

Dispersion free photoelectron wavepackets in multiphoton ionization

by

Pavan Muddukrishna

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AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

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Department of Physics
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

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Abstract

One of the ultimate goals in atomic, molecular and optical physics is understanding and controlling molecular chemical reactions which occur on extremely small spatio-temporal timescales. Experimentally observing the breaking and shaping of molecules is difficult and requires a camera which operates at times equal to or less than the molecular timescales. This state of the art camera is called the *laser*. Coupling it with the Chirped Pulse Amplification (CPA) technique allowed for the development of sub-picosecond pulses with high intensities. This advancement allowed for the rise of imaging techniques via electron rescattering such as Laser Induced Electron Diffraction (LIED) and theories such as Quantitative Rescattering (QRS) theory which have allowed for the extraction and analysis of molecular structure at high electron return energies (hundreds of eV)¹.

This dissertation studies an enhancement in electron yield within the rescattering plateau observed from experimentally collected Above Threshold Ionization (ATI) photoelectron spectra in the multiphoton ionization regime using LIED. The driving mechanism behind this phenomena has remained a mystery for the last 30 years. This dissertation first aims to understand experimental data and the enhancement through theoretically generated High Harmonic Generation (HHG) spectra. The time dependent behavior of the electronic wavepacket was studied when it returned to the parent ion. Rigorous analysis revealed the generation of a bimodal attosecond dispersion free electronic wavepacket at specific wavelengths and intensities that behaved similarly to the generation of a femtosecond pulse within a mode-locked oscillator. Additionally, it was found classical electron rescattering models, which are widely used to explain strong field phenomena, could *not* explain the electrons' dynamics and the enhancement within the multiphoton regime. The discovery of the dispersion free wavepacket reframes rescattering processes in the multiphoton regime.

The second part of this dissertation involves applying the dispersion free wavepacket to QRS for the extraction of electron-ion differential cross sections (DCS) from experimentally collected photoelectron angular distributions (PADs) at low electron return energies (tens of eV). PADs were collected of argon and smaller hydrocarbons at 1030 nm using a Double-sided Time of Flight (DToF) Vacuum chamber. The dispersion free wavepacket and QRS theory were subsequently used to extract electron yield representative of an electron-ion DCS. Further comparison with theory is still needed. This application takes the first steps in determining the viability of LIED and Quantitative Rescattering (QRS) theory as methods to extract molecular structure at low electron return energies. Furthermore it helps establish LIED's ability to image simpler hydrocarbons before proceeding towards more complex organic compounds.

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Approved by:

Major Professor
Cosmin I. Blaga

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Abstract

One of the ultimate goals in atomic, molecular and optical physics is understanding and controlling molecular chemical reactions which occur on extremely small spatio-temporal timescales. Experimentally observing the breaking and shaping of molecules is difficult and requires a camera which operates at times equal to or less than the molecular timescales. This state of the art camera is called the *laser*. Coupling it with the Chirped Pulse Amplification (CPA) technique allowed for the development of sub-picosecond pulses with high intensities. This advancement allowed for the rise of imaging techniques via electron rescattering such as Laser Induced Electron Diffraction (LIED) and theories such as Quantitative Rescattering (QRS) theory which have allowed for the extraction and analysis of molecular structure at high electron return energies (hundreds of eV)¹.

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Dedication

*Dedicated to my parents, my sister Bhavana, my brother-in-law Abhiram, my nephew
Atharva, and my niece Sahana.*

Chapter 1

Introduction

“The breakthrough is that the camera can see things that the human eye can’t see, and that we can use photography to access our world beyond what we know it to be.” - Shannon Perich, Smithsonian Curator

In the 1870’s, Leland Stanford, founder of Stanford University, began working with English photographer Eadweard Muybridge. Stanford was interested in resolving the infamous “un-supported transit” controversy which debated the motion of a horse as it gallops. At the time, horses were primary sources for motion, industry and even battle. Understanding their dynamics was of utmost importance. Stanford tasked Muybridge with capturing a horse’s motion with his camera. Normal exposure times for cameras were around 2 seconds, far too long to capture any significant motion from a horse. So, Muybridge created mechanical shutters which reduced exposure times to a *millisecond*². In June of 1878, Muybridge made history at a racetrack in California. Stanford’s horse galloped through 12 trip wires, each connected to a different camera. At each trigger point, the horse’s motion was captured and a series of stop-motion images were created (displayed in Figure 1). Muybridge, it seemed, had stopped time. His breakthrough demonstrated the necessity of a tool which recorded information at speeds faster than the motion of the studied object. This concept plays a key role of in the study of atomic and molecular dynamics.

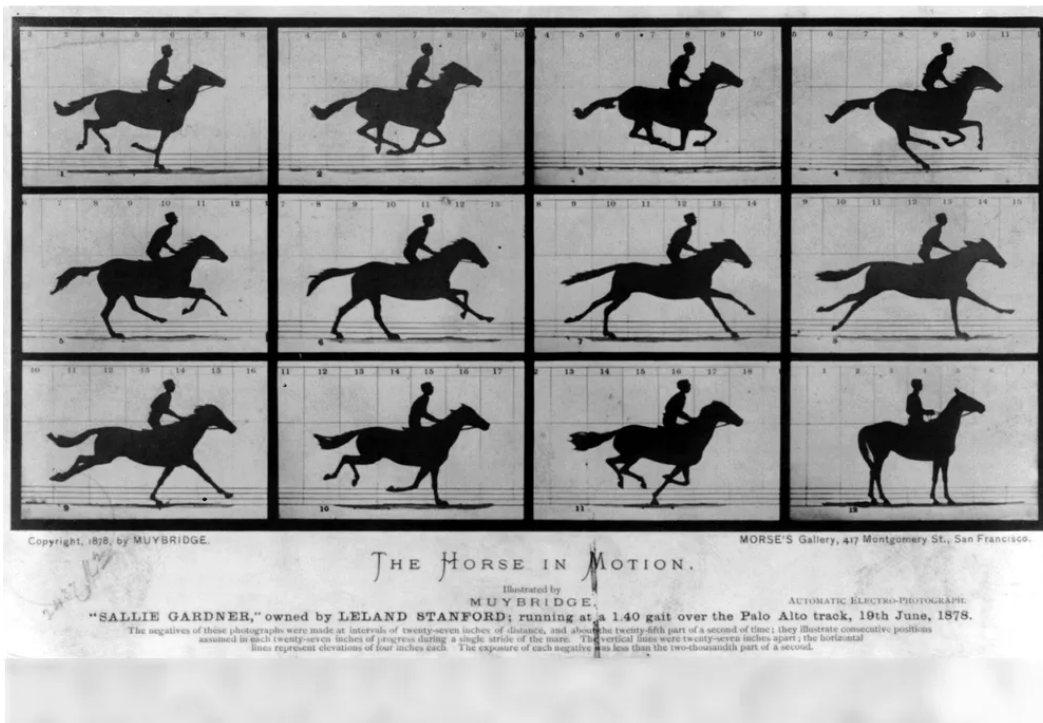


Figure 1.1: **Stop-Motion Images of a Galloping Horse.** Images of Stanford's galloping horse captured by Muybridge. The horse galloped through 12 trip wires, each triggering a separate camera. Muybridge developed a mechanical shutter which reduced the exposure time of his cameras from 2 seconds to a millisecond. Image credit goes to Haleema Shah².

The study of molecular motion and structure through electron diffraction has been a key goal in atomic, molecular and optical physics. Molecular transformations, such as bond breaking and bond forming, are critical in chemistry and biology and govern most chemical reactions. In addition, understanding their structure reveals novel properties of elements and helps refine techniques to ultimately control the reactions themselves. The timescale of molecular transformations is extremely small, some even on the order of femtoseconds (10^{-15} seconds), and internuclear distances are on the order of Angstroms (10^{-10} meters)³. Probing these molecules requires a camera which operates with similar spatial and temporal resolutions. Introducing...the laser.

The L.A.S.E.R. (Light Amplification by Stimulated Emission of Radiation) is based off Einstein's concept of stimulated emission: bound electrons can be stimulated to emit light

at a particular frequency. The experimental realization of a working laser dates back to the 1950s. The rest of this paragraph provides a brief glimpse into its historical development and further information can be found in " *A history of the laser: 1960-2019*" by M. Rose and H. Hogan in Photonics Spectra⁴. The M.A.S.E.R. (Microwave Amplification by Stimulated Emission of Radiation) was developed by Dr. Charles Hard Townes of Columbia University in 1954 with a central wavelength of 1 cm. Theodore Maiman of Hughes Research Laboratories constructed the first laser using a cylinder of synthetic ruby in May of 1960. In December of the same year, Ali Javan, William Bennett Jr. and Donald Herriott of Bell Labs developed the Helium-Neon (HeNe) laser with a central wavelength of 1.15 microns. Soon after, in 1964, Joseph E. Geusic and Richard G. Smith of Bell Labs developed the Nd:YAG (Neodymium-doped Yttrium Aluminum Garnet) laser. Finally, the Ti:Saph (Titanium-Sapphire) laser was developed by MIT's Peter F. Moulton, providing short pulses in the picosecond and femtosecond range. This laser is widely used in research labs today across the United States to probe and monitor atoms and molecules.

Extracting information of a chosen target relies on using one of the various imaging techniques developed over the last couple decades with our state-of-the-art camera. These techniques rely on the wave-particle duality of electrons for the creation of multi-dimensional electron diffraction images. Understanding the foundations of molecular imaging requires a look into the history of the wave-particle duality debate.

From the 1700s, physicists have often asked: "what is light?" and "how fast does light travel?". Many theories were proposed to answer these two fundamental questions. On the one hand, Sir Isaac Newton proposed light was made of tiny particles in his 1704 treatise *Opticks*⁵. Many principles, such as reflection could be explained using particle theory and fell in line with Newton's laws. However, in 1690, Christiaan Huygens, a Dutch mathematician, proposed light behaved like a wave in *Traite de la Lumiere*⁶. He used his *theory of wave motion of light* to explain reflection, refraction and transmission in what is better known today as *Huygen's principle*. In 1801, Thomas Young experimentally verified Huygen's wave theory in his famous double slit experiment, where he demonstrated the resultant wave interference pattern after light was impinged on a surface comprised of two slits⁷.

Major developments in the study of light occurred in the 1900s, when researchers committed their time into the study of black-body radiation. A black body absorbed all radiation and emitted more radiation than other bodies when in thermal equilibrium. The spectral distribution of the energy emitted by a black body is temperature dependent and spans a broad wavelength range. In October 1900, Max Planck presented his empirically correct radiation law to describe black-body radiation. It involved dividing the spectral distribution into discrete, frequency dependent energy packets scaled by a constant h , now known as Planck's constant⁸. In 1905, Einstein succeeded in explaining the photoelectric effect, or the emission of electrons when light hits a material, by proposing light was made of these tiny energy packets, or *quanta* of energy⁹. The maximum kinetic energy of the emitted electron after light struck the material would be $KE_{max} = h\nu - W$, where ν is the frequency of light and W is the work function, or the minimum energy required to remove the electron from the material. This explanation made light particle-like in nature, directly challenging Huygen's wave theory. It wasn't until 1924, when Louis de Broglie, a French physicist, attempted to formulate wave-particle duality⁹. The famous *de Broglie wavelength*, $\lambda_B = h/p$, where p is the momentum of the particle, indicates the wavelength at which wave-like properties become important. He proposed electron diffraction experiments as tests for the validity of his hypothesis.

Young's double slit experiment took place at a time when light was considered to be a particle *or* a wave. It wasn't until 1909, after Einstein's interpretation of the photoelectric effect, that Geoffrey Taylor confirmed wave-particle duality⁷. When the brightness of light going through the double slits was lowered, photons accumulated on the screen individually, like particles! This phenomena can be seen with electrons rather than photons in Figure 1.2. Therefore, under the right conditions, Young's 1801 experiment proved light is both a wave *and* a particle. Even 200 years later, the double slit experiment provides valuable insight into understanding modern electron diffraction imaging techniques for the study of atomic and molecular structure. Next, we study the mathematical phenomena of single and double slit diffraction and draw comparisons to atomic and molecular imaging.

Let's assume plane waves of wavelength λ are striking a screen with a circular aperture

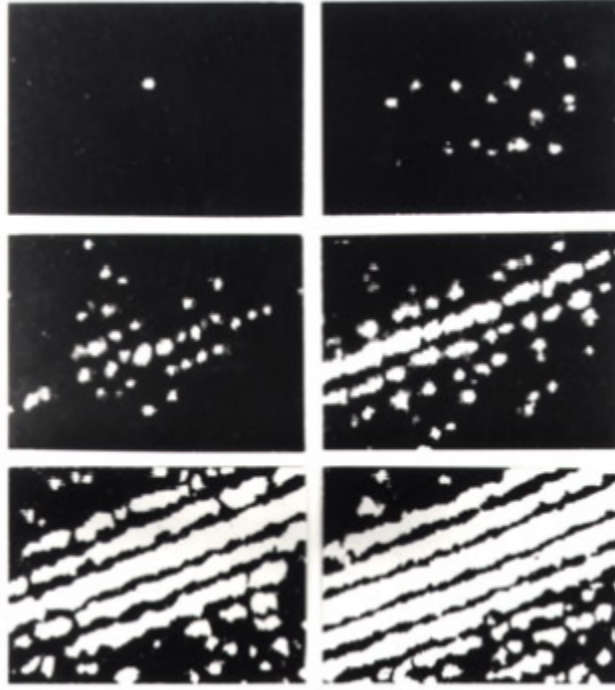


Figure 1.2: **Images of Final Detector Screen from Young's Double Slit Experiment at Different Electron Current Densities.** Images are taken directly from a TV monitor. If the electron current density is low, the electrons hit the final detector in Young's experiment as particles, as seen in the top left image. As the current density is increased, however, from top left to bottom right, an interference pattern develops, just as Young discovered in 1801. Image credit to Physics World Magazine⁷.

of radius a . The subsequent diffraction pattern fills a secondary screen in the far-field a distance x away from the first screen. The diffraction pattern is an experimental observable which measures the irradiance of light at a point P on the secondary screen a distance R away from the first screen, after diffracting at an angle θ ¹⁰. The scenario is depicted in Figure 1.3. Using spherical coordinates, the irradiance at point P is given by:

$$I(\theta) = I(0) \left(\frac{2J_1(ka \sin(\theta))}{ka \sin(\theta)} \right)^2 \quad (1.1)$$

where $I(0)$ is the irradiance at the center of the second screen, J_1 is the first-order Bessel function, and $k = 2\pi/\lambda$. The irradiance is plotted as a function of $ka \sin(\theta)$ in Figure

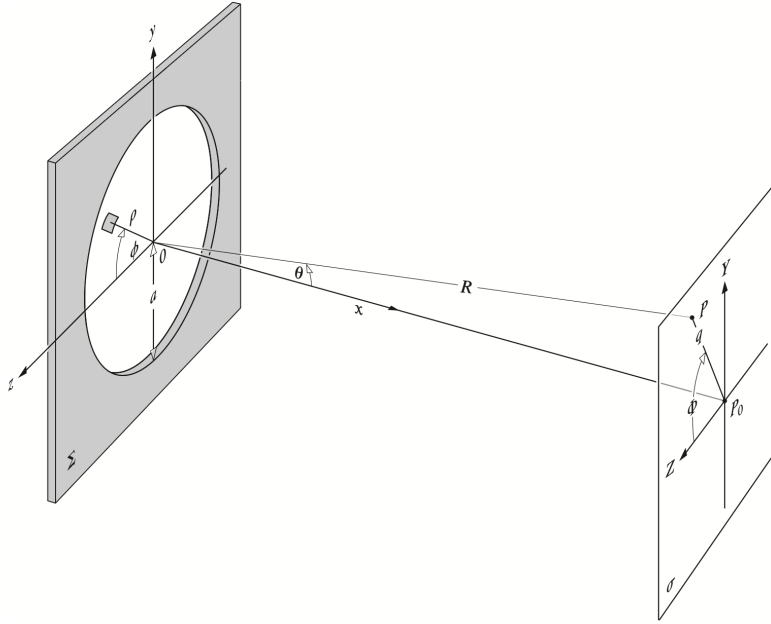


Figure 1.3: **Diffraction through a Circular Aperture.** Plane waves strike a screen Σ with a circular aperture of radius a and the subsequent diffraction pattern is cast on a secondary screen σ a distance x away. The irradiance of the light is calculated at a point P on σ a distance R away from Σ after diffracting at an angle θ . Image credit goes to Prof. Eugene Hecht¹⁰.

1.4a. The central peak corresponds to a bright circular spot known as an Airy disk, seen in Figure 1.4b. This Airy pattern consists of a series of light and dark rings, whose radius are determined by the zeros of the Bessel function. This means the experimentally measureable diffraction pattern *encodes* structural information about the size of the circular aperture and the Airy rings change if you adjust its diameter, as demonstrated in Figure 1.5.

The imaging techniques developed for probing gas-phase atomic structure make use of electron diffraction and the picture is not far from the concept of Airy rings. An electron, produced from an electron beam, collides with an atom, scatters off it at some angle, and hits a detector located some distance away from the atom. Here, the electron and atom play the role of the plane waves and circular aperture, respectively. The diffraction pattern that forms after the scattered electron hits the detector encodes structural information about the atomic target in the form of a differential elastic cross section (DCS). Fundamentally, a differential cross section measures the probability for electrons to scatter off the target

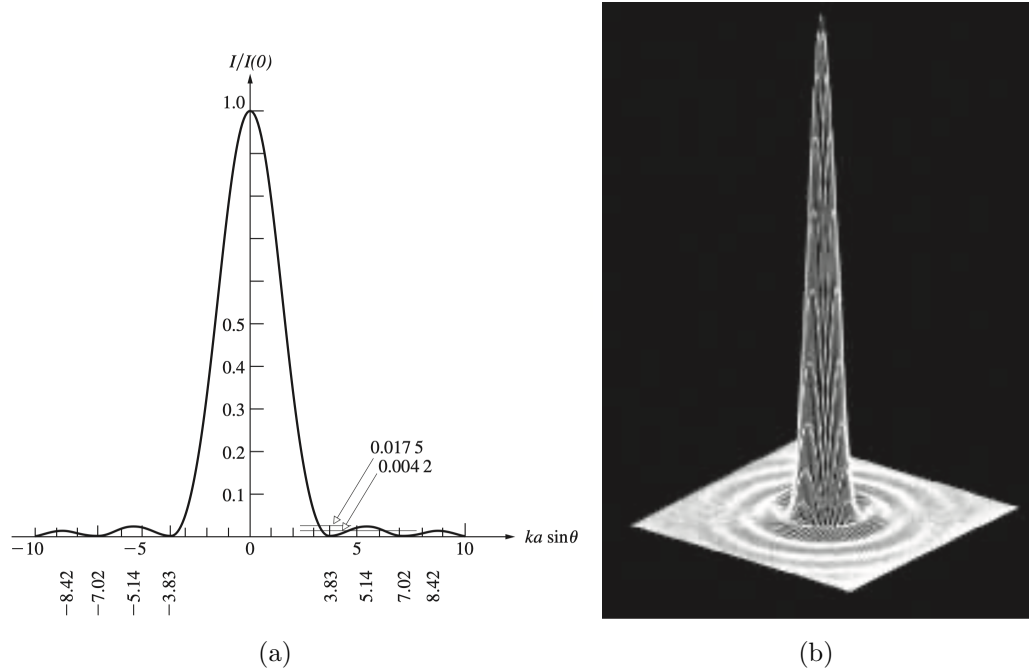


Figure 1.4: **Irradiance Distribution of Airy Rings.** (a) Irradiance plotted as a function of $ka \sin(\theta)$. I_0 represents the irradiance at the center of screen σ . (b) The maxima of the 1D distribution corresponds to a bright circular spot known as an Airy disk. The Airy pattern contains light and dark rings whose radius is dependent on the diameter of the circular aperture. Image credit goes to Prof. Eugene Hecht¹⁰.

in a solid angle $d\Omega$. Figure 1.6 shows theoretically calculated DCS for Argon and Xenon for electrons with kinetic energies of 100 eV¹¹. More maxima and minima are observed in Xenon's DCS compared to Argon due to its larger size (36 additional electrons). This is analogous to modifying Airy rings by changing the diameter of the circular aperture. The more complicated the atomic structure, the more complex the electron scattering, resulting in more peaks and troughs in the DCS. Analyzing this elastic cross section gives us direct information about the target atom.

Probing molecular structure also involves extracting a DCS. However, the methodology is more complicated due to the increased presence of atoms. We revisit Young's double slit experiment to understand molecular electron diffraction. Assume a monochromatic plane wave of wavelength λ impinges on a narrow slit. The diffracted wave then falls on a screen consisting of two narrow, parallel slits S_1 and S_2 whose centers are separated by a distance a , and two more diffracted waves are generated from the individual slits. These waves will

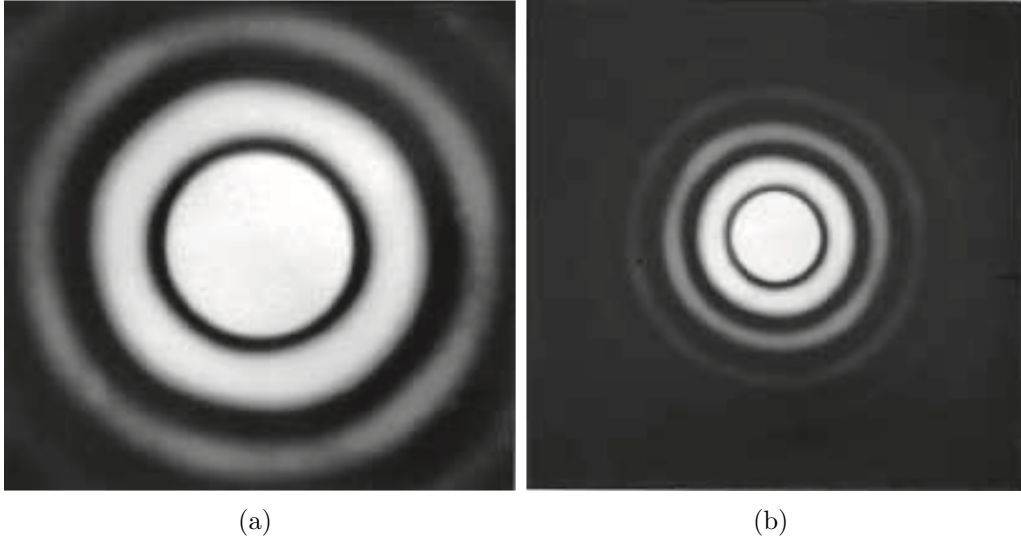


Figure 1.5: **Changes in Airy Pattern as a Function of Aperture Diameter.** Airy rings are shown with (a) 1 mm aperture diameter and (b) 0.5 mm aperture diameter. The clear change in the size and number of Airy rings shows how an experimentally observable diffraction pattern encodes structural information of the original object light diffracted off of. Image credit goes to Prof. Eugene Hecht ¹⁰.

constructively and destructively interfere, forming an interference pattern on a screen some distance s away from the two slits. The scenario and resultant interference pattern are shown in Figure 1.7. If the two waves produced from S_1 and S_2 travel a distance r_1 and r_2 , respectively, to interfere at a point P on the interference screen, the linear and angular position of the m th bright band is given by:

$$y_m = \frac{s}{a} m \lambda \quad (1.2a)$$

$$\theta_m = \frac{m \lambda}{a} \quad (1.2b)$$

The irradiance is given by

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \phi \quad (1.3)$$

where I_1 is the irradiance from the wave emitted from S_1 , I_2 is the irradiance from the wave emitted from S_2 , and ϕ is the relative phase between the two given by $\phi = k(r_1 - r_2) \approx k(ya/s)$ where $k = 2\pi/\lambda$. The resultant interference pattern depends both on slit

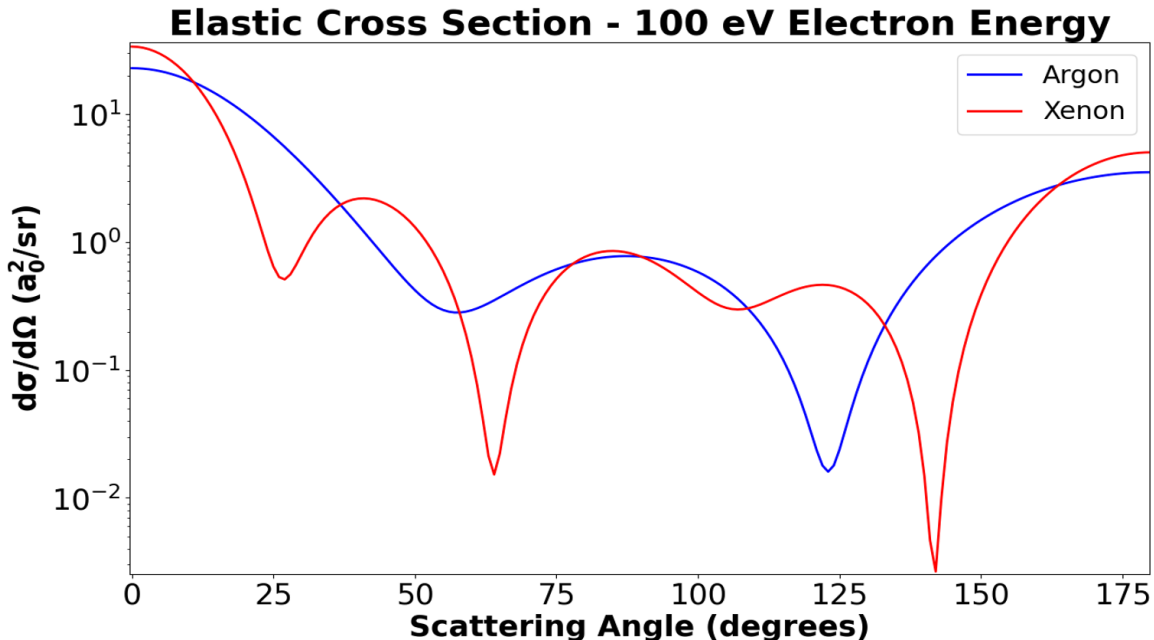


Figure 1.6: **Elastic Cross Sections of argon and xenon.** Elastic cross sections for argon (blue) and xenon (red) with an electron energy of 100 eV plotted as a function of scattering angle. The cross section is measured in units of a_0^2/sr or the Bohr radius squared per steradian. The more complex the atomic structure, the more complicated the scattering events, indicated by the greater number of peaks and troughs in Xenon's cross section. Analyzing the elastic cross section provides direct structural information about the target atom. More elastic cross sections can be generated using NIST Electron Elastic-Scattering Cross-Section Database, SRD 64¹¹.

separation and the distance from the slits to the final screen. If the two narrow slits in Young's experiment were replaced by small circular apertures, the resultant interference pattern would be Airy disks mixed with additional structure from the cosine term in Equation 1.3. This is shown in Figure 1.8.

The methodology behind probing molecular structure can be understood through the double slit experiment. Specifically, researchers are focused on extracting the bond length and respective bond angles of the target molecule. The most commonly used theoretical tool developed for this is known as the Independent Atom Model (IAM)¹². It assumes the atoms are fixed in space and have no interaction with each other. The high energy electron beam impinging on the target sees a potential which is a sum of the individual atomic potentials. If the molecule is placed in a fixed coordinate system, with origin O , then $\vec{R}_i$ and $\vec{R}_j$ represent

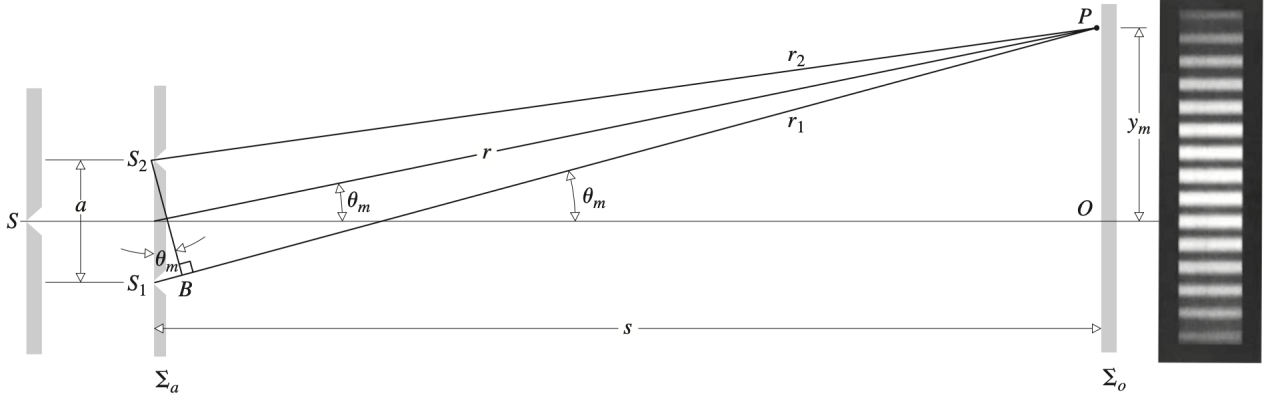


Figure 1.7: **Schematic of Young's Double Slit Experiment.** Monochromatic plane wave diffracts after falling on a narrow slit S . The wave then impinges itself onto Σ_a with two narrow slits, S_1 and S_2 , whose centers are separated by distance a . The two individual waves produced from the narrow slits travel a distance r_1 and r_2 at an angle θ , interfering at point P on Σ_o . The linear position from the center of Σ_o is given by y_m and the resultant interference pattern is shown. Image credit goes to Prof. Eugene Hecht¹⁰.

the distance from the individual atoms to the origin with $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ as their relative distance. Figure 1.9 shows a diagram of the situation. The DCS is given by:

$$I = I_A + \sum f_i f_j^* e^{i\vec{q}\vec{R}_{ij}} \quad (1.4)$$

The first term, I_A , represents the incoherent sum of the cross-sections from all atoms. The second term is known as the *molecular interference term* and explicitly depends on the interatomic distances. Symbols f_i and f_j are the complex scattering amplitudes from individual atoms. The DCS is equal to the norm-square of the scattering amplitude. Variable $\vec{q} = \vec{k} - \vec{k}_0$ is the momentum transfer term where $\vec{k}_0$ is the incident momentum of the electron and $\vec{k}$ is the momentum of the scattered electron. In elastic scattering, the magnitude of $\vec{k}_0$ and $\vec{k}$ are the same, only their direction is changed. According to Equation 1.4, it is q which determines the experimental spatial resolution, not the magnitude of k . Finer details of atomic structure can be resolved with larger q values. The two fixed atoms are analogous to the two circular apertures in the double-slit experiment with their diffraction pattern encoded in I_A , while the molecular interference term carries information about their interaction and acts as the cosine term in Equation 1.3. Like atomic electron diffraction, extracting the

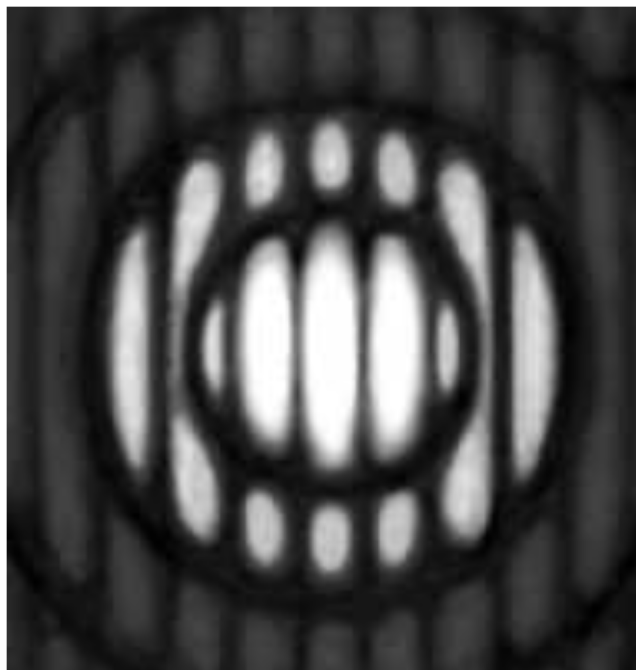


Figure 1.8: **Interference Pattern from Two Circular Apertures.** The resultant interference pattern if the two narrow slits in Young's experiments are replaced by two, small circular apertures. The pattern resembles an Airy disk but with extra structure from the relative phase between the two interfering waves. Image credit goes to Prof. Eugene Hecht ¹⁰.

elastic differential cross section proves crucial to understanding molecular structure.

The experimental imaging techniques developed over the last century have primarily utilized photons and electrons for the creation of diffraction patterns and are heavily rooted in wave/particle duality. Amongst all, electron diffraction is frequently used to probe the structure of atoms and small molecules in gas phase. The reason being electrons consist of charge and mass, meaning their cross sections are 5-6 orders of magnitude higher than photons¹³. As mentioned previously, electrons with energies on the order of hundreds of electronvolts (eV) are prepared using an external electron beam. These energies ensure the de Broglie wavelength of the particles are comparable to the chemical bond of the interrogated target. Additionally, the electrons are not sensitive to the valence electrons and mainly interact with the atomic nuclei. Therefore, the Independent Atom Model is invoked and the nuclei are fixed in space. The electrons scatter off the target and the resultant diffraction pattern formed from constructive and destructive interference of the scattered *waves* encode structural information following Equation 1.4. This is popularly known as Conventional

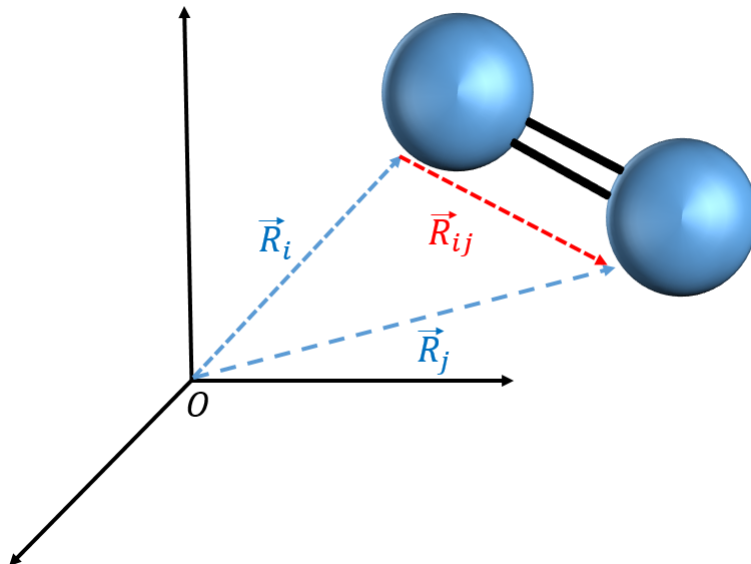


Figure 1.9: **Diagram for the Independent Atom Model.** The atoms of a diatomic molecule, shown with two blue spheres, are assumed to be fixed in space. Assuming a fixed coordinate system with origin O (black), the distance from the origin to each atom is given by $\vec{R}_i$ and $\vec{R}_j$ (blue vectors). The relative distance is given by $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ (red vector).

Electron Diffraction (CED). Using this technique on a gas-phase target coined the term Gas-Phase Electron Diffraction (GED) in 1930 when Mark and Wierl studied the structure of gas phase carbon tetrachloride. Both CED and GED are considered *static imaging* techniques as they investigate the target in equilibrium at a fixed point in time. They can extract the internuclear distance of molecules on the order of 0.001 Angstrom ($\text{\AA}$)¹¹³.

Although the static structure of molecules is important, the chemical reactions which occur in the world around us are constantly changing as a function of time. As mentioned previously, one of the main goals of atomic, molecular and optical physics is understanding how chemical bonds break, rotate and vibrate. That is, studying the off-equilibrium dynamics of atoms and molecules. Since molecular vibrations occur on the order of femtoseconds, the arrival of the femtosecond lasers opened the door for the creation of *dynamic imaging* techniques in the 1980s using electron diffraction. In addition to excellent spatial resolutions, these new techniques demanded femtosecond temporal resolutions to track chemical reactions as they evolved in time. Since its development, they have been used to study the

¹For context, chemical bond lengths are usually on the order of 1 $\text{\AA}$.

separation of the iodine atom from Trifluoroiodomethane (CF_3I) in 1983, structural changes of diiodotetrafluoroethane ($\text{C}_2\text{F}_4\text{I}_2$) in 1999, and the structural evolution of aluminum in 2003, just to name a few examples¹³.

Despite the many advancements made in atomic and molecular imaging, experimental laser physicists are always in search for new tools and techniques which would aid them in developing a *molecular movie* to "watch" bonds break and atoms migrate during a chemical reaction. The two projects in this dissertation contribute to this goal and technical details of both are explained at the end of Chapter 2.

The remaining five chapters of this thesis are structured as follows. Chapter 2 establishes the fundamentals of strong field-ionization, discussing ionization regimes, theoretical ionization models, and the Three-Step Model. Chapter 3 discusses the theoretical and experimental tools used to simulate and collect data. This includes computational logistics, concepts for calculating photoelectron and photoemission spectra, laser sources used and vacuum chamber specifications. Chapter 4 introduces the first project of this thesis which investigates the behavior of the electronic wavepacket under certain laser conditions and its potential application as a probing tool. Chapter 5 talks about the second project where experimental data of different targets are collected through a diffraction imaging technique for the study of a specific rescattering phenomena. Additionally, the data is used to conduct preliminary experimental elastic cross sections extraction using the aforementioned probing tool introduced in Chapter 4.

Chapter 2

Fundamentals of Strong Field Ionization

Strong field physics fundamentally involves the interaction of atoms or molecules with a strong electromagnetic (EM) field. It aims to induce, control and trace ultrafast processes. The intensity of an EM field is given by

$$I = \frac{1}{2} \epsilon_0 c E^2 \quad (2.1)$$

where ϵ_0 is the vacuum permittivity constant, c is the speed of light, and E is the electric field. For the purpose of this thesis, a *strong* electromagnetic field is defined as one whose intensity is non-negligible compared to the Coloumb field experienced by an electron within its atomic orbital. In the case of the hydrogen atom, the Coloumb field experienced by an electron in the first excited state is comparable to a field with a peak intensity of 10^{13} W/cm². Therefore, a *strong* electromagnetic field will be defined as one with an intensity between 10^{13} - 10^{14} W/cm². These field intensities allow us to focus on non-relativistic interactions, where the velocity of the charged particles remain significantly less than the speed of light¹⁴. An ultrafast process will be on the order of femtoseconds (10^{-15} s), comparable to the vibrational period of a molecule (tens to hundreds of femtoseconds)³.

The processes which arise from strong field ionization include double ionization, rescattering phenomena and more. However, fundamentally understanding their origins requires us to step into the theoretical world of strong field physics. This chapter introduces a brief background of strong field ionization, along with terms, concepts and phrases used repeatedly throughout this dissertation. All formulas in this chapter are written in atomic units, unless stated otherwise.

2.1 Ionization Regimes

To begin our journey, we start with the core of strong field physics: ionization. We choose an atom in its ground state, modeled by a Coulombic potential and expose it to an intense electromagnetic field. In order for ionization to occur, the field must provide enough energy to overcome the ionization potential (I_p) of the atomic target in its ground state. The relative intensity and energy of the field with respect to the atomic potential introduces two main regimes of ionization: the multi-photon regime and the tunneling regime.

At low field intensities, ionization can occur via the absorption of one or more photons. If the photon energy associated with the field $\omega > I_p$, then the atom can absorb a photon and eject an electron. This is known as *single-photon ionization*. The kinetic energy (KE) of the ionized electron from its ground state in this instance would simply be $KE = \omega - I_p$. However, if $\omega < I_p$, then the atom can only be ionized if it absorbs more than one photon. This is known as *multi-photon ionization*. In this case, the kinetic energy of the liberated electron would be

$$KE = N\omega - I_p \tag{2.2}$$

where N is the number of photons the atom absorbed.

An atom is not restricted to absorbing the N photons necessary to overcome the ionization potential. Instead, it can absorb more than the required number of photons in a process known as Above Threshold Ionization (ATI). In this case, the kinetic energy of the ionized electron is $KE = (N + S)\omega - I_p$, where S is the additional number of photons the target

absorbed. Details of ATI are discussed in Section 2.4.

If we now increase the field intensity, such that we rival the strength of the atomic potential, we transition to the tunneling regime. The electromagnetic field now distorts the Coulombic potential and ionization occurs when the electron escapes from the barrier formed from the perturbation. This is shown in Figure 2.1.

With differences established, we can now focus on categorizing the regime of our experiments. For this, we look to the work of L. Keldysh. In it, he used the Schrödinger equation to calculate the ionization rate for the ground-state of a hydrogen-like atom exposed to a strong, linearly polarized laser field¹⁵. From his calculations, he developed a simple theory, known as the Keldysh parameter (γ), defined as:

$$\gamma = T_t/(T/2) \quad (2.3)$$

where T_t is the tunneling time of the electron and T is the period of the laser field. If $\gamma < 1$, then the field is slowly varying with respect to the electron's tunneling time, allowing the electron to escape through the static barrier. However, if $\gamma > 1$, then the field oscillates faster than the tunneling time and ionization is instead possible via the absorption of multiple photons. The Keldysh parameter can also be explained as the amount of time it takes for an electron to tunnel through a barrier of length L ¹⁶. Given

$$L \approx I_p/F \quad (2.4)$$

where F is the peak electric field strength, and the velocity of the electron, v ⁱ

$$v \approx \sqrt{2I_p}/2 \quad (2.5)$$

its tunneling time, τ , would be

$$\tau = L/v \approx \sqrt{2I_p}/F \quad (2.6)$$

ⁱEquation 2.5 is valid in the classically forbidden region, or the region where the total energy of the electron is smaller than the combined Coulomb and field potential

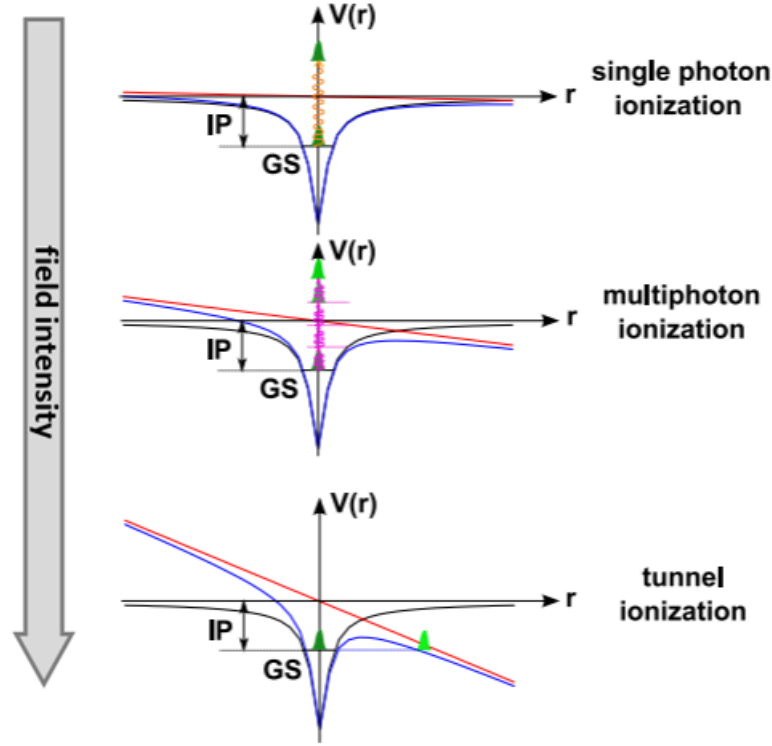


Figure 2.1: **Ionization Regimes as a function of Field Intensity.** From low to high field intensity: single photon ionization (top), multiphoton ionization (middle) and tunneling ionization (bottom). The field is represented in red, the atomic potential in black and the combined electromagnetic and Coulombic potential in blue. I_p is the ionization potential and GS is the ground state of the target. Image credit goes to Prof. Cosmin Blaga.

Substituting Equation 2.6 into Equation 2.3 yields

$$\gamma = \omega\tau = \omega\sqrt{2I_p}/F \quad (2.7)$$

where $\omega \propto 1/T$ is the frequency of the field.

Before we modify the Keldysh parameter any further, it is necessary to define the ponderomotive energy (U_p) as the cycle-averaged quiver energy of an ionized electron in an electromagnetic field. In atomic units¹⁶

$$U_p = F^2/4\omega^2 \quad (2.8)$$

and for linearly polarized light

$$U_p = 9.33I\lambda^2 \quad (2.9)$$

where λ is the wavelength of light used. Substituting equation 2.8 into equation 2.7 yields the well established formula for the Keldysh parameter

$$\gamma = \sqrt{I_p/2U_p} \quad (2.10)$$

2.2 Ionization Models for Atoms in an Electromagnetic Field

2.2.1 Analytical Models

Ammosov-Delone-Krainov (ADK) Model

The ADK model is used to calculate the ionization rate for adiabatic-tunneling ionization by infrared fields. An *adiabatic* process refers to a gradual change of a system's external conditions with time. The adiabatic approximation is used when the ionization time (measured as the inverse of the ionization rate) is short with the respect to the optical period of the field. To begin, we first study the ionization rate for a hydrogen-like atom in a static electric field. The combined potential is given by $V(r) = -Z/r + Fz$, where Z is the charge and F is the static electric field (polarized along the z axis). The hydrogenic wavefunction is modified to account for the influence of the external field and expressed in parabolic coordinates to handle the asymmetric tilted potential. The ionization rate is calculated by integrating the probability current density, j_z , in the $-z$ direction (since $F > 0$) over an open, orthogonal surface:

$$w_z = \int j_z dS \quad (2.11)$$

The probability current density is attained by solving the Time-Independent Schrödinger Equation in parabolic coordinates. We let $E = -\kappa^2/2$, where E is the eigenenergy of the

system. Doing this provides us with the following formula for the static ionization rate:

$$w_{static} = \frac{C_l^2 \frac{(2l+1)(l+|m|)}{2(l-|m|)!}}{2^{|m|}|m|!} \frac{1}{\kappa^{2Z/\kappa-1}} \left(\frac{2\kappa^3}{F}\right)^{2Z/\kappa-|m|-1} e^{-2\kappa^3/3F} \quad (2.12)$$

where l is the angular quantum number, m is the magnetic quantum number, κ relates to the ionization potential and C_l is a coefficient representing the amplitude of the electron wavefunction. We note that the momentum of the electron, $p \propto \sqrt{-\kappa^2/2}$. Using this relationship, equation 2.12 tells us the ionization rate is maximized when $p = 0$. A detailed derivation can be found in Prof. C.D. Lin's book on Attosecond and Strong-Field Physics¹².

Within the adiabatic approximation, F in equation 2.12 can be replaced by $|F(t)|$. We then calculate the cycle-averaged ionization rate using linearly polarized light, allowing for $F(t) = F_0 \cos(\omega t)$, where F_0 is the field amplitude. From this, the cycle-averaged ionization rate is:

$$w_{avg} = \frac{1}{T} \int_{-T/2}^{T/2} w(t) dt = \left(\frac{3F_0}{\pi\kappa^3}\right)^{1/2} w_{static}(F_0) \quad (2.13)$$

where T is the optical period. The probability of ionization within ADK theory is then calculated by using equation 2.13 and summing over the individual ionization probabilities of each cycle:

$$P_{ADK} = 1 - e^{-\int_{-\infty}^{\infty} w[|F(t)|] dt} \quad (2.14)$$

We note this holds for quasi-monochromatic fields. For short pulses, the adiabatic approximation breaks down, requiring the inclusion of the pulse envelope to better describe ionization dynamics.

The Strong-Field Approximation (SFA)

The Strong-Field approximation is a second model used to predict ionization probabilities. It begins with the work of Keldysh, Faisal and Reiss, who developed the Keldysh-Faisal-Reiss Theory, or KFR Theory. The ionization probability amplitude for an electron ejected with

a momentum $\vec{p}$ is:

$$M(\vec{p}) = -i \int_{-\infty}^{\infty} \langle \psi_{\vec{p}} | H | \psi_0 \rangle dt \quad (2.15)$$

where ψ_0 is the initial wavefunction. The final continuum state, $\psi_{\vec{p}}$, is given by a Volkov state ⁱⁱ

$$\psi_{\vec{p}}(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} \exp \left[i(\vec{p} \cdot \vec{r}) - \frac{1}{2} \int_{-\infty}^t \vec{v}_{\vec{p}}^2(t') dt' \right] \quad (2.16)$$

while the interaction Hamiltonian, H , is written in the Coulomb gauge:

$$H = -i\vec{A}(t) \cdot \nabla + \frac{\vec{A}(t)^2}{2} \quad (2.17)$$

where $A(t)$ is the vector potential of the field and the generalized momentum, $\vec{v}_{\vec{p}}(t)$, is $\vec{p} + \vec{A}(t)$. The differential ionization probability can be expressed as

$$\frac{dW(\vec{p})}{d^3p} = |M(\vec{p})|^2 \quad (2.18)$$

If we assume ionization by a monochromatic field with an optical period T and average over a cycle given

$$\left\langle \frac{\vec{v}_{\vec{p}}^2(t)}{2} \right\rangle_T = \epsilon_p + U_p \quad (2.19)$$

where $\epsilon_p = p^2/2$, then the differential ionization probability can be written as:

$$dW(\vec{p}) = \sum_n \delta(\epsilon_p + I_p + U_p - n\omega) R(\vec{p}) d\epsilon_p d\Omega_{\vec{p}} \quad (2.20)$$

where n is the number of photons, $R(\vec{p}) = \frac{\omega^2 p}{2\pi} |M_K(\vec{p})|^2$, $K = I_p/\omega$, and $M_K(\vec{p})$ is the partial transition amplitude. The delta function in equation 2.20 states that the allowed kinetic energies for an ionized electron is:

$$\frac{p_n^2}{2} = n\omega - (I_p + U_p) \quad (2.21)$$

ⁱⁱThe Volkov state is the analytical solution of the TDSE for a free electron in an oscillatory laser field in the absence of the atomic potential ¹²

with peaks separated by ω . These are known as Above Threshold Ionization or ATI peaks. We note that the threshold for ionization in equation 2.21 is shifted by the ponderomotive energy, U_p .

KFR Theory is the first-order theory of laser-matter interaction and its results are gauge dependent. The next steps are to improve SFA to the next order for strong field ionization.

We begin in the length gauge, where the interaction Hamiltonian, H_{int} , is $\vec{F}(t) \cdot \vec{r}$. The length gauge is preferred since the atomic and laser field potential are scalars that can be added directly to demonstrate the tilting of the Coloumb potential from the field. Additionally, the interaction Hamiltonian seamlessly connects the particles interaction with the electric field, an advantage when under the dipole approximation¹⁷. Next, the time evolution operator is used to solve the TDSE. The wavefunction, then, takes the following form at a time $t \rightarrow \infty$ when the laser field is off:

$$\psi(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} \int e^{i\vec{p} \cdot \vec{r} - ip^2 t/2} M(\vec{p}) d^3 p \quad (2.22)$$

where

$$M(\vec{p}) = \frac{-i}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} e^{-iS_0(\vec{p}, t_1)} \int e^{-i\vec{v}_{\vec{p}}(t_1) \cdot \vec{r}_1} \vec{F}(t_1) \cdot \vec{r}_1 \psi_0(\vec{r}_1) d^3 r_1 dt_1 \quad (2.23)$$

is the transition amplitude and

$$S_0(\vec{p}, t) = \int_t^{\infty} \left(\frac{1}{2} \vec{v}_{\vec{p}}^2(t') + I_p \right) dt' \quad (2.24)$$

is the action. To evaluate the transition amplitude, we turn to the saddle-point approximation. It assumes the main contribution for integrals of the form shown in equation 2.23 come from critical points¹⁸. The solutions to the saddle-point approximation are given by $\partial S_0 / \partial t = 0$ and are complex. The transition amplitude can be written as a summation over these complex solutions. The real part of the solution provides information on the time of emission of the electrons while the imaginary part relates to the rate of ionization in the semiclassical picture¹².

With two ionization models introduced, we can ask: how does ADK theory compare

to the SFA model? First, ADK theory applies to the tunneling regime while the SFA model mathematically applies to the full range of the Keldysh parameter. Second, ionization probabilities calculated with the ADK model agree more with TDSE than the SFA model. This is because the final continuum state in SFA is approximated to be a Volkov state which neglects effects from the atomic potential. Coulomb corrections can be made to improve SFA but will not be discussed here.

Ponderomotive Shift of Rydberg Electrons In equation 2.21, we noted that the ionization threshold is shifted by the ponderomotive potential. Let's investigate this further by considering the ponderomotive interaction between an electromagnetic field and a Rydberg electron.

A Rydberg electron is defined as one that is loosely bound to its parent ion. It is considered as “quasi-free” and its dynamics in a laser field are described by three coordinates: the atom's center-of-mass $\vec{R}$, the relative distance between the electron and the atom $\vec{r}$ and the quiver amplitude of the electron, ρ . Justifying a ponderomotive shift to the ionization potential requires a comparison of timescales and amplitudes. The quiver amplitude evolves with the period of the field. For 800 nm light, this would be approximately 2.6 femtoseconds. The relative motion between the electron and the atom evolves as n^3/Z^2 according to the Bohr model, where n is the nth electron from the core and Z is the charge. For large n (≈ 50), this would be on the order of picoseconds, or 1000 times longer than the period of the field. The quiver amplitude of the electron in an oscillating field is proportional to E_0/ω^2 . For 800 nm light at an intensity of 66 TW/cm² this is approximately 68 nm. Comparatively, the distance between a Rydberg electron and its nucleus, according to the Bohr model is proportional to $a_0 n^2/Z$, where a_0 is the Bohr radius. For large n , this is on the order of microns, or 1000 times larger than the quiver amplitude. Any changes to atomic or external potentials occur far from the electron and on much longer timescales. Therefore, it is safe to assume that the electron is quivering in an effective background potential, $V(\vec{R} + \vec{r})$, which can be subtracted from Schrödinger equation for the quiver motion¹⁹:

$$\left(\frac{-\hbar^2}{2}\nabla_\rho + \rho \cdot \vec{E}(\vec{R} + \vec{r})\cos(\omega t)\right)\phi(\rho, t; \vec{r}, \vec{R}) = i\hbar\frac{\partial}{\partial t}\phi(\rho, t; \vec{r}, \vec{R}) \quad (2.25)$$

The Volkov states are eigen-solutions to equation 2.25 and the eigen-energies are given by

$$E_{quiver} = \frac{|\vec{E}(\vec{R} + \vec{r})|^2}{4\omega^2} \quad (2.26)$$

which, as we recall from Section 2.1, is exactly the ponderomotive potential. The interaction between the field and the Rydberg electron can be described by adding equation 2.26 to the total Hamiltonian. This explains why the ionization potential is shifted by U_p in equation 2.21.

2.2.2 Numerical Calculations

TDSE in the Single Active Electron (SAE) Approximation

Simulations of strong field ionization processes such as High Harmonic Generation (HHG), Above Threshold Ionization (ATI) or Holography are nontrivial. In theory, given a N -electron system, you would need to solve the N -electron TDSE. Fortunately, these processes are assumed to be highly influenced by the interacting singly, ionized electron and distorted potential. This is the Single Active Electron (SAE) Approximation. In this model, all of the electrons surrounding the “active” one are considered to provide an effective potential. With this assumption, the potential can be written as a sum of a Coulomb and short-range potential¹²:

$$V(r) = \frac{-Z_c}{r} + V_{sr}(r) \quad (2.27)$$

where Z_c is the charge felt by the electron. The TDSE is written as

$$i\frac{\partial\psi(r, t)}{\partial t} = \left(-\frac{1}{2}\nabla^2 + V(r) + E(t)z\right)\psi(r, t) \quad (2.28)$$

where $E(t)$ is the linearly-polarized field propagating in the z -direction.

In practice, theorists use code written in their favorite programming language to numerically solve the TDSE under the SAE approximation. SAE-TDSE calculations are computationally efficient and scale well with changes in wavelength and intensity in comparison to multi-electron simulations. Additionally, the code itself is usually an extension of existing hydrogen TDSE codes. Even if multi-electron simulations do exist, single-electron calculations can still sweep large parameter spaces to identify certain features before running a heavier, more computationally expensive calculation²⁰. There are, however, two main disadvantages.

The most obvious pitfall of the SAE approximation is its failure to address multi-electron effects²¹. Specifically, it ignores electron-electron correlations, a phenomena that results in non-sequential double ionization (NSDI), discussed later in this dissertation.

Long computation times from spatial and temporal propagation are the second main disadvantage of SAE-TDSE calculations. Increasing the intensity requires a larger computational box and longer pulses requires more time steps²¹. Researchers continue to search for numerical efficiency of 1-electron TDSEs. For example, H.G. Muller proposed separating the Hamiltonian into tri-diagonal terms and using rotating reference frames in 1999²². Further efficiency was developed by Tulsy and Bauer in the development of QProp: “a position-space TDSE-solver for a single active electron bound in a spherically symmetric potential and subject to an external, time-dependent, space homogeneous electric field”²³. Calculation of photoelectron and HHG spectra for a variety of wavelengths and intensities is possible. QProp is open source, written in C++, and available for immediate download with detailed manuscripts.

Gauge Choice

The choice of gauge affects both the accuracy and computational efficiency of numerical calculations. Here we focus on two: the length and velocity gauge. Both come with their advantages and disadvantages depending on the distance between the electron and the parent ion.

In the length gauge, the TDSE is written as

$$i\frac{\partial\psi}{\partial t} = (H_0 + E(t)z)\psi \quad (2.29)$$

where H_0 is the field-free Hamiltonian and $E(t)$ is the electric field polarized in the z -direction. The length gauge is preferred for interactions close to the parent ion where the interaction is small²¹. This is because it directly couples the electric field and the position of the electron. However, when the electron travels far from the core after ionization, the large field-electron interaction coupled with the electron's quiver motion requires smaller time steps and more angular momentum functions. This leads to longer computation times.

If we write the vector potential as $\partial A/\partial t = -E(t)$, then the TDSE in the velocity gauge is written as

$$i\frac{\partial\psi}{\partial t} = (H_0 - iA(t)\frac{\partial}{\partial z})\psi \quad (2.30)$$

The phase factor which describes free-electron oscillatory motion is essentially eliminated, significantly reducing the amount of angular momentum functions needed to describe the wavefunction accurately for interactions far from the core. However, close to the ion, the interaction $A(t)p_z$ can be large, causing rapid oscillations, making equation 2.30 difficult to numerically integrate.

Running SAE-TDSE Calculations

Performing an SAE-TDSE calculation involves solving equation 2.28 given a wavelength, peak intensity and pulse duration. The field usually takes the form

$$E(t) = F(t)E_0\sin(\omega t + \phi(t)) \quad (2.31)$$

where $F(t)$ is the envelope function, E_0 is the amplitude of the field and $\phi(t)$ is the phase. The calculation starts by selecting a well-defined state, usually a superposition of eigenstates of the field-free Hamiltonian, generating the wavefunction on a radial grid, and then

propagating the wavefunction from a time t_i to a time t_{i+1} where $t_{i+1} = t_i + \delta t$.

Given a uniform radial grid, the wavefunction ψ_i for position x_i can be calculated with the three-point difference technique. It calculates ψ_i from ψ_{i+1} , ψ_i , and ψ_{i-1} . Further details are beyond the scope of this dissertation. The split-operator method is used to propagate the wave function along a uniform time grid. It first separates the initial wavefunction into momentum and position terms, propagating a half time-step in position space to lower the error to $\mathcal{O}(\delta t^3)$. Fourier transforms are subsequently performed in both position and momentum space to generate the wavefunction for the next time step in the grid²⁴. A more detailed discussion of the split-operator method can be found in Chapter 2 of “Strong Field Laser Physics” by Prof. K.J. Schafer.

The calculated time-dependent wavefunction generates observables like HHG spectra and angular distributions to compare with experimental data. They also simulate time-dependent quantities and excited state probabilities which greatly aid in understanding atomic and molecular dynamics.

2.3 The Three-Step Model

With ionization understood, we can now ask: what occurs to an electron after it is liberated by an intense electromagnetic field? One possibility is it drifts away (usually to a detector in an experiment). These are known as direct electrons. The ionized electron, now caught in an oscillating electric field, can also be accelerated back to the ionic core where it either elastically scatters, inelastically scatters, or recombines with the core, releasing a high energy photon in a process known as High Harmonic Generation (HHG). This sequence of ionization, acceleration in the field, and recollision with the core is known as the Three Step Model. In this section, we detail an electron’s journey in an oscillating electromagnetic field and make sense of its recollision dynamics with the parent ion.

2.3.1 Propagation in the Field

Although the electron is a quantum wavepacket, its dynamics in the electromagnetic field can be described classically at high energies due to the correspondence principle. Assume the electric field is given by $E(t) = E_0 \sin(\omega t)$, where E_0 is the field amplitude and ω is the frequency of the field. The vector potential is given by $A(t) = A_0 \cos(\omega t)$, where A_0 is the peak vector potential of the field. We note $A_0 = E_0/\omega$. The Hamiltonian for a charged particle in an electromagnetic field is:

$$H = \frac{(\vec{p}_{mechanical}(t))^2}{2} + V(\vec{r}) \quad (2.32)$$

where $\vec{p}_{mechanical}(t)$ is the momentum of the electron, or the mechanical momentum, and $V(\vec{r})$ is the potential. The *generalized* momentum is given by $\vec{p}_{generalized}(t) = \vec{p}_{mechanical}(t) + \vec{A}(t)$. The Simpleman Model assumes the influence of the field on the particle is stronger than the influence of the potential, neglecting $V(\vec{r})$ in equation 2.32. Under this model it can easily be shown that the generalized momentum is a constant of motion using the Hamilton-Jacobi equations. Assume the electron is ionized at time t_i . Recalling the ADK ionization rate maximizes when $p_{mechanical} = 0$, the generalized momentum becomes $p_{generalized} = A(t_i)$. Therefore the mechanical momentum at all times t after ionization given an initial ionization time t_i is given by

$$p_{mechanical}(t; t_i) = A(t_i) - A(t) \quad (2.33)$$

Integrating equation 2.33 from t_i to an arbitrary time t provides the position of the electron, $x(t; t_i)$, assuming $x(t_i) = 0$:

$$x(t; t_i) = \frac{E_0}{\omega} t \cos(\omega t_i) - \frac{E_0}{\omega} t_i \cos(\omega t_i) - \frac{E_0}{\omega^2} \sin(\omega t) + \frac{E_0}{\omega^2} \sin(\omega t_i) \quad (2.34)$$

An electron will return to the core when $x(t) = 0$. However, as mentioned previously, some drift towards a detector as direct electrons. At time $t \rightarrow \infty$ when the pulse vanishes ($A(\infty) = 0$), it is left with the momentum it gained initially from the vector potential of the

field:

$$p_{mechanical}(\infty; t_i) = A(t_i) = \frac{E_0}{\omega} \cos(\omega t_i) = p_{max} \cos(\omega t_i) \quad (2.35)$$

Equation 2.35 shows the maximum momentum the electron can have at detection is E_0/ω or $2\sqrt{U_p}$ (using Equation 2.8). Therefore, its maximum kinetic energy after ionization without further rescattering is

$$KE = \frac{p_{max}^2}{2} = 2U_p \quad (2.36)$$

2.3.2 Recollision

Tracking electron recollision dynamics through elastic scattering, inelastic scattering and recombination is done through the recollision model.

In section 2.3.1, the position of an electron in an electromagnetic field was solved classically. We concluded that an electron would return to the parent ion if $x(t) = 0$. The time the electron returns to the core is called the “return time” or t_r . Given the electron is ionized at some initial phase, $\phi_i = \omega t_i$, we can solve equation 2.34 and collect all times, $\phi_r = \omega t_r$, the electron returns to its parent. Let’s assume ionization occurs in the first half cycle of the pulse, or $\phi_i = [0^\circ, 180^\circ]$ ⁱⁱⁱ. We then iterate through each birth phase, solve equation 2.34, and collect all return phases for each birth phase. It is important that causality ($\phi_i < \phi_r$) is maintained. Figure 2.2 shows select electron trajectories for particular birth phases using the described methodology. The violet trajectories represent direct electrons and the green trajectories represent returning electrons. Clearly, direct electrons never cross $x(t) = 0$ while returning electrons return to the parent more than once. Performing this calculation for all birth phases between 0 and 180 degrees reveals a few important details. First, electrons born at $x(t_i) = 0$ between 0 and 90 degrees never return and are direct electrons. Second, the kinetic energy of an electron at *return* is given as

$$KE = \frac{1}{2} \dot{x}(t)^2 = 2U_p (\cos(\phi_r) - \cos(\phi_i))^2 \quad (2.37)$$

ⁱⁱⁱrecall that we have chosen our electric field to be a sine

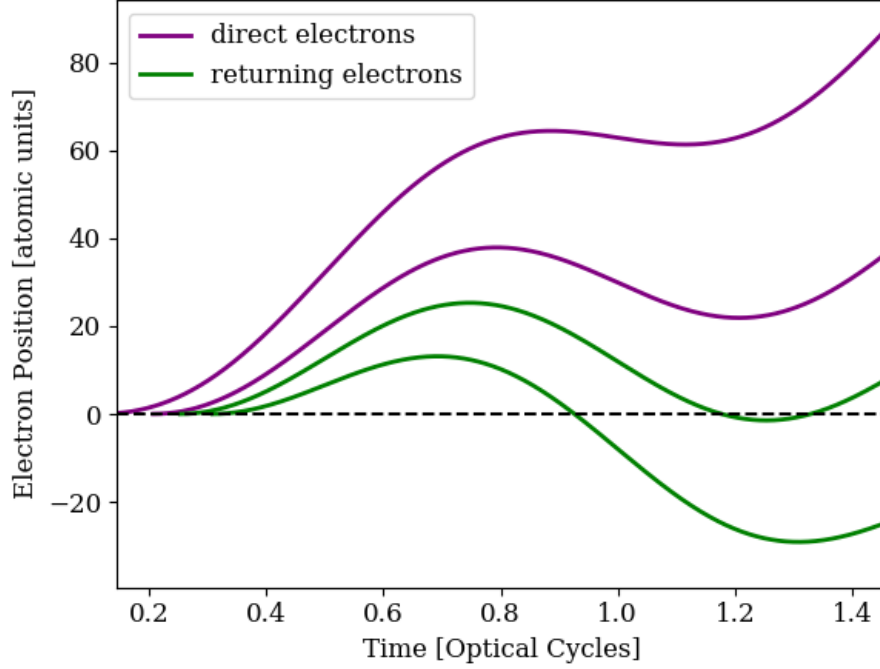


Figure 2.2: **Classical Electron Trajectories.** Electron trajectories plotted in atomic units as a function of time using a semiclassical approach. The violet trajectories represent direct electrons and never return to the parent ion after ionization. The green trajectories represent returning electrons and cross $x(t) = 0$, indicating the field accelerates these electrons back to its parent ion.

and the maximum KE it can have is $3.17U_p$. This occurs when the birth phase is $\phi_i = 108^\circ$ and the return phase is $\phi_r = 342^\circ$. Finally, plotting the kinetic energy distribution as a function of time reveals two classes of trajectories. *Long trajectories* are those which are born between $90^\circ < \phi_i < 108^\circ$ and return between $342^\circ < \phi_r < 450^\circ$. *Short trajectories* are those which are born between $108^\circ < \phi_i < 180^\circ$ and return between $180^\circ < \phi_r < 342^\circ$. This is shown in Figure 2.3. The naming convention is based on the total excursion time of the electron, or $t_{excursion} = t_r - t_i$.

Elastic Scattering

Elastic scattering conserves the kinetic energy of the electron in the center of mass frame while it scatters off the ionic core at an angle θ . In an experiment, the rescattered electron

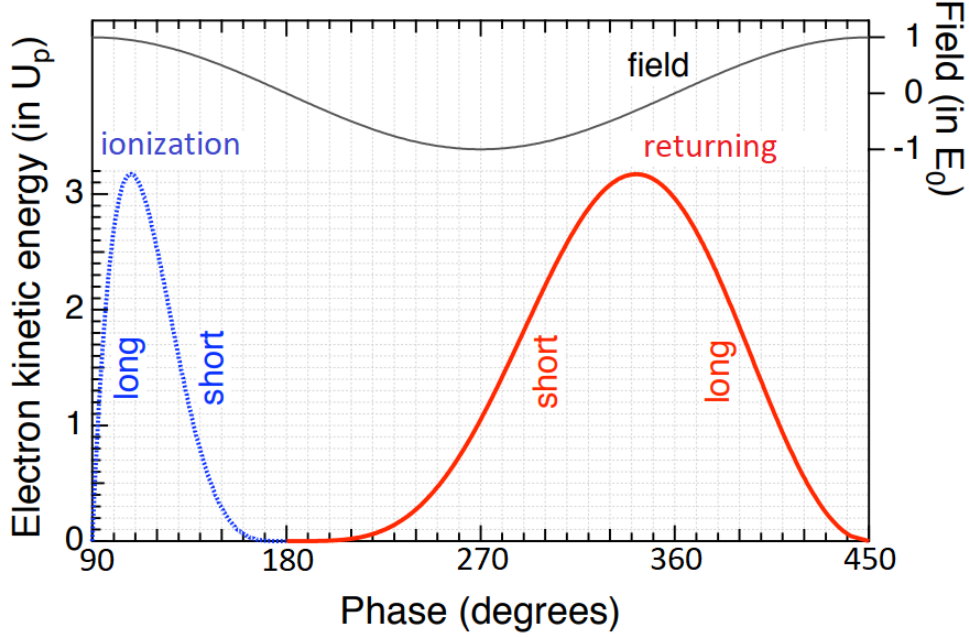


Figure 2.3: **Electron Return Energy Distribution.** The kinetic energy distribution for an electron is plotted for both ionization and return times as a function of phase. The maximum return energy is $3.17U_p$ and occurs at $\phi_i = 108^\circ$ and $\phi_r = 342^\circ$. The electric field is plotted in black. Additionally, long and short trajectories are defined based on the electron's excursion time on its trajectory, or $t_{excursion} = t_r - t_i$ where t_r is the time of return and t_i is the birth time.

eventually hits a detector with some accumulated energy and the kinetic energy distribution is recorded with a photoelectron spectra (PES). Figure 2.4 shows a typical photoelectron spectrum of Argon taken at 2 microns with a peak intensity of 200 TW/cm^2 . The x axis is the electron's kinetic energy in U_p units and the y axis is electron yield in arbitrary units. Direct electrons dominate between 0 and $2U_p$ while rescattered electrons dominate between $2U_p$ and $10U_p$. This region is called the *rescattering plateau* and its limit is $10U_p$. We use the recollision model to explain how electrons can accumulate energies above $2U_p$.

The full rescattering picture is described as such: after oscillating in the field, the electron is accelerated back to the core with some momentum p_r and elastically re-scatters at an angle θ_r . At the time of return, the mechanical momentum is $p_r = p_{max}(\cos(\phi_r) - \cos(\phi_i))$ along the laser polarization. Additionally, the electron is influenced by the field at the time of return, given by $A(t_r)$, before rescattering. This results in a final detected angle, θ_{det} which

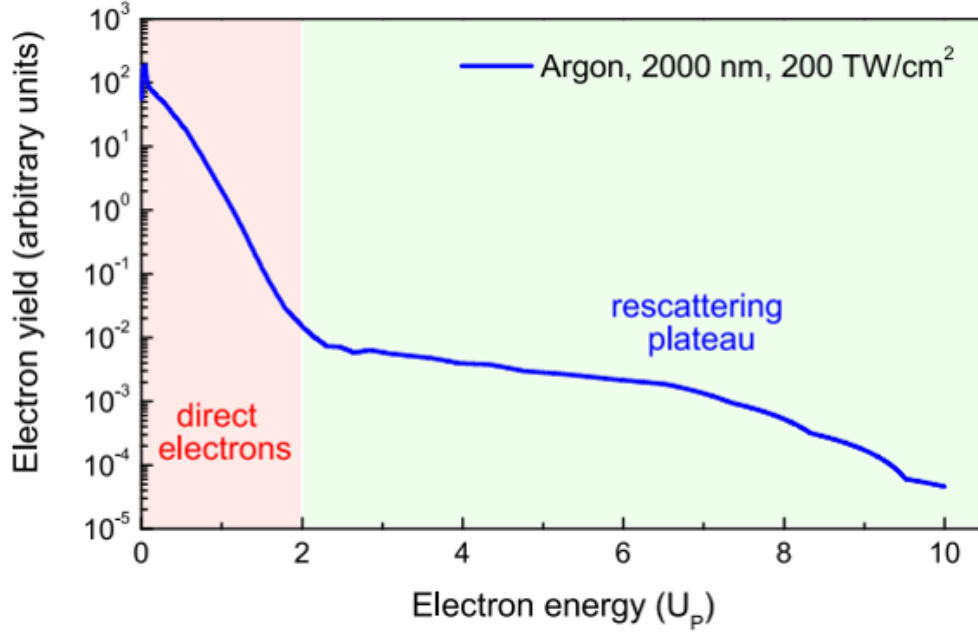


Figure 2.4: **Experimental Photoelectron Spectrum.** A typical, experimental photoelectron spectrum for Argon collected at 2 microns with a peak intensity of 200 TW/cm². The Keldysh parameter is 0.3, so this spectrum was collected in the tunneling regime. The electron's energy is given in U_p units. The direct electrons dominate the region between 0 and $2U_p$ while the region between $2U_p$ and $10U_p$ is populated by those electrons which have elastically re-scattered off of its parent ion. Image credit goes to Prof. Cosmin Blaga.

differs from the rescattered angle θ_r . The detected momentum, $\vec{p}_{det}$, is related to the return momentum and vector potential at the time of return through the generalized momentum: $\vec{p}_{det} + \vec{A}_{det} = \vec{p}_r + \vec{A}_r$. But since we assume no pulse at detection we are left with the following relationship:

$$\vec{p}_{det} = \vec{p}_r + \vec{A}_r \quad (2.38)$$

The situation above is depicted in Figure 2.5 in momentum space with parallel and perpendicular components relative to the linear polarization of the field. From section 2.3.1 we know $A_r = p_{max} \cos(\phi_r)$, with $p_{max} = 2\sqrt{U_p}$. Allowing for scattering in a two dimensional

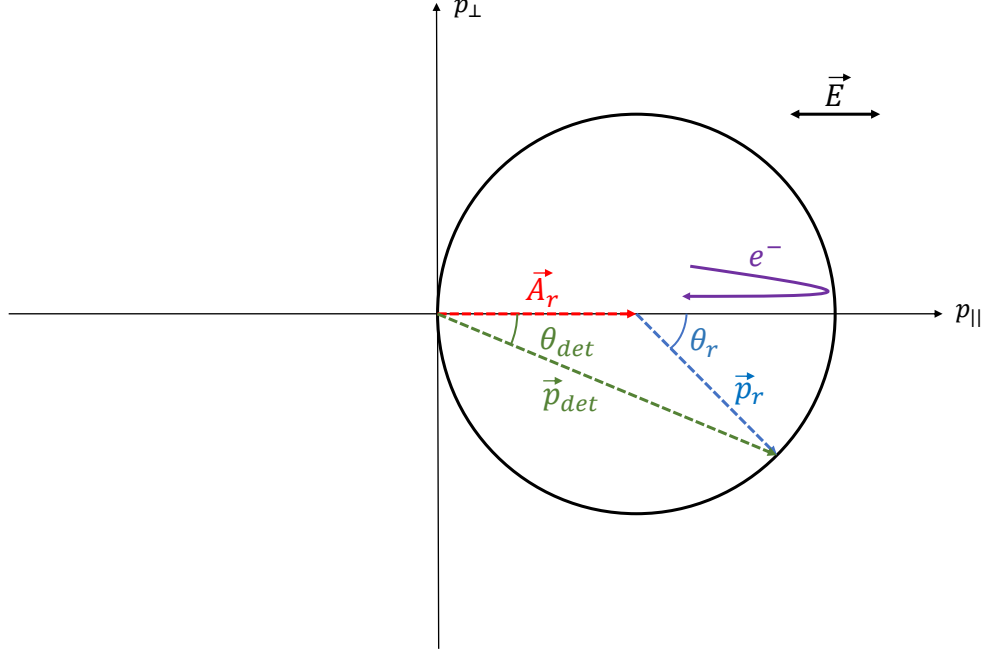


Figure 2.5: **Elastic Rescattering Diagram.** Rescattering picture modeled by vectors in momentum space with linearly polarized light. The electron is driven back to its parent ion after oscillating in the field (purple arrow). It returns with some return momentum, $\vec{p}_r$ (blue arrow), and elastically rescatters at some angle θ_r (blue angle). At the time of return the electron gains an additional kick from the vector potential $\vec{A}_r$ (red arrow). It is then detected at some angle, θ_{det} (green angle) with a total momentum of $\vec{p}_{det} = \vec{p}_r + \vec{A}_r$ (green arrow).

plane, the detected momentum becomes²⁵

$$\vec{p}_{det} = p_{max}(\cos(\phi_r) - \cos(\phi_i)) \begin{pmatrix} \cos(\theta_r) \\ \sin(\theta_r) \end{pmatrix} + \begin{pmatrix} p_{max}\cos(\phi_r) \\ 0 \end{pmatrix} \quad (2.39)$$

Using $E_{det} = \|\vec{p}_{det}\|^2/2$ the following equation is obtained for the detected energy:

$$E_{det} = 2U_p((\cos(\phi_i) - \cos(\phi_r))^2 + 2\cos(\phi_r)\cos(\theta_r)(\cos(\phi_i) - \cos(\phi_r)) + \cos^2(\phi_r)) \quad (2.40)$$

The maximum detected energy of $10U_p$ occurs at $\phi_i = 105^\circ$ and $\phi_r = 352^\circ$, where $\theta_r = 180^\circ$. This is known as a backscattering event, since the electron is re-scattering back along the

laser polarization.

Equation 2.39 shows the dependence of the detected energy on the electron's birth phase, return phase and rescattering angle. Additionally, the influence of the field on the electron at the time of return is key to accumulating detected energies larger than $2U_p$. This accumulation of higher energies allows for the distinction between direct and rescattered electrons in a photoelectron spectra.

Inelastic Scattering

In inelastic scattering, the kinetic energy of the electron is *not* conserved and some of it is transferred to the target, allowing for the promotion of a second electron into the continuum. This is known as nonsequential double ionization. Figure 2.6 shows the measured single and double ionization yields of Helium using a 780 nm, linearly polarized pulse. Curiously, the production of doubly charged helium ions is much higher than the yield predicted by the ADK ionization model. This is because the correlation between the first and second electron in the ionization process is neglected and gives rise to two types of double ionization models: sequential double ionization (SDI) and non-sequential double ionization (NSDI).

NSDI dominates below the saturation intensity ^{iv}, which is the point where SDI takes over. SDI involves the formation of a doubly-charged ion through two sequential electron ionization events: the first electron is field ionized from the neutral target followed by field ionization of the second electron from the singly charged ion. NSDI depends upon recollision of the first electron and can proceed via two paths: the first electron can directly ionize the second electron (this is known as the (e,2e) mechanism) or the second electron can be excited by the first electron and then ionize at a later time²⁶. The latter is known as Re-collision Excitation with Subsequent Ionization (RESI).

^{iv}saturation intensity: the intensity at which the probability of ionization becomes 1

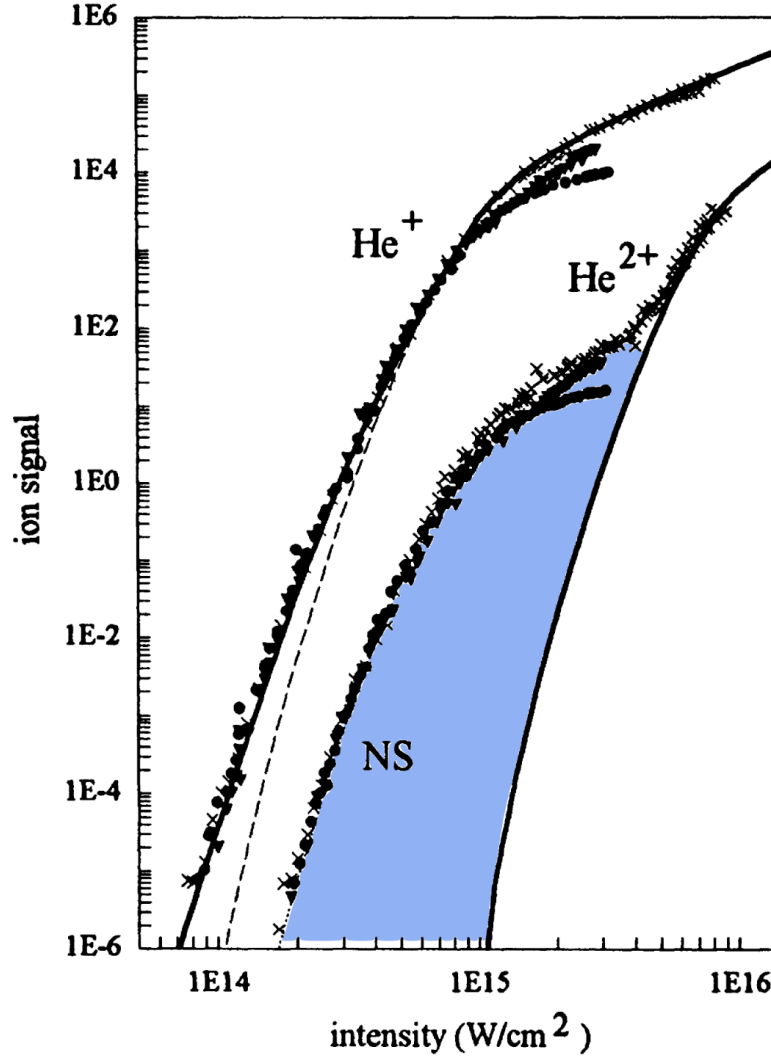


Figure 2.6: **Single and Double Ionization of Helium.** Experimentally measured Helium ions for a 780 nm, 100 fs linearly polarized field. SAE-TDSE calculations are shown as solid lines and ADK calculations are shown as dashed lines. Both calculations agree with the measurement at high intensity but ADK underestimates the yield at lower intensity. The solid curve on the right is the SAE-TDSE calculation made for sequential double ionization of Helium and the blue shaded region represents the (e,2e) mechanism responsible for non-sequential double ionization. Image credit goes to Prof. B. Walker²⁷.

Recombination

When the electron recombines with the parent ion, it emits a high energy photon in the process. Previous discussion calculated the maximum return energy of an electron at $3.17U_p$. Therefore, the maximum energy of the emitted photon is $E_{\text{photon}} = I_p + 3.17U_p$, where I_p is

the ionization potential. The kinetic energy at return was calculated classically for a certain birth phase, ϕ_i and return phase, ϕ_r . If (ϕ_i, ϕ_r) is a solution to $x(t_i, t_r) = 0$, then so is $(\phi_i + m\pi, \phi_r + m\pi)$, where m is an integer²⁸. This means a photon is generated every half-cycle of the field with an alternating phase, known as harmonics, and it can be shown that the harmonic spectrum consists of radiation bursts separated by odd integer multiples of the driving laser frequency. This phenomena is known as High Harmonic Generation (HHG). In 1994, Lewenstein developed a quantum mechanical way to understand HHG, now known as the Lewenstein model. In it, he predicts a cutoff energy that is slightly higher than the classical result²⁸. Despite this discrepancy, the Lewenstein model justifies the use of the semi-classical three step model for the prediction of temporal structure in harmonic spectra.

The emission of photons every half cycle occur on the order of attoseconds. This has made HHG a prime candidate for the creation of attosecond pulses. The production of these pulses are important because the timescale of electron motion within an atom or molecule is on the order of attoseconds (10^{-18} s)²⁹.

2.4 Laser Induced Electron Diffraction and Above Threshold Ionization

In Section 2.3.2, an experimentally collected PES was shown for Argon within the tunneling regime. This spectrum was created by direct electrons drifting towards a detector and those which have rescattered off the parent ion. Just like the Conventional Electron Diffraction imaging technique introduced in Chapter 1, these rescattered particles contain structural information of their parent ion. However, in contrast to CED, an electron beam is not prepared. Rather, the target's *own* electrons are used for probing its structure. This technique is known as **Laser Induced Electron Diffraction**, or **LIED**.

LIED is a relatively novel dynamic imaging technique developed over the last couple of decades and follows the elastic scattering phenomena of the rescattering model. It was first proposed by Zuo et al. in 1996 when they calculated momentum angular distributions of the

photoelectron spectra from ionization of H_2^+ . Since rescattering occurs on an optical-cycle timescale, it theoretically can achieve subcycle temporal resolutions, with the worst case scenario being the pulse duration itself. Additionally, the generation of the electron from the target itself makes table-top laser sources excellent candidates to perform experiments using a self-imaging approach. This is in contrast to Ultrafast Electron Diffraction, or UED, where electron pulses are generated by femtosecond laser sources from photocathodes and accelerated to tens or hundreds of keVs^{30 31}. The studies on trifluoroiodomethane, diiodotetrafluoroethane and aluminium mentioned in Chapter 1 were conducted using the UED technique^{32 33}. These experiments along with others have greatly enhanced our knowledge of structural changes of molecules on the atomic level in chemical reactions.

The advancements of temporal resolution in LIED and UED rely on the development of the laser compression technique. The development of femtosecond optical pulses allowed for the initial generation of electron ultrashort pulses with pulse durations on the picosecond level in UED. This resolution was brought down further to sub-picosecond levels by Siwick et al. in their study of the structural evolution of aluminum³⁴. The main limitation comes from repulsion between electrons in a single pulse, known as space charge effects, but pulsed relativistic electrons, with energies on the order of MeV, have been proven to reduce the duration to sub-100 fs and mitigate these effects^{35 36}.

The first experimental test of LIED on a dynamic system was performed in 2012. Prof. Cosmin Blaga field ionized oxygen and nitrogen molecules using three different wavelengths. Using the self-diffraction method, he extracted nitrogen's equilibrium bond length and measured a 0.1 Å displacement in oxygen's bond length over a period of 5 fs³⁷. This experiment validated LIED's ability to achieve sub-Angstrom spatial resolutions and femtosecond temporal resolution, buttressing its potential as a reliable ultrafast probe.

The PES in Figure 2.4 displays those electrons detected at 0° with respect to the laser polarization. Collecting electrons at all detected angles using LIED creates a 2D diffraction pattern known as a Photoelectron Angular Distribution (PAD) in detected momentum space. Figure 2.7 shows a general schematic for the LIED technique along with the resultant PAD collected for Argon at 2 micron³³⁸. These have been used to extract experimental elastic

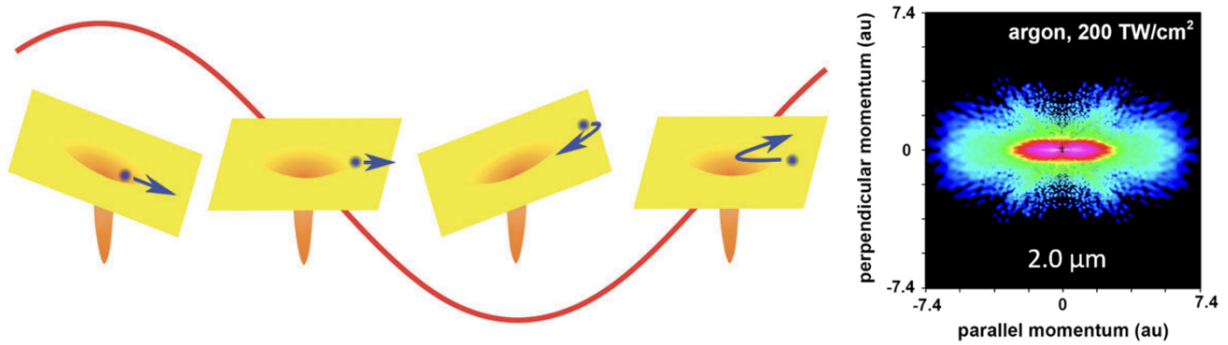


Figure 2.7: General Schematic of the LIED technique and the Resultant 2D Diffraction Pattern. The LIED imaging technique uses the target’s own electrons to probe its structure and is based on the rescattering model. Here the combined influence of the ion and the electric field (red) at different times are shown by the yellow potential surfaces. From left to right: the field ionizes an electron (blue ball). The electron is driven away from its parent ion by the field. Once the direction of the field changes, the electron is driven back to the target. Finally, the ionized electron rescatters off the ion and eventually hits a detector at some angle with a final detected kinetic energy. Collecting electrons at all detected angles creates the 2D diffraction pattern, or PAD, seen on the right in detected momentum space. The PAD in this figure was experimentally collected for Argon in the tunneling regime at 2 micron by Prof. Cosmin Blaga using linearly polarized light. The x axis is detected momentum parallel to the light polarization and the y axis is detected momentum perpendicular to the light polarization. Image credit goes to Prof. C.D. Lin, Dr. Junliang Xu and Prof. Cosmin Blaga³³⁸.

differential cross sections for the study of atomic and molecular structure. Further details of cross section extraction will be discussed in Chapters 3, 4 and 5 of this dissertation.

So far, the discussions on elastic scattering and LIED have been limited to the tunneling regime. Changing the wavelength of light in our experiment to 790 nm and dropping the peak intensity to 100 TW/cm² puts the ionized electron’s average quiver energy in the field at approximately 6 eV. This places us within the multiphoton regime. Figure 2.8 shows an experimentally collected PES by Prof. Cosmin Blaga at the Ohio State University using the aforementioned field parameters. This PES is known as an Above Threshold Ionization (ATI) spectrum. As mentioned in Section 2.1, ATI occurs when an atom absorbs more photons than are necessary to overcome the ionization potential. The individual peaks in the spectra are separated by one photon, as predicted from Equation 2.21 in the Strong Field Approximation. ATI was first demonstrated experimentally by Prof. Pierre Agostini

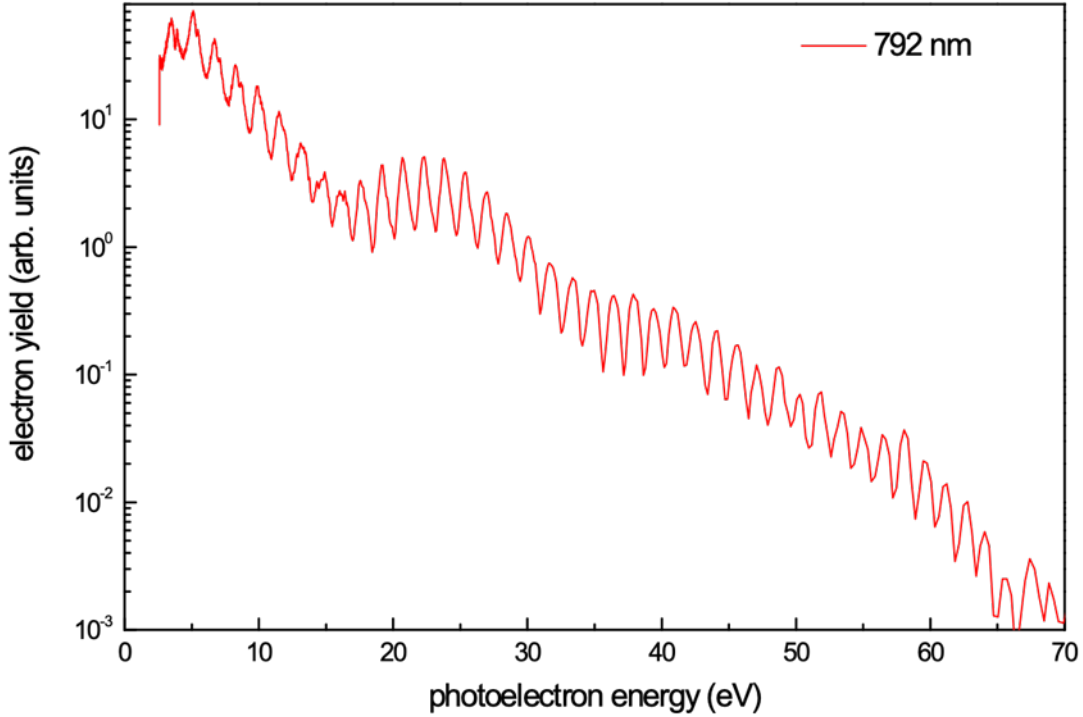


Figure 2.8: **Above Threshold Ionization (ATI) Spectrum.** Experimental ATI Spectrum collected by Prof. Cosmin Blaga at the Ohio State University for Argon at 792 nm with a peak intensity of $\approx 107 \text{ TW/cm}^2$. The quiver energy for the electron in the field is small, around 6 eV. Each peak in the spectrum is separated by one photon. An unexplained enhancement in electron yield is observed at around 24 eV, contrasting from the typical flat plateau and deviating from standard theoretical ionization rate models. Image credit goes to Prof. Cosmin Blaga.

in 1979 when he impinged an Nd:glass laser (photon energy of 1.17 eV) onto xenon³⁹. His photoelectron spectrum revealed two peaks separated by the photon energy of the laser.

It is important to note the stark difference in structure between the PES collected at 2 micron and the ATI spectra collected at 790 nm. The electron yield at 2 micron decreases in magnitude between 0 to $2 U_p$, plateaus between 2 to $7 U_p$, and again decreases between 8 to $10 U_p$. This behavior is standard and follows theoretical ionization rate models. However, the ATI spectra for 790 nm shows an enhancement in electron yield at approximately 24 eV, suggesting a departure from standard models and expectations. What causes this

enhancement is an unsolved mystery, and many have tried to understand its origins over the last 30 years. The motivation for the discovery of our new probing tool and the first project of this dissertation originally stemmed from a curiosity to understand this enhancement in electron yield. What follows is a timeline of key findings made in previous works.

1994: Paulus et al. published a paper titled *Plateau in Above Threshold Ionization Spectra*⁴⁰. In it they collected ATI spectra of noble gases at an intensity of 10^{14} W/cm², shown in Figure 2.9a. The key finding was the existence of an enhancement in the plateau region. They then focused on Argon specifically and collected ATI spectra at different peak intensities, shown in Figure 2.9b. The enhancement was well-resolved only at certain intensities and it was hypothesized as a single-electron effect.

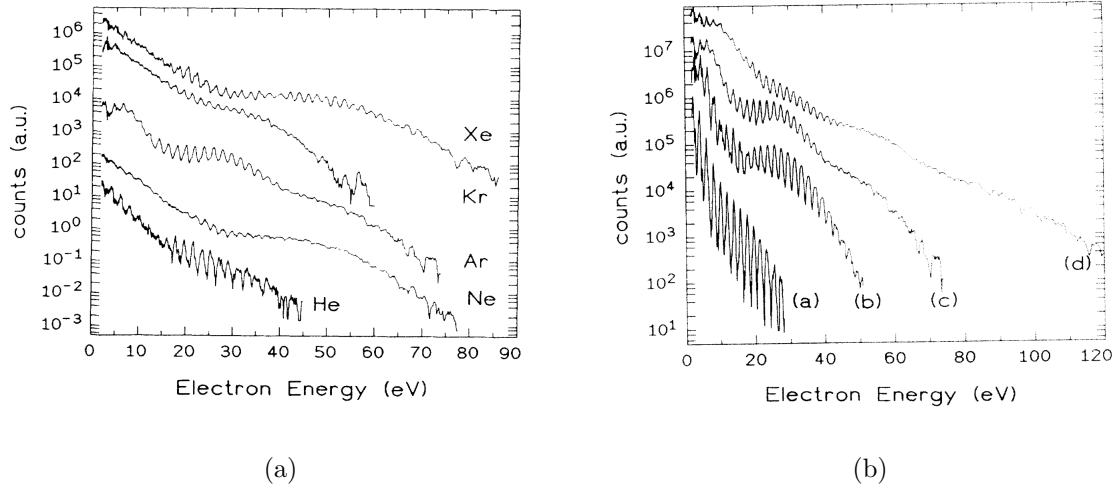


Figure 2.9: **Photoelectron spectra in noble gases and the discovery of the rescattering plateau.** a) ATI spectra collected for Helium, Neon, Argon, Krypton and Xenon at 10^{14} W/cm². Enhancement in electron yield observed in plateau region. b) ATI spectra collected for Argon at different intensities. From a) to d): 6×10^{13} W/cm², 1.2×10^{14} W/cm², 2.4×10^{14} W/cm², and 4.4×10^{14} W/cm². The enhancement is well-resolved only at certain intensities. Image credit goes to Prof. G.G. Paulus⁴⁰.

1997: Hansch et al. published a paper called *Resonant hot-electron production in above-threshold ionization* where they collected an ATI spectra of Xenon with 800 nm light at 10^{14} W/cm² and show a clear enhancement between 30-50 eV (Figure 2.10a)⁴¹. They then

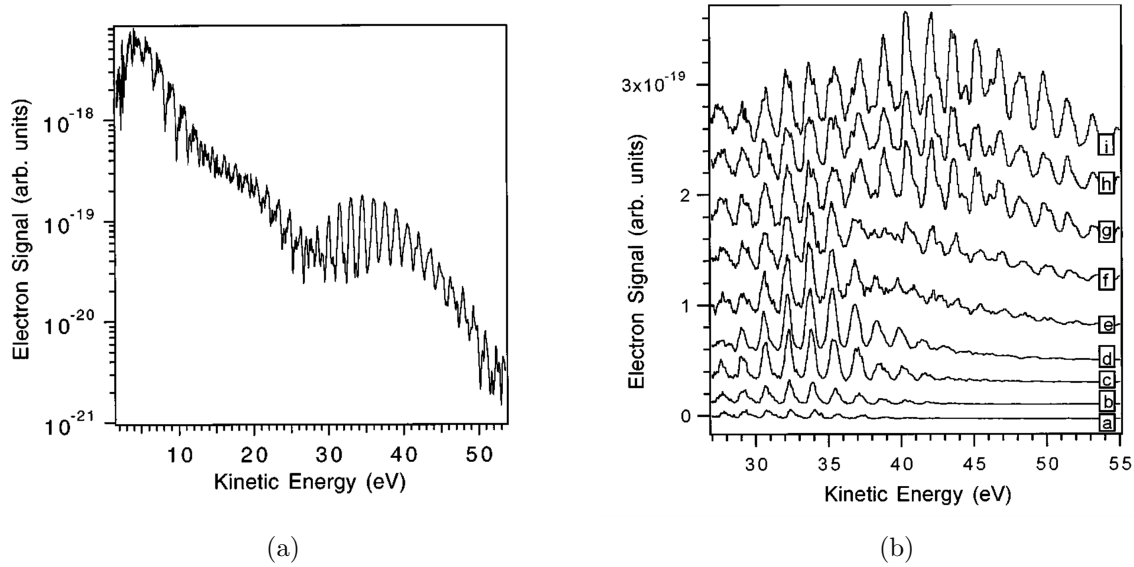


Figure 2.10: **Photoelectron spectrum of Xenon and an Experimental Demonstration of ATI Comb Invariance to Peak Intensity** a) ATI spectrum of Xenon at 800 nm with a peak intensity of $3 \times 10^{14} \text{ W/cm}^2$. Clear enhancement seen between 30-50 eV. b) ATI spectra collected of Xenon from a) 1.26 to i) $1.88 \times 10^{14} \text{ W/cm}^2$. The individual peaks do not shift as a function of energy and intensity. Combs of ATI peaks become well resolved between 40-45 eV as the peak intensity increases. Image credit goes to Prof. P Hansch⁴¹.

collected ATI spectra at varying intensities and found that individual ATI peaks do not shift in energy (Figure 2.10b). Instead, combs of ATI peaks become well resolved after a certain intensity. They hypothesized a resonant process must drive this enhancement.

1997: In the same year as Hansch, Hertlein et al. published a paper titled *Evidence for resonant effects in high-order ATI spectra*⁴². They collected ATI spectra of Argon at different intensities and noticed that the comb of individual peaks are actually made of smaller, triplet sub-peaks which do no shift in energy as a function of intensity, shown in Figure 2.11. The enhancement was hypothesized to be a single electron effect (in agreement with Paulus) and involved resonances embedded in continuum or bound states.

1999: Nandor et al. published a theoretical paper titled *Detailed comparison of above-threshold-ionization spectra from accurate numerical integrations and high-resolution mea-*

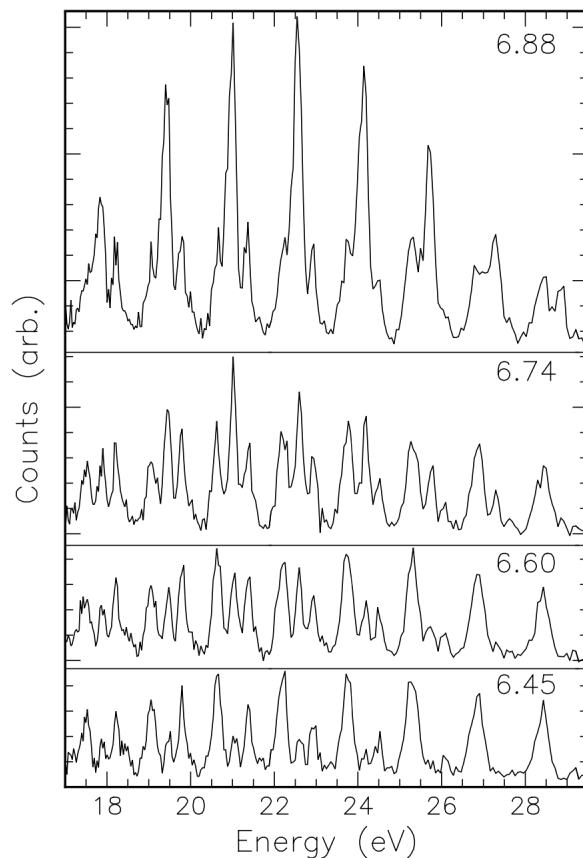


Figure 2.11: **ATI Spectrum of Argon and the Discovery of smaller, triplet sub-peaks.** ATI spectra of Argon between 6.45 and 6.88×10^{13} W/cm². The individual peaks are made of small, triplet sub-peaks which do not shift in energy as a function of intensity. Image credit goes to Prof. Marcus P. Hertlein⁴².

surements. They compared experimental Argon ATI spectra collected at 800 nm with theoretical spectra calculated using numerical Time Dependent Schrödinger Equation (TDSE) code under the Single Active Electron (SAE) Approximation, which considers only one active electron interacting with the field. Figure 2.12 shows experimental and theoretical PES for a given intensity. From this study they concluded that “the overwhelming majority of structures and features in the ATI photoelectron spectra of argon can be well modeled by a single-electron calculation”⁴³.

2001: Paulus et al. returned to publish *Channel-closing-induced resonances in the above-threshold ionization plateau*⁴⁴. Argon ATI spectra were collected at varying intensities and it

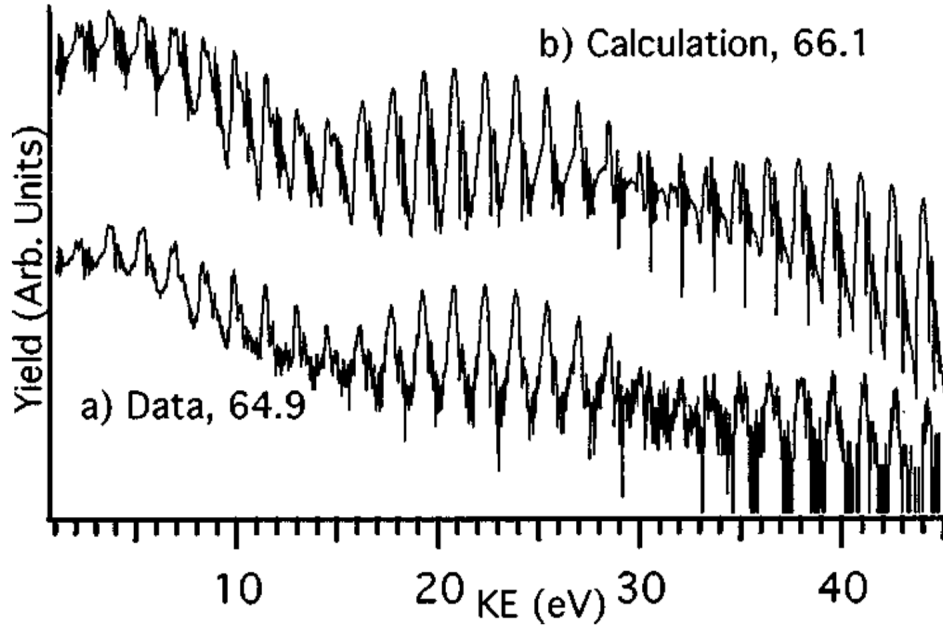


Figure 2.12: **Comparison Between Theoretically Generated and Experimentally Collected Photoelectron Spectrum of Argon.** a) Theoretical Argon ATI spectra obtained with numerical TDSE code under the SAE approximation at 66.1 TW/cm² b) Experimentally measured Argon ATI spectra using an 800 nm, 120 fs pulse at a peak intensity of 64.9 TW/cm². We note the excellent agreement between theory and experiment. Image credit goes to Prof. M.J. Nandor⁴³.

was concluded the enhancement “turns on” at a very specific intensity, known as the *leading* intensity, as seen in Figure 2.13. Paulus proposed a channel-closing condition to explain this phenomena. Using a zero-range potential which supports only one bound state with binding energy $E_{0,zr}$, the condition claims when the continuum threshold (shifted by U_p) is multi-photon resonant with the bound state, a channel closure occurs. This is mathematically given by: $E_{0,zr} + U_p = n\hbar\omega$, where ω is the frequency of light and n is the number of photons. Since $U_p \propto I$, the n -th channel closure corresponds to a specific intensity.

2003: Wassaf et al. published *Roles of resonances and recollisions in strong-field atomic phenomena: Above-threshold ionization*⁴⁵. Their goal was to understand the mechanism behind the enhancement with short and long range potentials using numerical TDSE code. They concluded multiphoton resonances and multiple electron recollisions caused the en-

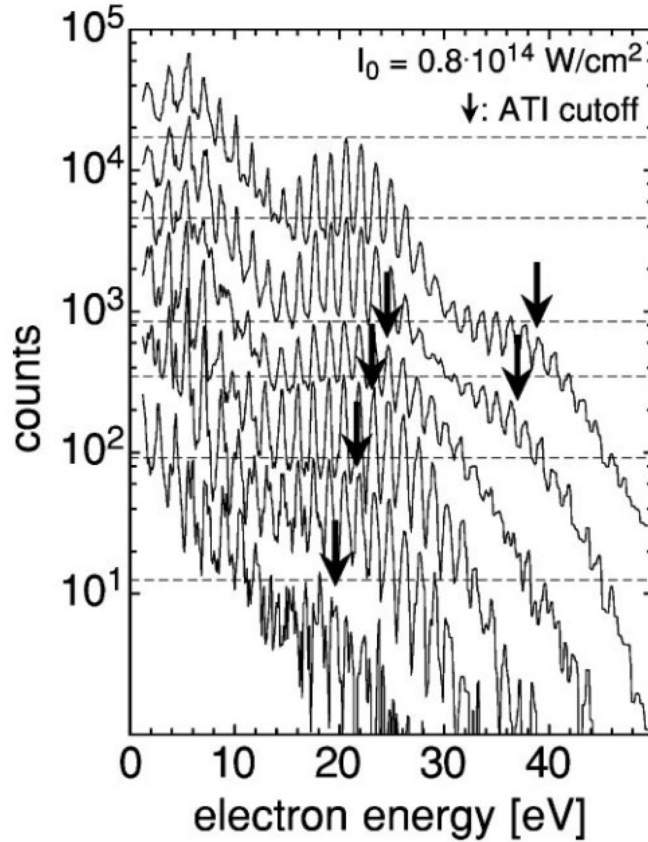


Figure 2.13: **Photoelectron Spectrum of Argon Collected at Varying Intensities and the Discovery of the Leading Intensity.** Argon ATI spectra collected between $0.5I_0$ (bottom) and $1.0I_0$ (top), where $I_0 = 8 \times 10^{13} \text{ W/cm}^2$. The horizontal dashed lines marks the maximum of the plateau for each spectra. The black arrows indicate the cutoff positions. The enhancement “turns on” at a very specific intensity, called the leading intensity, calculated from Paulus’ proposed channel-closing mechanism. Image credit goes to Prof. G.G. Paulus⁴⁴.

hancement with short-range potentials, but newly discovered metastable (long-living) Light Induced States (LIS) were responsible with long-range potentials. Details of the resonances and LIS are unnecessary for now. The point is recognizing the disagreement between Paulus and Wassaf over the the driving mechanism.

2009: Frolov et al. published *Analytic formulas for above-threshold ionization or detachment plateau spectra*⁴⁶. They derived closed-form analytic formulas for Above Threshold

Detachment (ATD) emission rates and electronic wavepacket assuming a short range potential which supports one weakly bound state. The concept behind ATD is the same as ATI except the starting point is a negative ion. These formulas helped explain qualitative features in ATD spectra and provided quantum justification for the classical rescattering model. They then were generalized to neutral atoms. The resulting Coloumb-modified formulas give results that agree very well with the high energy region of hydrogen ATI spectra obtained numerically from TDSE. This work provides analytical insight into how ATD and ATI rates depend on laser field parameters and how rescattering mechanisms play a role in ATI phenomena such as the enhancement.

The timeline presented serves both as an homage to those who dedicated their research towards understanding the enhancement and a summary on important discoveries and theories made. The phenomena is well-explained as a single electron effect, occurs at a special intensity, seen in multiple targets (atoms and molecules alike), does not shift in energy as a function of intensity, and agrees well with numerical TDSE calculations. However, the cause is unclear and its potential applications remain a mystery.

The foundations of strong field ionization established in this chapter are used abundantly in both projects presented in this dissertation. As mentioned previously, the first project aims to build upon the research done for understanding the enhancement. We believe the key to unlocking its driving mechanism lies in understanding the returning electronic wavepacket's behavior close to the ionic core. Therefore, instead of looking at the elastic scattering channel, we look at the *recombination* channel within the Three Step Model. This allows us to track the electron at time it *returned* to the parent ion through the generation of theoretical HHG spectra called Husimi plots. I should remind you, however, that we are ultrafast experimental physicists. We are always on the search for new probing tools which would aid us in extracting atomic and molecular structure. As our research unfolded, some of the astonishing properties of the electronic wavepacket shifted our focus from not only understanding the enhancement's driving mechanism but its application as a reliable ultrafast probing tool.

The second project in this dissertation uses the LIED imaging technique to achieve two experimental goals. The first was to further investigate the enhancement, specifically its dependence on pulse duration. The second aimed for the experimental observation of the enhancement in more complex molecules. This involves collecting PES along the laser polarization for each target with *low-energy* (tens of eV) rescattered electrons, placing us in the multiphoton regime. This project also focused on continuing to establish LIED as a reliable imaging technique. PADs of each hydrocarbon were collected and used to extract and analyze preliminary experimental Elastic Differential Cross Sections.

Before we jump into these projects and discuss our fascinating results, let's first take a look at the theoretical and experimental tools which aided us in our efforts.

Chapter 3

Experimental and Theoretical Tools

Physics is an observational science. The last several decades have seen the development of both theoretical and experimental tools for the observation and understanding of atomic and molecular dynamics. The first project in this dissertation involves experimentally collecting ATI spectra to observe the $6U_p$ enhancement in various targets. Additionally, theoretical high harmonic generation (HHG) spectra are generated to understand the driving mechanism behind the enhancement. The second project involves further understanding of the enhancement and the collection of photoelectron angular distributions. This chapter presents in detail experimental apparatus and theoretical tools used to acquire and analyze the results of this thesis.

3.1 Experimental Tools

Characterizing an ultrafast pulses' amplitude and phase is crucial when capturing atomic and molecular dynamics. Changes in pulse duration and shape can alter accurate measurement of chemical reactions which occur on such short timescales. This has lead to the development of techniques which measure the spectral and temporal profile of pulses. Before diving into the laser sources used to conduct experiments in the JRM Lab, we will first discuss one such technique known as Frequency-resolved Optical Gating (FROG).

3.1.1 Frequency-resolved Optical Gating (FROG)

Pioneered by Rick Trebino's research group at Georgia Institute of Technology, the FROG system is an instrument used to extract the spectral and temporal profile of ultrafast pulses. Specifically, it measures the *spectrogram* of a pulse, or the instantaneous frequency versus time. Theoretically, this instantaneous frequency is acquired through a gate function, $g(t)$, which scans the electric field in time⁴⁷. However, what is this gate function? In order to measure something in time, you need a tool which operates at a *shorter* timescale than the event itself. Therefore, the pulse *itself* is the gate function! Creating a spectrogram involves resolving the gated piece of the pulse.

Fundamentally, FROG is an autocorrelation measurement (the pulse is used to characterize itself). The most common FROG technique is known as Second Harmonic Generation (SHG) FROG, seen in Figure 3.1⁴⁸.

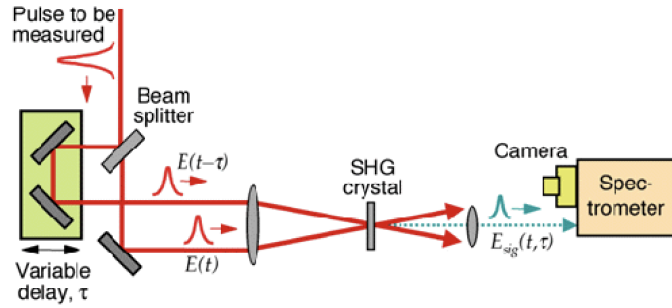


Figure 3.1: **Schematic of SHG FROG.** The fundamental beam is split using a beam splitter. A variable delay stage adjusts the time delay, τ between the fundamental beam, $E(t)$ and its replica $E(t - \tau)$. A lens focuses both beams down into an SHG crystal. When the two fields temporally overlap, $E_{sig}(t, \tau)$ is generated at double the frequency of the fundamental. This signal is then fed into a spectrometer. Image credit to Swamp Optics.⁴⁷

First, the fundamental beam, $E(t)$ is split using a beam splitter, and a delay stage controls the time delay, τ , between $E(t)$ and its replica, $E(t - \tau)$. Next, a lens focuses the two beams and are impinged on an SHG crystal. If the two fields temporally overlap in time, second harmonic signal, or $E_{sig}(t) = E(t)E(t - \tau)$, is generated (half the wavelength of the fundamental beam). A spectrometer measures this resultant signal at each time delay. Finally, a spectrogram is generated displaying the instantaneous frequency and intensity as

a function of time.

Retrieving the intensity and phase of the pulse from the spectrogram is known as the *two-dimensional phase retrieval problem*. Practically speaking, this is done using commercial software for the FROG. It first picks an initial $E_{sig}(t)$ and subsequently iterates until the two following constraints are satisfied⁴⁸:

$$E_{sig}(t, \tau) = E(t)E(t - \tau) \quad (3.1a)$$

$$I_{FROG}(\omega, t) = \left| \int_{-\infty}^{\infty} E_{sig}(t, \tau) \exp(-i\omega t) dt \right|^2 \quad (3.1b)$$

where $I_{FROG}(\omega, t)$ is the FROG signal trace. 3.1a places a theoretical constraint on the actual mathematical form of $E_{sig}(t, \tau)$, whereas 3.1b places an experimental constraint from the data collected through the spectrometer. An example of the final retrieved FROG trace can be seen in Figure 3.2a. Taking a horizontal lineout results in Figure 3.2b, or an intensity versus delay plot, where the FWHM of the resultant spectrum provides the pulse duration.

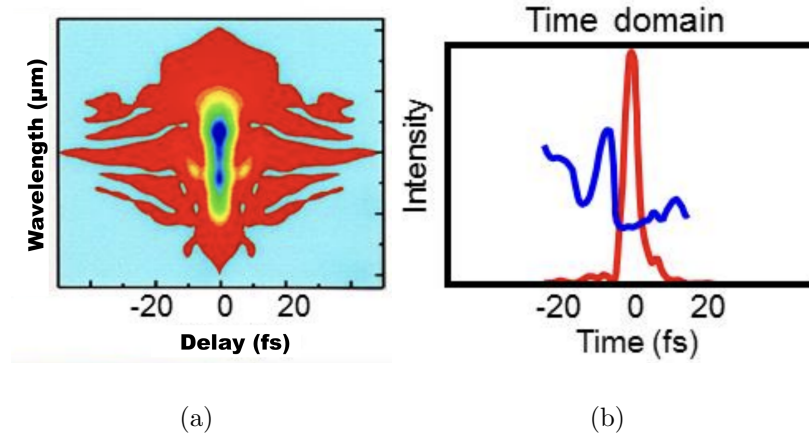


Figure 3.2: SHG FROG Trace and Resultant Spectrum in Time Domain. a) FROG trace generated from scanning $E_{sig}(t, \tau)$ across various time delay points and collecting the signal through a spectrometer. The FROG software reconstructs the intensity and phase of the pulse by placing constraints on $E_{sig}(t, \tau)$. b) Spectrum in the time domain (red) generated by taking a horizontal lineout of the retrieved FROG trace. Phase versus time plotted in blue. Image credit to Swamp Optics.⁴⁷

3.1.2 Laser Sources

To conduct experiments at strong-field intensities, ultrashort pulse energies are increased through an amplification process. However, the peak amplified energies can cause non-linear distortions and potentially damage crystals and other optical elements within the amplifier. This can be avoided, thankfully, by utilizing the Chirped Pulse Amplification technique, or CPA. Prof. Donna Strickland and Prof. Gérard Mourou were awarded the Nobel Prize in 2018 for their development of CPA. It consists of three main steps: stretching, amplification, and compression. Figure 3.3 shows a general schematic of CPA. First, a seeded output pulse (nJ energy pulses and fs pulse duration) from an oscillator is stretched in time, usually to picoseconds, using a grating-based stretcher. This new, stretched pulse is then passed through a multi-pass amplifier, which uses an external pump laser and a crystal (also known as a *gain medium*) to increase the pulse energy to millijoules (mJ), pass after pass, of the seeded, stretched pulse. Finally, the stretched, amplified pulse passes through a grating-based compressor, which shortens the pulse duration to femtoseconds. Both laser sources used in this dissertation utilize CPA.

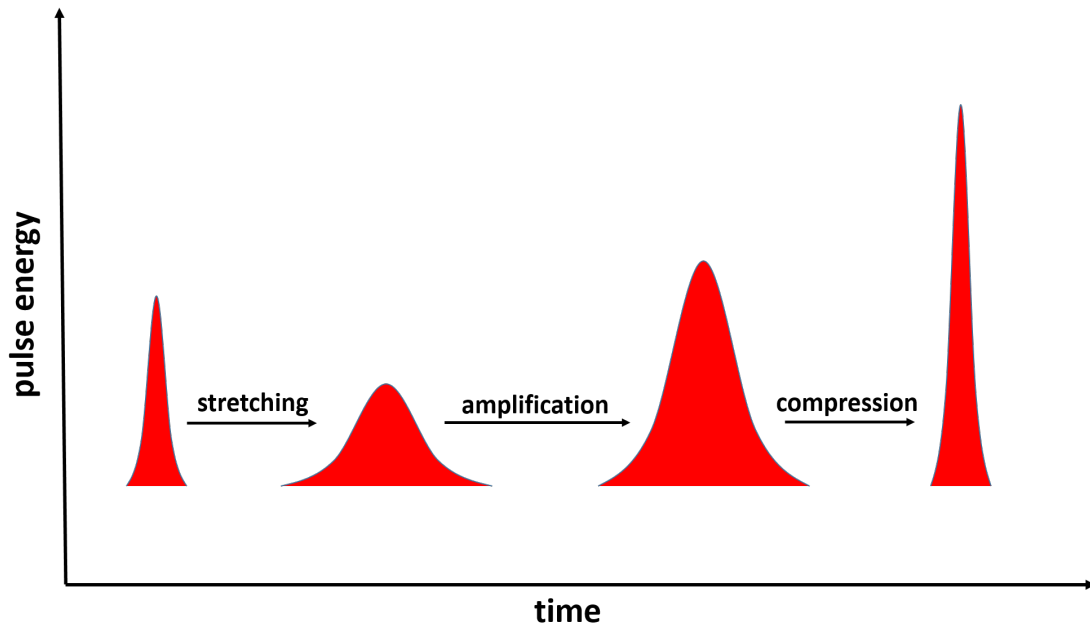


Figure 3.3: **General Chirped Pulse Amplification Schematic.** Schematic displaying the overall temporal and spatial evolution of the original seeded pulse from the oscillator from CPA. The pulse is stretched in time, amplified to high pulse energies and then compressed.

FLAME

An experimental PAD of argon presented in this dissertation was collected in FLAME, or Femtosecond LAsEr for Multicolor Experiments, within the James R. Macdonald Laboratory at Kansas State University. It consists of a Ti:Sapphire laser with a central wavelength of 805 nm (bandwidth of 60 nm), pulse energies up to 5 mJ, and a typical pulse duration of 24 fs, at a 3 kHz repetition rate. The laser is designed by Coherent, Inc. and is coupled with an optical parametric amplifier (OPA), which produces a broad spectrum of wavelengths.⁴⁹

The Coherent Vitara oscillator is used in FLAME which produces an 80 MHz frequency pulse train with an output power of 580 mW. It is pumped by a Verdi G-series green pump operating in continuous wavelength (CW) mode of 532 nm with an output power of 5 W. The output beam is then stretched in time beyond 200 ps and then sent through two amplification stages.

In FLAME, 15 passes are used to amplify the seeded pulse using a Coherent Revolution diode pumped Neodymium-doped Yttrium Lithium Fluoride (Nd:YLF) pump laser operating at 527 nm with an output power of 36 W. The multi-pass output is then subsequently fed into a single-pass amplifier (SPA) which utilizes the same Coherent pump laser. The amplified pulse is finally split and sent to an internal (7.5-30 fs) and external compressor (7.5-30 fs) for the high energy traveling-wave optical parametric amplifier of white light continuum (HE-TOPAS) and an 800 nm source with a peak power of 15.1 W⁵⁰. The 800 nm source was used to collect a PAD of argon.

KONZA

PADs of argon, methane, ethane, ethylene and acetylene were collected using Tangor 300 (designed by Amplitude Laser) within the KONZA laser room located at Kansas State University. It consists of a Yb:YAG (Ytterbium Doped Yttrium Aluminum Garnet) fiber laser oscillator operating at 40 MHz, producing nanojoule pulse energies and lases at 1030 nm⁵¹. This output is then stretched to hundreds of picoseconds using a fiber Bragg grating and amplified to microjoule pulse energies using a fiber amplifier and Yb rod amplifier.

Finally, after the beam is expanded through a telescope, it is further amplified with an Innoslab amplifier, producing pulse energies up to 3 mJ at a repetition rate of 100 kHz, and compressed with gratings to 450 fs⁵¹. To verify specs, the beam was expanded using a -75 mm diverging lens and its power stability was measured over 2 hours using a Gentec-EO power meter (UP55M-500W-H12-D0). The average power was 330 W with an RMS error of 0.0267%. The FROG trace seen in Figure 3.4 shows a pulse duration of approximately 450 fs with the compressor at a position of 22846 micrometers.

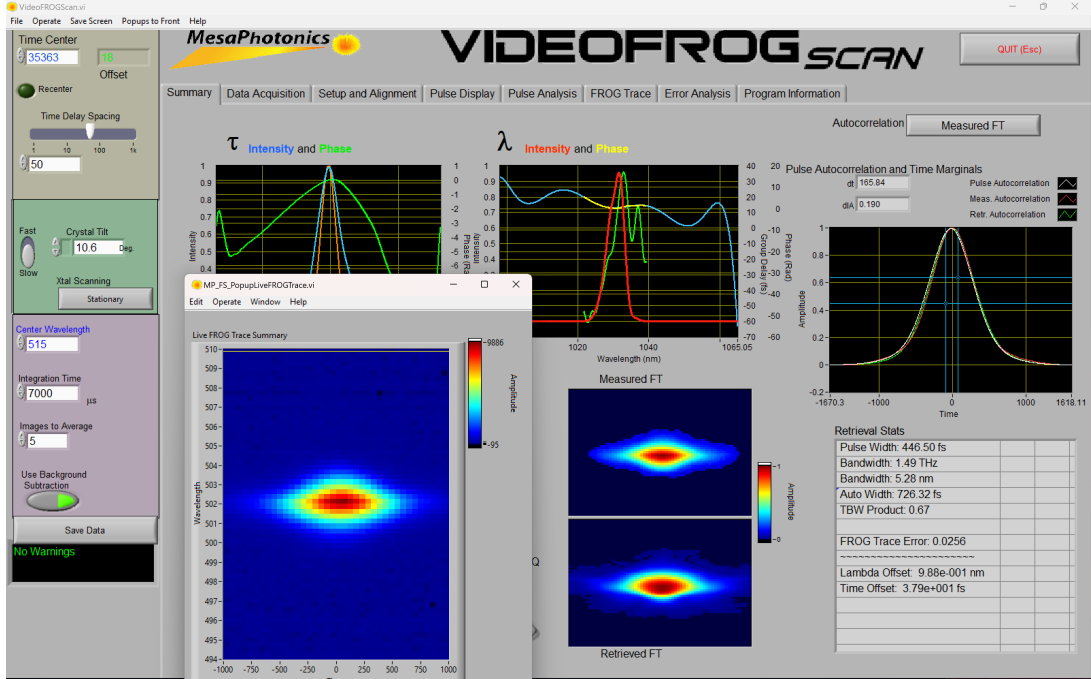


Figure 3.4: **Tangor FROG trace.** FROG trace collected for the output of the Tangor 300 using the SHG FROG technique. The Tangor operated at full power and the majority of beam was dumped using a 99% reflection, 1% transmission output coupler from Eksma optics. The transmitted beam was used to FROG. At full power, transmission was 4 W. Our group measured a pulse duration of approximately 450 fs.

Finally, the beam profile and spectrum, seen in Figure 3.5, was captured using a DataRay WinCamD-LCM detector and Ocean Optics Miniature Spectrometer, respectively. The DataRay software measured a beam diameter of approximately 5 mm.

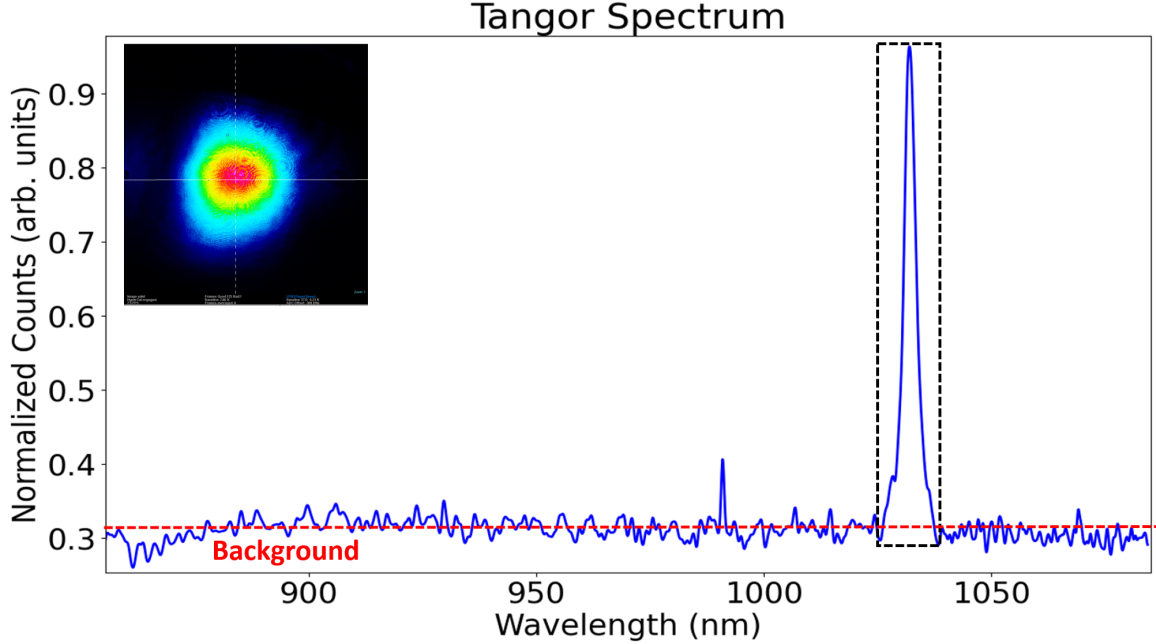


Figure 3.5: **Tangor Spectrum and Beam Profile.** Spectrum of Tangor 300 captured with a Ocean Optics Miniature Spectrometer. The spectrum measures a central wavelength of approximately 1030 nm (black dashed box). The beam profile in the top left was captured using a DataRay WinCamD-LCM detector before the beam was focused.

The RMS error for the beam’s power was measured to be approximately 1% after propagating through the time of flight chamber (discussed next) using a fast photodiode with a 1 ns rise time and the RIGOL Ultravision II oscilloscope which supports 10 GSa/s sampling and a frontend bandwidth of 4 GHz. The beam was transported to the time of flight chamber using 45° 2 inch (035-1030) and 0° 1 inch (035-1030-i0) 1030 nm mirrors from Eksma Optics. The main advantage of using the Tangor 300 comes from its high repetition rate, allowing for faster collection rates of experimental photoangular distributions.

3.1.3 Double-sided Time of Flight (DTOF) Chamber

The DTOF chamber was used to collect PADs of hydrocarbons. Built by Dr. Sajed Hosseini-Zavareh at Kansas State University, it is one meter in length consisting of two MCP detectors on either side, as seen in Figure 3.6⁵¹. The main advantage of using the DTOF spectrometer is its high energy resolution and its broad dynamic range (5-7 orders of magnitude). Electrons are collected at various angles by rotating the laser polarization with respect to the TOF

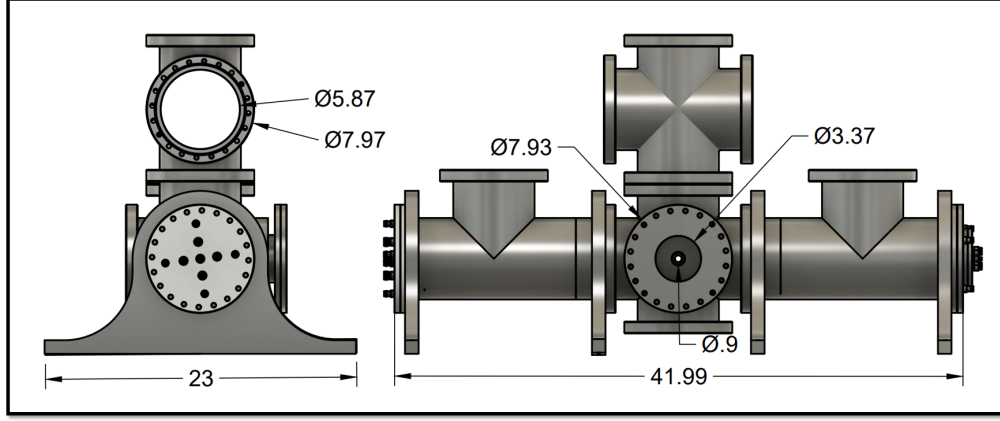


Figure 3.6: **Exterior of DTOF.** All numbers in this figure are in inches. Schematic of the DTOF skeleton. It is approximately 42 inches in length with two MCP detectors mounted on the left and right side. It is constructed with stainless steel flanges with an 8 inch outer diameter and a 6 inch inner diameter. There is also a 1 inch diameter and 1 mm thick recessed calcium fluoride input window from Newlight Photonics. The distance between the calcium fluoride window and the center of interaction is 3.5 inches. The DTOF is mounted on a cart, making it a portable experimental setup. Image credit: Dr. Sajed Hosseini-Zavareh⁵¹.

axis. The DTOF can also switch between ion and electron mode for the collection of both mass spectra and photoelectron spectra. The rest of this section provides details on the multianode MCP detector, field plates and data acquisition system used to collect data.

Multianode Detector

The multianode detector, designed by Dr. Sajed Hosseini-Zavareh, was used for the collection of photoelectron and mass spectra. It is formed by a dual Microchannel Plate (MCP) stack mounted in a Chevron configuration. MCPs are arrays which consist of 10^4 to 10^7 electron multipliers with channel diameters in the range of 10-100 μm ⁵². A typical MCP is shown in Figure 3.7.

An electron entering the MCP strikes the channel wall, resulting in a cascade of electrons from the applied electric field. MCPs can lead to electron multiplication factors of 10^4 to 10^7 ⁵². The overall signal enhancement depends on the applied electric field strength and the geometry of the MCP. Usually, a single anode collects the electron shower from the MCP. However, our home built multi-anode detector consists of five coaxial anodes each with a diameter of 12 mm given a 100 mm MCP plate, shown in Figure 3.8. Each anode is

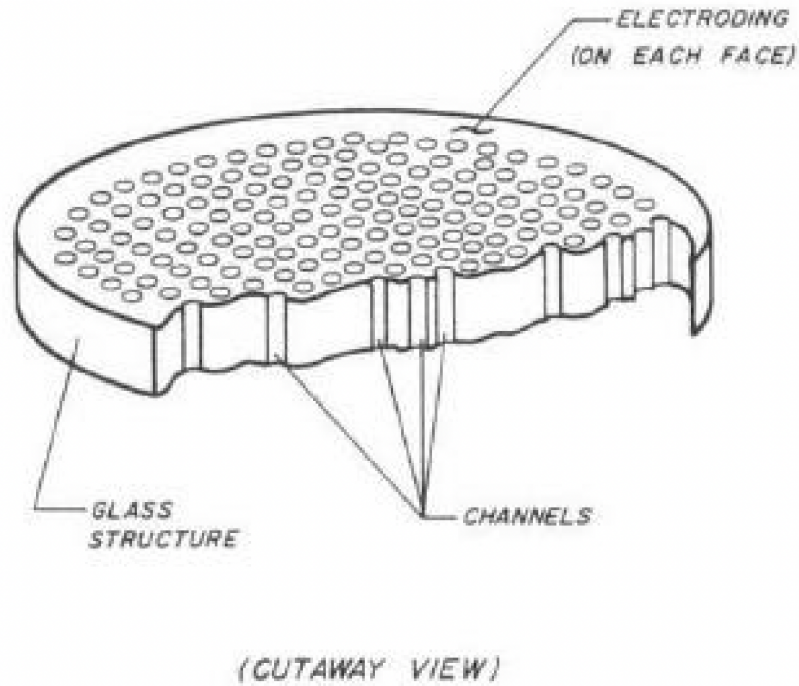


Figure 3.7: **Microchannel Plate (MCP)**. MCPs are arrays which consist of 10^4 to 10^7 electron multipliers with channel diameters in the range of 10-100 μm . They can lead to electron multiplication factors of 10^4 to 10^7 . Image credit to Dr. Joseph Wiza⁵².

separated by 1.25 inches and are located 17.6 inches from the center of interaction⁵¹. Simple trigonometry shows the anodes are separated by 4° . To avoid interference and overlap of detection regions between different anodes, a stainless steel mask is placed between the end of the MCP stack and the anodes. The main advantage of the multianode detector is its simultaneous detection of electrons at different polarization angles, expediting the data collection process. It can also switch between ion and electron mode by simply adjusting the bias voltage settings applied to the stack up to 2 kV using an Ortec 556 power supply⁵². Voltage of 2 kV is applied to the stack in electron mode and a voltage of -2 kV is applied to the stack in ion mode.

Field Plates and Voltage Optimization

The DTOF spectrometer consists of 6 field plates, seen in Figure 3.9. They are made of paramagnetic molybdenum and sprayed by Aerodag (Aerodag 16058) to create a conductive

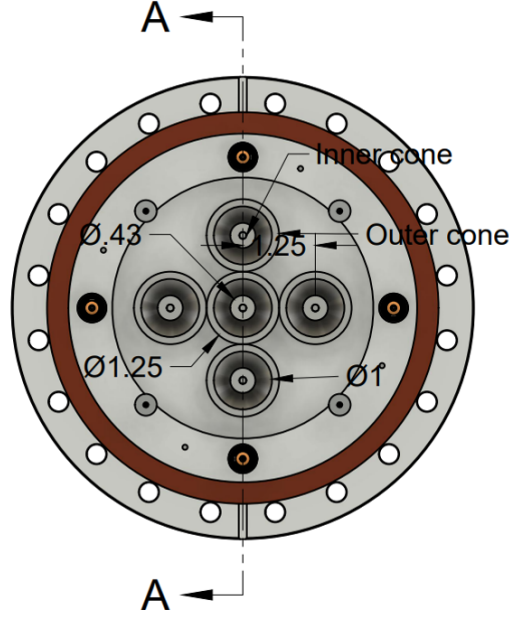


Figure 3.8: **Multianode Detector.** Multianode detector built by Dr. Sajed Hosseini-Zavareh. It consists of five coaxial anodes each with a diameter of 12 mm given a 100 mm MCP plate. Each anode is separated by 1.25 inches and are located 17.6 inches from the center of interaction, separating each anode by 4° . Image credit: Dr. Sajed Hosseini-Zavareh⁵¹.

graphite layer. This removes any patch effects, or effects which cause variations in the electric fields which alter the trajectory of low energy electrons. The distance between plates 3 and 4, called the extractor and repeller, respectively, is 0.75 inches. The alumina spacers (Kimball Physics AL2O3-SP-C-250) separating individual plates are each 0.25 inches. The field plates are grounded in electron mode due to the electron's higher charge-to-mass ratio than ions. However, in ion mode, a voltage V_1 is applied to plate 4 and a voltage $V_2 < V_1$ is applied to plate 3 while the rest of the field plates are grounded. The electrostatic field created from this voltage differential pushes the ions towards the detector. A voltage divider was connected to the plates to supply different voltages to different plates. It consists of one high voltage input and 6 outputs allowing for individual plate adjustments between 0 and 500 V. The power is supplied by a Tennelec Model TC 952 high voltage power supply. Determining V_1 and V_2 involved collecting TOF spectra of argon for time resolution optimization. The rest of this section details this study. Theoretically speaking, a single field plate could be used to extract ions. However, this would lead to poor resolution due to the spread of the ion's

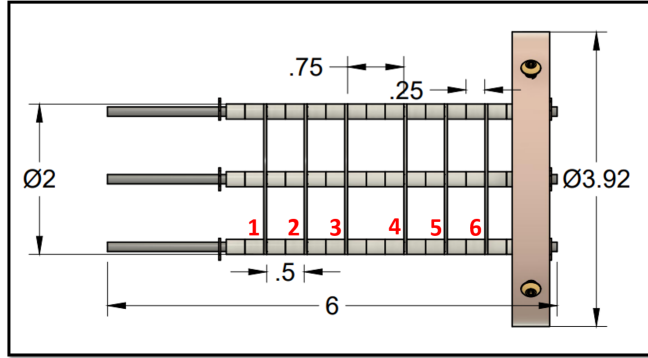


Figure 3.9: **DTOF Field Plates.** The DTOF spectrometer consists of 6 Aerodaged paramagnetic molybdenum field plates. The alumina spacers separating the individual plates are 0.25 inches. The distance between plates 3 and 4, called the extractor and repeller, respectively, is 0.75 inches. Image credit: Dr. Sajed Hosseini-Zavareh⁵¹.

initial space and kinetic energy distributions. Larger $\Delta t/t$ values would risk the overlap of different m/q peaks which correspond to different ions. Wiley and McLaren discovered that adjusting the electric field could compensate for these effects and is known as the Wiley-McLaren condition³⁸. Therefore, mass spectra of argon were collected at various extractor voltages, keeping the repeller voltage the same. The power out of the Tangor 300 was 1 W at a 20 kHz repetition rate and the pressure in the chamber was $\approx 5 \times 10^{-5}$ Torr. The goal was to find the smallest $\Delta t/t$ and identify at which voltage the argon m/q peak best fit a gaussian distribution.

The repeller voltage was set at 400 V while the extractor voltage was adjusted from 200 V - 300 V in steps of 10 V. Figure 3.10 shows raw mass spectra data of argon in time at 200 V, 220 V, 240 V and 300 V. Specifically, it focuses only on argon's peak located at $m/q = 40$. Each spectrum was fit with a Gaussian distribution and $\Delta t/t$ was calculated as the Full-Width Half Maximum (FWHM) divided by the peak position in time. At 200 V, the bump on the right observed in the raw data blue scatter plot indicates a non-satisfaction of the Wiley-McLaren condition. This is also observed at 220 V. At 300 V, despite the good fit, $\Delta t/t = 0.524\%$. A $\Delta t/t$ of 0.346% and best Gaussian fit was observed when the extractor voltage was adjusted to 240 V. So, for all mass spectra collected, the repeller and extractor

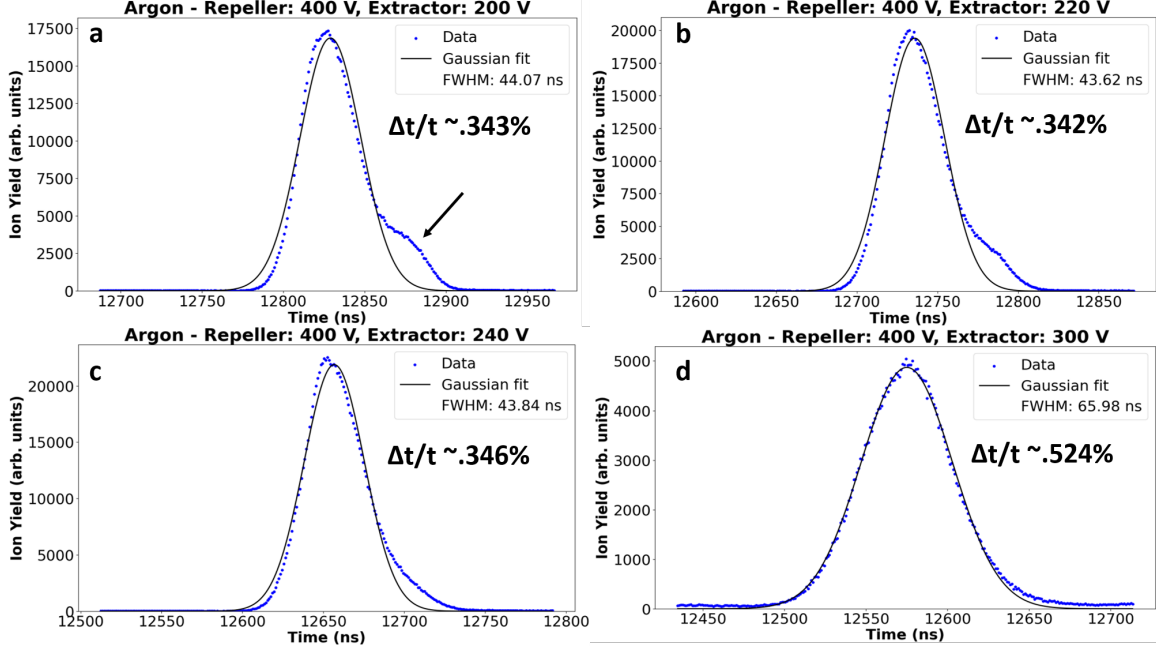


Figure 3.10: Mass Spectra of argon Collected at Varying Extractor Voltages with a Fixed Repeller Voltage. At a power of 1 W at a 20 kHz repetition rate and pressure of $\approx 5e-5$ Torr, mass spectra of argon were collected at extractor voltages of a) 200 V, b) 220 V, c) 240 V and d) 300 V with the repeller voltage fixed at 400 V. Each spectra plots ion yield versus time in ns. The blue scatter plots are raw data. The black plot is the Gaussian fit to the raw data. The unnatural rise in ion yield indicated by the black arrow come indicate a non-satisfaction of the Wiley-McLaren condition. The time resolution, $\Delta t/t$, is defined as the FWHM divided by the peak position in time.

were set to 400 V and 240 V, respectively.

Data Acquisition System (DAQ)

The electronics and software used to measure time of flight can be seen in Figure 3.11. We begin by describing the CAEN (Computer Automated Measurement and Control) V1290N Time-to-Digital Convertor (TDC). It measures the time difference between two events and outputs a digital signal for computer processing. The TDC resolution is set to 100 ps in ion mode and 25 ps in electron mode. This is because ions are heavier and slower moving compared to electrons. The double hit resolution is set to 5 ns to ensure the TDC can distinguish two events closely spaced in time. The 16 channel CAEN V1290N operates in trigger-matching mode, which defines a time window relative to a trigger signal (delayed

photodiode signal). Only events within this window are recorded and assigned times relative to the trigger. This is in contrast to other TDC modes, like Start TDC, which measure event times relative to a common start signal. Trigger matching mode allows for the capture of multiple events in quick succession relative to the trigger without the sequential processing required in other TDC modes. The four parameters used to set up this mode in the V1290N are:

1. **Match window:** The specific time interval in which events are recorded relative to the trigger signal. This window is $51.2 \mu\text{s}$ and $9 \mu\text{s}$ for ion and electron mode, respectively.
2. **Window offset:** A defined shift in time applied to the match window, changing the window's position relative to the trigger signal. The photodiode signal is delayed $+40 \mu\text{s}$ in ion mode and $+4 \mu\text{s}$ in electron mode using a Tennelec TC410A delay generator. The window offset is $-40.2 \mu\text{s}$ and $-4.2 \mu\text{s}$ relative to the trigger, or 200 ns before the photodiode signal. Events recorded at negative time values (photodiode signal defines the origin) are thrown out.
3. **Extra search margin:** Buffer time added to end of the match window allowing for event collection over a larger window. In this case, 25 ns is added on.
4. **Reject margin:** A set time interval defined in which events are ignored before the match window. In this case, the reject margin time interval is set to 25 ns.

Adjusting these settings and providing additional TDC commands are done from a linux computer via the VM-USB VME module. Once the TDC gathers time of flight data, the VM-USB can readout, record and transfer the data over to the computer for analysis. SpecTCL is a visualization software on the linux computer which displays the resultant histogram after data collection. The Readout software, interfaced with the VME module and TDC, records and exports data in binary format for further analysis in Python.

Data acquisition in our experiments uses 6 channels (ch0-ch5) of the TDC. Preprocessing of the raw signal from the MCP detector must be done to feed the correct signals into the TDC. First, a fast photodiode with a 1 ns rise time is activated by the laser. The signal

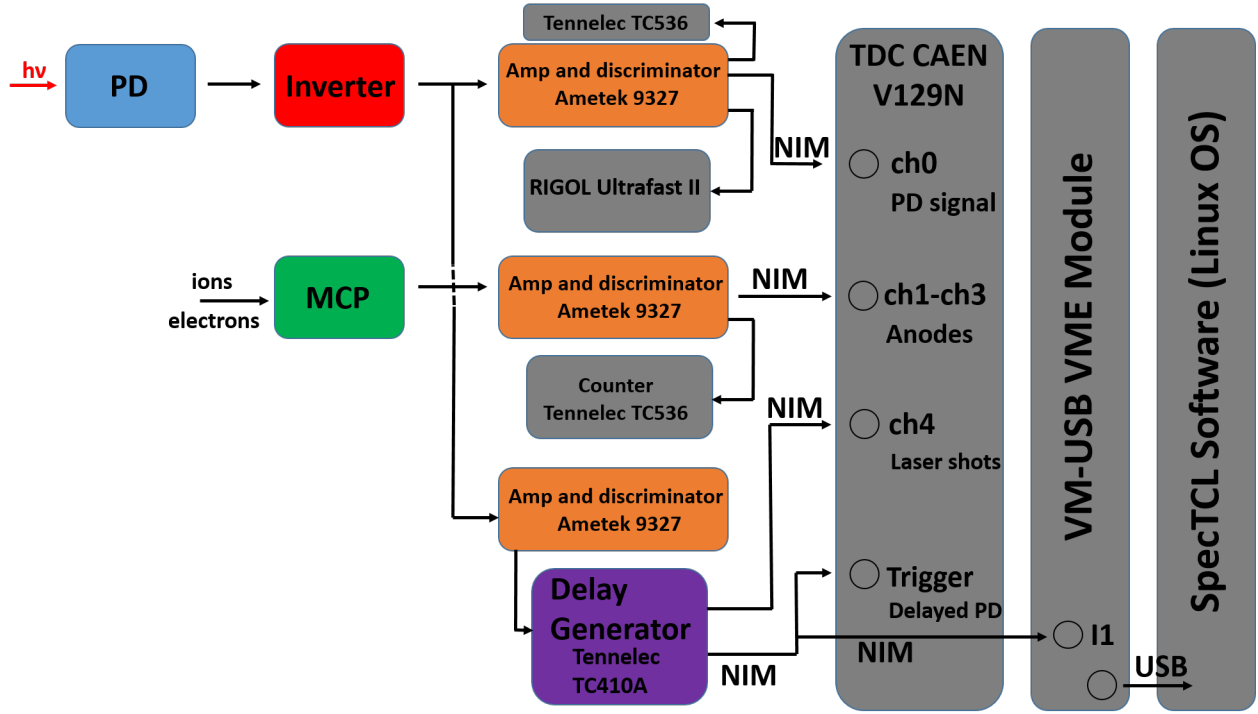


Figure 3.11: **DTOF DAQ Electronics.** The initial signal from a fast photodiode (blue) is inverted (red), split, amplified and discriminated (orange). One of the split signals is directed to ch0 on the TDC, a RIGOL Ultrafast II oscilloscope and a Tennelec 536 counter. The other split signal is sent to a delay generator (purple) and then into ch4 which measures laser shots and the trigger input of the TDC. ch1, ch2 and ch3 capture amplified and discriminated negative Nuclear Instrumentation Module (NIM) signals from the top, middle and bottom anodes, respectively, of the MCP (green) detector after charged particles hit the MCPs. This signal is also split and one part is sent to three Tennelec TC536 counters. Commands are sent to TDC from Linux computer via VM-USB VME module. The module also records and transfers data to the computer, where the SpecTCL software displays the resultant histogram.

from the photodiode is then inverted and split. Both split signals are then amplified and discriminated by the 9327-P 1-GHz Amplifier and Timing Discriminator made by AMETEK. One of the split signals is split again with one part directed to ch0 and the other to a Tennelec TC536 counter to measure the repetition rate. The other is directed to delay generators and subsequently into ch4 which measures laser shots and the trigger input. Ch0 and the trigger input serve to create the time window necessary for trigger matching mode. Laser shots are measured in ch4 due to overhead associated with TDC. Similarly, ch1, ch2 and ch3 capture amplified and discriminated negative Nuclear Instrumentation Module (NIM) signals from

the top, middle and bottom anodes, respectively, of the MCP detector after charged particles hit the MCPs. This signal is also split and one part is directed towards three Tennelec TC536 counters to measure counts from the three anodes. In electron mode, all three anodes are used, but only ch2 (middle anode) is used in ion mode.

Collecting PES and PAD

The collection of photoelectron spectra and photoangular distributions involves the following procedure, optics and software. First, the DTOF is set to electron mode and positive voltage is applied to the MCPs. Second, the output beam power of the Tangor 300 (1030 nm, 450 fs pulse duration, 100 kHz, linearly polarized light) is controlled using the combination of a half waveplate (HWP) from Newlight Photonics (WPM03-H-775-1550) and thin film polarizer from Eksma Optics (420-1698BBi70) . Third, the beam is focused into the chamber with a 150 mm plano convex lens (LA1433-C BK7 C coated). The lens is mounted on a 3d translation stage. After aligning the back reflection of the lens, it is important to adjust its z direction (direction of beam propagation) by moving the translation stage and optimizing the number of counts on the middle anode. Fourth, 2.0×10^{-4} Torr of the chosen target is injected into the chamber. Fifth, linear P-polarized light (horizontally polarized light with respect to the optical table) is required. This is so the electric field vector lies in the same plane as detection and oscillates along the direction of polarization, increasing the probability to detect rescattered electrons. Furthermore, it was shown in Chapter 2 that the static ionization rate was polarization dependent. However, the output beam of Tangor 300 is S-polarized (vertically polarized with respect to the optical table). Therefore, a HWP at 1030 nm from Newport Photonics (10RP02-50) is placed before the chamber to rotate and optimize the polarization. Optimization involves the following steps:

1. First, by eye, rotate the HWP until the counts on the middle anode are maximized.
2. Second, rotate the HWP position up to 8 degrees on either side of the initial value in steps of 2 degrees. At each position, collect a 2 minute photoelectron spectrum

3. Third, after the run is over, integrate the collected spectrum for each anode to attain the total yield and normalize to the number of laser shots. This will give the hits/shot.
4. Fourth, plot the hits/shot for each anode as a function of HWP angle. Identify the angle where the middle anode is maximized *and* there are roughly equal hit/shot across all anodes. Set your HWP to this angle.

Remember the multianode detectors are separated by 4° , meaning if the middle anode sees 0° polarization, the top and bottom anode see 4° and -4° polarization. HWPs rotate the polarization of linearly polarized light to twice the angle between the HWPs fast axis and the plane of polarization. Therefore, when plotting the hit/shot as a function of HWP angle, the peaks of each anode should be theoretically be offset by 2° .

For photoelectron spectra, the procedure is complete. The SpecTCL software (Linux OS) collects a histogram of electron yield versus time in ns for each anode and the total number of laser shots for a given run. The time bin size in electron mode is 25 ps. These histograms (and laser shots) are subsequently saved as .txt files ready for calibration in Python.

One additional step is required to collect a PAD. To detect electrons at various angles, the laser polarization must be rotated with respect to the TOF axis. Therefore a PAD is collected at one power by rotating the HWP between -2° and 47° in steps of 2° (-4° and 94° in steps of 4° polarization angles) and collecting a photoelectron spectrum at each detected angle, θ_d . These spectra (and laser shots) are subsequently saved as .txt files, ready for analysis.

As mentioned previously, electron collection is a field-free procedure. This means no voltage is applied to the DTOF's field plates.

Collecting Mass Spectra

Mass spectrum identify the atoms and molecules present within the chamber. It helps ensure the PES collected is of the target of choice and quantifies the amount of background contaminants (water, etc.) located within the chamber. Mass spectra collection involves similar steps to PES and PAD experiments, but with a few changes. The alignment procedure and

power adjustment of the Tangor 300 into the chamber remains exactly the same. However, the detection of ions is insensitive to the polarization of the laser, so the HWP at 1030 nm is not necessary. Additionally, the Tangor 300 is set to a 20 kHz repetition rate instead of 100 kHz. This will be explained when discussing mass spectrum calibration. The DTOF is switched to ion mode and negative voltage is applied to the MCPs. The TDC resolution is changed to 100 ps. As mentioned previously, 240 V and 400 V is applied to the extractor and repeller field plates. The electrostatic fields caused from the voltage differential push the ions towards the middle anode detector. The mass spectrum in time is collected using the DAQ system described previously and subsequently saved as a .txt file for calibration and analysis in Python.

DTOF Calibration

Since the Tangor 300 was a new laser and the DTOF's field plates had yet to be tested in electron mode, a PES, mass spectrum and PAD of argon was first collected as a test to ensure both systems were working correctly. It is a good reference atom which our group has studied extensively. Therefore, comparisons with previous data verifies a proper, working setup. The PES and PAD were collected at 8.6 W with a 100 kHz repetition rate while the mass spectrum was collected at 1 W at a 20 kHz repetition rate. The runtime for each polarization angle to collect the PAD was 20 minutes. This data is used to demonstrate calibration techniques in this section.

Calibration of Photoelectron Spectra

Given the time-of-flight (TOF) of an electron, t_{TOF} and the length of the spectrometer, L , the detected kinetic energy of the electron is given by:

$$E_{det} = \frac{1}{2}m_e \left(\frac{L}{t_{TOF}} \right)^2 \quad (3.2)$$

The actual time of detection, $t_{detected}$ is different than t_{TOF} due to cable lengths, etc. Therefore to account for this difference a time t_0 is added, making $t_{detected} = t_{TOF} + t_0$.

Therefore Equation 5.1 can be modified too:

$$E_{det} = \frac{1}{2}m_e \left(\frac{L}{t_{detected} - t_0} \right)^2 \quad (3.3)$$

Calibration of ATI spectra involves taking advantage of its properties. Attaining a proper spectra in energy involves adjusting L and t_0 until the ATI peaks are spaced one photon apart. This is done in a GUI, authored by myself. When raw data and wavelength are loaded in, initial values of t_0 and L are chosen. Then, sliders are used to adjust these two variables in real time until the desired spectrum is achieved. Additionally, the conversion of data from a function of time to a function of energy requires the yield to be multiplied by the Jacobian $dt_{TOF}/dE_{det} = (2E)^{-3/2}$. Calibrated PES of argon for the top, middle and bottom anode can be seen in Figure 3.12. Despite individual calibration, the three ATI spectrum are identical and the peaks are locked in energy. An enhancement in argon is observed across all three anodes at approximately 26 eV.

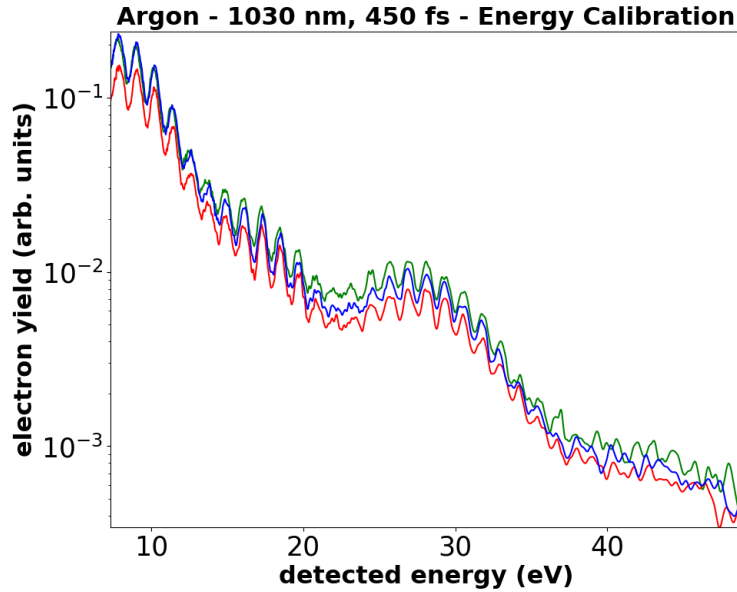


Figure 3.12: **Calibrated PES of argon for the Top, Middle and Bottom Anode of the Multianode detector collected with Tangor 300.** Calibrated ATI spectrum plotted in log scale for the top (red), middle (blue) and bottom (green) anode of argon collected at 8.6 W at 100 kHz repetition rate using the Tangor 300. Despite individual calibration, the spectrum are identical and the ATI peaks are locked in energy.

The relative error is given by:

$$\frac{\Delta E_{det}}{E_{det}} = 2 \frac{\Delta L}{L} + 2 \frac{\Delta t_0}{t_{detection} - t_0} \quad (3.4)$$

To calculate the relative error from experimental data, a gaussian is fit for a chosen ATI peak, where the FWHM is ΔE_{det} . The relative error for a high energy (≈ 54.5 eV) ATI peak was calculated to be approximately 1.21% using the middle anode ATI spectrum of argon. Because of the shorter flight time and inverse proportionately between $\Delta E_{det}/E_{det}$ and $t_{detection}$, this provides a worst-case scenario for the relative error. The results are shown in Figure 3.13.

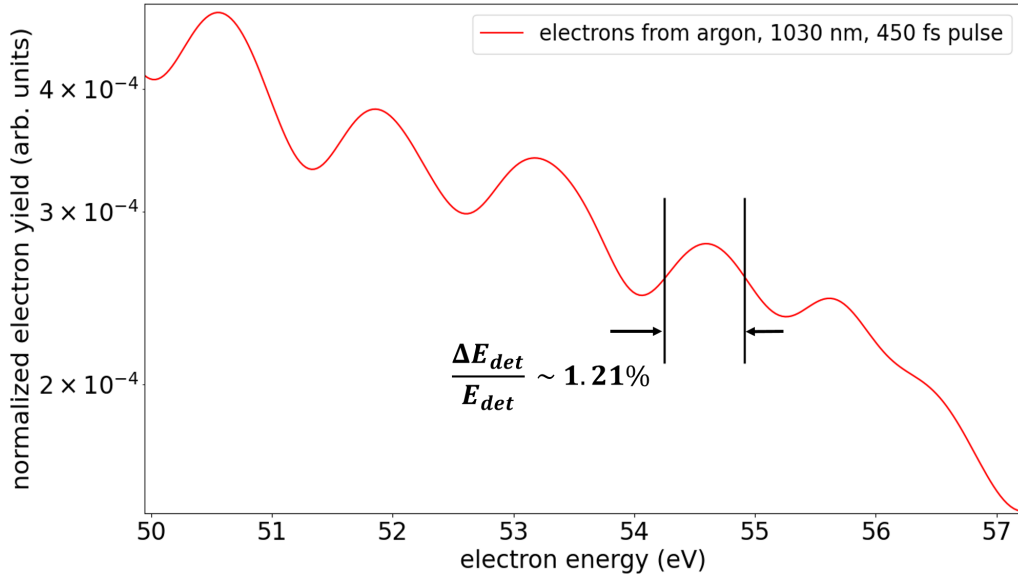


Figure 3.13: **Relative Error Calculations for High Energy ATI Peak using middle anode ATI Spectrum of argon.** $\Delta E_{det}/E_{det}$ was calculated for chosen ATI peak by fitting a gaussian and finding the FWHM. Relative error of approximately 1.21% calculated for chosen ATI peak around 54.5 eV.

Calibration of Mass Spectra

Collection of ions involves applying a voltage V_1 to plate 4 and a voltage $V_2 < V_1$ to plate 3. When a charge q is accelerated through a potential difference ΔV , the kinetic energy gained by the charge is $q\Delta V$. Therefore the velocity of an ion with mass m and charge q as it exits plate 3 is given by:

$$v = \sqrt{\frac{2q\Delta V}{m}} \quad (3.5)$$

Calibrating a mass spectrum involves converting t_{TOF} to m/q . Knowing $v = L/t_{TOF}$, equation 5.3 can be rearranged to give:

$$\frac{m}{q} = t_{TOF}^2 \frac{2\Delta V}{L^2} = t_{TOF}^2 k \quad (3.6)$$

where k is a constant with units $\text{kg/s}^3\text{A}$. Practically, when the raw data is loaded into the GUI, an initial k value is chosen and a slider adjusts the mass spectrum in real time. Comparison with existing NIST mass spectrum databases are made to ensure proper calibration.

As a quick aside, the previous section describing experimental collection of mass spectra mentioned the necessity to change the repetition rate of the Tangor 300 to 20 kHz. Let's see why. Rearranging Equation 5.4 gives:

$$t_{TOF} = \sqrt{\frac{mL^2}{q(V_1 + V_2)}} \quad (3.7)$$

Assume argon is injected into the chamber and a voltage $V_1 = 400$ V is applied to plate 4 and a voltage $V_2 = 240$ V is applied to plate 3. Knowing $L = 45$ cm, $m_{Ar} = 6.63\text{e-}26$ kg and $q = 1.6\text{e-}19$ C, the ion's time of flight, t_{TOF} is $11.43 \mu\text{s}$. At 100 kHz, a pulse is emitted every $10 \mu\text{s}$, meaning the ion is detected *after* the next laser pulse! For this reason, the repetition rate of the Tangor 300 is reduced to 20 kHz when running in ion mode so the ion's time of flight is faster than the emitted pulse train's periodicity.

A calibrated mass spectrum of argon can be seen in Figure 3.14. It verifies the PES and PAD collected is indeed of argon and shows relatively low amounts of water and other contaminants within the chamber.

Calibration of Photoangular Distribution

PAD calibration involves stitching together PES collected from -4° to 94° . The raw 2D (t_{TOF}, θ_{det}) map for argon can be seen in Figure 3.15a. For each anode, the 0° PES is

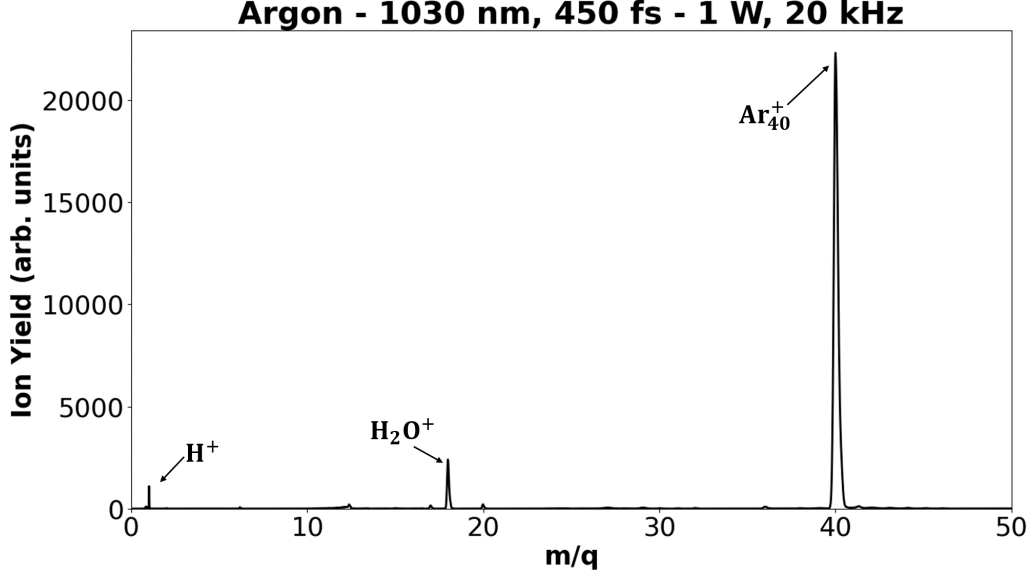


Figure 3.14: **Mass Spectrum of argon collected using Tango 300.** Mass spectrum of argon collected at 1030 nm, 450 fs at 1 W with a repitition rate of 20 kHz. Hydrogen, water and argon ion peaks are all labeled with black arrows on the mass spectrum.

calibrated using the steps mentioned in the previous section. Then, once in the energy domain, each spectrum is converted to detected momentum, p_{det} using $E_{det} = p_{det}^2/2$. The yield is also multiplied by the Jacobian $dE_{det}/dp_{det} = \sqrt{2E_{det}}$. This creates a 2D (p_{det}, θ_{det}) , seen in Figure 3.15b, which is finally converted to $(p_{parallel}, p_{perpendicular})$ using $p_{parallel} = p_{det}\cos(\theta_{det})$ and $p_{perpendicular} = p_{det}\sin(\theta_{det})$, where $p_{parallel}$ and $p_{perpendicular}$ are momentum parallel and perpendicular to the laser polarization, respectively. The yield is also divided by the Jacobian, p_{det} . This creates a PAD in one quadrant. The data is then interpolated (.2 angle spacing) and symmetrized across all four quadrants for visualization purposes.

An important consideration should be made when creating a PAD from all three anodes. As mentioned previously, the data collection process is expedited by collecting 3 detection angles simultaneously. If the middle anode sees electron at detection angle θ_d , then the top and bottom anode see electrons at detection angles $\theta_d + 4^\circ$ and $\theta_d - 4^\circ$, respectively. Therefore, when summing PADs from three anodes together, it is important to sum PES of the *same* angles together versus simply summing raw data of all three anodes from a singular run. The resultant PAD of argon in Figure 3.16 sums all anodes together. The red regions correspond to direct electrons and the blue region around 1.3 atomic units on the parallel momentum

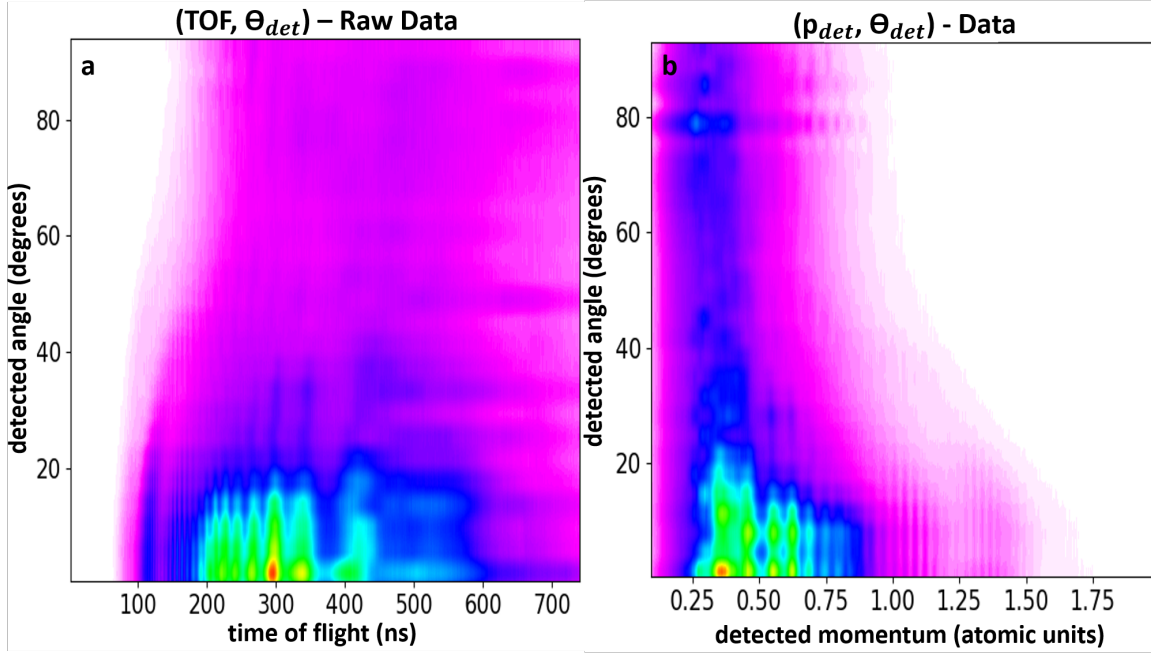


Figure 3.15: **Experimental 2D (t_{tof}, θ_{det}) and (p_{det}, θ_{det}) maps collected for argon from -4° to 94° detected angles.** PES were collected of argon at each detection angle in steps of 4 degrees by rotating a HWP every 20 minutes. Stitching together the PES at each angle and interpolating results in the (t_{tof}, θ_{det}) map shown in a). Calibrating the raw data to energy and then momentum results in the (p_{det}, θ_{det}) map shown in b).

axis corresponds to the enhancement region located within the rescattering region. This PAD was compared to one collected in FLAME *without* field plates. Figure 3.17 provides a side-by-side comparison of the data collected in KONZA and FLAME. As a note, data in FLAME was collected at the following parameters: 815 nm, 35 fs pulse duration, 30.5 mW at a 3 kHz repetition rate. Since there are no major differences between the two datasets, this test was a success.

Space Charge Effects

Another study conducted concerned the influence of space charge effects on mass spectra. In general, *space charge effects* are a result of the repulsion caused by particles of like charge⁵³. They influence the trajectory of slower moving or heavier ions as they head to the detectorⁱ. The greater the number of ions in the interaction region, the more space charge effects

ⁱThe trajectories of faster moving ions are also influenced, just not as much.

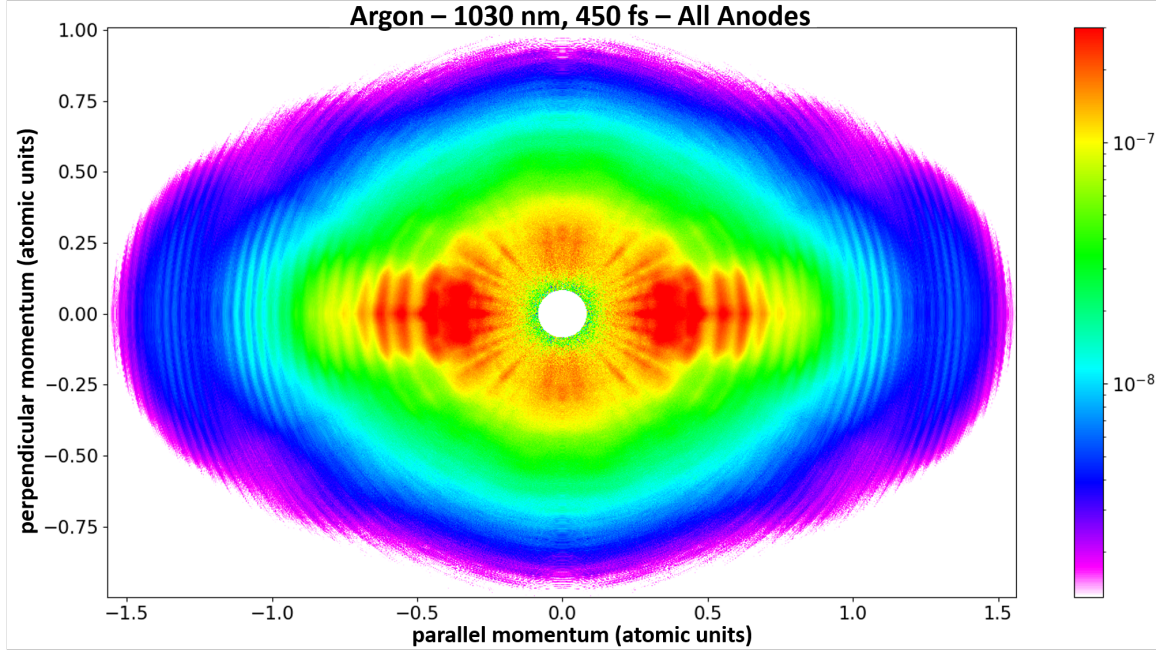


Figure 3.16: **Resultant Experimental argon PAD collected at 8.6 W, 100 kHz repetition rate.** argon PAD collected using the Tangor 300 and displayed in log scale. The red regions correspond to direct electrons while the blue regions map to rescattered electrons. The enhancement is observed at ≈ 1.3 atomic units on the parallel momentum axis.

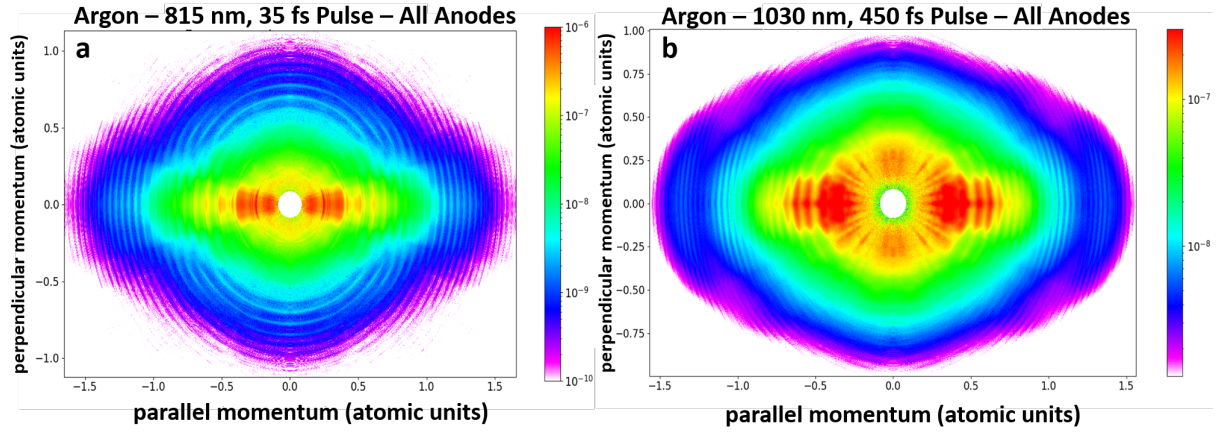


Figure 3.17: **Comparison of argon PADs collected in FLAME and KONZA.** a) argon PAD collected in FLAME at 815 nm, 35 fs pulse duration, 30.5 mW at a 3 kHz repetition rate. b) argon PAD collected in KONZA at 1030 nm, 450 fs pulse duration, 8.6 W at a 100 kHz repetition rate.

exist. Practically speaking, an increase in pressure *or* intensity leads to more ions, causing interactions between them, influencing their trajectories and decreasing the accuracy of the collected time of flight mass spectrum. To demonstrate this, mass spectra was first collected

of ethane ($m/q = 30$) at a fixed power, 0.65 W at a 20 kHz repetition rate, at varying pressures between 1.2×10^{-5} Torr and 2.0×10^{-4} Torr. The resultant mass spectra, zoomed in between m/q 25 and 32, are shown in Figure 3.18. As the pressure increases, the influence of space charge effects can be seen from the unnatural sloped rise in ion yield for m/q peaks greater than 28.

A similar study was subsequently conducted, except this time the pressure was kept constant at 4.9×10^{-5} Torr and the intensity of the Tangor 300 was adjusted between 1.1 W and 1.7 W at a 20 kHz repetition rate. The resultant mass spectra are seen in Figure 3.19. As expected, space charge effects are observed as the beam intensity increases. Therefore, compensating for space charge effects involved collecting mass spectra at lower pressures and pulse energies compared to PES parameters. This leads to the following question: do space charge effects have any influence on ATI spectra, specifically the enhancement? This will be addressed later in this chapter.

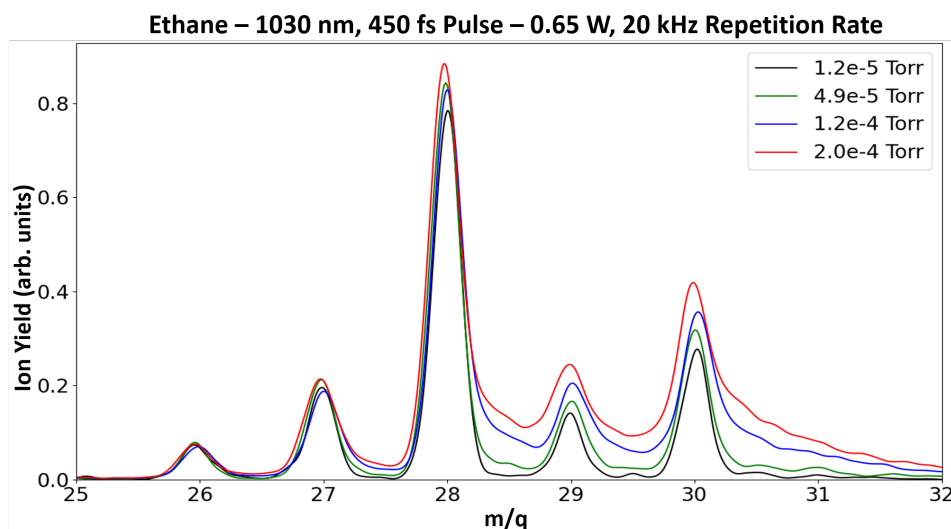


Figure 3.18: **Mass spectra of ethane collected at different Pressures at a Fixed Intensity to demonstrate Space Charge Effects.** The power in the chamber was set to 0.65 W at 20 kHz repetition rate and mass spectra of ethane was collected at 1.2×10^{-5} Torr (black), 4.9×10^{-5} Torr (green), 1.2×10^{-4} Torr (blue) and 2.0×10^{-4} Torr (red). As the pressure increases, space charge effects are observed by the unnatural rise in slope after an m/q of 28.

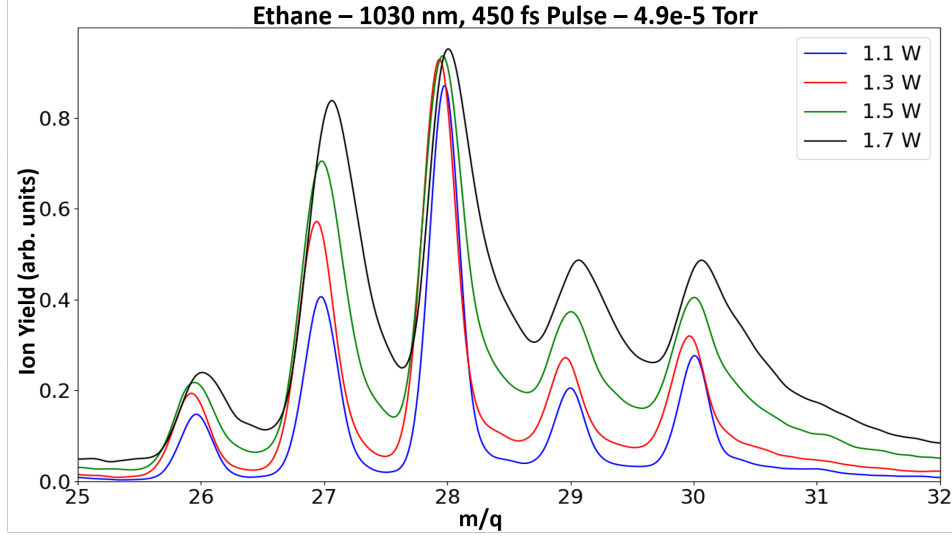


Figure 3.19: **Mass spectra of ethane collected at different Intensities at a Fixed Pressure to demonstrate Space Charge Effects.** The pressure in the chamber was set to $4.9\text{e-}5$ and mass spectra of ethane was collected at 1.1 W (blue), 1.3 W (red), 1.5 W (green) and 1.7 W (black). As the intensity increases, space charge effects are observed by the unnatural rise in slope after an m/q of 26.

3.1.4 Multi-pass Cell (MPC)

The MPC, located in KONZA, is a cell which allows for multiple passes of a laser beam through a gas medium. Specifically, it can be used for nonlinear pulse compression. The cell itself usually consists of two concave mirrors which the laser hits pass after pass, similar to a cavity. Experiments have shown that the nonlinear, on-axis phase shift, or the *B-integral*, per pass is small (< 1)⁵⁴. The measure of the B-integral is important as it can be used to estimate the strength of conditions such as self-focusing and spectral broadening of the pulse. The total accumulated non-linear phase shift along the optical z axis is given by:

$$\phi(t) = \int_0^L \frac{2\pi n_2}{\lambda} I(t, z) dz \quad (3.8)$$

where n_2 is the non-linear refractive index, λ is the wavelength, d is the thickness of the material, L is the total path length and $I(t, z)$ is the temporal intensity evolution⁵⁵. If the B-integral is large (3-5), self-focusing can occur. The radius of the beam becomes very small, greatly increasing its intensity above the damage threshold of optical elements. This means

the beam now has the potential of damaging gain medium and optics⁵⁶. Furthermore, the beam is shown to homogenize on the transverse axis within the cell after multiple passes.

For pulse compression, KONZA's MPC is filled with argon. The recommended input power from the manufacturer is 218 W or 70% of the Tangor output with a pulse duration of 450 fs at 1030 nm. With 840 mbar of argon in the cell, the beam traverses 11 passes on high-dispersive mirrors. At output, the power was measured by the manufacturer to be 205 W (94 % transmission) with a pulse duration of 55 fs. The characterized output beam profile can be seen in Figure 3.20.

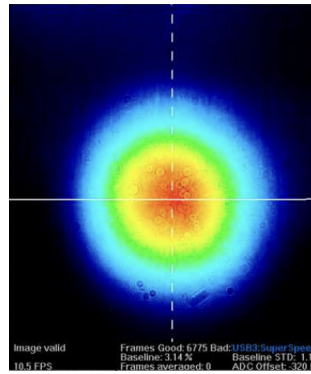
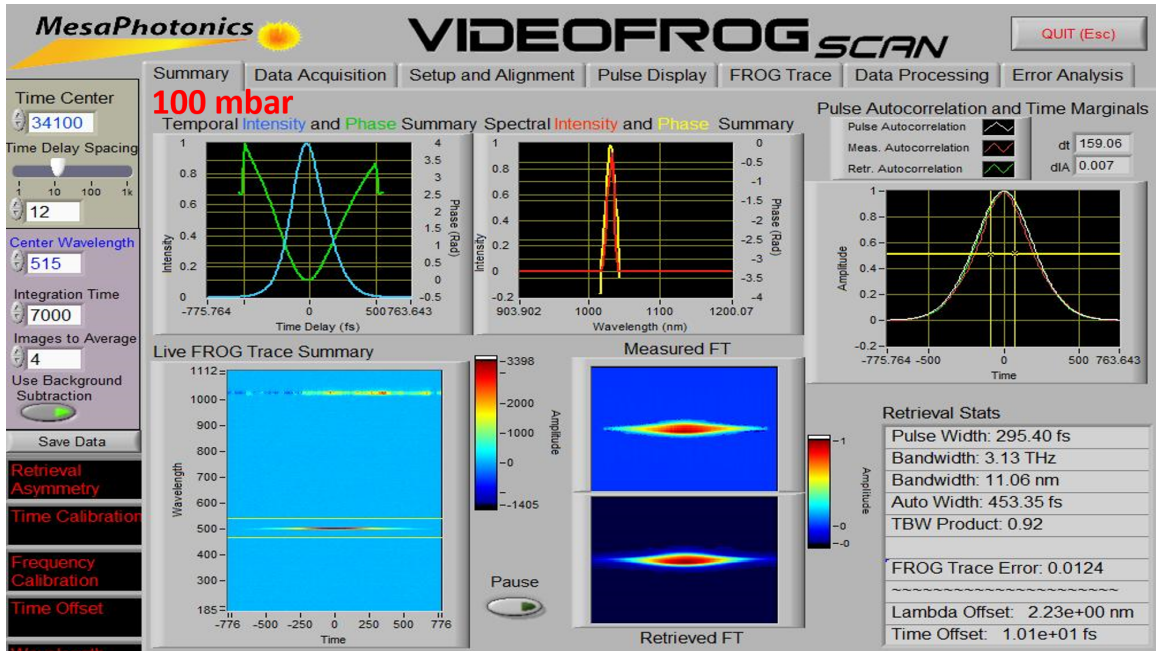
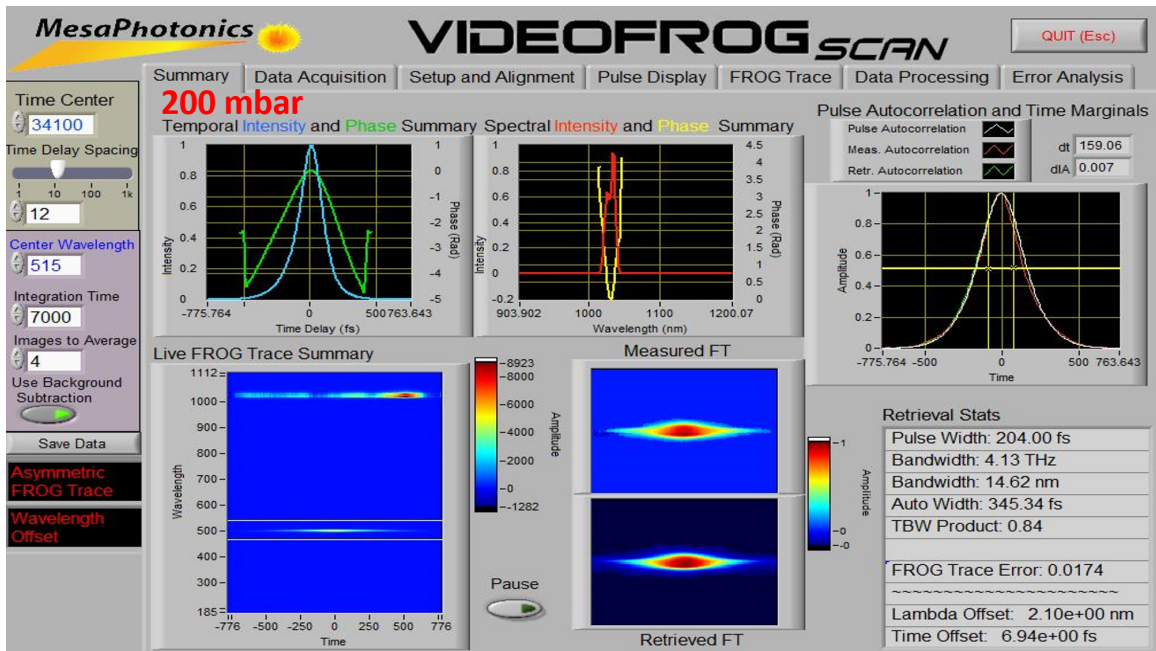


Figure 3.20: **Beam profile captured at output of MPC.** A 1030 nm, 450 fs beam enters the MPC at 218 W. After traversing 11 bounces on high-dispersive mirrors, the output beam has a measured pulse duration of less than 50 fs and a power of 205 W. The manufacturer captured the beam profile at output.

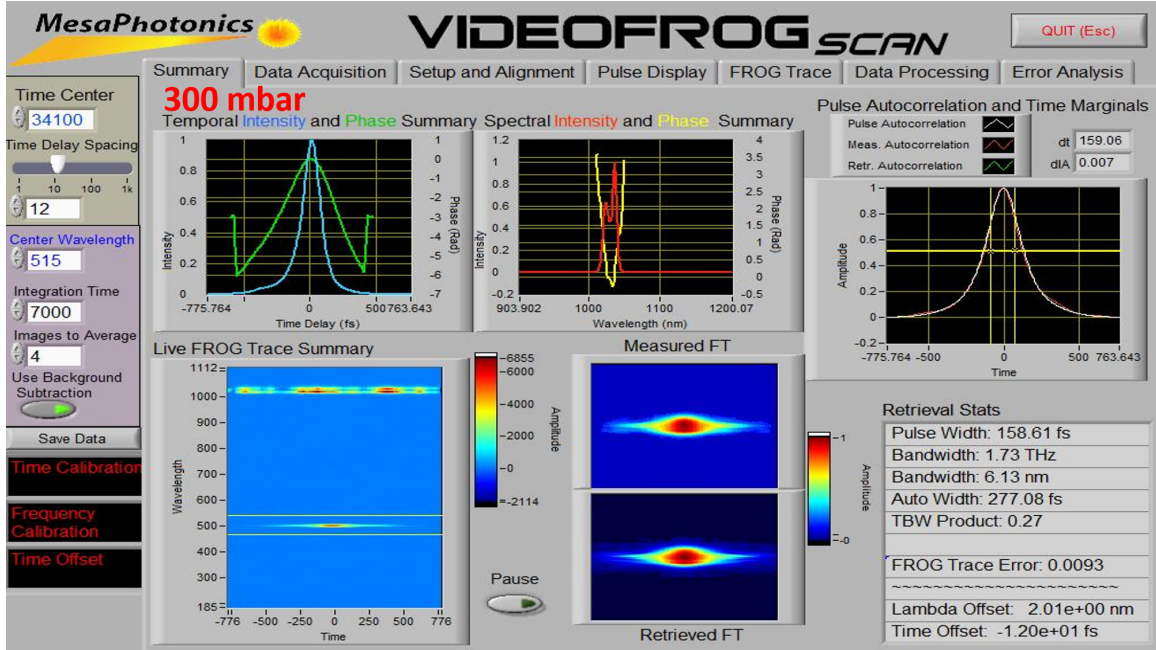
The pulse duration was also measured with 100 mbar, 200 mbar, 300 mbar and 500 mbar of argon in the MPC. The output beam was aligned to an SHG FROG setup located within the KONZA laser room. Explanation of SHG FROG can be found in Chapter 3.31. It should be noted the output beam's power was attenuated using the combination of a HWP (WPM03-H-775-155) and thin film polarizer (Eksma Optics, 420-1698BBi70). This is to avoid damaging the SHG crystal within the FROG setup. argon was subsequently filled into the MPC at the following pressures: 100 mbar, 200 mbar, 300 mbar and 500 mbar. At each pressure, the beam was FROGged and the pulse durations were measured to be 295 fs, 204 fs, 158 fs, and 85 fs, respectively. The resultant FROG traces for all four pressures can be found in Figure 3.21.



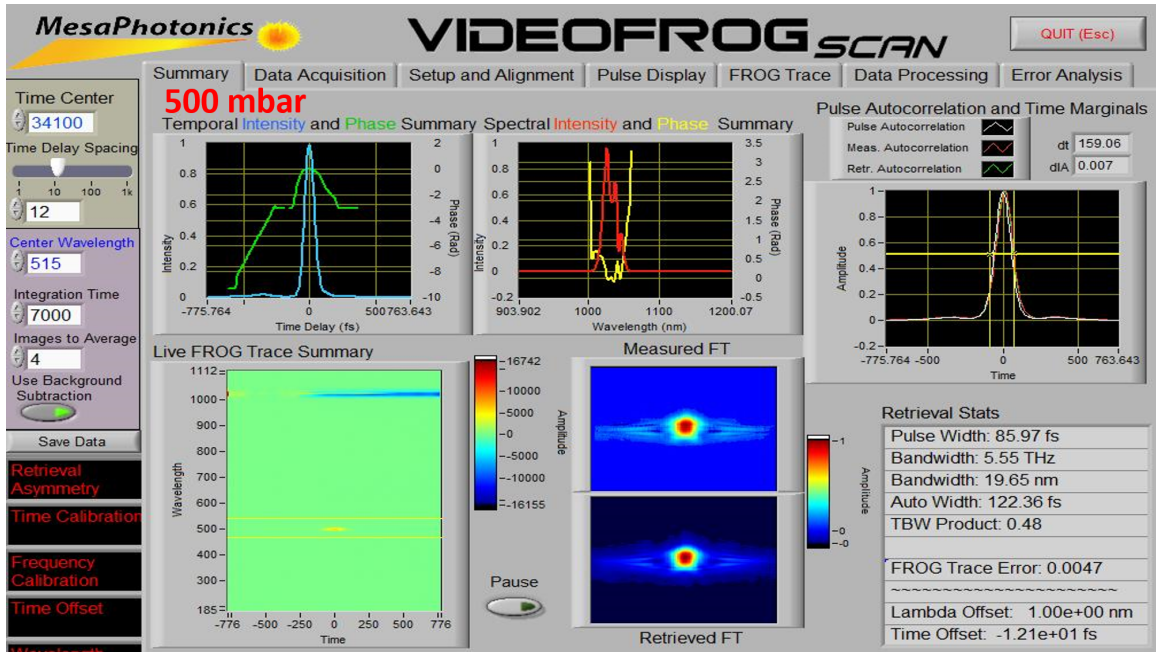
(a)



(b)



(c)



(d)

Figure 3.21: Measured Pulse Durations at Different argon MPC Pressures for 1030 nm Light Using SHG FROG. The FROG software from MesaPhotonics calculated the pulse duration for 1030 nm light after propagation through a) 100 mbar, b) 200 mbar, c) 300 mbar and d) 500 mbar of argon within the MPC. The pulse durations measured were 295.4 fs, 204.0 fs, 158.6 fs, and 86.0 fs, respectively.

3.2 Theoretical Tools

Computational Logistics

A summary of computational specifications for theoretical calculations are provided here. The propagation code which numerically solves the Time Dependent Schrödinger Equation under the Single Active Electron approximation (SAE-TDSE) is written in Fortran 77. This code provides the final, time-dependent electronic wavefunction given its initial wavefunction and one-electron binding potential. In order to obtain the photoelectron spectra, as well as slices of the radial wavefunction of a given energy, the final wavefunction is analyzed with a window operator using Fortran 90, defined later in this chapter. The photoemission spectra is calculated with Python 3. The operating system (OS) is Linux for Fortran and Windows for Python. The original propagation code was written by Kenneth Schafer of Louisiana State University (LSU). The dipole acceleration for different targets, intensities and wavelengths was calculated by Dr. Abraham Camacho Garibay of the Ohio State University.

Calculating Photoelectron Spectra (PES)

As mentioned in Section 2.3.2, PES measure the kinetic energy of direct and rescattered electrons at the time of detection. Simulating a PES involves calculating the probability of finding an electron with energy E . In theory, projecting the final wavefunction $\psi(\vec{r}, t_f)$ onto states of specific energies can fulfill this goal. These states are the eigenstates of the Hamiltonian which describes the behavior of the electron far from the core, or the asymptotic Hamiltonian. In practice, however, the storage of states is computationally unfavorable and a "window-function technique" is used.²¹ The window function is defined as

$$W(E, \gamma, n) = \frac{\gamma^{2^n}}{(H_0 - E_k)^{2^n} + \gamma^{2^n}} \quad (3.9)$$

where the window is centered around an energy E_k with resolution 2γ of polynomial order n . Higher n corresponds to a more precise rectangular window around E_k but comes at a computational cost. H_0 is the field-free Hamiltonian. This projection operator is subsequently

applied to the final wavefunction

$$|\Omega(\vec{r}, E)\rangle = W(E, \gamma, n)|\psi(\vec{r}, t_f)\rangle \quad (3.10)$$

which represents part of the wavefunction corresponding to energy $E \pm \gamma$. The probability of finding an electron with energy E is given by

$$P(E) = \langle \Omega(\vec{r}, E) | \Omega(\vec{r}, E) \rangle \quad (3.11)$$

If we expand equation 3.3 in a basis of radial functions and spherical harmonics, the probability becomes

$$P(E) = \int \Omega^*(r, E, \theta, \phi) \Omega(r, E, \theta, \phi) dr d\theta d\phi \quad (3.12)$$

Figure 3.22 shows a comparison between calculated and measured Above Threshold Ionization (ATI) spectra for argon at 66.1 TW/cm² and 64.9 TW/cm², respectively. The experimental spectrum was collected along the laser polarization using linearly polarized 800 nm, 120 fs pulses while the single intensity theoretical spectrum was obtained with velocity gauge SAE-TDSE calculations using a 45-cycle flat top pulse⁴³. The figure shows excellent agreement between calculated and experimental spectra.

Calculating High Harmonic Emission Spectra

High Harmonic Generation (HHG) spectra measure the relative intensity of emitted discrete frequencies, or harmonics, after an ionized electron accelerates and recombines with the parent ion. In an experiment, a gas of atoms is driven to emit harmonic radiation, which is modified when propagating through a non-linear medium²¹. Therefore, a full description of HHG spectra must account for macroscopic effects such as phase-matching, discussed in Chapter 4. For now, we will look at single-atom calculations which sufficiently describes its dynamics in a strong field. The emission spectrum for a single atom is calculated by taking

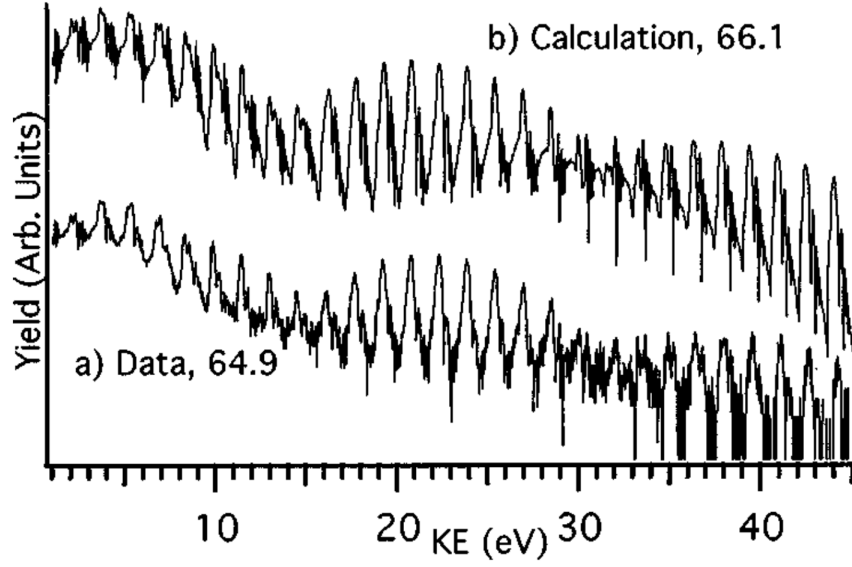


Figure 3.22: **Theoretical and Experimentally Measured ATI Spectra.** a) Theoretical argon ATI spectra obtained with SAE-TDSE calculations using a 45-cycle flat top pulse at 66.1 TW/cm² b) Experimentally measured argon ATI spectra using linearly polarized 800 nm, 120 fs pulse at a peak intensity of 64.9 TW/cm². We note the excellent agreement between theory and experiment. Image credit goes to M.J. Nandor⁴³.

the Fourier transform of the dipole expectation value over an optical period:

$$|D(\omega)|^2 = \left| \frac{1}{T} \int_0^T e^{i\omega t} d(t) dt \right|^2 \quad (3.13)$$

where $d(t)$ is the dipole moment and T is the period of the field. For linearly polarized light polarized along the z -axis, the dipole moment is defined as:

$$d(t) = \langle \psi(\vec{r}, t) | z | \psi(\vec{r}, t) \rangle \quad (3.14)$$

where $\psi(\vec{r}, t)$ is the final wavefunction calculated using numerical SAE-TDSE. Since recombination occurs near the parent ion, it is better to begin with the dipole acceleration, $a(t) = \frac{d^2}{dt^2} \langle z \rangle$, which prioritizes the behavior of the wavefunction near the core where the

electron experiences a larger force²¹. The spectrum relates to the dipole acceleration by:

$$D(\omega) = \frac{A(\omega)}{\omega^2} \quad (3.15)$$

where $A(\omega)$ is the Fourier transform of the dipole acceleration.

HHG spectra provides information about an atomic or molecular target at the time of return, or the time the ionized electron recombines with the parent ion. PES, on the other hand, only provides information at the time of detection. Therefore, studying the sub-cycle dipole response of an atom with the field at its return time provided information on the evolution of the electronic wavepacket. Given an electron that returns with an energy E_i and a photon emitted with energy $\hbar\omega_i = I_p + E_i$, the time dependence of emission is calculated by applying a window function around ω_i to the single-atom dipole acceleration spectrum²¹:

$$\epsilon_i(t) = e^{-i\omega_i t} \int e^{-i(\omega - \omega_i)t} (A(\omega)F(\omega - \omega_i)) d\omega \quad (3.16)$$

where $F(\omega - \omega_i)$ is the window function and $A(\omega)$ is the dipole acceleration calculated with SAE-TDSE using the Strong Field Approximation (SFA) discussed in Chapter 2. Sub-cycle dipole response is built by sliding $F(\omega - \omega_i)$ in ω . The result of this analysis, known as a Husimi plot, is demonstrated by Tate et al. in Figure 3.23 for argon at 2 μm with an intensity of 160 TW/cm²⁵⁷. The return energy of the electron is plotted as a function of return time in optical. Flat top pulses were used and a rectangular window function is chosen to sweep through different energies. The black solid lines are return energies calculated as a function of return time from the semi-classical model introduced in Section 2.3.2. The classical and quantum calculations agree for the first couple of cycles, where a noticeable interference pattern develops in the quantum plot as a result of multiple interactions between different electron trajectories. This will be further investigated in the next chapter.

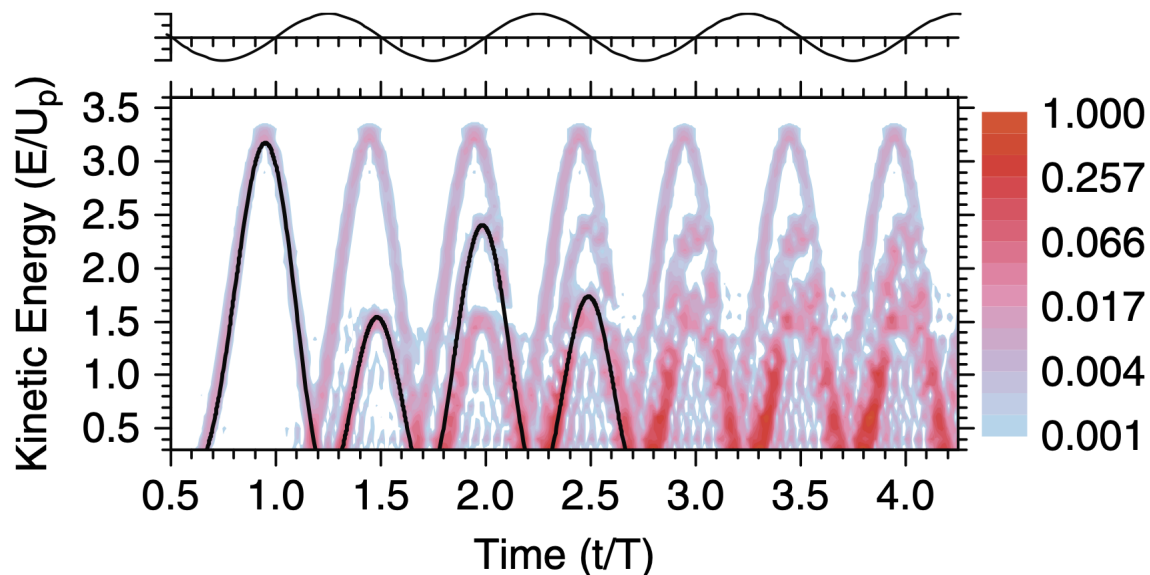


Figure 3.23: **Time Dependence of Photoemission Spectra** Time-dependent photoemission spectra calculated for argon at $2\ \mu\text{m}$ with an intensity of $160\ \text{TW}/\text{cm}^2$. Return energies (U_p units) are plotted as a function of return time (optical cycles). Calculations done with SAE-TDSE using SFA. Flat-top pulses are used with a rectangular window function. The black solid lines are return energies predicted by the semi-classical recollision model. The electric field is given by the black sinusoid at the top. Image credit goes to Prof. Jennifer Tate⁵⁷

3.3 Quantitative Rescattering Theory (QRS)

In 2009, Prof. Zhangjin Chen et al. introduced the Quantitative Rescattering Theory (QRS) for describing the production of rescattered photoelectrons and High Harmonic Generation⁵⁸. It provides a computationally efficient approach to generate key features in photoelectron angular distributions and HHG spectra in comparison to TDSE calculations.

3.3.1 QRS for Rescattered Photoelectrons

Photoelectron angular momentum distributions were studied under the SAE approximation for atomic targets using linearly polarized light. According to QRS, the distributions are expressed as

$$D(k, \theta) = W(k_r) \sigma(k_r, \theta_r) \quad (3.17)$$

where $\sigma(k_r, \theta_r)$ is the elastic DCS between free electrons, with return momentum k_r , and the target ion. The scattering angle, θ_r , is respect to the direction of the returning electron along the laser polarization. $W(k_r)$ is the momentum distribution of the electron, denoted as the returning wavepacket (RWP) by the authors. k is the measured momentum of the electron detected at an angle θ .

The validity of QRS was established by comparing the terms in Equation 3.9 with solutions of TDSE, quantum scattering theory and collected experimental photoelectron spectra⁵⁹. Let's highlights some key results.

Extracting the elastic DCS

To begin, the elastic differential cross section was extracted using QRS for argon at 800 nm with intensities of 100 and 140 TW/cm²⁵⁸. The idea is based on the classical recollision model highlighted in Section 2.3.2. Electrons with momentum k_r after elastically rescattering at an angle θ_r form a 2D circle in momentum space. We recall from Chapter 2.3.2, the generalized momentum is a constant of motion. Because of this the final detected momentum is given by $k_{det} = k_r + A_r$, where A_r is the vector potential at the time of return. k_r and A_r determine the radius and center of the circles, respectively. Electrons with a return energy of $3.17U_p$ which backscatter at $\theta_r = 180^\circ$ attain a detected kinetic energy of $10.007U_p$. This return energy corresponds to $k_r = 1.26A_0$, where A_0 is the amplitude of the vector potential. Morishita et al. called the electrons which lay along this shifted circle Back Rescattered Ridge (BRR) electrons and suggested a proportionality between the intensity of electrons along the ridge and the elastic DCS of the target ion by incident electrons of momentum k_r ⁶⁰.

Chen calculated $D(k, \theta)$ for argon using a five-cycle pulse at the aforementioned intensities by numerically solving TDSE for the time dependent wavefunction and projecting it onto eigenstates of a continuum electron with momentum $\vec{k}$ ⁵⁸. This momentum distribution is deemed "exact". A circle with radius $k_r = 1.22$ and center $A_r = k_r/1.26$ was fit onto $D(k, \theta)$ and the electron yield along the circle was extracted. This was compared to elastic DCS

calculated from TDSE. An electron was assumed to scatter off a model potential which was a combination of a Coulomb and short-range potential. The scattering amplitudes were calculated for each by solving for the final scattered wave function through partial-wave analysis and finally summed and squared to obtain the DCS. Figure 3.24 compares the cross sections generated from QRS Theory and quantum scattering theory. The results match quite well, validating QRS' ability to successfully extract elastic DCS.

The center of the circle chosen by the authors corresponds to the peak vector potential, A_0 . They chose it to be a constant because the vector potential at return does not change significantly in the narrow time window for electrons which accumulate a detected energy above $4U_p$. This removes dependence on intensity and wavelength, implying any changes to

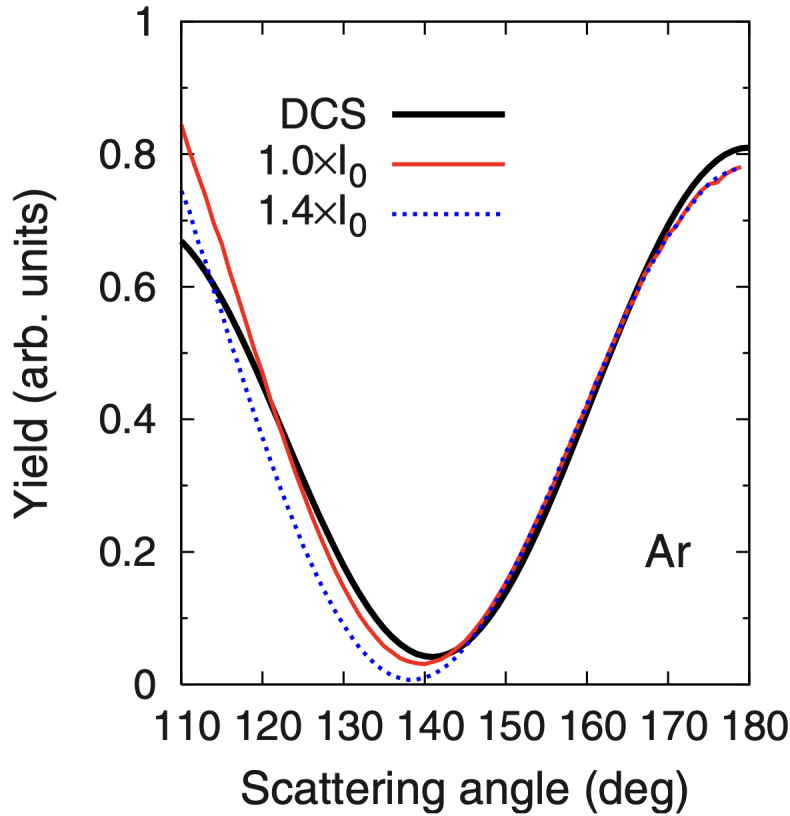


Figure 3.24: **Elastic DCS for argon at 800 nm: QRS Theory versus Traditional Quantum Scattering Theory** Electron yield extracted from angular distributions for momentum $k_r = 1.22$ for argon at 100 (red) and 140 TW/cm² (dashed blue) compared with DCS calculated from traditional quantum scattering theory using TDSE. Image credit to Prof. Zhangjin Chen⁵⁸.

the cross section are attributed to the target. The lack in change of structure in Figure 3.25 from varying intensities demonstrates this. The authors further investigate this implication by calculating the elastic DCS "exactly" at large angles for argon, krypton and xenon using quantum scattering theory. The structure of the individual cross sections are both complex and unique, as seen in Figure 3.4. The maxima and minima arise from interference of partial waves and cannot be reproduced with a hydrogenic atom, proving the strong dependence of the elastic DCS on the target.

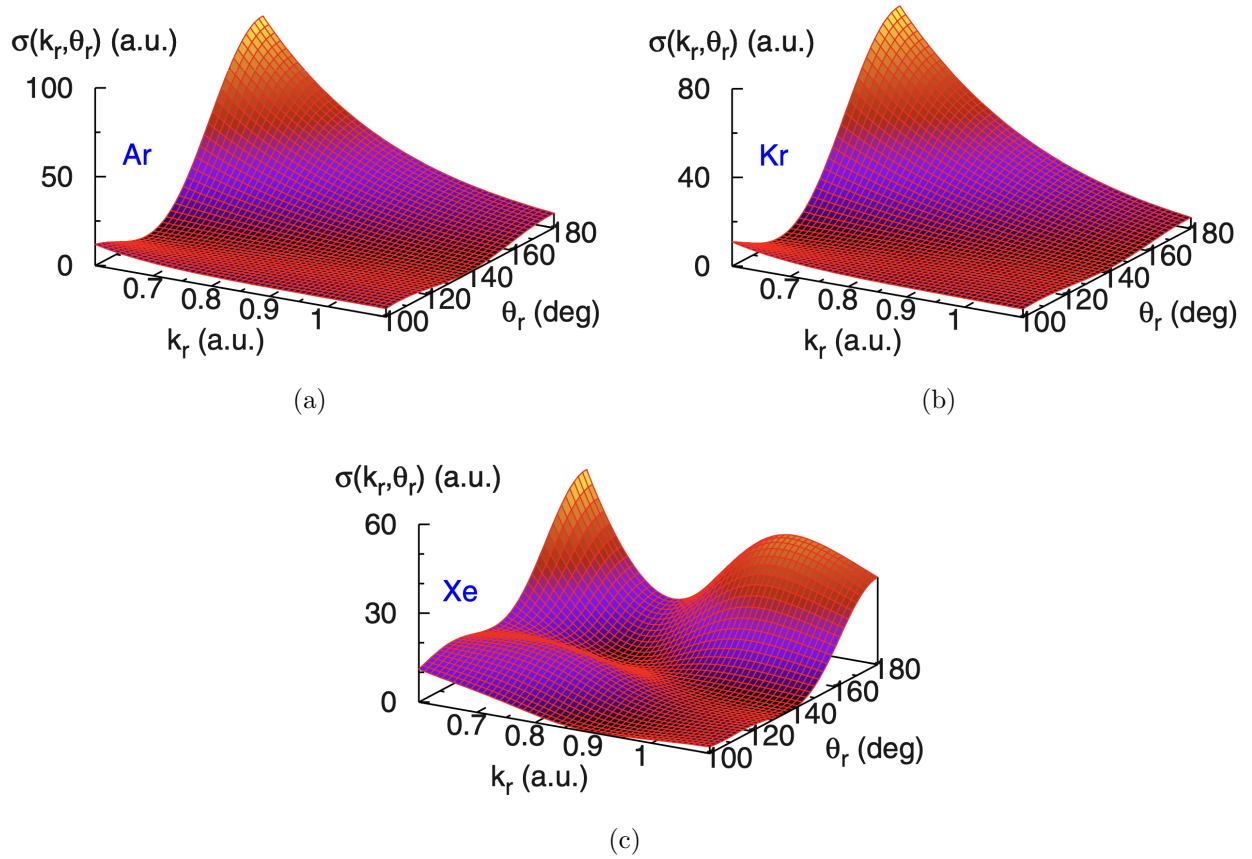


Figure 3.25: **Elastic DCS for Targets at Large Angles.** Differential Cross Sections calculated "exactly" from $k_r = 0.6$ to $k_r = 1.1$ at large angles, 110° - 180° for a) argon, b) krypton and c) xenon. Image credit to Prof. Zhangjin Chen⁵⁸.

Extracting the Returning Wavepacket

The RWP in Equation 3.9 is invariant to the scattering angle θ_r . To show this, $W(k_r) = D(k, \theta)/\sigma(k_r, \theta_r)$ was calculated "exactly" for two different intensities, where $D(k, \theta)$ was obtained through TDSE and $\sigma(k_r, \theta_r)$ was obtained through quantum scattering theory. The RWP was subsequently calculated by approximating $D(k, \theta)$ and $\sigma(k_r, \theta_r)$ using SFA2 and the plane wave Born approximation (PWBA), respectively. Both cases were for single ionization of argon in a 5 fs laser pulse with a wavelength of 800 nm. From Section 2.2.1, SFA2 assumes a Volkov state as the final wave function, includes electron-laser interactions, and describes rescattering off the parent ion to first order. Because of this, PWBA assumes the continuum electron wavefunctions as plane waves. The results are shown in Figure 3.26. Despite discrepancies in yield, the shapes of the RWP are nearly identical and do not change as a function of scattering angle.

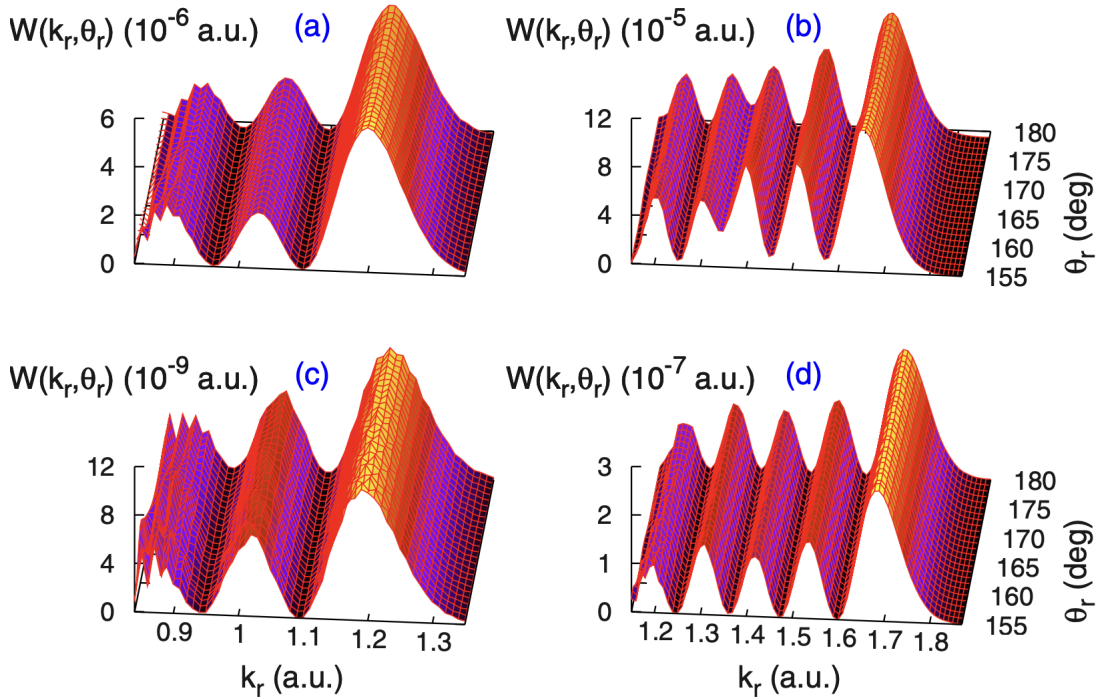


Figure 3.26: RWPs Calculated for for single ionization of argon in a 5 fs laser pulse with a wavelength of 800 nm with TDSE and SFA2 a),c) RWP calculated for 1.0×10^{14} W/cm² using TDSE and SFA2, respectively. b),d) RWP calculated for 2.0×10^{14} W/cm² using TDSE and SFA2, respectively. Image credit to Prof. Zhangjin Chen⁵⁸.

Target dependence of the RWP was also investigated. $W(k_r)$ was generated using TDSE and SFA2 for hydrogen, argon and xenon using an 800 nm, eight-cycle pulse with a peak intensity of 1.0×10^{14} W/cm². Figure 3.27 shows both the "left" and "right" RWPs for all targets using the two different calculations ⁱⁱ. To first order, TDSE and SFA2 agree. Additionally, the differences for the RWPs between targets are quite small, implying $W(k_r)$ mostly depends on field parameters. This would mean given the same pulse, any changes in the momentum distributions are attributed to the elastic DCS. Furthermore, the target independence implies the ability to calculate the RWP with SFA2 using a simpler, hydrogen-like target.

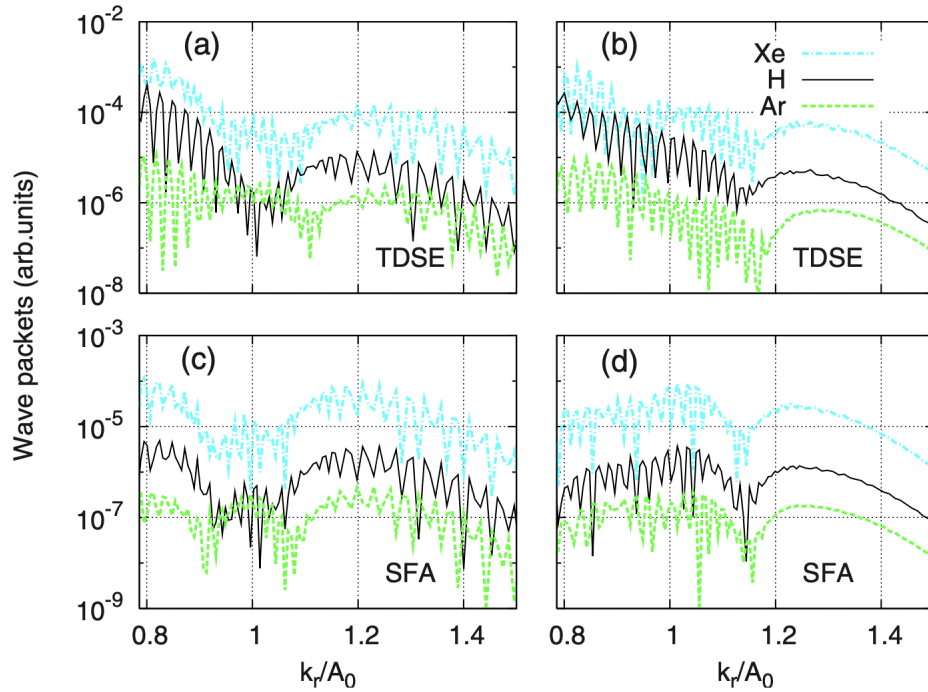


Figure 3.27: **RWPs for Various Targets Using TDSE and SFA2** All RWPs calculated at 800 nm with a peak intensity of 1.0×10^{14} W/cm² a) Left side RWPs for xenon (light blue), argon (green) and hydrogen (black) calculated using TDSE. b) Same as a) but the right side RWPs c) Left side RWPs calculated using SFA2 d) Same as c) but the right side RWPs. Image credit to Prof. Zhangjin Chen ⁵⁸.

ⁱⁱthe field distorts the left side and right side of the Coulomb potential every half cycle, meaning a wavepacket is released to the left and to the right every half cycle. If scattering occurs in the k_z and k_r plane, then left RWPs corresponds to $k_z < 0$ and right RWPs correspond to $k_z > 0$

Extracting Angular Momentum Distributions

A final test of QRS theory was producing accurate and reproducible 2D photoelectron momentum distributions. The elastic DCS was calculated by summing and squaring the scattering amplitudes of the model Coulomb and short-range potential. The RWP was obtained with

$$W(k_r) = D_{SFA2}(k, \theta) / \sigma_{PWBA}(k_r, \theta_r) \quad (3.18)$$

The RWPs calculated through TDSE and SFA2 behaved similarly, and changed little between targets, implying the use of simpler, hydrogenic models in calculations. The use of SFA2, the PWBA and a hydrogenic target increases the computation speed by a factor of 1000 in comparison to TDSE. However, this speed is only useful if momentum distributions calculated through QRS reproduce those generated by TDSE.

Figure 3.28 shows 2D angular momentum distributions for argon and xenon calculated with QRS and TDSE at the same field parameters: 800 nm, 5-cycle pulse with a peak intensity of 1.0×10^{14} W/cm². The results match quite well and according to QRS, any differences in the distributions between the two targets can be attributed to the elastic DCS. This provides some important consequences of using the QRS model: 1) faster calculations of RWP and momentum distributions, 2) physical explanations to describes differences in angular distributions, 3) Angular distributions collected experimentally can be used to extract an elastic DCS and 4) Keeping the target the same and changing the laser parameters can provide information on the RWP.

Volume Effects Points 3) and 4) can only be done if there is good agreement between momentum distributions experimentally collected and calculated distributions. Calculations done with QRS are usually at a single peak intensity. However, experimental distributions are collected over the full focal volume of the beam, with the peak intensity, I_0 , at the center. I like to think of the focal volume as the cross-section of an onion. The shape is not exactly identical but it will suffice for this explanation. The cross-section consists of rings of some volume. At the center is the peak intensity with the smallest volume. The next

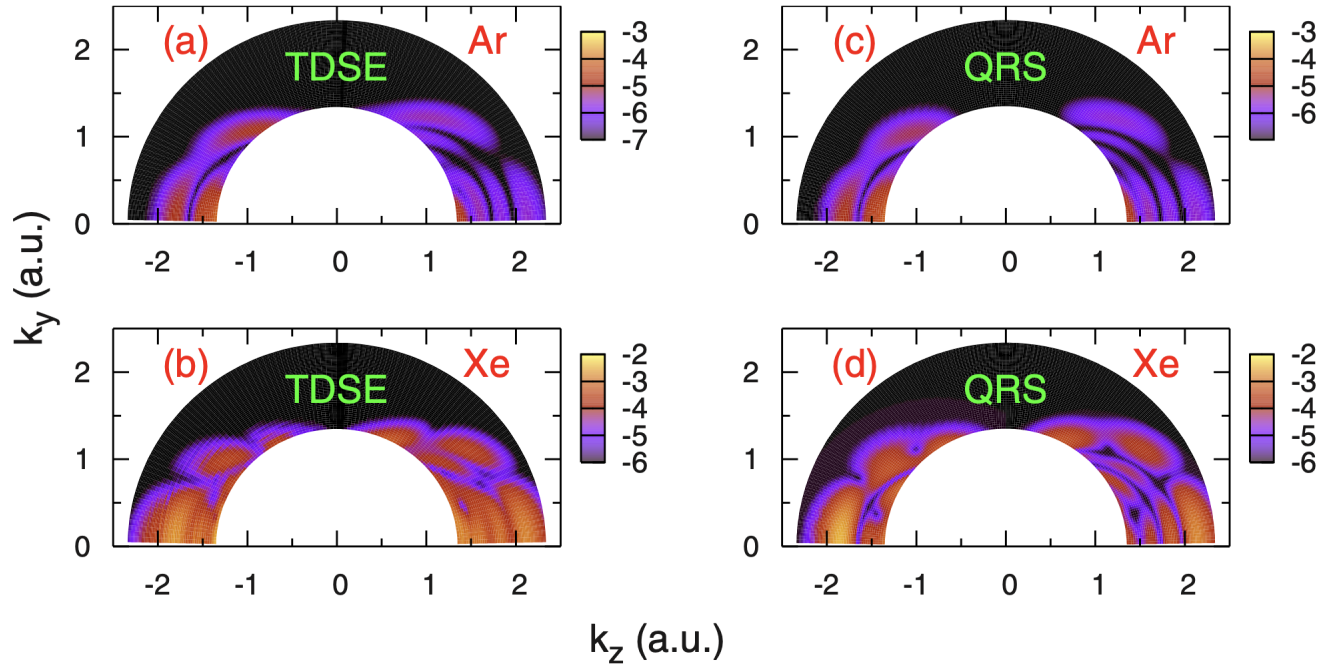


Figure 3.28: **Calculated 2D Momentum Distributions for argon and xenon** Comparison between momentum distributions calculated using a) TDSE and c) QRS for argon. Comparison between momentum distributions calculated using b) TDSE and d) QRS for xenon. A five-cycle, 800 nm pulse with a peak intensity of 1.0×10^{14} W/cm² was used for all calculations. Image credit to Prof. Zhangjin Chen⁵⁸.

ring over is of a lower intensity but with a larger volume. Continuing to move out from the center in this manner leads to rings of larger volumes and lower intensities. Each intensity associated with a ring is known as an *isointensity*. The measured experimental signal is an average of the contributions from all isointensities. This is better known as focal averaging. Therefore, theoretical models must include focal volume effects to accurately compare with experimental data. Figure 3.29 compares experimental photoelectron spectra with those calculated with QRS (volume effects included) for xenon and krypton using an 800 nm, 8 fs pulse at varying intensities. The results agree at high energies, however the discrepancies in xenon at low energies could possibly be due to the lack of multielectron effects in the SAE approximation. But, the general agreement between experiment and theory allows for RWP and DCS extraction from experimental momentum distributions.

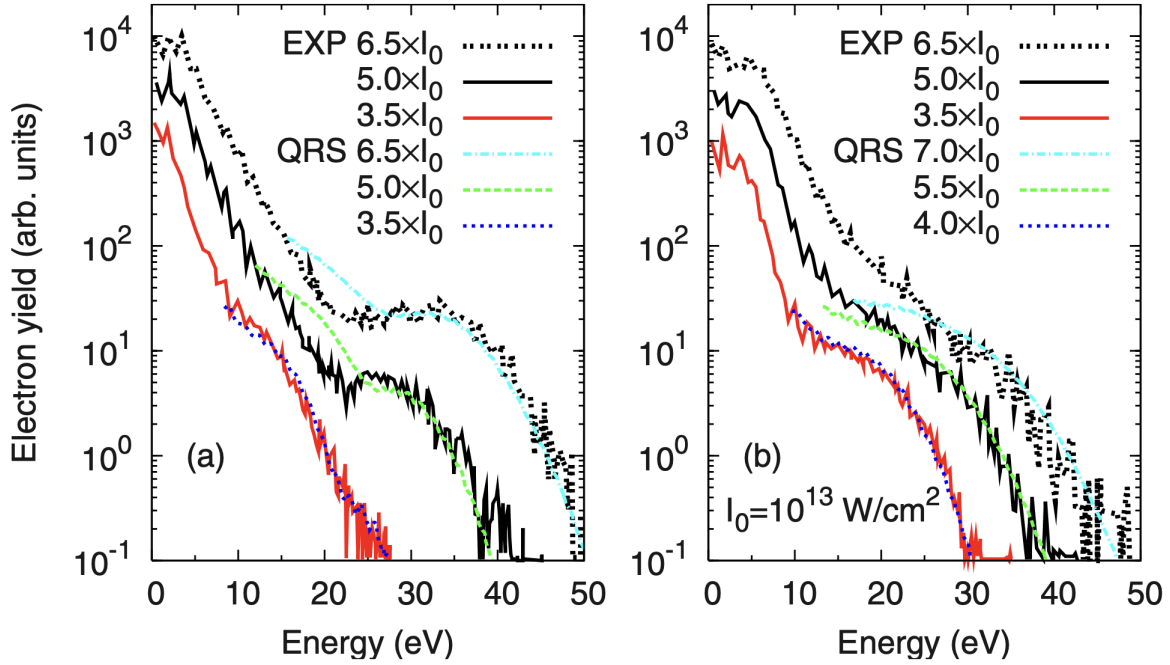


Figure 3.29: **Experimental and Calculated Photoelectron Spectra using QRS** Comparison between experimentally collected and calculated spectra using QRS for a) xenon and b) krypton at varying intensities. An 800 nm, 8 fs pulse was used for theoretical calculations and volume effects are included. Image credit to Prof. Zhangjin Chen⁵⁸.

3.3.2 QRS for HHG

In the same year as Chen, A.T. Le et al. published a paper on QRS for High Harmonic Generation from atoms and molecules. This section will only discuss HHG from atoms. Further details can be found in their paper⁶¹. Since HHG depends on the emission of a high energy photon after recombination, the authors calculate the induced dipole from the field on the atom. According to the QRS,

$$D(\omega) = W(E)d(\omega) \quad (3.19)$$

where $D(\omega)$ is the induced dipole, $|W(E)|^2$ is the flux of electrons returning with energy E , and $d(\omega)$ is the exact transition dipole. The electron energy relates to the photon energy by $I_p + E = E_{\text{photon}}$. The HHG spectra is given by $S(\omega) = |D(\omega)|^2$. The authors validated

QRS for HHG by comparing induced dipoles calculated using TDSE with those generated with QRS.

Obtaining the "exact" induced dipole involves numerically solving the TDSE under the SAE approximation. The steps for this have already been described in the previous section. Once the final time dependent wave function is calculated, the induced dipole is given in acceleration form by

$$D_A(t) = \langle \psi(\vec{r}, t) | \frac{\partial V(r)}{\partial z} | \psi(\vec{r}, t) \rangle \quad (3.20)$$

where $V(r)$ is a spherical potential and the field propagates along the z-axis. The "exact" transition dipole is given by

$$d_{\vec{k}, \vec{n}} = \langle \psi_i | \vec{r} \cdot \vec{n} | \psi_k^- \rangle \quad (3.21)$$

where ψ_k^- is the incoming scattering wave, $\vec{n}$ is the direction of light polarization and $\vec{k}$ is the momentum of the ionized electron. Here the authors assume the polarization is parallel to the z-axis. The scattering wave is numerically calculated using TDSE and partial wave analysis. The photorecombination DCS relates to the transition dipole by:

$$\frac{d^2\sigma}{d\Omega_{\vec{n}}d\Omega_{\vec{k}}} = \frac{4\pi^2\omega^3}{ck} |\langle \psi_i | \vec{r} \cdot \vec{n} | \psi_k^+ \rangle|^2 \quad (3.22)$$

where ψ_k^+ is the *outgoing* scattering wave ⁱⁱⁱ.

The authors calculate the transition dipole with QRS using two different approaches. The first is calculating the RWP using SFA. The previous section showed similar behavior between RWPs for SFA and TDSE. $D(\omega)$ and $d(\omega)$ are calculated using SFA and PWBA. The RWP is given by

$$W_{SFA}(E) = D_{SFA}(\omega)/d_{PWBA}(\omega) \quad (3.23)$$

and the induced dipole is calculated with

$$D_{QRS1}(\omega) = W_{SFA}(E)d(\omega) \quad (3.24)$$

ⁱⁱⁱPhotoionization and photorecombination are reverse processes. Equation 3.13 applies for photoionization and uses the incoming scattering wave, whereas photorecombination utilizes the outgoing scattering wave

The second approach uses a reference atom to calculate the RWP using TDSE. The reference is usually a hydrogen atom with an effective nuclear charge chosen to match the binding energy of the chosen atomic target. Because TDSE is used, this method is much more time consuming. The RWP is given by

$$W_{ref} = D_{ref}(\omega)/d_{ref}(\omega) \quad (3.25)$$

and the associated induced dipole is

$$D_{QRS2} = W_{ref}(E)d(\omega) \quad (3.26)$$

The two approaches have been named QRS1 and QRS2, respectively.

Figure 3.30a displays a comparison of RWPs calculated from exact TDSE, TDSE using a scaled hydrogen atom and SFA. The two TDSE calculations agree over a broad range of energy while the SFA calculation is within reasonable agreement. Figure 3.30b compares HHG spectra for argon using an eight cycle 800 nm pulse with a peak intensity of 2.5×10^{14} W/cm² calculated from TDSE, QRS1, QRS2 and SFA.

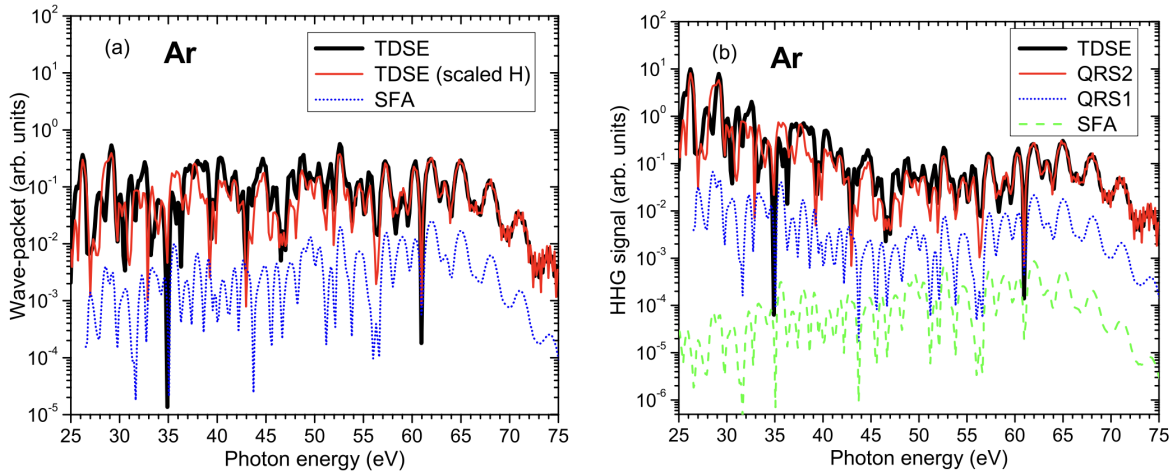


Figure 3.30: RWPs and HHG Spectra Calculated using Different Theoretical Models Calculations were made for argon using an eight-cycle 800 nm pulse with a peak intensity of 2.5×10^{14} W/cm². a) RWPs calculated from TDSE (black), TDSE using a scaled H atom (red) and SFA (dashed blue) b) HHG Spectra calculated using TDSE (black), QRS2 (red), QRS1 (dashed blue) and SFA (dashed green). Image credit to Prof. A.T. Le⁶¹.

There is clear agreement between TDSE, QRS1 and QRS2 while SFA deviates at lower photon energies. The corrections made to the induced dipole in QRS1 provide significant improvements over SFA and the results validate it as a dependable theory for analyzing HHG from atoms.

Chapter 4

Understanding the Enhancement and its Applications with Husimi Plots

This chapter serves to explain the cause of the enhancement and its universal behaviors through the use of photoelectron spectra and Husimi plots. As explained in Chapter 3.2, the Husimi spectrum captures the sub-cycle dipole response of the atom with the laser field at the time of recombination. This is important as the majority of information learned about the enhancement comes from PES, which measures the electron's behavior at the time of *detection*. The Husimi plots analyze the same electron dynamics, but at the time of *return*. They will simultaneously be used to showcase the development of an attosecond electronic soliton in a mirrorless cavity and its potential application for DCS extraction, probing of vibrational and rotational dynamics and explanation of fundamental strong field phenomena.

4.1 TDSE Calculations: Half-Integer Channel Closures and the $6U_p$ Enhancement

Before diving into the results from Husimi plots, this section briefly showcases two important universal phenomena of the enhancement recently discovered through TDSE calculations under the SAE approximation.

In Chapter 1 it was discussed how Paulus proposed a *channel-closing mechanism* to explain the enhancement occurring at a special, leading intensity⁴⁴. The condition claimed when the U_p -shifted continuum threshold is multi-photon resonant with the ground state, a channel closure occurs. Mathematically, this is given by $I_p + U_p = n\hbar\omega$. It is important to specify here that n , the number of photons, is a positive integer. Since U_p is linearly proportional to the laser intensity I , a specific, leading intensity can be correlated to the n th channel closure.

Analysis of theoretical calculations modifies Paulus' proposed mechanism. Theoretical ATI spectra were generated for argon, krypton, hydrogen and helium for different wavelengths and their leading intensities. Briefly mentioned in 3.3.1, experimental data is collected over the full focal volume of the Gaussian laser profile, where the peak intensity is located at the center of the profile with the smallest focal volume and each subsequent "peel", or iso-intensity, corresponds to a lower intensity with larger focal volume. The volume for an iso-intensity is given by

$$V(I_s, I_0) \approx \frac{4}{3} \left(\frac{I_0}{I_s} - 1 \right)^{0.5} + \frac{2}{9} \left(\frac{I_0}{I_s} - 1 \right)^{1.5} - \frac{4}{3} \arctan \left(\left(\frac{I_0}{I_s} - 1 \right)^{0.5} \right) \quad (4.1)$$

where I_0 is the peak intensity and I_s is the iso-intensity. The leading intensities for each wavelength and target were taken by choosing the iso-intensity which contributed the most to the total electron yield in the enhancement region when focal averaging was performed. The yield is the volume multiplied by the ionization rate. Figure 4.1 demonstrates such a calculation for argon at 665 nm conducted at two different peak intensities. The Gaussian profile of the beam can be seen in the top left and the normalized contributed electron yield to the enhancement can be seen as function of iso-intensity. Regardless of peak intensity, the leading intensity is approximately 110 TW/cm² for argon at 665 nm.

The wavelength and leading intensity were mapped to the n th channel closure using Paulus' mechanism, varying I_p depending on the target. Surprisingly, the leading intensities did not correspond to an integer channel closure, but to a *half*-integer channel closure.

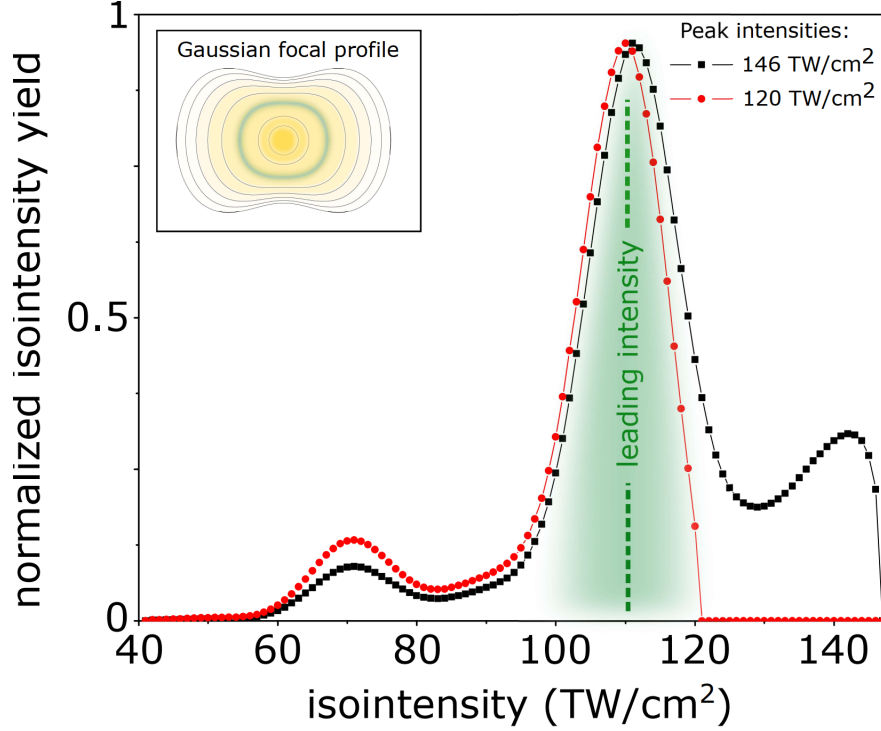


Figure 4.1: **Electron Yield Contributions to the Enhancement from Different Isointensities** TDSE calculations for electron yield contribution to the enhancement as a function of isointensities within the Gaussian focal profile at a peak intensity of 120 TW/cm² (red) and 146 TW/cm² (black). The calculations were done for argon at 665 nm. The Gaussian focal profile is shown in the top left and the green shaded region displays the intensity which contributes the most yield. Image credit to Prof. Cosmin Blaga.

Paulus' mechanism can be modified to

$$I_p + U_p = (n + 0.5)\hbar\omega \quad (4.2)$$

. The reason for the half photon is unknown, but TDSE calculations prove that it is a universal and reproducible feature across different atoms. Additionally, if the energy axis of the ATI spectra is normalized to U_p , then the enhancement always occurs at $6U_p$, regardless of the target. These two universal behaviors of the enhancement can be seen in Figure 4.2. It plots ATI spectra for a) the half-integer photon case or the "on resonance" case and b) the integer photon case or the "off resonance" case. U_p for the on resonance case ranges between 4.96 eV and 13.87 eV. U_p for the off resonance case ranges between 4.96 eV and 13.87 eV. Despite this broad range, the $6U_p$ enhancement can clearly be seen across all targets for the on

resonance case, but seemingly disappears for the off resonance case. Additionally, minimas in electron yield consistently occur at $4U_p$ and $8U_p$ for the on resonance case. Another maxima in electron yield is also consistently observed at $10U_p$ for the on resonance case. The general shape of the ATI spectrum is matching across all on resonance cases regardless of target and wavelength, but the same cannot be said when analyzing the off resonance spectrum. For example, the off resonance hydrogen spectra differ in shape, specifically around $8U_p$, in comparison to other targets. The reproducibility of the $6U_p$ enhancement across all targets and wavelengths justifies the modification of Paulus' channel-closing mechanism. Equation 4.2 will be used in calculating the leading intensities for a given wavelength, target and photon-channel closure.

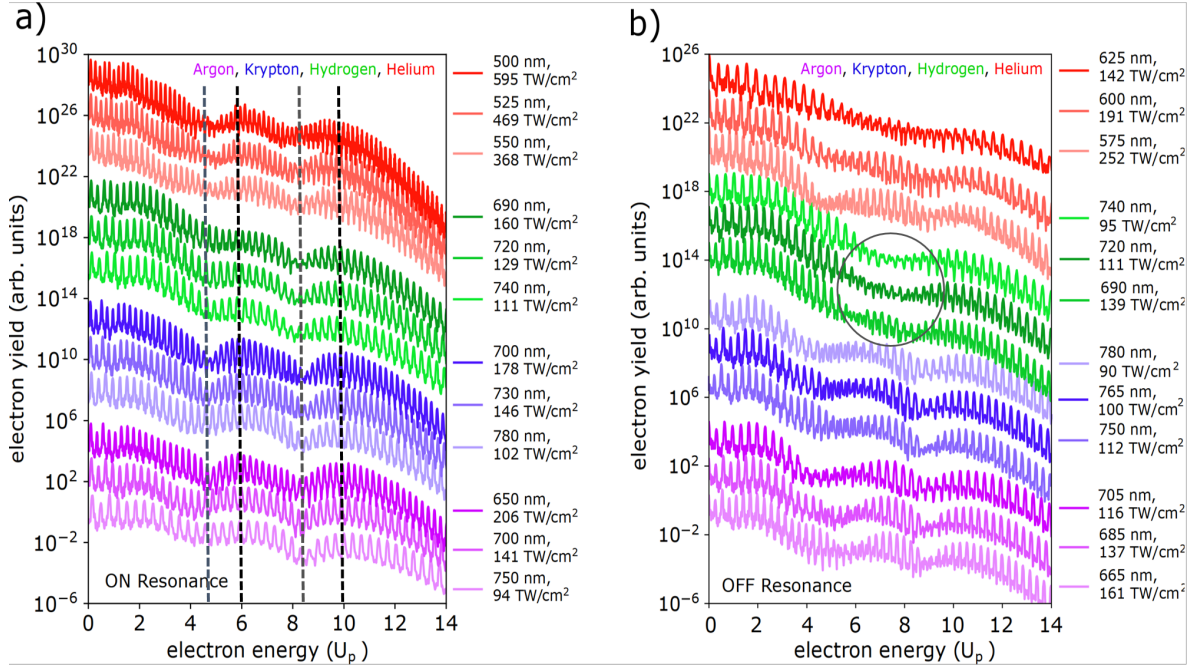


Figure 4.2: Theoretical ATI Spectra Calculated for On/Off Resonance Cases for Different Targets. ATI spectra calculated at different wavelengths and their corresponding leading intensities for argon (violet), krypton (blue), hydrogen (green) and helium (red) for a) the on resonance half-integer photon case and b) the off resonance integer photon case. The energy axis is in U_p units. A $6U_p$ enhancement (black dashed line), minimas at $\approx 4U_p$ and $\approx 8U_p$ (grey dashed lines), and maxima at $10U_p$ (black dashed line) are observed for the on resonance spectrum match, but the same cannot be said for the off resonance case. For example, the ATI spectrum of hydrogen differ in shape in comparison to other targets, specifically around $8U_p$, indicated by the black circle.

4.2 Husimi Plots: Results in the Tunneling and Multiphoton Regime

The computational logistics and mathematics for generating Husimi plots are described in Chapter 3.2. The dipole acceleration files for a given parameter were calculated using TDSE propagation code in the length gauge with a 10-cycle trapezoidal pulse with one cycle turn on and one cycle turn off. These acceleration files were then run through the "DipAcc-HHG-Scan.py" script, which took the Fourier transform of the dipole acceleration, calculated the dipole spectrum by dividing the transformed acceleration from the frequency squared and finally used a Gaussian time window with a fixed width to calculate the frequencies emitted within each time window. The output data was expressed in atomic units as a .dat file with a return time, return energy and corresponding frequency column. This file was then subsequently run through the "husimi.py" file authored by myself, which required 3 inputs: wavelength, intensity and ionization potential. This script properly reshaped the output file into a two-dimensional array and performed the necessary unit conversions to output a 2D Husimi plot with the return energy in U_p units and the return time in optical cycles.

As mentioned in Section 2.3.1, at high energies electron dynamics can be explained from a classical perspective. The first Husimi plot generated in this project serves as a benchmark. A spectrum is generated for argon at 2000 nm with an intensity of 160 TW/cm². This wavelength and intensity were selected for two reasons. First, these are the exact variables chosen by Tate et al. in their 2007 paper, providing a check on the reproducibility of data. Second, they place us within the tunneling regime (Keldysh parameter of 0.36) with a relatively high ponderomotive energy of ≈ 60 eV. We expect, then, the rescattering dynamics of the returning ionized electron can be described through the classical *long* and *short* trajectories within the recollision model. Figure 4.3 shows the calculated Husimi plot for argon at the aforementioned parameters. Tate's spectrum is overlaid on the bottom right. The black and red lines on top of the plot are the return energies predicted by the classical recollision model. These calculations are made with the "classic2.py" python

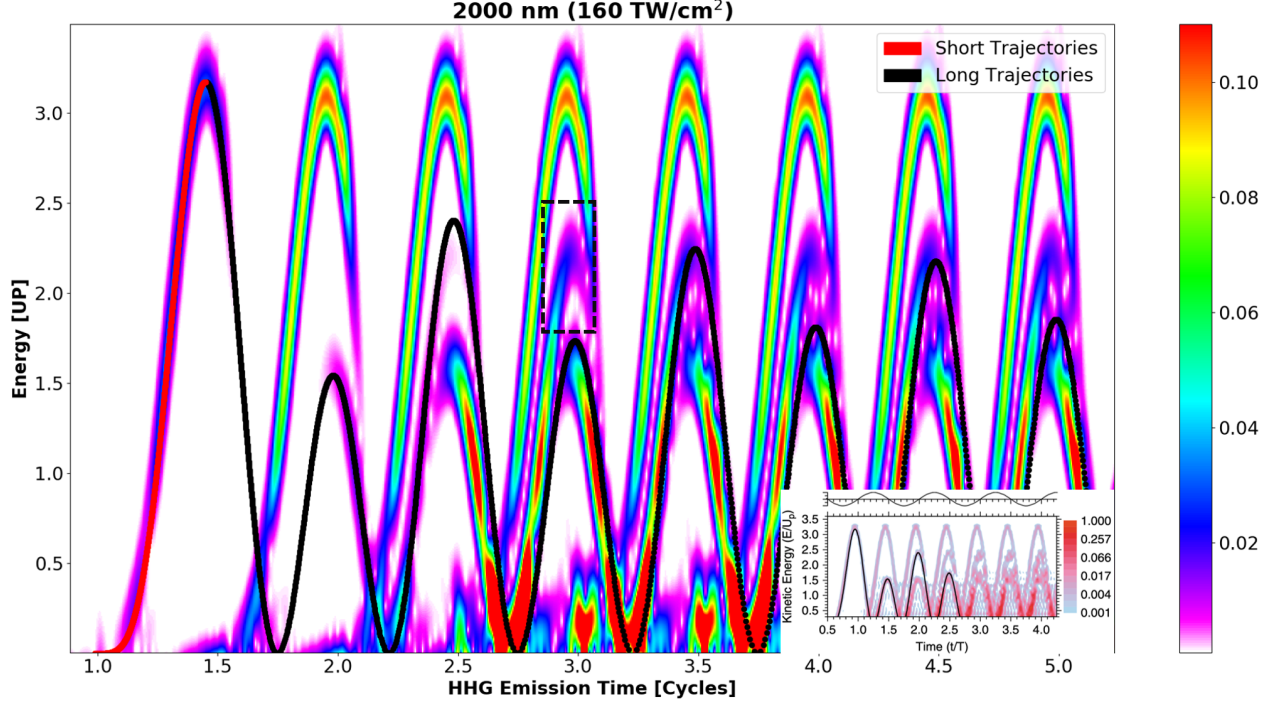


Figure 4.3: **Husimi Plot for argon in the Tunneling Regime** Husimi plot generated for argon at 2000 nm, 160 TW/cm². The return kinetic energy distribution (U_p units) is plotted as a function of the electron's return time (optical cycle units). The red and black lines on top of quantum calculation represent the return energies predicted by the classical recollision model. The red line corresponds to short trajectories. The black line corresponds to long trajectories. The structure developing around the third cycle, indicated by the dashed box, is caused from the interference of multiple long trajectories and the natural dispersion of the electronic wavepacket. Agreement is seen between our calculation and Tate's, whose spectrum is overlaid on the bottom right. The x and y axis of Tate's spectrum are in the same units as ours. Figure 3.23 in Chapter 3.2 of this dissertation shows a larger image of Tate's spectrum.

script which uses the methodology described in Section 2.3.2 and Equation 2.37 to output the kinetic energy at return given an initial birth phase and return phase. The red lines are those return energies which come from *short* trajectories and the black lines are those which originate from *long* trajectories. It is important to note here the classical model only assumes ionization in the first half cycle of the pulse, whereas the Husimi calculations assume ionization every half cycle. Resolving this would mean plotting multiple classical plots on top of the quantum results, each shifted by a half cycle. We notice the excellent agreement between the quantum and classical results on the first return centered at around 1.5 cycles. Additionally, the structure developing around the third cycle, indicated by the dashed box,

is caused from the interference of multiple long trajectories and the natural dispersion of the electronic wavepacket. Finally, the maximum return energy of the quantum Husimi plot is $3.17U_p$, which is the exact energy predicted by the classical model.

The enhancement observed in experimental ATI spectra occurs within the multiphoton regime at a specific intensity for a given target and wavelength. To better understand the electron's behavior under these conditions, Husimi plots were first generated for the same target, argon, at 790 nm. The leading intensity was calculated using Equation 4.1, setting I_p to 15.7 eV and $n = 12.5$ ⁱ. Under these parameters, the leading intensity is 66 TW/cm². This is the on resonance case. Off resonance Husimi plots were also generated for comparison at an intensity of 80 TW/cm².

Before discussing any results it should be noted that the Keldysh parameter is 1.43 and 1.30 for the on and off resonance cases, respectively, putting us in the multiphoton regime for both cases. U_p is 3.84 eV and 4.65 eV for the on and off resonance case, respectively. Figure 4.4a displays the Husimi plots for the on resonance case. Immediately looking at this figure, the electronic wavepacket behaves quite differently from the 2 μ m spectrum. The first characteristic observed is a cycle to cycle growth in HHG emission. Furthermore, these emission bursts occur in a narrow time window. For example, taking a lineout of the on resonance Husimi plot at $2.75U_p$ and fitting a Gaussian to the peak occurring at 5.37 cycles gives a FWHM of 505 attoseconds. The lack of wavepacket spread over time points to a partially *non-dispersive* wavepacket whose density grows at particular frequencies. Additionally, the maximum return energy far exceeds $3.17U_p$, both contrasting the tunneling case and suggesting that classical electron trajectories cannot describe the dynamics of the electronic wavepacket. It should be noted the classical trajectories do *not* take into account the influence of the ionic potential. This is not an issue at 2 μ m since the field oscillates slower than at 800 nm, allowing for increased electron excursion away from the ion, gaining kinetic energy in the process. However, at 800 nm, the field oscillates more quickly, driving the electron back to the ion more frequently. This limits its excursion distance, allowing for

ⁱThe choice of n is from the aforementioned TDSE calculations, which concluded that the 20-30 eV enhancement observed in ATI spectra for argon at 790 nm originates from this specific channel closure

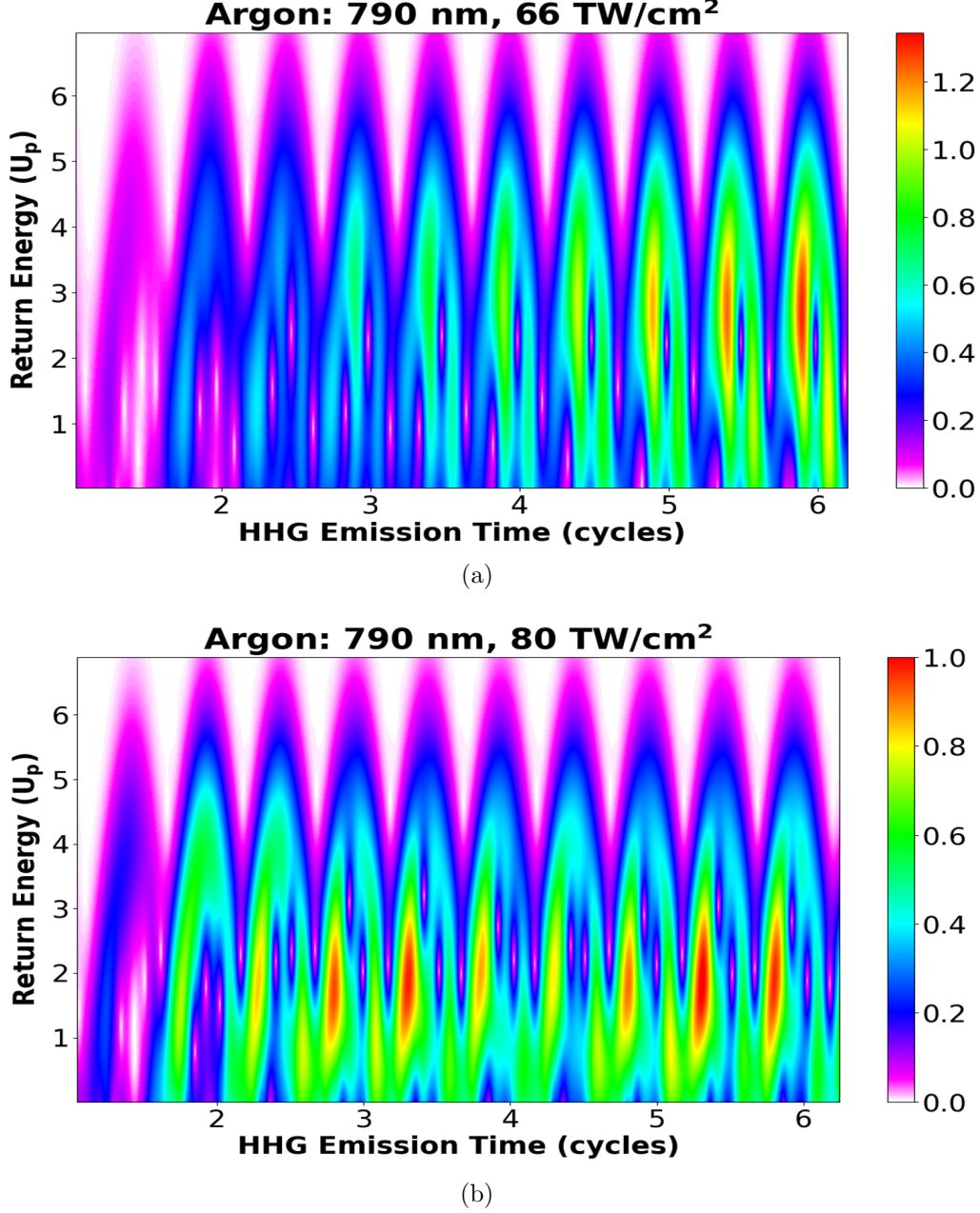


Figure 4.4: **argon On and Off Resonance Husimi Plots in the Multiphoton Regime.** Husimi plots generated for argon at 790 nm. a) On resonance case plotted at a leading intensity of 66 TW/cm² and b) Off resonance case plotted at an intensity of 80 TW/cm².

more influence of the potential on its dynamics.

The most striking contrast between the on and off resonance case in Figure 4.4 is the lack of cycle to cycle growth in emission at 80 TW/cm². To demonstrate this clearly, an energy lineout is taken along 2.75 U_p for both spectrum and plotted against each other in Figure

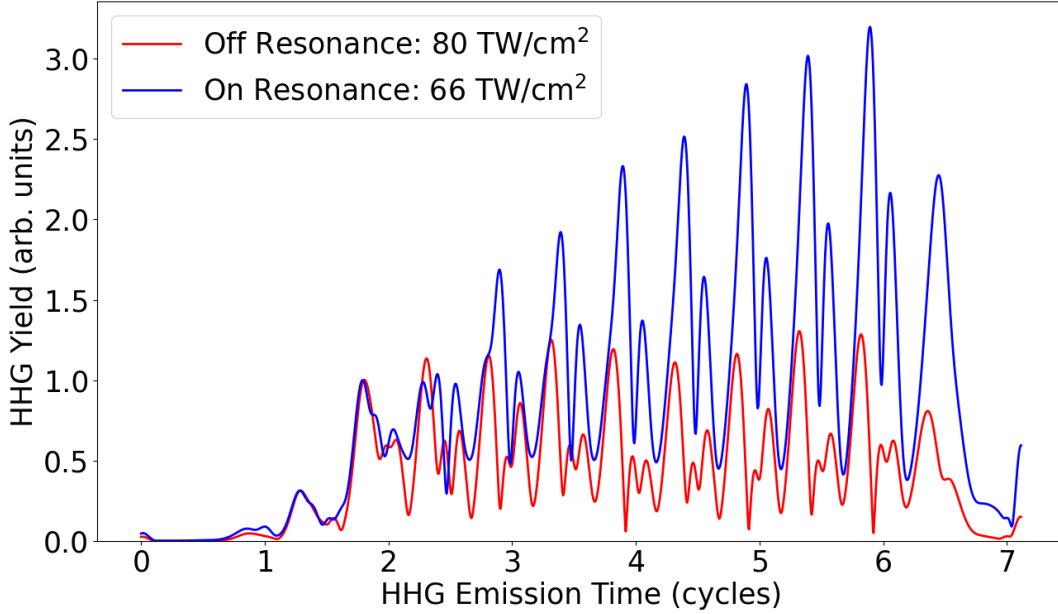


Figure 4.5: **Energy Lineouts for On/Off Resonance argon Husimi Plots** Energy lineouts taken at $2.75U_p$ from 2D on (blue) and off (red) resonance Husimi plots for argon at 790 nm. Both one dimensional lineouts have been normalized to their smallest peaks, respectively.

4.5. Both one dimensional lineouts are normalized to the first return. The on resonance cycle-to-cycle buildup again demonstrates a non-dispersive wavepacket whose density grows periodically when at the special, leading intensity.

Analogy to Modelocked Oscillators

At the right parameters, the Husimi spectrum reveal the creation of a bimodal attosecond electronic soliton which behaves similarly to a femtosecond laser pulse in a modelocked oscillator. An oscillator consists of a cavity and a pump source. The cavity is made of two curved mirrors, one of which is an outcoupler and generally transmits 5% of the light, a gain medium, such as a Ti:Sapphire crystal, and a dispersion control module, typically consisting of a pair of prisms. The pump source couples energy in the gain medium for amplification to occur within the cavity. The radiation passes through the gain medium many times by hitting the curved mirrors, amplifying after each pass until steady state is reached. The

prism pair serves to compensate for the dispersion accumulated after each pass. The laser cavity decides which frequency domain longitudinal modes are allowed for lasing. Maxwell's equations set the boundary condition that the electric field is zero at the end mirrors of the cavity. For a bare cavity of length L with no gain medium, the longitudinal frequency modes are given by⁶²

$$\nu_m = m\nu_0 = \frac{mc}{2L} \quad (4.3)$$

where ν_m is the m_{th} longitudinal frequency mode, ν_0 is the frequency of the fundamental mode, and c is the speed of light. We note m is a positive integer. Figure 4.6 shows a schematic of a cavity with a gain medium of length l and frequency-dependent index of refraction $n(\nu)$. In this case the longitudinal modes are given by

$$\nu_m = m\nu_0 = \frac{mc}{2(L-l) + n(\nu)l} \quad (4.4)$$

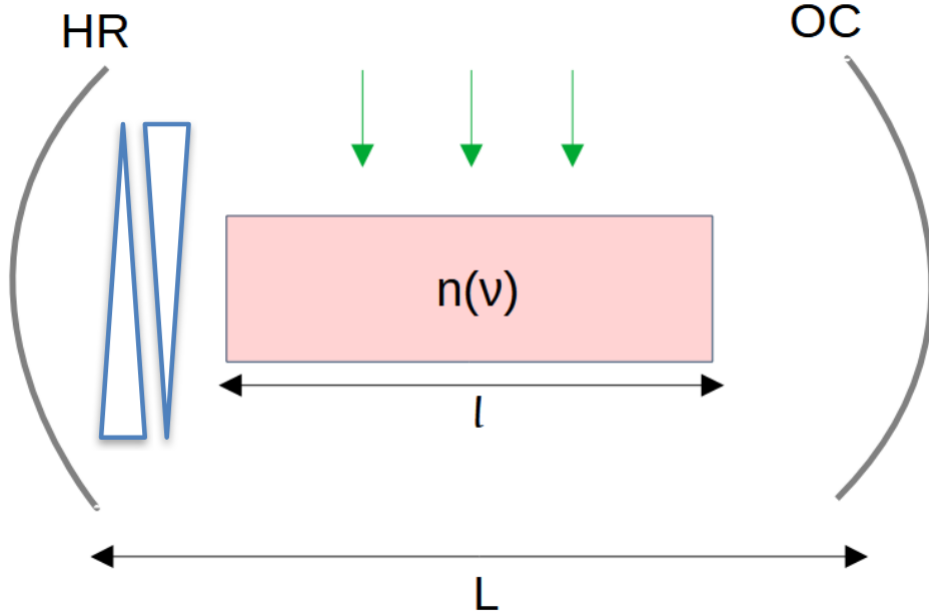


Figure 4.6: Laser Cavity Schematic. A cavity consists of a gain medium of length l (pink rectangle) with index of refraction $n(\nu)$, two curved mirrors separated by length L , one which is high reflectance (HR) and the other an output coupler (OC), and a prism pair for dispersion compensation (blue triangles). The gain medium is pumped by an external source (green arrows).

The difference between two modes would be $\nu_{rep} = c/(2(L - l) + n(\nu)l)$ and implies the output coupler produces a disperison compensated pulse train separated by the round trip time of the cavity, $1/\nu_{rep}$. For example, HITS oscillator operates at ν_{rep} of 80 MHz or a round trip time of 12 ns. Figure 4.7 displays the resulting frequency comb of longitudinal modes given a cavity of length L .

Tuning our wavelength and intensity parameters for a particular target given the channel closure condition has allowed us to trap a dispersion-free electronic wavepacket which circulates in a *mirror-less* cavity without dispersion with a cation as the gain medium and the backscattering events acting as an output coupler. As mentioned previously, classical trajectories do not account for the influence of the ionic potential. The running theory, then, is the potential itself acts as the prism pair and compensates accumulated dispersion experienced on the wavepacket.

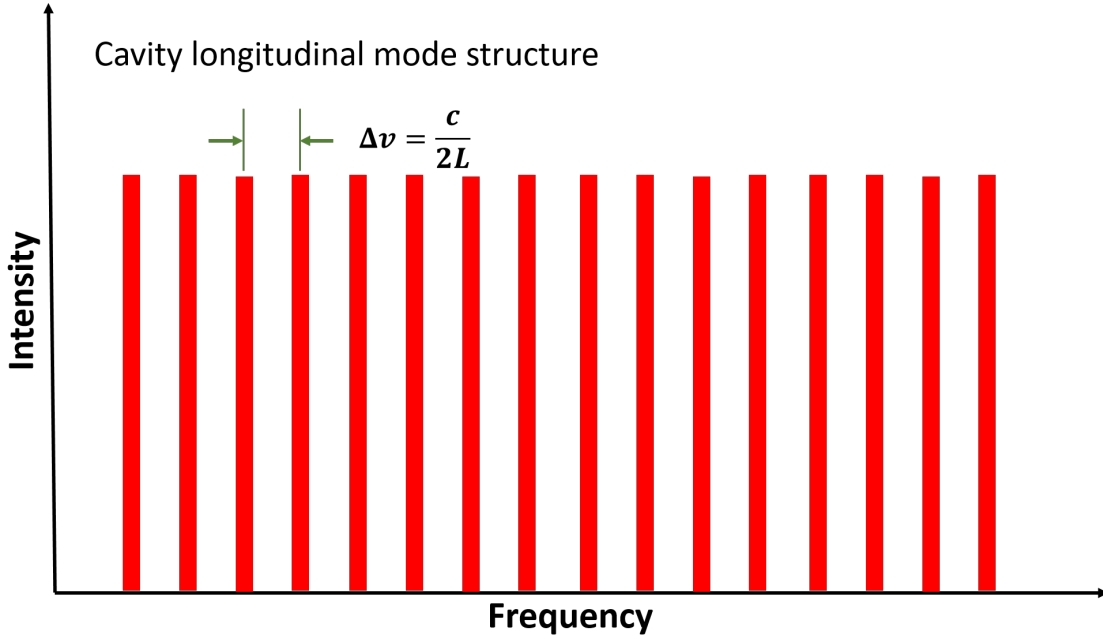


Figure 4.7: **Cavity longitudinal modes.** Frequency comb of longitudinal modes separated by $\nu_{rep} = c/2L$. The oscillator outputs a pulse train separated in time by $1/\nu_{rep}$.

Controlling Dispersion

The discovery of the soliton along with its target and wavelength independence sparked curiosity on the ability to control the dispersion of the electronic wavepacket. In other words, the soliton could be turned "on" and "off" by choosing an intensity and altering the wavelength of the field. To test this hypothesis, a Husimi spectrum was calculated for a chirped electric field. The chirp of a laser pulse is a measure of instantaneous frequency change as a function of time. This was done by stitching an off resonance, on resonance and off resonance field together. Setting $n = 12.5$ and the wavelength at 750 nm, Equation 4.2 tells us the leading intensity would be 94 TW/cm². This is the on resonance field. The corresponding off resonance fields occur at 729 nm ($n=12$) and 770 nm ($n=13$). The chirped electric field can be seen in Figure 4.8. The resultant Husimi spectrum calculated for this field is shown in Figure 4.9. As predicted, off resonance behavior is observed up to the 8th cycle, where the on resonance field "turns on" with cycle to cycle growth of emission,

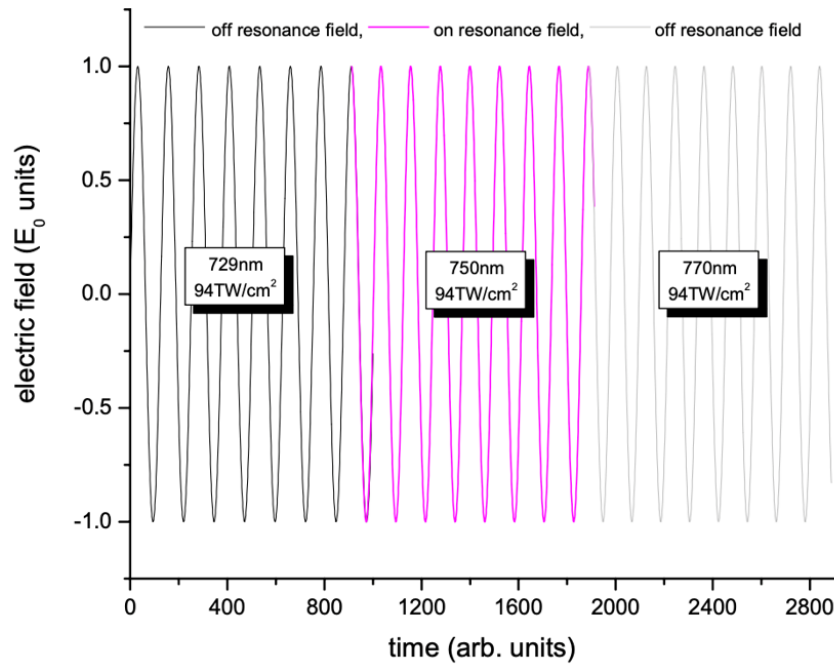


Figure 4.8: **Chirped Electric Field.** Chirped electric field created by stitching off resonance field, on resonance field and off resonance field together. The y axis has been normalized to the electric field amplitude. The x axis is time in arbitrary units. Equation 4.2 was used to calculate the necessary wavelengths at a leading intensity of 94 TW/cm² for $n=12$ (black), $n = 12.5$ (pink) and the $n=13$ (gray) photon channel closure.

and subsequently "turns off" after the 15th cycle, where a ramp down of the soliton occurs after one cycle with a potential revival around the 18th cycle. What we have theoretically shown, then, is the ability to control dispersion by tweaking the field parameters to the proper wavelength and intensity using the channel closure condition or Equation 4.2. The calculations made for the Husimi plots so far were done for a 10 cycle trapezoidal pulse. To align more with experimental parameters, a long sine-squared pulse was used to generate Husimi plots of argon for both the on (66 TW/cm²) and off resonance (80 TW/cm²) cases. The goal was to demonstrate soliton formation and dispersion control with a realistic laser pulse. The field in question is given by:

$$E(t) = \sin\left(\frac{\pi t}{\tau}\right)^2 \sin(\omega t) \quad (4.5)$$

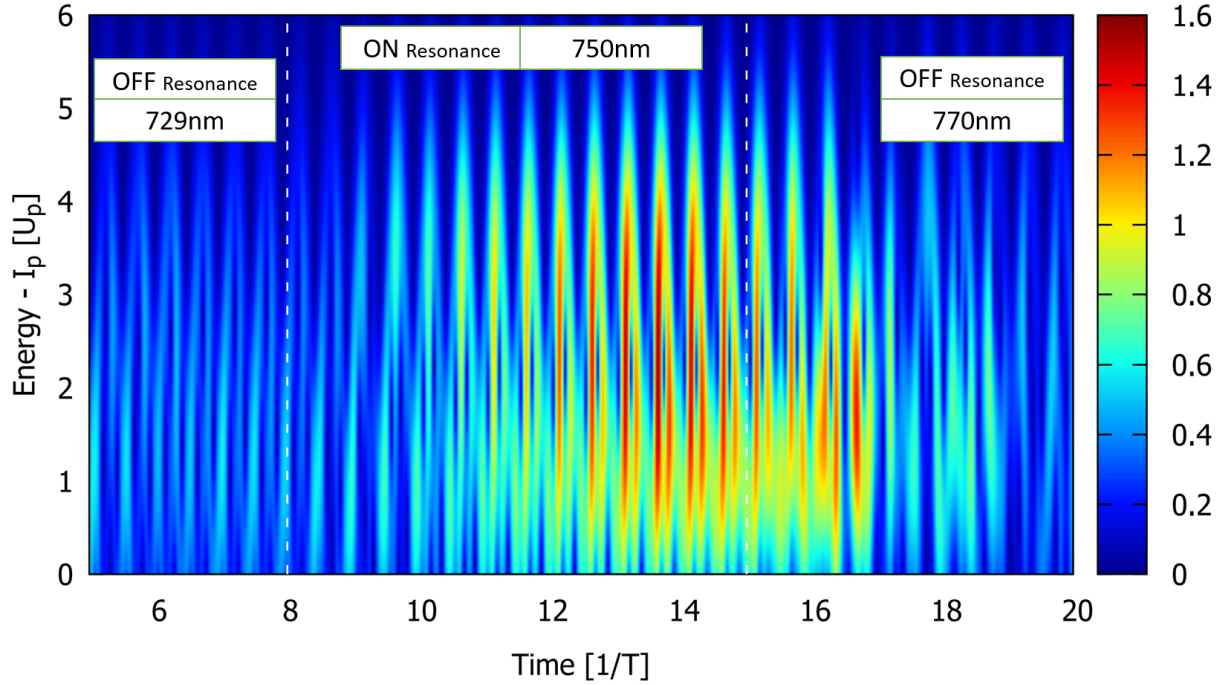


Figure 4.9: Resultant Husimi Spectrum Calculated for a Chirped Electric Field. Husimi spectrum calculated for the chirped electric field seen in Figure 4.1. The x axis is return time in cycles and the y axis is return energy in ponderomotive units. Off resonance behavior (no cycle to cycle emission growth) observed up to 8th cycle, where the on resonance field "turns on" at 750 nm with sharp cycle to cycle emission growth up to the 15th cycle, followed by a soliton ramp down over one cycle with a possible revival around the 18th cycle.

where τ is the length of the pulse, ω is the laser frequency and t is time. Its amplitude goes from 0 at $t = 0$, to 1 at $\pi/2$, again back to zero at τ . After that time, the pulse is gone and is only active for one half sine cycle of the envelope. Figure 4.10a displays the generated Husimi plot for the off resonance case and the resultant energy lineout taken at $3U_p$ in Figure 4.10b with the sine-squared field intensity in gray.

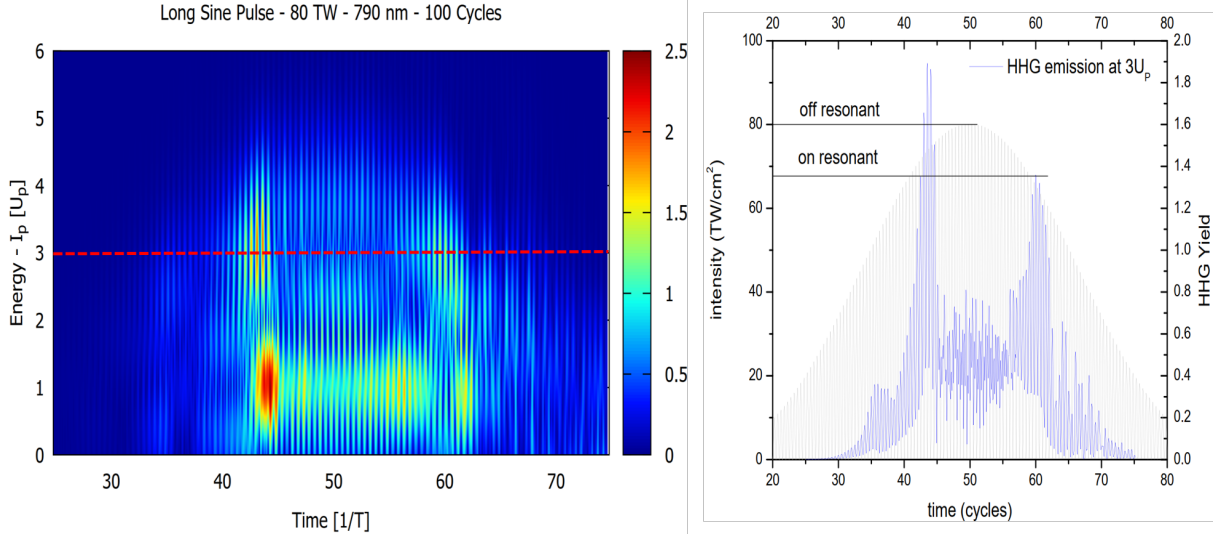


Figure 4.10: **790 nm argon Husimi Spectrum Calculated for a Long Sine-Squared Pulse at 80 TW/cm²** Left: Generated Husimi spectrum given a 100 cycle sine squared pulse calculated at 80 TW/cm² for argon at 790 nm. Red dashed line indicates $3U_p$ lineout. Right: Energy lineout taken at $3U_p$ in blue overlaid with the field in gray. Two emission windows are seen at the instantaneous intensity corresponding to the on resonance leading intensity. The off and on resonance intensities are denoted by the two black horizontal lines.

The key observation here are the two main emission windows separated in time where the instantaneous intensity matches the leading intensity. This again demonstrates the ability to control dispersion and cavity gain by adjusting the pulse duration of our field. Similarly, Figure 4.11a shows the generated Husimi plot for the on resonance case and the corresponding lineout at $3U_p$ in Figure 4.11b. Here, chirp-free emission is seen only near the peak of the field. Only one, narrow emission window is observed in comparison to the off resonance case, before and after which the soliton breaks apart. However, two conclusions are drawn from both Husimi plots: the soliton exists even when using a realistic sine-squared pulse and adjusting the pulse duration of the field allows for control of dispersion and gain.

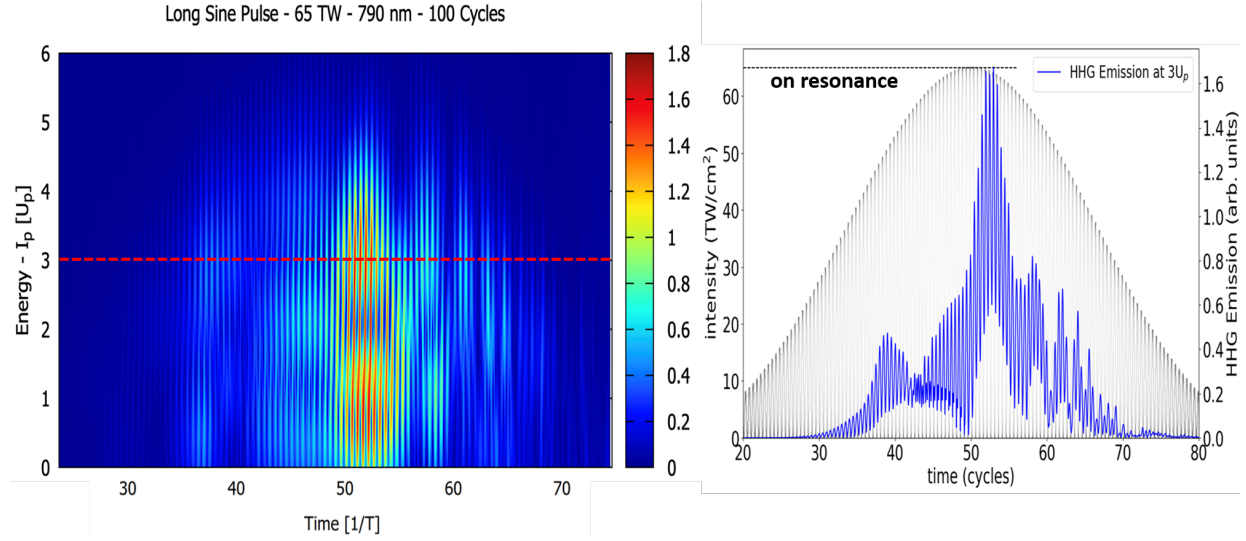


Figure 4.11: **790 nm argon Husimi Spectrum Calculated for a Long Sine-Squared Pulse at 65 TW/cm²** Left: Generated Husimi spectrum given a 100 cycle sine squared pulse calculated at 65 TW/cm² for argon at 790 nm. Red dashed line indicates $3U_p$ lineout. Right: Energy lineout taken at $3U_p$ in blue overlaid with the field in gray. A single emission window is seen near the peak of the field corresponding to the leading intensity denoted by the black, dashed horizontal line.

Soliton Stability

Despite the excellent discoveries made about the soliton and the ability to control wavepacket dispersion, the previous studies had only been calculated for up to 8 cycles. To investigate the soliton's stability, another Husimi spectrum was generated for argon, 790 nm, 66 TW/cm² (on resonance case). However, this calculation was done for a much longer period of time, approximately 60 cycles, or 157.8 fs. The resultant spectrum is shown in Figure 4.12a. A couple of important observations can be made here. First, the most frequent return energies occur at $2.75U_p$ and $1.25U_p$. These energies are indicated by dashed black horizontal lines in Figure 4.12a. Second, the horizontal lineouts displayed in Figure 4.12b and Figure 4.12d, taken at these two energies, show the periodic buildup of emission saturates at approximately 7 cycles and stabilizes thereafter. Finally, to demonstrate the consistency of these frequent return energies, a simple study was conducted. For $2.75U_p$, a lineout in time was first taken at an earlier cycle (near saturation) where the density of emission was maximum. This occurred at 6.89 cycles. A second lineout was then taken at a later cycle where the density of emission

was maximum. This occurred at 59 cycles. The two vertical lineouts in energy were then plotted in Figure 4.12e. The same methodology was applied for the return energy of $1.25U_p$, except the two return times were chosen to be 7.07 and 59.15 cycles. These lineouts are plotted in Figure 4.12d and clearly confirm $1.25U_p$ and $2.75U_p$ as the most frequent return energies, regardless of the return time. In fact, if the time of return positions are taken and converted to the vector potential at the time of return, the HHG emission is maximized at $.68A_0$ for $2.75U_p$ and $0.91A_0$ for $1.25U_p$, where A_0 is the peak vector potential ⁱⁱ.

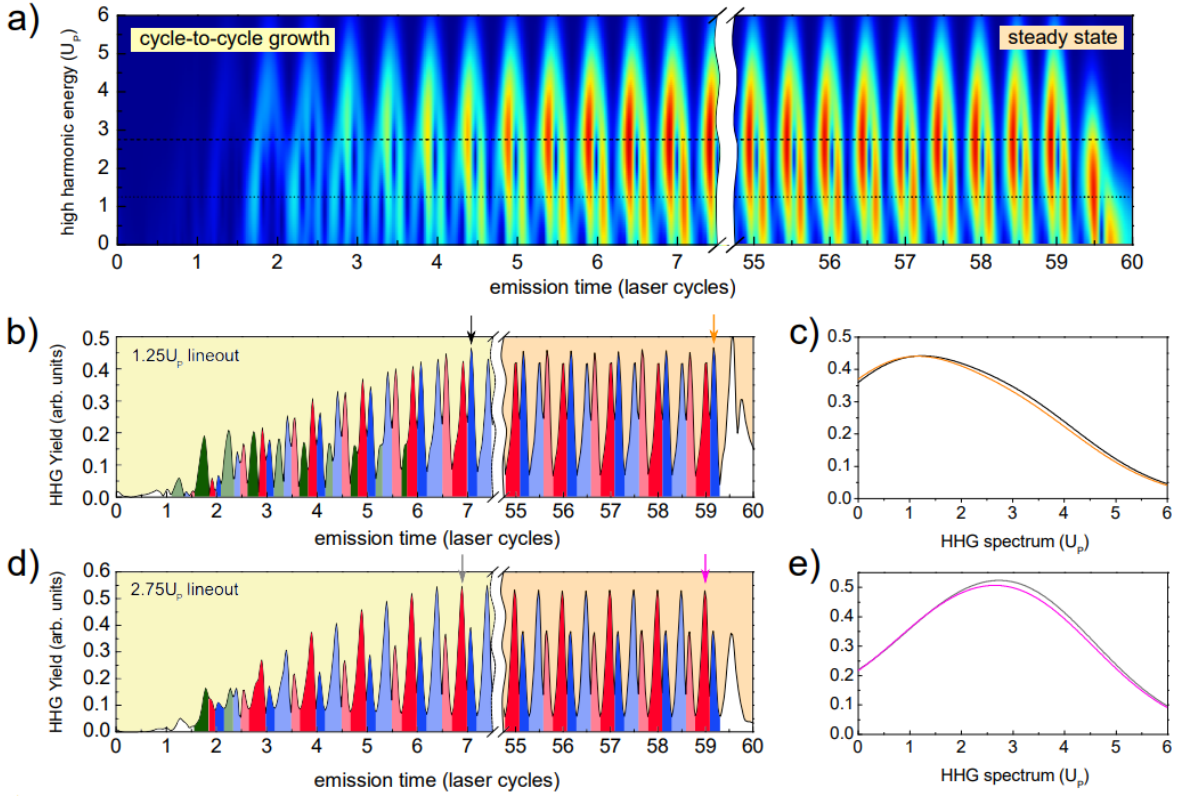


Figure 4.12: **Argon 60 Cycle Husimi Plot and Analysis** a) 60 cycle Husimi plot generated for argon at 790 nm with a leading intensity of 66 TW/cm². Only the first 7 cycles and last 5 cycles are shown. The black dashed horizontal lines indicate the return energies of $1.25U_p$ and $2.75U_p$. b) Energy lineout taken at $1.25U_p$. Only the first 7 cycles and last 5 cycles are shown. c) Vertical time lineouts taken at 7.07 cycles (black) and 59.15 cycles (orange). These return times are indicated by the black and orange arrows in 4.7b. d) Energy lineout taken at $2.75U_p$. Only the first 7 cycles and last 5 cycles are shown. e) Vertical time lineouts taken at 6.89 cycles (gray) and 59 cycles (pink). These return times are indicated by the gray and pink arrows in 4.7d. Credit to Prof. Cosmin Blaga for this image.

ⁱⁱwe recall A_0 is equivalent to $\sqrt{4U_p}$

The Enhancement: Pulse Duration Dependence

Further understanding the stability of the dispersion free wavepacket involved studying its behavior over various cycles. This could be done by generating Husimi spectrum over different cycles, but this is computationally challenging, especially for calculations over 100 cycles. However, the installation of the Tangor 300 and MPC in JRM Lab provided the opportunity to perform this exact study experimentally by observing how the enhancement changed as a function of pulse duration. As mentioned in Chapter 3, the Tangor 300 operates at 1030 nm, 450 fs with a peak pulse energy of 3 mJ at a 100 kHz. The MPC, described in Chapter 3.1.4, can be filled with argon at varying pressures to adjust the pulse duration of the Tangor 300 output. So, the ultimate goal was: collect photoelectron spectra of argon at varying pulse durations using the Tangor 300, the MPC and the DTOF vacuum chamber.

Chapter 3.1.1 described the procedure to measure the pulse duration with 100 mbar, 200 mbar, 300 mbar and 500 mbar of argon in the MPC. The FROG traces displayed in that section measured pulse durations of 295 fs, 204 fs, 158 fs and 85 fs, respectively. Next, the beam was sent to the DTOF chamber using 45° 2 inch (035-1030) and 0° 1 inch (035-1030-i0) 1030 nm mirrors from Eksma Optics. The procedure outlined in the Chapter 3.1.3 was used to collect photoelectron spectra was followed. Peak to peak fluctuations of 2.5 % were measured using the RIGOL Ultravision II oscilloscope after putting the beam on a fast photodiode (1 ns rise time). At each pressure of the MPC, an intensity scan was done by collecting photoelectron spectra at various powers to determine where the enhancement was best resolved. The runtime of each scan varied between 10 and 20 minutes, and this was compensated by normalizing each spectrum to the total number of laser shots. An example of such a scan can be seen in Figure 4.13 when 500 mbar of argon was injected into the MPC. At lower powers, two enhancements are observed at approximately 25 eV and 42 eV! Equation 4.2 tells us these correspond to the $n = 16.5$ and $n = 18.5$ channel closure. Knowing the enhancement occurs at $6U_p$, U_p would be 4.11 eV and 6.52 eV, respectively. As the intensity increases, the first enhancement at 25 eV washes away from direct electron contamination and a new one can be seen at approximately 63 eV, corresponding to the n

= 21.5 photon channel closure with U_p being 10.13 eV. Since, the ponderomotive energy is linearly proportional to the intensity of the field, this behavior is not unexpected.

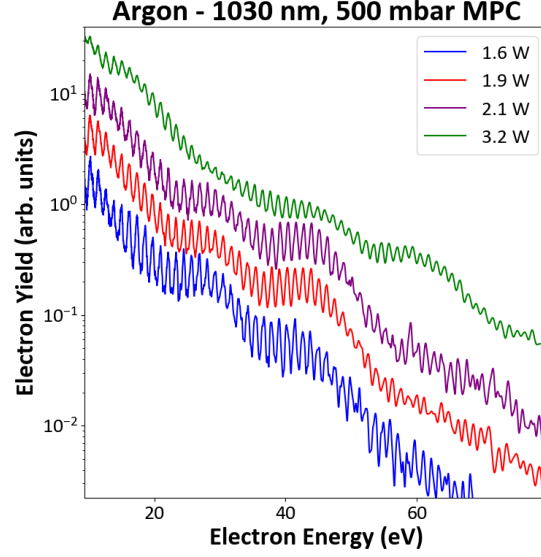


Figure 4.13: **Intensity Scan of argon ATI Spectra with 500 mbar of argon Injected into MPC.** ATI Spectra of argon collected at 1.6 W, 1.9 W, 2.1 W and 3.2 W with 500 mbar of argon within the MPC. This pressure corresponded to a pulse duration of approximately 85 fs. At lower powers, an enhancement is observed at 25 eV and 42 eV. At 3.2 W, the 25 eV enhancement washes away from direct electron contamination and a third enhancement appears at 63 eV.

The results of the pulse duration study are shown in Figure 4.14a. All spectra shown were 20 minute runtimes. The immediate observation made was the invariance of the enhancement as a function of pulse duration. Specifically, it does not shift in detected energy as the pulse duration increases. To investigate this further, a 1D Gaussian filter was used to smooth the ATI peaks, seen in Figure 4.14b. Then, a peak finding algorithm was used to determine where the two enhancements occurred for each spectra ⁱⁱⁱ. The quantified peak values can be seen in Table 4.1. The standard deviation for the first and second enhancement from this dataset and sample sizes are both 0.3 eV, quantifying the lack of enhancement energy shift as a function of pulse duration. This could be a reflection on the intensity dependence of the enhancement. As long as the required leading intensity is within the focal volume of

ⁱⁱⁱScipy Python package was used for this analysis. Specifically `gaussian_filter1d` for smoothing and `argrelextrema` for peak finding.

Table 4.1: **Peak positions in energy for first and second enhancement observed in argon at different pulse durations.**

Pulse Duration (fs)	First Peak Position (eV)	Second Peak Position (eV)
85.97 ± 0.34	28.6 ± 0.3	43.5 ± 0.5
158.61 ± 1.47	28.1 ± 0.3	43.0 ± 0.5
204.00 ± 3.54	28.3 ± 0.3	43.4 ± 0.5
295.40 ± 3.66	28.9 ± 0.3	43.8 ± 0.5

the beam, the ATI peaks which form the envelope are locked in place, regardless of peak intensity. Further experimentation and analysis are planned for the future. This involves collecting PADs at different pulse durations for different targets.

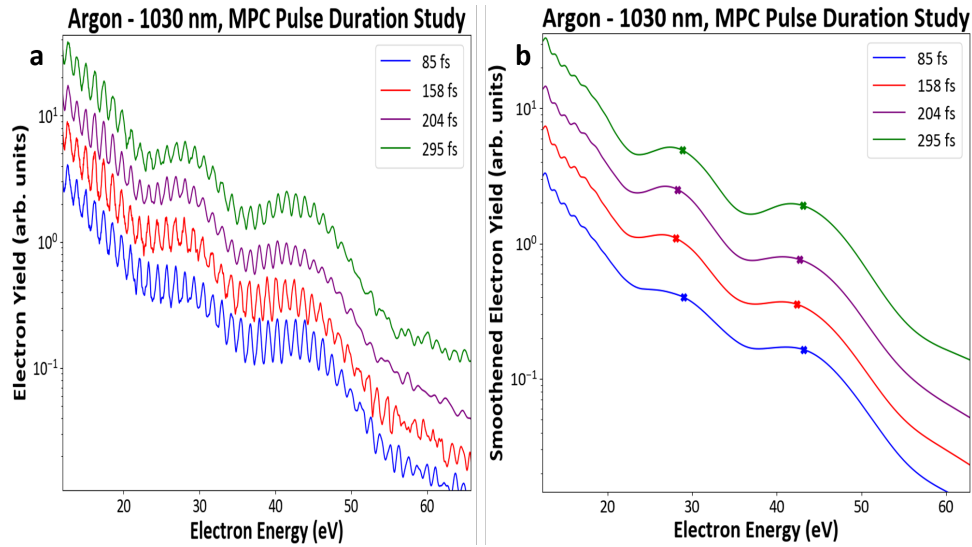


Figure 4.14: **ATI spectra of argon collected at varying Pulse Durations.** a) ATI Spectra of argon collected at 85 fs, 158 fs, 204 fs and 295 fs. All spectra were for 20 minute runtimes. The pulse durations were varied by injecting different mbar of argon into the MPC. Two enhancements are observed at 28 eV and 43 eV for all pulse durations. The enhancements do not shift in detected energy as a function of pulse duration. b) argon ATI spectra were smoothed using a 1D gaussian filter at each pulse duration. Then, a peak finding algorithm was used in Python to determine the peak positions in energy of each enhancement. These peak positions are marked with an x on each spectra.

Non-Dispersive Wavepacket: Target Dependence?

The next step to understanding our wavepacket was studying its dependence on different wavelengths and targets. So, Husimi plots were generated for argon at 650 nm and for different targets to see if the same phenomena was observed. Figure 4.15 displays four on resonance Husimi plots for argon, xenon, hydrogen and helium. The most important result to notice is *all* four spectrum show a sharp cycle to cycle build up of HHG emission, regardless of target and wavelength. Further quantitative analysis is discussed later in this chapter. For now, this study reveals the non-dispersive nature of the electronic wavepacket is not unique to argon at 790 nm, 66 TW/cm².

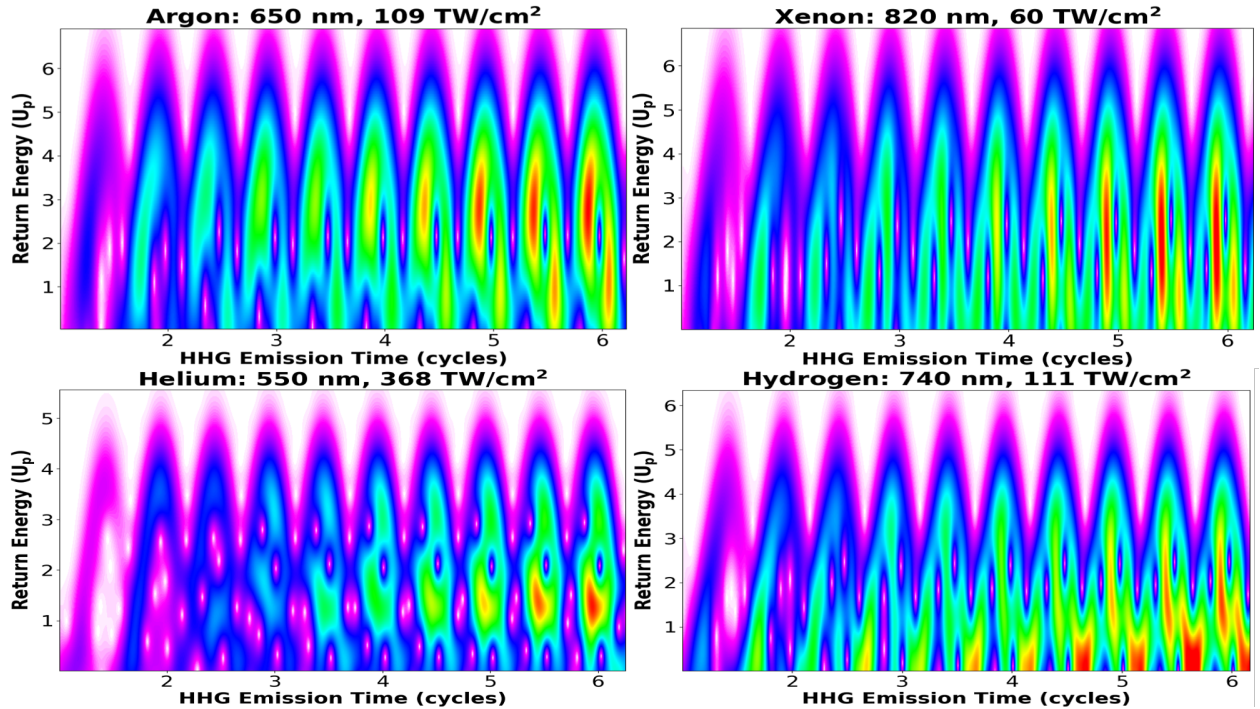


Figure 4.15: **On Resonance Husimi Plots for Different Wavelengths and Targets**
Top left: Husimi plot for argon at 650 nm with a leading intensity of 109 TW/cm². Top right: Husimi plot for xenon at 820 nm with a leading intensity of 59.9 TW/cm². Bottom left: Husimi plot for helium at 550 nm with a leading intensity 368 TW/cm². Bottom right: Husimi plot for hydrogen at 740 nm with a leading intensity of 111 TW/cm². The y and x axes are the return energy in U_p units and return time in optical cycles.

4.3 Husimi Plots: Explaining the $6U_p$ Enhancement

In section 2.3.2, the full elastic rescattering picture equated the overall detected momentum of a rescattered electron to the vector sum of the momentum the electron gains at the time it returns to the parent ion plus the vector potential at the time of return, or $\vec{p}_{det} = \vec{p}_r + \vec{A}_r$. The detected energy is $E_{det} = \|\vec{p}_{det}\|^2/2 = (\vec{p}_r + \vec{A}_r)^2/2$. The Husimi plots provide the return energy, E_r of the electron at the time it returns to the parent ion, t_r . Since $p_r = \sqrt{2E_r}$ and $A_r = A_0 \cos(\omega t_r)$, the plots provide both the variables necessary to map the HHG emission distribution to a final, detected energy. The 60 cycle argon Husimi plot was used for this analysis. In the last section, we learned the cycle-to-cycle build up of HHG emission stabilized after the 7th optical cycle and the most frequent return energies were $1.25 U_p$ and $2.75 U_p$. Mapping to detected energies can theoretically be done then by extracting the A_r and p_r values from an arbitrary cycle along the Husimi plot. For this analysis, two vertical lineouts in time were taken in time at approximately 19.87 and 20.05 cycles, where the density of HHG emission was maximized. These lineouts are seen as the shaded pink and orange distributions in Figure 4.16a and Figure 4.16b. To no surprise, the most frequent return energies are still $1.25 U_p$ and $2.75 U_p$. Subsequent horizontal energy lineouts are taken between 1 to $7 U_p$ in $.25 U_p$ steps. Each lineout looks like 4.12b and a peak finding algorithm is used to find the return time where HHG yield is maximized around 19.87 and 20.05 cycles. These extracted time values correspond to the red and blue scatter plots in Figure 4.16a and Figure 4.16b. Each (E_r, t_r) pair is converted to (p_r, A_r) using the aforementioned equations and finally mapped to a detected energy. The black scatter plots in Figure 4.16a and Figure 4.16b provide the mapped detected energies for a given (p_r, A_r) .

A couple of exciting discoveries made from this analysis begin to connect the dots of a 30 year old mystery. First, the most frequent recombination energies return at a time which map to a detected energy of $6U_p$! To make this obvious, a $6U_p$ horizontal dashed line has been intersected with a $2.75U_p$ and $1.25U_p$ vertical dashed line. Second, the y-scale of both plots in Figure 4.14 only span a).07 and b).007 cycles, a very short amount of time. Both time scatter plots were further investigated to find at which return frequencies the electronic wavepacket

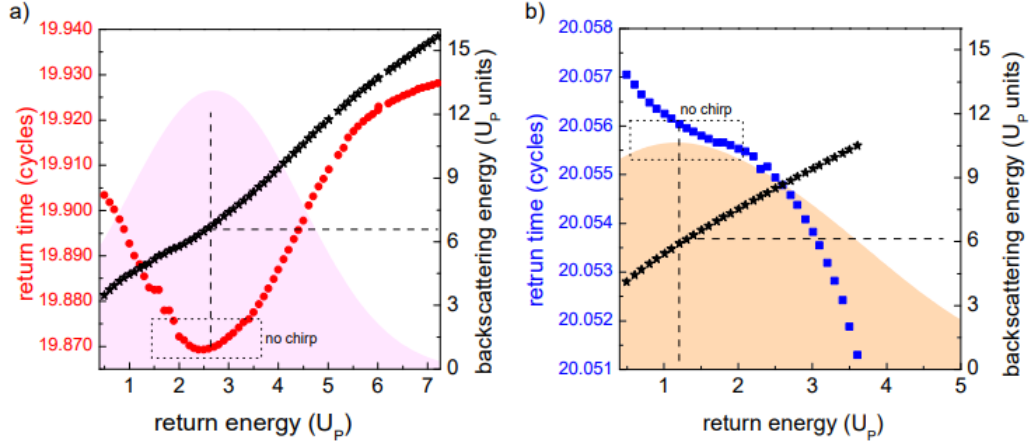


Figure 4.16: Mapping Return Energies and Return Times to Detected Energies

All lineouts and calculations made from 60 Cycle On resonance argon Husimi Plot at 790 nm. Vertical lineout in time taken at a) 19.87 cycles shown as shaded pink distribution, peaking at $2.75U_p$ and b) 20.05 cycles shown as shaded tan distribution, peaking at $1.25U_p$. Scatter plot in a) red and b) blue are extracted time values in optical cycles indicating where HHG yield is maximized. They are found from horizontal lineouts taken between 1 to $7U_p$ in $.25U_p$ steps and peak finding around a) 19.87 cycles and b) 20.05 cycles. Mapped detected energies for each individual (p_r, A_r) pair shown in black scatter plot. A dashed vertical line is drawn at a) $2.75U_p$ and b) $1.25U_p$ and a horizontal dashed line is drawn at $6U_p$ for both figures. The x axis is return energy in U_p units, the y axis on the left is the return time in cycles and the y axis on the right is the detected energy in U_p units. Image credit to Prof. Cosmin Blaga.

dispersed the least. As mentioned previously, the chirp of a light pulse measures the rate of change in the instantaneous frequency. A previously unchirped laser pulse can become chirped through chromatic dispersion after light travels through a medium with a wavelength dependent index of refraction. Similarly, measuring the rate of change in the return energy through the time scatter plots is a reflection on the dispersion of the electronic wavepacket as it evolves in time. The smaller the change, the more stable and non-dispersive the electronic wavepacket for a particular return energy. The energies with the smallest change over time are marked in Figures 4.16a and Figure 4.16b in dashed boxes labeled "no chirp". Amazingly, these return energies correspond to $2.75U_p$ and $1.25U_p$! This explains why the density is highest at these return energies. Overall, the results shown in Figure 4.16 strongly support the aforementioned theory: an ionized trapped, stable electronic wavepacket, caught in an oscillating field, returns to the parent ion cycle after cycle, its density growing with little

to no dispersion and largest at $2.75U_p$ and $1.25U_p$, before eventually backscattering with a kick from the field's vector potential and resulting in an enhancement of electron yield at a detected energy of $6U_p$.

Differential Cross Section Correction This chapter has consistently equated the HHG emission to the spectral density of the electronic wavepacket. This is done under the assumption of the Quantitative Rescattering Theory (QRS) from Section 3.3.1. Equation 3.17 states the returning wave packet is equal to the induced dipole divided by the exact transition dipole. The induced dipole squared provides us with our Husimi plots and the exact transition dipole relates to the photorecombination DCS from Equation 3.19. Therefore, to fully analyze and understand the behavior of the wavepacket's spectral density, we would need to divide the Husimi plots by the target's photorecombination cross section. This work has not been done yet but is planned for the future.

4.3.1 $6U_p$ Explanation in Other Targets and Wavelengths

The soliton and Husimi plots for argon at 790 nm provided an explanation for the $6U_p$ phenomena. However, is this explanation unique to only this target and this wavelength? Section 4.2 provided on resonance Husimi plots for helium, xenon, hydrogen and argon at 650 nm. Lineouts for each target were taken at energies where the soliton was approximately most dense, and a chosen peak in time, around 5.9 cycles (most soliton growth), was fit to a Gaussian distribution to extract its position and Full Width Half Maximum (FWHM). Then, this value was converted to A_0 units for comparison. Figure 4.17a plots the resultant lineouts for all targets. The analyzed time peak positions for helium, argon (790 nm), argon (650 nm), hydrogen and xenon were $5.92 \pm .10 T$, $5.88 \pm .10 T$, $5.86 \pm .10 T$, $5.89 \pm .06 T$ and $5.89 \pm .06 T$, respectively, where T is the period. Regardless of the target, the electronic wavepacket returned to the ion at roughly the same time! Subsequent lineouts were then taken at these positions in time and fit to another Gaussian distribution to extract the peak positions in energy. These are plotted in Figure 4.17b. Again for helium, argon (790 nm), argon (650 nm), hydrogen and xenon these peaks were located at $1.3U_p$, $2.6U_p$, $2.6U_p$, $1.6U_p$

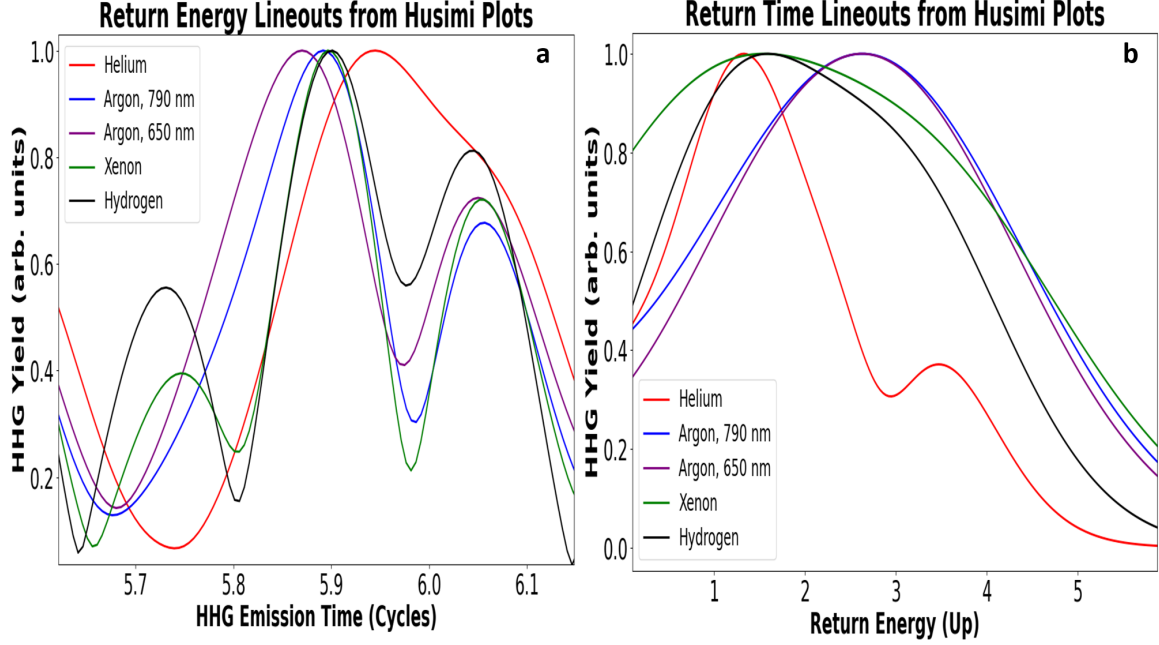


Figure 4.17: **Return Energy and Time Lineouts Extracted from On Resonance Husimi Plots for Multiple Targets** a) Energy lineouts were extracted at $1.25U_p$, $2.6U_p$, $2.6U_p$, $1.75U_p$ and $1.75U_p$ from on resonance Husimi plots for helium (red), argon (790 nm, blue), argon (650 nm, purple), xenon (green) and hydrogen (black) to identify the return times of the electronic wavepacket by fitting a Gaussian to the data. These were found to be $5.92 \pm .10 T$, $5.88 \pm .10 T$, $5.86 \pm .10 T$, $5.89 \pm .06 T$ and $5.89 \pm .06 T$, respectively, where T is the period. b) Lineouts in time were extracted at the aforementioned time values for helium (red), argon (790 nm, blue), argon (650 nm, purple), xenon (green) and hydrogen (black) to determine the return energies of the wavepacket by fitting a Gaussian to these plots. They were found to be $1.3U_p$, $2.6U_p$, $2.6U_p$, $1.6U_p$ and $1.9U_p$, respectively.

and $1.9U_p$, respectively. Finally, the positions in time and energy were converted to A_r and p_r and these were mapped to a detected energy. Amazingly, these were calculated to be $5.5U_p$, $6.7U_p$, $6.7U_p$, $5.7U_p$ and $5.8U_p$ for helium, argon (790 nm), argon (650 nm), hydrogen and xenon, respectively! Regardless of target, the electronic wavepacket returns to the ion at the same time and the soliton explains the $6U_p$ enhancement.

4.4 Husimi Plots: Applications

Analyzing HHG spectra has deepened our understanding of electron dynamics at the time of return within the multiphoton regime. The non-dispersive wavepacket provided us with

a new lens by which to explain phenomena such as the $6U_p$ enhancement. Additionally, its stability and target independence provides itself as a tool for many applications. First, its target independence and universality allows for the potential to extract differential cross sections. Second, its stability across many cycles allows for the wavepacket to probe the target multiple times over 100 fs, meaning vibrational and rotational modes can be investigated. Finally, the Husimi plots debunk the use of classical trajectories in the multiphoton regime and provide potential explanations for electron-electron correlation phenomena such as NSDI.

4.4.1 Extracting Differential Cross Sections

The methodology for extracting an elastic DCS is highlighted in Section 3.3.1 and is based on the classical recollision model from Section 2.3.2. A circle is placed on a 2D experimentally collected angular distribution, where the momentum at return, p_r and the vector potential at return, A_r determine the radius and center of the circle. The electron yield is collected along this circle as a function of the rescattering angle, θ_r . From QRS, Equation 3.17 states the yield collected from the angular distribution is proportional to the elastic DCS and the returning wavepacket is dependent mostly on the laser parameters only. We recall the Husimi plots provide *both* the momentum at the time of return and the vector potential at the time of return, the exact parameters we need to fit our circle!

As a preliminary test, we use our Husimi plots to fit a circle onto a photoelectron angular distribution of argon collected with the DTOF chamber located in FLAME, discussed earlier in Chapter 3. As a reminder, data in FLAME was collected at the following parameters: 815 nm, 35 fs pulse duration, 30.5 mW at a 3 kHz repetition rate. Details of the 800 nm source in FLAME and the DTOF chamber can be found in Section 3.1.2 and Section 3.1.3 of this dissertation. Figure 4.18 shows the general methodology for extracting a DCS from a PAD using the Husimi plots. First, photoelectron angular distributions of argon are collected at 815 nm. Second, Husimi plots are generated for the on resonance case for argon at 790 nm. The vector potential at return, A_r and the return momentum p_r are subsequently found from

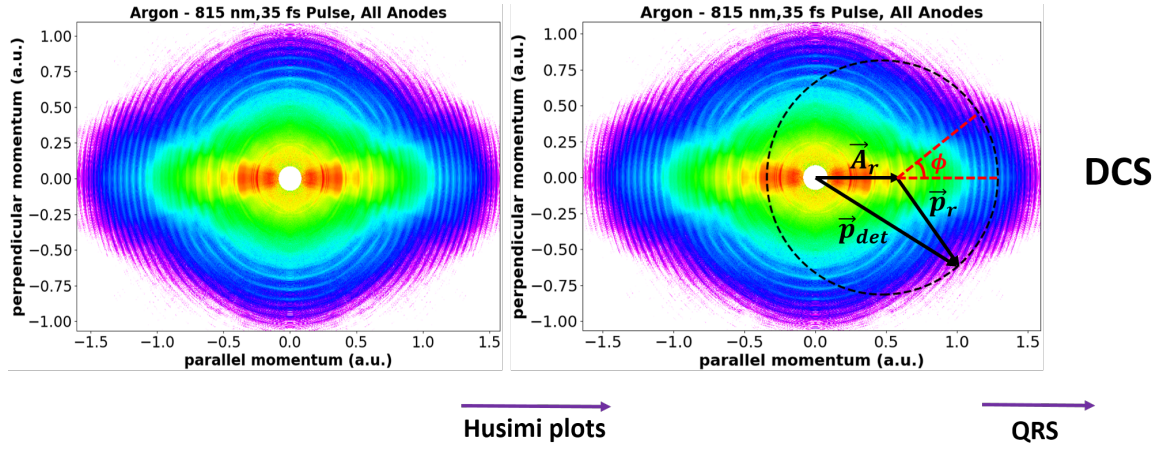


Figure 4.18: **DCS Extraction Methodology using Husimi Plots.** First, we collect photoelectron angular distributions for argon at 815 nm. Next, we use the Husimi plots calculated at the same parameters to obtain p_r and A_r in atomic units. These will be the radius and center of the circle, respectively. Finally the yield is extracted along the circle as a function of ϕ , the rescattering angle. The x and y axes of the PAD are momentum parallel (pperp) and perpendicular (ppara) to the laser polarization, respectively, in atomic units.

the Husimi spectrum. For 790 nm argon, the electronic wavepacket returns with an energy of $p_r = \sqrt{5.5U_p}$ at $A_r = .68A_0$ and $p_r = \sqrt{2.5U_p}$ at $A_r = .91A_0$. Finally, the circle is placed on the 2D momentum distribution with a radius of p_r and center of A_r and the yield is extracted along θ_r . Figure 4.19 displays the resultant yield as a function of scattering angle for a return energy of $2.75U_p$ (return momentum of $\sqrt{5.5U_p}$) and compares the extracted yield to theoretical elastic electron-ion DCS calculated by Prof. A.E.S Green for a similar return energy⁶³. Further comparison with theory is needed and caution should be taken in calling these results a "Differential Cross Section".

4.4.2 Interrogating Vibrational and Rotational Dynamics Using an Electronic Soliton

Another fundamental property of the soliton is its stability. The 60-cycle Husimi plot calculation for argon demonstrated this. As a note, 790 nm light corresponds to a period of 2.6

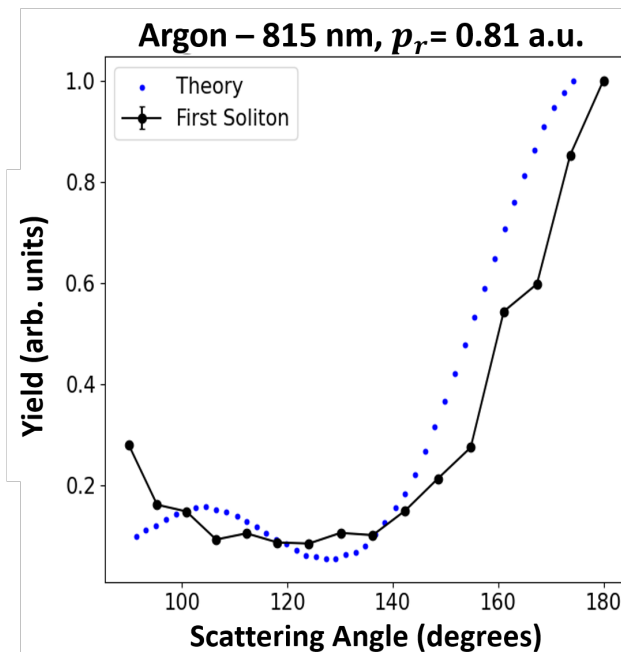


Figure 4.19: **790 nm argon DCS Extracted using On Resonance Husimi Plots.** Normalized DCS extracted at varying peak intensities for a return energy of 0.39 a.u., or a return momentum of 0.88 a.u. using on resonance argon Husimi plots at 790 nm.

fs, meaning the soliton was stable for 156 fs^{iv}! The vibrational period of molecules is on the order of tens of femtoseconds, whereas the rotational period is on the order of nanoseconds. Since the soliton lasts for the duration of the pulse, it is a potential candidate for interrogation of these molecular dynamics. Additionally, experimental focal averaging of Gaussian beams need not be a factor since the enhancement is seen as long as the correct wavelength and intensity parameters are used. Using the soliton as an experimental probing mechanism has not been tested on molecules yet but will be pursued in the near future.

4.4.3 Revisiting Fundamental Strong Field Phenomena

Analysis of Husimi spectra emphasizes the importance of the phase contribution from the returning electronic wavepacket. The key to the enhancement is the fact that the returning wavepacket is *dispersion free* at certain return frequencies. In other words, the phase asso-

^{iv}if we could, we would run the calculation for more cycles, but it's computationally expensive

ciated with the wavepacket at these return frequencies is "flat" (no chirp). This results in the constructive interference of the bimodal wavepacket which consistently returns to the parent ion with the same return phase cycle after cycle. This phase-sensitive phenomena which survives focal averaging calls for the modification of theoretical tools such as QRS. The factorization of the momentum distribution into contributions from the returning wavepacket and the elastic DCS in QRS theory simplifies calculations. However, the phase information is lost as it focuses on calculating the magnitude of the wavepacket. Therefore, QRS theory cannot describe interference effects or phenomena which depends on the phase of the electronic returning wavepacket.

Stepping back even further, the discovery of the dispersion free wavepacket begins to reframe rescattering processes in the multiphoton regime. The attosecond soliton, not classical long and short trajectories, dictate electron dynamics in the continuum. Additionally, the results presented in this chapter point to the necessary inclusion of the ionic potential's influence on electron dynamics. This helps explain why SFA would struggle to explain the enhancement with its assumption of a Volkov state as the final continuum state. To what extent can the soliton explain rescattering phenomena? Specifically, at what Keldysh parameter does the soliton fail and the classical model take over? Answers to these questions can contribute greatly to modifying rescattering models.

The dispersion free wavepacket can also help explain other strong field phenomena, such as NSDI. In the "Inelastic Scattering" section of Chapter 2.3.2, Figure 2.6 showed the measured single and double ionization yields of helium at 780 nm collected by Prof. B. Walker et al. The production of doubly charged helium ions was much higher than that predicted by the ADK ionization model. At the time, the group claimed a second electron can only be knocked off if the return energy of the first electron was greater than the binding energy of He^+ (54.4 eV). For this, they assumed the maximum return energy of the electron was $3.17U_p$ and calculated the needed intensity. Since this threshold was not observed in the experiment, the group concluded rescattering could not explain the higher production of double charged ions. They instead proposed nonsequential ionization occurred through a "simultaneous two-electron ejection either through a shakeoff or threshold mechanism in-

volving some form of electron correlation”²⁷ v. However, the discovery of the soliton calls for a revisit of the underlying mechanism which drives NSDI. Within the multiphoton regime, Husimi plots generated for helium in Figure 4.15 show return energies beyond $5U_p$! With these new, higher return energies, the intensity necessary to knock off a second electron lowers, and reopens the possibility of rescattering driving nonsequential ionization. Additionally, since the ADK ionization model applies within the tunneling regime, we would not expect it to agree with the rescattering model driven by the soliton. An originally closed door now remains ajar for further investigation on electron-electron correlation phenomena.

Another fundamental goal in strong field physics is the generation of shorter pulses for the study of electron motion. In Chapter 2.3.2, "Recombination", HHG was discussed as a prime candidate for the generation of attosecond pulses. In general, a driving beam is impinged on a solid or gas medium which catalyzes the HHG process, outputting an extreme Ultraviolet (XUV) field, resulting in an attosecond pulse train. A schematic can be seen in Figure 4.20. In practice, however, this process is quite difficult since researchers must control a variety of sensitive factors.

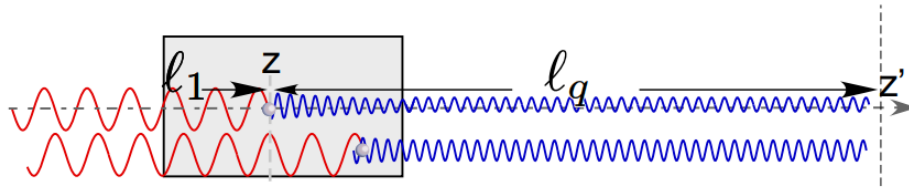


Figure 4.20: **Phase mismatch in HHG.** For two atoms within the gas medium (gray rectangular box), the driving laser (red field) must traverse two different lengths (l_1), resulting in a length mismatch and dephasing between the two resultant XUV fields (blue field) as they also traverse two different lengths (l_q) to the detector (gray dashed line). Image credit: Dr. Thierry Ruchon⁶⁴.

For example, the solid or gas medium used consists of an ensemble of atoms. For two atoms, the driving laser must traverse two different lengths to produce the XUV field, resulting in a length mismatch and dephasing between the two resultant XUV fields. This is known as a phase mismatch and results in lower XUV conversion efficiency. *Phase matching*

^vshakeoff: while the first electron tunnel ionizes, the second electron is ionized with some intensity dependent probability

involves finding the necessary conditions to sum the resultant XUV fields coherently and depends on the geometry of the beam, the driving beam's intensity, the pulse duration and the gas medium⁶⁴. However, our soliton provides a way of producing attosecond pulses with less constraints. The returning electrons inherently sum with the same phase since they are caught within an oscillating field, a coherent source! Therefore, the phase matching condition is not needed. By experimentally tweaking the wavelength and intensity to satisfy the channel-closure conditions, the soliton sheds light on a new way to control and increase the production of attosecond pulses by laxing the sensitive phase matching constraint.

Chapter 5

Applying the Dispersion Free Wavepacket to QRS

Section 4.4.1 highlighted the potential application of the dispersion free wavepacket in extracting an elastic electron-ion DCS. The extraction methodology depends on QRS theory, which was introduced in Section 3.2. It factorizes the photoelectron angular momentum distribution into the averaged spectral density of the returning wavepacket and the elastic DCS. Additionally, as mentioned in Chapter 4, QRS theory focuses on calculating the magnitude of the wavepacket and interference effects like the enhancement, which depends on its phase, are washed out from focal averaging effects. In general, the DCS is easier to calculate for electron energies on the order of hundreds of eV¹. It was shown for molecules consisting of light atoms, the DCS extracted from these electrons were accurate for collisional energies around 100 eV using QRS in the SAE approximation and the IAM model¹. However, we perform LIED experiments using *low-energy electrons* less than 10 eV. Specifically, the leading intensity for argon at 790 nm is 66 TW/cm², making $U_p \approx 3.84$ eV. This leads to the following question: is QRS theory under the SAE approximation still valid for investigating the enhancement and for more complex molecules with low energy electrons? This question was investigated on methane, ethane, acetylene and ethylene. Why these hydrocarbons? These are essential petrochemical compounds, thus the interest in studying their

chemistry at femtosecond levels. Second, the radicals of these small molecules are fragments in photoinduced dissociation of larger molecules. Therefore, the experimental data collected and analyzed establishes LIED’s ability to image simpler hydrocarbons before proceeding towards more complex organic compounds. This first step involves collecting photoelectron spectra and photoelectron angular distributions of these hydrocarbons.

5.1 Enhancement Existence in Hydrocarbons?

The previous section and experimental studies discussed in Chapter 2.4 observed the enhancement in multiple atoms and simpler, diatomic molecules. But what about our chosen simple hydrocarbons? The procedure to collect PES outlined in Section 3.3.3 was followed and ATI spectra for methane, ethane, and ethylene were collected at varying intensities. As a reminder, 1030 nm light was used at a 100 kHz repetition rate with a 450 fs pulse duration. Figure 5.3 displays the scans for the three targets. Let’s look at them individually.

Looking at Figure 5.1a, an enhancement is observed at ≈ 15 eV for methane ($I_p = 12.56$ eV) at lower powers. Using Equation 4.2 and calculating $6U_p$, this corresponds to the $n = 12.5$ photon channel closure. As the intensity increases, another enhancement appears at ≈ 30 eV, mapping to the $n = 14.5$ channel closure. Additionally, the first observed enhancement seemingly disappears as the intensity increases. This is due to an increase in the $2U_p$ cutoff and direct electrons mask the first observed enhancement. Similarly, in Figure 5.1b, an enhancement appears at ≈ 21 eV and ≈ 35 eV for ethane ($I_p = 11.55$ eV). Remarkably, these also correspond to the $n = 12.5$ and $n = 14.5$ photon channel closures. Ethylene’s ($I_p = 10.51$ eV) intensity scan (Figure 5.1c) shows two enhancements occurring at ≈ 20 eV and ≈ 27 eV, corresponding to the $n = 11.5$ and $n = 12.5$ channel closures. Finally, acetylene’s enhancement occurs at ≈ 21 eV, again corresponding to $n = 12.5$. Figure 5.1d plots all targets’ ATI spectra for comparison.

Decreased ATI contrast occurs in both methane and ethane at higher intensities. Occurrence in both molecular targets suggests this phenomenon depends more on field parameters than molecular structure. At higher intensities, electrons gain more energy from the field,

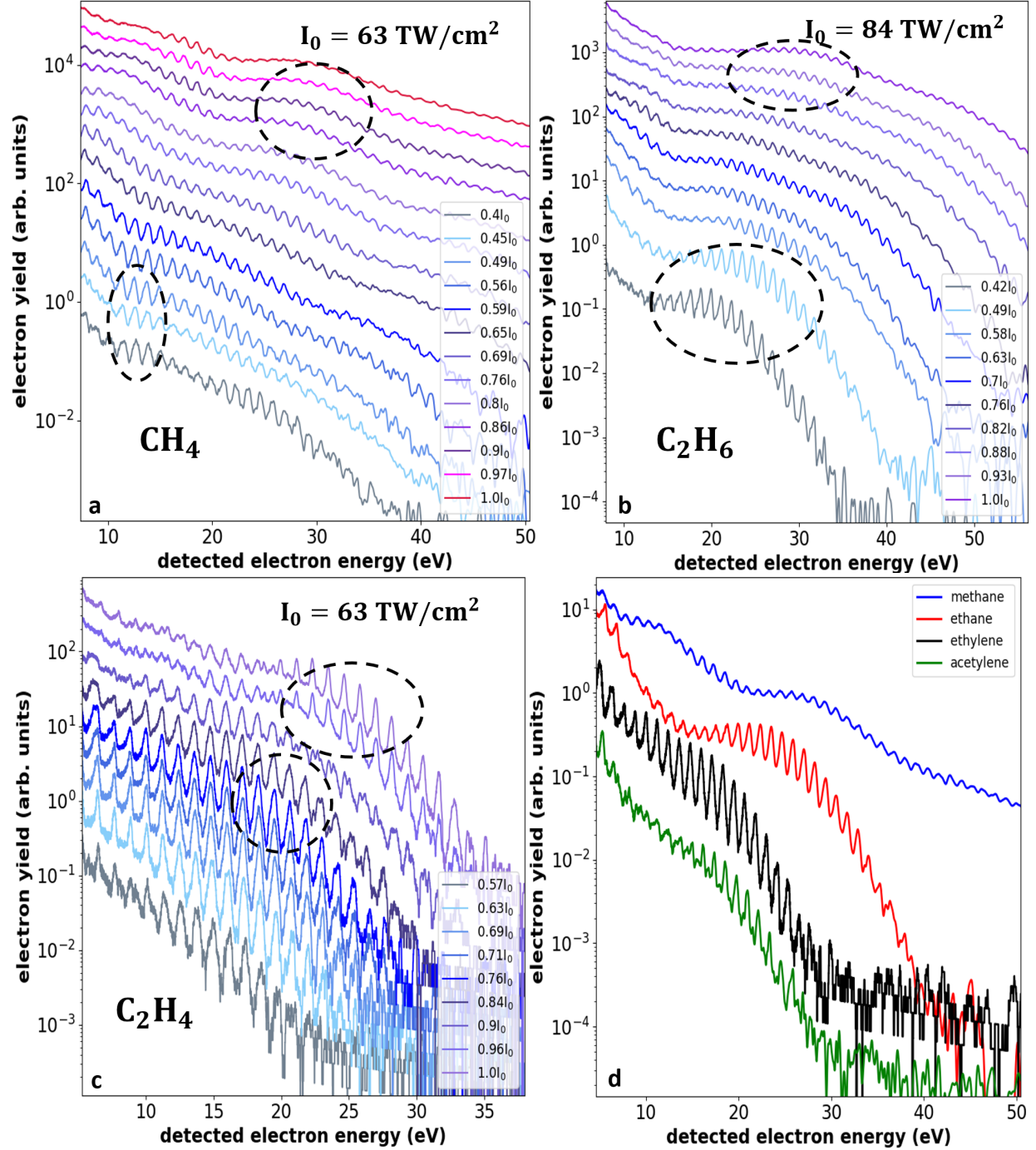


Figure 5.1: **Photoelectron Spectrum of Hydrocarbons collected at Varying Intensities with Tangor 300.** PES collected at varying intensities for a) methane, b) ethane, c) ethylene. Acetylene's enhancement can be seen in d) where all four targets' ATI spectrum are plotted together. Two enhancements were observed in methane, ethane and ethylene, while an enhancement at ≈ 21 eV is seen in acetylene. All enhancements are indicated with black dashed ovals.

extending the $2U_p$ cutoff. This results in greater interference from contributions of electrons

originating at different isointensities within the focal volume, causing the observed reduction in ATI peak contrast within the spectrum. Additionally, at lower intensities, molecular ionization is orientation dependent⁶⁵. This is explained by molecular ADK (MO-ADK) theory, which can be used to calculate the ionization rate of molecules in a laser field. Specifically, at lower intensities, the ionization rate is largest when the initial electronic cloud is aligned with the field direction⁶⁵. As the intensity increases and approaches the saturation intensity, the probability of ionization nears unity regardless of molecular orientation. This uniformity in ionization results in molecular orientation averaging causing a decrease in ATI resolution at higher intensities observed in hydrocarbon PES.

The intensity scan of hydrocarbons experimentally supports the half-integer photon closure theory introduced in Chapter 4. Given n , I_p and the wavelength, Table 5.1 calculates the corresponding leading intensity for both the first and second order enhancement for each hydrocarbon.

Target	$6U_p$ Location (eV)	I_p (eV)	U_p (eV)	n	Leading Intensity (TW/cm ²)
methane	15	12.56	2.5	12.5	25
methane	30	12.56	5	14.5	50
ethane	21	11.55	3.5	12.5	35
ethane	35	11.55	5.8	14.5	60
ethylene	20	10.51	3.3	11.5	34
ethylene	27	10.51	4.5	12.5	46
acetylene	21	11.41	3.5	12.5	37

Table 5.1: **Mapped Leading Intensity for Each Hydrocarbon's Enhancement.**

Additionally, the data shows the locking of ATI peaks making up the enhancement after the peak intensity meets and passes the leading intensity, reinforcing the observations made by Hansch in 1997. To illustrate this locking, a vertical line is drawn through a chosen ATI

peak within the enhancement region in Ethylene’s intensity scan, seen in Figure 5.2. As the peak intensity increases and passes the leading intensity of 34 TW/cm², the ATI peak locks in place and does not shift in detected energy despite a continual increase in the peak intensity. This experimentally demonstrates that the enhancement depends on the *leading* intensity rather than the peak intensity.

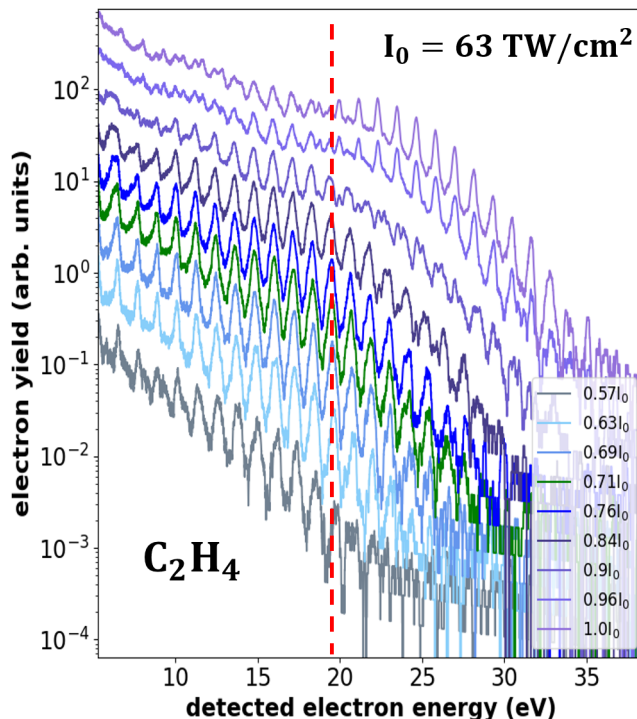


Figure 5.2: **Demonstration of ATI Locking in Ethylene PES.** ATI spectra collected of Ethylene at various peak intensities. The first order enhancement occurs at a leading intensity of 34 TW/cm² and at approximately 20 eV. Once the peak intensity surpasses the leading intensity, at approximately 0.7I₀ (green ATI spectrum), the ATI peaks making up the envelope of the enhancement lock in place. This can be seen by the ATI peaks lining up with the red dashed line consistently after surpassing the leading intensity.

5.2 Enhancement Dependence on Space Charge?

In Chapter 3.1.3, collection of ethane mass spectra at various pressures and intensities demonstrated the influence of space charge. But does it have any influence on the enhancement region in ATI spectra? The specific concern for our group was if running at higher pressures of 2.0×10^{-4} Torr would artificially change the structure of the enhancement. So, a study

was conducted on methane and ethane. PES were collected of both targets at a fixed intensity where the enhancement was observed but at different pressures. Figure 5.3 plots PES for all pressures of both targets, except the electron yield is normalized to the enhancement for comparison. Clearly, the structure of the enhancement does not change as a function of pressure and therefore is *not* influenced by space charge. This means collecting PES at a higher pressure of 2.0×10^{-4} Torr for the sake of more statistics and faster runtimes should not be an issue.

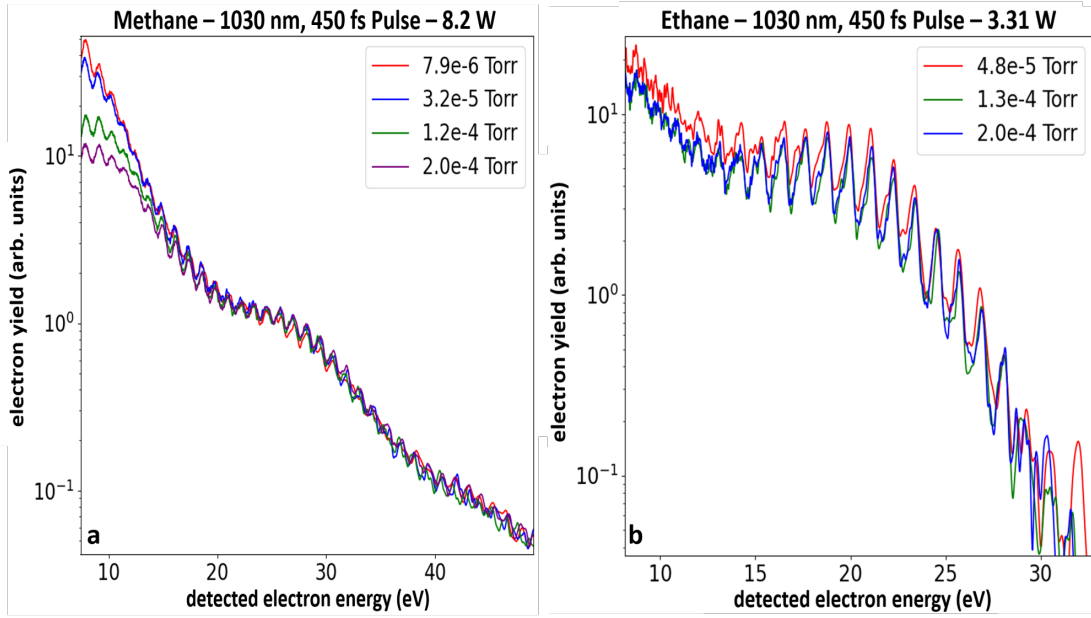


Figure 5.3: **PES of methane and ethane Collected at Fixed Intensity but different Pressures to study Space Charge Effects on the Enhancement.** a) methane PES collected at 7.9×10^{-6} Torr (red), 3.2×10^{-5} Torr (blue), 1.2×10^{-4} (green) and 2.0×10^{-4} Torr (purple). The power was held at 8.2 W at a 100 kHz repetition rate. b) ethane PES collected at 4.8×10^{-5} Torr (red), 1.3×10^{-4} Torr (green), and 2.0×10^{-4} Torr (blue). The power was held at 3.31 W at a 100 kHz repetition rate. All PES are normalized to the enhancement for comparison. For both targets, the structure of the enhancement does not change as a function of pressure.

5.3 Investigating Molecular Structure: PAD Collection

The PES study concluded the existence of the enhancement in *all* chosen hydrocarbons. Its observation poses the next following question: can the enhancement and QRS theory be used to investigate molecular structure in more complex molecules at low return energies? The first step involves collecting PADs of the same hydrocarbons at a particular intensity.

The PADs for methane, ethane, ethylene and acetylene were collected at the following approximate peak intensities given a 10 mm beam diameter before focus: 121.0 TW/cm², 48.4 TW/cm², 56.5 TW/cm², and 58.3 TW/cm², respectively. For all targets, a 20 minute PES was collected at each polarization angle. The results are shown in Figure 5.4. Even visually, subtle differences in the resultant diffraction pattern are observed from target to target. For all PADs, the red hue in the center corresponds to low energy direct electrons which have *not* rescattered off the parent ions. The cutoff for these electrons are $2U_p$, into the green region of the PADs. The blue areas map to the rescattering plateau observed in 1D PES and is also the location of the enhancement. The probability of ionization is highest along the laser polarization.

5.4 Extracting Electron-Ion Yields

Electron yield is extracted from the PADs at a certain return momentum by fitting a circle onto the angular distributions. In the tunneling regime, the parameters of this circle would be chosen from classical long trajectories. However, in Chapter 4.2, it was shown they could *not* explain the behavior of the electronic wavepacket in the multiphoton regime. But the soliton can! Therefore, the idea is to use our Husimi plots to choose a p_r and A_r which determines the radius and center of the circle, respectively. QRS then tells us the yield extracted along this circle is reflective of the elastic DCS.

The on resonance Husimi plots for argon at 790 nm revealed two solitons with return times of $0.68A_0$ and $0.91A_0$ and the most frequent return energies of $2.75U_p$ and $1.25U_p$,

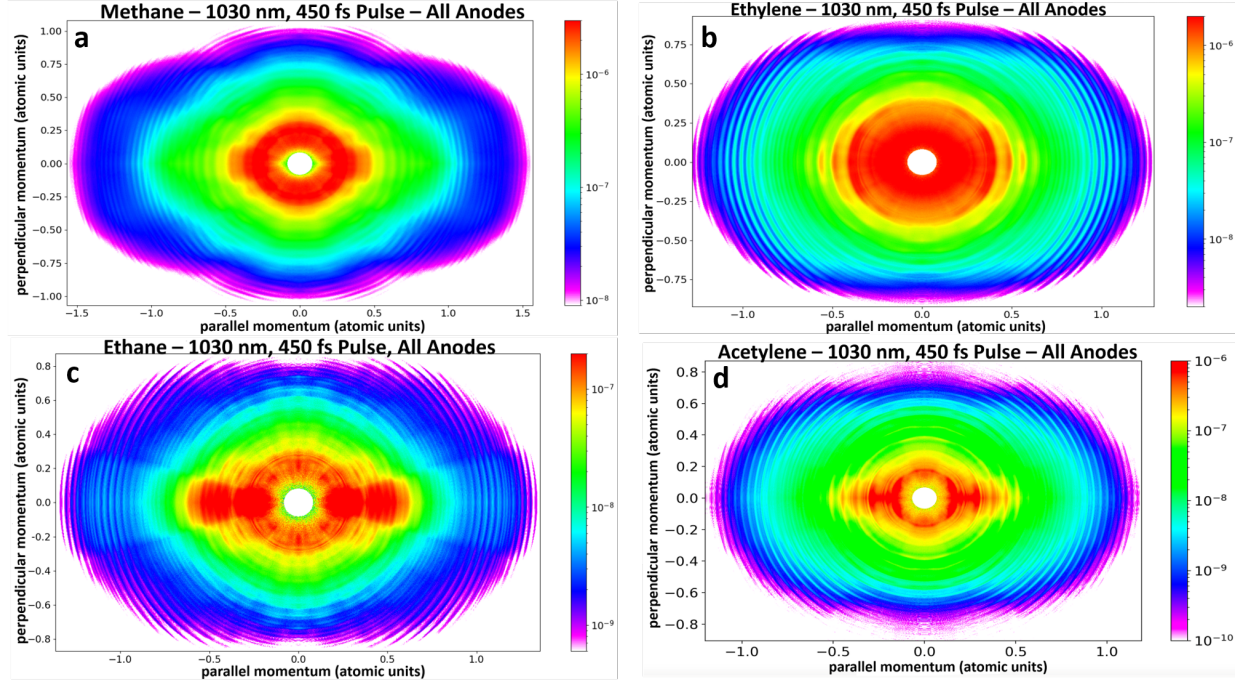


Figure 5.4: **PADs of Hydrocarbons collected with Tangor 300.** PADs of a) methane, b) ethylene, c) ethane and d) acetylene collected at approximately 121.0 TW/cm², 56.5 TW/cm², 48.4 TW/cm² and 58.3 TW/cm², respectively.

respectively. Since testing of QRS is currently limited to higher energies, the higher frequency soliton was chosen for this study. We recall this p_r and A_r combination corresponds to a detected energy of $6.8U_p$. A fitted circle with radius $p_r = \sqrt{5.5U_p} \pm 2\%$ and center $A_r = 0.68A_0$ was used to extract electron yield from both the 800 nm and 1030 nm PADs of argon collected in FLAME and KONZA, respectively. The 1030 nm PAD of argon with the overlaid momentum circle is seen in Figure 5.5. Clearly, along the laser polarization, the circle passes through the desired enhancement region.

The steps to extract electron yield do not directly use the $(p_{\parallel}, p_{\perp})$ PAD. First, given a p_r , A_r , and the detected angle, θ_d , the scattering angle, θ_r , is calculated by:

$$\theta_r = \pi - \theta_d - \sin^{-1} \left(\frac{A_r}{p_r} \sin(\theta_d) \right) \quad (5.1)$$

Next, given $p_{r,min} = p_r - 2\%$, $p_{r,max} = p_r + 2\%$ and a fixed A_r , PES at each scattered angle is integrated between a minimum detected momentum, $p_{det,min}$ and a maximum detected

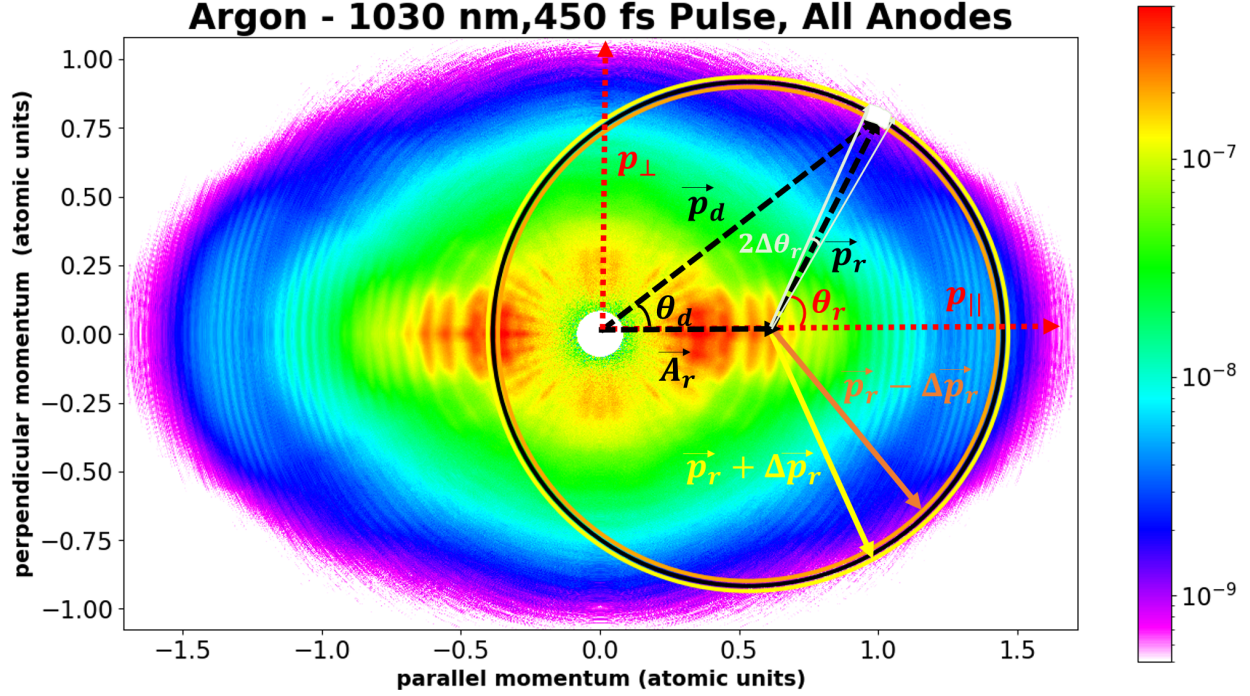


Figure 5.5: **Fitted momentum circle overlaid on argon, 1030 nm PAD using p_r and A_r values extracted from Husimi plots for electron yield extraction.** The higher energy soliton at $p_r = \sqrt{5.5U_p} \pm 2\%$ and $A_r = 0.68A_0$ was used to extract electron yield within the white sector for each scattering angle, θ_r , given Δp_r and $\Delta\theta_r$. The orange and yellow circles plot the momentum circles for $p_r - \Delta p_r$ and $p_r + \Delta p_r$, respectively, while the black circle plots the momentum circle for p_r given A_r . Clearly, the circle passes through the enhancement region located at ≈ 1.3 a.u. along the parallel momentum axis.

momentum $p_{det,max}$ given by:

$$p_{det,min} = \sqrt{A_r^2 + p_{r,min}^2 - (2A_r p_{r,min} \cos(\theta_r))} \quad (5.2a)$$

$$p_{det,max} = \sqrt{A_r^2 + p_{r,max}^2 - (2A_r p_{r,max} \cos(\theta_r))} \quad (5.2b)$$

Finally the standard deviation of the summed yield is calculated using population standard deviation or

$$\sigma = \sqrt{\frac{\sum_i (a_i - \bar{a})^2}{N}} \quad (5.3)$$

where a_i represents each value in the population, $\bar{a}$ is the population mean and N is the size of the population. Figure 5.6 compares the extracted yield to theoretical elastic electron-ion DCS calculated by Prof. A.E.S Green for similar return energies⁶³. Angles below 100 degrees

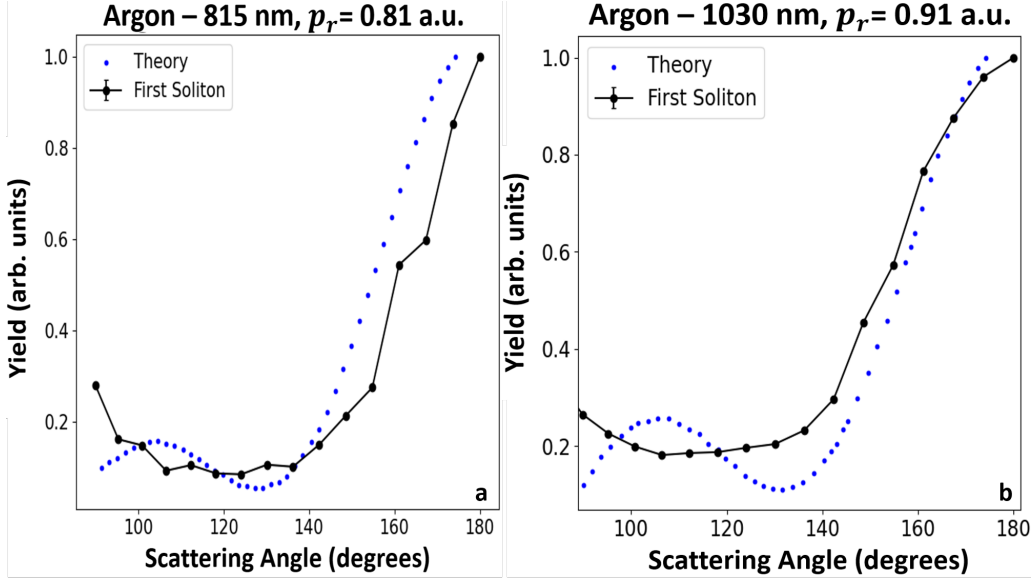


Figure 5.6: **Comparison between theoretical cross sections and experimental electron yields extracted from PADs for argon at 815 nm and 1030 nm.** a) Electron yield extracted from PAD of argon collected at 815 nm for a return momentum of 0.81 a.u. shown in black. The blue plot is theoretical cross section calculated at the same return momentum for 800 nm light. b) Electron yield extracted from PAD of argon collected at 1030 nm for a return momentum of 0.91 a.u. shown in black. The blue plot is theoretical cross section calculated at the same return momentum for 800 nm light.

were not considered due to direct electron contamination. Although the general trend looks similar, discrepancies do exist at $\approx 100^\circ$ and hard conclusions cannot be made about the validity of our extraction methodology and QRS at low return energies. For now, it is best to use caution when equating the extracted yield with a DCS.

The same electron yield extraction methodology outlined in the previous paragraph was also tried on methane, ethane and ethylene. However, without generated Husimi plots of these targets, how do we choose a p_r and A_r ? In Chapter 4.3.1, it was shown regardless of target, the electronic wavepacket returned to the parent ion at $\approx 324^\circ$. Additionally, the mapped detected energy at this return time when choosing the most frequent return energy in each target's respective Husimi plot was $\approx 6 U_p$. It should also be noted that the most frequent return energies are *not* invariant to the target choice. Therefore, A_r was fixed at a ϕ_r of 324° and p_r was calculated for each target given E_{det} was $6U_p$. The extracted yields for methane, ethane and ethylene at p_r of 0.8 a.u., 0.66 a.u. and 0.67 a.u. are seen in Figure

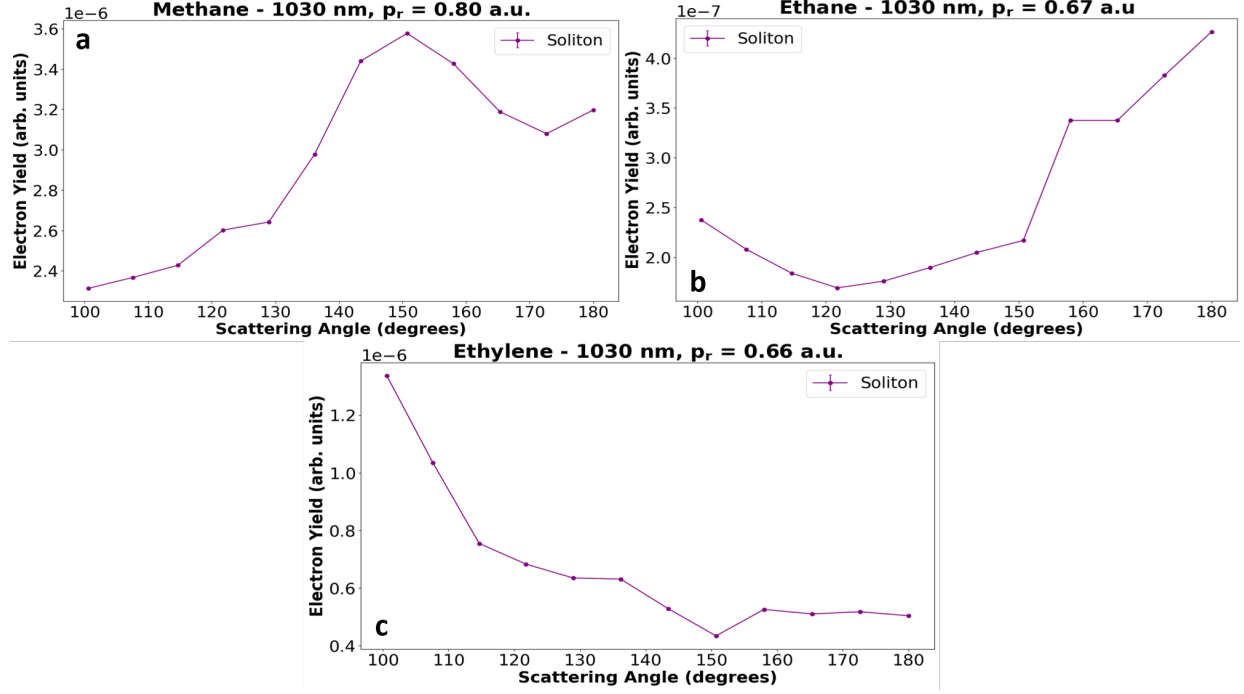


Figure 5.7: **Extracted electron yields for Hydrocarbons.** Extracted electron yields for a) methane, b) ethane and c) ethylene with A_r fixed at a return phase of 324° and p_r calculated given $E_{det} = 6U_p$. Clear differences are observed in yield trends between the targets but further analysis and comparison with theory must be done to make any conclusions.

5.7. Clear differences in yield trends are observed between all three targets.

Comparing and contrasting these cross sections begins with understanding the structural differences of our hydrocarbons. Figure 5.8 displays a ball and stick model for methane, ethane and ethylene. Methane, with a single carbon atom, is the simplest of the targets with its tetrahedral geometry shown in Figure 5.8a. It consists of single bonds between the central carbon atom and the four hydrogen atoms. The H-C-H bond angles are all equal at 109.5° . Both carbons in ethane, seen in Figure 5.8b, have four single bonds with tetrahedral geometry (1 carbon bond and 3 hydrogen bonds). The C-C-H bond angles equal 111.2° . Ethylene's molecular structure, displayed in Figure 5.8c, is trigonal planar, meaning each carbon is surrounded by three other atoms in the same plane. The two carbons are connected by a double bond, while the carbon-hydrogen bonds are single bonds. The C-C-H bond angle is 121.3° . The single carbon center and symmetry of methane allows for simpler scattering dynamics and less interference effects in comparison to the C_2 targets, resulting

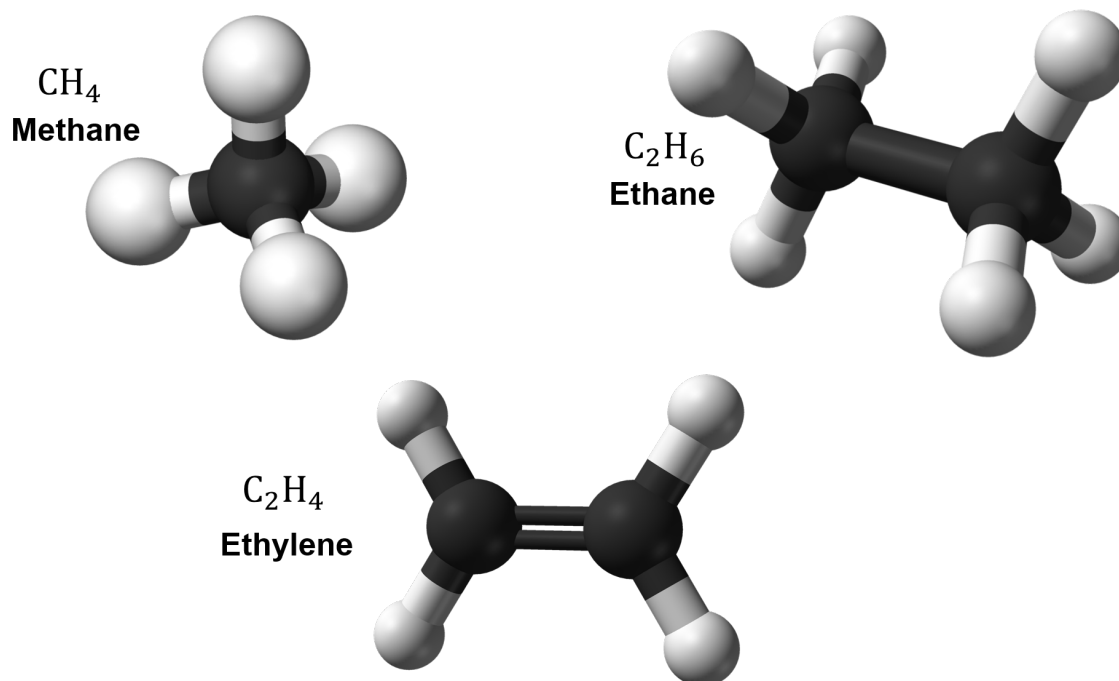


Figure 5.8: **Ball and Stick Model of methane, ethane and ethylene.** Ball and stick model showing molecular geometry of a) methane b) ethane and c) ethylene. The white sphere is hydrogen and the black spheres is carbon.

in a more structured cross section. This can be seen by the distinct peak in methane's DCS at approximately 150° . This is analogous to the simpler interference pattern seen from single-slit scattering in comparison to double-slit scattering. The slits corresponds to the atomic centers and the interference pattern maps to the elastic electron-ion differential cross section.

To further analyze our results, the extracted yield for each hydrocarbon is compared and contrasted with respective theoretical DCS calculated at similar return energies seen in Figure 5.9. Theoretical and experimental absolute differential cross sections for elastic electron scattering by methane from Cho et al. are shown in Figure 5.9a⁶⁶. Before discussing similarities and differences, we note our methane results are electron-ion DCS whereas the absolute differential cross section is electron scattering off neutral methane. Additionally, the return energy for our methane data is ≈ 8 eV whereas the incident energy for the absolute cross section is 10 eV. The biggest difference in the two cross sections is the lack

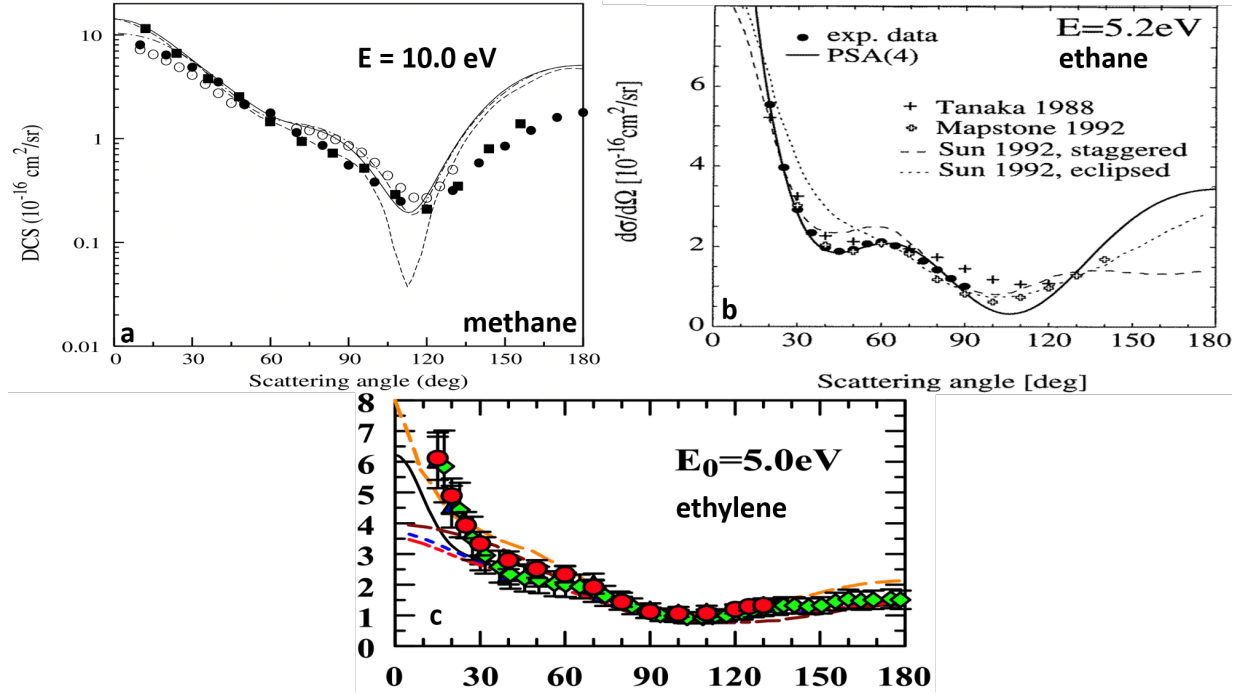


Figure 5.9: **Theoretical and Experimental DCS of methane, ethane and ethylene.** Theoretical and experimental elastic electron-neutral DCS for a) methane, b) ethane and c) ethylene at an incident electron energy of 10 eV, 5.2 eV, and 5 eV, respectively. For all plots, solid lines are theoretically calculated DCS while scatter plots are experimental data.

of the peak at 150° in Figure 5.9a, observed in Figure 5.7a. However it is important to note the difference in scaling between the two datasets. The data in Figure 5.7a spans only 1.2 units whereas Figure 5.9a covers nearly four orders of magnitude. Therefore the prominent peak can arguably be a small variation in electron yield. However the general differences in trend between the two plots could be due to the difference in electron energies and the state of methane. The scattering angle of electrons with identical kinetic energy will differ if the target is an ion or a neutral atom, due to variations in electrical charge⁶⁷. However, a minima at $\approx 110^\circ$ is seen in both cross sections. Figure 5.9b provides theoretical and experimental elastic electron-neutral differential cross sections of ethane from Merz et al. at a similar incident energy of our ethane electron-ion data⁶⁸. Both cross sections exhibit the same overall trend between 100° and 180° . However, the electron-neutral DCS reaches a minima at approximately 110° , whereas our data has a minima in yield at approximately 120° . Again, this discrepancy could be due to the difference in the state of the target (ion

versus neutral). Finally, Figure 5.9c showcases elastic theoretical and experimental electron-neutral DCS of ethylene from Khakoo et al. at a incident energy similar to the ethylene data in Figure 5.7c⁶⁹. The local minima observed at approximately 150° in our data cannot be seen in the electron-neutral DCS. Additionally, the sharp rise in electron yield at 100° in our data could be direct electron contamination and is not observed in Figure 5.8c. However, the overall trend and modulations are similar between the two datasets.

Another factor contributing to the discrepancies between the cross sections in Figures 5.7 and 5.9 comes from the nature of the returning electronic wavepacket. The extracted electron yield in Figure 5.7 derives from a circle placed on the enhancement region within the PAD. Husimi spectrum tell us the enhancement occurs from a bimodal non-dispersive wavepacket. Furthermore, because the PADs were collected using LIED, the ionized electron maintains phase coherence, as discussed in Chapter 4, with the field throughout its rescattering journey.

In contrast, the experimental DCS shown in Figure 5.9 were collected using a prepared electron beam. This generally produces incoherent wavepackets, where there is no defined phase relationship between two electrons or the electron and the target⁷⁰. The interaction between the bimodal, coherent wavepackets can therefore result in interference effects which alter or modulate the extracted elastic DCS. This is analogous to the additional interference pattern observed in scattering from two circular apertures, discussed in Chapter 1, due to the relative phase between the two interfering wave¹⁰.

These explanations provide further insight into the comparison between our data and previous studies. However, further validation of the extraction methodology and deeper understanding of the trends observed in Figure 5.7 requires comparison with theoretical data.

Chapter 6

Conclusions and Future Work

This dissertation focused on understanding the cause of an enhancement observed at $6U_p$ in experimental ATI spectra within the multiphoton ionization regime. It was shown to occur within multiple targets at a special, leading intensity within the focal volume of the beam given the wavelength. Traditionally used classical electron trajectories could not explain the phenomena. So, theoretical time dependent HHG spectra were generated to understand the behavior of the electronic wavepacket when it returns to the parent ion. Remarkably, at the given wavelengths and leading intensities, a bimodal attosecond electronic dispersion free wavepacket was discovered whose density built cycle after cycle. It behaved similarly to light within a modelocked oscillator. Further analysis was done to understand its properties. For example, regardless of target, the wavepacket returned to the parent ion at approximately the same cycle. Adjusting the chirp of the electric field allowed for dispersion control and the development of the dispersion free wavepacket was also observed when using a sine-squared, realistic laser pulse. Additionally, a 60 cycle HHG spectra calculation demonstrated its stability after steady state was reached around 7 cycles. The most frequent return energies of the two dispersion free wavepackets generated were $2.75U_p$ and $1.25U_p$. These return momenta and corresponding return times remarkably mapped to a detected energy of $6U_p$! A 30 year old mystery had been solved: the ionized electronic wavepacket returns to the parent cycle after cycle, its density growing with little to no dispersion at certain frequent

return momenta, before eventually backscattering and detected with an accumulated kinetic energy of $6U_p$.

The discovery of the bimodal dispersion free wavepacket reframes rescattering in the multiphoton ionization regime. This phase-sensitive phenomena which survives focal averaging calls for the modification of theoretical tools such as QRS. Furthermore, it is this wavepacket, not classical long and short trajectories, which dictates electron dynamics in the continuum. Finally, the generated Husimi spectra point to the necessary inclusion of the ionic potential's influence on electron dynamics. The failure of classical long and short trajectories to explain the enhancement in ATI spectra ultimately calls for a modification of the famous semiclassical electron rescattering model.

The existence of the dispersion free wavepacket at certain wavelengths and intensities in multiple targets sparked curiosity of its applications. First, its stability makes it a prime candidate for the interrogation of vibration and rotational dynamics. Second, it can be used to revisit explanations of strong field phenomena such as NSDI. Additionally, the dispersion free wavepacket sheds light on a new way to control and increase the production of attosecond pulses. Finally, its universality and stability opens the door for its potential as a tool to probe molecular structure and extract elastic differential cross sections.

The wavepacket was subsequently applied to QRS for the extraction of electron-ion DCS. The goal was to study LIED's and QRS's viability in studying molecular structure at low electron return energies, on the order of tens of eV. The targets investigated were methane, ethane, acetylene and ethylene. The radicals of these small molecules are fragments in photoinduced dissociation of larger molecules. Therefore this study also begins to establish LIED's ability to image simpler hydrocarbons before proceeding towards more complex organic compounds. Photoelectron angular distributions were collected of argon and the aforementioned hydrocarbons using the Tangor 300 at 1030 nm. The dispersion wavepacket and QRS theory were subsequently used to extract electron yield as a function of scattering angle. Further comparison with theory is needed and caution should be taken in calling the resultant data elastic electron-ion differential cross sections.

Future work involves further application of LIED within JRM lab and collaborations with

theorists. The studies done on the enhancement in this dissertation used a monochromatic field. Gas phase experiments are currently underway to study the enhancement's dependence when subject to an intense bichromatic field. The ultimate goal is to coherently control the enhancement by adjusting the relative phase between the two fields. Additional lab work involves developing an OPA pumped by 1030 nm to shift to longer wavelengths with the ultimate goal of creating molecular movies through UV pump, LIED probe experiments. On the theoretical side, the near future involves calculating elastic differential cross sections for argon and the hydrocarbons investigated in the second project to compare with experimental results. These will be extremely beneficial in validating LIED and QRS theory at low electron return energies.

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Appendix A

Atomic Units

Quantity	Name/Formula	Symbol	SI Units
mass	electron mass	m_e	$9.1093837 \times 10^{-37}$ kg
action	reduced Planck constant	$\hbar$	$1.0545718 \times 10^{-34}$ J·s
charge	fundamental charge	e	$1.6021766 \times 10^{-19}$ C
length	Bohr radius	a_0	$5.2917721 \times 10^{-19}$ m
velocity	electron's velocity in 1st Bohr orbit	v_0	2.1876913×10^6 m/s
energy	Hartree energy	E_H	$4.3597439 \times 10^{-18}$ J
time	a_0/v_0	t	$2.4188843 \times 10^{-17}$ s
electric field	e/a_0^2	E	5.1422063×10^{11} V/m
frequency	v_0/a_0	f	4.1341375×10^{16} sec ⁻¹