

Ultrafast molecular imaging studies with laser-induced electron diffraction
at high repetition rates

by

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ABSTRACT

Laser induced electron diffraction (LIED) is a technique developed in the 1990s that leverages high-intensity ultrashort pulse lasers to capture femtosecond dynamics and provide detailed imaging capabilities of molecular and atomic structures. For decades, conventional gas phase electron diffraction (CED) has been the preferred method for determining inter-nuclear separations of isolated molecules at equilibrium [1], with modern implementations achieving spatial resolutions at the femtometer scale. However, the reliance on an electron gun in CED has limited its temporal resolution, making it difficult to capture atomic motion during chemical transformations. The electrostatic repulsion within the electron bunch, restrict the electron pulse duration to approximately 1 picosecond.

Approximately thirty years after the invention of the first laser in 1960 [2], the development of chirp pulse amplification (CPA) [3] in the 1980s revolutionized atomic, molecular, and optical (AMO) physics by enabling sub-picosecond pulses with high intensities, facilitating the generation of ultrashort electron pulses. This advancement also opened new possibilities for dynamic molecular imaging through intense laser-matter interactions. In recent years, ultrafast electron diffraction (UED) has emerged using CPA technology to generate electron guns with temporal resolutions down to 100 fs. Along with UED, LIED was developed to overcome the limitations of CED, offering femtosecond temporal resolution.

The foundation of the LIED was shaped after discovery of the three-step model [4–6] in strong field physics (SFP) during the 1990s. When atoms and molecules are exposed to high intensity laser pulses, electrons are tunnel ionized. Post ionization, the liberated photoelectrons are accelerated and decelerated in the cycle of the laser field, and might recollide with the ion parent and could elastically rescatter. The latter defines the whole concept of LIED under the three step model. Until now, extensive studies has been done

in LIED for atoms [7, 8], diatomic molecules [9, 10], small hydrocarbon molecules [11, 12], and large molecules [13].

Our ultimate goal in the Blaga group here at James R. McDonald laboratory (JRML) is to demonstrate pump-probe studies on molecules using the LIED technique. Although LIED has been a powerful tool for imaging molecules, recording a photoelectron angular distribution (PAD) currently takes several hours with 1 kHz lasers and standard time-of-flight (TOF) chambers. This process becomes even more time-consuming when PADs need to be collected at multiple time delays for pump-probe studies, taking up to a day for 10 different delays.

In this dissertation, we accomplished two main objectives. First, we enhanced JRML’s LIED experimental capabilities by improving data collection rates by three orders of magnitude. We achieved this by developing a well-suited spectrometer for LIED, utilizing a high repetition rate laser, and implementing a fast data acquisition system.

We constructed a specialized time-of-flight (TOF) setup for LIED experiments, featuring a one-meter double-sided TOF (D-TOF) equipped with two custom-built multi-anode multichannel detectors, with total of 10 anodes. This configuration reduces data collection time by an order of magnitude compared to standard single-anode TOFs. Additionally, the combination of the D-TOF (providing a tenfold reduction) and a Yb-based 100 kHz laser (providing a hundredfold reduction) decreases the data collection time by three orders of magnitude compared to standard single-anode TOFs integrated with 1 kHz laser sources. Coupled with a fast data acquisition system capable of handling the high data rates, the D-TOF setup has dramatically improved our experimental efficiency.

Second, we studied subtle molecular differences by undertaking the first LIED study of butane isomers. This work highlights the potential of LIED to resolve structural differences with high precision, advancing our understanding of molecular structures. we provide theoretical and experimental evidence demonstrating the ability of LIED to effectively distinguish between n-butane and isobutane. Our findings also shows LIED’s potential for

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Dedication

Dedicated to my parents, grandmother, uncles, brother, and Raha Samani

Chapter 1

Introduction

1.1 Historical Overview

The invention of pulsed lasers via Q-switching in 1962 [15] marked the beginning of nonlinear optics and strong field physics (SFP) [16, 17]. Pulse durations of these early Q-switched lasers were on the order of μs . Although the intensity ($10^{13} W/cm^2$) generated by early Q-switched lasers was low compared to modern standards, it was sufficient to observe multiphoton ionization in gases [16, 17]. Initially, the scientific community turned to perturbation theory to model the multiphoton ionization [18] given that the laser's field strength was smaller than the intra-atomic fields [18].

In subsequent years, the pulse duration of Q-switched lasers reached the nanosecond scale. A major breakthrough took place in late 1970's with the discovery of above threshold ionization (ATI) by Agostini et al., [19] who found that xenon atoms ionize by absorbing more than the minimum number of photons required. These excess energies show up as peaks with one photon spacing in the photoelectron spectra (PES). Higher order peaks, which involve the absorption of more photons, often cannot be explained by lower order perturbation theory, which assumes weak interactions and fails to account for the nonlinear processes involved in multiphoton ionization.

The ionization yield found from experiment for higher order peaks could not be explained by lower orders of perturbation theory. Considering only the lower orders of perturbation theory, one would expect that the yield between two peaks should decrease while going to higher orders. The perturbative expansion in terms of the field strength did not converge, as the contributions from higher-order terms remained significant. This non-convergence indicated that higher-order interactions are not negligible and must be considered in a better framework.

Leonid V. Keldysh developed a more complete theoretical framework to describe ionization processes in atoms and molecules subjected to strong electromagnetic fields [20]. Keldysh's theory assumed that the oscillation period of the laser field was much longer than the time it takes for an electron to tunnel out of the atom. This allows the ionization process to be treated as if the electric field is static during the tunneling event. Later on in 1986 Ammosov, Delone and Krainov (ADK) [21] included a Coulomb correction factor in Keldysh's work.

Moving forward, the advent of femtosecond laser technologies [22–25] in 1985 led to new discoveries in SFP. Three related observations emerged: high-order ATI plateau [5, 26], non-sequential ionization (NSI) [27, 28], and high-order harmonic generation (HHG) [6, 29]. The original work by Keldysh did not encompass these specific phenomena since it primarily addressed the ionization process in SFP, laying the groundwork for understanding multiphoton and tunneling ionization. The discoveries of high-order ATI plateau, NSI, and HHG, and their interpretations through another model, came later and built upon the foundational understanding provided by Keldysh's theory. In 1993, these phenomena were effectively interpreted through the rescattering model explained by Schafer et al. [5] and shortly after by Corkum et al. [6], who described the process where an electron, after being ionized by an intense laser field, is driven back to the parent ion by the oscillating electric field of the laser. Upon returning to the ion, the electron can undergo elastic scattering, recombination (HHG), and inelastic scattering.

As soon as the rescattering mechanism was established, scientists wondered if it could be used as a structural probe. The idea of using electrons as a static imaging technique goes back to the 1930s when the first conventional electron diffraction (CED) was done by Mark and Wierl [30], who studied carbon tetrachloride in gas phase using a 10-60 keV electron gun. Electron guns were providing very good spatial resolutions, but lacked temporal resolution due to the electrostatic repulsion of the electron bunch. The development of femtosecond ultrashort pulse lasers provided alternatives to CED’s electron gun, one of which is ultrafast electron diffraction (UED). The significant improvement in time resolution was achieved with the advent of the laser pulse compression technique. Newly available femtosecond optical laser pulses were utilized to generate ultrashort electron pulses via the photoelectric effect [31–34]. This advancement successfully reduces the electron pulse duration to the sub-100 fs [34] in recent years. In UED, electron pulses are generated by ultraviolet (UV) femtosecond lasers impinging on a photocathode and are accelerated to energies ranging from tens and hundreds of keVs to several MeV [34–36]. These experiments have significantly advanced our understanding of structural changes at the atomic level in chemical reactions [37].

Along with UED, LIED was developed to overcome the limitations of CED. LIED is a self-diffraction technique with promising spatio-temporal resolution to probe ultrafast molecular dynamics. The electrons ionized in the high-intensity laser field are elastically scattered within the optical cycle of the laser field from the ion parent, providing temporal resolution down to several femtoseconds. The remaining part of this subsection provides the reader with a non-comprehensive list of LIED results as reported in the literature.

LIED was first proposed through the work of Zuo et al. in 1996 [38] where they calculated momentum angular distributions of the PES from intense ultrashort pulse ionization of H_2^+ . Then in 2008, Okunishi et al. [39] and Meckel et al. [40] measured the photoelectron momentum angular distribution of Ne, Ar, and Xe generated by 800-nm, 100-fs laser pulses via LIED.

On the theoretical front, in 2009 Chen et al. [41] laid a solid theoretical foundation

for LIED, namely the quantitative rescattering theory (QRS). According to the QRS, the measured electron yield in a PAD can be factorized into products of the returning electron wavepacket that only depends on laser parameters and thus contains no structural information and a field-free electron-ion elastic differential cross section that contains the structural information. They proved the validity of the QRS model using the results from the solution of the time-dependent Schrödinger equation for atomic targets within the single active electron approximation.

Additionally, in 2012, Xu et al. presented comprehensive studies on noble atoms using LIED [7], detailing the extraction of field-free differential cross-section (DCS) for argon, krypton, and xenon over a broad energy spectrum ranging from 50 to 200 eV. They applied the QRS theory to analyze the measurements and confirmed that longer wavelengths are more favorable in LIED as they produce higher electron return energies.

The first successful extraction of quantitative DCS using longer wavelengths was done by Blaga et al. [9] in 2012. They also showed that LIED is a capable tool for dynamically imaging molecules. In an LIED pump-probe scheme, a pump pulse initiates a dynamic process within the system, while the LIED probe maps the time-dependent positions of the atoms. The clock is initialized by tunnel ionization (pump) and the probe is a field-driven wave packet that rescatters with the parent molecular core at a later time, approximately one optical cycle. Varying the wavelength is equivalent to adjusting the delay between the pump and probe pulses. They demonstrated that using tunable mid-infrared pulses, the measured O_2^+ bond length was 100 ± 5 pm, shorter than that of the neutral. They measured this displacement to occur at a time interval of 5 fs. This experiment showed that LIED could achieve a spatial resolution of 5 pm and a temporal resolution of 5 fs. Later on, Wolter et al. reported observing molecular dynamics by directly observing molecular bond breaking using a mid-infrared high repetition rate laser [12], where they reported imaging the molecular structure of acetylene (C_2H_2) 9 fs after ionization using a mid-infrared laser.

In 2014, Xu et al. [10] presented a technique called fixed-angle broadband laser-driven

electron scattering (FABLES) or Fourier-transform LIED (FT-LIED). Using this technique, they retrieved the bond length information of the N_2 molecule by taking the Fourier transform of the photoelectron energy distribution observed along the polarization direction of intense ultrafast light pulses. The technique takes advantage of the scattering wave packet created by strong-field tunnel ionization to study the molecular structure of its ion parent with picometer spatial resolution. When the Fourier transform of the PES was analyzed, it was demonstrated that internuclear separations in N_2 molecules could be precisely determined with 10 pm spatial resolution. Soon after, in 2015, Pullen et al. [11] used FABLES to include O_2 and various polyatomic molecules (C_2H_2) [42], considering molecular alignment in their work. Subsequently, LIED was applied to more complex systems such as ammonia, benzene, etc. [13, 43–48].

1.2 Motivation

In the near future our group’s goal is to do pump-probe using the LIED technique and study the dynamics of the molecules and chemical transformations. With a 1kHz laser and a single electron detector, recording just one PAD, as reported in previous work took 4-6 hours [9]. In a standard pump-probe setup using LIED, this would require half a day for each time delay, assuming stable experimental conditions throughout. Consequently, to create a molecular movie, significant improvements in data collection rates are reacquiring cutting-edge technology to expedite the process while ensuring sufficient statistics and high resolution.

So far, previous LIED results were recorded with general-purpose experimental chambers that weren’t designed specifically for LIED which will be discussed in chapter 3. During my PhD work, we have built a double sided time of flight (D-TOF) that is completely dedicated to LIED. We achieved this goal by developing novel multianode detectors, incorporating faster electronics that can operate with 100 kHz lasers and a dual TOF arm design.

Compared to previous work done with non-LIED designed TOF, our new LIED chamber provides one order of magnitude higher data collection rates and will be discussed later. This setup is currently operational and being used to collect data for various experiments. Chapter 2 of this thesis describes the design, the operation and the performance of the chamber in detail. D-TOF is currently integrated with our newly acquired Yb-based high average power 100 kHz repetition rate pulse laser making it a powerful tool to decrease the PADs data collection time by two orders of magnitude compared to 1 kHz laser sources. The chamber was ran successfully with FLAME, a 3 kHz repetition rate laser system. However, upon the commissioning of JRML’s new 100 kHz laser, the faster electronics were allowed to showcase their performance. Combined, we can now acquire PADs with 3 orders of magnitude improved rates compared to 1 kHz laser sources and single anode TOFs. This dissertation will present results that substantiate these advancements.

Our second goal was to use LIED to distinguish between isomers by conducting the first LIED study of butane isomers. Traditional electron diffraction methods have been valuable for examining molecular structures. However, these techniques may struggle to differentiate between molecular isomers due to their limited sensitivity to nonadjacent bond structures and electronic configurations. LIED presents a compelling alternative, as the yield of the self-imaging electron is highly influenced by the shape of valence orbitals, resulting in distinct diffraction patterns for isomers with different electronic structures. In my thesis, we provide theoretical and experimental evidence demonstrating the ability of LIED to effectively distinguish between n-butane and isobutane. The underlying principle is clarified through the modeling of multiorbital tunnel ionization of the molecules and the subsequent rescattering of the ionized electron with the molecule. Our findings shows LIED as a powerful technique for identifying molecular isomers and highlight its potential for concurrently probing the nuclear and electronic structure of a molecule.

1.3 Overview of Dissertation

This dissertation begins by exploring the historical development of SFP, followed by a detailed theoretical background.

Chapter 3 presents all experimental details: the two TOF-chambers used (the Ohio State general purpose TOF for the butane study) and the JRML’s novel LIED-dedicated chamber’s design and assembly, along with actual data as part of this thesis. In addition, we will discuss the fundamentals of the ultrashort pulse generation and the three types of lasers utilized in both experiments.

In Chapter 4, we will explore the fundamental theories underlying the LIED technique. This discussion along with the experimental results will demonstrate how our findings underscore LIED’s effectiveness as a robust method for identifying molecular isomers. Lastly, in chapter 5 we put important conclusions together.

Chapter 2

Theoretical Concepts in Strong Field Physics

Before delving into a detailed exploration of strong field ionization and electron rescattering, it is essential to address several fundamental aspects of strong field physics.

2.1 What is Strong Field Physics?

Strong field physics is the science of understanding the interaction between a strong laser field and matter. The question arises of how big the aforementioned electromagnetic field magnitude should be to be considered strong. An electric field is considered strong when it is non-negligible compared to the average Coulomb field experienced by the electron in its atomic orbital [49]. For example, in the case of the hydrogen atom, the electron is bounded to the proton at the distance of the Bohr radius $a_0 \approx 0.529\text{\AA}$ with a strength of

$$|\vec{E}| = \frac{e}{4\pi\epsilon_0 a_0^2} \approx 5.142 \times 10^{11} \frac{V}{m} \quad (2.1)$$

The Coulomb field experienced by the electron is equivalent to the peak intensity of a

laser field of

$$I = \frac{1}{2}\epsilon_0 c E^2 = 3.509 \times 10^{16} \frac{W}{cm^2}, \quad (2.2)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light, and e is the electron charge. For multi-electron atomic systems, the electric field experienced by the outer valence shell electron is lower due to a larger distance to the nucleus because of the $\frac{1}{r^2}$ scaling of the Coulomb field and screening effects by the inner shell electrons.

2.2 The Ponderomotive Potential

The ponderomotive energy, denoted as U_p , represents the cycle-averaged kinetic energy of a free electron subjected to the influence of an oscillating electromagnetic field. To illustrate this concept, let's consider the scenario of a free electron interacting with a linearly polarized electric field characterized by the following form:

$$\vec{E}(t) = E_0 \cos(\omega t) \hat{z} \quad (2.3)$$

Here, $\vec{E}(t)$ represents the electric field as a function of time, with E_0 being the amplitude of the electric field, ω denoting the angular frequency, and t representing time. In the non-relativistic limit, we can express the force acting on this electron as:

$$m_e \frac{d^2 x}{dt^2} = e E_0 \cos(\omega t) \quad (2.4)$$

In this equation, m_e shows the mass of the electron 9.109×10^{-31} kg, and e represents the charge of the electron. By integrating and averaging equation 2.4 over a single cycle of the electric field, we can establish the definition of the ponderomotive energy, as follows [50, 51]:

$$U_p = \frac{E_0^2 e^2}{4m_e \omega^2} \quad (2.5)$$

This ponderomotive energy characterizes the average energy resulting from the oscillatory motion of the electron within the electromagnetic field. The concept of ponderomotive energy holds significant importance and will be frequently referenced throughout this dissertation.

While Equation 2.5 accurately describes the ponderomotive energy, it is often more convenient to express U_p in terms of the laser intensity defined as:

$$I(E_0) = \frac{1}{2}\varepsilon_0 c E_0^2 \quad (2.6)$$

Here, ε_0 represents the vacuum permittivity, c is the speed of light, and E_0 denotes the amplitude of the electric field. Substituting this laser intensity expression into the definition of ponderomotive energy, we arrive at the following formulation:

$$U_p = \frac{e^2}{8\pi^2 m_e \varepsilon_0 c^3} I \lambda^2 \quad (2.7)$$

For the sake of practicality, Equation 2.7 is often expressed in a more convenient form using parameters that are commonly known and utilized in laboratory settings. This alternate expression is as follows:

$$U_p[eV] = 9.33 \times I[10^{14}W/cm^2] \times \lambda^2[\mu m] \quad (2.8)$$

This form of the equation provides a straightforward way to compute the ponderomotive energy in electronvolts based on the laser intensity in units of 10^{14} watts per square centimeter (W/cm^2) and the wavelength of the laser in micrometers (μm).

For an 800 nm laser at a peak intensity of $10^{14}W/cm^2$, U_p is 6 eV.

2.3 The AC Stark Shift

In the presence of an oscillating electric field, an atom's energy levels undergo a well-known phenomenon called the AC Stark effect. At the intensities of laser fields commonly employed in strong-field physics, the Stark shift is significant and cannot be disregarded [52]. To gain a better understanding, let's briefly delve into the AC Stark effect.

The Hamiltonian for an electron interacting with this electric field and an atomic potential, $V(\vec{r})$, can be expressed as:

$$H = \frac{(\vec{p} - e\vec{A})^2}{2m_e} + V(\vec{r}) \quad (2.9)$$

Here, $\vec{E} = -\frac{\partial \vec{A}}{\partial t}$, while $\vec{p}$ and $\vec{r}$ show the momentum and position vectors of the electron, respectively. Employing perturbation theory, we can determine the shift in the energy level (n -th level) as follows [52–54]:

$$\delta E_n = -\frac{1}{4}\chi_n(\omega)E_0^2 \quad (2.10)$$

The parameter $\chi_n(\omega)$ corresponds to the dynamical polarizability of the n -th level and is defined as [52–54]:

$$\chi_n(\omega) = 4 \sum_m |(d_z)_{n,m}|^2 \frac{2(E_m - E_n)}{(E_m - E_n)^2 - \omega^2} \quad (2.11)$$

In this expression, E_n represents the energies of the unperturbed atom, and d_z is the projection of the dipole moment along the electric field axis. Although this result originates from perturbation theory and may not hold in the strong-field limit, for the purpose of comprehending this effect, this perturbative expansion suffices.

While this is typically a complex operation, simplification can be achieved by focusing on highly excited states or Rydberg states ($n \gg 1$). Under this assumption, the dynamic

polarizability approaches its asymptotic limit as $\omega \gg |E_m - E_n|$, $\chi_n(\omega) \propto -\omega^{-2}$. With this result, Equation 2.10 can be further simplified to [52–54]:

$$\delta E_n = \frac{eE_0^2}{4m_e\omega^2} \quad (2.12)$$

A direct comparison between Equation 2.5 and Equation 2.12 reveals an exact match. The higher-lying states near the continuum are expected to shift by an amount equivalent to the ponderomotive energy, U_p . Therefore, given a particular peak intensity, the amount of energy required to ionize an electron from the ground state shifts from I_p to $I_p + U_p$ [55]. Figure 2.1 schematically illustrates this impact on the energy states of the atom as a function of laser intensity, with the shifting of the ground state being relatively weaker and hence neglected.

Additionally, Figure 2.1 shows an interpretation that as the intensity increases, the electron yield in the lower-order ATI decreases. This is due to the peak intensity of the laser field crossing a channel closure. While this particular ATI peak does not completely vanish, as the laser pulse contains a continuous distribution of intensities within the focus, the channel remains open at lower intensities within the focal volume. In the case of a short pulse, the electron does not escape the focus before the pulse ends. Consequently, the detected energy of the electron is equivalent to its energy at the moment of ionization.

Also, in the short pulse regime, the ponderomotive shift of the continuum due to adjustments in laser intensity results in a corresponding shift of the ATI peaks to lower energies. As the laser intensity increases, each ATI order is expected to shift to lower energies by an amount equal to the change in U_p .

2.3.1 Channel Closure

As discussed in the previous section, the AC Stark shift shouldn't be neglected in SFP. Each successive ATI peak corresponds to the absorption of an additional photon by the electron.

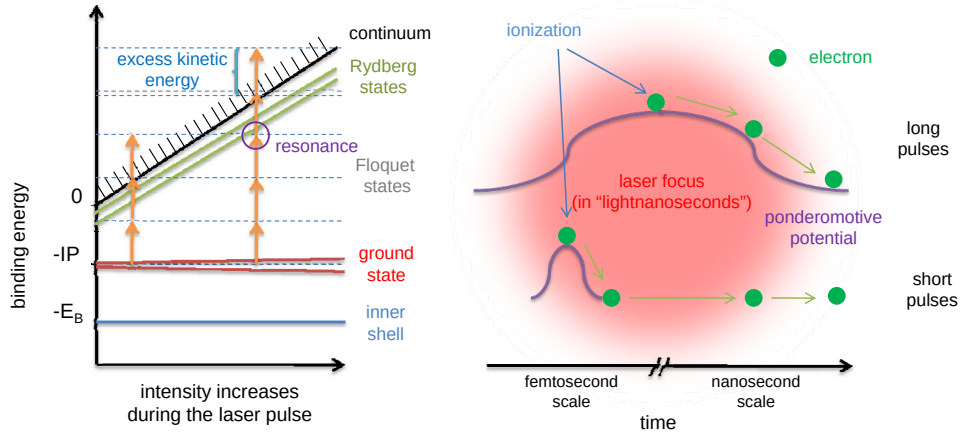


Figure 2.1: Energy level shifts due to the AC Stark effect. Left image: As the laser intensity increases, the energy levels shift due to the AC Stark effect. The magnitude of this shift is proportional to the polarizability of each level and the square of the electromagnetic field strength. Right image: The interaction between the pulse duration and the time it takes for the ionized electron to escape the laser focus determines the detected electron energy.

With the increase in ponderomotive energy, the continuum states shift to higher energy levels, consequently requiring a greater minimum number of photons for ionization [56–58]. This phenomenon is known as channel closure and directly results from the AC Stark shift. At lower intensities, if N photons are required to ionize an electron, as the laser intensity rises and shifts the states to higher energies, $N + 1$ photons become the minimum requirement for ionization. Figure 2.1 illustrates this principle, and as the intensity continues to rise, it leads to the crossing of additional channel closures, demanding an even higher photon count for ionization.

It is essential to note a distinction between a short pulse and a long pulse. The determination of a short pulse is based on the time it takes for the ionized electron to escape the laser focus and it will be calculated in this section. Immediately following ionization, an electron's energy is given by:

$$E_f = N\hbar\omega - (I_p + U_p) \quad (2.13)$$

Here, N represents the number of absorbed photons. Please note that the intensity dependence term is embedded in U_p . In the case of a long pulse, the electron has sufficient time to escape the laser focus, during which it experiences a force of $-\nabla U_p$ [59] where U_p depends on the spatial distribution of the laser intensity. This results in the electron gaining energy equal to U_p , offsetting the impact of the AC Stark shift on the detected electron's energy. In a long pulse scenario, each ATI order appears at the same intensity, regardless of the laser intensity, as shown schematically in Figure 2.1. Additionally, Figure 2.1 shows that as the intensity increases, the electron yield in the lower-order ATI decreases. This is due to the peak intensity of the laser field crossing a channel closure. While this particular ATI peak does not completely vanish, as the laser pulse contains a continuous distribution of intensities within the focus, the channel remains open at lower intensities within the focal volume.

In the case of a short pulse, the electron does not escape the focus before the pulse ends. Consequently, the detected energy of the electron is equivalent to its energy at the moment of ionization. Also, in the short pulse regime, the ponderomotive shift of the continuum due to adjustments in laser intensity results in a corresponding shift of the ATI peaks to lower energies. As the laser intensity increases, each ATI order is expected to shift to lower energies by an amount equal to the change in U_p .

2.4 Ionization Regimes in a Strong Laser Field

Photoionization is a result of an electromagnetic wave or a photon interacting with an atomic or molecular system. To describe this interaction in quantum mechanics, ionization of an atom was first addressed by Einstein [60] in 1905 through the photoelectric effect when SFP didn't exist.

In the ground state, atoms and molecules are bound systems, and ionization can occur when an electromagnetic (EM) field transfers enough energy to overcome their I_p . When

the $\hbar\omega$ of the EM field is greater than the I_p , an atom can absorb a photon and emit an electron with a K.E. equal to the difference between the two values: $KE = \hbar\omega - I_p$. This phenomenon is the essence of the photoelectric effect. Even a single photon with $\hbar\omega > I_p$ is sufficient to ionize the atom, resulting in a high ionization rate at very low intensities. In such cases, perturbation theory within the framework of nonrelativistic quantum mechanic is commonly applied, treating the atomic Hamiltonian as the unperturbed Hamiltonian and the EM field Hamiltonian as the perturbation.

On the other hand, if the photon's energy is insufficient to overcome the I_p ($\hbar\omega < I_p$), the atom can only be ionized by absorbing multiple photons while satisfying energy conservation:

$$KE = N\hbar\omega - I_p \quad (2.14)$$

Where N is the minimum number of photons required for $KE < \hbar\omega$. Since N can be quite large in equation 2.14, achieving a measurable nonlinear ionization rate W_N necessitates absorbing many photons by the atom. Assuming no intermediate resonances, the general expression for the nonlinear ionization rate W_N using perturbation theory for low intensity is given by [61, 62]:

$$W_N = \sigma_N(\omega, \epsilon) \frac{I^N}{\omega^N}, \quad (2.15)$$

where $\sigma_N(\omega, \epsilon)$ is the multiphoton absorption cross section, I is the intensity related by the EM field, and ϵ is the field's ellipticity. It is important to note that the cross-section is independent of intensity. Single photon ionization ($N = 1$) [61, 62] can be seen as an approximate case of multiphoton ionization.

As intensities increase sufficiently, equation 2.15 is no longer applicable. ATI is one indicator of entering the higher-order regime, wherein the atom absorbs more photons than the minimum requirement [63]. Moreover, it is possible for the ionization rate W_{N+S} , with S representing the excess number of absorbed photons, to exceed W_N .

At even higher intensities, the EM field's strength becomes comparable to the atomic

potential, leading to another mechanism called tunnel ionization. In this case, the ionization rate is no longer described by a power law in terms of intensity but rather follows an exponential relationship [20] and it will be proved in 2.4.1 :

$$W \sim \exp \frac{-2(2I_p)^{3/2}}{3E_0} \quad (2.16)$$

Since this is the regime investigated in this document, in the following pages we will discuss this process and its predictions in detail for both atoms and molecules. Finally, at the highest intensities, the external field strength overcomes the atomic potential. This can be viewed as the asymptotic case for tunnel ionization, when the barrier is completely suppressed. For this reason, this regime is referred to us as over the barrier ionization (OTBI) and the intensity is described by [61]:

$$I_{\text{OTB}} = \frac{\pi^2 c^3 \epsilon_0 I_p^4}{2Z^2 e^6} \quad (2.17)$$

where c is the speed of light, ϵ_0 is the permittivity of free space, and Z is the charge of the ion after ionization. I_{OTB} is the upper bound on ionization. Above this intensity, the electron freely escapes the core. This process can be fully understood classically and will not play an important role in the discussions in the remainder of this dissertation. However, all experiments presented hereafter will have kept the laser intensity below this threshold.

All the above mechanisms are presented graphically in Figure 2.2, as a function of field strength and the photon energy: At the top of the plot, where the electric field strength is low, the regime of single ionization is depicted. The I_p is represented by a black line, indicating the energy required to remove an electron from the atom or molecule. The laser field is shown in red, representing the applied electromagnetic field. The total potential, which combines the atomic potential and the laser field, is displayed in blue. The electron wave packet resulting from ionization is represented by a green structure. Moving down in the plot, as the electric field strength increases, the regime of multiphoton ionization is illustrated. The ionization occurs through the absorption of multiple photons. The same

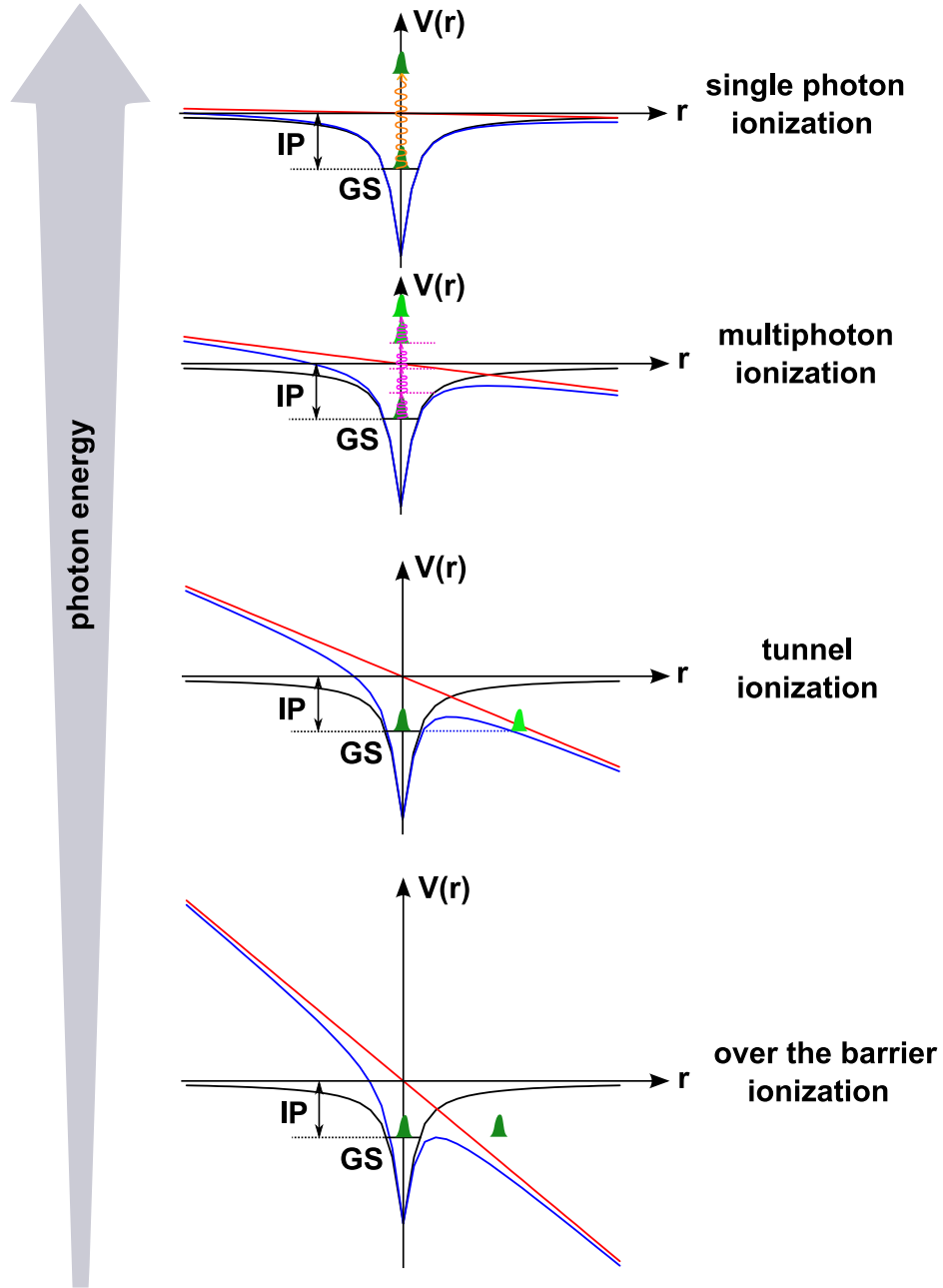


Figure 2.2: The figure depicts the ionization regimes as a function of electric field strength. It is a 3D plot with the vertical axis representing the strength of the electric field. The plot is divided into four regions from top to bottom, each corresponding to a specific ionization regime.

color scheme is used to represent the I_p , laser field, total potential, and electron wave packet as in the single ionization regime. Further down in the plot, when the electric field strength is high, the regime of tunnel ionization is shown. The ionization process involves the electron tunneling through the barrier created by the combined effect of the atomic potential and the electric field. The I_p , laser field, total potential, and electron wave packet are visualized using the same colors as in the previous regimes. At the bottom of the plot, where the electric field strength is extremely high, the regime of over-the-barrier ionization is depicted. In this regime, the external field strength dominates over the atomic potential, resulting in the suppression of the barrier. Similar to the other regimes, the I_p , laser field, total potential, and electron wave packet are represented using their respective colors.

At this point, it becomes crucial to address a significant question: How can we make sure whether ionization of an atom or molecule occurs through multiphoton or tunneling processes? The answer becomes apparent when considering specific factors.

A viable approach would involve conducting a comprehensive calculation of the ionization rates for both multiphoton and tunneling processes to determine the dominant mechanism. There is a way to roughly estimate the ionization behavior. In 1965, L.V. Keldysh [64] introduced a fundamental theoretical framework that has played a crucial role in understanding the ionization of atoms and molecules when exposed to intense oscillating fields, such as those generated by ultrafast lasers.

2.4.1 Overview of Keldysh Theory

In the non-relativistic framework, the Hamiltonian of an electron influenced by an atomic potential $V(\vec{r})$ and an oscillating external laser field $\vec{E}(t)$ is represented by

$$H(t) = \frac{\vec{p}^2}{2m_e} + e\vec{r} \cdot \vec{E}(t) + V(\vec{r}) \quad (2.18)$$

Equation 2.18 is formulated in the length gauge. In the velocity gauge we have, $H(t) = [\vec{\mathbf{p}} - e\vec{\mathbf{A}}(t)]^2/2m + V(\vec{\mathbf{r}})$, where $\vec{\mathbf{A}}(t)$ is the vector potential of the laser ($\vec{\mathbf{E}}(t) = -\partial\vec{\mathbf{A}}(t)/\partial t$) and e is the electron charge magnitude. Assuming the size of an atom is much smaller than the wavelength of the optical field the spatial dependence of the $\vec{\mathbf{E}}(t)$ can be neglected which is called dipole approximation. The probability amplitude for an electron transition from a ground state ψ_0 to a continuum state $\psi_{\vec{\mathbf{p}}}$ with momentum $\vec{\mathbf{p}}$ is given by [20]

$$M(\vec{\mathbf{p}}) = \lim_{t \rightarrow +\infty, t' \rightarrow -\infty} \langle \psi_{\vec{\mathbf{p}}}(t) | U(t, t') | \psi_0(t') \rangle, \quad (2.19)$$

where $U(t, t')$ denotes the time evolution operator of $H(t)$. This expression raises the question of how to accurately compute $M(\vec{\mathbf{p}})$. The conventional perturbation approach to ionization considers the electron to remain in a stationary state of the atom post-ionization, which is not entirely precise since the electron is still subjected to the oscillating laser field, meaning it experiences acceleration due to this time-variant field. This consideration is negligible for weak fields but is crucial in strong field ionization scenarios. The transition amplitude according to Keldysh's approach is [20]

$$M(\vec{\mathbf{p}}) = \frac{i}{\hbar} \int_{-\infty}^{\infty} dt_0 \langle \psi_{\vec{\mathbf{p}}}^{(V)}(t) | e\vec{\mathbf{r}} \cdot \vec{\mathbf{E}}(t_0) | \psi_0(t_0) \rangle \quad (2.20)$$

The state $\psi_{\vec{\mathbf{p}}}^{(V)}(t)$ is described by the Volkov function:

$$\langle \vec{\mathbf{r}} | \psi_{\vec{\mathbf{p}}}^{(V)}(t) \rangle = \frac{1}{(2\pi\hbar)^{3/2}} \exp \left[\frac{i}{\hbar} \left(\vec{\mathbf{p}} \cdot \vec{\mathbf{r}} - \frac{m}{2} \int_{-\infty}^t \vec{\mathbf{p}}(t')^2 dt' \right) \right], \quad (2.21)$$

And the relationship between the kinetic and canonical momentum is

$$m\dot{\vec{\mathbf{r}}}(t) = \vec{\mathbf{p}} + e\vec{\mathbf{A}}(t), \quad (2.22)$$

Equation 2.22 states that the vector potential of the laser is $\vec{\mathbf{A}}(t)$, which is related to the

electric field $\vec{\mathbf{E}}(t)$ by $\vec{\mathbf{E}}(t) = -\frac{\partial \vec{\mathbf{A}}(t)}{\partial t}$. The Volkov state is the eigenstate of a free electron in the field $\vec{\mathbf{E}}(t)$. Using it as the final state implies that the interaction between the electron and its parent ion after ionization is neglected. In other words, a key difference between the perturbative approach and Keldysh approach is that the former neglected the effect of the laser field for the final state [20] while the latter neglected the effect of the atomic potential for the final state. In reference [64], Keldysh presented the calculations of total ionization rate, that is, $w_0 = \int |M|^2 d^3\vec{\mathbf{p}}$, for a monochromatic field $E_0 \cos(\omega t)$. Under the approximation that (i) the laser field amplitude is small compared to the atomic field and (ii) the atomic potential is a short-range potential, an analytic expression for w_0 was obtained. It was expressed as an infinite sum in which each term can be interpreted as the partial rate due to the absorption of N photons, and the minimum N has to be such that the energy sum of the photons is at least not smaller than the effective I_p . That is, each term represents an ATI order. In the expression of w_0 there is a crucial parameter γ which is now called the Keldysh parameter:

$$\gamma = \frac{\omega \sqrt{2mI_p}}{eE_0}, \quad (2.23)$$

where ω is the laser frequency. This dimensionless parameter characterizes the dynamical regime of ionization as we will examine. The ionization rate for the two extreme cases of γ are

$$w_0 \propto \begin{cases} \left(\frac{E_0}{\omega}\right)^{2[K_0]} & \gamma \gg 1 \\ (\sqrt{I_p}E_0)^{1/2} \exp\left(-\frac{2(2I_p)^{3/2}}{3E_0}\left(1 - \frac{\gamma^2}{10}\right)\right) & \gamma \ll 1 \end{cases} \quad (2.24)$$

where $K_0 = \frac{I_p}{\hbar\omega}$ and $\lceil \cdot \rceil$ is the ceiling function. For $\gamma \ll 1$, on the other hand, is called the “tunneling limit”. In the limit $\omega \rightarrow 0$ (i.e. $\gamma \rightarrow 0$), the exponential term becomes $\exp\left(-\frac{2(2I_p)^{3/2}}{3E_0}\right)$ which coincides with the expression for the tunnel ionization of an atom by a static field shown in Equation 2.16. As a simple illustration of tunnel ionization, Figure 2.3 shows a narrow square potential well under the influence of a static external field E .

Initially, an electron is in the well with an energy of $-I_p$. Due to the external field, the

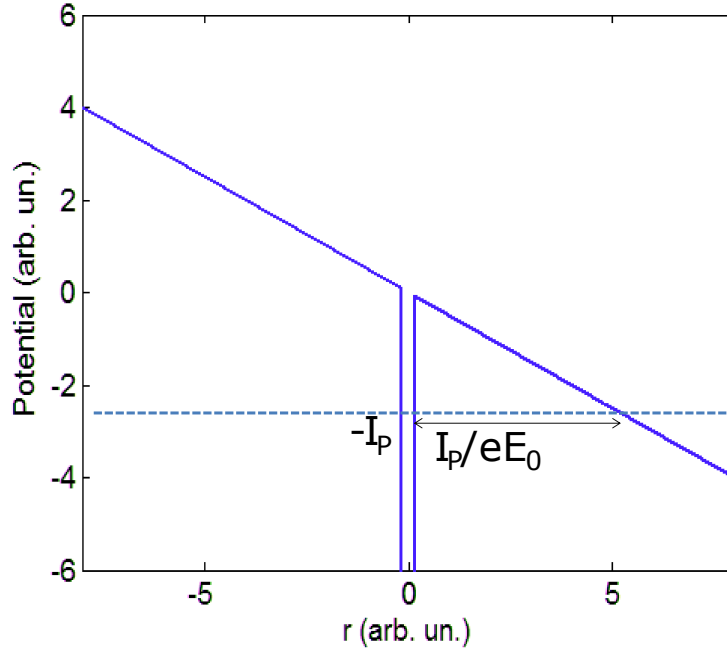


Figure 2.3: A square potential well under the influence of a strong constant electric field.

potential is “tilted”, thus a barrier of a width of I_p/eE_0 is formed. Ionization occurs if the electron tunnels through the barrier. If the external field is an optical field, it alternates as a function of time and as a result the potential barrier also varies in time. For every half of an optical period the barrier is switched from one side to the other. In this scenario, one could imagine that a crucial criteria for tunneling to happen is that the electron has to tunnel through the barrier “fast” enough so that it could escape before the barrier is “closed”.

Figure 2.4 provides a visual representation of this process. Near the peak of each half-cycle, when the field approaches its maximum value, the atomic potential is suppressed, creating a nonzero probability for a bound electron to tunnel into the continuum. To achieve a substantial tunneling probability, the atomic potential must be suppressed significantly within a fraction of the laser’s cycle duration.

In Keldysh’s model, once the electron has tunnelled out of the atomic potential, it propagates under the influence of the laser field, with the effects of the atomic potential

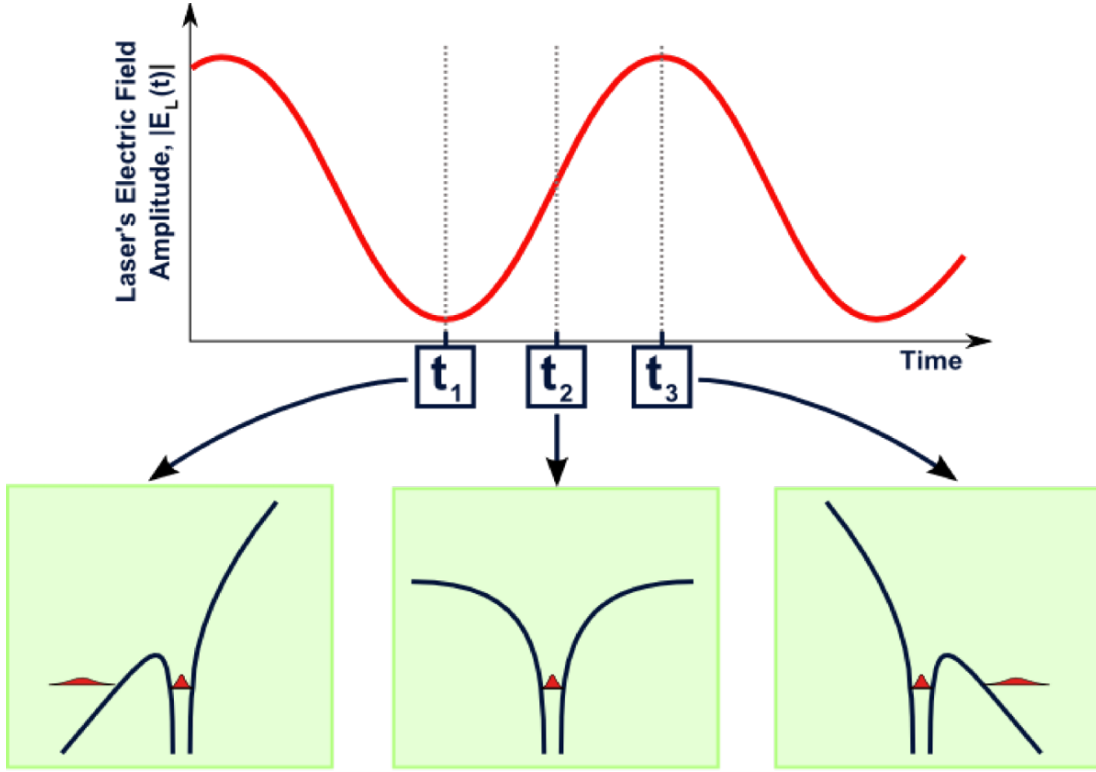


Figure 2.4: Tunnel ionization of an electron interacting with a linearly polarized laser field. In panels (a), (b), (c) the combined potential of the atom and laser is shown at three different times during a laser cycle. At the peaks t_1 and t_3 the atomic potential is distorted such that the electron can tunnel ionize.

neglected. In another approach, Keldysh introduced the adiabaticity parameter γ , often referred to as the Keldysh parameter, to show the significance of tunnel ionization in the interaction between the target and the light field. This parameter is expressed as [20]:

$$\gamma = \frac{\text{tunneling time}}{\text{optical angular period}} = \frac{\omega}{\omega_t} \quad (2.25)$$

The Keldysh parameter represents the ratio of the tunneling frequency ω_t and the frequency of the external field ω . When the tunneling time is short compared to the optical period, tunnel ionization plays an important role. To use Equation 2.25 effectively, it is essential to define what Keldysh meant by the tunneling time of the electron. Keldysh defined the tunneling time as the time it takes for a classical electron with a velocity v to traverse

a potential barrier of thickness d . For a bound electron in the ground state, the average velocity is $v = \sqrt{2I_p/m_e}$ [20], where m_e denotes the electron's mass. The width of the barrier is determined as $d = I_p/eE_0$, where E_0 is the laser field amplitude, and e represents the electron charge. The tunneling time is calculated as [20]:

$$t_t = \frac{d}{v} = \frac{\sqrt{2m_e I_p}}{eE_0} \quad (2.26)$$

Inserting Equation 2.26 into Equation 2.25, the Keldysh parameter can be expressed as Equation 2.23. While Equation 2.23 is accurate, the Keldysh parameter is often more conveniently expressed in terms of the ponderomotive energy. By substituting the ponderomotive energy into Equation 2.23, the Keldysh parameter can be written as:

$$\gamma = \sqrt{\frac{I_p}{2U_p}} \quad (2.27)$$

If γ is much less than 1, tunnel ionization dominates the interaction, showing that the tunneling frequency surpasses the field frequency. On the other hand, if γ is much greater than 1, the assumption of tunnel ionization no longer holds, and multiphoton ionization becomes the ionization mechanism. Second and third plots of Figure 2.2 illustrate these limiting scenarios.

The conventional interpretation of γ involves using it as a metric to differentiate between the two primary regimes of strong field ionization:

It is essential to understand that the adiabacity parameter γ should be used as a rough guide rather than an exact parameter to identify whether a process is predominantly governed by multiphoton ionization or tunneling ionization. When γ is approximately equal to 1, it corresponds to the transition regime where characteristics of both MPI and TI are present [65].

2.5 Ionization Models for Atoms and Molecules in an Electromagnetic Field

2.5.1 PPT and ADK Formulas

As previously mentioned, Keldysh's formula faced challenges in accurately reflecting experimental observations due to the neglected influence of the atomic core on the photoelectron wavefunction. The Perelomov, Popov, and Terent'ev (PPT) formula, introduced shortly after Keldysh's publication, offered an improvement by accounting for the long-range Coulomb interaction [66, 67]. This formula was applicable to different atomic ground states across quantum numbers l and m . Historically, Keldysh, PPT, and other models did not gain traction until technological advancements in the 1980s enabled the use of intense short pulsed lasers. The Ammosov, Delone, and Krainov (ADK) formula, a product of this period, is a simplification of the PPT formula for the case of $\gamma \ll 1$ and is favored for its simplicity in practical applications, even when $\gamma \approx 1$ [68]. Only the ground state is considered in these models, excluding any discrete bound states. The focus of the current chapter is to assess the practicality of PPT and ADK by comparing them against experimental data and theoretical models for the intensity-dependent ionization yield of different atomic species under various laser wavelengths and polarization states.

We begin by recapping the PPT and ADK theoretical frameworks to interpret ionization rates under strong electromagnetic fields. For a more in-depth derivation, references to the foundational papers are provided [66, 67]. Analogous to Keldysh's formulation, the PPT ionization rate is a summation, with each term corresponding to the ATI process of absorbing multiple photons [66–69]:

$$w_{\text{PPT}}(E, \omega) = \sum_{q \geq q_{\min}} w_q(E, \omega), \quad (2.28)$$

where E and ω symbolize the amplitude and frequency of the laser field, respectively. The effective ionization threshold is encapsulated by the parameter $q_{\min}$. The complete cycle-

averaged PPT formula is given as [66–69]:

$$w_{\text{PPT}}(E, \omega) = c_{n^* l^*}^2 f(l, m) \left(\frac{2}{En^{*3}} \right)^{2n^* - |m| - 1} (1 + \gamma^2)^{\frac{|m| + 3/2}{2}} g(\gamma) A_m(\omega, \gamma) e^{-\frac{2(2I_p)^{3/2}}{3E} g(\gamma)}, \quad (2.29)$$

with $g(\gamma)$ defined as:

$$g(\gamma) = \frac{3}{2\gamma} \left[\left(\frac{1}{1 + \frac{1}{2\gamma^2}} \right) \sinh^{-1} \gamma - \frac{\sqrt{1 + \gamma^2}}{2\gamma} \right], \quad (2.30)$$

and $A_m(E, \omega)$ is:

$$A_m(E, \omega) = \frac{4\gamma^2}{\sqrt{3\pi} |m|! (1 + \gamma^2)} \sum_{q \geq q_{\min}} e^{-\alpha(\gamma)(q - \nu)} w_m(\sqrt{\beta(\gamma)(q - q_{\min})}), \quad (2.31)$$

$$w_m(x) = \frac{x^{2|m|+1}}{2} \int_0^1 \frac{e^{-x^2 t} t^{|m|}}{\sqrt{1-t}} dt, \quad (2.32)$$

$$\alpha(\gamma) = 2 \left(\sinh^{-1} \gamma - \frac{\gamma}{\sqrt{1 + \gamma^2}} \right), \quad (2.33)$$

The function $\beta(\gamma)$ and frequency ratio ν are given by:

$$\beta(\gamma) = \frac{2\gamma}{\sqrt{1 + \gamma^2}}, \quad \nu = \frac{I_p}{\omega} \left(1 + \frac{1}{2\gamma^2} \right), \quad (2.34)$$

where the coefficient c_{n^*} is:

$$c_{n^*}^2 = \frac{2^{2n^*}}{n^* \Gamma(n^* + l^* + 1) \Gamma(n^* - l^*)} \quad (2.35)$$

and the function $f(l, m)$ is defined as:

$$f(l, m) = \frac{(2l + 1)(l + |m|)!}{2^{|m|} (|m|)! (l - |m|)!}. \quad (2.36)$$

In the equations above, E represents the field amplitude, $n^* = 1/\sqrt{2I_p}$ is the effective quantum number, and $\Gamma(x)$ denotes the gamma function. The quantum numbers l and m are associated with the orbital and magnetic quantum numbers, respectively. These are defined with respect to the quantization axis determined by the laser polarization direction. The factor $(2/En^{*3})^{2n^*}$ in Equation 2.29 incorporates the long-range Coulomb interaction and $\sqrt{3E\pi n^{*3}}$ is the result of cycle averaging. It is noted that the $m = 0$ orbital predominantly contributes to ionization as its electron density is chiefly distributed along the quantization axis, where all nonzero m orbitals present nodes that are not conducive to the ionization of the electron.

For circular polarization, the cycle-averaged PPT rates are given by [68, 69]:

$$w_{\text{PPT}}^s(E, \omega) = \frac{c_{n^*l^*}^2 I_p}{4\sqrt{2\pi} q_{\min}^{3/2}} \left(\frac{2}{En^{*3}} \right)^{2n^*} \left(1 + \frac{1}{\gamma^2} \right)^{1/2} \times \sum_{q \geq q_{\min}} (1 + \zeta) \sqrt{(1 - \zeta)} \left(\frac{1 + \gamma^2}{\zeta^2 + \gamma^2} \right)^{3/4} e^{-\frac{4q_{\min}}{1+\zeta} \tanh^{-1} \left(\sqrt{\frac{\zeta^2 + \gamma^2}{1 + \gamma^2}} - \frac{\zeta^2 + \gamma^2}{1 + \gamma^2} \right)}, \quad (2.37)$$

for s orbitals,

$$w_{\text{PPT}}^{p_0}(E, \omega) = \frac{3c_{n^*l^*}^2 I_p}{16\sqrt{2\pi} q_{\min}^{5/2}} \left(\frac{2}{En^{*3}} \right)^{2n^*} \left(1 + \frac{1}{\gamma^2} \right)^{3/2} \times \sum_{q \geq q_{\min}} (1 - \zeta^2) \sqrt{(1 - \zeta)} \left(\frac{1 + \gamma^2}{\zeta^2 + \gamma^2} \right)^{5/4} e^{-\frac{4q_{\min}}{1+\zeta} \tanh^{-1} \left(\sqrt{\frac{\zeta^2 + \gamma^2}{1 + \gamma^2}} - \frac{\zeta^2 + \gamma^2}{1 + \gamma^2} \right)}, \quad (2.38)$$

for p orbitals with $m = 0$,

$$\begin{aligned}
w_{\text{PPT}}^{p\pm}(E, \omega) = & \frac{3c_{n^*l^*}^2 I_p}{8\sqrt{2\pi} q_{\min}^{3/2}} \left(\frac{2}{En^*3} \right)^{2n^*} \left(1 + \frac{1}{\gamma^2} \right)^{3/2} \\
& \times \sum_{q \geq q_{\min}} \left(\sqrt{\frac{\zeta^2 + \gamma^2}{1 + \gamma^2}} \mp \zeta \text{sign}(m)^2 \right) \frac{1}{\sqrt{1 - \zeta}} \left(\frac{1 + \zeta^2}{\zeta^2 + \gamma^2} \right)^{3/4} \\
& e^{-\frac{4q_{\min}}{1+\zeta} \tanh^{-1} \left(\sqrt{\frac{\zeta^2 + \gamma^2}{1 + \gamma^2}} - \frac{\zeta^2 + \gamma^2}{1 + \gamma^2} \right)},
\end{aligned} \tag{2.39}$$

For p orbitals with magnetic quantum number $m = \pm 1$, the minimum photon number $q_{\min}$ for circular polarization is related to the ponderomotive energy U_p and I_p by $q_{\min} = [(2U_p + I_p)/\omega]$. Here, ζ is defined as $2q_{\min}/q - 1$. The ionization rate for $m = 0$ states is notably smaller compared to the $m = \pm 1$ state.

The ionization rate according to the Ammosov-Delone-Krainov (ADK) model is given by [68]:

$$w_{\text{ADK}}(E) = c_{n^*l^*}^2 f(l, m) I_p \left(\frac{2}{En^*3} \right)^{2n^* - |m| - 1} \exp \left[-\frac{2(2I_p)^{3/2}}{3E} \right]. \tag{2.40}$$

The ADK model's formula for instantaneous ionization rates can be extrapolated from the general equation by considering the $\gamma \rightarrow 0$ limit, signifying ionization in a static electric field, and omitting cycle-averaging prefactors. Due to the ADK formula's frequency-independent nature, it does not offer predictions on the wavelength dependency of ionization rates. This holds true for instantaneous rates regardless of the polarization type. By analyzing the electron tunneling rate through a Coulomb potential in a static field, the formula is further validated.

The atomic parameters for the atoms under study are listed in a table. To determine the ionization probability of an atom by a laser pulse, the following rate equation is utilized:

$$\frac{dP_0}{dt} = -w(E(t))P_0, \tag{2.41}$$

where P_0 denotes the probability of the atom remaining not ionized. The population of the

atomic ground state is represented by P_0 , which is initially set to 1. The atomic parameters for PPT and ADK calculations are tabulated below:

Element	I_p (eV)	n^*	$c_{n^*}^2$	I_{BSI} (TW/cm ²)
Ne	21.56	0.794	4.244	862
Ar	15.79	0.929	4.116	246
Kr	13.99	0.986	4.025	153
Xe	12.13	1.059	3.882	86
Na	5.14	1.627	2.290	2.8
K	4.34	1.770	1.890	1.4
Mg	7.65	1.334	3.163	13.3
Zn	9.39	1.203	3.532	31

Table 2.1: Atomic parameters for PPT and ADK calculations [14].

The ionization probability is then given by:

$$P = 1 - \exp \left(- \int_{-\infty}^{+\infty} w(E(t)) dt \right), \quad (2.42)$$

where $F_0(t)$ is the pulse envelope with a sine-squared shape defined as:

$$\vec{E}(t) = \begin{cases} E_0 \cos^2 \left(\frac{2\omega t}{11n} \right) \cos(\omega t) \hat{z}, & \text{if } -\frac{11n\pi}{4\omega} < t < \frac{11n\pi}{4\omega} \\ 0, & \text{otherwise} \end{cases} \quad (2.43)$$

where n is the full width at half maximum (FWHM) pulse duration in terms of the number of optical cycles.

As shown in Figure 2.5 ionization probability of krypton atoms driven by a 0.8 μm wavelength laser is analyzed using PPT and ADK models. The PPT model typically estimates a higher ionization probability than ADK, possibly because the former depends on the photon energy $\hbar\omega$, while the latter is similar to the PPT's limit as $\omega \rightarrow 0$. Thus, any PPT estimations with non-zero ω will likely predict a higher probability than ADK. PPT's prediction shows local minima against an increasing trend, aligned with intensities satisfying the condition $N\hbar\omega - I_p - U_p = 0$, where N_{min} is the threshold photon count needed for ionization,

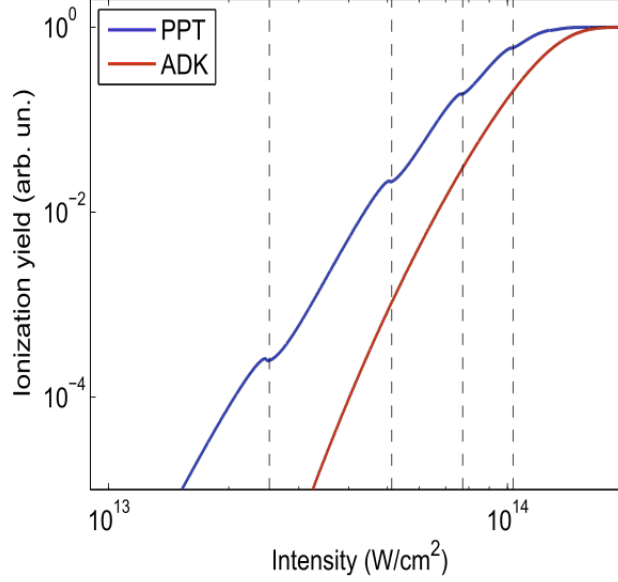


Figure 2.5: Comparison between PPT and ADK ionization yield as a function of laser intensity for krypton atom at 0.8 μm driving wavelength. Reproduced from [68].

leading to the channel closure effect. With the increase in laser intensity, N_{min} must rise as the prior energy $N_{\text{min}}\hbar\omega$ becomes insufficient for atom ionization, hence, the local minimum in ionization probability at channel closure intensities. In the described experiments, ions are produced from a full Gaussian laser beam focus. Therefore, focal volume averaging is taken into account in the calculations. To match with experimental results, focal averaging effect is taken into account in the reported PPT and ADK computations.

2.5.2 Keldysh-Faisal-Reiss Strong Field Approximation

KFR represents a preliminary model for the interaction between lasers and atoms. This model, originally known as the Keldysh theory, has been expanded into what is sometimes called the KFR theory to take into account the insights from Faisal and Reiss. It is also called strong field approximation (SFA). Unlike experimental results on real atoms, Keldysh's formula is constrained by removal of the Coulomb interaction between the photoelectron and the originating ion. ADK proposed its formula for tunnel ionization rate, similar to the PPT formula in the limiting case where $\gamma \ll 1$. Both PPT and ADK formulations are used

in calculating the ionization probability. When calculating the momentum distribution of photoelectrons, the SFA, or KFR, is the method most commonly used. The detailed formulations of KFR can be found in the review article by Milošević [70]. In quantum mechanics, the accurate transition amplitude from an initial state $|i\rangle$ to a final state $|f\rangle$ is shown as:

$$M_{i \rightarrow f}(t) = -i \int_{-\infty}^t \langle i | V(t') | f \rangle dt', \quad (2.44)$$

where $V(t)$ is the interaction potential, with the assumption that variables except the time are omitted. In 1963, Keldysh proposed a simplified version of this formula by disregarding the atomic potential's effect on the final state, a method always maintaining gauge invariance. In the length gauge, where $V(\vec{r}, t) = \vec{r} \cdot \vec{E}(t)$, the wave function of a "free" electron within an electromagnetic field which is known as Volkov wave function can be described as:

$$\langle \vec{r} | f^V(\vec{P}, t) \rangle = \frac{e^{i\vec{r}(\vec{P} + \vec{A}(t))}}{(2\pi)^{3/2}} \exp \left\{ i \int_t^\infty \left[\frac{(\vec{P} + \vec{A}(\tau))^2}{2} \right] d\tau \right\} \quad (2.45)$$

where $\vec{A}(t)$ is the vector potential. Briefly speaking, Volkov wavefunction, named after Dmitry Volkov who first described it in 1935, represents a wavefunction for a free electron moving in a plane electromagnetic wave. It's a quantum state of an electron that is not bound to an atom but is under the influence of a classical electromagnetic field as shown in 2.45. The action, which is connected to ADK theory, is given by:

$$S(t) = \frac{1}{2} \int_t^0 \left[\vec{p} + \vec{A}(\tau) \right]^2 d\tau + I_p t, \quad (2.46)$$

and the transition amplitude is expressed as:

$$\mathbf{M}_{\vec{P}}^{\text{direct}} = i \frac{Z^{5/2}}{\pi \sqrt{2}} \int_0^{kT} \frac{\exp(iS(t))}{\partial S(t)/\partial t} dt, \quad (2.47)$$

Given that T shows the laser pulse period, Z the atomic number, and k an integer, the transition amplitude detailed in the equation can be computed through the saddle point

method. This involves identifying the roots in the integrand's denominator, which are typically complex. The real components of these roots represent the crucial phases when the electron is going from a bound to a continuum state, representing the fact that these phase have the same vector potential. Consequently, the transition amplitude can be extracted as addition of two terms. Since the ionization rate, is related to the squared of the sum, an interference term shows up. This term is not found in the ADK framework, which was developed for a static case, so neglects the oscillatory phase data. This neglect leads to a loss of phase information in the ADK transition amplitude. Employing the saddle point technique, the ultimate transition amplitude within Keldysh's model is shown as:

$$\mathbf{M}_{\mathbf{P}}^{\text{direct}} = -\frac{Z^{5/2}}{\sqrt{2}} \sum_{n=1,2} \frac{\pi \exp[iS(t_n)]}{E(t_n) (I_p + p_{\perp}^2)^{1/2}} \exp\left[-\frac{(2I_p + p_{\perp}^2)^{3/2}}{3E(t_n)}\right], \quad (2.48)$$

where the summation is executed over two saddle points. The rest of the steps needs to be done numerically by finding the saddle points for each electric field value.

Although SFA does not directly reproduce ionization rates from TDSE calculations, the overall shape of the spectra in both models are similar [71]. In contrast, ionization rates estimated by the ADK model have shown closer agreement with TDSE outcomes. This discrepancy largely arises because, in SFA, the continuum electron is modeled using the Volkov wavefunction 2.45, which omits the potential effects from the atomic ion core. The history of the KFR theory and its modification is also reviewed in [72].

2.5.3 Time Dependent Schrödinger Equation in the Single Active Electron Approximation

The most significant benefit of using TDSE over previous theoretical models is its high accuracy, as it accounts for the atom's excited states and thoroughly characterizes the long-range Coulomb potential under the laser field's influence, the ground state, and all excited states. Since the method provides a time dependant wave function, any information can be

extracted. However, one drawback is that it takes a lot of computational effort and time due to the complication of the problem.

As a proof of how powerful this model is, here are two Figures for TDSE simulations shown in Figure 2.8, using the widely accessible Qprop software [73].

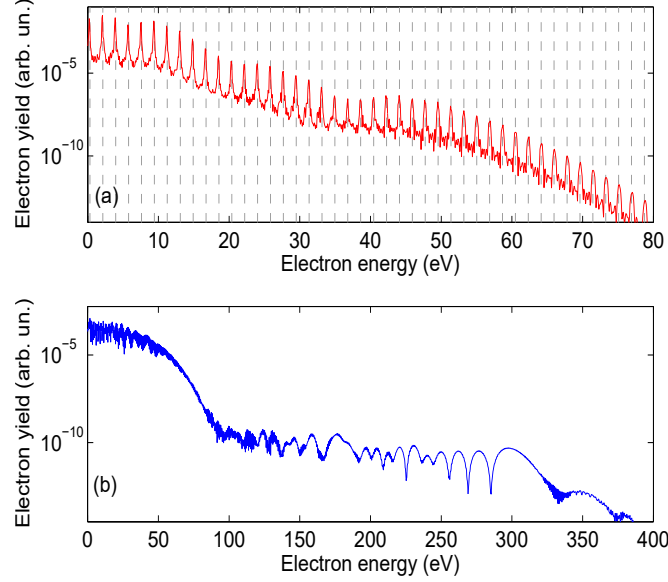


Figure 2.6: TDSE simulations of photoelectron energy spectrum from a hydrogen atom irradiated by a laser pulse at (a) 680 nm in the multiphoton regime and (b) 1800 nm in the tunneling regime. Reproduced from [74].

Figure 2.8 demonstrates the TDSE simulations of the photoelectron energy spectrum from a hydrogen atom when it is irradiated by laser pulses at two distinct wavelengths. Panel (a) shows the condition where $\gamma = 1.26$, placing us firmly within the multiphoton ionization domain. This regime is characterized ATI peaks, with adjacent peaks separated by the photon energy matching the laser's central wavelength (1.82 eV). Shown in panel (b) of Figure 2.8, where the laser's wavelength is 1800 nm, we enter the tunneling regime characterized by $\gamma = 0.47$. In this domain, the photoelectron spectrum divides distinctly into a dual-part profile. At the lower end of the energy spectrum, we observe an initial peak at zero, which then descends exponentially towards a definitive cutoff point. Past this threshold, the spectrum increases into a plateau phase, where the yield stabilizes and extends relatively flat until reaching a second cutoff at the higher energy boundary of the

spectrum. The initial low-energy portion is attributed to direct electrons, while the latter high-energy term results from rescattered electrons. A more comprehensive exploration of this phenomenon will be discussed with the assistance of the semi-classical model detailed next subsection.

Nonetheless, TDSE simulations are an invaluable resource, often serving as a standard for evaluating the precision of theoretical models across various scenarios.

2.6 Interpreting Electron Dynamics: The Semi-classical Perspective

This section introduces a semi-classical approach, frequently referred to as the three-step model. This model has gained attraction for its ability to show electron's full behavior while tunneling ionization happens and how it rescatters while it's in intense laser electromagnetic field. The model's foundational concept starts from the electron's quantum tunneling. Following this quantum tunneling through a potential barrier, the electron remains subject to the dominant laser field's effects. The model assumes the electron is removed far away from the core then its motion can be described by the laser field. The simplified motion equation for an electron influenced by a linearly polarized laser light can be written as follows:

$$m_e \frac{d^2x}{dt^2} = -eE_0 \cos(\omega t), \quad (2.49)$$

where E_0 represents the laser amplitude, ω is the angular frequency of the laser, and x denotes the electron's displacement.

In this model, we apply the following simplifications: (i) we ignore relativistic effects since the electron velocity v is significantly less than the speed of light c ; (ii) the laser's temporal pulse profile is neglected due to the recollision dynamics occurring on a sub-optical cycle; (iii) spatial dependence of the field is not considered. By integrating the governing equation

of motion, we arrive at the equations for the displacement $x(t; t_0)$ and velocity $v(t; t_0)$ of the electron as follows:

$$x(t; t_0) = \frac{eE_0}{m_e\omega^2} [\cos(\omega t) - \cos(\omega t_0) + \omega(t - t_0) \sin(\omega t_0)], \quad (2.50a)$$

$$v(t; t_0) = \frac{eE_0}{m_e\omega} [\sin(\omega t) - \sin(\omega t_0)]. \quad (2.50b)$$

Consider an electron just after it has tunneled through a Coulomb potential barrier. We start by assuming the electron's initial momentum is negligible. According to Equations 2.50, the electron's movement is a mix of oscillatory and linear drift motions. Illustrations in Figure 2.7(a) shows the electron's position $x(t; t_0)$ over time for various initial conditions t_0 when electron is tunneling out. Additionally, Figure 2.7(b) presents the field's amplitude and the vector potential as functions of time. It is important to note that U_p , as defined in Equation 2.5, is the cycle-averaged potential energy corresponding to the field. We consider that the oscillatory motion will dissipate after the laser field is gone and we will be left with drifting term. This term is what we measure its momentum and is known as PES as shown in Figure 2.8. Figure 2.8 shows a typical PES for Argon taken at $2 \mu\text{m}$ with $200 \text{ TW}/\text{cm}^2$ intensity.

The drift momentum's value is dependent on the initial phase t_0 . For the case that electrons don't interact with the parent ion, the K.E. of the the drift spans from 0 for $t_0 = \frac{\pi}{2\omega}$ to a maximum of $2U_p$ as shown in Figure 2.8.

The amplitude of the field vector potential and the ionization rate, peaks at $t = 0$ and is at its minimum at $t = \frac{\pi}{2\omega}$, resulting in a photoelectron energy spectrum yield that decreases as a function of K.E. and has a cutoff at $2U_p$ as shown in Figure 2.8. These electrons are called direct electrons.

As shown in the Figure 2.7a, some electron trajectories pass the zero line and they are the electrons that interact with the ion parent at a later time. These electron's return energy E_r , or K.E. upon return to the original position, is bound between zero and a maximum of

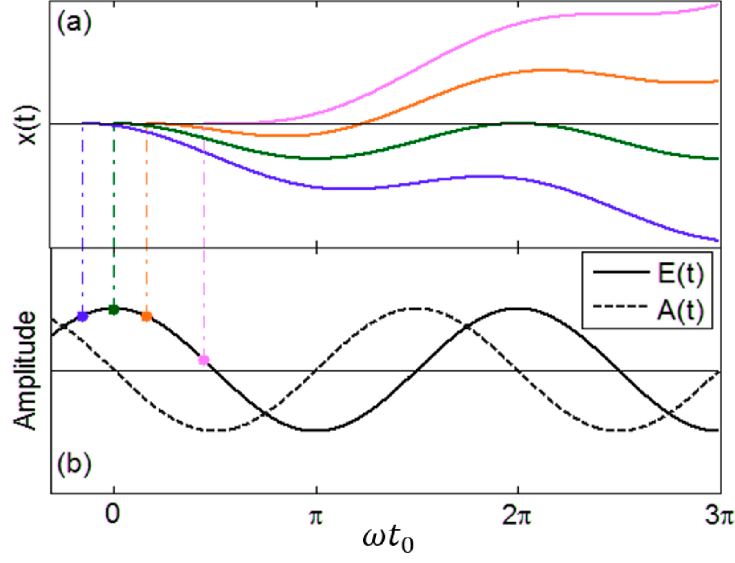


Figure 2.7: Classical electron trajectories. Upper panel: x versus ωt with different values of t_0 . $\omega t_0 = -0.5$ (purple); $\omega t_0 = 0$ (green); $\omega t_0 = 0.5$ (orange) and $\omega t_0 = 1.4$ (pink). Lower panel: amplitude (in arbitrary units) of electric field $E(t)$ and vector potential $A(t)$ vs ωt .

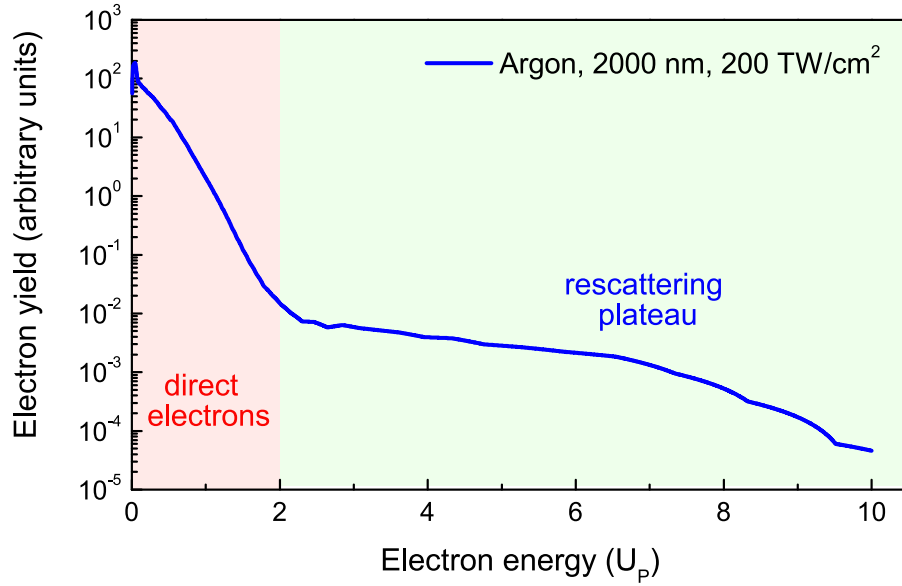


Figure 2.8: A typical photoelectron spectrum in the tunneling regime. The red region extending up to $2U_p$ is dominated by the direct electrons, while the blue region extending up to $10U_p$ arises from rescattering. Reproduced from [9].

$3.17U_p$, which a range of possible electron trajectories post-ionization can be derived.

let's consider the first return of the electron. The momentum k_r at the time of return to

the origin is as followed:

$$k_r \equiv m_e v(t_r; t_0) = \frac{eE_0}{\omega} [\sin(\omega t_r) - \sin(\omega t_0)] \quad (2.51)$$

When $\omega t_0 = 17^\circ$ or 0.29 radians as shown in Figure 2.9 (dashed line), the electron returns with a maximum K.E. of $3.17U_p$. For example, At $\omega t_0 = 13^\circ$ or 0.22 radians, the electron returns at $\omega t_r = 270^\circ$ or 4.7 radians. There are two distinct initial phases leading to different electron trajectories: long and short. Long and short refer to the time difference $t_r - t_0$.

Electrons born (ionized) after 0.29 radians return first and are called short trajectories. To be more accurate, we refer to the birth of the electrons multiple times in this work. Although we describe the electrons as being born, they are actually wave packets. As mentioned previously, the ADK model gives the probability of the ionization rate of the electrons as a function of time. Those electrons born before 0.29 radians return later and are called long trajectories. As it is shown in Figure 2.9 long trajectories occur from 0 to 0.29 radians, while short trajectories occur from 0.29 to $\pi/2$ radians. It is even possible to have more than two returns. For phases above 0.29 radians, the electron returns exactly twice (with the exception of the phase at 0.29 radians), while for phases from 0 to 0.29 radians, there are multiple returns. All multiple returns correspond to long trajectories. long trajectories' ionization rate is higher than the short trajectories since they are born at the peak.

The recollision phase, where the electron interacts with its parent ion, is a critical component of the three-step model. This interaction can result in elastic or inelastic scattering, or even recombination. During elastic scattering, the electron's momentum may change direction but keeps its magnitude, with only two possible outcomes in a one-dimensional model: forward (0°) or backward scattering (180°).

Backscattering, in particular, has an important impact by reversing the electron's momentum at the time of recollision. This interaction can potentially yield higher drift momentum compared to non-scattered paths. Consequently, the K.E. measured (E_f) varies

from 0 to as much as $10U_p$ as shown in Figure 2.8. Also shown in 2.8 from 2 to $10U_p$ is populated by rescattered electrons and is called the rescattering plateau. For the case of $\omega t_0 = 14^\circ$, for which $\omega t_r = 265^\circ$, the photoelectron will have maximal K.E. of $10U_p$ for $\theta_r = 180^\circ$. Figure 2.9(b) shows the correlation between E_r and E_f for long and short trajectories. Figure 2.9 also shows that below $10U_p$, there are two sets of birth-return times that would give the same K.E. except for $\omega t_0 = 14^\circ$ or 0.24 radians ($\omega t_r = 265^\circ$ or 4.6 radians). Electrons born before 14° would return after 265° , while those born after 14° would return before 265° . If the electrons are scattered in the forward direction, they would emerge as low-energy electrons with energies below $2U_p$.

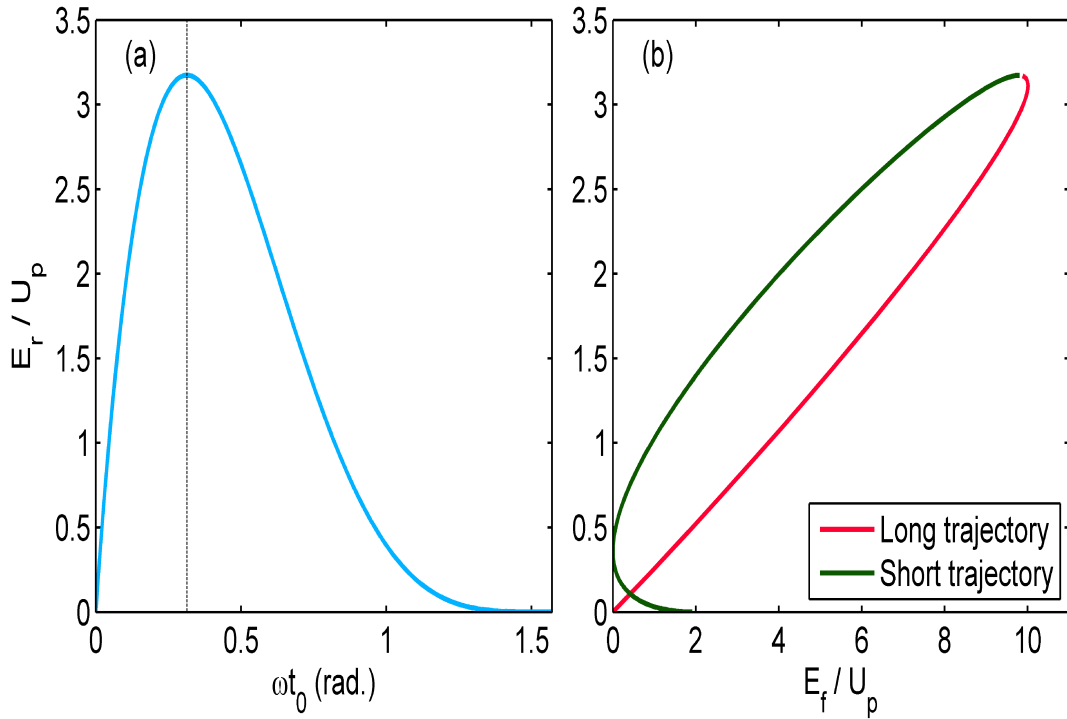


Figure 2.9: K.E. of rescattering electrons. (a) Return energy of the electron E_r as a function of ωt_0 . (b) Relation between E_r and E_f .

When an electron undergoes inelastic scattering upon its return, it imparts energy to the parent ion's bound electrons, potentially leading to the ejection or excitation of additional electrons. This event is known as nonsequential ionization (NSI).

As shown in 2.10 reproduced from [75], in the case of recombination, the electron goes back the ground state and emits a photon, a process that is called high-harmonic generation (HHG). This mechanism is important in generating attosecond pulses of light [76] and has significantly contributed to the exploration of ultrafast dynamics within electrons, as reviewed in [77].

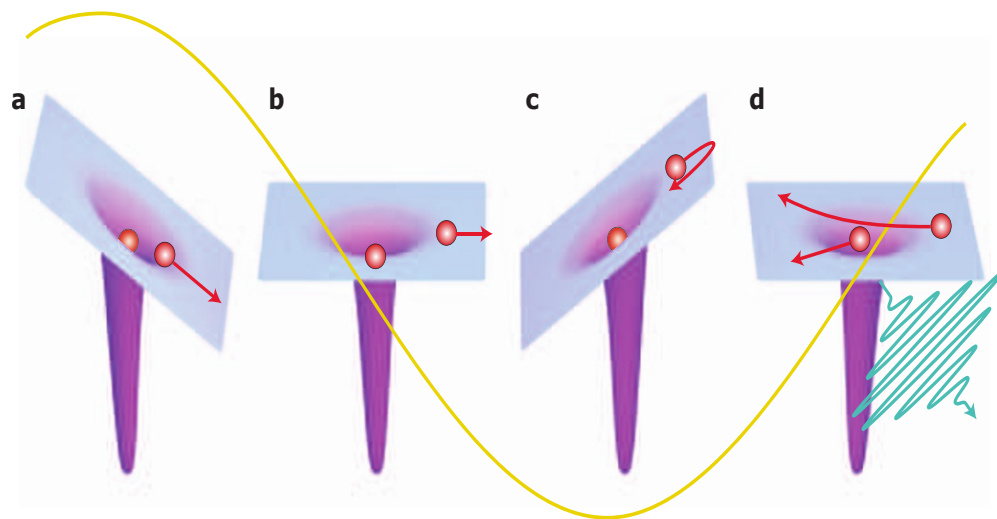


Figure 2.10: The three-step model of high-harmonic generation (HHG). (a-d) An intense femtosecond near-infrared or visible pulse (yellow) extracts an electron wave packet from an atom or molecule. First, the electron is pulled away from the atom near the peak of the optical field (a) and accelerated (b). When the optical field reverses, the electron is driven back (c) where it can ‘re-collide’ during a small fraction of the laser oscillation cycle (d). This process allows the parent ion to experience an attosecond electron pulse that can be used directly, or its K.E., amplitude, and phase can be converted to high harmonics upon recollision. Adapted from [75].

2.7 Nonsequential ionization

When the electron returns to the core, it can have energy several times greater than the I_p of the parent ion. Under such conditions, the electron might eject multiple electrons, as documented by Walker et al. [28]. In their study, illustrated in Figure 2.11 (adapted from [28]), they measured the yields of both single and double ionizations from helium using 780 nm, 100 fs linearly polarized light pulses. If the ADK rate is applied for sequential electrons,

it underestimates the production of He^{++} . The large discrepancy observed in Figure 2.11 (the blue region) comes from the fact that the impact of first ionized electron to eject the second electron is underestimated.

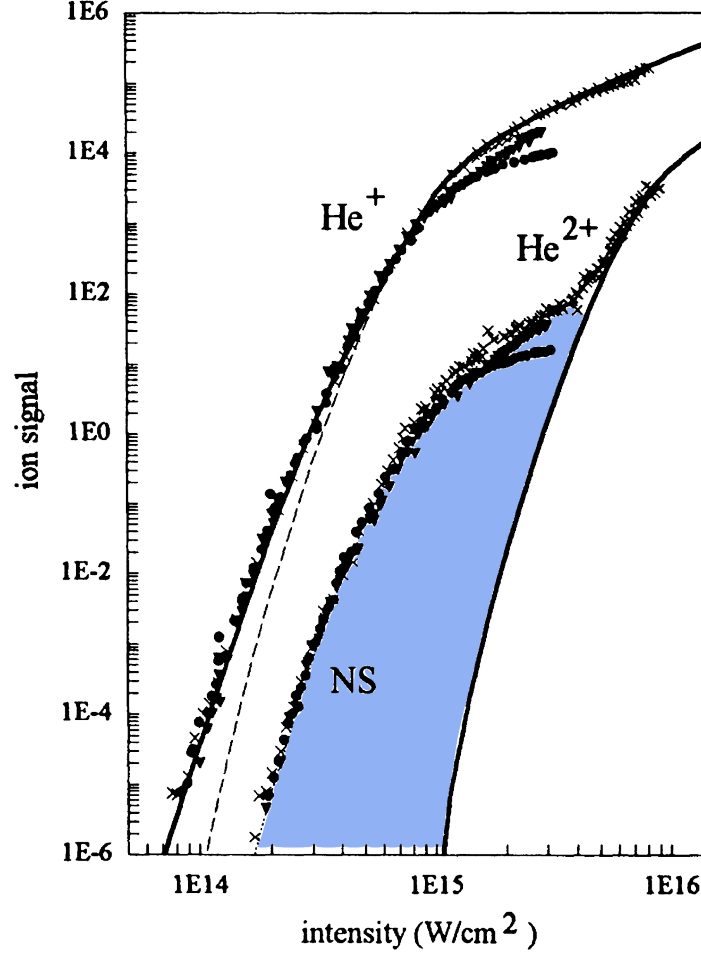


Figure 2.11: Double ionization of helium. The dotted line represents the ADK rate calculated for single ionization, while the solid lines are the TDSE-SAE numerical calculations. The blue shaded area represents the inelastic $e, 2e$ enhancement. Adapted from [28].

Corkum [6] proposed that when the tunnel-ionized electron returns to the core, it can ionize the second electron (e - $2e$ process), a phenomenon that is known as inelastic scattering. Therefore, at the time of rescattering, the first electron must possess sufficient energy ($\geq 54.4\text{eV}$) to liberate the second electron. This interaction is typically modeled using the Lotz ionization cross-section. Chaloupka et al. [78] has demonstrated detailed electron-ion

coincidence measurements for understanding of this process. The dynamics involved are complex due to significant electron correlations, to the extent that even if the returning electron has insufficient energy to excite the ion, the process can still happen. Also, the ADK model significantly underestimates the ionization rate when the Keldysh parameter is approximately 1.

Chapter 3

Experimental Setup

Within our research team, a significant area of exploration is the future utilization of pump-probe studies using the LIED technique. One of my primary goals was to construct a state-of-the-art, double-sided time of flight (D-TOF) setup dedicated to LIED. While sharing common features with standard TOF setups, which provide excellent energy resolution and a dynamic range of 6-7 orders of magnitude, our D-TOF setup stands out due to the inclusion of two home-built multi-anode microchannel plate (MCP)-based detectors. These detectors significantly reduce data collection time by an order of magnitude.

This setup was bench-tested with our ultrashort pulse 3 kHz laser source, FLAME, and performed as designed. The fully operational D-TOF is now integrated with our high-speed Yb-based 100 kHz repetition rate laser system (Tangor 300 Amplitude laser) operating at 1 μm . Preliminary data collection has shown that the combination of D-TOF and Tangor 300 reduces data collection time by three orders of magnitude as compared to 1 kHz laser sources and single anode detectors. Prior to integrating the D-TOF with Tangor 300, the DAQ system was thoroughly tested to ensure that the electronics could handle the fast rate.

While developing the D-TOF, I had the rewarding opportunity to collaborate with DiMauro-Agostini group at Ohio State University (OSU). There, we utilized a TOF setup integrated with a 1 kHz CPA-pumped 3-4 μm optical parametric amplifier (OPA) laser sys-

tem, favorable for LIED, to undertake the first LIED study of isomers and study subtle molecular differences.

In this chapter, I will provide comprehensive details about the CPA laser systems used in my studies. Additionally, I will describe the D-TOF experimental setup designed, built, tested, and deployed at the James R. McDonald laboratory. This includes an overview of the vacuum components, the pumps working in tandem with the D-TOF, the methodologies for venting and initiating the vacuum process, the design of the detector spectrometers and the results obtained, the electronics, the Data Acquisition (DAQ) system, the 3 kHz laser system, the Yb-based 100 kHz laser source, the 1 kHz laser system used at OSU, the OPA system, and the TOF setup at OSU.

3.1 Laser Sources

The first laser was demonstrated in 1960 [2]. Soon after, the study of intense laser physics made significant progress. The effort to make laser pulses shorter and stronger led to new methods like Q-switching [15], modelocking [79], and CPA [3]. Figure 3.1 represent a historical overview of this journey .

This section will outline the laser systems that have been key to my experiments. It will detail the Ti:Sapphire CPA system, notable for its 800 nm wavelength operation and its role in powering the OPA systems.

3.1.1 Generation of Intense, Ultrafast Laser Pulses

Soon after Maiman’s pioneering laser [2] in 1960, Hellwarth and McClung presented the generation of laser pulses via Q-switching [15] in 1961, when they used a Kerr cell as an optical shutter along with a ruby rod to produce 300 kW peak power laser with pulse duration of 0.12 μ s and repetition rate of 100 kHz. Q-switching is a technique to produce brief laser light pulses by periodically manipulating the laser’s energy losses. The Q factor

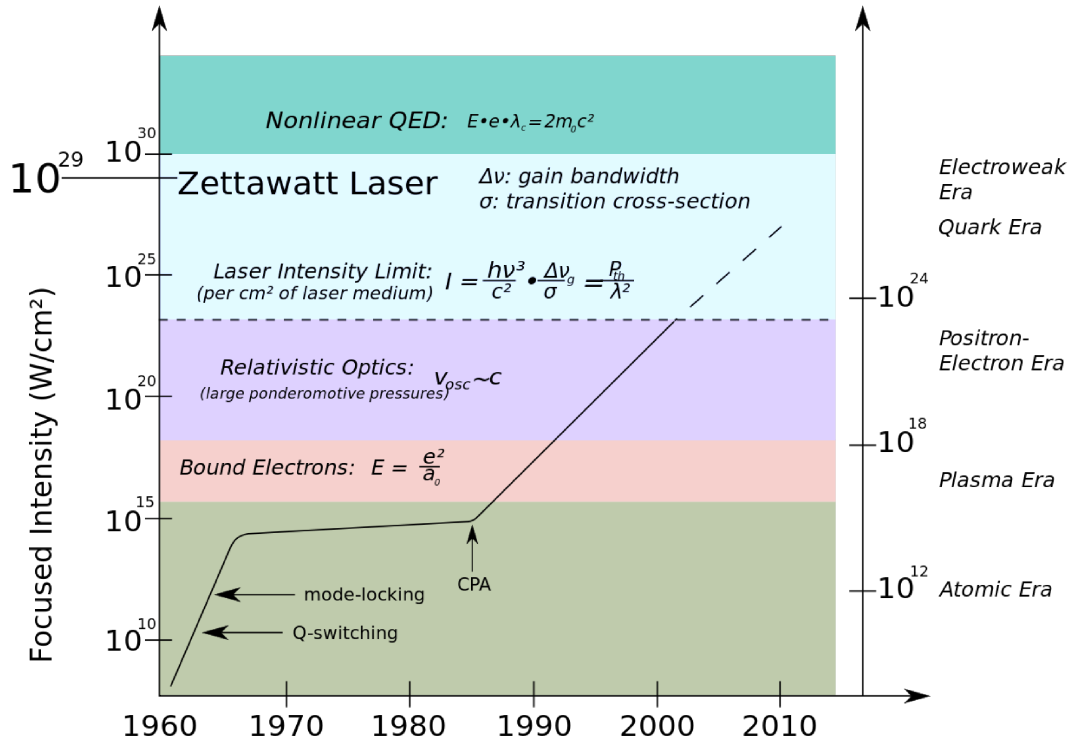


Figure 3.1: Maximum laser intensity over time since the first laser in 1960. The invention of CPA has been a fundamental breakthrough, allowing for a dramatic increase in laser peak intensities, achieving levels previously unattainable. Adapted from [80].

(quality factor) is a measure of a laser cavity's capacity to store electromagnetic energy. The higher Q-factor results in shorter pulses. Modulating the Q factor can be achieved by placing an optical switch within the laser cavity. Deactivating the switch causes energy accumulation in the gain medium. While the switch is on, stimulated emission continues to be supplied to the gain medium and results in a compact laser pulse. Q-switched lasers are routinely employed to generate ns pulse duration.

The next success in generating short laser pulses was achieved with the advent of mode-locking [79], a technique that enabled the generation of laser pulses as short as a few femtoseconds. modelocking essentially provides the same cavity round trip times for all frequencies, which, when they are perfectly modelocked, one can produce ultra-short pulses. modelocking process causes the longitudinal modes to interfere destructively throughout

most of the cavity, with the exception of specific regions where constructive interference occurs that results in a short pulse. To generate ultrashort laser pulses, the gain medium plays an important role. The gain medium's bandwidth must be substantial enough to accommodate the desired pulse duration. Time-bandwidth product is a principle used to check this which shows a pulse's temporal width Δt , to its corresponding frequency bandwidth $\Delta\nu$, with the Gaussian pulse serving as a common model. The relationship between Δt and $\Delta\nu$ is expressed by the inequality $\Delta\nu\Delta t \geq 0.44$ (only true for Gaussian pulse temporal profiles), showing the bandwidth necessary for a pulse of specific duration. For example, consider the Ti:Sapphire, a solid-state medium used for generating few femtosecond laser pulses. A typical Ti:Sapphire oscillator has a cavity length on the order of 1.9 meters, resulting in a mode spacing around 80 MHz. The medium's bandwidth is greater than 100 THz and centered near the 800 nm, which gives over a million longitudinal modes. Proper modelocking and dispersion management within such an oscillator can result in pulses as short as 5 femtoseconds. However, these pulses have low energies on the order of nJ. Despite this, modelocking is the optimal method for producing short pulses. To use these pulses for intense laser fields, amplification is required.

In 1985, a technique called chirped pulse amplification (CPA) as shown in Figure 3.2 was developed by Strickland and Mourou [3], which revolutionized the amplification of ultrashort laser pulses. Strickland and Mourou recieved the Nobel prize in 2018 for this technique.

For many experiments mJ-level pulses were required at the time, not nJ. This requires the drop of repetition rates, as 80 MHz repetition rates at mJ pulses would require Megawatt-class lasers.

In CPA, the pulses are first stretched temporally. Figure 3.3 shows a reflective, Martínez-type stretcher [81]. As shown in Figure 3.3, the ultrashort pulse's colors or frequencies are dispersed in time known as positive group delay dispersion (GDD) when passing through the stretcher. This causes red colors to travel faster and blue colors to travel slower. Thus the spectrum's red part precedes the blue, stretching the final pulse while reducing peak

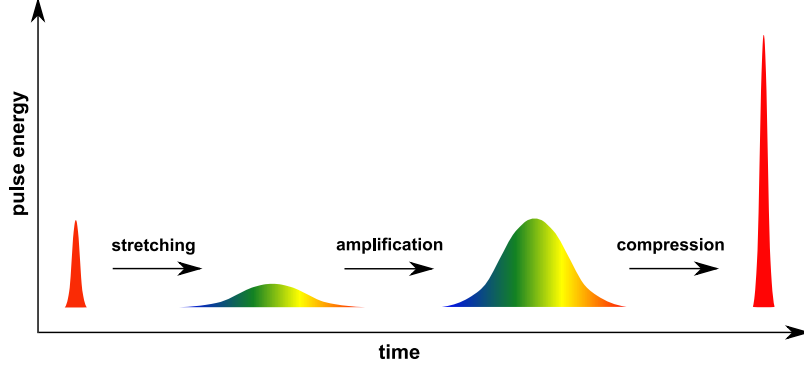


Figure 3.2: Schematic representation of a CPA system. Ultrashort laser pulses undergo temporal stretching to decrease the peak power during amplification. Next they are amplified. Finally, the pulses are compressed.

power. G1 and G2 represent diffraction gratings, L1 and L2 are convex lenses, RR is a retroreflector, and M shows the output mirror. The critical stretcher parameters, l for the stretcher length and i for the input angle, determine the stretching factor. This process decreases the laser's peak power to prevent any potential damage during amplification. For Ti:Sapphire lasers, the technique can stretch a pulse from femtoseconds to hundreds of picoseconds. Post-stretching, the laser pulse for our case undergoes two amplification

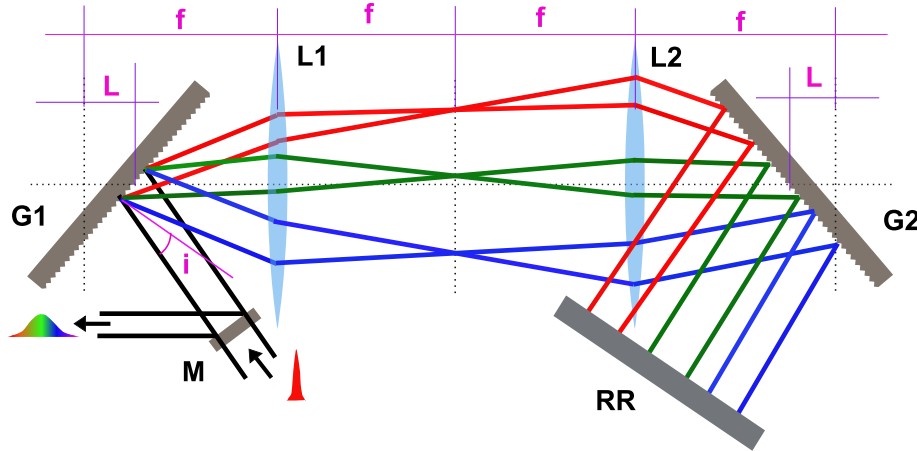


Figure 3.3: The Stretcher: The frequencies within an ultrashort pulse injected into the stretcher are spatially dispersed, leading to a stretched pulse with a much lower peak power.

stages and please notice that not all CPA laser systems have two amplification stages. The

primary stage, could be a regenerative amplifier or simply the regen, attenuates the 80 MHz pulse train emerging from the stretcher to 1 kHz frequency through a Pockels cell. The Pockels cell is an electro optical modulator (EOM) that works like a very fast optical switch. Combination of the Pockels cell and a half wave plate manages the polarization of the laser pulse such that it permits a singular pulse from every 80,000 to buildup of the regen amplifier. This selection is crucial for increasing the energy per pulse. For instance, if there is an output average power of 8 W at a pulse repetition rate of 80 MHz, the energy per pulse would be 1 μ J. However, at a repetition rate of 1 kHz, the energy per pulse would increase to 8 mJ. References for this methodology can be found in [82], [23], and [22]. when the pulse is inside the regenerative cavity, it repeatedly goes through a Ti:Sapphire crystal and is overlapped with a high power Q-switched green pump laser. The pulse energy is then amplified by 6 orders of magnitude from nJ into mJ . The second stage of amplification is similar except that there is no cavity. This time the amplified seed is sent to a Ti:Sapphire single pass linear overlapped with a Q-switched green pump and further amplification in pulse energy happens just by few factors. The advantage of this amplification configuration that first the seed is amplified by the regen amplifier and next a single pass or mutlipass amplifier is due to the fact that being a cavity, the regen amplifiers provide high gain for low-energy seed pulses, significantly increasing their energy before they enter the single pass amplifier. This pre-amplification reduces the load on the single pass amplifier to reach the final desired pulse energy. Additionally, regen amplifiers improve pulse quality and stability by cleaning up the pulse and enhancing its spatial and temporal profiles, ensuring that the single pass amplifier receives a more stable and well-defined pulse. Following amplification, the pulse is temporally compressed to tens of fs as shown in Figure 3.2.

This process is performed using a compressor, which introduces negative GDD to the colors and shortens the pulse. By carefully adjusting the input angle i and the compressor length L , one can control the negative GDD to achieve the desired pulse compression, effectively reversing the initial stretching process.

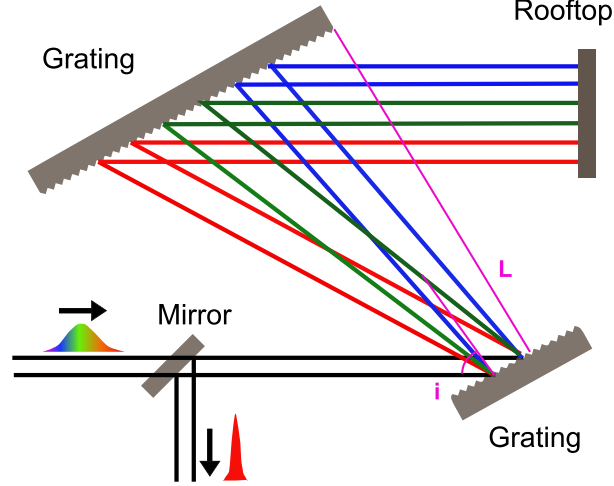


Figure 3.4: The Compressor: Essentially a stretcher in reverse, it is comprised of two gratings and a rooftop retro reflector. The input angle i and the compressor length L determines the negative GDD.

3.1.2 The Ti:Sapphire Laser System Used at OSU

One of the main laser systems that was utilized for the experiments presented in this dissertation consists of two primary components: a commercial $0.8 \mu m$ Ti:Sapphire laser system (Spitfire ACE PA, Spectra Physics) and a custom-built optical parametric amplifier which adjusts the output wavelength of the Ti:Sapphire laser to a tunable range between $3\text{-}4 \mu m$.

The output parameters of the Ti:Sapphire system are illustrated in Table 3.1.

Parameter	Value
Pulse Energy	12 mJ
Pulse Duration (FWHM)	80 fs
Central Wavelength	800 nm
$1/e^2$ Beam Diameter	11.5 mm
Repetition Rate	1 kHz

Table 3.1: Output parameters of the Ti:Sapphire system

The initial laser pulse in this setup comes from a commercially available Ti:Sapphire oscillator system named Spectra Physics Mai Tai. This oscillator generates a pulse trains 80 MHz repetition rate approximately 10 nJ of energy and pulse duration of about 50 fs.

The corresponding bandwidth for such a pulse duration is 22 nm. Next, the pulse goes to the CPA system, where it is stretched to 200 ps. Post-stretching, the laser pulse proceeds to two amplification stages. First, it's amplified by a 24 mJ, 527 nm Q-switched Spectra Physics pump from 10 nJ to 8 mJ with repetition rate of 1 kHz. Thermal stability of the crystal is maintained at -15°C via a thermal electric cooler to prevent thermal lensing.

Next amplification is done with a 25 mJ, 527 nm pump from the same Spectra Physics with the crystal held at -15°C. Post single-pass amplification, pulse energy rises to approximately 15 mJ.

After the amplification processes, the laser pulse duration is compressed to 80 fs. In the configuration of the compressor as shown in 3.4, two sets of Spectrogon gratings are employed in this specific laser, with dimensions of 64 mm by 64 mm and 140 mm by 120 mm, and a groove density of 1500 grooves per millimeter. Adjusting the compressor parameters such as the incident angle i and grating separation L , allows for precise control over the pulse duration.

3.1.3 Mid-infrared Optical Parametric Amplifier Used at OSU

Optical parametric amplifiers (OPAs) are used to produce laser light with variable wavelengths. Experimentally, this was first achieved by Franken et al. in 1961 [83] where they focused a pulsed ruby laser operating at 694 nm into a quartz crystal, producing a wavelength of 347 nm. An interesting anecdote about this publication is that the dense, small image at 347 nm was mistaken for a smudge by the editor, due to the black-and-white format of the publications at the time, and was consequently removed from the final published paper, as shown in Figure 3.5. They mentioned a brief theory of OPA in their work, but the theoretical aspects of the OPAs were demonstrated through the works of [84, 85] afterwards.

The mechanism happens when intense laser fields interact with a dielectric nonlinear material such as beta barium borate (BBO), leading to creation of new frequency components that are absent in the original incident radiation field. To have a stable OPA, a stable pump

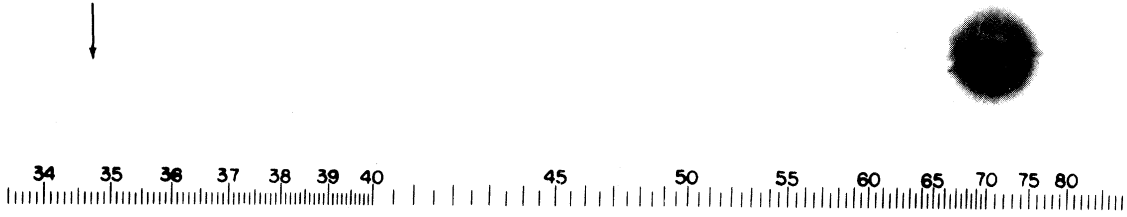


Figure 3.5: First indication of the OPA. The wavelength scale is in units of 100 Å. The arrow at 3472 Å indicates the small but dense image produced by the second harmonic. Reproduced from [83].

laser, typically a Ti:Sapphire laser for mid-infrared region is utilized. BBO crystal-based OPAs are prominent for their high output pulse energy (1 mJ). The maximum wavelength for these BBO crystals is around $2.5 \mu\text{m}$ due to their absorption properties. Alternative crystals that can achieve wavelengths greater than $3 \mu\text{m}$ include KTiOAsO_4 (KTA), KTiOPO_4 (KTP), and KNbO_3 . Here I describe custom-built KTA crystal-based OPA designed at OSU to generate submillijoule laser pulses between 3 to $4 \mu\text{m}$ favorable for LIED.

Basic Principles of Optical Parametric Amplification

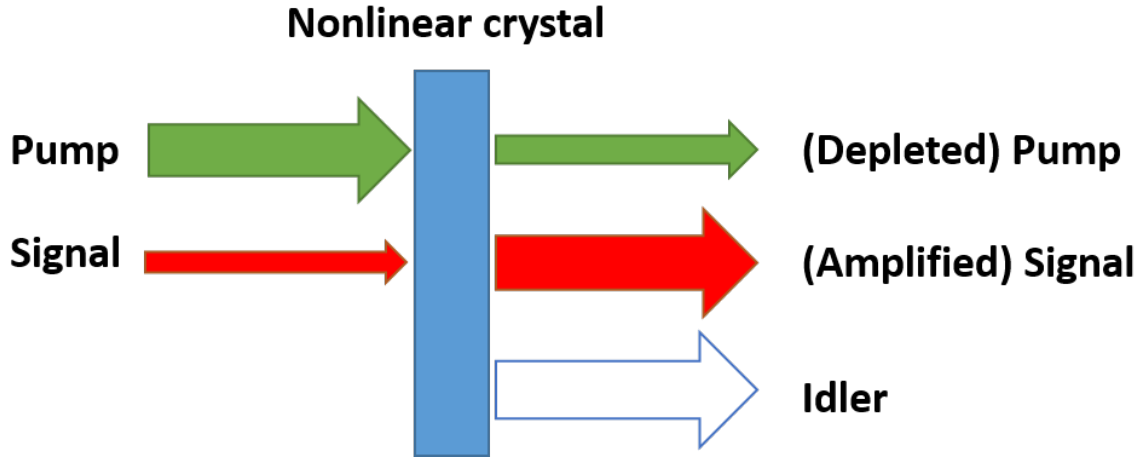


Figure 3.6: Schematic diagram of optical parametric amplification.

OPA involves the interaction of two laser beams within a nonlinear crystal to generate a third beam, known as the idler as shown in Figure 3.6. The pump beam, with higher energy,

transfers energy to the signal beam, resulting in the signal's amplification and the creation of the idler beam. OPA and difference frequency generation (DFG) are similar nonlinear processes. However, OPA typically refers to the scenario where the lower frequency beam is significantly weaker than the higher frequency beam. This process follows the conservation of energy, expressed as:

$$\hbar\omega_p = \hbar\omega_s + \hbar\omega_i \quad (3.1)$$

where ω_p is the pump frequency, ω_s is the signal frequency, and ω_i is the idler frequency. Following that, the relationship in wavelength between the pump (λ_p), signal (λ_s), and idler (λ_i) wavelengths in an OPA system is given by:

$$\frac{1}{\lambda_p} = \frac{1}{\lambda_s} + \frac{1}{\lambda_i} \quad (3.2)$$

Phase matching is also a critical condition for the efficient interaction of light waves in nonlinear optical processes such as OPA. It involves the alignment of wavevectors of the pump ($\mathbf{k}_p$), signal ($\mathbf{k}_s$), and idler ($\mathbf{k}_i$) waves according to the equation:

$$\hbar\vec{\mathbf{k}}_p = \hbar\vec{\mathbf{k}}_s + \hbar\vec{\mathbf{k}}_i \quad (3.3)$$

This condition ensures momentum conservation during the frequency conversion process. The wavevector $\vec{\mathbf{k}}$ is related to the refractive index $n(\omega)$ of the medium by the equation:

$$k = n(\omega)\frac{\omega}{c} \quad (3.4)$$

In the case of collinear propagation, the phase matching condition can be expressed as:

$$n(\omega_p)\omega_p = n(\omega_s)\omega_s + n(\omega_i)\omega_i \quad (3.5)$$

Phase matching - getting all the light waves to move together — is vital, especially when

changing the color of the laser light. This coordination largely depends on the type of crystal through which the light passes. Each crystal interacts with light frequencies differently, which is why we need to select the right crystal for the desired color range.

All nonlinear crystals such as KTA are birefringence materials. This means that they have two different indices of refraction based on the light wave's polarization passing through them. To achieve phase matching in KTA, we align the pump (the light that initiates the process) and idler (the newly created light color) beam polarization along the extraordinary axis (e). Meanwhile, the signal beam polarization (the light we want to strengthen) aligns with the ordinary axis (o). This arrangement is termed type-IIA phase matching and is essential for our experiments with KTA crystals to be successful. Equation 3.5 demonstrates that by adjusting the crystal tilt, we can achieve phase matching across various frequencies.

An integral part of an OPA setup, which actually doesn't deal with amplifying the light itself, is starting the process. This is done by generating an initial "seed" beam -which will be used as the signal later on, at a different frequency from the pump beam. To supply both pump and seed beams using a single laser, the most common method is white light continuum generation [86]. White light generation (WLG) was demonstrated in 1970 through the work of Alfano and Shapiro where they showed that by sending a narrow green beam at 532 nm through borosilicate glass, a broad spectrum of light could be generated, spanning 4000 to 7000 Å from blue to red. This was the result of nonlinear optical effects, primarily self-phase modulation (SPM) caused by self focusing on solids and liquids, and was termed WLG or later as "Supercontinuum" (SC) which now spans from UV to MIR wavelengths.

Here, WLG is achieved by focusing a femtosecond few μJ laser beam onto a transparent medium sapphire window [87]. Afterwards, a particular spectral component of interest is filtered and amplified in the nonlinear crystal [88].

Practical Aspects of Optical Amplification

When using lasers to amplify light in materials, we need to be careful about two main things: how strong the laser is and how long the light travels inside the amplifying material. We want a strong laser to get more amplified light, but not so strong that it damages the material. For example, for the case of KTA crystal we can only handle about 200 GW/cm^2 [89] before getting damaged.

To get the most amplification, we also want the light to travel through a long piece of this crystal. But there's a catch. Material dispersion affects the interaction length, as a group velocity mismatch (GVM) between pulses of different frequencies can occur, causing them to temporally separate and reduce amplification. This mismatch can cause the amplification to weaken or stop altogether. Phase matching bandwidth also plays a role, limiting the effective crystal length for amplification, particularly because a laser pulse spectrum has only its central frequencies satisfying the phase matching condition.

Given that the previous conditions are satisfied, 800 nm beam with an intensity of 200 GW/cm^2 is overlapped in KTA with the $1 \mu\text{m}$ signal beam produced from WLG is amplified by a factor of 200. Next, to further amplify the signal, it is redirected to a second KTA crystal. This process is iterated through several crystal stages as shown in Figure 3.7.

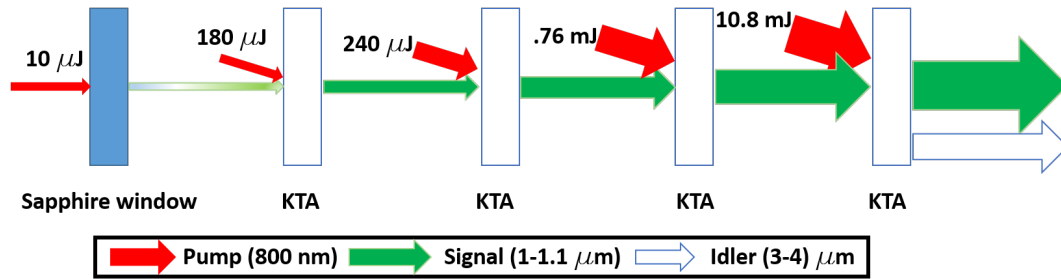


Figure 3.7: Schematic of the mid-IR OPA at OSU

After the final stage of amplification, we're left with an outcome of a 0.75-0.4 mJ mid-infrared beam, ranging from 3-4 μm with a pulse duration of 100 fs. For the case of the 3 μm which is the wavelength of interest for us, the output pulse energy is 0.75 mJ.

3.1.4 The Ti:Sapphire Laser System Used at KSU

In October 2020, our laboratory took a significant leap forward with the acquiring of the femtosecond laser for multicolor experiments (FLAME) laser system from Coherent (Legend Elite Duo). FLAME is a fully integrated, turnkey system that represents the culmination of well-established laser technology. Specifically customized for our laboratory's research purposes, FLAME is designed to facilitate a range of pump-probe experiments. FLAME was utilized at the time for bench-testing my apparatus at JRML.

The output parameters of the Ti:Sapphire system are illustrated in Table 3.2.

Parameter	Value
Total power	15 W
Pulse Energy	5 mJ
Pulse Duration (FWHM)	30 fs
Central Wavelength	800 nm
$1/e^2$ Beam Diameter	11 mm
Repetition Rate	3 kHz

Table 3.2: Output parameters of the FLAME Ti:Sapphire system

The initial laser pulse in this setup comes from a commercially available Ti:Sapphire oscillator system named Coherent Vitara. The oscillator works via an Optically pumped semiconductor laser (OPSL) Verdi G-series green pump 532 nm working at continuous wavelength (CW) mode with operating output of 5 W. This oscillator works based on the Kerr lens modlocking technique and it produces a pulse train at an 80 MHz frequency with output power of 580 mW which makes energy of each pulse approximately 7.25 nJ. Modelocking bandwidth of the oscillator could vary between 100-125 nm based on the model used which makes the pulse duration less than 15 fs. Next, the beam is directed into a special spatial filter (SSF). The SSF routes the beam from the oscillator through a notch-filter which reduces the intensity around 800nm and creates two peaks on either side with valley at 800nm. This is to make use of the Ti:Sapphire crystal gain profile and create a flat spectrum at the amplifier output which is known as gain narrowing. Then, the pulse proceeds to the CPA system, where the pulses are stretched temporally beyond 200 ps.

Post-stretching, the laser pulse proceeds to two amplification stages. The primary stage, called the Legend-Elite regen, drops the 80 MHz pulse train emerging from the stretcher using a Signal Delay generator Elite (SDG-Elite) to 3 kHz frequency via a Pockels cell. the amplification in the regen happens using a Revelation diode-pumped, intra-cavity doubled, Q-switched Nd:YLF laser of 527nm green pump laser set at working current of 18.5 A with output power of roughly 36 W which is overlapped with the seed. The pulse is channeled into the regen cavity, repeatedly in a Ti:Sapphire crystal. Pumping is facilitated by a Revelation diode-pumped, intra-cavity doubled, Q-switched Nd:YLF laser of 527nm green pump set at working current of 18.5 A with output power of roughly 36 W. Thermal stability of the crystal is maintained at -11.7°C via a thermal electric cooler to prevent thermal lensing.

Second stage amplification is done in a Ti:Sapphire single-pass amplifier (SPA). Here, a 37.37 W pump power with current of 19.2 A, 527 nm pump from the same coherent pump laser is employed, with the crystal held at -9.6°C.

Lastly, the laser pulses split into two each with its own compressor, which one is an internal compressor (7.5 W- 30 fs) used to compress the pulse for a commercial high energy traveling-wave optical parametric amplifier of white light continuum (HE-TOPAS), and other half will be sent to an external compressor (7.5- 30 fs) used as an 800 nm source.

3.1.5 The Yb:YAG 100 kHz High Intensity Laser Source

The initial laser pulse in this setup comes from a modelocked Yb:YAG fiber laser oscillator with repetition rate of 40 MHz and pulse energies of few nanojoules which is pumped with fiber coupled diode lasers at 940 nm and lases at 1030 nm. Yb-doped laser crystals, with a very low quantum defect of around 9% and the relatively high thermal conductivity of the yttrium aluminium garnet (YAG) host (14 W/mK), have become the preferred material for high peak and average power lasers. Next, the laser light goes into a pulse picker which enables variation of the repetition rates up to 4 MHz while maintaining the same average power. Next, the beam is temporally stretched with a fiber Bragg grating (FBG) to hundreds

of ps and subsequently amplified in a fiber amplifier followed by Yb rod amplifiers (pre-Amp 2 and 3) to pulse energies of hundreds of μJ . After beam expansion through telescopes, it is further amplified in the main InnoSlab amplifier as detailed in [90]. This main amplifier is optimized for 300W of average power at repetition rate of 100kHz. Finally, the pulses are compressed with a grating compressor down to 450 fs.

3.1.6 TOF Spectrometer Used at OSU

Briefly, my research at OSU involved collecting the PES at different laser polarization angles and for that we used a TOF setup. TOF spectrometer situated in an ultra-high vacuum (UHV) chamber, is sustained by robust turbomolecular pumps a 345 liter/sec pump (Leybold Turbovac TMP361) and a 360 liter/sec pump (Leybold Turbovac 360 CSVG). The chamber's background pressure is approximately 10^{-9} torr, as shown in Figure 3.8. The laser, denoted as "L", goes through a lens and an input window "IW" then in the chamber. The focal point of the laser in the chamber makes the interaction region, where ionization events occur. The spectrometer is capable of detecting both ions and electrons, with the detection methodologies shown later on in this section. The objective is to measure the TOF of these particles, reflecting their drift from the ionization point to the detector.

The experimental setup includes shielded tubes, referred to as Mu-Metal "MM" to prevent the external magnetic fields modifying the angular distribution of the electrons while the TOF is detecting the electrons, and an electrostatically shielded box, the "Faraday cage" or "FC", to avoid any external magnetic field on the electrons and ensure precision in the measurements.

To introduce experimental targets to the area of interaction, for gaseous targets at ambient conditions ranging between 10^{-9} and 10^{-4} torr, a connection is established to a gas reservoir regulated by a valve for precise flow control, added by turbomolecular pumps to maintain constant gas conditions suitable for experiment at pressure of interest. We operate within a gas pressure range, constrained by the chamber's background pressure at the lower

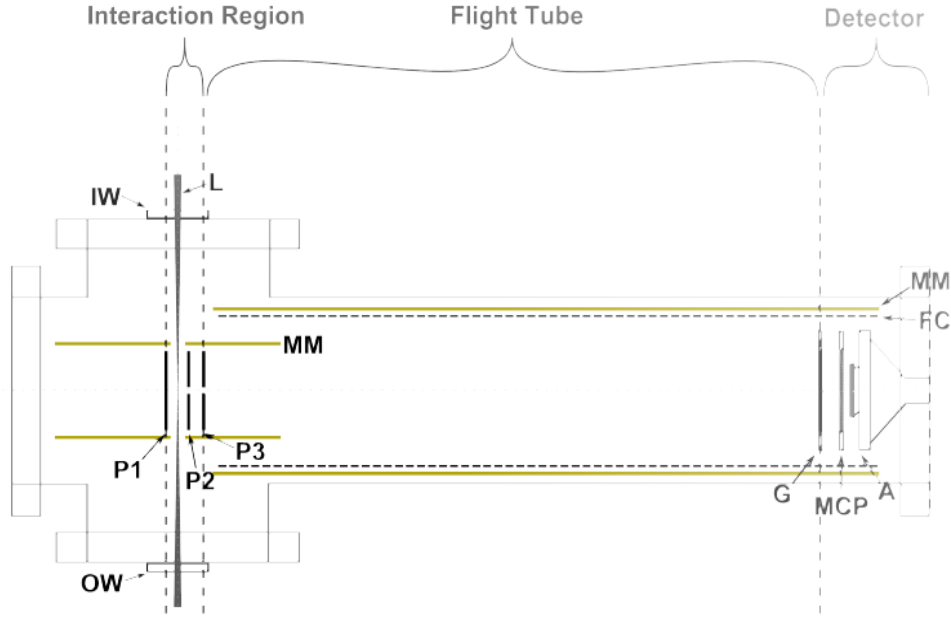


Figure 3.8: Schematic diagram of TOF spectrometer (top view). L: laser; IW: input window; WW: output window; P1,P2,P3: Electrostatic field plates for accelerating ions; MM: mu-metal; FC: Faraday cage; G: grounded grid; MCP: multichannel plates; A: collecting anode. Reproduced from [91]

end and by detector saturation at the upper end.

MCP Detector Used at OSU

The MCP detector is designed to detect both electrons and ions. It is made of multitude of parallel microchannels, each coated with a conductive material, which amplify the incoming particles' signal. The amplification occurs as the striking particle induces secondary emissions, enhancing the original signal significantly.

The rapid detection capability of the MCP detector, with a response time under one nanosecond, makes it an ideal choice for the experiment. Details regarding the specific MCP detector model can be found in Figure 3.9 of this section.

The detector, made by R. M. Jordan Company, is featuring plates with microchannels that are 25 micrometers in diameter. The channels' length-to-diameter ratio is 40:1, and their orientation at 8 degrees to the plate surface optimizes particle capture. The double

stack (Chevron) configuration of the plates increases the gain of the incident electron by 6 orders of magnitude as shown in Figure 3.17.

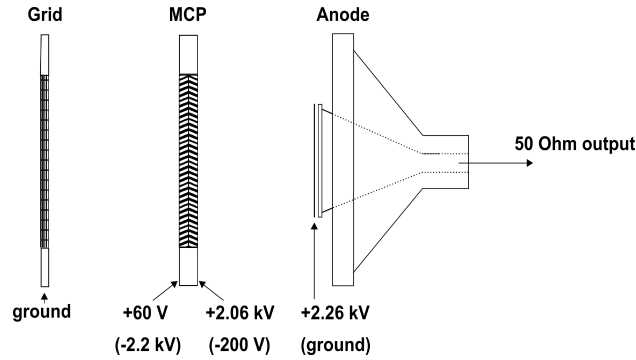


Figure 3.9: Schematic diagram of the MCP detector. The diagram shows the electrical setup for both electron and ion detection modes. Voltages are applied as follows: Ground at 0 V, Grid at +60 V, Front MCP at +2.06 kV, Back MCP at +2.26 kV, and Anode at ground potential. Reproduced from [91].

A stainless steel grid shields the detector from external magnetic and electric fields, maintaining the integrity of the detection process. The grid aperture measures 1.750 inches. A voltage of magnitude of 2 kV is applied to Chevron stack for both electron and ion detection. The MCP detector has impedance-matched MCP stack to ensure uniform gain across the MCP, approximately 10^5 times. In electron mode, a 60 V potential difference propels the electrons towards the detector, enhancing detection efficiency. For ion mode, pre-accelerated ions are detected by amplifying the electronic signal at the detector's end. A gold-coated Kapton foil is utilized to decouple the high voltage from the signal pulse, minimizing impedance with a 50Ω impedance matched anode. Reflections along the high voltage lines are removed by installing three low pass RC filters. Separate Bertan power supplies provide the necessary voltages, set to 2.06 kV for electron mode and -2.20 kV for ion mode, as indicated in Figure 3.9.

Data Acquisition System

The data collection system acts like a precise “stopwatch” that tracks time intervals and manages data storage and transfer. This stopwatch is a high-precision time to digital converter (TDC), specifically a LeCroy TDC4208 or 2228A model. It begins timing when it receives a START signal and stops with a STOP signal. The timing resolution can be adjusted between 50 ps, 100 ps, 285 ps, or 1 ns, depending on the TDC model. Ionization events are recorded when the laser pulse hits an InGAS photodiode, triggering the timing mechanism.

The timing mechanism within the setup inherently includes a time offset when measuring the TOF which is coming from the cables and electronics and it can be precisely determined. For timing initiation, an InGaAs photodiode is positioned to intercept a fraction of the laser beam redirected by a CaF_2 window. The signal from the photodiode is amplified (Ortec 574) and then shaped by a constant-fraction discriminator (Ortec 574) to produce a standardized negative pulse nuclear instrument module (NIM) signal, marking the START for the TDC.

The STOP pulse is selected from the detector’s signal, which is initially amplified (Ortec VT120C) and then refined by a picosecond-precision timing discriminator (Ortec 9307). This final pulse is then fed to the TDC, ensuring accurate TOF measurements for each laser pulse, encompassing multiple parameters.

For every laser pulse, the system has the capacity to detect several particles, which translates into numerous STOP signals. The TDC has a limit of recording eight STOP signals for each laser shot. The TDC’s operation necessitates two extra NIM signals in addition to the START and STOP signals. These are known as the “end-of-window” (EOW) and “clear” (CLR) pulses. The sequence in which the TDC registers the signals for every laser shot is as follows: START, up to eight STOPs, then EOW, and finally CLR. Upon receiving the EOW signal, the TDC stops to read any further STOP signals. It then proceeds to transfer the recorded TOF data to a controller (CAMAC CC32). Then, the CLR pulse erases all recorded data, preparing the TDC for the next sequence of START and STOP

signals corresponding to the next laser shot. These EOW and CLR pulses are produced by a delay/pulse generator (Stanford DG535), which is in sync with the laser’s 1kHz operational frequency.

3.1.7 Double-sided Time of Flight Setup at KSU

The TOF spectrometer provides high energy resolutions and a broad dynamic range between 5-7 orders of magnitude. For example, $\frac{\Delta E}{E} = 0.5\%$ for a TOF of length 0.5 meter and electron energy of 500 eV given that the time bin is 100 ps. However, its detection capabilities are limited to electrons within a narrow solid angle, typically less than 5° . To observe electrons ejected at varying angles relative to the laser’s polarization, it is necessary to rotate the laser polarization in relation to the TOF axis. The time for collecting enough statistics to make a histogram for one photoelectron angle could be done faster if the a 100 kHz repetition rate laser and a multianode detector is used.

For that, the LIED dedicated D-TOF system is designed to speed up the measurement of PADs to just a few minutes for each angle, especially when used with 100 kHz high-repetition laser sources. This efficiency is due to its two advanced, in-house developed MCP-based detectors located on opposite sides. Moreover, the D-TOF is versatile, working with both electrons and ions, allowing it to collect more comprehensive data. This cutting-edge TOF system is the latest addition to the JRML. It’s tailored for rapid LIED studies and its portable design means it can be used with various laser setups within the facility.

This section offers a comprehensive overview of the D-TOF’s structural design, its assembly process, operational guidelines, and user instructions.

D-TOF’s Outer Design

The D-TOF apparatus is mounted on a portable cart measuring 4 by 2 feet. This cart is equipped with wheels that have a lockable stand to ensure stability during experiments. It is important to ensure the setup is aligned with the optical table before engaging the stands.

Beneath the D-TOF structure, there are standard 19-inch racks used for installing various equipment. The D-TOF unit has a length of one meter and is constructed using stainless steel flanges with an 8-inch outer diameter and a 6-inch inner diameter, as illustrated in Figure 3.10. There is a 1-inch-diameter calcium fluoride (CaF_2) input window with 1 mm thickness from Newlight Photonics recessed 2.93 inches from the edge, allowing for the attachment of lenses with short focal lengths, such as 100 mm. Consequently, the space between the CaF_2 window and the central point of interaction measures 3.5 inches. The uncoated CaF_2 has the average light transmission 94% and minimal chromatic aberration with Abbe number of 94 at 800 nm. Additionally, it provides the group velocity dispersion (GVD) of $27.8 \text{ fs}^2/\text{mm}$ at 800 nm [92]. The D-TOF system is supported by four brackets, which link it securely to the mobile cart.

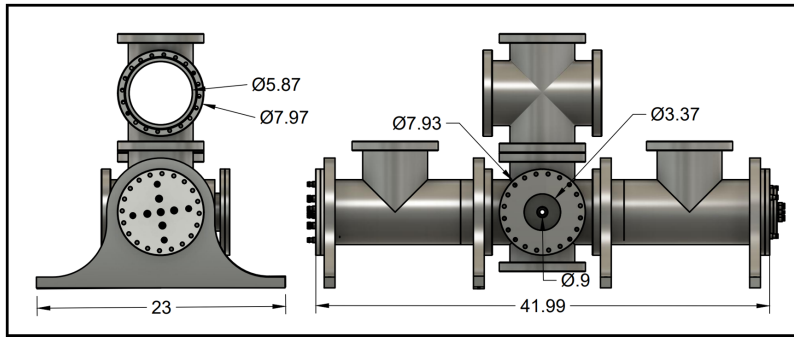


Figure 3.10: D-TOF dimensions: dimensions are in inches

For precision in experiments, it's crucial to align the laser beam meticulously from the optical table to the exact center of interaction within the D-TOF apparatus. Misalignment can cause the beam to strike the gold-plated mu-metal tube in the D-TOF, risking damage to the apparatus and creating unwanted electron ionization on the gold surface, which appears as noise in the PES being measured. To avoid these issues, the alignment process begins with a Helium-Neon (HeNe JDS uniphase Model 1508P-0) laser, following specific alignment protocols. Here is the alignment procedure:

1. Position a HeNe laser on the optical bench, aligning it with a minute circular aperture

approximately a few hundred micrometers in diameter to generate precise, symmetrical Airy patterns.

2. Guide the Airy patterns towards the last set of flat mirrors on the bench, ensuring they are then projected through the CaF_2 window.
3. Confirm the diffraction pattern is perfectly symmetrical upon hitting the wall after exiting through the output window. The symmetry of the pattern signifies accurate beam alignment at the interaction center.
4. Place two irises on the mounts flanking the D-TOF setup and another two on the bench post the last mirrors.
5. Install the lens (LA1433-B f=150 mm plano convex Thorlabs) on the xyz translational stage (Newport) with the CaF_2 window in its line of sight.
6. Adjust the lens's translational stage to obtain a symmetrical diffraction pattern beyond the last iris.
7. Align the lens's back reflection both vertically and horizontally to the irises on the bench by fine-tuning the lens tilt using the set screws on its mount.
8. Repeat this alignment process whenever the setup is relocated or the spectrometer is disassembled and reassembled.

When varying laser wavelengths, be weary to align the z-axis translation due to changes in the focal position. For instance, a laser beam initially at zero position with a beam waist $\omega_0 = 1$ mm and wavelength $\lambda = 0.8\mu\text{m}$ will encounter a lens with a focal length $f = 100$ mm. To find the focus position, we calculate the Rayleigh length $z_R = \frac{\pi\omega_0^2}{\lambda} = 125\pi$ cm and use the ABCD matrix for lens focusing:

$$L = \begin{bmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{bmatrix} \quad (3.6)$$

The ABCD matrix is:

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ -\frac{1}{100 \text{ mm}} & 1 \end{bmatrix} \quad (3.7)$$

The post-lens q parameter is given by:

$$q' = z' + iz'_R = \frac{Aq + B}{Cq + D} \quad (3.8)$$

Solving for q' yields:

$$q' = -f \frac{z_R^2}{f^2 + z_R^2} + i \frac{f^2 z_R}{f^2 + z_R^2} \quad (3.9)$$

For $\lambda = 0.8\mu\text{m}$, the calculated $z' = 99.93$ mm. Repeating the calculations for $\lambda = 3\mu\text{m}$, with $z_R = 33\pi$ cm, we get $z' = 99.07$ mm. Therefore, the difference in focal positions for various wavelengths necessitates slight adjustments on the z-axis translation stage.

The D-TOF Spectrometer

The details of the D-TOF spectrometer setup are depicted in Figures 3.11 and 3.12. It operates in two modes: ion mode and electron mode. For electrons, the spectrometer is functioning in a field free mode, with all the plates grounded. Since some electrons can have very low kinetic energy, they shouldn't be affected by any external electric field. Therefore, the field plates (1-6) illustrated in Figure 3.12 are made of paramagnetic molybdenum and they are sprayed by graphite to remove any patch effects. Patch effect causes a nonuniform E-field distribution on the field plates. Furthermore, any external magnetic field such as Earth's magnetic field affects the resolution. Thus, the entire spectrometer is surrounded by gold plated nonmagnetic mu-metal shields (MμShield Corporation). This assembly includes two mu-metals. The longer section, termed the long-arm mu-metal (LM), extends to 25.5 inches and has an internal diameter of 4 inches, featuring half-inch holes near its center for

laser access and gas introduction.

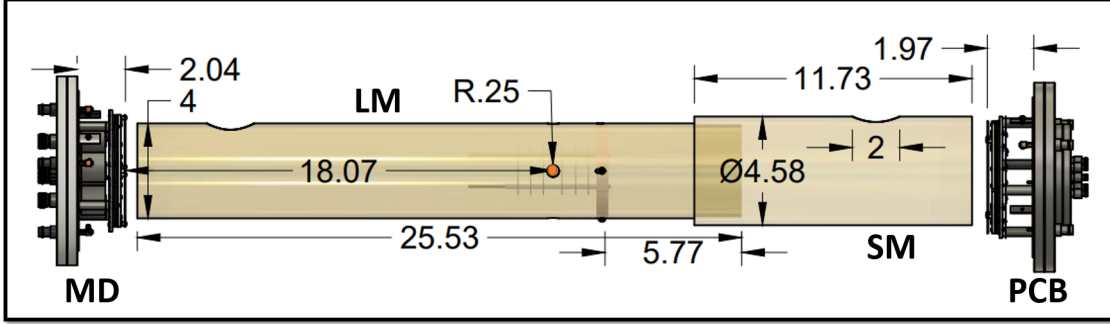


Figure 3.11: [D-TOF spectrometer for Ion and electron detection] Schematic diagram of D-TOF spectrometer (Front view). orange spot: center of interaction; MD: MCP-based multi-anode detector; LM: Long- arm mu-metal; SM: Short-arm mu-metal; PCB: MCP-based printed circuit board detector

The selection of a half-inch entry aperture for the LM is based on ensuring that the laser beam, even in the least favorable scenario, would not be obstructed at the LM's input. Let's analyze the least favorable condition to confirm whether the beam will be truncated by the LM's half-inch aperture. We'll assume a laser wavelength of $3\mu m$ and a beam quality factor (M^2) of 1.5, which is considered sub-optimal. The beam's diameter must not exceed the diameter of the 1-inch CaF_2 window, so we'll consider a large beam diameter of $D=16$ mm which satisfies the 3ω criteria [93] and it is above the typical beam diameters used in our experiments. With a $f=100$ mm focal length lens, the beam diameter at the focal point can be determined by [94]:

$$2\omega_0 = \frac{4M^2\lambda f}{\pi D} \quad (3.10)$$

Using this formula, the calculated beam diameter at the focus is $35.8\mu m$, and the corresponding Rayleigh length z_R :

$$z_R = \frac{\pi\omega_0^2}{M^2\lambda} = 224\mu m \quad (3.11)$$

With the Rayleigh length at the focus, we can compute the beam diameter two inches away from the focus, right at the LM's entry point, using:

$$\omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2} \quad (3.12)$$

The resulting beam diameter is ~ 8 mm, which is still less than the diameter of the LM's entry aperture. Thus, even in the worst case, the beam is not clipped by the LM input. Furthermore, the field plate assembly, integrated inside the LM and affixed by screws, is furnished with sliders enabling a 0.4-inch adjustment range.

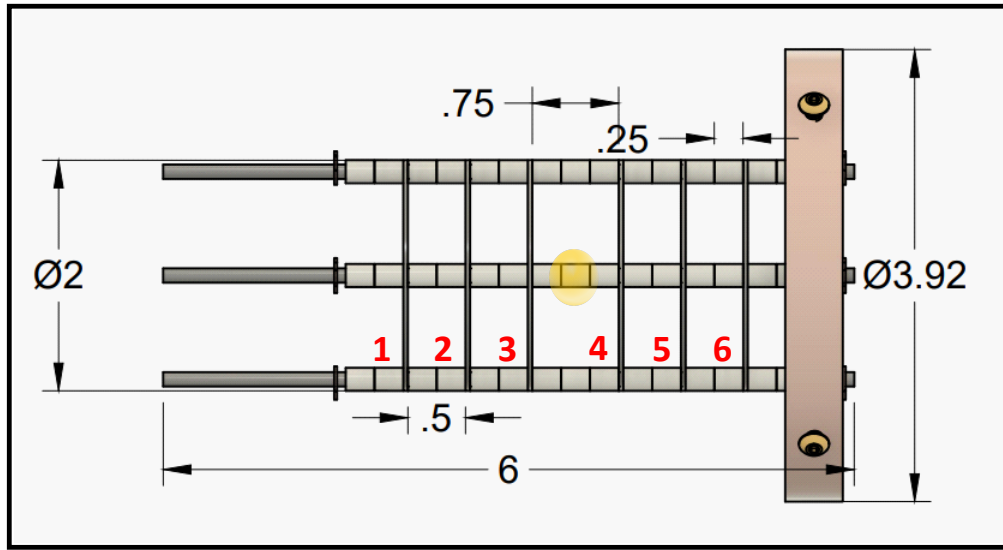


Figure 3.12: Diagram showing the detailed dimensions of the D-TOF field plates assembly in inches, with the plates labeled from 1 to 6 all with the size of 2 inches. The distance between the plates 3 and 4 is 0.75 inches and the yellow point located in the middle of them indicates the center of interaction. Each spacer's length is 0.25 inches, and the length of the rods are 6 inches. Positive voltages could be applied to plates 1, 2, 3, and 4 to extract ions towards the left detector, or to plates 3, 4, 5, and 6 to extract ions towards the right detector.

The short-arm mu-metal (SM) on the right side spans 11.7 inches with an internal diameter of 4.5 inches. Both LM and SM are perforated with a 2-inch pattern to enhance vacuum efficiency and reduce magnetic field near the turbo pumps, with an overlap of 2 inches to ensure a minimized magnetic field presence.

These features contribute to an optimized field-free environment for electron spectroscopy studies. As shown in Figure 3.13, measurements of the magnetic field (B-field) for the mu-metals were conducted in various orientations, from East to West and North to South, utilizing a Hall probe sensor capable of detecting changes in the magnetic field down to the nano Tesla level. The purpose of these measurements was to confirm the effectiveness of the mu-metals in reducing the magnetic field relative to the surrounding environment. The values are normalized for better comparison. Notably, efforts were concentrated on reducing the external radial B-field within the mu-metal, as the radial B-field primarily affects the electrons due to the Lorentz force.

As the measurements show, the radial B-field inside the LM and SM are depleted down to values less than 0.2 from North to South compared to the earth's radial field of 0.70 and to 0.10 from East to West compared to the earth's radial field of 0.85 and this is a good sign that electrons and especially the low energy electrons wouldn't be affected by the surrounding magnetic field. D-TOF is equipped with two in-house constructed MCP-based detectors positioned laterally as shown in Figure 3.11, the left houses a multi-anode detector (MD) while the right accommodates a printed circuit board (PCB) detector. Further elaborations on these detectors will be provided in subsequent sections.

The spectrometer could also detect the mass spectrum for ions while operating in the ion mode. After the target gas or molecule is ionized in the center of interaction -orange point in Figure 3.11 and yellow sphere in Figure 3.12 -, the ions will be repelled towards the MCP-based detector by applying a series of constant positive electric voltages on the field plates. This technique was originally developed by Wiley and McLaren [95] where they minimized the ions' non-zero velocity distribution and achieved a good mass resolution. In their work, Wiley and McLaren used a two-stage ionization-acceleration volume that focuses the ions into a detector at the end of the field free region. In their work, they refer to "volume" as the spatial region within the mass spectrometer where ionization and initial acceleration of ions occur. For our case, for a given charge-to-mass ratio (q/m), voltages were applied to

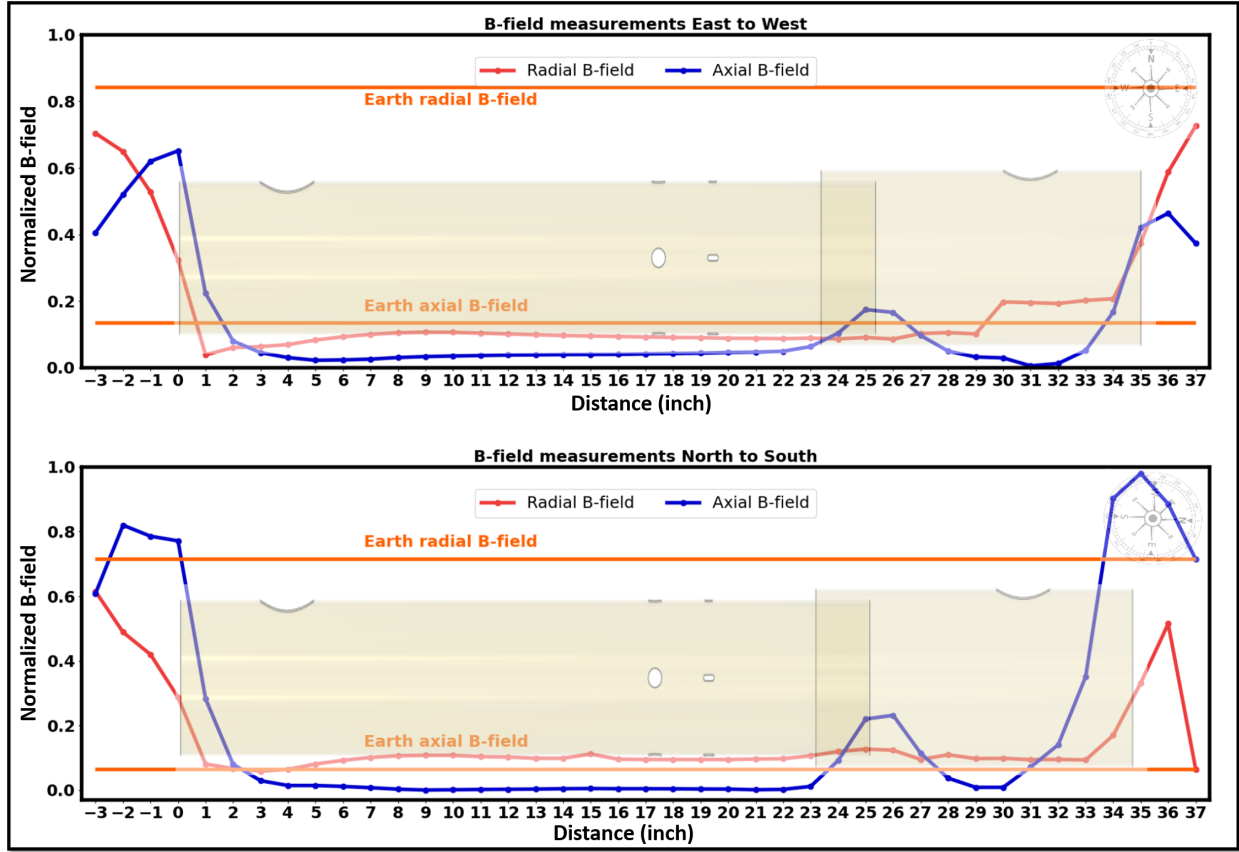


Figure 3.13: Calculated radial and axial B-fields for mu-metal measured from East to West and North to South. The top plot shows the B-field measurements along the East-West axis, and the bottom plot shows the measurements along the North-South axis. The Earth's normalized radial and axial B-field values are indicated for reference. The data highlights the variations in the magnetic field strength across the distance, normalized for comparison. Notably, efforts were concentrated on reducing the external radial B-field within the mu-metal, as the radial B-field primarily affects the electrons due to the Lorentz force.

the field plates 4, 3, 2 and 1 depicted in Figure 3.12 to extract the ions to the left detector (multi-anode detector) as shown in Figure 3.11 or voltages were applied to field plates 3, 4, 5, and 6 to extract the ions to the right detector (PCB detector) as shown in Figure 3.11.

The D-TOF Spectrometer Lattice Assembly

The core area of the D-TOF spectrometer, enclosed by mu-metal, is termed the **lattice**. Familiarity with the lattice structure is essential for any updates or changes. Detailed lattice

assembly instructions are as follows:

1. alumina tubes, specifically AL2O3-TU-C-125 from Kimball Physics, are secured to the inner and outer sides of the oxygen-free copper plate. This plate, sourced from McMaster-Carr (8966K82), is enhanced with graphite spray (Bonderite L-GP G Acheson Aerodag G) and a layer of gold plating (by Klein Plating Works). The assembly is held together using copper Beryllium lock rings, provided by Kimball Physics.
2. Spacers made of alumina, Kimball Physics AL2O3-SP-C-250, are positioned between plates of molybdenum that have been Aerodagged. These plates are prepared with threading to accommodate brass screws (McMaster-Carr 97715A400). Kapton insulated wires (Accu-Glass products 100675), suitable for ultra-high vacuum, establish the electrical connections for the field plates. Detailed procedures for the electrical setup and surface preparation can be found in the specific subsections [3.1.7](#) and [3.1.7](#).
3. The sequence of components, leading up to the final field plate, is arranged as follows:
 - Two spacers and each spacer has length of 0.25 inch.
 - First field plate with inner diameter (ID) of 0.53 inch
 - Two spacers
 - Second field plate with ID of 0.45 inch
 - Two spacers
 - Third field plate with id of 0.25 inch
 - Three spacers
 - Fourth field plate with id of 0.25 inch
 - Two spacers
 - Fifth field plate with id of 0.45 inch
 - Two spacers

- Sixth field plate with id of 0.53 inch
- Two spacers
- Copper lock ring

The positioning of the first field plate, which is the furthest from the copper plate, is our label reference during the wiring process.

4. A half-inch hole on the copper plate's top allows for routing of Kapton wires, as illustrated in Figure 3.14.
5. The completed stack, depicted in Figure 3.12, is inserted into the LM and secured with button-head hex screws (McMaster-Carr 97715A102).

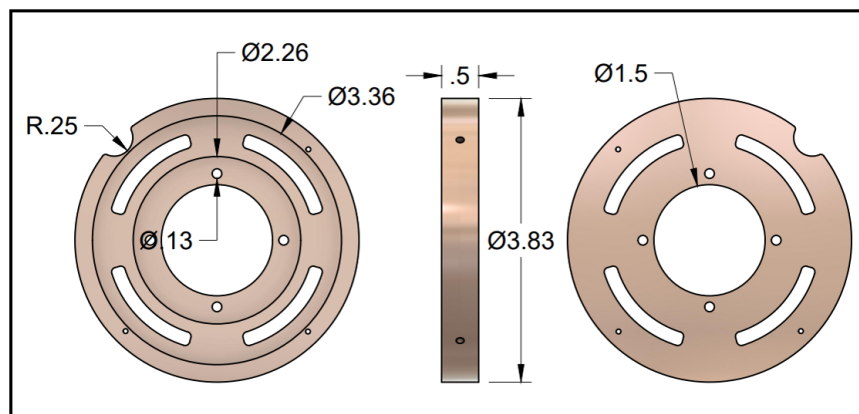


Figure 3.14: Copper plate dimensions.

Aerodag Spraying the Field and Copper plates

The Aerodag brand's designation is derived from Aerodag 16058, a graphite lubricant aerosol used for coating field plates within the D-TOF spectrometer, as elucidated in section 3.1.7. This coating process is pivotal for generating a conductive graphite layer, which is essential for mitigating patch effects on electrons. To ensure surface uniformity during the aerodagging procedure, follow these steps and refer to the Aerodag G Material Safety Data Sheet (MSDS) for safety information at [MSDS Link](#).

1. Have protective gear, including a face mask and gloves, before beginning the spraying process.
2. Insulate the hot plate and its cable with aluminum foil to prevent electrical short circuits, as graphite is conductive.
3. Activate the hot plate under a fume hood and set its temperature to 70°C , a previously determined optimal temperature for achieving the best surface finish without excessive aerodag evaporation.
4. Connect the Kapton wires with 2-56 brass screws, tighten them to the field plates, place the field plates on the hot plate, and wait for one minute since heat evaporates the bubbles on the molybdenum surface and creates a smooth surface.
5. Point the tip of the spray away from the field plate and start spraying it in a left and right motion.
6. Wait for a few minutes to get a uniform surface area again and redo step 5.
7. Wait for a moment, rotate the field plate 180° and redo step 5. Rotating the field plate during the application ensures an even distribution of the coating, preventing unsprayed areas. The interim periods allow the heat to eliminate any surface bubbles, resulting in a consistent layer across the plate.
8. Carefully invert the field plate and set it onto the hot plate, taking care to retain the graphite coating intact. Use the brass screw for stability when positioning the field plate on the hot plate.
9. Redo steps 5-7 for the remaining surface.
10. Ensure that every spot is aerodagged especially the edges. Finally, one should achieve a uniform metallic surface.

If a smooth surface is not obtained, wipe the field plate using Acetone and a lint free tissue. Then redo aerodagging.

Copper plate is aerodagged for the same reason. One is required to do the same instructions for the copper plate too. Except when placing them on the hot plate, the waiting time would be longer because copper plate is a larger material.

D-TOF Field Plate Wiring and Voltage Power Supply

To direct ions towards the detector, it's necessary to set different voltages across the field plates. This is done by connecting a voltage divider to the plates. The system includes a TC952 high voltage power source. The voltage divider, housed in a black box on the D-TOF cart, features one SHV input for the power source and six outputs linked to a 9-pin female connector cable (product number 100020 from Accu-Glass). This setup allows for independent voltage adjustments on each of the six plates, with a range from 0V to 500V. A display with a selector switch is available to monitor the voltage on each plate. Users should ensure that the input to the voltage divider does not exceed 500V since that's the max voltage the pins could tolerate. For reference on how the pins are connected to the voltage indicators and field plates, please refer to Table 3.3. In electron mode, the field plates are set to ground.

Pin number	Indicator number	Field plate number
1	1	1
2	2	2
3	3	3
4	4	4
5	5	5
6	6	6

Table 3.3: Pin connection order to the voltage divider indicators and the field plates

The same wiring was done for the field plates inside the D-TOF using UHV compatible materials and they were connected to a 9-Pin UHV subminiature-C connector (100040 Accu-Glass products). Figure 3.15a shows the connection order for each field plate through the

connector. Please notice that the numbers order is mirror image with the Figure 3.15b.

Finally, both connectors will be connected to a 9C-133 9-Pin feed through on a 1.33 inch Conflat Flange (CF)(100021 Accu-Glass production) as shown in Figure 3.15c. The numbering on the feed through shows the outside where the connector in Figure 3.15a is connected to.

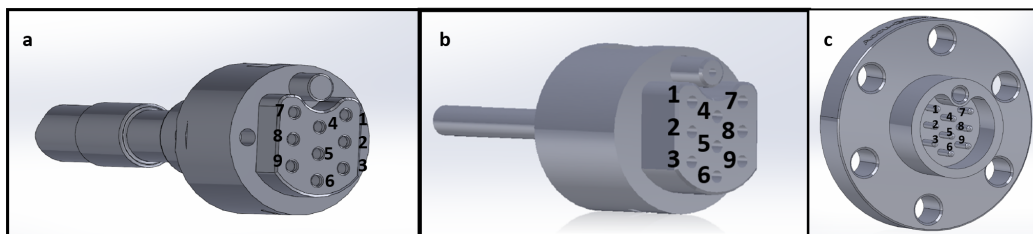


Figure 3.15: a: 9 pin connector field plate order, b: 9 pin connector UHV field plate order, c: CF flange for field plate connectors

In ion mode, particularly under Wiley McLaren conditions, the repeller voltage—assigned to field plate number four—is established at 350 volts. Concurrently, the optimized voltage for the extractor, associated with field plate number three, is regulated at 230 volts. All remaining plates are maintained at a voltage of zero.

The D-TOF Detectors Spectrometer

Ions and electrons initiate their trajectory at the interaction center, moving towards the detectors. For the D-TOF spectrometer, we have developed two home-built state-of-the-art detectors using a stack of MCPs arranged in a Chevron configuration. It's worth acknowledging the collective advancements made by various research groups in the evolution of imaging, single, and multi-anode detectors over the years, which have laid the groundwork for our current technology [96–107]. Our innovative multi-anode detectors are uniquely engineered for electron spectroscopy, with capabilities extending to mass spectrometry. Unlike traditional works that primarily focus on ion detection for mass spectrometers, where the substantial mass difference between ions and electrons diminishes the urgency for detector speed, our design prioritizes rapid response times essential for electron detection. Moreover,

while standard ion-mode detectors require minimal adjustments due to low signal variation from the ground, electron-mode operation demands precise capacitive decoupling due to the MCPs’ biasing at voltage levels above 2.2 kV. Our design intricately addresses this by decoupling the channels in both detectors. Moreover, the electronic components used inside the detectors eliminate the cross-talk issue among the channels.

We believe our detector stands at the forefront of current technology, adept at meeting the stringent speed requirements of electron spectroscopy—requirements that far surpass those for ion spectroscopy. This dual functionality ensures that if electron detection is achieved with high fidelity, ion detection will naturally follow suit. We acknowledge that some existing electron detection systems rely on CCD arrays, which, despite their utility, may not match our detector’s speed and can suffer from high cross-talk, nonlinearity issues, efficiency, and reliability concerns.

In presenting our detectors, we aim to build upon the collective knowledge and respect the contributions of the scientific community, ensuring that our discourse remains considerate of other research groups and their pivotal work.

Before delving into the specifics of our MCP-based detectors, it’s crucial to understand the fundamental role MCPs play within them. Therefore, we will first explore the characteristics and performance of MCPs as integral components of our detection systems.

Microchannel Plate

MCP was initially created for image enhancement but found broader use due to its sensitivity to particles and photons, making it especially useful in nuclear science. Its inception dates back to 1930 [108], with the actual development occurring in the 1960s through international collaborative efforts [109–112]. The unique electrical properties of MCPs allow for their miniaturization, a process that benefits from fiber optic production techniques.

They are compact arrays of $10^4 - 10^7$ electron multipliers as illustrated in 3.16, each with diameters between 10-100 micrometers. MCP thickness closely matches the length

(L) of its channels. The proportion of a channel's length to its diameter (d) is known as alpha $\alpha = L/d$, and this ratio, along with the material's inherent secondary emission factor, influences the MCP's amplification ability. Typically, MCPs are constructed with an alpha ratio ranging from 40 to 60. Its working mechanism is such that the channels act

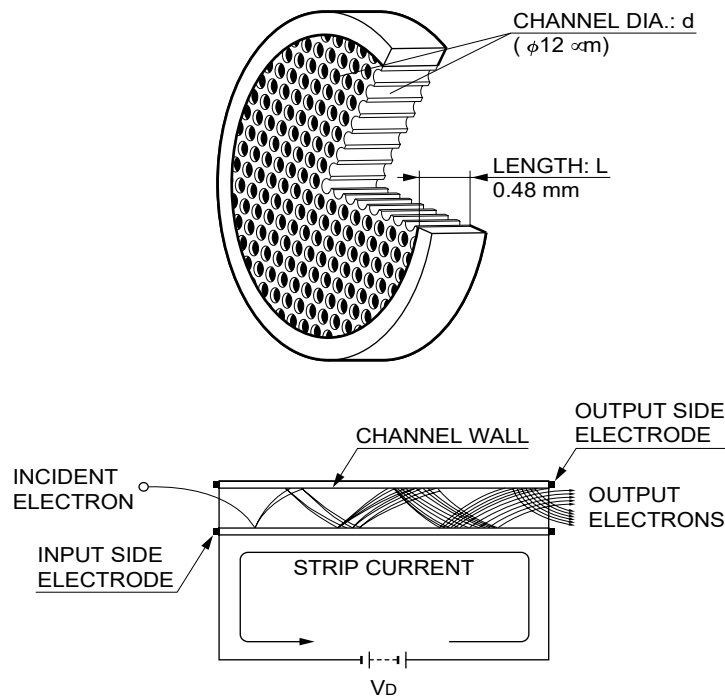


Figure 3.16: MCP schematic. Reproduced from [112]

like individual dynodes. Within a vacuum, when electrons enter MCP at the end where the potential is lower, they hit the channel wall, resulting in the emission of additional electrons. These secondary electrons gain speed from the electric field inside the channel and as they move, they strike the walls, creating more secondary electrons. This process repeats if the material of the channel has a secondary electron emission ratio above one, leading to a multiplying cascade of electrons along the channel [113]. Figure 3.17 adopted from [112] shows a graph of gain against applied voltage for a typical channel Multiplier.

MCPs are coated with conductive materials to serve as input and output electrodes. The resistance between these electrodes is typically around $10^9 \Omega$. MCPs can enhance electron signals by factors of $10^4 - 10^7$. MCP assemblies used for TOF measurements come with

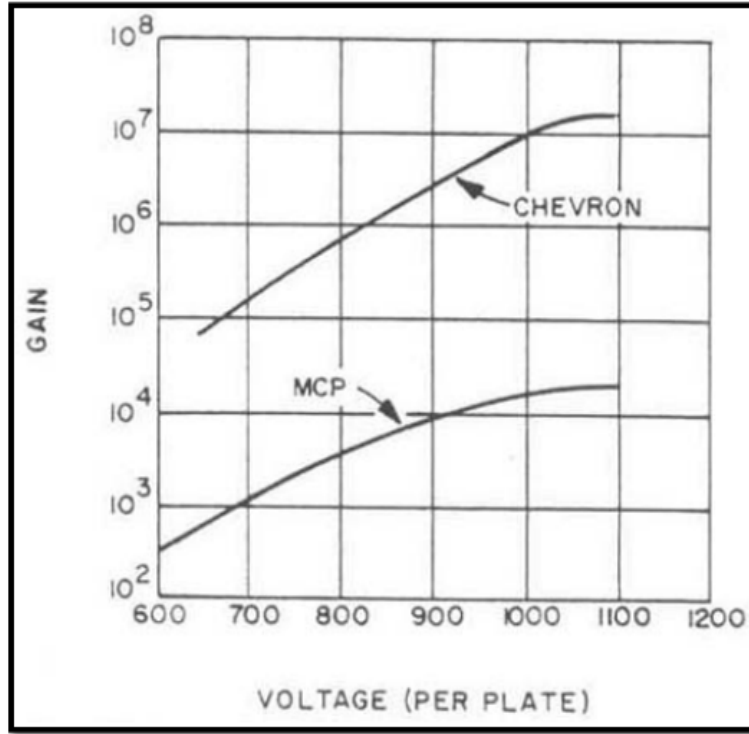


Figure 3.17: Gain vs voltage characteristic for a straight channel MCP and a Chevron at input current signal of 10^{-12} Amp/ cm^2 . Reproduced from [112].

a swift response time, which varies from 450 ps to 1.5 ns at full width at half maximum (FWHM). Spatial resolution is constrained by the channel architecture, with 12-micrometer channels typically spaced 15 micrometers apart center-to-center. Not all the MCPs surface could detect particles. They have an active area. Open Area ratio (OAR) is the ratio of the channel open area to the entire effective area. For example if the OAR of an MCP is 60%, This means that 40% of the signal can not be detected.

The dead time of the MCP -the brief period following an event during which the device is unable to record another event- is significantly reduced due to the parallel operation of its numerous channels. MCP with channels that are 25 micrometers in diameter typically holds around 5.5×10^5 individual channels. The total resistance measured from one electrode to the other across the MCP is typically around $3 \times 10^8 \Omega$, resulting in an approximate resistance of $R = 2.75 \times 10^{14} \Omega$ per channel. Considering the MCP as a parallel plate capacitor, with

a 1 mm thickness and filled to half its volume with a Corning 8161 glass dielectric (having a dielectric constant, ϵ , of 8.3), results in an estimated capacitance of roughly 200 pF or about $C=3.7 \times 10^{-16}$ F for each channel. Due to the channel walls discharging during the multiplication process, the final 20% of the channel length does not contribute to this process, necessitating a recharge through a resistance of $2.75 \times 10^{14} \Omega$, leading to a recharge time constant, or channel recovery time, of roughly $T=RC=20$ ms per channel.

Although every channel in an MCP has an inherent dead time on the order of milliseconds, the sheer number of channels, approximately 10^5 to 10^6 , operating independently, significantly reduces the overall effective dead time of the MCP to between 10^{-7} and 10^{-8} seconds.

The lifetime of MCP is influenced by the alteration of the channel wall's ability to emit secondary electrons, which occurs due to the constant bombardment by electrons—particularly in parts of the channel where amplification is highest. As a result, over time and with continued usage, the MCP's amplification capability gradually decreases. For example as measured in B.R. Sandel et. al. [114] for Chevron plates, with the gain of 1×10^6 with each pulse through both plates and a pulse frequency of 100 kHz/cm², the second plate will reach a total accumulated charge of about 0.05 C/cm² after 850 hours of operation.

Moreover, operating the MCP at a high voltage of approximately 1 kV per stage necessitates maintaining a high vacuum environment. Poor vacuum conditions can lead to increased noise due to ion generation within the channels which reduces MCP lifespan, and causes potential damage from discharges. To remove these issues, it is essential to maintain a vacuum level of 1×10^{-4} torr or lower during MCP operation.

Multi-anode Detector

Here at JRML, we have created a versatile detector for TOF spectrometry that can identify both ions and electrons. This detector can switch between detecting ions and electrons simply by adjusting the bias voltage settings, without needing to alter the physical config-

uration. Its multi-anode structure allows for the simultaneous capture of electron spectra from various emission angles. The anodes are coaxial and as shown in Figure 3.18 separated by 1.25 inch and a distance of 17.6 inches from the center of interaction (4° separation) makes each anode with collection data angle of 1.5° . The coaxial anodes are connected to $50\ \Omega$ impedance type-N connectors. Figure 3.18 on the right shows a section view of the anodes. Therefore, The inner and outer cones are tapered such that they match type-N connector impedance. This impedance matching prevents any pulse reflection or ringing in the signal pulse. The cone shapes are engineered with high precision to meet exact measurements based on the following equation [115]:

$$Z = 60 \ln \left(\frac{\cot \frac{1}{2}\alpha_1}{\cot \frac{1}{2}\alpha_2} \right) \quad (3.13)$$

where α_1 represents the half-angle at the apex of the inner cone, α_2 represents the half-angle of the apex of the outer cone, and Z represents the impedance in units of Ohm. For $Z = 50\ \Omega$, the inner taper has the semi-angle $\alpha_1 = 8.6^\circ$ and the outer taper $\alpha_2 = 19.8^\circ$.

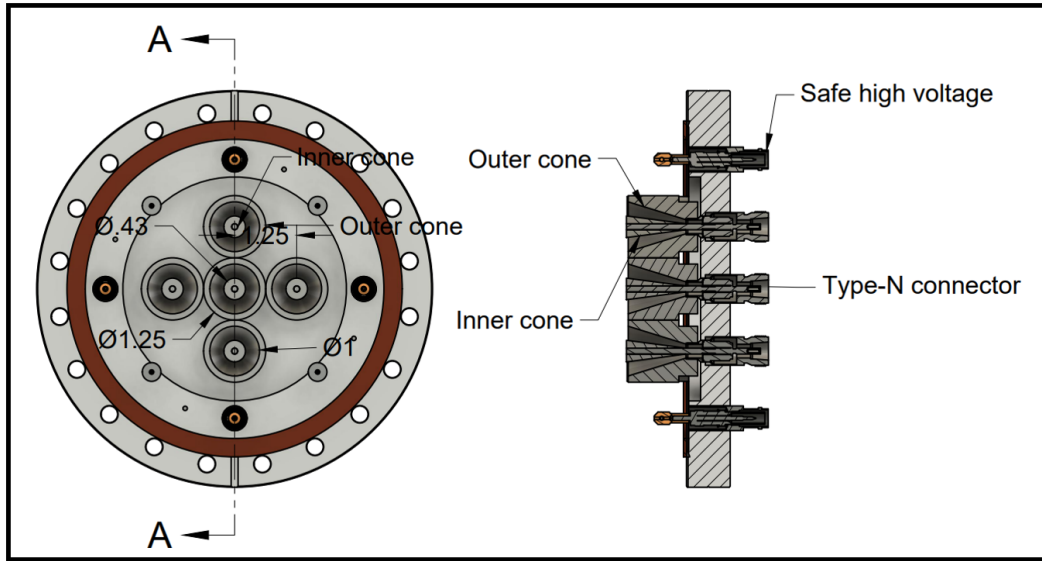


Figure 3.18: Left: Top view of the multi-anode schematic. Right: Section view of the top view which shows how the anodes are connected to the type-N connectors and illustrates a better tapered view of the inner and outer cones.

The multi-anode design significantly boosts the rate at which data is gathered, directly proportional to the number of anodes incorporated, which in this case is five. To prevent interference or 'cross-talk' between the anodes, a mask is placed between the end of the MCP stack and the anodes, complemented by the application of electronic filters. The anodes consistently perform without any differences in efficiency, and the signal quality and noise levels are comparable to those found in traditional detectors with a single anode.

The detector is formed by a dual MCP stack mounted in a Chevron configuration. Biased up to 2 kV, the MCP stack generates a brief shower of electrons when a charged particle hits the front of the MCP. In a commercial MCP detector (for an ion mode only MCP detector, see [Jordan detector](#)), a single conical anode collects the electron shower and generates the signal. The signal is amplified, discriminated and its arrival time relative to a known event (typically the arrival of a pulsed laser that generates the single charged particle) is measured. The angular resolution of the detector is therefore $2\theta = \arctan(D/L)$, where D is the diameter of the MCP detector and L is the length of the spectrometer. In this invention, we have developed a multi-anode design that improves the angular resolution of the detector. For a 100 mm diameter MCP plate, we have employed 5 anodes, each with a 12 mm diameter. This improves the angular distribution by a factor greater than 8. Furthermore, the 5 anodes allow data collection at 5 different emission angles concomitantly. Finally, each anode is DC decoupled, allowing the detection for both electron and ions.

As illustrated in Figure [3.19a](#), the electron shower generated by the MCP stack is collected by copper-clad Kapton foils (LF9110R Dupont) glued to 50 Ω conical anodes. Biased 200 V higher than the back of the MCP stack, the copper-clad Kapton foil and the conical anode form a DC decoupling capacitor. The electron shower collected on the copper side of the Kapton foil is slowly discharged to the power supply through a 1k Ω resistor. All anodes are connected to the same power supply. A 10 nF bypass capacitor filters any high frequencies that might come from the power supply.

The bypass capacitor purpose is also to provide a significant charge to the MCP to fa-

cilitate a rapid recovery following the initial electron avalanche. Because of the length of the power supply cable and its inherent transmission delay (approximately 3 nanoseconds for 2 feet of cable), the power supply adapts to the charge depletion within a few nanoseconds. The use of such bypass capacitors is common in radio frequency (RF) applications, where they are positioned adjacent to RF operational amplifiers on circuit boards to ensure resilience against high voltage, in this case, up to 2 kV. A 10 nF capacitor would suffice, as the energy stored in a 10 nF capacitor at 2.2 kV is about 22 mJ. Given that each MCP pulse yields a maximum of 10^8 electrons ($q = n \times e = 1.6 \times 10^{-11}$ C) and each electron acquires 2.2 keV of energy, the capacitor has more than enough energy for 12.5×10^{13} electrons to power the MCP for over 100,000 hits without needing to draw additional power. The combination of a 1 k resistor and the 10 nF capacitor creates a low-pass RC filter with a very brief time constant of 1 μ s, which is short enough to recharge between laser shots.

The bias voltage of the anodes is 0V (ground) in ion detection mode and 2.2 kV in electron mode. In both modes, the signals collected by the anodes have amplitudes ranging from -5 mV to -60 mV with a DC level at ground. It's worth to mention the engineering behind the electronic component task in Figures 3.19a. The RC circuit in the multi-anode detector for DC decoupling purposes, is a circuit made up of a Kapton foil (similar to a lollipop) with a thin layer of adhesive (torrSeal) made of resin as shown in Figure 3.19b. The combination is a capacitor in series with signal, and the 50 Ohm impedance of the output (tied to ground) on the signal line. For a swift signal response, which means shorter rise and fall times, it is essential that the capacitance of the Kapton is minimal. To calculate the rise and fall time, we know that the diameter of the lollipop is 10 mm with an area of $A \approx 7.854 \times 10^{-5} \text{ m}^2$. The dielectric thickness d of the combined layers (0.5 mm resin and 25 μ m Kapton) is 0.525 mm (or $0.525 \times 10^{-3} \text{ m}$), and the effective dielectric constant ϵ_r needs to be calculated.

The effective permittivity ε_{eff} for the combined layers in series is given by:

$$\frac{d}{\varepsilon_{\text{eff}}} = \frac{d_1}{\varepsilon_{r1}} + \frac{d_2}{\varepsilon_{r2}} \quad (3.14)$$

Substituting the given values:

$$\frac{0.525 \times 10^{-3}}{\varepsilon_{\text{eff}}} = \frac{0.5 \times 10^{-3}}{4.0} + \frac{25 \times 10^{-6}}{3.0} \quad (3.15)$$

$$\frac{0.525 \times 10^{-3}}{\varepsilon_{\text{eff}}} = 0.125 \times 10^{-3} + 8.33 \times 10^{-6} \quad (3.16)$$

$$\frac{0.525 \times 10^{-3}}{\varepsilon_{\text{eff}}} = 0.13333 \times 10^{-3} \quad (3.17)$$

$$\varepsilon_{\text{eff}} = \frac{0.525 \times 10^{-3}}{0.13333 \times 10^{-3}} \approx 3.94 \quad (3.18)$$

To calculate the capacitance, the capacitance C of a parallel plate capacitor is given by:

$$C = \frac{\varepsilon_0 \cdot \varepsilon_{\text{eff}} \cdot A}{d} \quad (3.19)$$

Where: ε_0 is the permittivity of free space (8.854×10^{-12} F/m), $\varepsilon_{\text{eff}} = 3.94$, $A \approx 7.854 \times 10^{-5}$ m², and $d = 0.525 \times 10^{-3}$ m.

Substituting these values into the formula, we get:

$$C = \frac{8.854 \times 10^{-12} \text{ F/m} \times 3.94 \times 7.854 \times 10^{-5} \text{ m}^2}{0.525 \times 10^{-3} \text{ m}} \quad (3.20)$$

Simplifying the expression, we find:

$$C = \frac{2.74 \times 10^{-15}}{0.525 \times 10^{-3}} = 5.22 \times 10^{-12} \text{ F} \quad (3.21)$$

Therefore, the capacitance C is approximately 5.22 pF.

Given the resistance $R = 50\ \Omega$ and the capacitance $C \approx 5.22\ \text{pF}$, the time constant τ of the RC circuit is calculated as:

$$\tau = R \cdot C \quad (3.22)$$

Substituting the given values, we obtain:

$$\tau = 50\ \Omega \times 5.22 \times 10^{-12}\ \text{F} \quad (3.23)$$

Thus, the time constant τ is:

$$\tau = 261 \times 10^{-12}\ \text{s} \approx 261\ \text{ps} \quad (3.24)$$

The frequency f associated with the time constant τ is given by:

$$f = \frac{1}{2\pi\tau} \quad (3.25)$$

Substituting the time constant $\tau = 261\ \text{ps}$, we get:

$$f = \frac{1}{2\pi \times 261 \times 10^{-12}\ \text{s}} \approx 610\ \text{MHz} \quad (3.26)$$

The rise time and fall time are approximated as:

$$t_r \approx t_f \approx 2.2\tau \quad (3.27)$$

This approximation comes from the fact that it takes about 2.2 times the RC time constant for the voltage to change from 10% to 90% of its final value.

Given the time constant $\tau = 261\ \text{ps}$:

$$t_r \approx t_f \approx 2.2 \times 261\ \text{ps} \approx 574.2\ \text{ps} \quad (3.28)$$

Therefore, the rise time and fall time for the composite dielectric layer with a 0.5 mm resin layer and a 25 μm Kapton layer are approximately 574.2 picoseconds. Please notice that the above is a rough calculation of the signal's response time since we can't exactly measure the thickness of the adhesive and the dielectric constant of the adhesive was assumed to be resin, which constitutes most of the adhesive. However, the experimental data shown in Figure 3.22a demonstrates a fall time of 478.2 ps and a rise time of 717.3 ps captured by multi-anode detector, which does not follow the simplified approximation of 2.2 times the RC time constant for rise and fall times. This discrepancy can be attributed to several factors: The actual rise and fall times can be influenced by the measurement equipment's response and bandwidth, which might not perfectly capture the theoretical values. Real-world components often exhibit non-ideal behavior that deviates from the simple RC model. These factors can result in rise and fall times that differ from the simplified theoretical predictions.

When attaching the Kapton foil to the anode, it is crucial to use a very thin layer of adhesive (torrSeal) and ensure it is evenly spread to avoid excessive thickness. However, there is a limit to how thin you can go before encountering issues. If the Kapton layer is too thin, it can produce a stronger negative pulse, which is desired, but it may also cause an unwanted positive overshoot immediately following.

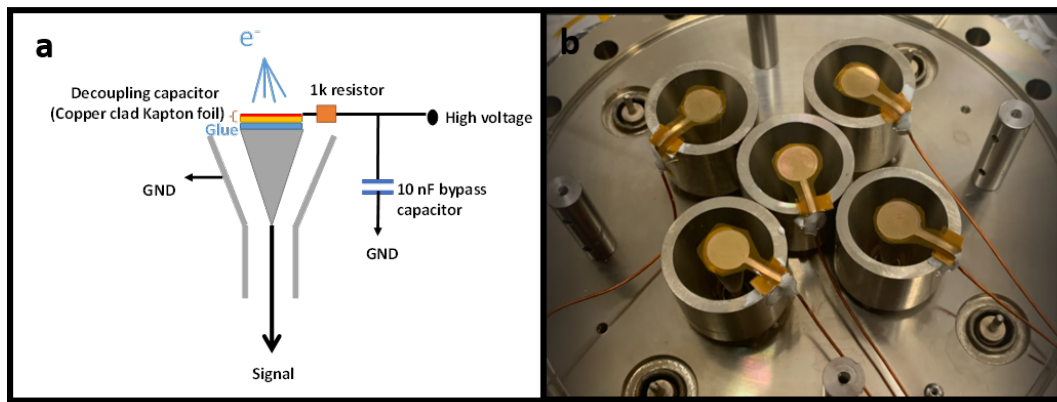


Figure 3.19: The circuitry and diagram for an individual anode.

The detector is presented in detail in Figure 3.20a. From top to the bottom the spectrometer includes (1) Aerodag sprayed molybdenum plate grounded to a Stainless Steel (SS) flange, (2) alumina rod spacers to isolate molybdenum from the top SS plate, (3) Macor ring attached to the top SS plate to electrically isolate the molybdenum plate from the top SS plate, (4) Top SS plate connected to a Super High Voltage (SHV) connector, (5) the MCP stack sandwiched between the two SS plates which are isolated by alumina rod spacers and the bottom Macor made ring, (6) bottom SS plate connected to SHV connector isolated from top SS plate and bottom SS mask, (7) Macor made ring to electrically isolate the bottom SS plate from top SS plate and the second SS plate mask (8) second SS plate mask connected to SHV connector, (9) alumina rod spacers to electrically isolate the SS mask from the SS rods, (10) SS rods which hold the MCP stack, (11) home built SS outer conic anode tack welded to the SS flange, (12) home built inner SS conical anode tack welded to a radio type-N connector, (13) copper-clad flexible Kapton flexible printed circuit boards glued on the inner conic anodes, (14) 8" SS conflat flange, (15) Kovar made type-N electrical feedthrough connectors carrying the fast signals. Figure 3.20b shows the multi-anode detector.

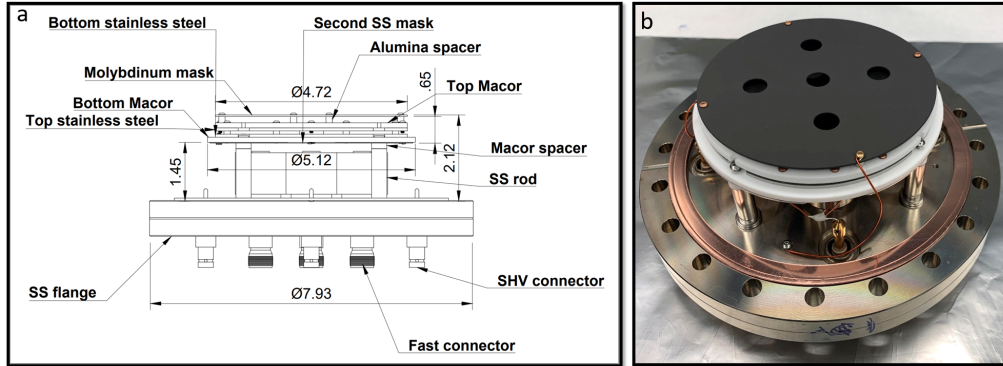


Figure 3.20: a: The multi-anode detector schematic. b: The multi-anode detector.

The MCP integrated into the detector's design is shaped like a rectangle, with a total active area that measures $100 \text{ mm} \times 15 \text{ mm}$, which equates to 1500 mm^2 . When taking into account the cumulative surface area of the three smaller inner cones beneath the stack of

MCPs, which is $36\pi \text{ mm}^2$ each, it turns out that just about 22% of the MCP's available active area is being utilized.

Multi-anode detector's performance was checked and it shows promising results compared to commercial single anode MCP-based detectors. As an example, Figure 3.21 displays an output waveform recorded in ion mode (-1525 V applied voltage) using a high-speed MCP assembly F4655-13 from Hamamatsu detectors shown in their catalogue, which has an effective area of 14.5 mm in diameter. This assembly has a two-stage MCP with a channel diameter of $4 \mu\text{m}$. The thickness of the two-stage MCP is less than 0.5 mm. Consequently, this Figure shows the electron response time, a rise time of 293 ps and a fall time of 539 ps.

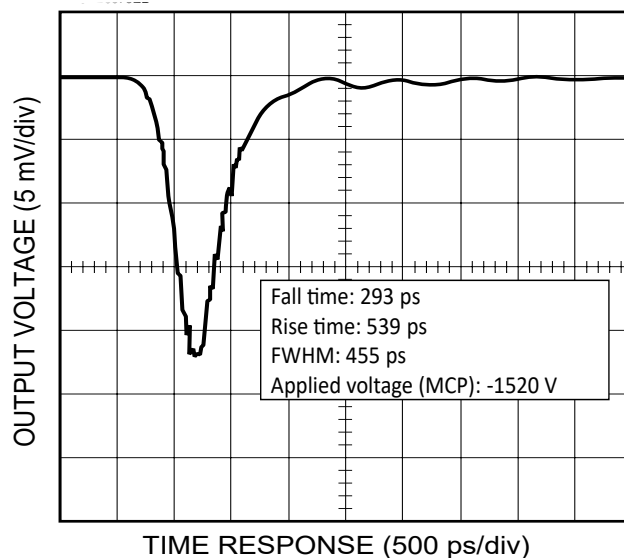


Figure 3.21: Output waveform recorded with a high-speed MCP assembly. The waveform shows a rise time of 293 ps, a fall time of 539 ps, and a full width at half maximum (FWHM) of 455 ps. The applied voltage to the MCP is -1520 V. Reproduced from [116].

Figure 3.22 demonstrates the performance of the multi-anode detector operating in electron mode with a +2 kV applied voltage to the MCP stack while the ion gauge was on at pressure of 7.4×10^{-8} torr and dark counts were measured. Figure 3.22a presents a typical raw electron signal recorded by a Tektronix CSA7404 4 GHz 20 Gs/s signal analyzer from the middle anode (Anode 2). The recorded signal features a fall time of 482.2 ps, a rise time of 717.3 ps, and a FWHM of 2.07 ns, with the oscilloscope triggered at the -5 mV leading edge.

When measuring fall times with an oscilloscope, it's important to account for the bandwidth and rise time (or fall time) of the oscilloscope itself. The oscilloscope's own limitations can affect the accuracy of the measurement. Oscilloscopes have a specified rise time, which is usually related to their bandwidth. This specification indicates how quickly the oscilloscope can respond to a change in the signal. The rise time (fall time) of the oscilloscope can be approximated using the bandwidth (BW) with the formula $t_{\text{scope}} \approx \frac{0.35}{\text{BW}}$. The observed rise time (or fall time) on the oscilloscope is a combination of the actual signal's rise time (t_{signal}) and the oscilloscope's rise time (t_{scope}): $t_{\text{observed}} = \sqrt{t_{\text{signal}}^2 + t_{\text{scope}}^2}$. One can rearrange the above formula to solve for the actual rise time of the signal: $t_{\text{signal}} = \sqrt{t_{\text{observed}}^2 - t_{\text{scope}}^2}$. As shown in Figure 3.22a, given the observed fall time on the oscilloscope is $t_{\text{observed}} = 478.2$ ps and the oscilloscope rise time specification is $t_{\text{scope}} = 80$ ps, we can calculate the actual fall time of the signal: $t_{\text{signal}} = \sqrt{(478.2 \text{ ps})^2 - (80 \text{ ps})^2} = \sqrt{228670.44 \text{ ps}^2 - 6400 \text{ ps}^2} = \sqrt{222270.44 \text{ ps}^2} \approx 471.49$ ps. So, the actual fall time of the signal is approximately 471.49 ps, which is slightly less than the measured 478.2 ps. The measured fall time of 478.2 ps includes the contribution from the oscilloscope's own response time. The actual fall time of the signal is indeed less than the observed value, approximately 471.49 ps in this case. Figure 3.22b shows a histogram of 2100 electron fall time traces, with each bin containing 80 events. This plot reveals the temporal resolution of anode 2, measured to be 500 ± 50 ps. Similar measurements were conducted for the top anode (anode 1) and bottom anode (anode 3) using 1000 traces, with the oscilloscope triggered at the -5 mV leading edge and time referenced at 0 seconds. The temporal resolutions were determined to be 560 ± 50 ps for anode 1 and 380 ± 50 ps for anode 3. Figure 3.22c examines cross-talk among the anodes, showing the signal when the oscilloscope was triggered at the middle anode. No cross-talk was detected between the anodes. Figure 3.22d displays the pulse height distribution (PHD) of electrons for 2100 traces from the middle anode, triggered at -5 mV. The distribution indicates minimum peak voltages detected by anode 2, ranging from -0.030 V to -0.010 V, with a peak around -0.015 V and weighted around -0.013 V.

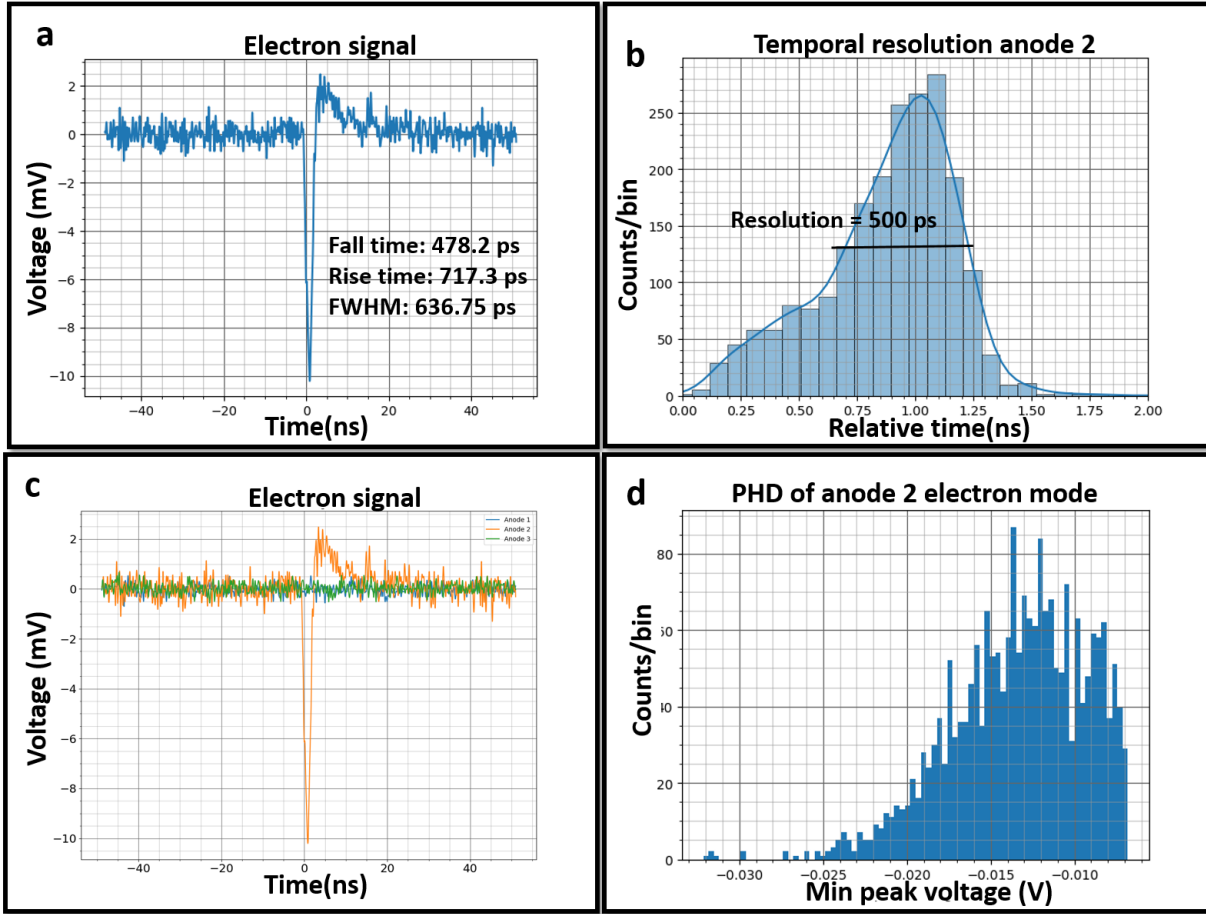


Figure 3.22: Performance of the multi-anode detector in electron mode with a +2 kV applied voltage to the MCP stack. a: Typical raw electron signal recorded by a Tektronix CSA7404 4 GHz 20 Gs/s signal analyzer from the middle anode (Anode 2). Oscilloscope triggered at the -5 mV leading edge. b: Histogram of 2100 electron fall time traces for Anode 2, with each bin containing 80 events. The temporal resolution is measured to be 500 ± 50 ps. c: No cross talking among the electron signals. d: pulse height distribution (PHD) of electrons for 2100 traces from the middle anode, triggered at -5 mV.

PHDs for the three anodes were measured using a 12-bit, 250 MHz, 1.25 Gs/s RIGOL DHO924 digital oscilloscope with the trigger set at -5 mV leading edge for all measurements, capturing 2000 traces per anode. The PHD for anode 1 (Figure 3.23a) shows a peak pulse height of 31 hits with a maximum of 19.62 mV and a minimum of 3.01 mV. The peak-to-peak (Pk-Pk) value is 15.82 mV, with a mean pulse height of 8.93 mV, a median of 8.19 mV, and a mode of 7.86 mV. The bin width is 261.1 μ V, and the standard deviation (sigma) is

2.42 mV. For anode 2 (Figure 3.23b), the PHD reveals a peak pulse height of 33 hits, with a maximum of 18.97 mV and a minimum of 2.58 mV. The Pk-Pk value is 16.44 mV, the mean is 7.41 mV, the median is 7.26 mV, and the mode is 6.53 mV. The bin width is 210.1 μ V, and the sigma is 2.03 mV. The PHD for anode 3 (Figure 3.23c) shows a peak pulse height of 34 hits, a maximum of 24.06 mV, and a minimum of 2.48 mV. The Pk-Pk value is 21.58 mV, with a mean pulse height of 9.25 mV, a median of 9.15 mV, and a mode of 8.34 mV. The bin width is 259.9 μ V, and the sigma is 2.46 mV. These measurements indicate that anode 3 has the highest mean pulse height and variability, while anode 2 has the narrowest distribution, suggesting less variability in detection performance. variability in detection performance refers to the consistency and spread of the pulse height measurements for each anode. Here's a detailed explanation:

Mean pulse height: This is the average value of the pulse heights recorded. A higher mean indicates that, on average, the anode detects stronger pulses.

Standard deviation (Sigma): This measures the spread of the pulse heights around the mean. A higher standard deviation indicates greater variability, meaning that the pulse heights are more spread out and less consistent.

Pk-Pk Value: This is the difference between the maximum and minimum pulse heights recorded. A higher Pk-Pk value indicates a wider range of pulse heights detected, which also suggests greater variability.

Median and Mode: These are additional measures of the central tendency. The median is the middle value when all pulse heights are ordered, and the mode is the most frequently occurring pulse height.

When an anode has higher variability, it means that the pulse heights it records are less consistent. This could indicate fluctuations in detection efficiency or noise levels across the MCP or different impedance at certain regions on the MCP too. Conversely, lower variability suggests that the anode consistently detects pulses with similar heights, indicating more stable performance.

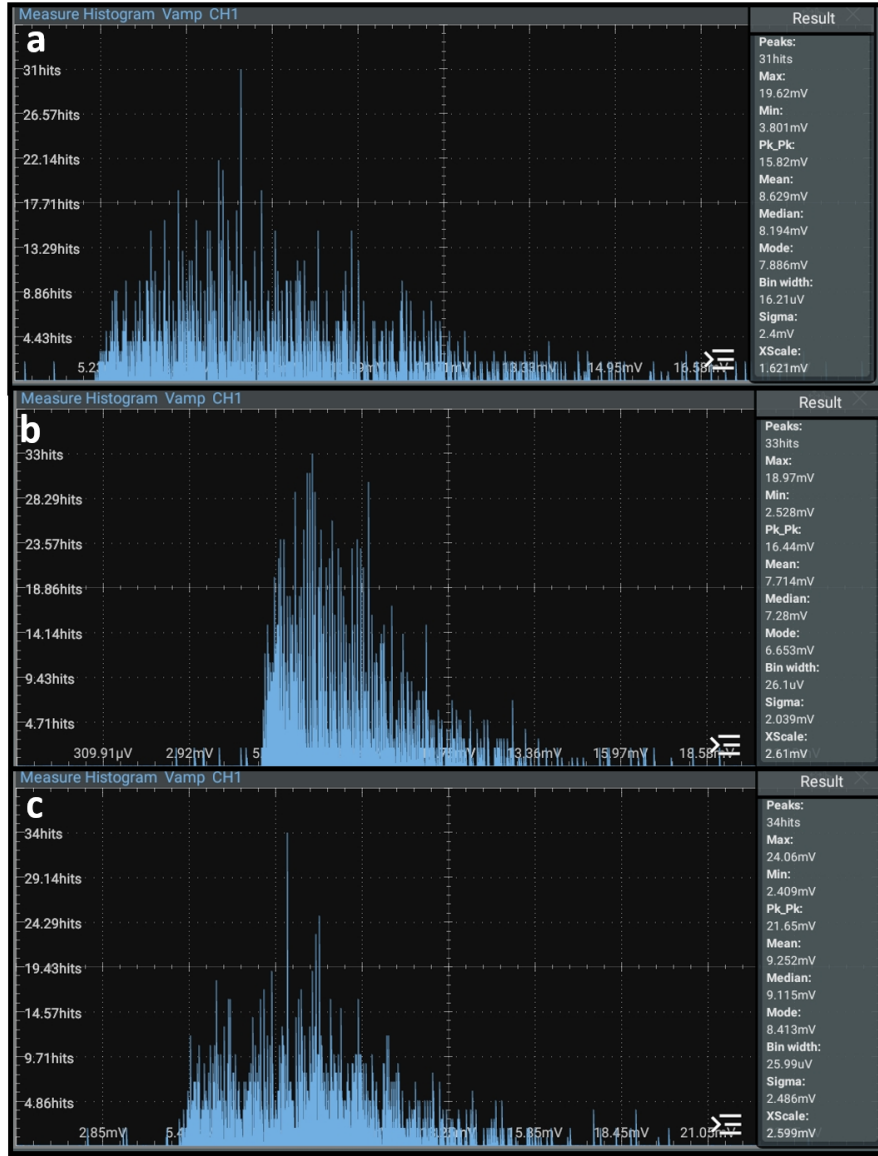


Figure 3.23: PHD of the multi-anode detector in electron mode with a +2 kV applied voltage to the MCP stack. a: PHD of anode 1. b: PHD of anode 2. c: PHD of anode 3.

The performance of the multi-anode detector in ion mode was evaluated specifically for anode 2 while voltage of -2 kV was applied to the MCP stack (the middle anode) using a Tektronix CSA7404 4 GHz, 20 Gs/s signal analyzer. The oscilloscope was triggered at -5 mV. The ion signal recorded in Figure 3.24a, shows a sharp fall time of 640 ps and a rise time of 1 ns, and FWHM of 940 ps. The peak value of this signal is -15.5 mV and generally

speaking, the signal's peak value for ion is higher corresponding to electrons since ions are 2000 heavier. This indicates the detector's capability to accurately capture rapid changes in ion signals.

Further analysis of the temporal resolution of anode 2 in ion mode for 1000 traces is presented in Figure 3.24b. The histogram of the relative time distribution reveals a temporal resolution of 820 ± 30 ps, demonstrating the detector's precision in timing measurements.

Additionally, the PHD for anode 2 in ion mode, shown in Figure 3.24, illustrates the variation in peak voltage. The histogram indicates a consistent performance of the anode in detecting ion signals with varying amplitudes.

These results collectively confirm the efficacy of the multi-anode detector in ion mode, highlighting its high temporal resolution and reliable signal detection capabilities.

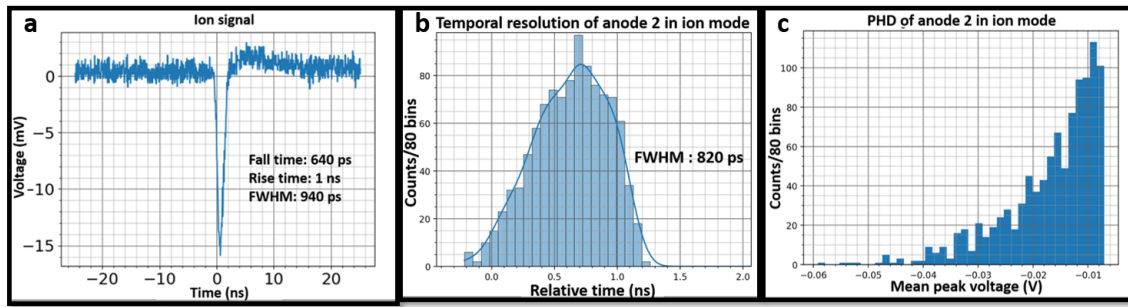


Figure 3.24: a: Ion signal recorded. The fall time is 640 ps, rise time is 1 ns, and FWHM is 940 ps. b: Temporal resolution of anode 2 in ion mode. The histogram shows a FWHM of 820 ± 30 ps, indicating high precision in timing measurements. c: PHD of anode 2 in ion mode.

Printed Circuit Board Detector

We designed and built a printed circuit board (PCB) MCP detector with a new anode geometry for the D-TOF spectrometer, capable of detecting both ions and electrons. The motivation of this work was to increase the effective area of the anodes, overcoming the limitations imposed by the outer cone in traditional multi-anode detectors. The operation in ion or electron detection mode is achieved via a change in the operational bias voltages,

without any physical setup changes. The PCB geometry allows us to use 85% area of the MCP to record electron spectra at multiple electron emission angles. Compared to our multi-anode detector the area efficiency has increased by 63%. Furthermore, compared to our multi-anode Figure 3.25a and commercial version, we are not confined by the bulky physical geometry of conical anodes because ultra high vacuum (UHV) compatible subminiature version A (SMA) connectors 50 Ω impedance matched are (A0645-2-W MPF products) used in the new design as shown in Figure 3.25b. Simply put, 5 conical anodes (5*1.25" diameter) can be replaced with 12 SMA connectors. Moreover, cross-talk between the channels is eliminated by employing electronic filtering.

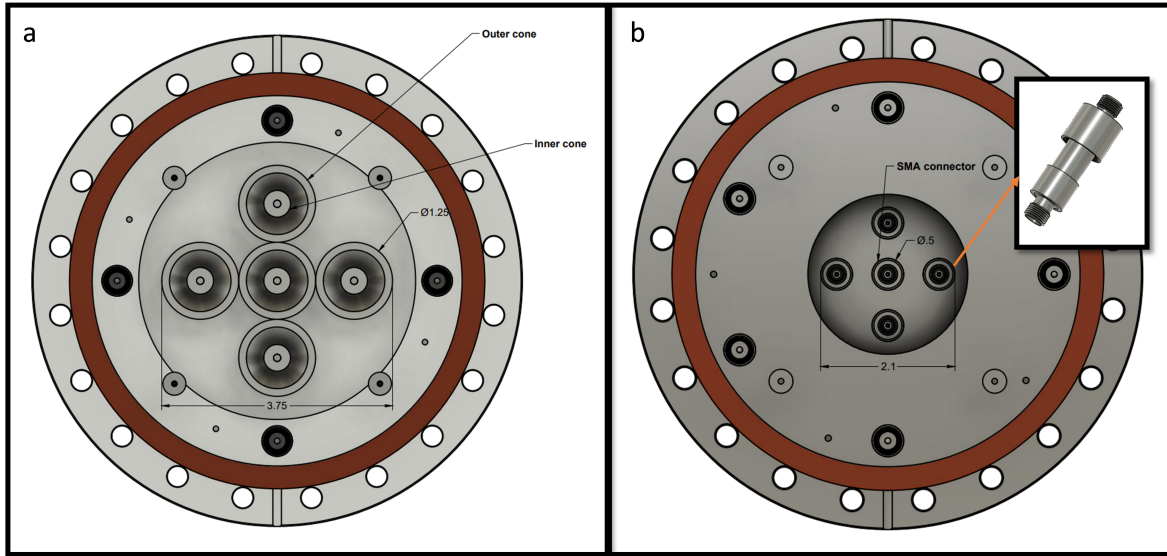


Figure 3.25: a: shows our five anode TOF detector geometry: To maintain the 50 Ω impedance match, we are confined by the outer cone geometry. b: shows our five SMA connector geometry and the subset is a complete picture of the 50 ohm impedance matched commercial SMA connector.

In this configuration, a custom-built Ultra-High Vacuum (UHV) compatible printed circuit board (PCB) is employed. The material used for the PCB is an AP911R double-sided, copper-coated Kapton foil laminate, sourced from Dupont, and crafted into a circular shape. Electronic pathways are carefully etched onto this base material. To increase the structural integrity of the otherwise pliable foil, a stainless steel ring is mounted on its underside.

Wiring provides connectivity between the front and back surfaces of the PCB. On the PCB's front side, electron shower generated by varied angles by the MCP stack is intercepted by copper-coated paddles, as illustrated in Figure 3.28. Positioned approximately 200 V above the back of the MCP stack, these paddles, together with the Kapton foil, act as a DC decoupling capacitor. Paddles on the back panel are connected to SMA connectors through coaxial UHV compatible connector to cable - SMA Male cables (A110756.52 Accuglass). Figure 3 demonstrates the gradual transfer of electrons from the paddles on the front to those on the back, which are linked to the same power source via 1kohm resistors. A 10 nF capacitor on the back side filters out any high-frequency noise that might be introduced by the power supply. The copper paddles are biased at 0V (earth) for ion detection mode and at 2 kV for electron detection mode. Regardless of the mode, the paddles register signal amplitudes ranging from -5 mV to -60 mV, with a ground-level DC baseline.

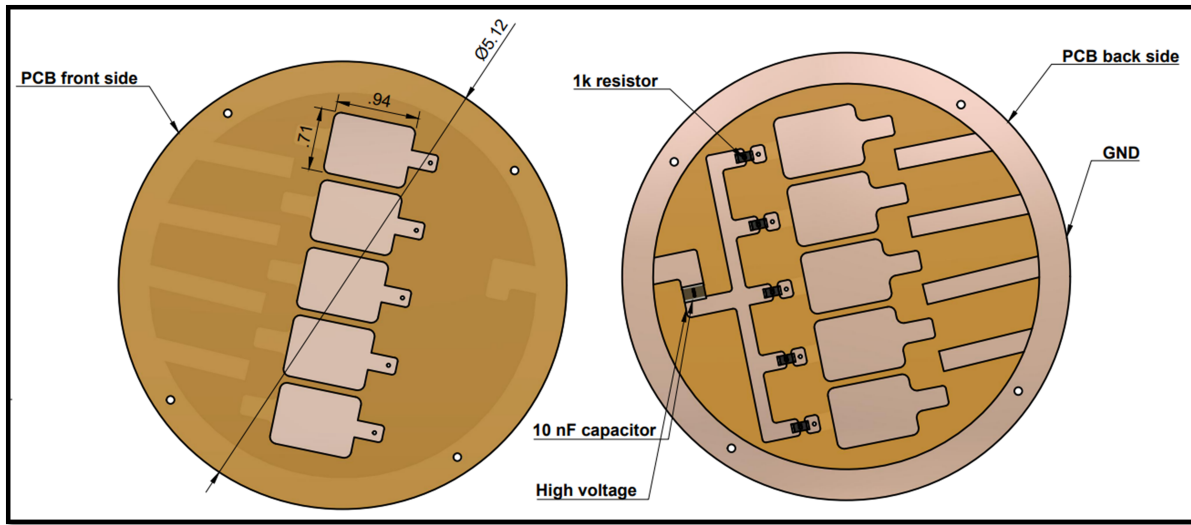


Figure 3.26: PCB front and back side. The front side consists of the paddle which stores the charge. The back side consists of a 10nF bypass capacitor, high voltage route, ground, and 1k resistors. The pink color shows the copper and brown is the Kapton foil.

The detector is presented in detail in Figure 3.27. From top to the bottom the spectrometer includes (1) Aerodag sprayed molybdenum plate grounded to a stainless steel (SS) flange, (2) alumina rod spacers to isolate molybdenum from the top SS plate , (3) Macor

ring attached to the top SS plate to electrically isolate the molybdenum plate from the top SS plate, (4) Top SS plate connected to a super high voltage (SHV) connector, (5) the MCP stack sandwiched between the two SS plates which are isolated by alumina rod spacers and the bottom Macor made ring, (6) bottom SS plate connected to SHV connector isolated from top SS plate and bottom SS mask, (7) Macor made ring to electrically isolate the bottom SS plate from top SS plate and the second SS plate mask (8) Macor spacers which isolate the PCB board from MCP stack, (9) PCB board glued to a thin SS ring, (10) SS rods which hold the MCP stack, (11) Commercial UHV compatible SMA cables connected to the PCB and the SMA connector, (12) commercial UHV compatible 50 ohm impedance match SMA connectors tack welded to the SS adaptable flange (the connector is a feed through that carries the fast signal), (13) 8" zero reducing SS flange connected to the adaptable SS flange.

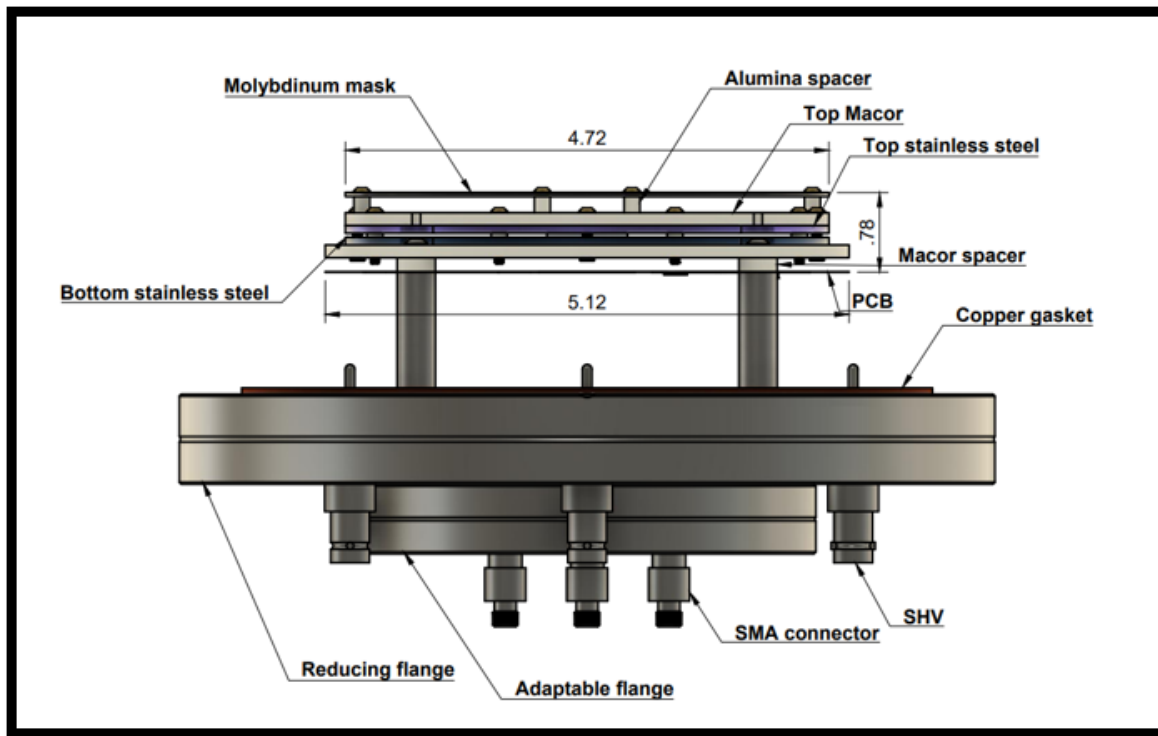


Figure 3.27: The detector stack design details and dimensions in inches.

Figures 3.28a and b shows the top and side view of PCB detector.

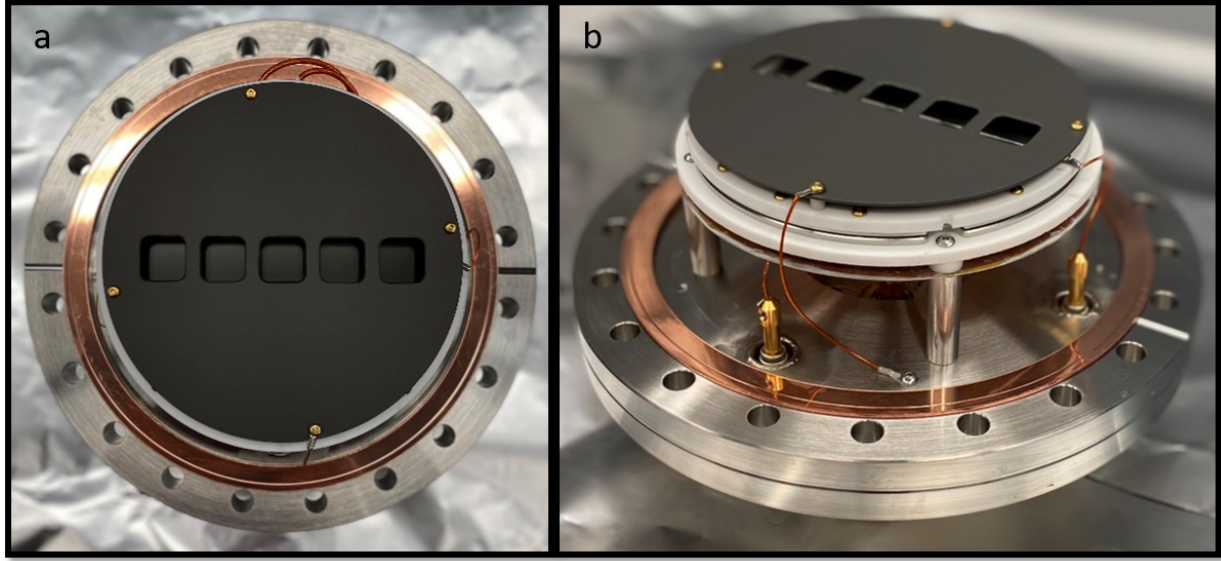


Figure 3.28: a: PCB detector's top view. b: PCB detector's side view.

A preliminary test of the PCB detector was conducted in both electron and ion modes to evaluate its signal capture effectiveness. Figure 3.29 shows the voltage-time characteristics for the middle anode under electron (a) and ion (b) signals.

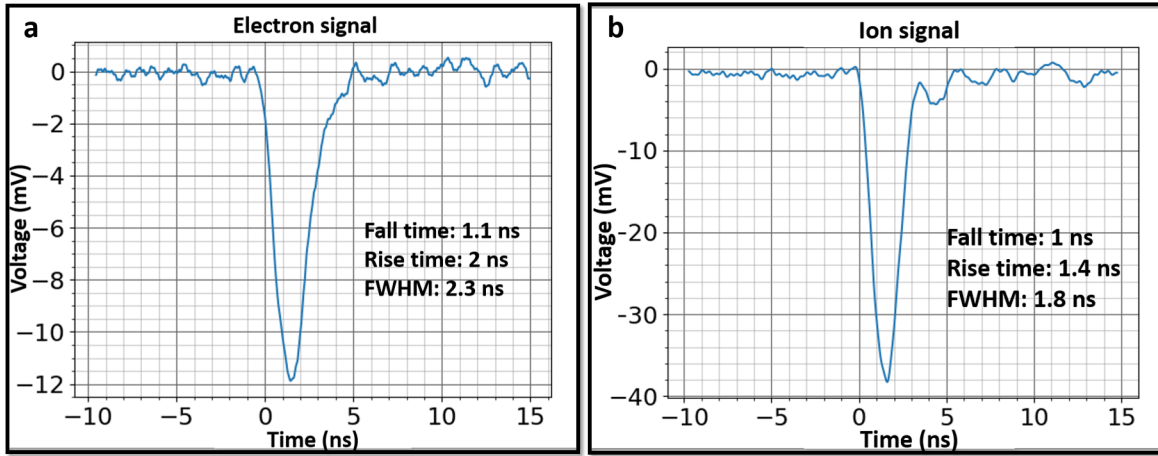


Figure 3.29: a: Electron signal. b: Ion signal.

In electron mode, a voltage of +2 kV was applied to the MCP stack, with a background pressure of 9×10^{-8} torr in the D-TOF to measure a dark count for each case. The data was captured using a Tektronix CSA7404 4 GHz, 20 Gs/s signal analyzer, with the signal

triggered at -5 mV. As shown in Figure 3.29a, the PCB detector's response time in electron mode exhibited a fall time of 1.1 ns, a rise time of 2 ns, and a FWHM of 2.3 ns, with a peak signal value of -12 mV.

Furthermore in ion mode, a voltage of -2 kV was applied to the MCP stack under the same pressure conditions. The data was recorded using the same signal analyzer, also triggered at -5 mV. The ion signal, shown in Figure 3.29b, demonstrated a fall time of 1 ns, a rise time of 1.4 ns, and an FWHM of 1.8 ns, with a peak signal value of -38 mV. Response time values in both modes show the detector's capability to accurately capture fast transient events. It should be noted that Figure 3.29 represents a typical preliminary signal captured by the PCB detector and does not imply a limitation in capturing signals with shorter fall times than those mentioned. More detailed data, including PES, mass spectra, and PAD, will be presented in this chapter and the next, demonstrating the PCB detector's performance.

3.1.8 MCP Read Out and Voltage Divider

MCPs function solely to amplify the signal, so the use of a compatible readout apparatus in the MCP-based detector such as anode is necessary to capture the data. Moreover a device is required to provide the necessary voltages to the MCP detector stack. With that said, the voltage divider is the device that consists of several resistors connected in series, which divides the input voltage among its resistors to provide the necessary operating voltages for different stages of the MCP detector.

For ions and electrons, since the polarity of the power supply matters, the right power supply polarity and the appropriate voltage divider should be used. For positive ions, a circuit that keeps the MCP stack input at a negative high voltage is used. Conversely, for electrons or negative ions, a circuit that holds the MCP stack input at ground or slightly positive high voltage is preferred. Since the MCP detector operates at very low current levels, it's significant to choose the right resistor values to protect the MCP stack from any

possible damage at any operation mode. In circuits with various routes for electricity to travel, the path that has the least resistance is where most of the electrical current flows. This concept is applied in designing voltage dividers for MCP detectors, to ensure they operate effectively whether they're detecting ions or electrons.

As shown in Figures 3.30 and 3.31, since the MCP stack components (Mask, Chevron, and anodes) have a very high resistance ($R_{\text{Mask}} = 50 \text{ G}\Omega$, $R_{\text{Chevron}} = 20 \text{ M}\Omega$, and $R_{\text{Anode}} = 20 \text{ M}\Omega$), the resistors R_1 , R_2 , and R_3 parallel to each MCP component should be adjusted such that most of the current applied by the high voltage power supply runs through the voltage divider's resistors.

The high voltage power supply used for the ion and electron voltage dividers, is an Ortec 556 that can be switched between a negative and a positive polarity. The maximum current produced by the power supply is 1 mA, but since we didn't want to push the power supply to it's limit, we designed the voltage dividers such that their maximum current in the line was 0.5 mA (500 μA).

For the electron mode MCP detectors, the voltage divider is constructed of resistors considering that the detector stack has its inherent resistance. The resistors R_1 , R_2 , and R_3 have values of 150 k Ω , 3.85 M Ω , and 400 k Ω respectively. The 3.85 M Ω series resistor functions as a current limiter to safeguard the power supply in the event of an MCP short to the ground, such as during an arc fault. Normally, the MCP exhibits 20 M Ω resistance; but when it shorts, its resistance drops a lot, which would be a problem if the now few hundred ohms MPC sits across a 2.2 kV supply. The 3.85 M Ω resistor therefore limits the current supplied by the power supply to 0.5 mA in the worse case scenario.

For the ion mode MCP detectors as shown in Figure 3.31, an input voltage of 2.5 kV with negative polatity was fed to the system. The resistors R_1 , R_2 , and R_3 have values of 600 k Ω , 4 M Ω , and 400 k Ω respectively. As mentioned previously, the 4 M Ω series resistor functions as a current limiter to safeguard the power supply.

In addition, every resistor in the ion or electron mode voltage divider circuit, experiences

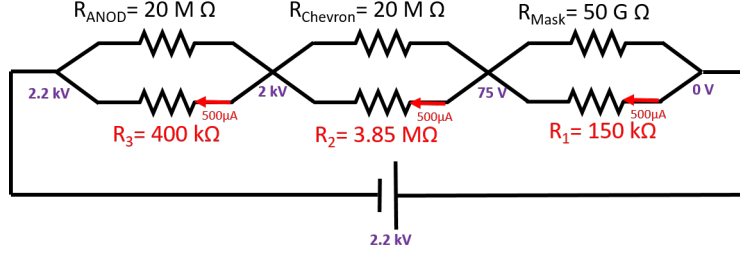


Figure 3.30: Voltage divider configuration in electron mode.

a voltage drop that will lose its energy in the form of heat. This is because the electrical energy is transformed into thermal energy. Each resistor configuration, is designed to handle a certain amount of power, known as its power rating, which indicates the maximum amount of energy it can safely dissipate without being damaged. For example As shown in Figure 3.30, the voltage drop on the R_2 is 1.925 kV. Therefore, the dissipated heat is calculated to be 0.96 W. consequently, the resistor's selected power rating should be selected to be higher than the dissipated heat.

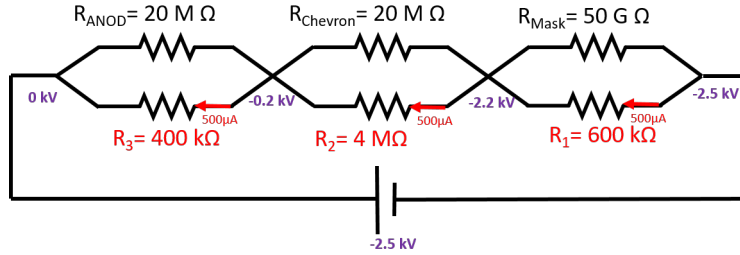


Figure 3.31: Voltage divider configuration in ion mode.

3.1.9 D-TOF Data Acquisition System

The electronics configuration used to measure time of flight is detailed in Figure 3.33. The principal component of this setup is the Time to Digital Converter (TDC), which, as its name indicates, measures the time interval between two events and converts this measurement from analog to digital format for analysis by a computer. This system is based on the high performance CAEN V1290N (Computer Automated Measurement and Control) TDC. The

TDC has 16 channels. TDC's resolution is adjustable from 800 ps, 200 ps, 100 ps, and 25 ps (our case). It's double hit resolution is adjustable between 5 ns (our case), 10 ns, 30 ns, 100 ns. Double hit resolution is the minimum amount of time required by TDC to distinguish between two separate timing signals or "hits." If two signals arrive within this period, the TDC may not be able to distinguish them as separate events. This value for modern TDCs can be as low as 3-5 nanoseconds, meaning they can differentiate hits that are spaced very close together in time. V1290N, operates in trigger matching mode to handle time measurements in experiments. In this mode, this device does not use a common start or stop method; instead, it establishes a time window during which hits are accepted. The hits within this window are then assigned absolute times relative to a time origin also known as trigger. This is different from other TDC modes where a precise time reference is used for all channels. In trigger matching mode, the TDC can be configured to accept a maximum number of hits per event, which is a per-module maximum rather than per channel. To elaborate more, common Start TDC is like a sprint race where all runners start at the same time when the starting gun goes off. The "common start" is the gunshot, and all the runners (signals) race towards the finish line (the TDC) at different speeds (times). The TDC measures how long it takes each runner to reach the finish line from the moment the gun fires. For trigger matching mode, imagine this as a race where runners can start at different times, and there's a time window (like a gate). The TDC is like a camera taking snapshots of the runners as they pass through this window. If they're in the window, their picture (or time) gets taken, and if they're outside the window when the snapshot is taken, they're not included. The TDC in this mode is collecting snapshots only during this "open window" time, and it's like saying, "I'm only taking pictures from this time to this time; whoever passes through, I'll snap a photo." To obtain the full resolution of the TDC in trigger matching mode, it's important to extend the trigger matching window to include the gate signal and digitize the gate signal in one of the channels (ch0). For example, imagine you're waiting to jump into double dutch rope and you want to make sure you have enough

time to fit in without getting caught by the ropes. The trigger matching window is like the time you have to jump in. Extending it means you're making sure there's enough time for the gate signal (or the moment you start jumping) to be included in the time you're watching. Now, once you're jumping in the ropes, someone is making a slow-motion video so you can see exactly when you jumped in. Digitizing the gate signal is like making that slow-motion video on a camera (TDC channel) so you can see exactly when the action happened. Figure 3.32 shows the TDC diagram working in trigger matching mode. The trigger matching control on the V1290 is managed through four programmable parameters. **Match window**, **window offset**, **extra search margin**, and **reject margin**. Imagine you're playing a game where you need to catch fireflies, but you can only do this during a certain time at night, and you have a special net that opens and closes automatically.

The **match window** is like the specific time when your net is open. You can catch fireflies only during this time. For TDC working in ion mode this window is set at $51.2\ \mu\text{s}$ (max dynamic range) and for electron mode, it is set at $9\ \mu\text{s}$.

The **window offset** is the time between when you spot a firefly and when your net actually opens. If you spot a firefly too early, you need to wait for the net to open at just the right time. The window offset is referenced to the trigger input as shown in Figure 3.32. The trigger input (Delayed PD signal) is a positive value of $+40\ \mu\text{s}$ for ion mode and $+4\ \mu\text{s}$ in electron mode. The window offset is shifted by $-40.2\ \mu\text{s}$ for ions and $-4.2\ \mu\text{s}$ for electrons relative to the trigger. For both ion mode and electron mode, the window offset is set such that it starts slightly earlier (200 ns) than the photodiode (PD) signal at negative time. Following that, recorded hits arriving at the negative time values are dumped.

The **extra search margin** is like giving yourself a head start. After the official time ends, you're already looking around for fireflies to catch, just in case they show up late. In program, a 25 ns extra search margin is added to the window.

The **reject margin** is like the extra time before your timer starts. Even if you see them, you won't try to catch them because it's earlier than your set time. In the program it is

Specified that the reject margin prior to the match window to be 25 ns.

In summary, in this game, the fireflies are like the signals the TDC is trying to catch (ch1 for ion mode and ch1-ch3 for electron mode). The game starts with the "trigger input," as shown in Figure 3.32 using a TENNELEC TC410A delay generator (4 μ s for electron mode and 40 μ s in ion mode) as shown in Figure 3.33 and the net opens at the "window offset" time, stays open for the "match window width," and then closes, with a little extra time added just in case ("extra search margin"). If any fireflies come during the "reject margin" times, they're too early, and you ignore them.

The same trigger signal is fed to the I-1 input at VM-USB VME module. The VM-USB VME module works with the CAEN TDC as part of the data acquisition system by serving as the bridge between the linux box computer and the CAEN TDC. This module can send control commands from the computer to the CAEN TDC. These commands could be to start or stop measurements, configure the TDC settings, or to initiate data readout. Once the time of flight data is captured by the TDC, the VM-USB module can trigger the readout process, record the data, and transfer the data from the TDC to the computer for analysis.

SpecTcl is a software designed for the visualization of histograms and analysis of data. It's often utilized in conjunction with the Readout software. Readout is the experiment control software that is interfaced with The VME crate and digitization modules such as TDC that is inserted into that crate. Once the data is recorded by the Readout, they are typically exported into binary formats, which can be conveniently imported into specialized analysis tools like MATLAB or Python for analysis.

For additional information on the data collection system, SpecTcl program, and updates to the Readout process, the guides and tutorials authored by Kevin Carnes on [JRML DAQ systems](#), [VME DAQ](#), [SpecTcl](#), and [Readout](#) are recommended to the users.

Given that the TDC cannot process raw signals from the detector, a preprocessing step is required. As shown in Figure 3.33 six channels of the TDC are being utilized. Channels zero (ch0) and the trigger input are dedicated to initiating the trigger matching mode on

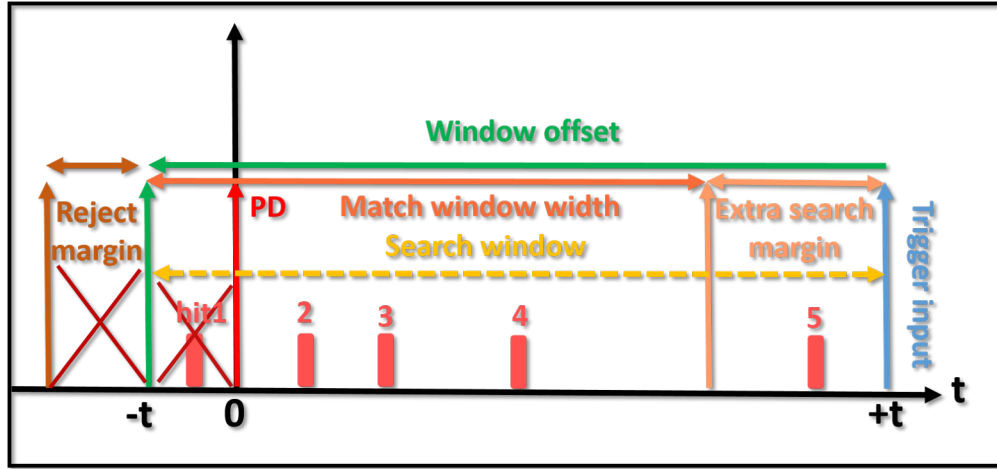


Figure 3.32: V1290A/N Trigger Matching Mode timing diagram.

the TDC, thereby establishing the timing window. The ch0 signal is specifically generated through a fast photodiode (1 ns rise time) activated by the laser at the ionization event. The initial signal from the photodiode is inverted and then split. Both branches of the split signal are then amplified and discriminated using a 9327-P 1-GHz Amplifier and Timing Discriminator made by AMETEK. Although amplification may be considered unnecessary due to the potential for adequate enlargement of the photodiode signal, the light intensity impinging on the photodiode is regulated with neutral density filters. One of the split signals is directed to ch0 while the other is sent to delay generators, which serve as the source for the trigger signal and laser shot counts. The reason we log the number of laser shots to ch4, is a necessary measure due to the overhead associated with the TDC. Furthermore, channels one through three (ch1-ch3) capture the signals from charged particles detected by the MCP after traversing a distance L within the spectrometer. Therefore, signals from the anodes of the MCP detector—top anode on ch1, middle anode on ch2, and bottom anode on ch3 in electron mode, or only ch2 active in ion mode—are first amplified and discriminated by the same type of AMETEK equipment. This device yields fast negative NIM pulses that experience minimal time shift. These pulses are then fed into channels one through three (ch1-ch3) on the TDC as discrete events.

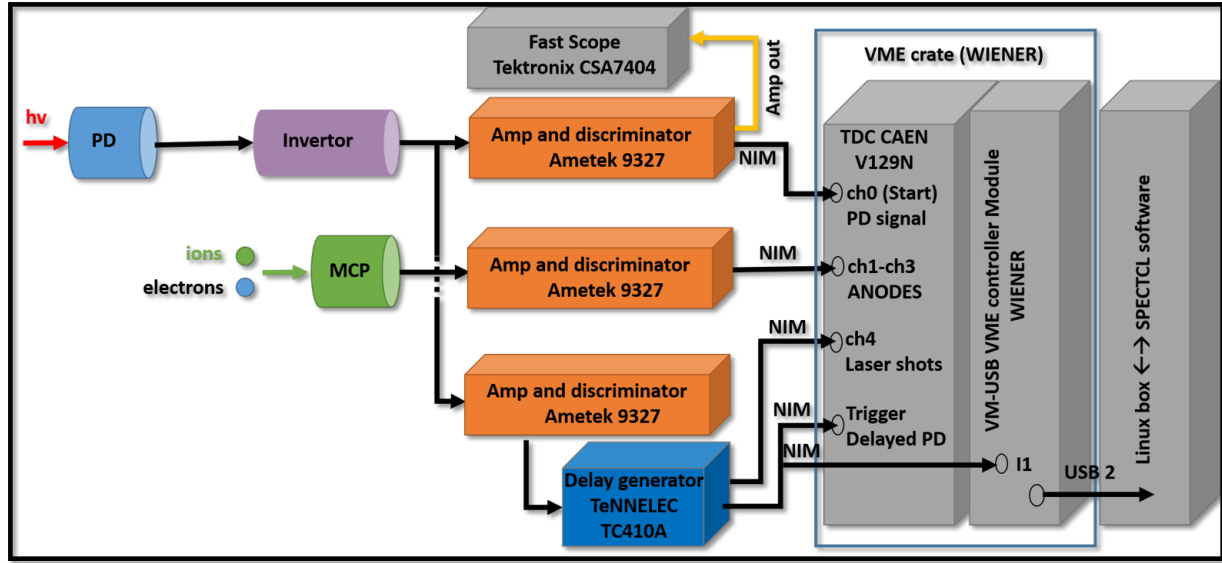


Figure 3.33: DAQ electronics diagram.

D-TOF Vacuum System

The D-TOF is an analysis chamber that studies the evolution of molecules in High Vacuum (HV) ($10^{-3} - 10^{-8}$ torr) and Ultrahigh Vacuum (UHV) ($10^{-8} - 10^{-12}$ torr). For D-TOF the background pressure reaches down to 10^{-9} torr. At such a low pressure one deals with molecular flow regime and basically at this region the chance of molecules to interact with the walls of the chamber is more frequent than colliding with each other. For example, the mean free path λ for air at room temperature of 20°C is 79nm. Now compare the latter value with the mean free path λ for air at room temperature of 20°C for HV (5×10^6 cm) and UHV (5×10^9 cm). As another example, the time required for monolayer formation of the air molecule at 20°C assuming the molecule diameter of 3×10^{-8} cm and sticking probability of 1 can be derived from equation 3.29 [117].

$$t = \frac{2.5 \times 10^{-6}}{P(\text{torr})} \text{ s} \quad (3.29)$$

According to equation 3.29, to maintain a clean surface for a useful time period, one requires the gas pressure of less than 10^{-9} torr. With that said to get a clean surface to have an

analyze chamber, a lot of effort has been done. This section presents the D-TOF pumping system. For more information about the details please see [118]. First, the D-TOF vacuum schematic is given. Next, the procedures for pump down, venting, and purging the D-TOF vacuum chamber are given along with existing safety protocols in FLAME lab.

D-TOF Vacuum Generation

The D-TOF is a mobile experimental chamber dedicated to mass and electron spectroscopy. Figure 3.34 shows the vacuum schematic of the D-TOF in the FLAME lab.

The D-TOF is connected to a Pfeiffer (A100L) multistage Roots backing pump with a pumping speed of $100 \text{ m}^3/h$ which pumps the setup down to a pressure of 10^{-2} torr. Outside FLAME, there are two independent Roots pump. One is connected to UHV line as shown in Figure 3.35, other is connected to the High gas line. The D-TOF and most of the vacuum setups existing in FLAME are connected to the UHV line.

As shown in Figure 3.34, the red dash line shows the self-contained parts of the D-TOF. This means that the only pumps that stay unchanged when moving from one lab to another are the turbo molecular pumps P1 and P2. Turbo molecular pumps P1 and P2 are Leybold Turbovac MAG W 600 ip, with pumping speed of 520 l/s for argon. It is important to mention that turbo pump's circumferential speed are on the order of average thermal speed of the molecules derived from the Maxwell-Boltzman distribution. Equation 3.31 shows the average thermal velocity of the molecules.

$$V_{avg} = \sqrt{\frac{8.R.T}{\pi.M}} = 146\sqrt{\frac{T}{M}} \quad \frac{m}{s} \quad (3.30)$$

Where $R=83.14 \frac{\text{mbar.l}}{\text{mol.k}}$ is the gas constant, T is the temperature in kelvin and M is the molar mass. Table 3.4 shows average thermal velocity for different molecules.

Furthermore, part of D-TOF's gas line is connected to Edwards dry scroll pump with 1800 rpm and pumping speed of $15.1 \text{ m}^3/h$ to purge the gas line as shown in Figure 3.34.

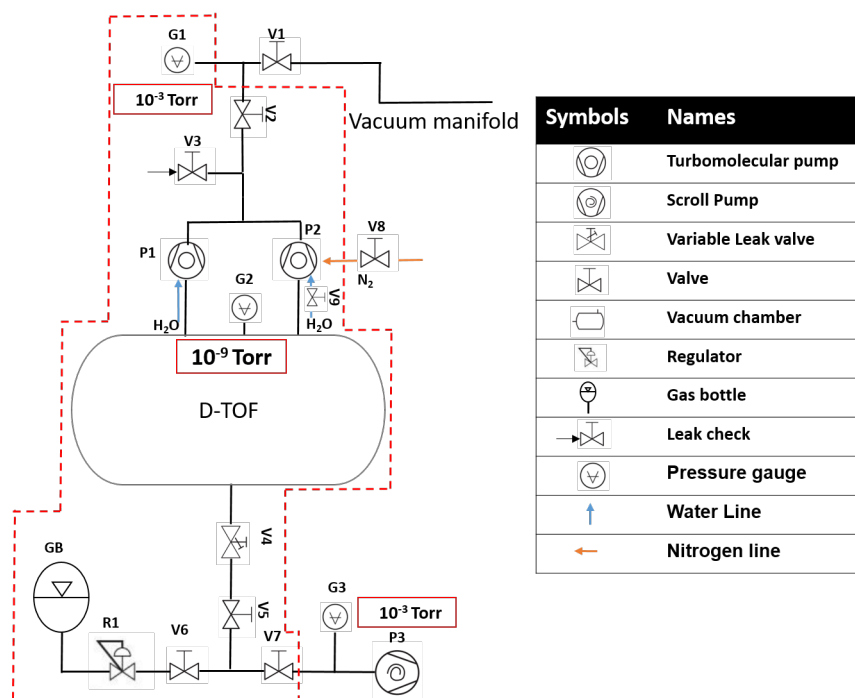


Figure 3.34: D-TOF vacuum schematic in FLAME lab. Red dash line shows D-TOF parts mounted on the stand. The self-contained part consists of 6 valves V2-V7. Valves V5-V7 are used for the gas line and purging line, valve V3 for leak-checking and valve V4 is a Varian precision leak valve. The D-TOF uses two Leybold Turbovac MAG W 600 ip turbo molecular pumps P1 and P2, one hot cathode ion gauge with digital controller G2 to read High vacuum pressure, a thermocouple pressure reader head with analogue reader G1 for rough vacuum pressure, and a gas bottle GB connected to a regulator R1. The parts outside of the red dash line include an Edwards dry scroll vacuum pump P3 and a G3 thermocouple pressure reader serving as the purge line and the vacuum manifold connected to a Pfeiffer (A100L31324) multistage Roots pump for rough vacuum. Speedi valve V1 Connects the D-TOF system to the vacuum manifold in FLAME. A dedicated nitrogen gas line V8 is used for venting. Both turbos are water cooled in series through valve V9.

The D-TOF is connected to a Pfeiffer (A100L) multistage Roots backing pump with a pumping speed of $100 \text{ m}^3/h$ which pumps the setup down to a pressure of 10^{-2} torr. Outside FLAME, there are two independent Roots pump. One is connected to UHV line as shown in Figure 3.35, other is connected to the high gas line. The D-TOF and most of the vacuum setups existing in FLAME are connected to the UHV line.

As shown in Figure 3.34, the red dash line shows the self-contained parts of the D-TOF. This means that the only pumps that stay unchanged when moving from one lab to another

Gas	Molecular Mass M	Mean thermal velocity (m/s)
H_2	2	1761
He	4	1245
H_2O	18	587
Ne	20	557
CO	28	471
N_2	28	471
Air	28.96	463
O_2	32	440
Ar	40	394
CO_2	44	375

Table 3.4: V_{avg} as a function of molar mass M

are the turbo molecular pumps P1 and P2. Turbo molecular pumps P1 and P2 are Leybold Turbovac MAG W 600 ip, with pumping speed of 520 l/s for Argon.

The D-TOF gas delivery system is connected to an Edwards dry scroll pump P3 that achieves pumping speed of $15.1 \text{ m}^3/h$ to purge the gas line.

All the aforementioned pumps are oil-free vacuum pumps. Without baking, the turbo molecular pumps produce UHV inside D-TOF down to 10^{-9} torr. If the Roots pump manifold is not available, the turbos can be used with a dedicated dry pump. Before we start the pumping procedures, let's introduce some terms.

Roots pump: Roots vacuum pump is an oil-free rotary positive-displacement pump. It has two symmetrically-shaped two-lobe or three-lobe impellers which are connected to toothed gears. Rotation of the gears causes the counter rotation of the lobes in the motor housing and the impellers scoop out the air. Since Roots pump are oil free, small compression ratio of 10-100 can be attained [118].

Turbo molecular pump: They operate in the molecular flow regime and their construction is similar to air-craft jet turbine engine. Series of oppositely canted static and motive propellers on a common shaft that have between 20000 to 90000 rpm which makes their edge speed comparable to average molecular velocities [117]. When the gas molecules come down to the column of propellers, as the propeller rotates, they exhaust the molecules

down. The spacing between the static and motive propellers are on the order of millimeter so that essentially larger tolerances could be obtained. The compression ratio k_0 of the turbo molecular pump depends on the molecular mass of the molecules $\log k_0 = \sqrt{M}$. As an example, given the compression ratio of $k_0(He)=3 \times 10^7$ from experiment, for $k_0(N_2)$ we have:

$$\frac{\log k_0(He)}{\log k_0(N_2)} = \sqrt{\frac{4}{28}} = 0.37 \longrightarrow k_0(N_2) = 1.6 \times 10^9 \quad (3.31)$$

which agrees to one order of magnitude with the experimental value of $k_0(N_2) = 2 \times 10^8$. As a result, since the compression ratio depends on the molecular weight, it's very high for oil vapor back-streaming from the pump bearing or exhaust. Therefore, turbo pump provides almost an oil-free vacuum. Magnetic suspension bearing in the turbo pumps is the most recent development which make them free of any lubricant or grease. The turbo pumps in D-TOF usually run with either Roots pump or a scroll pump as a backing pump. With the vacuum chamber at atmospheric pressure, the backing pump is activated and draws the gas right through the body of the turbo pump and brings the pressure down to the order of few millitorr. After sometime the turbo pump will be activated and at full speed after a full day brings the D-TOF pressure down to low 10^{-8} torr.

Scroll pump: It consists of a fixed scroll, movable scroll and a discharge port. The gas is absorbed from the inlet and transformed into the center of the scroll set. As the rotation progresses, the gas pockets form at the center of the scroll housing. In the middle of the scroll housing is a discharge port which exhausts the compressed gas out of the system.

D-TOF Pump Down Procedure

Now that we know the purpose of each vacuum pump as discussed in section 3.1.9, in this section we focus on the pump down procedure and safety protocols. As mentioned in section 3.1.9 the D-TOF is a mobile system. As a result, it can be used with any JRM laser systems. Since D-TOF will be operating in various lab spaces, it is critical to obey all safety protocols.

These can change from lab to lab. Therefore, before pumping down the system, the user should consult with the safety officer in charge.

Moreover, it is important to know the reason behind each action done while working with the vacuum setups, electronics, and laser systems in the lab to avoid any mistakes and damages. The following is a step by step D-TOF pump down procedure in FLAME.

1. Ensure that the D-TOF cart is tightened to the ground. The D-TOF is mounted on a cart that has four wheels with four individual adjustable feet that can be dropped to the ground using a ratchet wrench. Thus, the setup is secured and the turbo pumps with suspended magnetic ball bearings are safe.
2. Ensure that the water line V9 to the pumps are open with water flowing and the nitrogen gas line valve V8 is closed as shown in Figure [3.34](#).
3. Ensure that valve V1 is closed. This valve connects the D-TOF to vacuum manifold and it must be closed for any pump down or venting process.
4. Connect the leak checker or pump cart to Valve V3 and open the valve.
5. Check that valve V2 is open.
6. Turn on the leak checker and start pumping the D-TOF down.
7. Once pressure reaches to 200 millitorr, turn on the D-TOF turbo pumps.
8. Wait until the turbo pumps work at full speed and at this point an optional leak check could be performed. check procedure in section [3.1.11](#) for leak checking.
9. Once the turbos are at full speed, close leak check valve V3 and open valve V1.
10. Turn off the leak checker and seal valve V3 with a KF blank and clamp.

3.1.10 D-TOF Vent Down Procedure

There are times when the D-TOF needs modifications or one requires to move the setup to another lab to use another ultrashort pulse laser system. Therefore, a vent down process becomes necessary. The following venting process is for the case that the gas line is closed and no experiment is running in the D-TOF.

1. Close the gas bottle GB and precision variable leak valve V4 and open valve V7 as shown in Figure 3.34.
2. Close Valve V1 to isolate the D-TOF from the vacuum manifold.
3. Turn off the turbo pumps.
4. Open the valve V3, detach the clamp from valve V3 while the blank KF flange is kept in place.
5. Open the nitrogen line V8. When the D-TOF reaches the atmospheric pressure, the blank flange will automatically fall down.
6. If the D-TOF is open for modification, make sure to open the nitrogen line valve when you are ready to unseal any part of D-TOF. Then cover the open and detached part with aluminum.
7. Close the nitrogen gas line and put the KF blank flange and the clamp back on.

D-TOF Purging Procedure

Before running an experiment, the gas line must be free of any contaminants. This is done by repeatedly purging the gas line.

1. Ensure that the variable leak valve V4 is closed.

2. Open valve V5 with V6 closed. Open valve V7. P3 will pump the gas line up to Variable valve V4.
3. Close valve V7, open gas bottle GB valve for pressure of less than 500 psi and adjust the regulator R1 for pressure of approximately 10 psi. Open valve V6.
4. Close valve V6 and open valve V7. This process purges the gas line. Wait until the pressure decreases to less than 200 mtorr and close the valve V7.
5. Repeat steps 3 and 4 three or four times.
6. With valve V7 is closed and Valve V6 opened, open the variable leak valve V4 for your desired pressure and start the experiment. Make sure that the pressure in the setup doesn't go above 10^{-4} torr while the MCP detector is on. This will damage the MCPs.

Design Considerations for Power Outages

Figure 3.35 shows the FLAME lab vacuum system schematic. As shown in Figure 3.35, the FLAME room has two different vacuum lines called Ultra High Vacuum (UHV) line and a High Gas (HG) line. The D-TOF, COLTRIMS, KAMP, RABBIT, and Eric Wells's setup are connected to the UHV line. This line consists of five Pneumatic valves V1 and V4-V6 (MDC vacuum KGV-2000V). These valves are working with compressed air. If they detect any pressure higher than a user-defined value, they will shut off automatically.

For the case of a power outage, there are three possible situations. Long-term power outages, short-term power outages. For the case of long-term power outages the turbos completely spin down. On the other hand for the short-term case turbos don't have the time to spin down.

During a long-term power outage, if COLTRIM and KAMP are running gas in their experiment, The D-TOF won't be affected since Pneumatic valves V3-V6 will be closed when they detect any high pressure. In contrast, if the D-TOF, RABBIT, or Eric's setup

are running gas in their experiments, all the UHV lines on the right of valve V6 will be affected by each other. For that, an electro-Pneumatic valve replaced with V2 from Figure 3.34 connected to a voltage drop box, will be installed on D-TOF and turbo pumps will be connected to a voltage drop box. Voltage drop box prevents the electronics from turning back on automatically after a power outage. The reset button should be pressed to reactivate the turbos. This procedure prevents any possible damage to the D-TOF and the other two setups. The D-TOF will not be damaged during a long-term power outage if the pressure is less than 10 psi. After a long-term power outage, the user is required to close the gas line and go through the pump down procedure in section 3.1.9

For the case of the short-term power outages, the D-TOF will be isolated from the UHV line and the turbos will completely spin down. If no experiment is running, the user only needs to turn the turbo pumps back on and open the vin valve when they operate at full speed. If the pressure inside the chamber ($> 10^{-3}$ torr), do pump down.

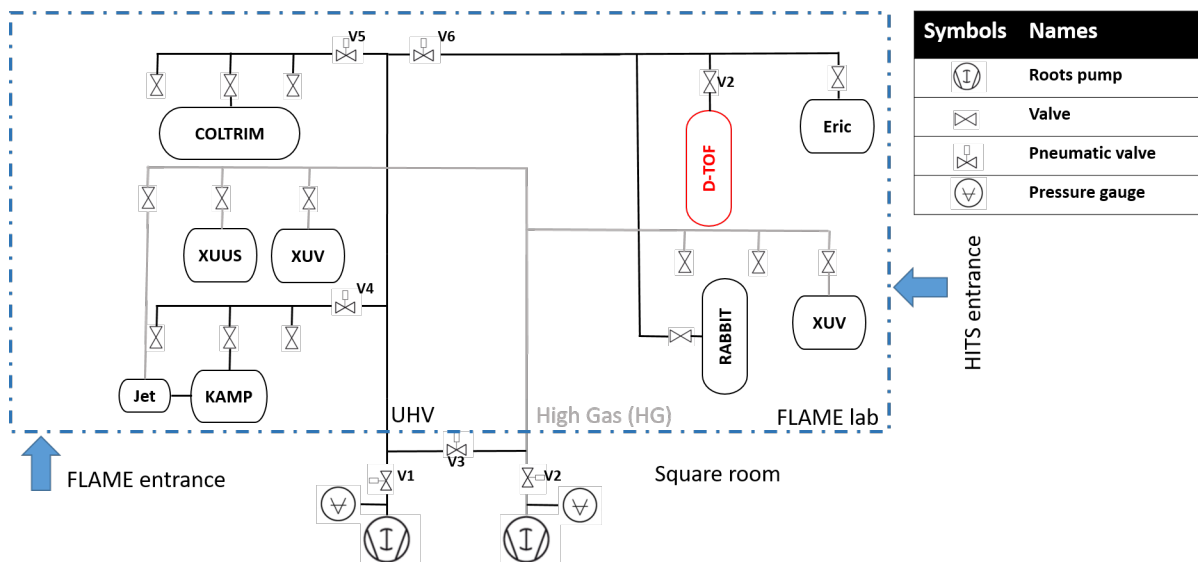


Figure 3.35: FLAME lab vacuum schematic

3.1.11 D-TOF Helium Leak Checking Procedure

JRM is equipped with a Lybold PhoeniXL 300 module Helium leak checker that performs leak checking on vacuum setups. Figure 3.36 shows the leak checker diagram. Here I summarized the operation of PhoeniXL 300 module.

- By pressing the start button, valve V1 and V2a are opened and the sample test (D-TOF) is evacuated through the external pump. All other valves are closed at this.
- When the inlet pressure P1 drops to less than 11 torr, valves V2a and V2b are opened and leak checker starts working in the **gross mode**. In this mode leak rates down to $10^{-8} \frac{\text{mbar.l}}{\text{s}}$ can be detected.
- After the inlet pressure drops to 0.2 torr, leak checker will switch to **fine mode** and reaches to its full sensitivity detection. In this mode, valves V2a and V2b are closed and valve V4a is opened and the gas flow goes through the turbo molecular pump instead.
- When the leak check is stopped, all the valves except valve V2a are closed.
- Valve V3 is opened for venting the leak checker.

The following is the instruction to use the Phoenix leak checker as a pump leak check for D-TOF.

1. Ensure that D-TOF's valve V1 is closed and V2 is open as shown in Figure 3.34.
2. Connect leak checker's inlet port to valve V3 in Figure 3.34.
3. Open Valve V3 in Figure 3.34.
4. Plug in the leak checker and turn on the external roughing pump.
5. Turn on PhoeniXL 300 module.

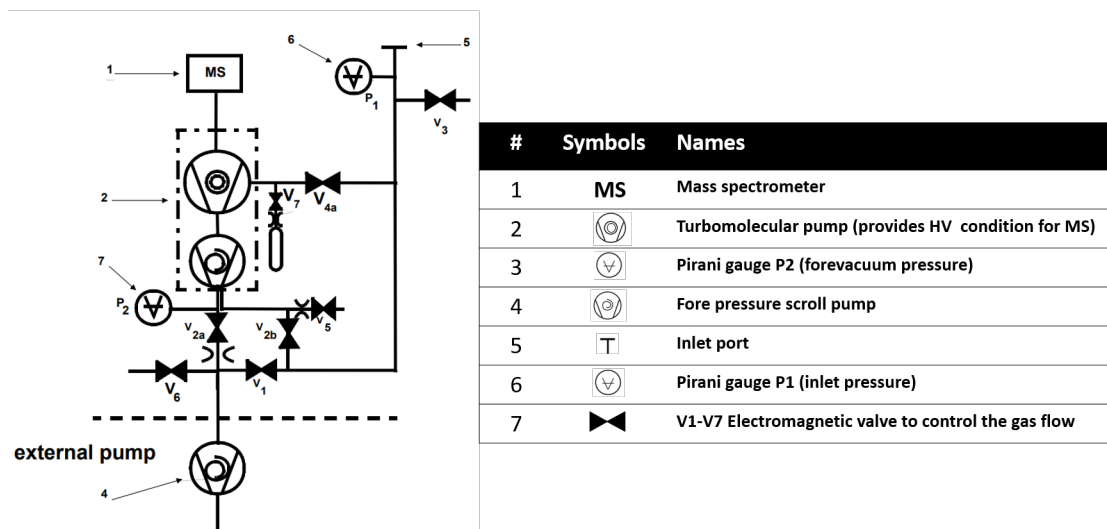


Figure 3.36: Leybold PhoeniXL 300 Module Leak checker vacuum diagram

6. Wait until the leak checker's turbo pump starts working at full speed. Push the start the start button, then wait for pressure < 0.6 torr and it switches to fine mode.
7. Open the Helium gas bottle and adjust the regulator such that little pressure is sensed when gas is sprayed on your lips.
8. Spray helium to D-TOF's different junctions and each time wait few seconds for the leak checker's response. It is recommended to start leak checking at the top of the chamber.
9. If the leak checker's Mass Spectrometer MS doesn't show any change in pressure on the screen, the D-TOF doesn't have any physical leak.
10. Close valve V3 on D-TOF, and seal it with a KF blank and a clamp.
11. Press leak checker's stop button.
12. Press vent button, turn off the leak checker, and disconnect it from D-TOF.

3.2 Electron Spectrometer Calibration

From the TOF (t_{TOF}) of an electron and the traveled distance (L), the kinetic energy of the electron can be determined using the equation:

$$E = \frac{1}{2}m_e \left(\frac{L}{t_{TOF}} \right)^2 \quad (3.32)$$

Typically, the energy is on the range of zero to a few keV, making relativistic effects negligible (the rest mass energy of an electron is 0.51 MeV). There is a systematic offset between the detected ($t_{\text{detection}}$) and the actual TOF (t_{TOF}) due to the cables and electronics, expressed as $t_{\text{detection}} = t_{TOF} + t_0$. Thus, t_{TOF} is modified to $t_{\text{detection}} - t_0$, with $t_{\text{detection}}$ being the TDC's timing and t_0 the delay that needs to be identified. This adjustment yields the revised formula:

$$E = \frac{1}{2}m_e \left(\frac{L}{t_{\text{detection}} - t_0} \right)^2 \quad (3.33)$$

Figure 3.37a illustrates the electron counts as a function of $t_{\text{detection}}$ from the ionization of argon atoms at the MPI regime, revealing the ATI. The Tangor 300 (Amplitude LASER) was used with a power of $8.62 \pm 2\%$ W (Tangor output at 43%) and a pulse duration of 450 fs for this measurement.

The D-TOF pressure was set at 2×10^{-4} torr. A 150 mm focusing lens (LA1433-C BK7 C coated) plano convex lens was used, and the runtime was set at 10 minutes. The inset shows the zoomed in ATI between 60 to 200 ns. This region is one of the region of interest in our group currently under study. Similarly, Figure 3.37b shows the electron counts as a function of $t_{\text{detection}}$ for ATI peaks captured by the PCB detector with the FLAME laser. The laser power was set at $29.5 \pm 5\%$ mW, with a wavelength of 815 nm, a pulse duration of 30 fs, and a focusing lens of $f = 100$ mm (LA1509-B Thorlabs) was used. The D-TOF pressure was set at 2×10^{-4} torr, and the runtime was 180 minutes. As seen in Figure 3.37, the ATI peaks are not equally spaced in time; however, they are equally spaced in energy,

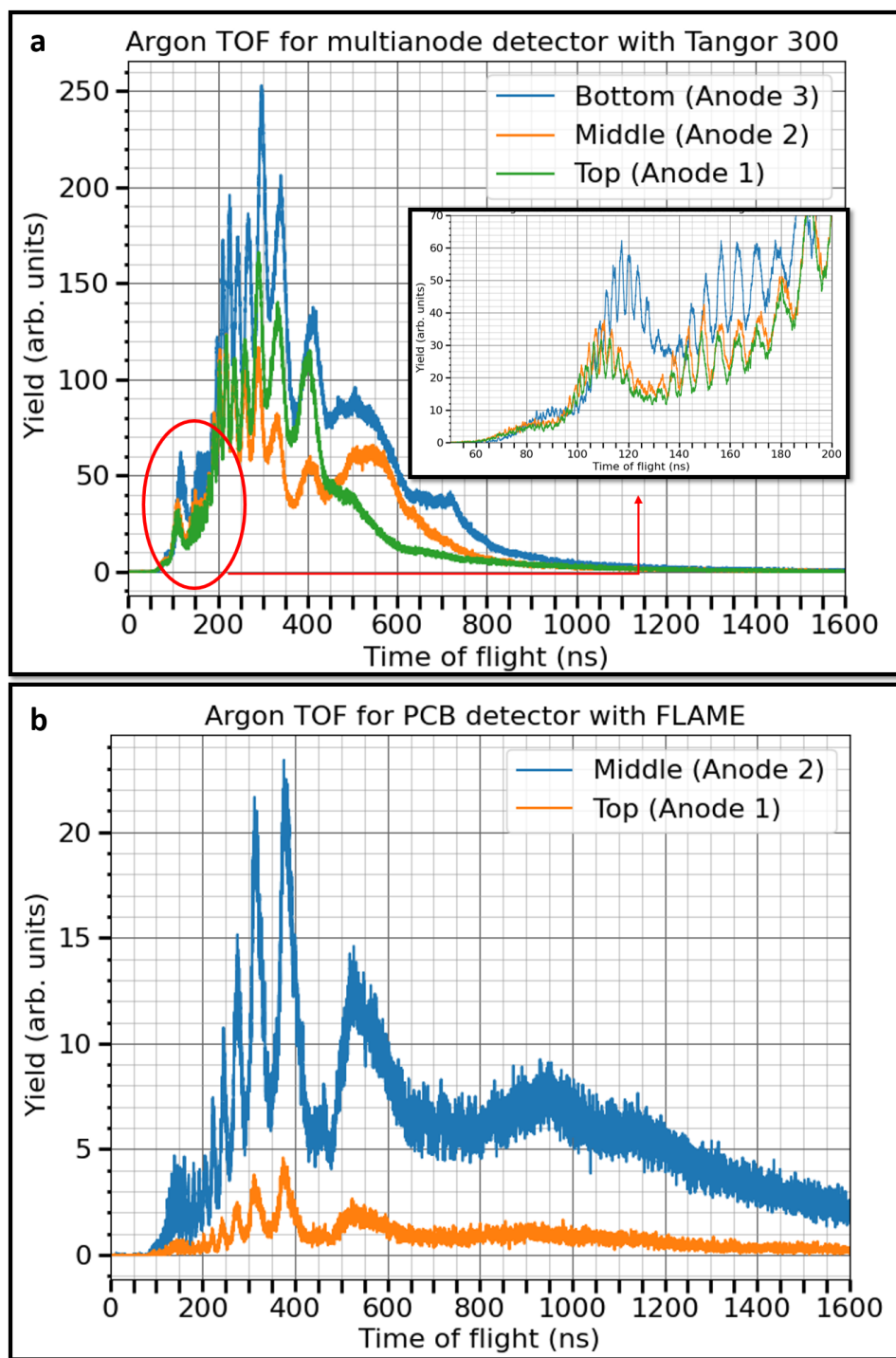


Figure 3.37: a: TOF captured by multi-anode detector taken by Tangor 300 . The inset shows zoomed in plot at the ATI between 60 to 200 ns. b: TOF captured by PCB detector taken by FLAME laser.

corresponding to the laser photon energy of 1.20 eV for 1030 nm and 1.52 eV for 815 nm. The ATI characteristic helps to determine t_0 and L . Since the time-to-energy conversion scale depends on t_0 and L , the spacing of the peaks in the converted spectrum also depends on these parameters. Thus, the appropriate t_0 and L can be identified by finding the best fit of the ATI peaks to the photon spacing.

Consequently, Figure 3.38a shows the calibrated TOF in energy for Figure 3.37a and the inset shows a zoomed in picture within 15 to 40 eV.

Figure 3.38b depicts the calibrated data for 3.37b respectively. Note that converting the signal as a function of time (f_t) to a function of energy (f_E) necessitates the conversion Jacobian dt_{tof}/dE . From Equation 3.32, it follows that $dt_{tof}/dE \propto E^{-\frac{3}{2}}$.

In this setup, only electrons emitted along the TOF axis (with a finite acceptance angle of $\pm 2^\circ$) will reach the detector. For example, the spectrum in Figure 3.38 was measured with the laser polarization parallel to the TOF axis, so the measured electrons were those emitted along the laser polarization. To measure PES at a different emission angle θ , the angle between the TOF and the laser polarization must be set to θ . This can be achieved by rotating the laser polarization using a half-wave plate.

We can easily determine the relative error from Equation 3.32 based on the relative errors of two parameters:

$$\frac{\Delta E}{E} = 2 \frac{\Delta L}{L} + 2 \frac{\Delta t_0}{t_{detection} - t_0} \quad (3.34)$$

For very low energy electrons, their time of flight ($t_{detection}$) is very long, and from the above equation, it is evident that the calibration fit is primarily influenced by the relative error in the spectrometer's length. Conversely, for very high energy electrons, the denominator of the last term on the right side of Equation 3.34 can be quite small, making the relative error highly sensitive to t_0 . Additionally, the relative error in energy is not uniform across the spectrum due to the presence of the $t_{detection}$ term in E. The performance of the D-TOF spectrometer is illustrated in Figure 3.39a and is compared with the performance

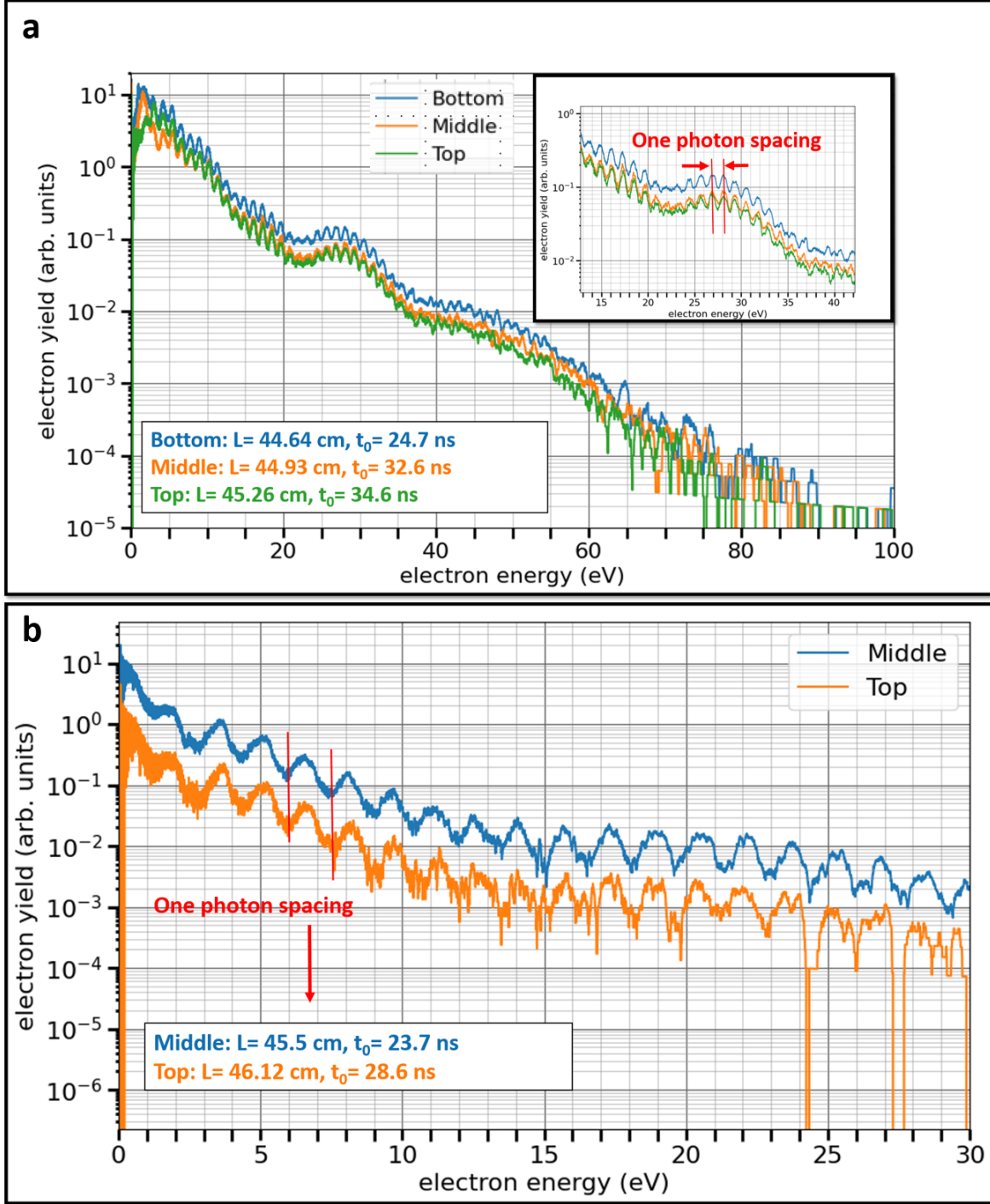


Figure 3.38: a: shows the PES for the multi-anode detector taken with the Tangor 300 LASER. The inset shows a zoomed in picture from 15-40 eV. b: The PES captured with the PCB detector taken with the FLAME LASER.

of the TOF spectrometer at OSU, shown in Figure 3.39b. Figure 3.39a provides a detailed view of the photoelectron spectrum (PES) for the first ATI peaks and the corresponding Rydberg structures.

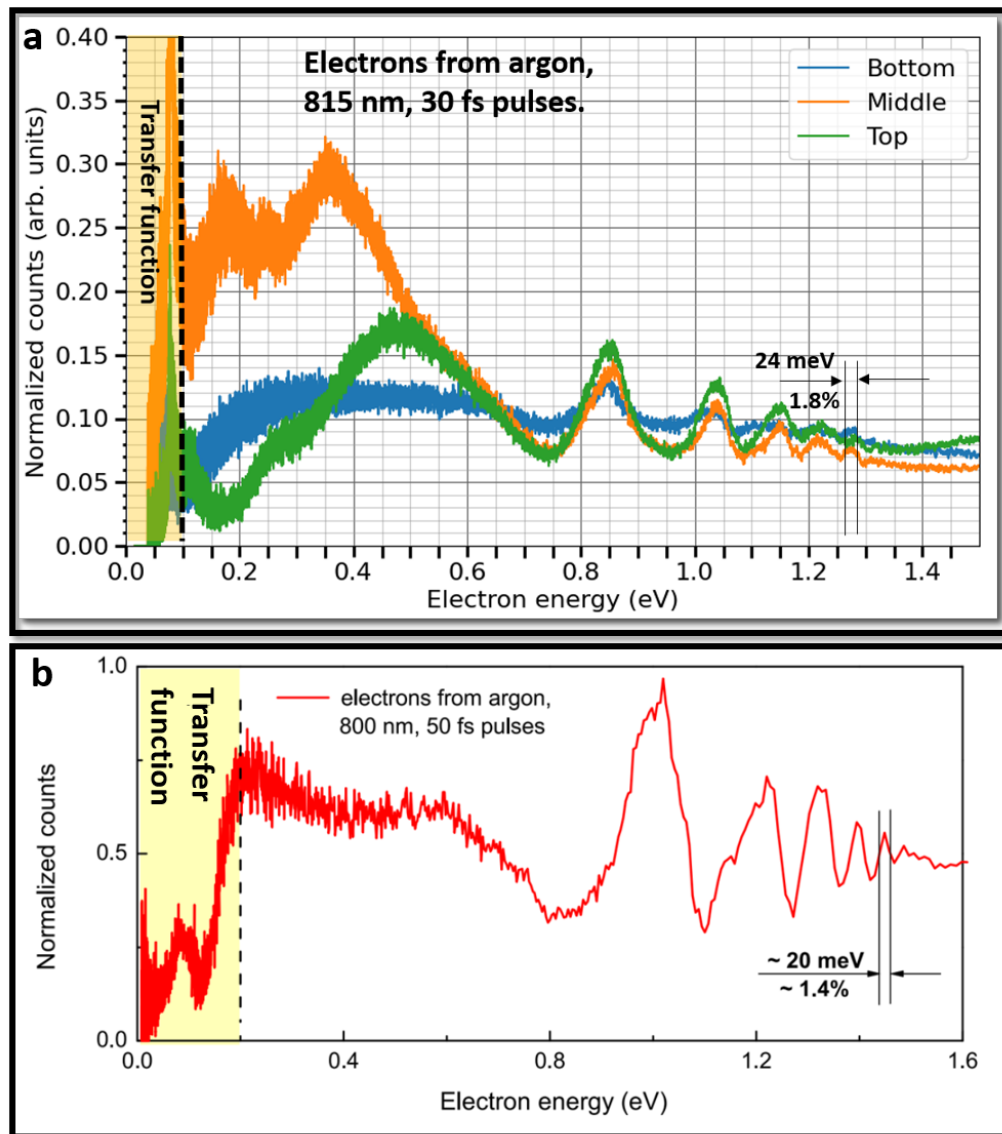


Figure 3.39: a: Performance of the D-TOF spectrometer for electrons from argon using 815 nm, 30 fs pulses. b: Performance of the TOF spectrometer at OSU for electrons from argon using 800 nm, 50 fs pulses.

These were obtained using the FLAME laser with a pulse energy of 65 mW, a pulse duration of 30 fs, a wavelength of 815 nm, and a chamber pressure of 1×10^{-4} torr. The

data indicates that below 0.1 eV, the transfer function of the D-TOF spectrometer reaches down to zero eV, whereas for the TOF spectrometer at OSU, the transfer function starts below 0.2 eV, which is characteristic of field-free TOF spectrometers. The relative energy resolution of the selected Rydberg peak for the D-TOF is 1.8%, which is comparable to the relative energy resolution of 1.4% for the TOF spectrometer at OSU.

3.3 Mass Spectrometer Calibration

In TOF setup, measuring the PES does not directly reveal the final state of the ion parent atoms or molecules. For instance, detecting two electrons from a single laser pulse could either stem from a double ionization of one atom or from two separate single ionization of two different atoms. While one scenario might be more likely than the other, it is impossible to distinguish between them using only electron spectroscopy. The goal of ion measurement is to determine the charge state distribution of the ionized target atoms. Additionally, for molecules, we can identify the fragment distribution resulting from dissociation, provided that the fragments are charged.

To conduct TOF mass spectrum measurements of ions, static voltages are applied to the molybdenum plates shown in Figure 3.12. The electrostatic fields generated across these plates accelerate the ions toward the MCP detector. The main difference between electron and ion measurements is that the velocity gained by the electrons originates from the laser field, whereas the ions gain most of their velocity from the applied static field. The electrostatic field collects most of the ions in the middle anode. First, Positive V_2 voltage is applied to plate 4 (450 V) and the ions at the center of interaction are repelled towards the aperture of plate 3 due to the electric field produced. Next, positive V_1 voltage ($V_1 < V_2$) is applied to plate 3 and the ions will be extracted. Plates 2 and 1 are grounded. After passing through the aperture of plates 2 and 1, the ions drift along the field-free region of the flight tube and reach the MCP detector. For optimal resolution of the ion mass spectrum, the

voltages are adjusted to satisfy the Wiley-McLaren condition [95]. The velocity of an ion with mass m and charge q at the aperture of plate 3 (extractor) is given by

$$v = \sqrt{\frac{2qV}{m}} \quad (3.35)$$

where V is the electric potential at the ionization position and for our case ($V = \frac{V_1+V_2}{2}$) (the laser focus), and the initial velocity of the ion is assumed to be negligible. Thus, the relationship between the mass-to-charge ratio of an ion and its TOF is:

$$t_{TOF} = \sqrt{\frac{m \times L^2}{q(V_1 + V_2)}} \quad (3.36)$$

where V is the electric potential at the ionization position and for our case ($V = \frac{V_1+V_2}{2}$) (the laser focus), and the initial velocity of the ion is assumed to be negligible. Thus, the relationship between the mass-to-charge ratio of an ion and its TOF is:

$$t_{TOF} = \sqrt{\frac{m \times L^2}{q(V_1 + V_2)}} \quad (3.37)$$

where m is the mass of the atom or molecule under study, L is the length of the ToF spectrometer, and q is the charge of the ion parent. Let's perform some calculations based on Equation 3.37 for singly ionized argon ($m_{Ar} \approx 6.6 \times 10^{-26}$ kg) while voltages $V_1 = 450$ V and $V_2 = 250$ V are applied to the field plates. $L = 45$ cm for the case of the D-TOF and $q = 1.6 \times 10^{-19}$ C.

By plugging these values into Equation 3.37:

$$t_{TOF} = \sqrt{\frac{6.6 \times 10^{-26} \text{ kg} \times (0.45 \text{ m})^2}{1.6 \times 10^{-19} \text{ C} \times 700 \text{ V}}} \quad (3.38)$$

$$t_{TOF} \approx 1.0937 \times 10^{-5} \text{ s} = 10.937 \mu\text{s}$$

For the Tangor 300 laser operating at 100 kHz, each laser pulse is emitted every 10 μ s, meaning the ion parent reaches the MCP detector after the next laser pulse. One way to address this issue, the repetition rate of the laser should be reduced to be slower than the TOF of the ion parent. In our setup, we set the Tangor 300 to a 20 kHz repetition rate, corresponding to 50 μ s. Figure 3.40 shows the Methane mass spectrum. Figure 3.40a shows the methane Mass spectra reproduced from national institute of standard technology (NIST) [119] which they utilized gas chromatography to record this data and Figure 3.40b shows the methane mass spectra recorded by the PCB detector using the Tangor 300 with 1 W power while the repetition rate was set at 20 kHz due to the reason mentioned earlier.

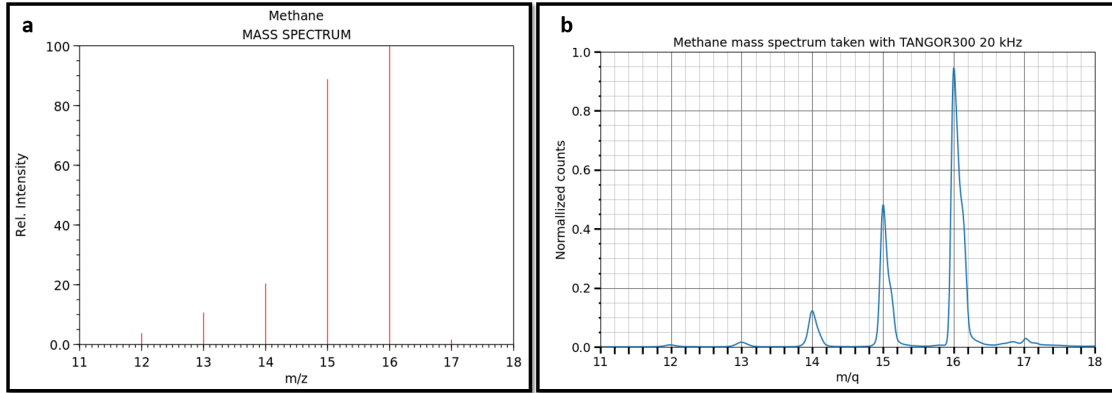


Figure 3.40: a: Mass spectrum of Methane taken with electron impact. reproduced from [119]. b: Mass spectrum captured by PCB detector taken by tangor300.

For this data, repeller voltage V_1 was set at 400 V and the extractor voltage V_2 was varied between from 200 V to 270 V in steps of 10 V and integrated number of Counts for CH_4^+ (the peak located at $m/q=16$) from mass spectra were calculated for the same runtime of 10 minutes for different extractor voltages and optimized value was found to be 240 V as shown in Figure 3.41. The rest of the field plate voltages were set at 0 V.

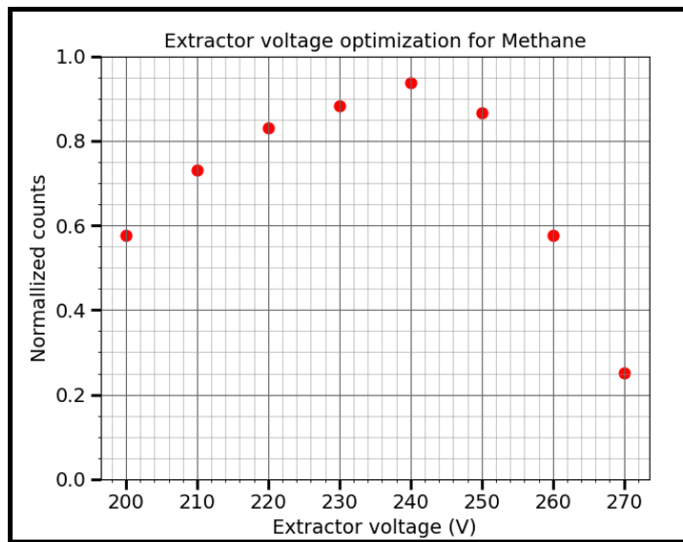


Figure 3.41: Extractor voltage optimization for methane.

3.4 Experimental Detail for Recording Photoelectron Angular Distribution

Photoelectron angular distributions (PADs) were obtained for multi-anode detector using Tangor 300 with wavelength of 1030 nm, pulse duration of 450 fs, pulse energy of 62.5 μJ , and intensity of $60 \pm 5 \text{ TW/cm}^2$. The target gas, argon in this case, was introduced effusively via a precision leak valve. Operating pressure of 2×10^{-4} torr was adjusted to ensure high data collection rates without space-charge effects. A linearly polarized laser with a positive lens $f = 150$ mm (LA1433-C BK7 C coated Plano convex lens) was used to minimize the focal volume and background gas contribution. As shown in Figure 3.42a, the angle φ between the laser polarization and D-TOF spectrometer axis was controlled with a zero-order half wave plate (HWP) as indicated in 3.42a.

The collection angle of each anode is $\pm 0.7^\circ$ (12 mm diameter and a flight tube of 45 cm long). Rotating the HWP every 2° , changes the detected angle by 4° . Given the geometry of the setup, the angular distributions were recorded exclusively for electrons emitted in the plane perpendicular to the laser propagation direction (aligned along the

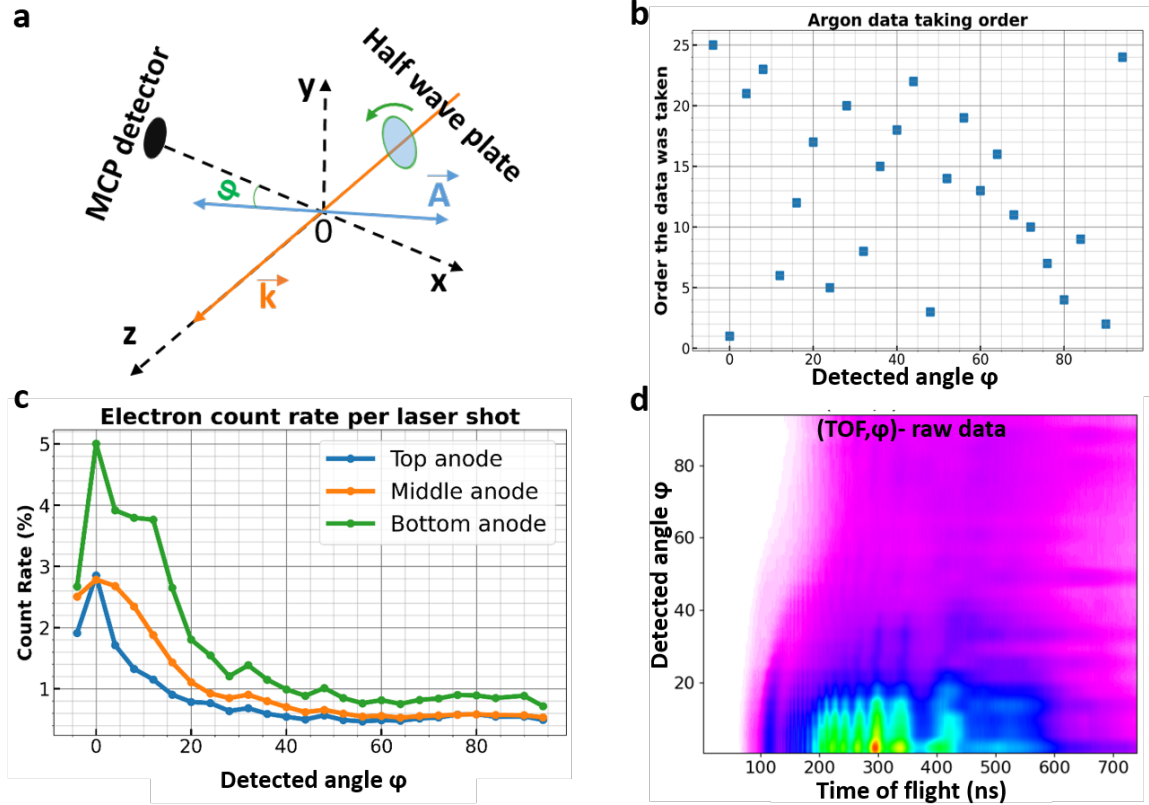


Figure 3.42: Setup for recording photoelectron angular distribution (PAD). a: Experimental setup for recording TOF in the x-y plane for various angles φ between the spectrometer axis and the laser polarization. b: Order of data collection for each angle (example data at $1.03 \mu\text{m}$ at intensity of $60 \pm 5 \text{ TW}/\text{cm}^2$ in argon is used). c: Count rate plotted as data was acquired, with smooth curves indicating stable experimental conditions. d: Raw TOF angular distributions dataset plotted in logarithmic scale for the summation of all anodes in multi-anode detector.

z-axis as shown in as shown in Figure 3.42a). However, the emission exhibits cylindrical symmetry along the laser polarization axis when linearly polarized light is used, thus the distribution in the x-y plane appears identical to that in the x-z plane. To obtain the 2D PAD, spectra for detected angle φ from -4° to 94° in 4° steps were collected randomly using a python random generator as shown in Figure 3.42b to eliminate systematic errors due to experimental condition changes. The reason for collecting TOF data at angles -4° and 94° is due to the separation of the anodes by 4° (3.175 cm separation from center to center and a flight tube length of 45 cm). Therefore, if the middle anode detects an angle φ , the detected

angles for the top and bottom anodes are $\varphi + 4^\circ$ and $\varphi - 4^\circ$, respectively. Consequently, to create a complete PAD for the top and bottom anodes, data must also be collected at these angles. The electron count rates for each anode were collected and monitored while collecting the TOF at each angle as shown in Figure 3.42c. Significantly different count rates for consecutive angles typically indicate a change in experimental conditions, prompting a thorough check of the entire setup for consistency. After completing the angular distributions of anodes for all angles, the summed up TOF data is plotted on an intensity graph with a logarithmic scale as shown in Figure 3.42d.

3.5 Procedure to Obtain 2D Angular Distribution Momentum Plots

After collecting the data for each angle of all anodes, the TOF data shown in Figure ??d was converted to momenta (as shown in Figure 3.43).

For this transformation, the required Jacobian is $J_1 = p^2$, where p is the measured momentum. Subsequently, the data was converted from a (p, φ) plot to a (p_x, p_y) plot using the appropriate Jacobian $J_2 = p$ and by interpolating the angular dependence for all momenta. This transformation is illustrated in Figure 3.44 for top, middle, bottom and summation of all the anodes for multi-anode detector. The (p_x, p_y) plot is presented for all four quadrants, but the data was recorded for only one quadrant and then symmetrized for display purposes (this was done only after verifying that the HWP produced symmetric distributions across the entire range). A close examination of Figure 3.44 reveals that the center of the images (warm colors) contains most electrons. These low momentum electrons are direct electrons that have not scattered and are not useful for LIED. As we will discuss later, they cause the differential cross section (DCS) in Figure 3.44 to start at $\theta = 20^\circ$ rather than $\theta = 0^\circ$. However, the LIED-relevant region comprises the green and blue areas, representing higher momentum electrons that have rescattered on their parent ion, revealing

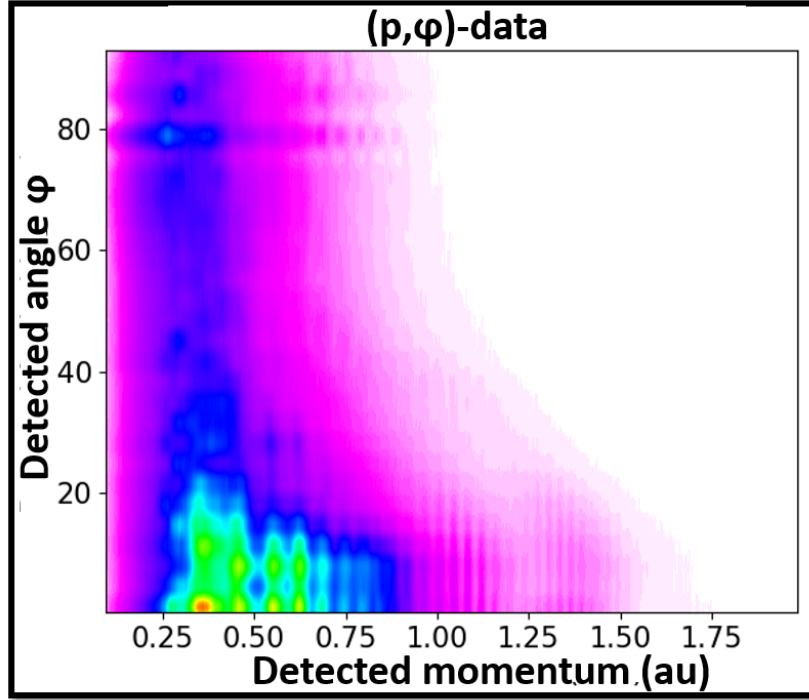


Figure 3.43: The (p, φ) distribution obtained from the TOF data for argon using Tangor 300 for multi-anode detector.

spatial information. These electrons are significantly fewer compared to direct electrons. Therefore, to obtain a good PAD and DCS, it is crucial to record data with good statistics in this region. For the data in Figure 3.44, this was achieved using 100 kHz repetition rate Tangor 300 at acquisition times (10 minutes per φ value).

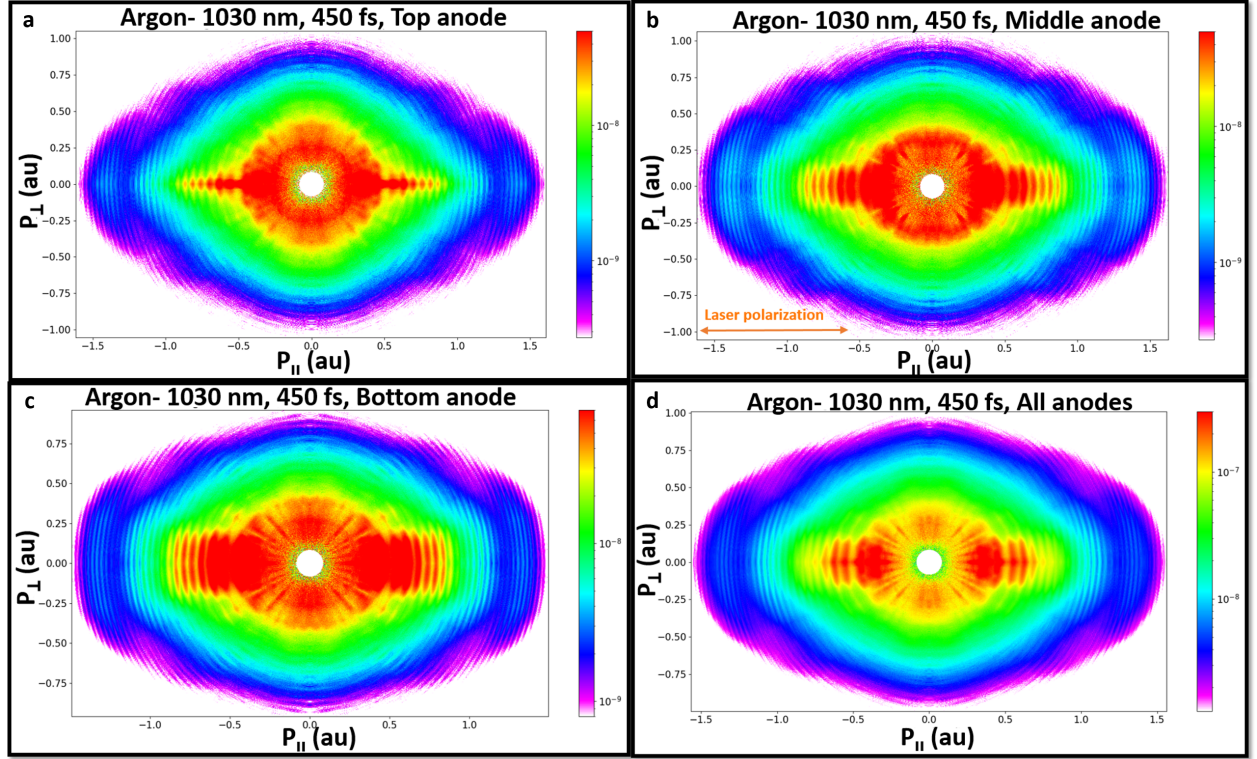


Figure 3.44: Momentum distribution in Cartesian coordinates obtained from the (p, θ) data for Argon at 1030 nm, 450 fs. (a) Top anode, (b) Middle anode, (c) Bottom anode, (d) All anodes combined. The distribution shows the detected momentum $p_{\parallel}$ versus $p_{\perp}$.

Chapter 4

Experimental Findings and Theoretical Analysis of LIED in Molecular Isomers

This chapter starts with an analogy between the diffraction of light and the diffraction of electrons. This comparison serves as a foundation to better understand the principles behind electron diffraction, leveraging the well-established concepts of LIED. Using this analogy, I delve into the procedure to extract the electron yield from the 2D momentum obtained from PAD and how it's linked to Quantitative Rescattering (QRS) theory. The QRS theory provides a robust framework for interpreting the PAD data, which is crucial for deriving accurate DCS values. The electron yield showcased as an example in this chapter is derived from the PAD presented in the previous chapter, all highlighting the practical operational efficacy of the D-TOF spectrometer in LIED experiments.

Furthermore, I will show the results regarding the butane isomers. In the results LIED offers a compelling alternative because the electron yield of the molecules under study highly depends on the shape of valence orbitals, thereby creating distinct diffraction patterns for isomers with different electronic structures. In this chapter, we present theoretical and

experimental evidence demonstrating the capability of LIED to effectively distinguish between n-butane and isobutane. The underlying principle is elucidated through modeling of the multiorbital tunnel ionization of the molecules and the subsequent rescattering of the ionized electron with the molecule. Our findings highlight LIED as a powerful technique for identifying molecular isomers and shed light on its potential for simultaneously probing nuclear and electronic structure of a molecule. For the case of the electronic structure, Analysis of multiorbitals of butane isomers were taken into account in the ionization rate and in the DCS extracted from LIED model which is called the tunneling ionization independent atom model, tunneling ionization rate of the isomers is involved. The trend of the latter DCS agrees well with the experiment, while the trend of the DCS obtained from the IAM significant deviates from the experiment. The agreement between the theory and experiment suggests that LIED can resolve structural differences among isomers because it is sensitive not only to their molecular structure but also to the shape of their valence orbitals.

4.1 From Diffraction of Light to LIED

Diffraction and interference are crucial techniques for imaging. To elaborate, let's consider the example of Fraunhofer diffraction from a circular aperture. When a laser strikes a small opaque circular object, it creates a pattern known as the Airy disk, observable on a far distant screen as shown in Figure 4.1a.

At any specific laser wavelength, the intensity of light, $I(\theta)$, varies with the deflection angle θ relative to the central maximum as shown by the equation:

$$\frac{I(\theta)}{I(0)} = \left[\frac{2J_1(kD \sin(\theta))}{kD \sin(\theta)} \right]^2 \quad (4.1)$$

where $k = \frac{2\pi}{\lambda}$ is the photon wavenumber, D is the diameter of the aperture, and J_1 is the first-order Bessel function.

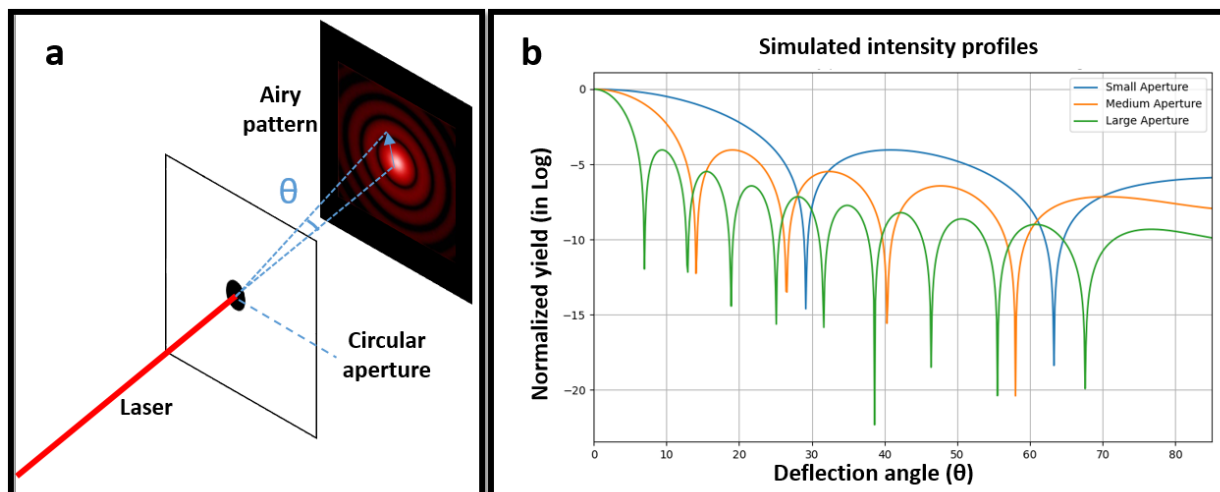


Figure 4.1: (a) A typical setup for observing diffraction through a circular aperture. When a laser beam illuminates the aperture, it produces the characteristic Airy disk pattern of concentric rings on a screen positioned behind the aperture. (b) Simulated intensity profiles as a function of deflection angle θ , plotted for three different aperture sizes: small, medium, and large. The arrows indicate the angular positions of the first diffraction minimum.

Figure 4.1b illustrates the normalized radial intensity distribution for three different aperture sizes: small ($D = 1 \mu\text{m}$), medium ($D = 2 \mu\text{m}$), large ($D = 4 \mu\text{m}$), and laser wavelength of 800 nm. With increasing aperture size, the number of minima and maxima, determined by the zeros of the Bessel function, increase. Measuring the light wavelength and the angles where intensity fades allows precise determination of the aperture's diameter.

Additionally, if the laser encounters two separated obstacles at a distance R , the resulting interference pattern grows more complex, resulting in an intricate Airy pattern across each aperture, creating fringes whose separation is dependent on R . Therefore, when the wavelength of light is known, examining the diffraction and interference patterns enables the accurate determination of both the diameter D of the obstacle and its separation R .

Similarly, a diatomic molecule can be conceptualized as two atomic structures separated by a distance R . Historically, the interaction of X-rays with matter has been weak, limiting their use in structural analysis of isolated molecules until the innovation of high-brightness synchrotron and free-electron laser sources [120].

The significant shift in perspective occurred in 1924, introduced by Louis de Broglie, who suggested that matter possesses inherent wave-like characteristics, shown by the relation $m \cdot v = \frac{h}{\lambda}$ where m and v represent the mass and velocity of a particle, h is Planck's constant, and λ denotes the wavelength. For example, for an electron with a kinetic energy of 100 eV ($1\text{eV} = 1.6 \times 10^{-19}$ Joules), the corresponding de Broglie wavelength is $\lambda_{\text{dB}} = \frac{h}{(2m_e E)^{1/2}} = 1.23 \times 10^{-10}$ m, where $m_e = 9.31 \times 10^{-31}$ kg and $h = 6.626 \times 10^{-34}$ J-s.

Since electrons are charged particles, their scattering cross section is significantly higher, by five to six orders of magnitude, compared to X-rays [121]. This attribute has made electron diffraction a preferred method for the detailed study of small molecules in the gas phase.

Before starting to study a detailed molecular analysis, it is worth examining the simplest cases, which are atoms. When atoms are subjected to electron beam scattering, they reveal intricate patterns that vary with atomic size. Figure 4.2 presents elastic differential cross sections for a 100 eV electron beam scattering on argon (Ar), krypton (Kr), and xenon (Xe). The data, extracted from NIST [122], underscores that larger atoms, such as xenon, result in more complex diffraction patterns. Thereby, this is exactly what the single aperture data in Figure 4.1b shows.

The comparison between light and electron concludes when addressing the theoretical treatment of light, typically modeled as a classical field, as detailed in equation 4.1. For electrons, the approach transitions to quantum mechanics, starting from the inhomogeneous Schrödinger equation for elastic scattering as given by [121]:

$$\Delta\psi + p^2\psi + \frac{2m_e e}{\hbar^2}\Phi\psi = 0 \quad (4.2)$$

The total wavefunction $\psi = \psi_0 + \psi'$, ψ , combines the incoming wave, ψ_0 , satisfying $\Delta\psi_0 + p^2\psi_0 = 0$, with the spherical scattered wave, ψ' , influenced by potential Φ . For cylindrical symmetry [121]:

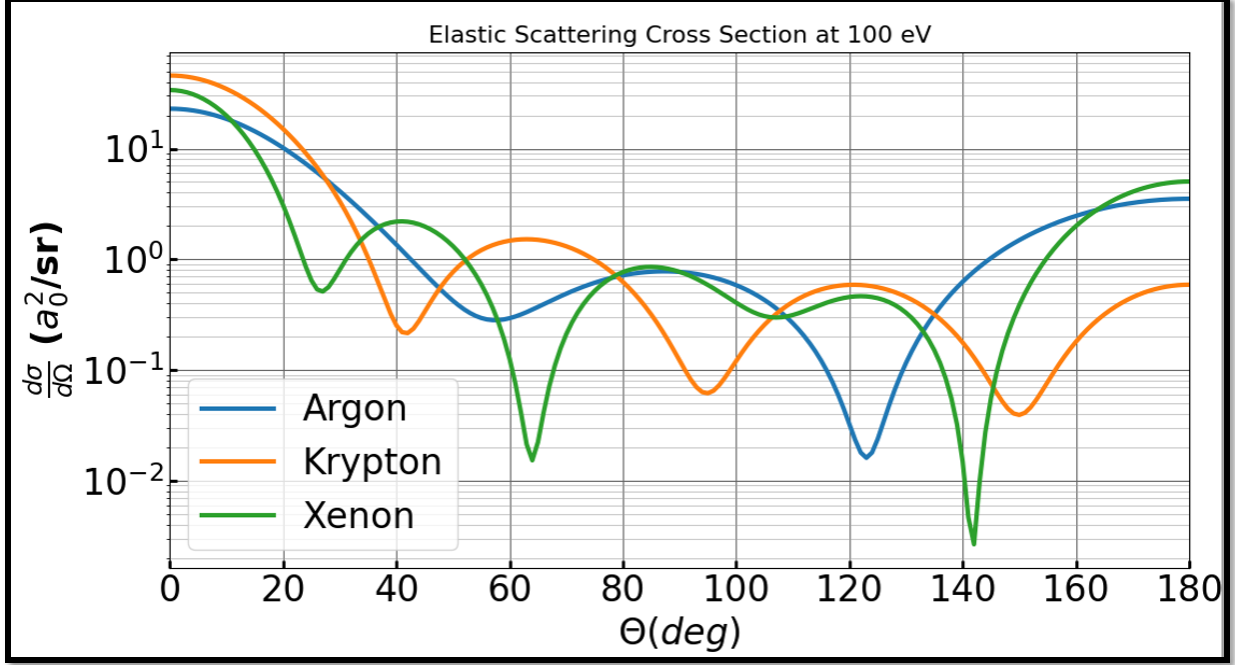


Figure 4.2: Elastic differential cross sections of a 100 eV electron beam scattering off noble gases Argon (Ar Z=18), Krypton (Kr Z=36), and Xenon (Xe Z=54), extracted from [122]. This figure illustrates the increased complexity in diffraction patterns corresponding to larger atomic sizes, evidenced by a greater number of minima and maxima.

$$\psi' = \frac{A}{R} f(p, \phi) e^{ipR} \quad (4.3)$$

where A is a normalization constant, and $f(p, \phi)$ is the complex scattering amplitude. Expanding this using partial waves [121]:

$$f(p, \phi) = \frac{1}{2ip} \sum_{j=0}^{\infty} (2l+1)(e^{2i\delta_l} - 1)P_l(\cos(\phi)) \quad (4.4)$$

Where $P_l(\cos(\phi))$ denotes the Legendre polynomial of order l . The phase shifts δ_l , dependent on the electron's energy and the potential Φ , interpret the delay the incoming electron wave undergoes as it passes by the atom. Ultimately, the expression for the intensity of the scattered electrons, I_s , is derived by calculating the probability current, resulting in [121]:

$$I_s(p, \phi) = \frac{I_0}{R^2} |f(p, \phi)|^2 \quad (4.5)$$

Here, I_0 denotes the incoming electron intensity. Given that the dependency on R^{-2} conforms to the well-established inverse square law for spherical waves, it is crucial to recognize that all angular dependencies in the scattering process are encapsulated within the scattering amplitude.

Calculating scattering amplitudes typically presents significant challenges that extend beyond the scope of this chapter. Notably, at electron energies exceeding 5 keV, the potential Φ can generally be addressed using the static-field approximation, with the atom considered as a static charge distribution [123]. However, in the setting of LIED, where electron energies usually fall within the 50 to 300 eV range, these simple static-field and static-exchange approximations prove insufficient, necessitating more complex models [124]. Nevertheless, as illustrated in Figure 4.4, even at energies as modest as 100 eV, contemporary theoretical models show excellent agreement with experimental results, underscoring the efficacy of LIED as a precise and valuable tool for ultrafast molecular imaging.

Developing a theoretical framework for scattering signals from molecules is inherently complex. Nonetheless, the kinetic energy of incoming electrons usually far exceeds the binding energies of valence electrons, which are predominantly responsible for electron scattering at large angles. In this context, the scattering experiments are less influenced by the molecular chemistry.

In the independent atom model (IAM), it is assumed that the scattering from one atom does not affect the scattering from its neighbors. The scattered wave from a molecule composed of N atoms fixed in space can be described by the equation [121]:

$$\psi(\vec{\mathbf{R}}) = \frac{KA}{R} e^{ip_0 R} \sum_{i=1}^N f_j(\phi) e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{R}}_i} \quad (4.6)$$

Where $|\vec{\mathbf{q}}| = |\vec{\mathbf{p}} - \vec{\mathbf{p}}_0| = 2p \sin(\phi/2)$ is the momentum transfer and $\vec{\mathbf{R}}_i$ are the coordinates

of the i^{th} atom as shown in Figure 4.3. Given that molecules in a gas are randomly oriented, the measured scattering signal results from an incoherent sum of all possible orientations.

Given that each molecular orientation occurs with equal probability, when we introduce the internuclear separations, represented as $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$, it becomes possible to perform a spatial average of equation 4.5. This averaging process results in a derived scattering signal expressed as $I_s(p, \phi)$ [121]:

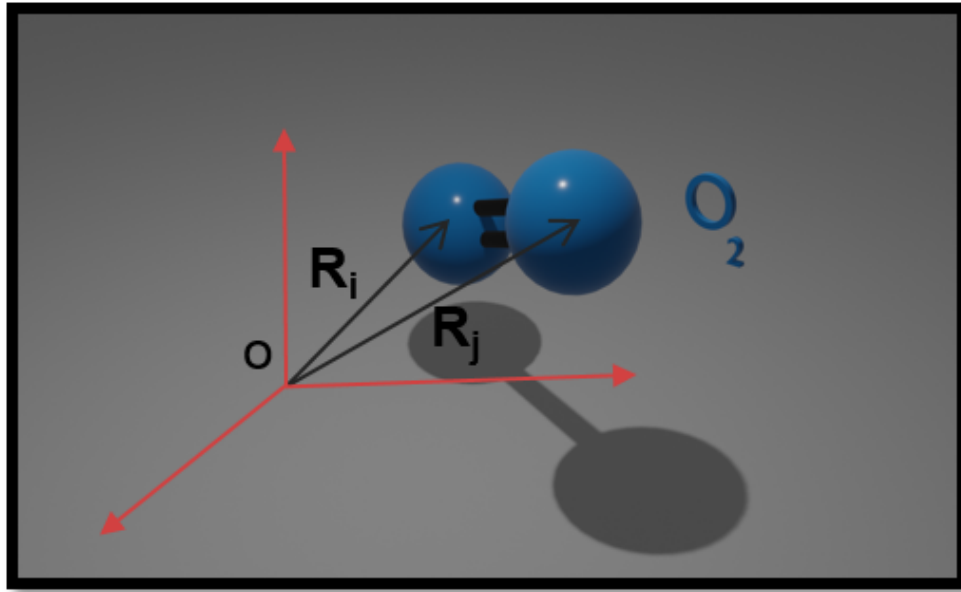


Figure 4.3: Illustration of the independent atom model (IAM). The coordinates $\vec{R}_i$ and $\vec{R}_j$ represent the positions of the i^{th} and j^{th} atoms, respectively. The internuclear separation, represented as $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$.

$$I_s(p, \phi) = \frac{K^2 I_0}{R^2} \left[\sum_{i=1}^N |f_i(p, \phi)|^2 + \sum_{i=1}^N \sum_{j=1, i \neq j}^N f_i(p, \phi) f_j^*(p, \phi) \frac{\sin(qR_{ij})}{qR_{ij}} \right] \quad (4.7)$$

Since I_0 is typically a constant, K is a scalar, and R is approximately also a constant for most GED experiments so far, we will ignore the pre-factor $\frac{K I_0}{R^2}$ in the rest of the text. The primary term on the right-hand side of the equation typically represents a purely atomic scattering factor which lacks molecular structure information but provides the largest contribution to the differential cross section (DCS). The subsequent term, termed the molecular

term, allows for the extraction of structural details via the internuclear distances R_{ij} (bond lengths), although this only accounts for about 5–10% [121] of the total measured DCS. High signal-to-noise ratios (SNRs) are crucial for accurately determining R_{ij} from the DCS measurements.

The resolution of R_{ij} relies on the momentum transfer q , which is dictated by the incoming. For optimal resolution, a wide momentum transfer range is advantageous to capture several extremas of $\sin(qR_{ij})/qR_{ij}$. For example, a typical internuclear distance of 1 Å under a DCS spanning a momentum transfer of 7 Å⁻¹ exhibits two extremas, suitable for achieving spatial resolutions in the picometer range or better. However, further increases in q yield diminishing returns due to its presence in the denominator of the molecular contrast term, necessitating exceptionally low noise measurements for extracting subtle molecular contrasts against the dominant atomic background [121].

The process of implementing LIED initially seems straightforward, but it is not. one would expect to illuminate the target with a linearly polarized, ultrafast laser pulse and analyze the resulting data. However, extracting the DCSs from the measured 3D PES introduces several complexities. One major issue is that the scattering momentum and angle of the electron is different than the one at the time of detection since the laser field is involved (unlike UED and CED). This interaction not only affects the electron’s momentum after collision but also necessitates modifications in the analysis of experimental PADs. Moreover, several interaction effects need further exploration, including the changes in ionization rates based on molecular alignment, laser intensity, and wavelength. The nonlinear dynamics of the laser-matter interaction require the consideration of focal averaging as the molecules experience varying intensities depending on their position within the laser focus. Lastly, although the DCSs extracted provide valuable data, the modeling of these interactions in LIED can be challenging, especially since the collision energies are typically lower than those observed in CED or UED. This often makes the IAM less applicable and poses additional theoretical challenges.

After more than a decade of research, significant advancements have been made in both the theoretical and experimental aspects of electron diffraction. These developments will be illustrated systematically. For instance, as shown in Figure 4.4, effective implementation of LIED can be seen. This figure displays a comparison between LIED DCS obtained

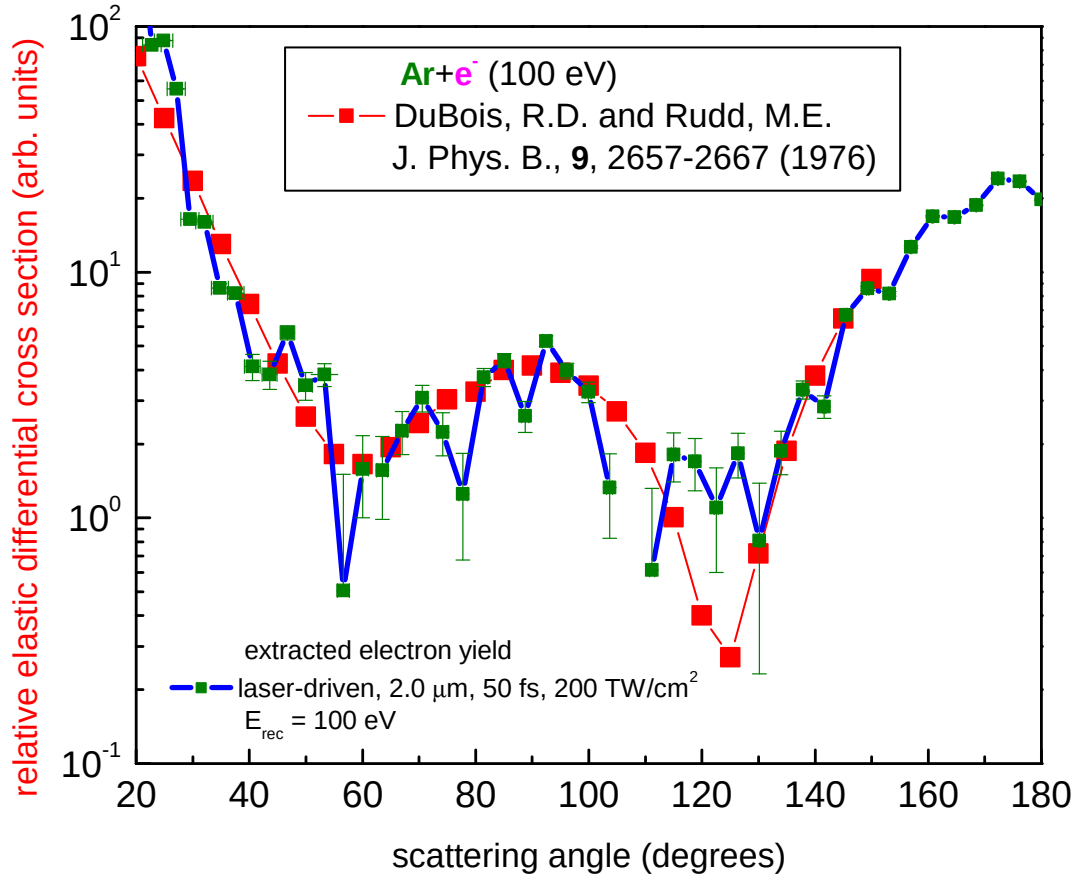


Figure 4.4: Comparison between conventional electron diffraction (shown with red symbols) and LIED (shown with green symbols) for argon atoms at an electron rescattering energy of 100 eV. Reproduced from [125].

under intense laser conditions and classical electron-neutral argon collision data from 1976 [125], highlighted with red symbols. The accuracy in replicating the diffraction minima and maxima locations is evident. With the incident electron momentum $|p| = 5.1 \text{ \AA}^{-1}$,

a momentum transfer covering the range from 20 to 180 degrees spans 1.8 to 10.2 $\text{\AA}^{-1}$. By looking at the equation 4.12, this range is sufficiently broad to enable observation of internuclear distances with up to 0.1 $\text{\AA}$ resolutions.

Furthermore, it is noted that while targets in CED were neutral atoms, in LIED they are often cations, as the electrons rescatter from the parent ion. The error bars present in the LIED data of Figure 4.4, mainly due to limited data collection statistics, are expected to improve as data collection techniques enhance.

4.2 LIED Requirements

The maximum kinetic energy achievable by rescattering electrons corresponds to approximately $3.17U_p$. Enhancing this energy while maintaining the intensity below OTBI regime ($2.46 \times 10^{14} \text{ W/cm}^2$ for Argon) for the target under study can be achieved by increasing the laser wavelength. For instance, with a $3\mu\text{m}$ wavelength at intensity of $1 \times 10^{14} \text{ W/cm}^2$, the maximum kinetic energy at return would be 265.3 eV which is significantly less than the hundreds of keV used in GED and UED. The flux of rescattering electrons at such low energies suggests that using keV energies to generate diffraction images with LIED might not be practical. As shown in Equation 4.5, inverse fourier transform of the coherent term would reveal effective retrieval of the bond lengths provided that the q or momentum transfer $q = 2p \sin(\phi/2)$ is a large number. LIED benefits from the fact that ϕ is large but p is small which still makes the q a large number. This contrasts with the approach in GED or UED, where p needs to be large.

To achieve higher energies for rescattering electrons, mid-infrared lasers must be utilized to leverage the λ^2 scaling of the ponderomotive energy. In this way, LIED is comparable to GED or UED, where laser-induced electrons are utilized to generate diffraction images, enabling direct measurement of interatomic distances through the IAM.

4.3 Transition from Quantum to Classical Treatment in Photoionization

Previously, we considered photoionization through quantum mechanics. In the following analysis, however, we will treat the photoelectron classically as a point particle after ionization. In this approach, we connect the detected electron momentum p and its detected angle ϕ along the laser polarization during the recoil to the photoelectron's momentum during the return p_r and the angle θ_r it scattered off its ion parent.

The justification for this classical method is illustrated in Figure 4.5 where Tate et al. [126] indicated that by integrating the TDSE within the single active electron framework in Argon, quantum and classical results converge during XUV photon emission phases. Figure 4.5 is a plot of the intensity of the emitted harmonics as a function of energy and time for a pulse wavelength of $2\ \mu\text{m}$ with peak intensity of $160\ \text{TW}/\text{cm}^2$. The time axis, in optical periods, begins 1/2 cycle into the pulse, when harmonic emission first becomes possible. As shown in Figure 4.5, the TDSE results (colorlines) closely match the semiclassical prediction (black lines) for the 1st, 2nd, 3rd, and 4th electron returns. The time dependence of these trajectories (black lines) is derived purely from classical mechanics. Even a quantum system like a returning photoelectron shows classical behaviors. This result confirms that even if the returning photoelectron wavepacket is a quantum system, it can be treated as a classical electron that is ionized in the field at time of birth t_b with zero momentum and returning time at t_r . This quantum result also shows the earlier classical approximation of ignoring the ionic potential after collision was reasonable, thus it allows us to connect the detected electron to the rescattered electron and provides accurate DCS extraction with long trajectories. Therefore, the experimental results showcased in this chapter for the butane isomers DCS are also treated classically.

For this classical approach, Hamiltonian dynamics offers a convenient method to describe the classical electron in the laser field when the ionic potential $V(\vec{r})$ is neglected. The

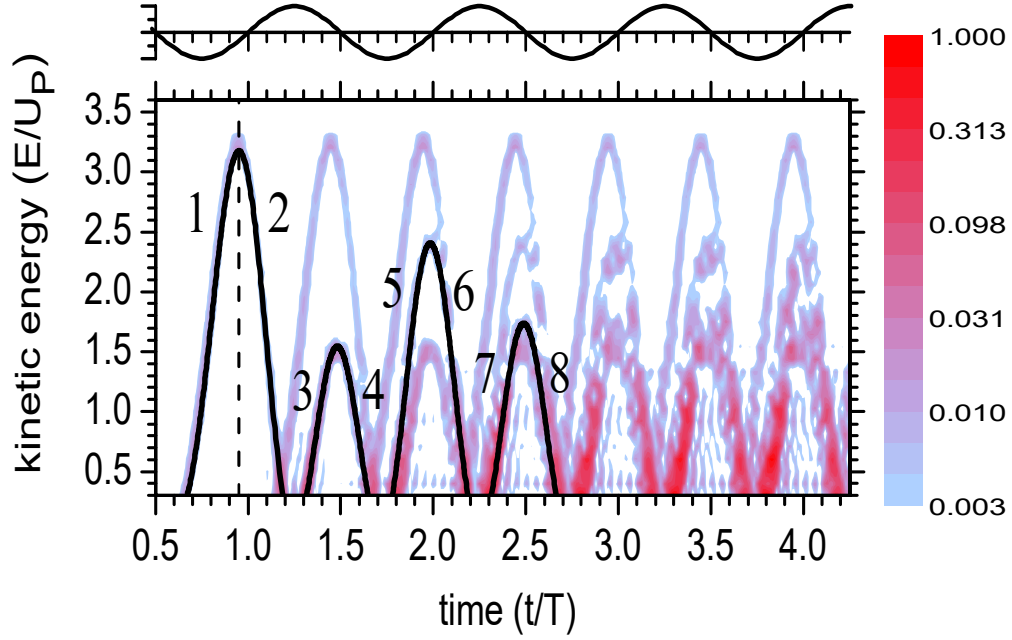


Figure 4.5: High-harmonic generation emission occurs as a photoelectron wavepacket returns to its parent atom. This emission was calculated using TDSE for argon with 2 μm pulses at a peak intensity of 160 TW/cm^2 . Reproduced from [126].

classical Hamiltonian of an electron oscillating in the laser field, expressed in atomic units, is given by:

$$H = \frac{(\vec{p}(t) - \vec{A}(t))^2}{2} \quad (4.8)$$

where $\vec{p}(t)$ and $\vec{A}(t)$ represent the mechanical momentum and the vector potential at time t , respectively. As can be seen from Equation 4.8, the generalized momentum $\vec{P}(t) = \vec{p}(t) - \vec{A}(t)$ remains constant from birth to rescattering and from rescattering to detection. At birth, the mechanical momentum is approximated as zero. And at detection, the vector potential vanishes since the laser pulse is not present. Thus, the mechanical momentum at the instant t_r before rescattering is:

$$\vec{p}(t) = \vec{A}(t_r) - \vec{A}(t_{\text{birth}}). \quad (4.9)$$

This equation can be integrated between t_{birth} and t_r to obtain the electron position

$x(t_r; t_i)$. The details of this approach was shown in chapter 2. By finding the roots of the transcendental equation $x(t_r; t_i) = 0$, the return times of all classical returns are determined. For more information regarding the classical trajectories, see chapter 2. Once return times t_r are known, using the equation $E_r = p_r^2/2$, the return momenta p_r and the return kinetic energies are calculated. The return energies of classical trajectories are shown in Figure 4.5 as solid black lines as a function of t_r , assuming ionization during the first half cycle. The first classical returns, labeled as 1 and 2, are the short and long trajectories, respectively. They are the most energetic, with the two trajectories merging into one at their maximum return energy of $3.17U_p$. The next returns have their birth times when the long trajectory was launched, but they revisit the parent ion at later times. The second return is labeled as 3 and 4 which the maximum return energy for the second return is $1.5U_p$. Slightly more energetic is the third return, labeled as 5 and 6. The fourth return, labeled 7 and 8, is more energetic than the second but less than the third. Generally, the contribution of multiple returns diminishes in increasing order as the spectral density of the returning electron wavepacket decreases due to its expansion perpendicular to the laser polarization direction.

Continuing with the classical model, if the electron is scattered by the ion at angle θ_r and time t_r , after it exits the laser field, it will gain an additional kick given by $A_r = A(t_r)$ which needs to be calculated since $E_{det} = (p_r + A_r)^2/2$, where E_{det} is the kinetic energy of the detected electron and $E_{det} = p^2/2$.

At the time of rescattering, the electron wavepacket diffracts on its parent ion. Classically, this event is interpreted as the incoming electron with momentum $\vec{p}_0$ is elastically scattered with momentum $\vec{p}_r$. The electron yield, is a function of p_r and rescattering angle θ_r . After rescattering, the electron leaves the vicinity of the parent ion and once again, its motion can be described using the ionic potential-free Hamiltonian. Therefore, while the generalized momentum immediately after rescattering is conserved until detection, we obtain the electron momentum at detection $\vec{p}$:

$$\vec{p} = \vec{p}_r + \vec{A}_r \quad (4.10)$$

The last two equations enable us to assign, for a given detected electron momentum $\vec{p}$, a rescattering momentum $\vec{p}_r$ and the vector potential at rescattering $\vec{A}_r$. However, these solutions are not unique, as several classical trajectories might contribute. However, at a detected energy of $10U_p$, only one classical trajectory contributes, allowing us to assign a unique $(\vec{A}_r, \vec{p}_r)$. As seen in Figure 4.5, above $2.5U_p$ rescattering energies, only two types of classical trajectories exist. Several key findings emerge from the analysis of electron trajectories in the backscattering geometry ($\theta_r = 180^\circ$). Firstly, the most energetic collisions at the detector produce electrons with energies up to $10U_p$, primarily due to the recollision occurring near the peak of the vector potential, or close to the zero crossing of the laser's electric field. Secondly, at energies near the peak return, the long and short trajectories are almost degenerate, reducing the uncertainty in assigning $(\vec{A}_r, \vec{p}_r)$ to the maximum detected electron energies. These observations lead us to conclude that the highest energy electrons detected in a measured PAD are ideal for LIED since they have the highest electron momentum transfers suitable for the IAM.

4.4 The Quantitative Rescattering Theory and Electron Yield Extraction

Determining the relative elastic electron-ion DCS from experimental angular distributions is straightforward. However, linking the detected electron yield directly to the DCS has not been straightforward in the context of early LIED experiments by Okunishi et al. [39] and Meckel et al. [40], where though PADs were compared with DCS, the authors did not equate them directly. Subsequently, Chen et al. [41] established a solid theoretical basis for LIED through the introduction of the QRS. QRS theory proves that the electron yield

$I(p, \phi)$ observed can be expressed as the product of the returning electron wavepacket $W(p_r)$ and the field-free DCS $\sigma(p_r, \theta_r)$:

$$I(p, \phi) = W(p_r)\sigma(p_r, \theta_r) \quad (4.11)$$

Here, $W(p_r)$ represents the returning electron wavepacket (RWP), and $\sigma(p_r, \theta_r)$ is the field-free DCS. This formulation shows that, unlike earlier assumptions, the detected electron yield and the DCS are connected through the QRS without directly equating the two initially. Numerical integration of the TDSE and strong-field approximation (SFA2) validate this relationship, where RWP depends solely on the laser parameters and is largely independent of the molecular structure under study which allows precise evaluation from SFA2. Thus, molecular structure primarily lies within the DCS. In summary, for a given p_r , the RWP is a straightforward numerical factor in the product. The electron yield, measured along a circle with radius p_r and offset Δr from the origin as specified in Equation 4.10, is what we seek to determine as the DCS. Please note that when the integration of the yield is performed, in transition from (p, ϕ) or $(p_\perp, p_\parallel)$ to (p_r, θ_r) , the appropriate Jacobian needs to be applied to ensure conservation of normalization. The integration limits, Δp_r and $\Delta \theta_r$, should be as minimal as possible to maintain strong statistical integrity and optimal signal-to-noise ratio. Figure 4.6a graphically demonstrates this procedure, noting that the vector potential offsets for circles at $p_r - \Delta p_r$, p_r , and $p_r + \Delta p_r$ are not identical, thus the area of integration varies with the angle θ_r . By adhering to this method, precise DCSs can be derived, as shown in Figure 4.6a. Figure 4.6b shows the extracted electron yield at $p_r = 0.76a.u. \pm 2\%$. Please notice that 4.6 is just an example to introduce the steps to extract the electron yield. The PAD shown in the figure is taken at the MPI regime and extracting the DCS does not convey any physical meaning. As it was mentioned before, LIED happens at the tunneling ionization regime. We will show more intuitive electron yields in the next sections.

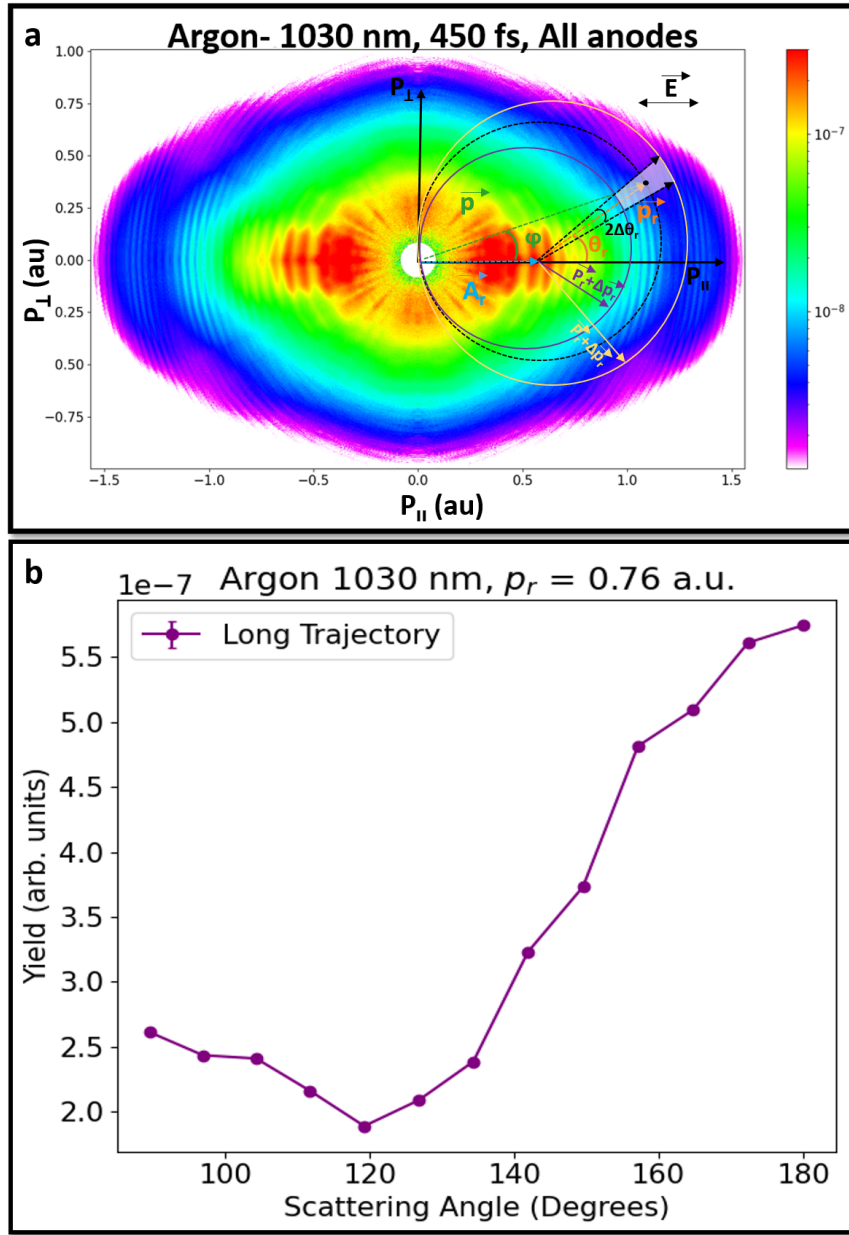


Figure 4.6: a: The extraction of electron-ion DCS are analyzed for electrons that elastically scatter with initial momentum p_r and are subsequently detected with momentum p . b: extracted yield from at $p_r = 0.76a.u. \pm 2\%$

4.5 Identification of Molecular Isomers Using Laser Induced Electron Diffraction

Distinguishing structural differences among isomers is a fundamental challenge in the physical sciences. Isomers are molecules with the same chemical formula but possessing different structures and distinct physical or chemical properties. Isomerization, the transformation from one isomer to another [127–130], plays a pivotal role in processes such as vision [131, 132] and energy storage [133]. Over the years, different techniques have been employed for structural imaging or identification of isomers in the gas phase. High harmonic spectroscopy has demonstrated the ability to unambiguously distinguish between isomers [134, 135], while Coulomb explosion imaging has been used recently to differentiate the absolute geometry of isomers [136–138]. In contrast, despite being widely used for imaging molecular structure, gas electron diffraction (GED) [139–141] and UED [37] have encountered challenges in discerning structural disparities among rotational isomers (or conformers). The subtle changes in the diffraction signal caused by such differences have made it difficult to reliably differentiate between isomers using GED or UED.

The challenges encountered in using GED or UED to identify isomers originate from their limited sensitivity to non-adjacent bond structures. The elastic scattering intensity of GED and UED for randomly oriented molecules can be well-approximated using the IAM [142–144], expressed as

$$I(p, \phi) = \left[\sum_{i=1}^N |f_i(p, \phi)|^2 + \sum_{i=1}^N \sum_{j=1, i \neq j}^N f_i(p, \phi) f_j^*(p, \phi) \frac{\sin(qR_{ij})}{qR_{ij}} \right] \quad (4.12)$$

Consequently, GED and UED lack sensitivity to changes in the distance between non-adjacent atoms. Although aligning the molecule with an additional laser pulse may mitigate some information loss due to orientation-averaging [143, 144], aligning all the isomers experimentally under the same conditions is nontrivial and impractical.

In contrast to GED and UED, LIED [38, 40] could be a promising approach for probing structural disparities among isomers. To emphasize again, LIED is based on the three-step model [5, 6]: The molecule first undergoes tunnel ionization (TI) by an intense infrared (IR) laser pulse. Subsequently, the ionized electron is then accelerated by the laser and driven back to recollide with the ionic core. It has been demonstrated that the distribution of the elastically backscattered electrons carry rich structural information about the ionic target [7, 9, 10, 12, 39, 42–47, 145–147]. According to the QRS [41, 148], the Equation 4.13 for a molecule oriented at Euler angles $\eta = (\alpha, \beta, \gamma)$ can be expressed as

$$I(p, \phi, \eta) = W(p_r, \eta) \sigma(p_r, \theta_r, \eta) \quad (4.13)$$

The electron wavepacket, denoted by $W(k_r, \eta)$, exhibits only a weak dependence on momentum for mid-infrared (IR) lasers and is proportional to the total ionization (TI) rate $w(\eta)$ [41]. As mentioned before, in LIED, the backscattered electrons are of particular importance as they collide with the ionic core at higher scattering energies [41], which enables the cross section σ to be approximated using the IAM for the neutral molecule [149]. Consequently, the orientation-averaged photoelectron distribution, denoted as I_{TI} , can be approximated as follows [7]:

$$I_{TI}(p, \phi) = \sum_i |f_i(p_r, \theta_r)|^2 \int w(\eta) dR + \sum_i f_i(p_r, \theta_r) f_j(p_r, \theta_r)^* \int e^{iq \cdot R_{ij} w(\eta)} dR. \quad (4.14)$$

Assuming the wavepacket W is independent of p_r and we call Equation 4.14 TI-IAM. Due to the anisotropy of $w(\eta)$, I_{TI} depends on $q \cdot R_{ij}$ rather than $q R_{ij}$ which makes it sensitive to molecular bond lengths and angles. When the measured photoelectron distribution $I_{TI}(p, \phi)$ is transformed to the laser frame with $p = p_r - A_r$, it can be identified as the TI-weighted DCS used to analyze rescattering. Given that isomers possess different molecular symmetries, the orientation dependence of their TI rates varies [14, 150–153]. Therefore, Equation 4.14 suggests that the TI-DCS extracted from LIED could serve as a means to distinguish

molecular isomers.

Previous studies often ignored the importance of TI rates mentioned in [149] in their structural analysis, particularly when the molecules in question were relatively simple [9, 10, 12, 42–47, 146, 147]. However, in complex molecular systems, incorporating TI rates can significantly alter the TI-DCS when compared with experimental DCS. This comparison offers new insights into molecular structure. This study shows the scientific part of the thesis and the importance of TI rates in the effective application of LIED for differentiating isomers of n-butane and isobutane and confirming the method’s ability to capture detailed molecular features that distinguish these isomers. We perform LIED experiments for n-butane and isobutane and compare the experimental DCS with the DCS calculated using the IAM and TI-IAM. We identify distinct features between the extracted DCS for n-butane and isobutane, demonstrating that LIED can clearly distinguish the two isomers. The experimental DCS for n-butane notably deviates from those predicted by IAM. When the multiorbital TI rates are included, a significantly improved agreement is obtained. Our findings suggest that LIED is sensitive not only to both distances between adjacent atoms but also to the shape of valence orbitals of molecules. This means that since LIED identifies the isomers of molecules, and bondlength information can be extracted from DCS too, it can be a great tool to study the nuclear and electronic structures at the same time.

We begin with some background information on the target molecules. Notably, n-butane has two stable conformers: *anti* and *gauche*. The energy of the *gauche* conformer exceeds that of the *anti* by approximately 34.7 meV. These conformers are divided by an energy barrier estimated at 139 meV [154]. At room temperature, the distribution between the *anti* and *gauche* forms of n-butane is approximately 65:35, as indicated by GED studies and electron momentum spectroscopy. In our theoretical analysis, we treat these two forms of n-butane separately. Figure 4.7 illustrates the geometry and TI rate of *anti* n-butane, *gauche* n-butane, and isobutane. Each of these species possesses three pairs of adjacent carbon-carbon bonds measuring $2.8a_0$ and ten pairs of adjacent CH bonds each measuring

$2.2a_0$.

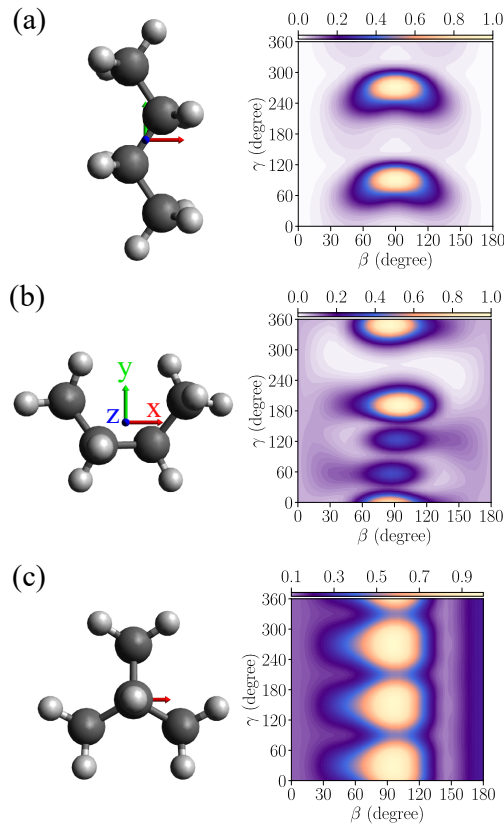


Figure 4.7: Geometry and multiorbital tunnel ionization rate of (a) n-butane (*anti*), (b) n-butane (*gauche*), and (c) isobutane. The laboratory frame, which is the same for all species, is defined in (b). The laser polarization is assumed to be along the z axis (the blue axis). The Euler angles for the tunnel ionization rate are defined by the $z-y-z$ extrinsic rotation convention, in which the molecule is first rotated by γ about the z axis, followed by β about the y axis (the green axis).

To calculate the TI rates, the structural parameters of the Kohn-Sham orbitals for *anti*, *gauche*, and isobutane were analyzed using the Octopus density functional theory software [155]. In this analysis, only the orbitals whose binding energies are within 1 eV of the highest occupied molecular orbital (HOMO) are considered. Consequently, for *anti*, *gauche*, and isobutane, the top four, three, and three HOMO levels were examined, respectively.

From Figure 4.7, we see that the three species have distinct orientation dependence for the total TI rate. In particular, the TI rate of *anti* and *gauche* are more localized compared to that of isobutane. The rate of *anti* is localized around $\beta = 90^\circ$ and $\gamma = 90^\circ/270^\circ$, such

that the rate is maximized when the laser polarization is along the y axis, while the rate of gauche is localized around $\beta = 90^\circ$ and $\gamma = 0^\circ/180^\circ$, such that the rate is maximized when the laser polarization is along the x axis. The strong dependence of TI rates on the molecular orientation suggests that the DCS extracted from the LIED experiment should deviate from that of the IAM, thereby enabling the identification of the butane isomers.

In Figure 4.8a, we compare the DCS from 70° to 180° at 50 eV calculated using the IAM for all three species as well as the 65:35 mixture of anti and gauche. As expected from the similarity in the adjacent bond structures, the DCSs from the IAM are almost indistinguishable among the species and mixture. The averaged differences between the DCSs over 70° to 180° are at most 3%, which is too small to be easily distinguished in experiments. Therefore, the results suggest that GED and UED, which rely on the use of the IAM, may not be able to distinguish the structural differences between randomly oriented isomers.

To showcase the capability of LIED for distinguishing molecular isomers, we performed the LIED experiments for n-butane and isobutane. The PES were collected in a field-free electron TOF apparatus equipped with MCP-based detectors (length 0.525 m, background pressure 3×10^{-8} Torr, collection angle 1.5°). Each isomer was delivered to the target using a precision leak valve at a pressure of 10^{-4} Torr. The TOF data was digitized using a TDC with 150 ps/bin, providing a relative photoelectron energy resolution of about 1%. Both targets were irradiated with $3 \mu\text{m}$, $80 \mu\text{J}$, 100 fs pulses at 1 kHz repetition rate. Focused with an $f = 100$ mm CaF_2 lens, the laser delivered $40 \pm 6 \text{ TW}/\text{cm}^2$ on the target. The details of the laser system can be found in chapter 3. The angular distributions were collected one angle at a time by rotating the laser field polarization direction with respect to the TOF spectrometer axis using as zero order HWP. The waveplate rotation was fully motorized. To eliminate the influence of small laser intensity drifts, at each angle PES were collected for 30 seconds, followed by a random waveplate rotation to a new angular position, with a minimum angular step of 2° . For each isomer, a full angular distribution was recorded over

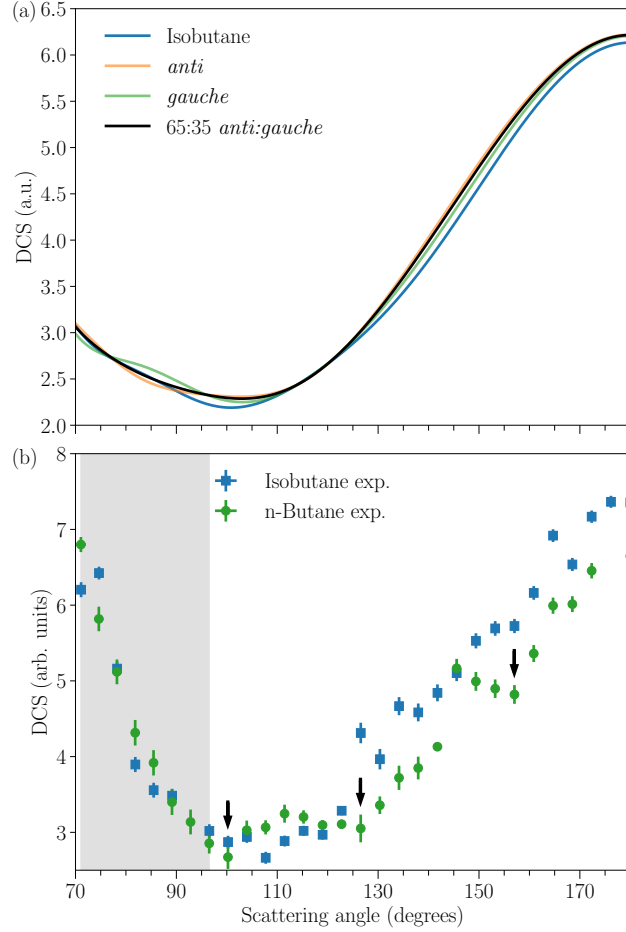


Figure 4.8: The DCS at scattering energy of 50 eV for n-butane and isobutane, obtained from (a) the IAM and (b) the LIED experiments. In (a), the DCSs obtained for n-butane (*anti*, *gauche*, and the 65:35 mixture) and isobutane are differed by less than 3% on average. Meanwhile, in (b), the two DCSs extracted from experiments exhibit clear differences between the isomers: There are three minima for n-butane (indicated by the black arrows) and the DCS of n-butane around 180° is about 10% lower than that of isobutane. Data in the shaded area are contaminated by signals from direct electrons.

8 hours. Details about the transformation from the photoelectron distribution $I_{TI}(p, \phi)$ to the TI-DCS $I_{TI}(p_r, \theta_r)$ can be found in [7, 9, 156].

The TI-DCS extracted from the experiment for n-butane and isobutane are shown in Figure 4.8b. For a fair comparison, the TI-DCS for n-butane and isobutane are normalized with respect to their direct electrons signal. The signals for scattering angles less than 100° are neglected since they are likely to be contaminated by direct electrons. Unlike the DCS

from the IAM, the two extracted TI-DCSs show clear differences: There are three minima for n-butane at around 100° , 125° , and 155° , and the DCS of n-butane around 180° is about 10% lower than that of isobutane. Figure 4.8b thus provides clear evidence that LIED can resolve the structural differences between isomers.

To elucidate the mechanism of LIED, we compared the DCS obtained from the IAM and TI-IAM with the experimental results. Figure 4.9a and b compare the calculated DCS with the experimental DCS for n-butane and isobutane. Since the experimental data are averaged over $\pm 20\%$ of the electron kinetic energy at 50 eV, the theoretical DCSs are averaged uniformly over the scattering energy of 40 to 60 eV.

The extracted DCS for both isomers are then normalized using the least square fit to the theoretical TI-DCS. In the case of isobutane, a remarkable agreement is found between the DCS calculated using the TI-IAM and extracted from the experiment. Comparing between the results from TI-IAM and IAM, the TI-DCS is about 10% lower than the DCS from the IAM at around 180° , while their qualitative behavior are very similar. This is unsurprising given that the orientation dependence of isobutane TI rate has a three-fold symmetry, such that it is more isotropic than that of n-butane. On the other hand, for n-butane (65:35 *anti:gauche*), the trend of the TI-DCS agrees well with the experiment, while the trend of the DCS obtained from the IAM significant deviates from the experiment. The agreement between the theory and experiment suggests that LIED can resolve structural differences among isomers because it is sensitive not only to their molecular structure but also to the shape of their valence orbitals.

Despite the agreement for the trend, the TI-DCS for n-butane fails to reproduce the three minima marked in Figure 4.8b. The primary reason for this discrepancy is likely the inadequacy of the IAM at 50 eV in accurately approximating the DCS of ion-electron collisions with the DCS of neutral-electron collisions. Increasing the peak laser intensity and wavelength used in the experiment could resolve this issue, as the rescattering energy scales with the peak intensity and the square of the laser wavelength. Another possible reason

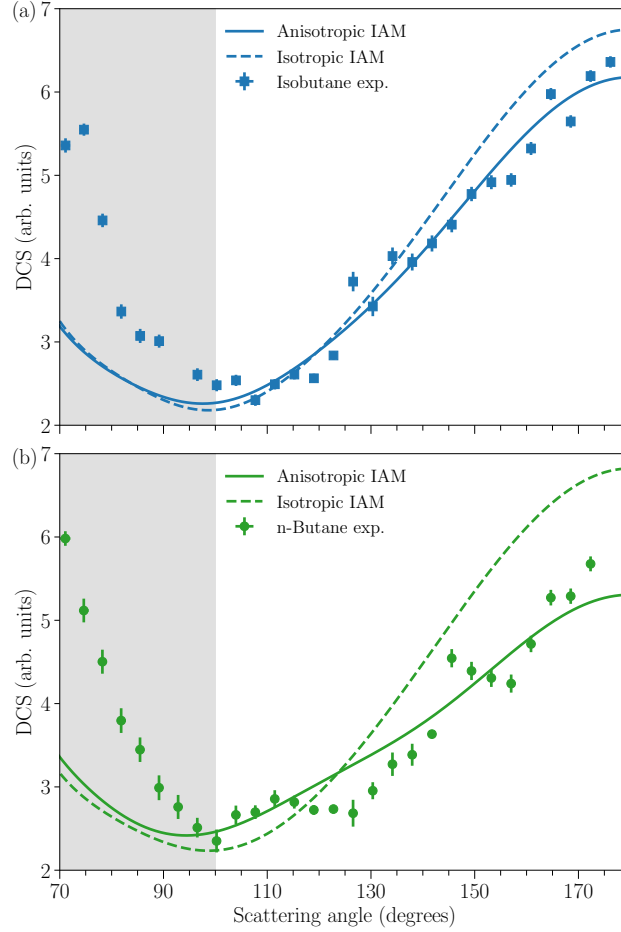


Figure 4.9: (a) Comparison between DCS extracted from experiments for isobutane at 50 eV and the convoluted DCS calculated using the IAM (dashed lines) and TI-IAM (solid lines). The DCS from the TI-IAM shows good agreement with the experiment. (b) Same as (a), but for n-butane. The DCSs are calculated with 65% *anti* and 35% *gauche*.

behind the disagreement between theory and experiment for n-butane could be the nuclear motion before or after tunnel ionization. To investigate this, we performed real-time time-dependent density functional theory calculations for molecular ions using Octopus [155]. However, our analysis indicates that the effects of nuclear motion before and after TI do not significantly alter the qualitative behavior of the convoluted DCS.

Chapter 5

Conclusion and Future Work

In this document, we outline the home-built LIED dedicated D-TOF, equipped with a high-speed, Yb-based 100 kHz CPA laser (Tangor 300 Amplitude LASER). We start by detailing the design process using Fusion 360 and SolidWorks, which helped in the precise construction and assembly of our D-TOF spectrometer. We also discuss the engineering principles and physics knowledge applied to assembling the chamber components, including setup configuration, electronics, data collection, and testing protocols.

We highlight the performance of the D-TOF in handling both ion and electron modes, showcasing the results of rigorous tests. Initially, we sought external collaborations for building multi-anode detectors. When this did not succeed, we took on the challenge of developing our own MCP-based detectors. Our in-house built detectors now match the performance of the best single-anode detectors available on the market.

To tackle challenges such as magnetic field interference affecting electron paths, we devised a design that effectively neutralizes these effects. Furthermore, we incorporated electronic components directly within the chamber to avoid any noise from the inductance of the long wires applied to the RF signal we are collecting. Although integrating these electronics was challenging due to potential contamination risks in the UHV D-TOF chamber, we managed to create contamination-free detectors. These detectors maintain an exceptionally

low background pressure of 4×10^{-9} torr in D-TOF.

Additionally, it was our pleasure to share all our knowledge in building the D-TOF with our collaborators at Ohio State University Nexus lab. They have constructed a mostly similar D-TOF setup known as symmetric double time of flight (SDTOF), which is now fully operational.

Lastly, on the scientific front we have demonstrated that LIED can distinguish isomers unambiguously due to its sensitivity on the nuclear geometry and the shape of valence orbitals. Our results are in sharp contrast with the IAM employed by the GED and UED, in which the DCS is insensitive to the structural differences between isomers due to similar adjacent bond structures. We anticipate LIED to be a robust technique for probing structural differences between isomers. In particular, analysis of the measured 2D electron spectra could offer valuable insights into the molecular structure [46, 149, 157]. On the other hand, combining with some pump pulses to excite the target molecule, LIED could be utilized to probe the transient nuclear and electronic structure of the excited state. A key technical challenge lies in using a weaker laser pulse but with longer wavelengths to drive LIED on excited states of a neutral molecule, which have similar ionization potentials as the alkali atoms. Using LIED as a dynamical probe could be highly rewarding. First, the pulse duration of mid-IR laser is getting closer to the single-cycle limit [158, 159], much shorter than the current limit of hundreds of fs in UED. Additionally, LIED signal for the excited state is likely to be free from the background of the unpumped target, as the laser intensity of the probe is too weak to ionize the neutral ground state. Thus, we look forward to the development of LIED as a background-free probe with picometer and femtosecond spatio-temporal resolution for nuclear and electron dynamics in generic molecules.

In the near future we will investigate the application of LIED at JRM lab, particularly with its use on more complex molecular targets undergoing chemical reactions. The recent integration of our D-TOF with the Tangor 300 laser has substantially enhanced LIED's applicability. This combination has dramatically improved our data collection efficiency,

reducing hours of work to just minutes under stable experimental conditions. The operating wavelength of the Tangor 300 is 1030 nm, and we are currently developing an OPA pumped by the Tangor 300 to shift to longer wavelengths (3-4 μm), which are more suitable for LIED applications. Our ultimate goal is to create molecular movies through UV pump, LIED probe experiments.

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