60} is extracted from the DCS (red squares). The theoretical calculation (blue line) is performed through the IAM for a 100eV electron rescattering energy. For determining bond lengths the position of the peaks is more important than their amplitude.

as in Fig. 5.7. The red distance corresponds to C\textendash{}C separations within the same ring, \(~1\text{--}2.5\text{Å}\). Blue corresponds to internuclear distances between carbons in neighboring rings, \(~3.5\text{--}4.5\text{Å}\). The orange distance of \(~5.5\text{--}6.5\text{Å}\) relates to carbons separated by approximately three carbon rings. Finally, purple corresponds to the full cage size distance of \(~7\text{Å}\).

5.4 Discussion and Outlook

Several things could be done to gain better resolution. First, we could sample the q range in finer steps. This would require collecting data in smaller angular increments by decreasing the acceptance angle of our MCP detector. Also, if we could increase the intensity of our MIR laser or move to a longer wavelength (for example 4\textmu m instead of 3.6\textmu m) then the rescattering energy could be increased; thereby allowing a better spatial resolution due to an increased momentum transfer range \([111]\). However, there is a balancing act between improving spatial resolution and acquiring sufficient statistics in the data within a reasonable amount of time. If we decrease the acceptance angle, our count rates will decrease. Also, the DCS tends to decrease at higher scattering energies which would further decrease our count rates. The collection time for the angular distribution presented in Fig. 5.4 was approximately 10 hours. We could also increase the return energy used for extraction simply by increasing the statistics in the plateau portion of the photoelectron angular distribution. Recall that we extracted a DCS for 100eV electron return energies but 3.17U\textsubscript{p} is close to 300eV. We are currently in the process of building an oven which will
Figure 5.7: Extracted bond distances in Å in C_{60}. Panel (a) shows our experimental (red) and calculated (blue) results. Panel (b) was measured through CED, image reproduced from [117]. The colors indicated the families of bond distances we observed.

Figure 5.8: The families of bond lengths we extracted. The colors correspond to those in Fig. 5.7. Figure reproduced from [117].
Figure 5.9: The DCS as a function of scattering angle. Experimental data is shown by the green squares. The IAM calculation using the known C$_{60}$ bond lengths is in black. These are the same results as were shown in Fig. 5.5. The red and blue lines are the IAM calculations for a hypothetical C$_{60}$ molecule which is 5% smaller or larger respectively.

achieve higher temperatures and will therefore increase the target density in the interaction region allowing us to collect better statistics for higher energy electrons in a reasonable time frame.

In the current data we did not observe any features that we could conclusively attribute to the plasmon resonance; at least from our initial analysis. One of the overarching motivations for this project was to observe fast C$_{60}$ dynamics. Specifically, we were interested in performing a pump-probe experiment where an 800nm pump beam could excite the molecule and LIED at MIR wavelengths would act as the probe. By varying the delay we could look for femtosecond scale changes in the nuclear structure of C$_{60}$ when the plasmon resonance was excited. However, currently this is not feasible due to the amount of time required to run a complete angular distribution. In order to get a better intuitive feeling for the expected change in the DCS if the C$_{60}$ molecule were a different size we performed a few more IAM calculations. Figure 5.9 shows our experimentally retrieved DCS (green squares) along with the calculation for the equilibrium width of the C$_{60}$ cage (7.113Å) and a hypothetical molecule which is 5% larger or smaller. The shifting of the diffraction pattern is clear but it also shows the precision we will need to achieve to observe such fine structural changes.
Chapter 6
CONCLUSIONS

In the strong-field regime the laser field can have a highly complex and fascinating influence on the target species. In this dissertation we have more closely examined several of these effects on atoms and molecules. The majority of previously published work has been performed at visible and NIR wavelengths but further exploration of the MIR regime has demonstrated the existence of equally interesting phenomena. The use of MIR light allows us to explore extreme nonlinear optics in a whole new class of species which have lower ionization potentials. Further, intense, long-wavelength (MIR) laser sources are essential for extracting target specific structural information (for example: differential cross-sections and bond lengths) due to the higher electron rescattering energies.

In Chapter 3 we investigated the ionization dynamics of sodium and potassium at MIR wavelengths. The alkali metals at MIR wavelengths are of interest because they are approximately the Keldysh scaled equivalent of the noble gases at NIR wavelengths, which have been studied extensively. Comparing these two sets of species allows us to gain further insight into which observed features are universal and which are species dependent. By examining the ion yield curves and comparing them to ADK calculations we found that population transfer to intermediate, strongly coupled, excited states (the p-states in alkali metals) before subsequent ionization significantly contributes to the total measured ion yield. Previously published results of noble gas targets at visible/NIR wavelengths have shown good agreement with ADK calculations by only accounting for direct ionization from the ground state. In the alkali photoelectron spectra we observed that the strength of the rescattered (plateau) electrons exhibits a larger species dependence than in the noble gases. The electron yield in the plateau of potassium is approximately 2–3 orders of magnitude higher than in sodium. This was found to agree well with the difference between the elastic scattering DCS for the two species. Finally, we experimentally measured the angular distributions in these two species and extracted the elastic scattering DCS by analyzing the rescattered photoelectrons. By comparing our results to previous measurements in the noble gas atoms we conclude that in order to extract an accurate DCS from a 2D photoelectron...
momentum distribution it is important to have a Keldysh parameter value far into tunneling regime and preferably less than 0.6. To our knowledge, this is the first experimental demonstration of extracting the DCS in the alkali atoms through this technique.

In Chapter 4 we studied the dependence of the photoelectron energy spectra in the noble gases as a function of wavelength in the visible/NIR regime. We determined experimentally that the energetic position of the plateau enhancements is strongly dependent on the target atom and the wavelength but not the peak laser intensity. By performing SFA and TDSE calculations we attributed the origin of these enhancements to intra-cycle long trajectories which rescatter with the core. Further, we showed that the position in energy and shape of the enhancements depends strongly on the target specific ground state wavefunction. How the form of the exiting wavefunction influences the rescattering process is still under investigation. Finally, through further TDSE calculations, we demonstrated that there is a ‘dominant intensity’ region which predominantly contributes to the enhancements and accounts for the observed intensity independence of this feature. Further theoretical analysis is necessary to understand the observed increase in ATI contrast associated with the enhancement regions and to uncover the origin of these ‘dominant intensities’.

Finally, in Chapter 5 we demonstrated the first known application of laser induced electron diffraction (LIED) on a macromolecule, specifically C$_{60}$, using 3.6$\mu$m light. All previously published results have been performed on atoms or diatomic molecules. We were able to extract four families of bond lengths characteristic to the C$_{60}$ molecule. Our results were in agreement with previously published studies performed through conventional electron diffraction. These findings clearly demonstrated that LIED can be used successfully to extract target specific structural information. However, one of the major motivations for beginning this project was to use a pump beam to excite the C$_{60}$ plasmon resonance and then use LIED as the probe in order to image the C$_{60}$ structural changes as a function of time. Currently the amount of time necessary to measure a single angular distribution and our spatial resolution for bond length extraction are limiting the feasibility of observing this behavior. Nonetheless, this initial study shows great promise for applying strong-field methods for ultra-fast molecular imaging purposes.


139


