

Imaging Molecular Structures with Femtosecond Laser Pulses:

Experimental Apparatus Development and Computational Geometry Reconstruction

by

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I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final versions, as accepted by my examiners.

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ABSTRACT

A joint facility with the University of Waterloo and the Advanced Laser Light Source has been constructed, in order to explore the behavior of ions and electrons during ultrafast molecular dynamics. The sophisticated apparatus known as the Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) has been constructed in Waterloo. A COLTRIMS, or reaction microscope, comprises seven essential components: the Time of Flight (TOF) spectrometer, the delay-line detectors, the signal acquisition system, the vacuum system, the cooling system, the magnetic coils, and the analysis software. Detailed assembly procedures, problem diagnosis tests, operational procedures and initial tests using femtosecond laser pulses, to initiate dynamics, are reported.

To investigate the geometric structure of a molecule immediately preceding the initiation of a Coulomb explosion, by a few-cycle laser pulse, an optimized Coulomb explosion geometry reconstruction framework is developed, and explained in detail and validated using both simulation data and experimental data. The application of the geometry reconstruction optimization method, to experimental data resulting from the ionization of asymmetric molecules N_2O and OCS by sub 7fs laser pulses, demonstrates its effectiveness of the framework.

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DEDICATION

Dedicated to time.

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List of Abbreviations

CEI	Coulomb Explosion Imaging
TOF	Time of Flight
COLTRIMS	COLd Target Recoil Ion Momentum Spectroscopy
ALLS	Advanced laser light source laboratory
PIPICO	Photoion-Photoion Coincidence Map
KER	Kinetic Energy Released
MCP	Micro Channel Plate
ATI	Above Threshold Ionization
SFA	Strong Field Approximation
OBI	Over-the-Barrier Ionization
SPI	Single Photon Ionization
TI	Tunneling ionization
CPA	Chirped Pulse Amplification

Chapter 1 Introduction

1.1 Motivation

The evolution of atomic and molecular physics is closely connected with the development of optics. Optics provides a window into the atomic and molecular field, facilitating the exploration of the microscopic world. In 2018, the Nobel Prize in Physics recognized the significance of Chirped pulse amplification (CPA) [1], a technique for generating high-intensity, ultra-short optical pulses. Then, in 2023, the Nobel Prize once again acknowledged research in optics, specifically the experimental methods for generating attosecond light pulses. This involves the application of a semi-classical three-step model [2] to describe the motion of electrons in a strong laser field. Advancements in high-intensity laser technology have not only improved the laser quality but also further facilitated research into interactions between lasers and atoms or molecules.

The study of molecular dynamics and their interactions with intense fields has attracted significant attention, leading to the development of various experimental and theoretical techniques. Examples include high-harmonic spectroscopy [3][4][5], laser-induced electron diffraction [6][7][8], Coulomb explosion imaging (CEI) [9][10][11][12] and Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) [13][14][15]. This work focuses on the CEI and COLTRIMS. CEI involves the explosive removal of multiple electrons revealing the original molecular structure by measuring the momenta of the fragmented ions. COLTRIMS uses a combination of electric and magnetic fields and measures the 3D momentum vectors of both electrons and ions during an ionization process, providing detailed insights into ionization dynamics and electron-ion correlations.

1.2 Organization

The purpose of this thesis is to explore molecular structures using femtosecond laser pulses. The research is systematically organized into two parts: the construction of COLTRIMS and geometry reconstruction.

Chapter 2 reviews atom ionization processes and the dissociation of H_2 in strong laser field.

Chapter 3 studies COLTRIMS. This includes detailed description of its essential components, diagnostics for signal problems, procedures for conducting experiments and a calibration test.

Chapter 4 focuses on simulating the Coulomb explosion imaging concerted process and examines two geometry reconstruction methods using simulated data.

Chapter 5 shows the application of the optimization geometry reconstruction method, analyzes real experimental data from N_2O and OCS molecules.

Chapter 6 discusses future work.

Chapter 2 Background

2.1 Atomic strong field ionization

Strong field ionization is a fundamental process in the study of the interaction between intense laser fields and atoms, especially when the laser photon energy is significantly smaller than the ionization potential of the initial atomic state. In this scenario, characterized by high laser intensity and significantly low electromagnetic wave frequency, the ionization occurs as if the laser electric field were almost constant. This regime allow for the application of the strong field approximation (SFA) [16][17][18], where it assumed that an active electron, once ionized, interacts primarily with the laser field and not significantly with its parent core.

The Keldysh parameter [16], γ , is named after the distinguished physicist Lenoid V. Keldysh. The Keldysh parameter serves as a fundamental indicator to explain the ionization mechanisms induced by intense laser fields and to understand the resulting laser-matter dynamics.

$$\gamma = \frac{\text{tunneling time through the barrier}}{\text{wave period of the applied field}} = \sqrt{\frac{I_p}{2U_p}} \quad \text{Equation 2. 1}$$

$$U_p = \frac{e^2 E^2}{4m_e \omega^2} \quad \text{Equation 2. 2}$$

I_p represents the ionization potential, which is the energy required to remove an electron from the ground state to the ionization state. U_p represents ponderomotive energy, which is the average kinetic energy of the oscillations of a free electron and can be calculated as in Equation 2. 2 for a monochromatic laser field [19]. e and m_e are the charge and the mass of the electron. E is the electric field strength of the laser, and ω is the laser frequency.

The potential of an atom in a strong laser field is the combination of Coulomb potential and the laser field potential. If $\hbar\omega > I_p \gg U_p$, single photon ionization (SPI) can occur [20]. If $\hbar\omega < I_p$, ionization types are indicated as follows.

In Figure 2. 1, (A) shows the atomic Coulomb potential without a laser field. The photon energy is much smaller than the ionization potential, so the electron is trapped in the potential barrier. As shown in Figure 2. 1 (B), a laser field is applied while the strength is weaker compared to the Coulomb potential and $I_p > \hbar\omega \gg U_p$. Multi photon ionization (MPI) occurs when absorbed n photons and $n\hbar\omega \geq I_p$ [20]. Another case, the free electron can absorb more photons, when $I_p > U_p > \hbar\omega$ the above threshold ionization (ATI) occurs [20]. As shown in Figure 2. 1 (C), as the laser field strength increasing, the potential barrier is getting lower, the

energy required to free an electron I_p is getting smaller as the dashed black line is closer to the start position. This is the tunneling ionization (TI) when $U_p > I_p \gg \hbar\omega$ [21][22]. As shown in Figure 2. 1 (D), when the laser field is stronger than the internal binding field, the electron can be removed without the need to overcome an energy barrier, which is referred as over the barrier ionization (OBI) with $\gamma \ll 1$ [23].

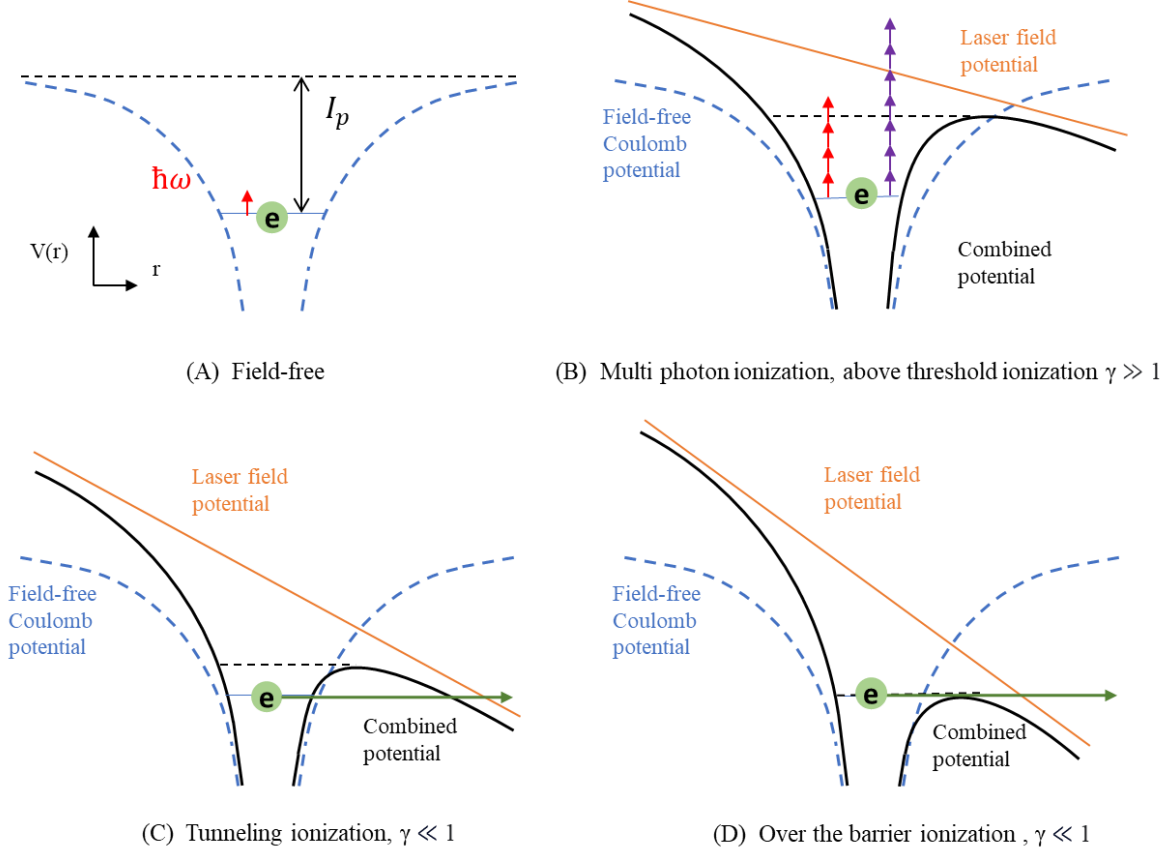


Figure 2. 1: The atomic potentials induced by a laser field. (A) Field free potential with only the Coulomb potential. (B) Multi-photon ionization in red and above threshold ionization in purple. (C) Tunneling ionization. (D) Over the barrier ionization. Dashed blue line represents the field free Coulomb potential, the orange line represents the laser field potential, the black curves represent the combined potential. The black double headed arrow represents the ionization potential I_p , the red arrow represents the photon energy $\hbar\omega$.

2.2 Molecular strong field dynamics

H_2 is a fundamental model to study different kinds of interactions with an intense laser field. In general, the double ionization process is sequential [24][25], which means $H_2 \rightarrow H_2^+ \rightarrow H^+ + H^+$. The one-electron molecule H_2^+ when irradiated by an intense field will either photodissociate $H_2^+ + n\hbar\omega \rightarrow H + H^+$ or ionize via a Coulomb explosion $H_2^+ + m\hbar\omega \rightarrow H^+ + H^+ + e^-$.

The dissociation process behavior of H_2^+ can be described by bond softening, above threshold dissociation, vibrational trapping (bond hardening). The dressed potential energy curves (PEC) can be calculated by Floquet theory [26][27] as shown in Figure 2. 2. When the internuclear distance is fixed and the laser intensity is increased slowly, the diabatic curves are involved into the adiabatic ones. Consider the ground state $|g,n\rangle$, and if the protons slowly move apart, it will follow the adiabatic curve to the state $|u,n-1\rangle$. This is called bond softening [31][32][34], because it tends to lower the potential barrier and to weaken the restoring force in the well. Vibrational trapping, also known as bond hardening [34][36], refers to the unlikely case where the dissociating molecule becomes trapped in the upper potential well.

For a higher laser field, if the molecule starts from the initial state $|g,n\rangle$, the dissociation of H_2^+ occurs by absorbing three photons, which are then directed towards the $|u,n-3\rangle$ state. As the internuclear distance increases, the molecule has two possible dissociation pathways: it can emit one photon and transition to the $|g,n-2\rangle$ state, at the end, this results in the dissociating wavepacket corresponds to the photo-dissociation by two photons. This process is called above threshold dissociation [33][35] because more photons are absorbed than the minimum necessary. Alternatively, it can continue dissociating to the $|u,n-3\rangle$ state, which involves a total of three absorbed photons.

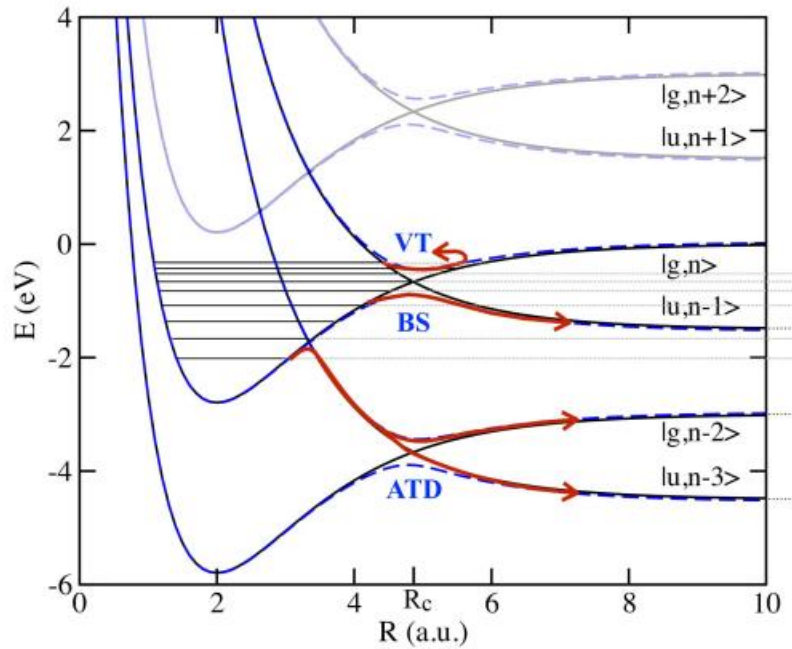


Figure 2. 2: Dressed potential energy curves for H_2^+ . The black curves represent diabatic potentials, the blue dashed curves represent adiabatic dressed potentials. $|g,n\rangle$ is the ground state H_2^+ , $|u,n-1\rangle$ is the first excited state dressed with one photon and they can be dressed by different number of photons. Figure is from [28].

2.3 Review of reaction microscope

The COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) technique [37][38][13], now more commonly known as the “reaction microscope”, was developed by Ullrich and Schmidt-Bocking in Frankfurt [15][74] in 1988.

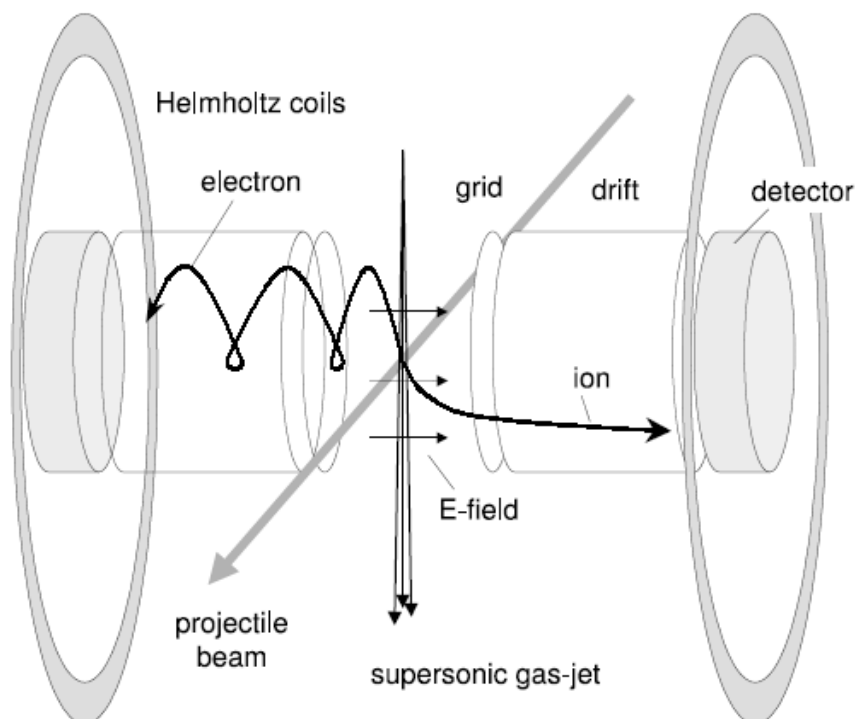


Figure 2.3: The COLTRIMS apparatus or “reaction microscope” adapted from [15]. The supersonic gas-jet is ionized by the projectile beam, which could be highly charged ions or electrons, or more recently a focused laser pulse. The electric field guides the ions and electrons to opposite detectors, while the Helmholtz coils provide a magnetic field that confines the electrons.

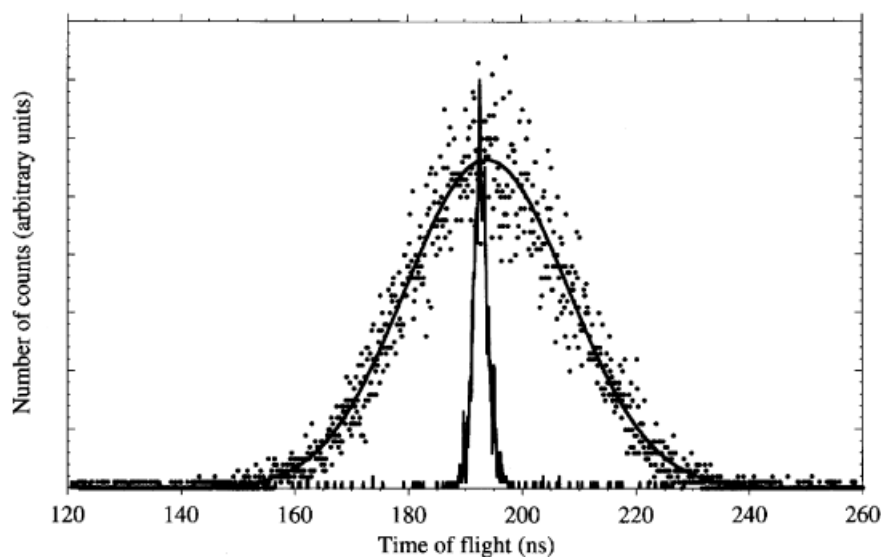


Figure 2.4: Number of counts vs. time of flight for ion results from room temperature gas (black points) compared to from a supersonic gas jet (middle thin distribution). The deviation of the TOF from the mean value is proportional to the momentum of the ions in the direction of electric field. Figure is from [73].

This advanced technique is instrumental in investigating the dynamics of electrons and ions in an atom or a molecule as it is ionized by intense fields. By using a combination of electric and magnetic fields, all charged fragments and electrons from an atomic or molecular multiple ionizations are projected onto position sensitive detectors [1]. The three-dimensional momentum vectors of these particles can be determined from their measured time of flight and position information. The supersonic gas jet can provide a thin gas beam, which has velocity only in the direction of gas jet. Figure 2.4 shows data from reference [73] which compares, the time-of-flight distribution of ions from room temperature gas and ions from a supersonic gas jet. The deviation of the TOF from the mean value is proportional to the momentum of ions in the direction of electric field. This means the supersonic gas jet provides a very small velocity in the direction of electric field. The supersonic gas jet is essential for maintaining the condition of only one molecule in the laser focus in order to operate in a coincidence mode.

The COLTRIMS technique has been successfully employed by various research groups. The Frankfurt group in 2013[80] showed that electron localization and asymmetrical breaking of molecular bonds are ubiquitous, even in symmetric laser pulses. The group in University of Ottawa have made important contributions performing experiments examining the behavior of H_2 molecules [78] (2009), they proposed a new method to obtain molecular frame photoelectron angular distributions from H_2 molecules ionized by intense laser pulses. Kubel et al. [76] (2019) demonstrated an all-optical method to imagine an ultrafast valence electron wave packet in real time with a time resolution of few femtoseconds. Mi et al. [71] (2023) demonstrated a new pathway to form D_3^+ from the D_2 - D_2 dimer by analyzing the ion

momentum. Lai et al. [72] (2023) reconstructed N_2 molecular orbital from the electron momentum. The group in East China Normal University identified a unique three-body fragmentation pathway of SO_2 involving the formation of a fast-rotating O_2 intermediate [75](2020). Qiang et al. [79] (2020) reported the experimental observation of quantum wave-packet echoes in a single Ar molecule. The COLTRIMS technique has significantly advanced our understanding of molecular dynamics, offering insights into the molecular structures and electron behavior.

Here we will review some recent work which demonstrates the setup, to make detailed measurements of both ion and electron behaviour during molecular dynamics initiated by ultrafast laser pulses. The unique design of COLTRIMS employs both electric field and magnetic field to guide the ions and electrons which result from an ionization event, in opposite directions, enabling their detection by two time and position sensitive delay-line detectors. This setup allows for the precise measurement of position and time information (x,y,t), which can then be converted into momentum for each ionic particle.

Recent studies have shown by Mi et al. [71] successfully demonstrated a new pathway to form D_3^+ from D_2 - D_2 dimer by analysing the ion momentum. Lai et al. [72] reconstructed molecular orbital from the electron momentum.

Mi et al. [71] studied D_2 - D_2 dimers using COLTRIMS with femtosecond laser pulses of 790nm, 25 fs, and repetition rate of 10kHz. They found a pathway to form the molecule D_3^+ from the D_2 - D_2 dimer, during the ionization process.

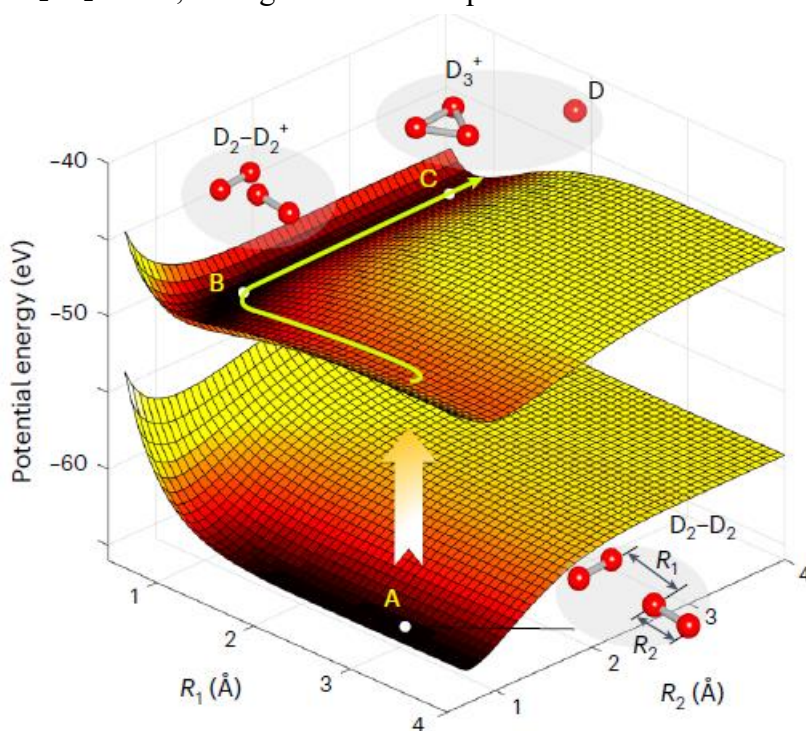


Figure 2.5: Calculated potential energy surfaces of a D_2 - D_2 dimer and the schematic pathway of D_3^+ formation. The lower potential energy surface represents the ground state potential

energy of the neutral D_2 dimer, and the higher one represents the potential energy of first ionization state. Figure is from [71].

As shown in Figure 2.5, the D_2 dimer starts from point A which is the lowest energy point of the ground state. When an electron is removed from the dimer, the system moves to the $D_2-D_2^+$ energy surface and starts moving along the pathway colored by a yellow line. Point B is where the $D_2-D_2^+$ has minimum energy, however the system can continue to evolve along the shallow potential indicated by the yellow line to point C. where it has rearranged with the formation of molecule D_3^+ and a deuterium atom D.

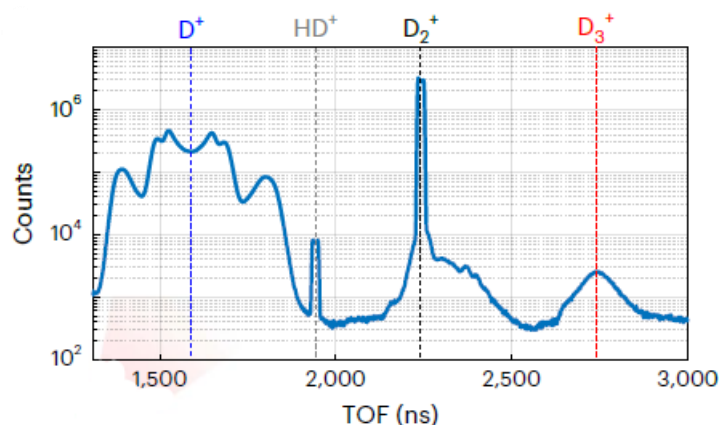


Figure 2.6: Measured time of flight spectrum for photoions. The blue, grey, black and red dashed lines represent the center of the time of flight for D^+ , HD^+ , D_2^+ and D_3^+ . Figure is from [71].

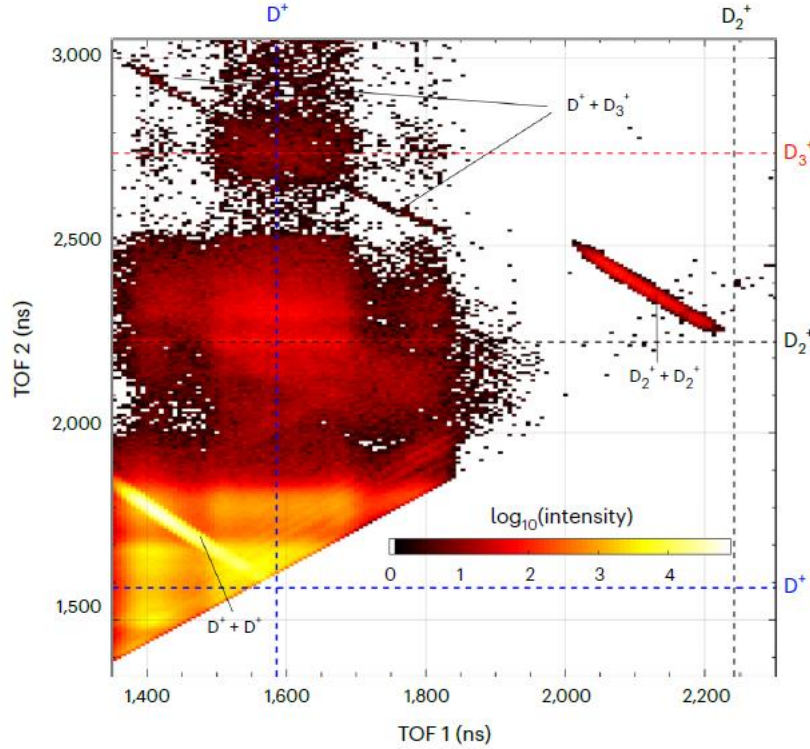


Figure 2.7: Measured photon-ion photo-ion coincidence spectrum. The TOF1 and TOF2 represent the time of flight of first ion and the time of flight for the second ion. The sharp lines show that the first and second ions originate from dissociation of a molecule. Figure is from [71].

As shown in Figure 2.6, the COLTRIMS can identify the species of positive ion fragment, from the time of flight of all the ions. For this experiment, D^+ , HD^+ , D_2^+ and D_3^+ are identified from the spectrum, indicating that D_3^+ has been generated. To understand the process, however, the correlation of the fragment ions was essential. In order to reveal this, a second probe pulse was used by the authors to ionize to the $2+$ state. This allowed them to identify the channel $D_2-D_2^+ \rightarrow D_3^++D$, from $D_2-D_2^+ \rightarrow D_3^++D^+$. In order to do that though they needed to use the capabilities of COLTRIMS, to correlate, every ion detected, with every other ion and electron. This is the result of having only one molecule in the laser focus per laser pulse and storing all detection events individually and not averaging any parameters. This allows the authors to construct a photo-ion photo-ion coincidence spectrum. As shown in Figure 2.7, time of flight for the first ion and second ion from one molecule can be plotted as separately as x and y axis. The sharp diagonal lines represent three different observed channels. The top line represents the D^+ and D_3^+ channel. The Coulomb explosions of D_2-D_2 dimer are also observed. The middle diagonal line shows the $D_2^+ + D_2^+$ explosion, and the bottom one shows the $D^+ + D^+$ explosion. Finally by varying the time between the pump and probe pulses and measuring the magnitude of the $D_3^++D^+$ signal, the authors were able to measure the time for the dimer to evolve into D_3^++D on the singly charged potential as $\tau = 330 \pm 55$ fs.

Kunitski et al. [56] used the COLTRIMS approach to study an exotic triatomic cluster He_3 which in this context means a helium trimer in which the three atoms are connected in a loosely bound Efimov state. In order to do this the authors, employ triple coincidence by

ionizing the trimer to a triply ionized state He_3^{3+} which Coulomb explodes to the $\text{He}^+ + \text{He}^+ + \text{He}^+$ channel with all three ions detected. This can allow the structure of the trimer to be reconstruction using also called inversion method, which involves starting from the measured ion momenta and tracing back to determine the original geometries, assuming a pure Coulomb repulsion. The authors employed a look-up table method to reconstruct the helium trimer.

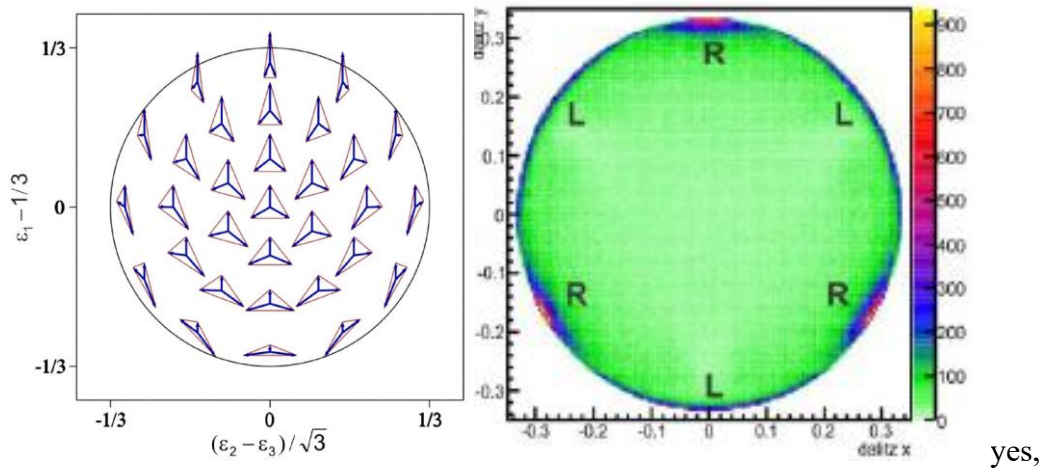


Figure 2.8: (left) theoretical Dalitz plot for helium trimer. (right) reconstructed Dalitz plot. Figure is from [56].

Kunitski et al. [56] utilised a Dalitz plot approach to extract data points, which were then used to simulate the experimental process and store both the data points and momenta into a large table. A measured set of ion momenta is compared to the look-up table to find the corresponding geometry. As shown in Figure 2.8, the left plot is the theoretical Dalitz plot, and the right plot is the reconstructed Dalitz plot.

COLTRIMS is also flexible in the source of ionization which it can utilize, with many recent contributions focusing on the molecular dynamics initiated by light from X-ray free electron lasers (XFL). An important recent study of geometry reconstruction, performed by Boll et al. [49] using COLTRIMS and XFL, which has successfully reconstructed the geometric structure for 2-iodopyridine ($\text{C}_5\text{H}_4\text{IN}$).

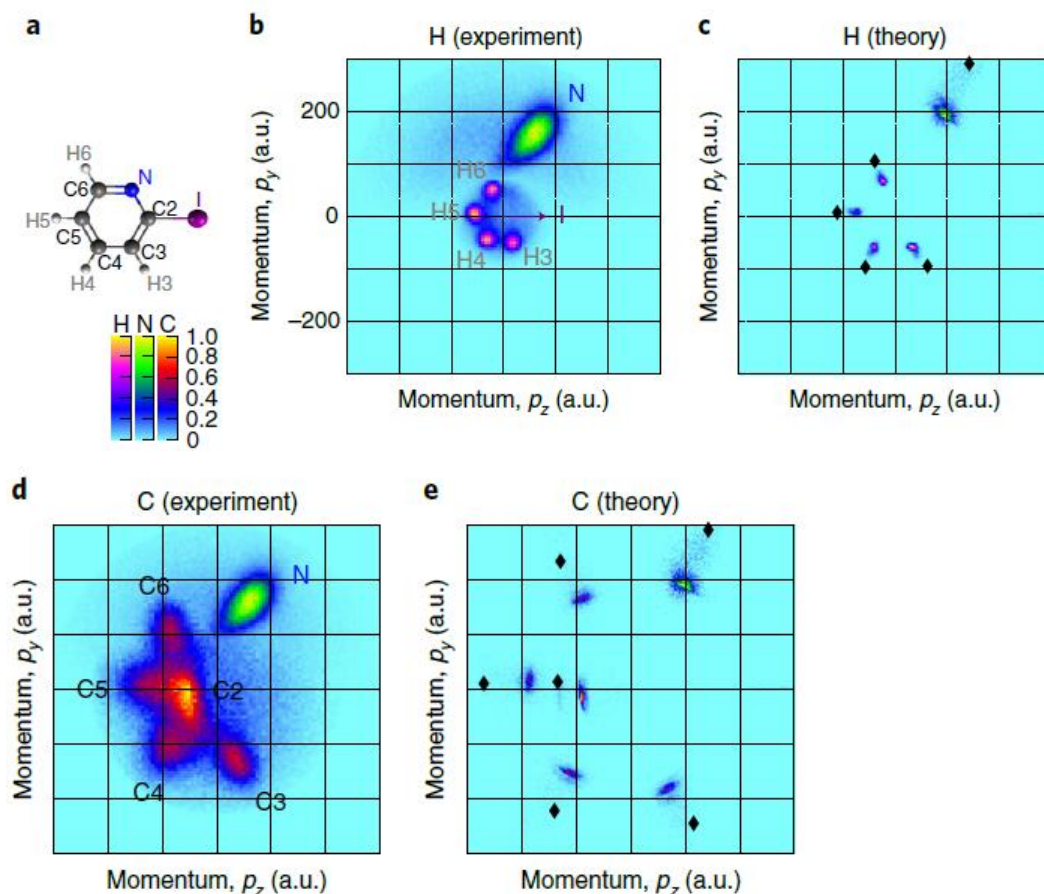


Figure 2.9: (a) structure for 2-iodopyridine (C_5H_4IN). (b) measured Newton plot and (c) calculated Newton plot. Newton plot shows the relationship between each momentum component. Figure is from [49].

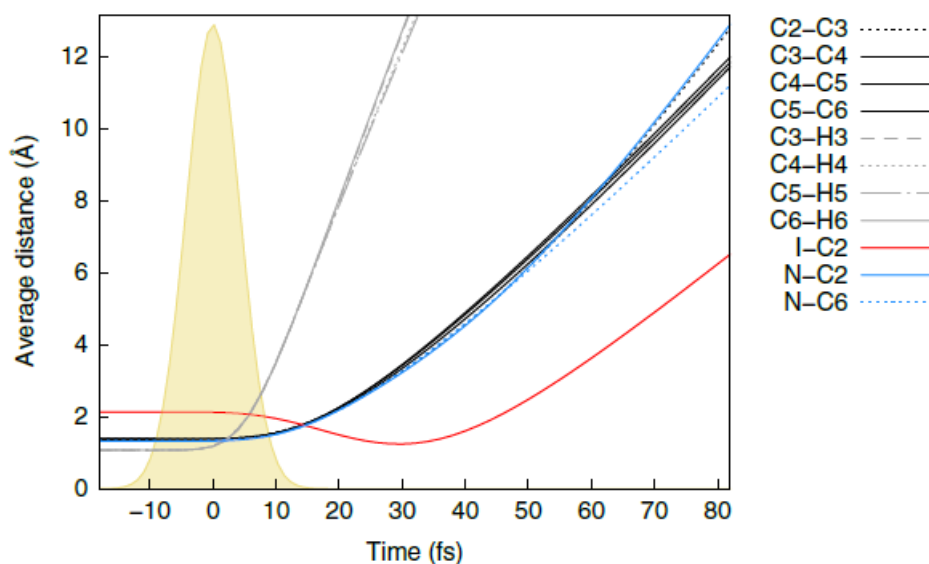


Figure 2.10: reconstructed bond lengths for 2-iodopyridine. The yellow area shows the assumed X-ray pulse shape, which is in the form of a Gaussian curve. The lines represent the bond lengths. Figure is from [49].

This geometry reconstruction method is a forward method, which means first modeling the structure of the molecule using a simulated ground vibrational state distribution, and then modeling the ionization process and Coulomb explosion resulting from the laser ionization event. This simulation is then visualized using the same Newton plotting technique used to visualize the experimental data. By comparing the simulated momentum and measured momentum the quality of the molecular model and the ionization dynamics model can be assessed. The 2-iodopyridine experiences Coulomb explosion, resulting in ion fragments I⁺, N⁺, C⁺ and H⁺. The authors employed the XMDYN theoretical toolkit, which combines atomic ab initio X-ray physics with molecular dynamics in a Monte Carlo scheme. As shown in Figure 2.9, the experimental momentum results (b) and (d) are consistent with the simulation results (c) and (e). The agreement validates the structural and ionization dynamics shown in Figure 2.10.

Lai et al. [72] studied the molecular orbital of N₂ molecule from the electron momentum. This experiment was performed with COLRIMS and 800nm, 30 fs and 5kHz femtosecond laser.

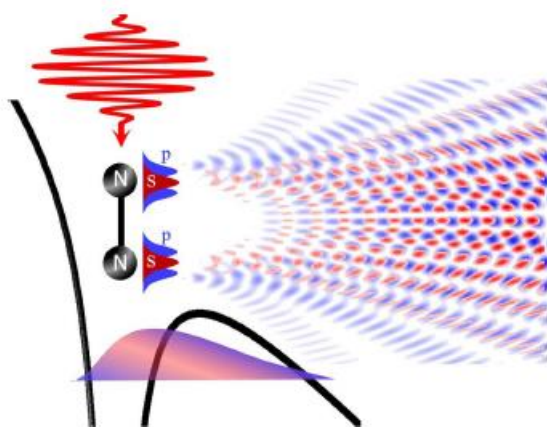


Figure 2.11: the schematic of laser induced electron tunnelling spectroscopy. The molecular potential is distorted by a laser field. The highest occupied molecular orbital of N₂ can be written as a linear combination of the 2s atomic orbital and 2p atomic orbital. As an electron is ionized from the molecule, the electron wave packet experiences orbital interference from the two centers, causing a modulation in the molecular frame photoelectron angular distributions. Figure is from [72].

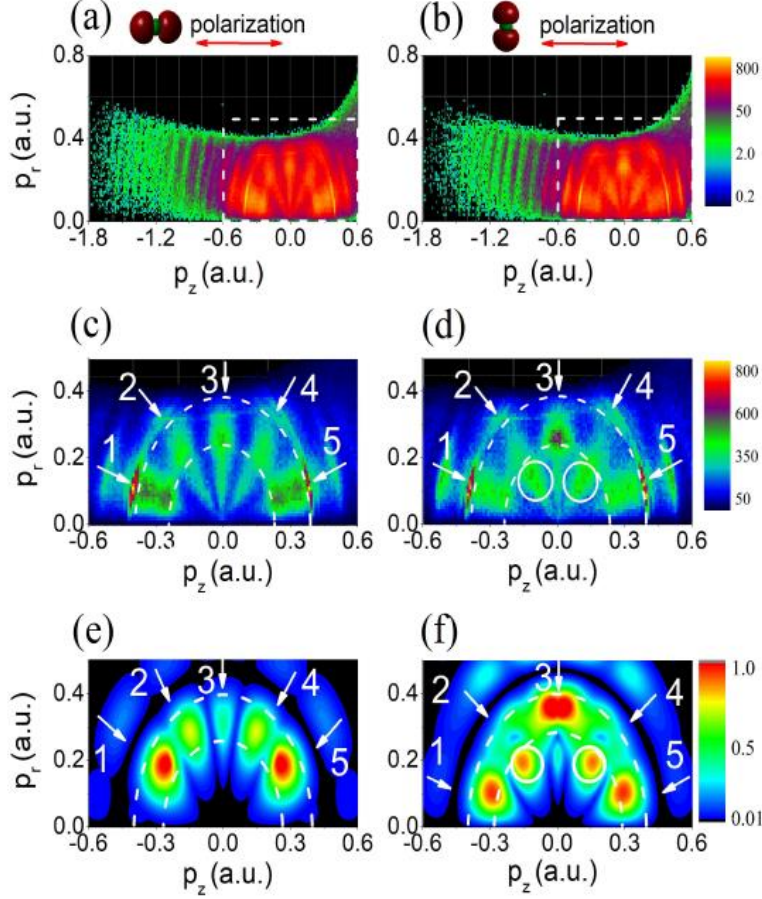


Figure 2.12: (a) and (b) are the experimental results of electron momentum for the parallel and perpendicular alignments of the molecular N₂ with respect to the laser polarization. (c) and (d) are the enlarged view of the low-energy region in (a) and (b). (e) and (f) are simulated photoelectron angular distribution. Figure is from [72].

According to molecular orbital theory, the molecular orbitals of N₂ can be written as a linear combination of atomic molecular orbitals. As shown in Figure 2.11, electrons ionized from the 2s and 2p atomic orbitals interfere with each other, causing a modulation in the photoelectron angular distribution. By analyzing the interference patterns, the authors of [72] were able to determine the weighted coefficient and the relative phases of different atomic orbitals, and then reconstruct the molecular orbitals. As shown in Figure 2.12, the measured electron momentum can be obtained from COLTRIMS. The experiments were performed for both horizontal laser polarization and vertical polarization. p_z represents the component electron momentum that is parallel to the polarization, and p_r represents the momentum perpendicular to the polarization. From (a) and (b), for momenta smaller than 0.6 a.u., the photoelectron angular distribution shows a radial fan-like patterns. There are five radial stripes in both plot (c) and (d). For the horizontal polarization case (c), each stripe maximizes the same energy band as indicated by the dashed semi-circles. While for the vertical polarization case (d), the second and fourth stripe maximize at the lower energies as indicated by the two circles. The authors use the linear combination of atomic orbitals (LCAO) approach to reconstruct the

electronic wavefunction of N_2 from this information, they also develop a Strong Field approach which they term the Coulomb quantum-orbit strong-field approximation to simulate the electron momentum for the experiments as shown in the figure (e) and (f), which are consistent with the experimental data.

Chapter 3 Reaction Microscope Construction

3.1 Introduction

The Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) technique [37][38][13], now more commonly known as the “reaction microscope”, was initially devised by the research group of Horst Schmidt-Bocking at the university of Frankfurt, and is an advanced technique to investigate the dynamics of electrons and ions in a molecule as it is ionized by intense fields. All charged fragments and electrons from an atomic or molecular multiple ionization are projected onto position sensitive detectors [1] using a combination of electric and magnetic fields. From the measured time of flight and position information, the three-dimensional momentum vectors can be determined.



Figure 3.1: Image of UW-ALLS COLTRIMS. UW: University of waterloo in Waterloo, Ontario. ALLS: Advanced laser light source laboratory in Varennes, Quebec.

COLTRIMS apparatus consists of seven primary components: the spectrometer, the delay-line detector, the signal system, the vacuum system, the cooling system, magnetic coils and Cobold software. At the heart of the COLTRIMS is the coincidence condition, where all

information about each ion and electron detected, is recorded and stored for each individual laser pulse, and nothing is averaged. This allows the behavior of a molecule under thousands of separate interactions to be observed. The condition relies on the fact that only one interaction event per laser shot is allowed, which guarantees that the detected fragments come from the same molecule. To achieve this, a vacuum environment, a supersonic gas jet and a focused laser beam are essential. The vacuum and cooling systems are critical for maintaining a stable low pressure (10^{-10} mbar) environment for laser-induced interactions with molecules. The focusing mirror is designed to focus the laser beam to a small spot ($100\text{-}10000\text{ }\mu\text{m}^3$), resulting in significantly increased intensity that is proportional to the square of the laser's electric field. In order to ensure that target density is low enough to maintain only one molecule in the laser focus, per laser shot, the target gas is delivered by a supersonic jet, which is achieved using a nozzle, a skimmer, apertures and 4-jaw slit. The spectrometer and magnetic coils generate external electric field and magnetic field, respectively, which direct ions and electrons to follow trajectories that can be analyzed. Meanwhile, delay-line hexanode, micro channel plate, and signal system enable the precise collection of data from these interactions.

3.2 Vacuum system

To conduct measurements effectively, a high-vacuum setting is imperative. Without an adequate vacuum environment, the interaction of photon beam with the surrounding gas would make it difficult to drive particles towards detectors and collect effective data. Typically, the surrounding gas refers to the air, which primarily consists of H_2O and the ionization of H_2O could generate a significant number of H^+ ions. Furthermore, in order to prevent the influence of thermal energy and obtain accurate momentum measurements, it is crucial to provide a cold target. The supersonic jet is achieved by directing gas from a higher-pressure region, typically a few bars, into a low-pressure chamber (around 10^{-4} bar), passing through a nozzle, skimmer, slit and apertures then finally entering the interaction main chamber.

Figure 3.2 illustrates the layout and components of the vacuum systems, showing how the chambers and pumps are interconnected, along with pressure measurement components to monitor the vacuum levels. This is a three-stage thin jet source system. COLTIMS consists of five chambers and seven pumps. The high gas load in the jet source chamber is pumped by a big turbo pump Pfeiffer HiPace 1800 with a speed of 1450 l/s, the scroll pump serves as the backing pump for the big turbo pump. The jet source chamber is pumped by the Pfeiffer Hipace 1800 turbo molecular pump and backed by a scroll pump (Edwards XDS35i) or by an Ecocube pump (Pfeiffer Hipace 80 and backing pump MVP 015-2, pump speed of 67 l/s). The second stage chamber and third stage chamber are individually pumped by two Pfeiffer Hipace 80 turbo molecular pump with a pump speed of 67 l/s. The main chamber is pumped by the Pfeiffer Hipace 700 turbo molecular pump, which has a pump speed of 685 l/s. And the jet dump

reaction chamber and the jet dump chamber. Seven turbomolecular pumps are connected to the five chambers. The two Hipace 80 turbo pumps evacuate the gas from the second and third stage chambers into the jet source chamber, the Hipace 1800 turbo pump evacuate the gas from the jet source chamber. The Hipace 300 turbo pump evacuates the gas from the jet dump chamber, and the Hipace 700 evacuates the gas from the reaction chamber. The scroll pump is the backing pump of Hipace 1800. The EcoCube is the backing pump of Hipace 300 and Hipace 700. The dashed lines represent the connections of the cooling system. Details for gas handling and EcoCube can be found in Figure 3.4.

Table 3.1: Operation pressures of chambers and valves.

Detection area	Jet source	Second stage	Third stage	reaction chamber
Pressure (mbar)	$10^{-4} - 10^{-3}$	10^{-6}	10^{-8}	10^{-10}
Detection area	Jet dump	Valve #1	Valve #2	Valve #3
Pressure (mbar)	10^{-10}	10^{-2}	10^{-4}	10^{-1}

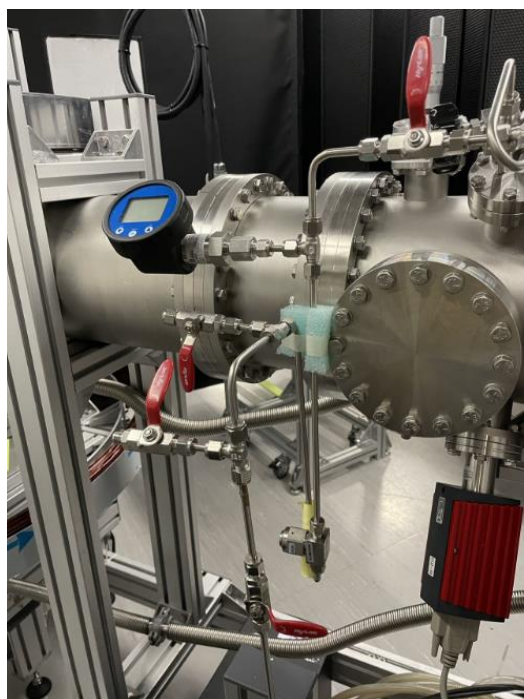


Figure 3. 3: Picture of the external gas line.

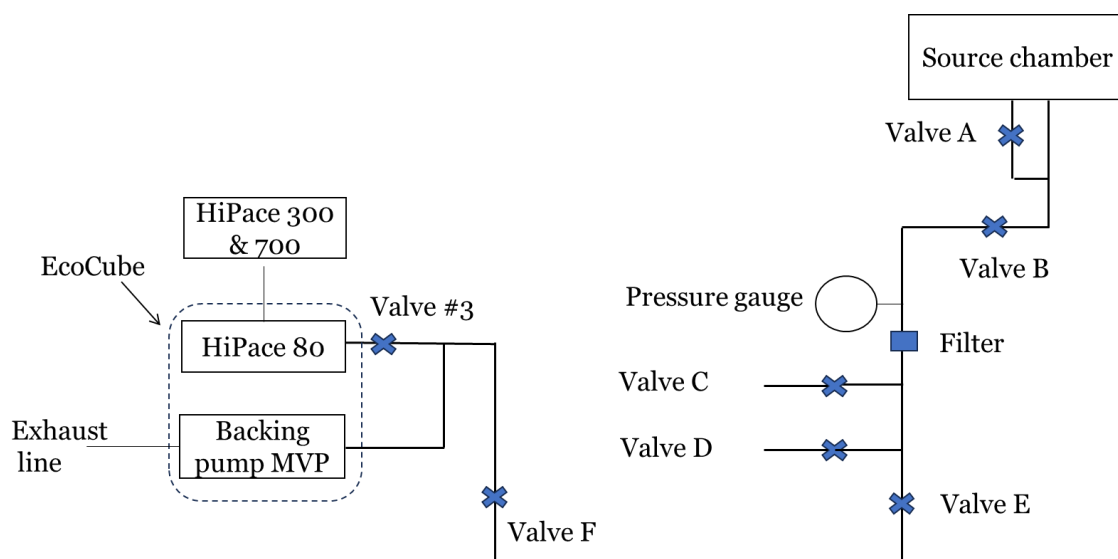


Figure 3.4: Diagram of the external gas line. The gas cylinder can be connected to valve C or D. The range of the pressure gauge is 0-5 bar. The EcoCube is a combination of a HiPace 80 and a backing pump MVP.

As shown in Figure 3.4, the gas is pumped from the jet dump chamber and the reaction chamber to the HiPace 80 by the HiPace 300 and 700. Following this, valve #3 is situated between the exhaust of the HiPace 80 and the MVP, it must be closed before the MVP is used to evacuate the external gas line. When pumping out the gas line, valve #3 is closed before valves B, E and F should be open. During experiments, valves E and F must be closed, and valve #3 must be open.



Figure 3. 5: Power control for vacuum system designed by UW electronics store.

As shown in Figure 3.2, the vacuum system consists of different kinds of pumps and the associated pressure display control units and electronics valves that require power, with

different current requirements. A power control system for the COLTRIMS is designed, as shown in Figure 3. 5. The system pumping procedure can be found in Appendix A.5.

3.3 Supersonic gas jet

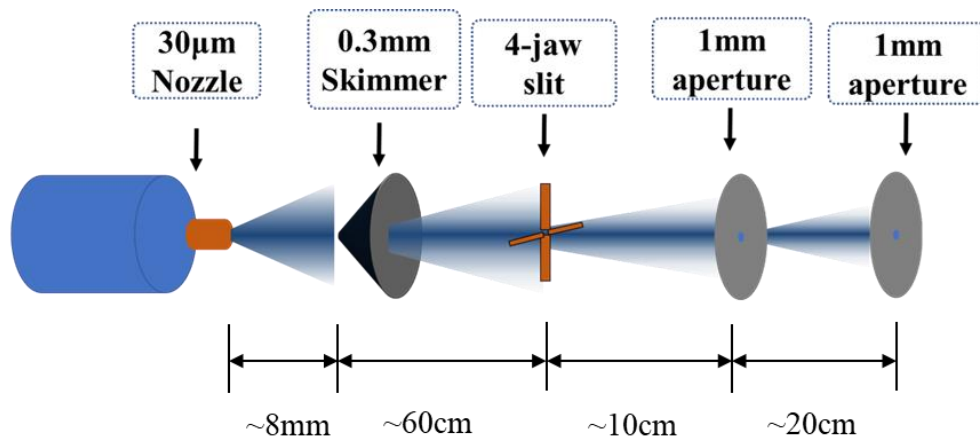


Figure 3.6: Collimation of jet. The gas jet comes from the gas nozzle, before passing through the skimmer, 4-jaw slit, and two apertures.



Figure 3.7: The interior of the jet source chamber. The red line shows the path of the gas line from outside the chamber to the gas nozzle.

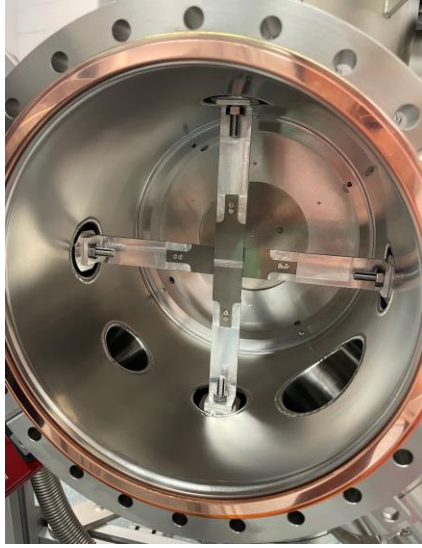


Figure 3.8: The adjustable 4-jaw slit. The 4 jaws are connected to 4 micrometer screws on the outside.

As shown in Figure 3.7, inside the jet source chamber, the gas nozzle is connected to the outside gas cylinder by a spiral tube. As shown in Figure 3.6, a 0.3mm-diameter skimmer is mounted on the divider between the jet source chamber and the second stage chamber, with the tip towards the nozzle. The nozzle is fixed on a rod, while the position is adjustable slightly by two micrometer screws outside the chamber. As shown in Figure 3.8, inside the collimator chamber, the 4-jaw aperture is adjustable by 4 micrometer screws to adjust the width and height of the gas line.

Figure 3.6 shows the collimation of jet. The gas jet initially exits with some velocity from a 30 μ m-diameter nozzle, then pass through a 0.3mm-diameter skimmer. The orientation of the skimmer's tip is directed toward the nozzle, facilitating a transition from a narrower opening to a wider one. The skimmer can narrow the gas jet and select the central coldest part by filtering the outer portion. Additionally, an adjustable 4-jaw slit system can further narrow the molecular beam. The supersonic gas jet is essential for maintaining the condition of only one molecule in the laser focus in order to operate in a coincidence mode.

3.4 Focused laser beam

In the fundamental transverse mode TEM_{00} , the Gaussian intensity distribution [43][44][45] as shown in Equation 3. Where the total power P can be calculated by the measured the average power from power meter, pulse duration and repetition rate. Beam waist $w(z)$ has minimum value w_0 can be calculated by Equation 3. . z_R refers the Rayleigh length, and it is where the Gaussian beam has expanded by a factor of $\sqrt{2}$.

$$I(r, z) = \frac{2P}{\pi w(z)^2} e^{-2r^2/w(z)^2} \quad \text{Equation 3. 1}$$

$$P = \frac{E}{\tau} = \frac{P_{av}}{f_{rep} \tau} \quad \text{Equation 3. 2}$$

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2} \quad \text{Equation 3. 3}$$

$$z_R = \frac{\pi w_0^2}{\lambda} \quad \text{Equation 3. 4}$$

$$w_0 = \frac{2f\lambda}{\pi d} \quad \text{Equation 3. 5}$$

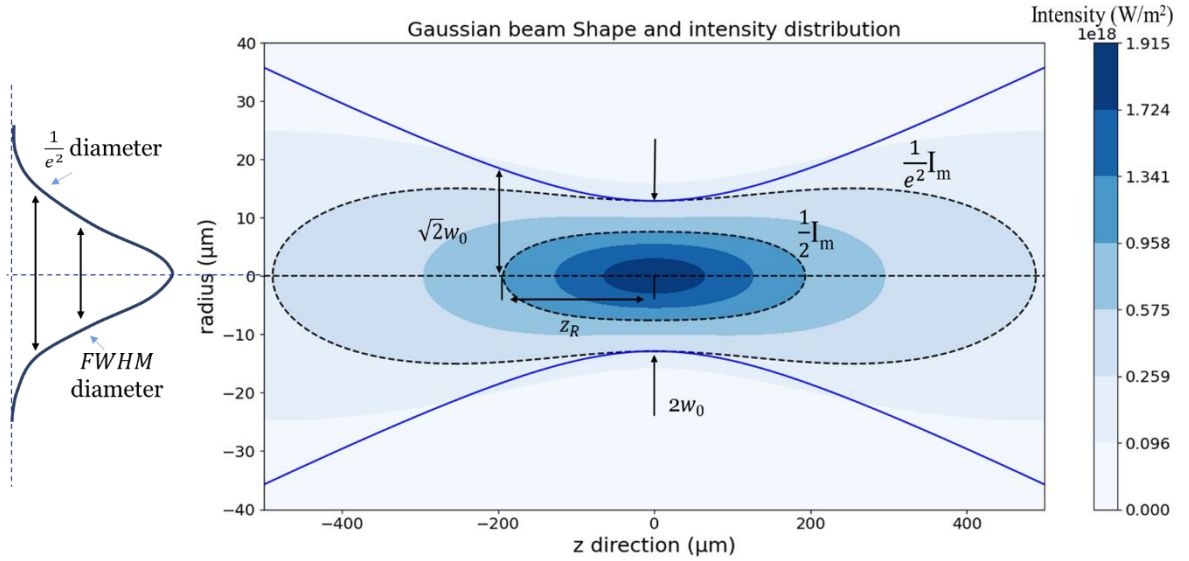


Figure 3.9: Gaussian beam shape and intensity distribution at focal spot. Pulse duration τ is 30fs, wavelength λ is 2700nm, repetition rate f_{rep} is 20 kHz, average power P_{av} is 3000 mW, focal length f is 75mm and beam diameter d is 10mm. The z direction corresponds to the laser's direction. The intensity is illustrated by color, with darker blue indicating higher intensity. The larger dashed oval outlines the intensity at $1/e^2$ of maximum intensity I_m . The smaller dashed oval outlines the intensity at $1/2$ of maximum intensity I_m . The blue hyperbola lines represent the Gaussian beam profile, with the beam waist located at $2w_0$. The left plot shows the diameters of a Gaussian beam.

As shown in Figure 3.9, intensity and beam profile at focal spot has been illustrated. The minimum beam waist is $2w_0 = 25.78\mu m$, the Rayleigh length is $z_R = 193.37\mu m$. The peak

intensity can be calculated, $I_m = \frac{2P}{\pi w_0^2} = \frac{P\pi d^2}{2\lambda^2 f^2} = 1.915 \cdot 10^{18} \text{ W/m}^2$. The focal spot, whereas the intensity is $\frac{1}{2} I_m = 0.958 \cdot 10^{18} \frac{\text{W}}{\text{m}^2}$, is about 386.74 μm in z direction, and 16.57 μm in x and y direction. The focal spot with $1/e^2 I_m = 0.259 \cdot 10^{18} \frac{\text{W}}{\text{m}^2}$, is about 976.35 μm in z direction, and 25.78 μm in x and y direction.

3.5 Magnetic coil

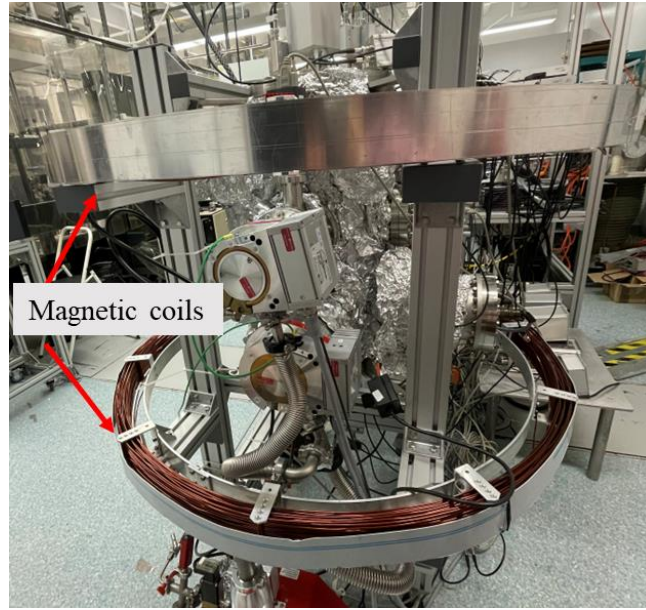


Figure 3.10: Picture of magnetic coils.

The electrons born in the interaction region can move all possible directions with energies ranging from a few electron volts to higher values depending on the laser intensity. A homogeneous magnetic field is needed to capture all electrons, and this is accomplished by a Helmholtz configuration [41]. In this setup, two identical copper circular coils with a radius of 60 cm are positioned 60 cm apart along the same line. Electric current flows through both coils in the same direction. This current generates magnetic fields around each coil, and when combined, they create a nearly uniform magnetic field in the space between the coils.

3.6 Spectrometer

The spectrometer is the central part of the COLTRIMS experiment to guide the ions and electrons onto detectors. The spectrometer contains two 3-layer HEX 75 delay line detectors, which have zero dead time, high precision, multi-hit micro channel plates (MCP). A single drift

region is maintained by copper electrodes which are connected to each other by a resistance chain. The electric field directs the positively charged ions to the ion detector, whereas electrons are captured by a homogeneous magnetic field and fly to the electron detector. The field strengths can be changed for individual experiment. A homogeneous electric field is built up inside the spectrometer by connecting copper electrodes with a series of $100\text{k}\Omega$ resistors.

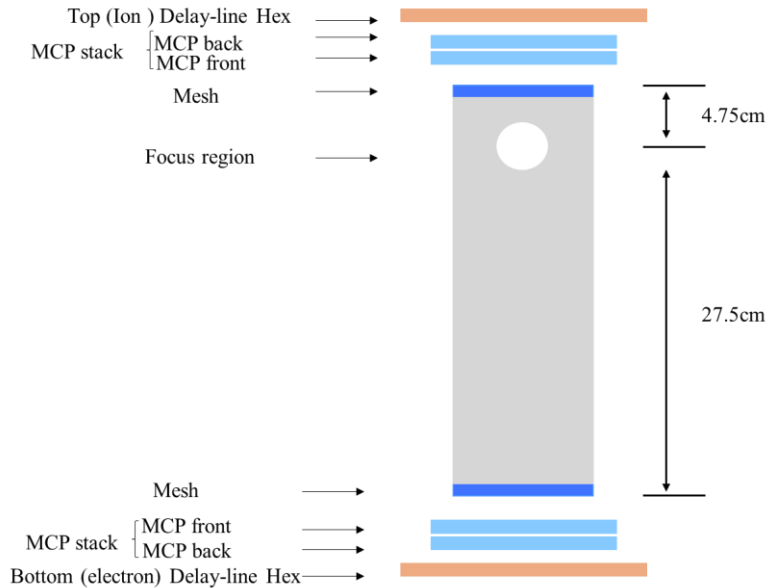


Figure 3.11: Diagram of the spectrometer and detector.

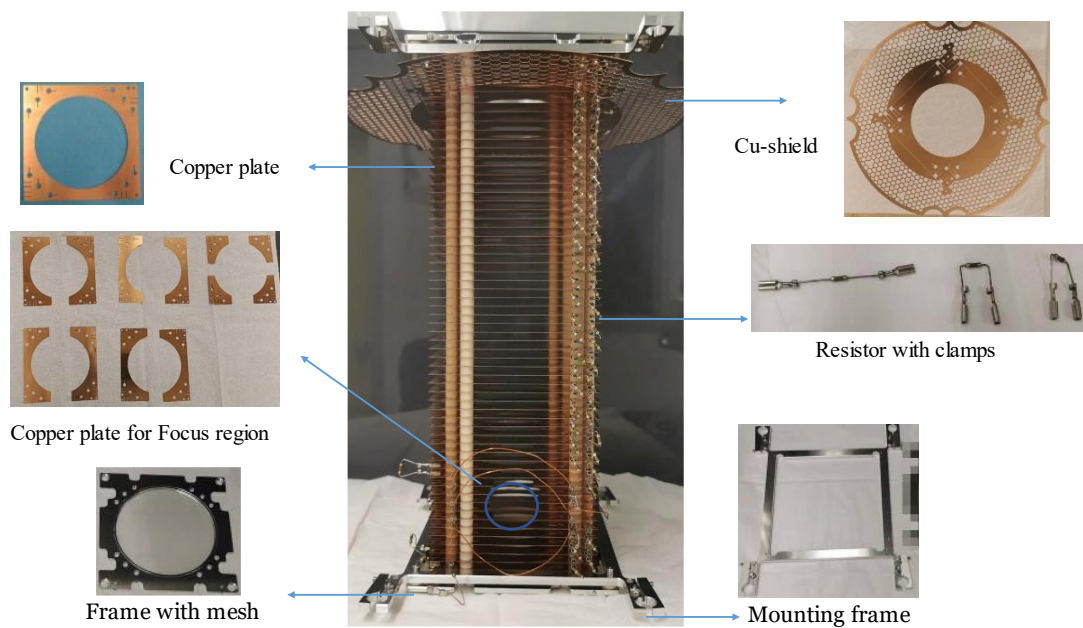


Figure 3.12: Spectrometer and its components. From end to end, meshes and copper plates are connected by resistors.

3.7 Delay line detector

The ion detector and electron detector are exactly same, and both consist of two main parts: the three-layer hexagonal delay-line (Hexanode) [40][41] and the micro channel place (MCP) [42]. The position and time information of particles are detected by delay-line hexanode and MCP.

3.7.1 Micro channel plate

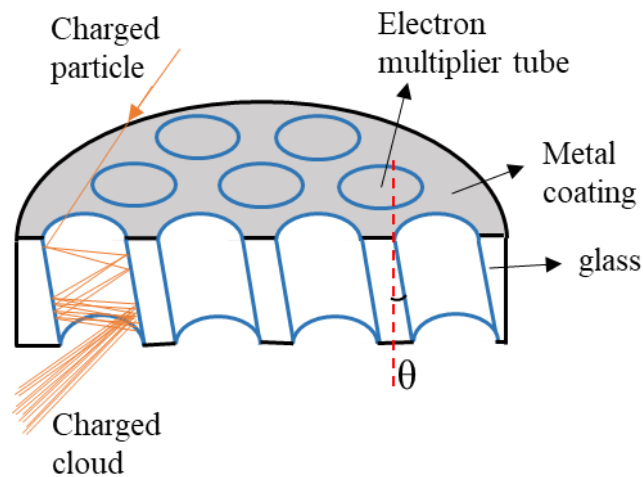


Figure 3.13: Diagram of a micro channel plate.

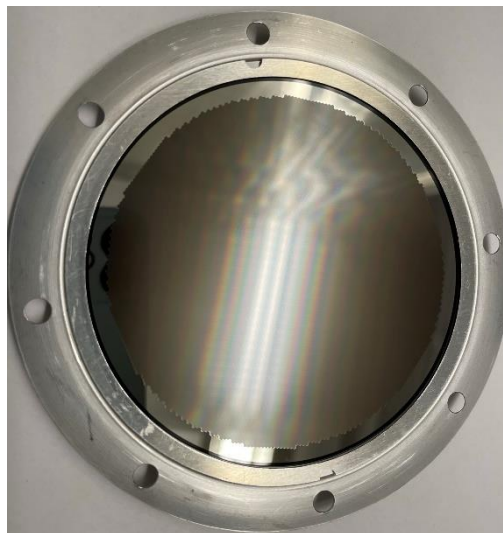


Figure 3.14: Picture of a micro channel plate.

The main purpose of micro channel plate is electron multiplication and record the time of flight. As shown in Figure 3.14, a micro channel plate is a glass wafer with metal coating on

both surfaces, featuring numerous individual electron multiplier tubes (channels) [42]. These channels are parallel to each other and have a slight angle θ , around 20° relative to the surface normal. Each channel has a diameter of 12 micrometers. On each MCP, there is a 'V' shape marking indicating the front side. The open area ratio, which is the ratio of integrated pore area to the total disc area is at least 70%. A single MCP is measured to have a resistance about $20\text{M}\Omega$, with a diameter of about 87 mm. when a charged particle enters a channel and undergoes multiple collisions with the channel wall, it emits an electron cloud. Ultimately, a single MCP can achieve an electron multiplication factor about $10^3 - 10^4$. Each MCP stack contains two micro channel plates in series with a relative angle between two 'v' marks to increase gain to $10^6 - 10^7$.

3.7.2 Three-layer hexagonal delay-line

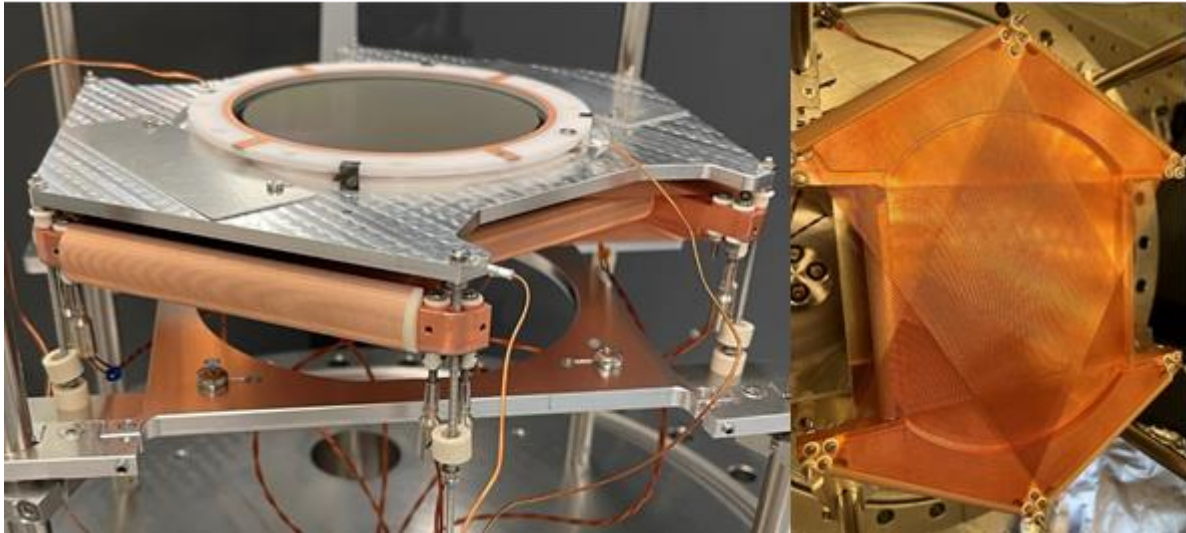


Figure 3.15: Pictures of a delay line detector including a MCP stack and a 3-layer hexagonal delay-line.

The charged clouds emitted from the MCP stack impact the hexagonal delay-line, from which position information is derived. Typically, a delay-line detector has two layers. However, a third layer to make it a hexagonal delay line can provide additional data for multi-hit cases. The three layers (A, B, C) are at an angle of 60° to each other. When a charged cloud hits one layer, it generates a signal pulse. This pulse propagates in both directions towards the ends of the delay line. Each layer includes a signal wire and a reference wire, with the signal wire maintained at a higher potential compared to the reference wire. This arrangement ensures that the charged cloud is mostly collected by the signal wire. In the case of multiple layers, the electron cloud is detected by all signal wires, providing more position information, and enhancing precision.

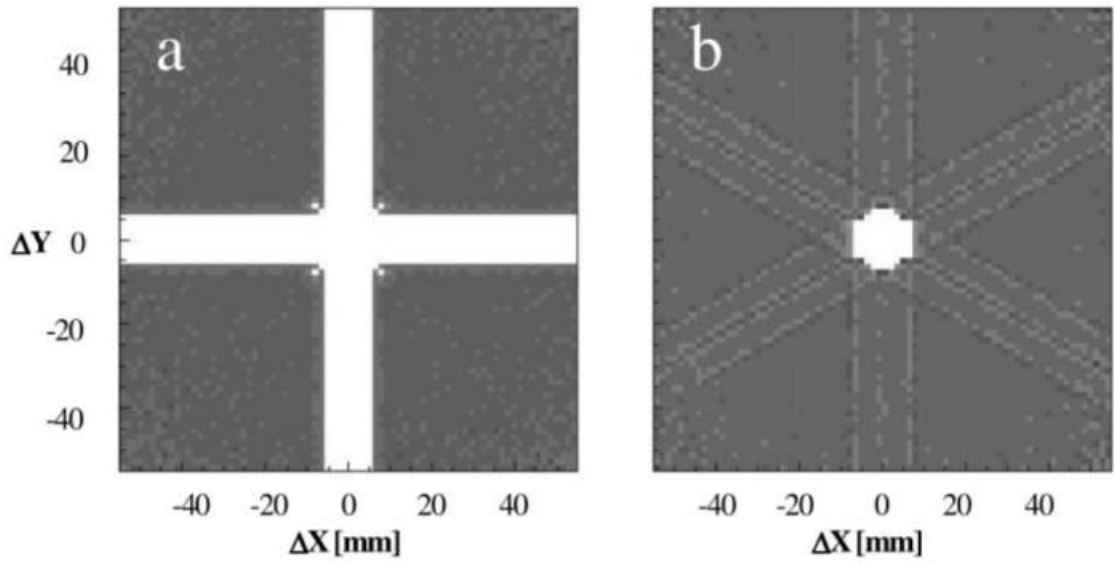


Figure 3.16: Monte Carlo simulation of the dead regions for two particles that arrives with relative positions Δx and Δy on a double layer delay-line (a) and on a three-layer delay-line (b). Only in the dark regions, the position and time of both particles can be reconstructed. The relative arrival time of the two particles in this simulation is 2.5ns for (a) and 0ns for (b). Figure adapted from [82].

As shown in Figure 3.16, the dead region for a three-layer delay-line is significantly smaller compared to a double layer delay-line, and it can detect simultaneous particles. The three-layer delay-line is only blind when particles arrive at the same time and at the same position. The third layer provides additional time information to resolve the simultaneous particle hits and reduce the dead region.

3.7.3 Measurement

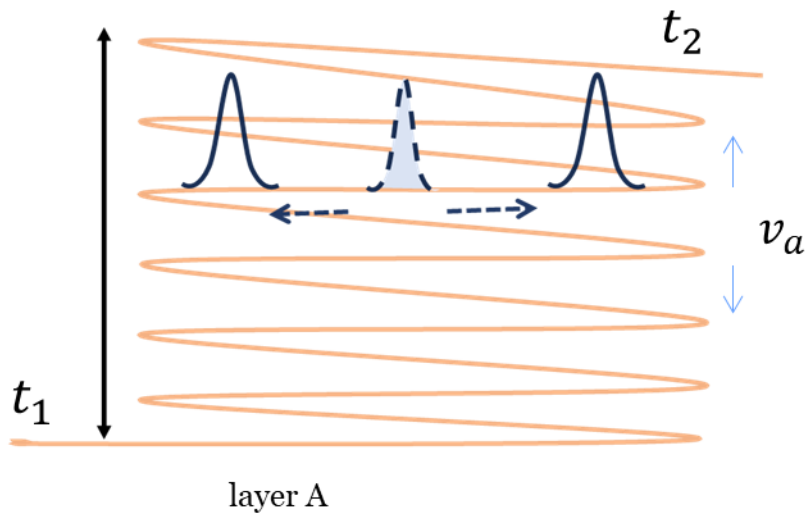


Figure 3.17: Diagram of a single layer.

$$A = \frac{1}{2} v_a (t_1 - t_2)_a \quad \text{Equation 3.6}$$

$$B = \frac{1}{2} v_b (t_1 - t_2)_b \quad \text{Equation 3.7}$$

$$C = \frac{1}{2} v_c (t_1 - t_2)_c + O \quad \text{Equation 3.8}$$

$$X_{AB} = A + O_x \quad \text{Equation 3.9}$$

$$Y_{AB} = \frac{1}{\sqrt{3}}(A - 2B) + O_y \quad \text{Equation 3.10}$$

$$X_{AC} = X_{AB} \quad \text{Equation 3.11}$$

$$Y_{AC} = \frac{1}{\sqrt{3}}(2C - A) + O_y \quad \text{Equation 3.12}$$

$$X_{BC} = B + C + O_x \quad \text{Equation 3.13}$$

$$Y_{BC} = \frac{1}{\sqrt{3}}(C - B) + O_y \quad \text{Equation 3.14}$$

The position on a single layer is coded by the arriving time difference from signals in opposite corners of the anode as shown in Figure 3.17. The position A layer A can be calculated by Equation 3.6. v_a represents the velocity in the direction perpendicular to the wire. Following a similar principle, the positions B and C on the layer B and layer C can be determined using equations 3.7 and 3.8. The two-dimensional position on the hexanode can be determined from any two layers using equations 3.9-3.14. The signals from the third layer serve as a redundant source of information in situations when signals are lost. The parameter O is an offset value, which should align the detected position for all three layers. It needs to be selected in such a way that the position lines for calculated A, B, C intersect at a common center, which means A should be zero when both B and C are zero.

3.8 Reconstruction of momentum for ions and electrons

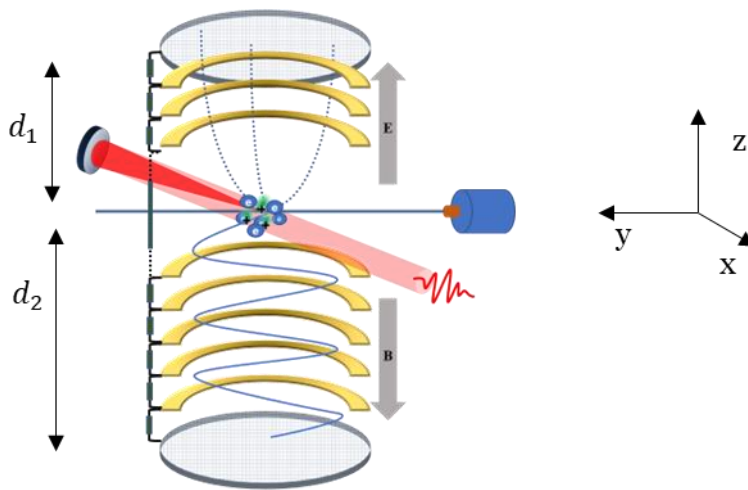


Figure 3.18: trajectory of ions and electrons in the spectrometer. The gas jet is along the y-axis, the laser is along the x-axis, and the spectrometer is along the z-axis. The vertical distance from

the top detector to the focusing position is d_1 , the vertical distance from the bottom detector to the focusing position is d_2 .

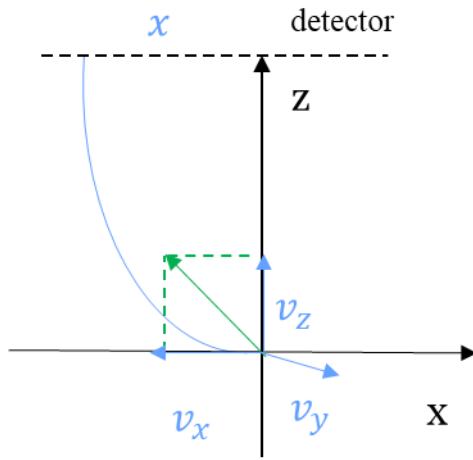


Figure 3.19: an example of trajectory for ions in xz-plane. The dashed line represents the ion detector, x is the displacement in x direction. The initial velocity can be divided into x , y and z components. The trajectory of an ion follows a projectile motion.

$$TOF_0 = \sqrt{\frac{2d_1m}{qE}} \quad \text{Equation 3.15}$$

$$p_x = m \frac{x - x_0}{t} \quad \text{Equation 3.16}$$

$$p_y = m \frac{y - y_0}{t} \quad \text{Equation 3.17}$$

$$p_z = \frac{qE}{2} \frac{TOF_0^2 - t^2}{t} \quad \text{Equation 3.18}$$

From the measured position and time information (x,y,t) , momentum of ions can be reconstructed by equations 3.15-3.18. Ions in the spectrometer move towards the top detector due to the electric field and follow a projectile motion. The (x_0, y_0, TOF_0) represents when an ion flies to the detector with zero initial velocity. The motion in the y direction determines the time of flight. The velocities in the x and y directions can be easily calculated by dividing displacement by time. To determine the momentum in the z direction, one can utilize the relationship that ions with zero initial velocity, will have the same displacement in z direction.

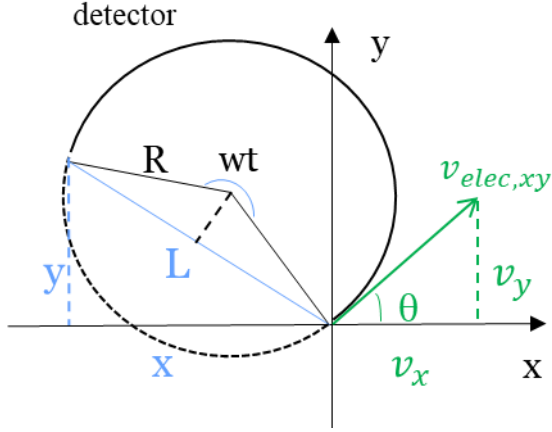


Figure 3.20: trajectory of electrons in the xy-plane. The initial velocity can be divided into x, y and z components. v_z is the velocity perpendicular to the xy-plane, v_x and v_y are the velocity in the xy-plane. The trajectory of an electron follows a circular motion in the xy-plane, while in z-direction it follows a path of uniformly accelerated motion.

$$T = \frac{2\pi m_e}{eB} \quad \text{Equation 3.19}$$

$$v_{e,xy} = \frac{eBR}{m_e} \quad \text{Equation 3.20}$$

$$R = \frac{x^2 + y^2}{2 |\sin(\frac{wt}{2})|} \quad \text{Equation 3.21}$$

$$p_x = \frac{wm_e}{2} \left(x \cot \frac{wt}{2} - y \right) \quad \text{Equation 3.22}$$

$$p_y = \frac{wm_e}{2} \left(y \cot \frac{wt}{2} + x \right) \quad \text{Equation 3.23}$$

$$p_z = \frac{eE}{2} \frac{TOF_0^2 - t^2}{t} \quad \text{Equation 3.24}$$

$$TOF_0 = \sqrt{\frac{2d_2 m_e}{eE}} \quad \text{Equation 3.25}$$

Electrons follow spiral trajectories from the interaction region to the bottom detector, influenced by both a homogeneous electric field and a homogenous magnetic field. As shown in Figure 3.20, electrons follow a circular motion. The initial velocity is the component in xy-plane. The final position on the detector (x,y) is on the circle. The radius can be calculated by equation 3.21, and the period for a full circle can be determined by the equation 3.19. The x and y component of velocity can be calculated by equation 3.22- 3.24.

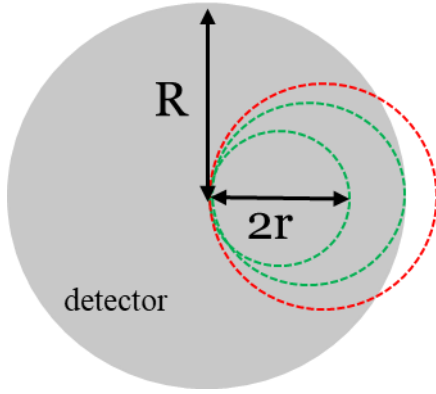


Figure 3.21: Electron trajectories on a detector. R is the radius of the detector, and $2r$ represents the diameter of the circular motion. $2r < R$ is required for detection purpose. The green dashed lines remain within the detector, while the red dashed line extends beyond the detector.

For ions, the displacement in the xy -plane should be less than the radius of the detector, R . For electrons, $2r$ should be less than R as shown in Figure 3.21. Electrons will return to their initial (x, y) position after each period T , so the condition $t \neq nT$ must be satisfied.

3.9 Signal system

To ensure the proper collection of all signals, signal verification procedures are essential. First, inspect cable connections within the chamber, specifically from detectors and spectrometers to flanges. Then, examine cable connections outside the chamber, tracing them from flanges through the electronics to the computer. Additionally, verify the delay-line signals by using a pulse generator and assess the MCP signals by applying appropriate high voltages. Finally, assess the signal detection process within the Cobold software by conducting dark count tests. These steps collectively help ensure the proper functioning and connectivity of the entire system.

3.9.1 Cable connections

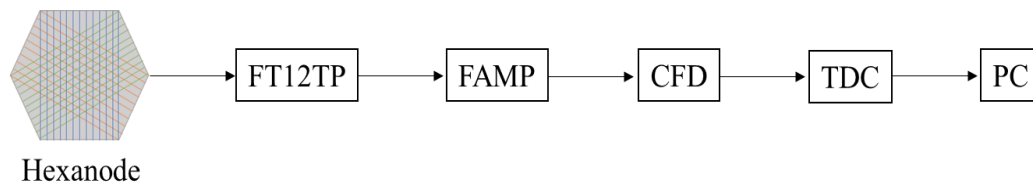


Figure 3.22: A signal pathway from hexanode to PC. Hexanode: the delayline detector. FT12TP: 12-pin feedthrough decoupler. FAMP: signal amplifier. CFD: constant fraction discriminator. TDC: time-to-digital converter. PC: computer.

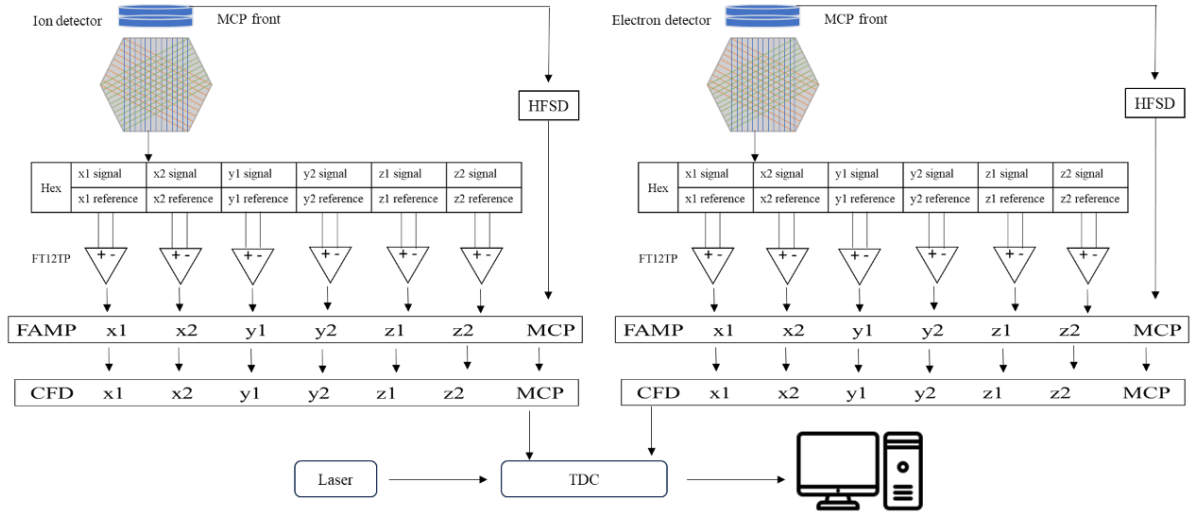


Figure 3.23: The diagram of the signal from detectors to computer.

The signal processing in COLTRIMS involves collecting signals from detectors and routing them to the computer. The initiation is triggered by a signal from the laser photodiode. Then signals from detectors are collected, including 12 delay line signals from the 3-layer delay lines, and 1 signal from the MCP front. These signals pass through the FT12TP feedthrough decoupler and a high frequency signal decoupler (HFSD). The signal decoupler is a passive device to pick up high frequency signals from FT12TP. Afterward, 7 signals are amplified by FAMP (the amplification factor is adjustable, ranging from 0 to 70) and routed for timing and digitizing circuits. The signals are then processed into NIM signals by the CFDs and fed into the time-to-digital converter (TDC). In a standard COLTRIMS setup, all measurements involve timing represented as analog voltage pulses, which can vary in amplitude. To address uncertainty, constant fraction discriminators (CFDs) are used. These CFDs trigger at a fixed fraction of a pulse's amplitude by combining it with a delayed and inverted copy of itself, ensuring consistent and precise triggering for accurate measurements. A TDC functions like synchronized stopwatches. Each arriving pulse starts a clock, and when the stopping line is triggered, all clocks freeze for readout by the system.

When the buildup the COLTRIMS or open the main chamber, cable connections should be checked before and after assembling the flanges by continuity tests for each part, starting from the delay line and MCP, extending all the way to the feedthrough, ensuring that resistances are within the specified range. Cable connection details can be found in Appendix A.2.3 and A.3. Resistance check procedures and checklists can be found in Appendix A.4.

3.9.2 Check delay-line signals.

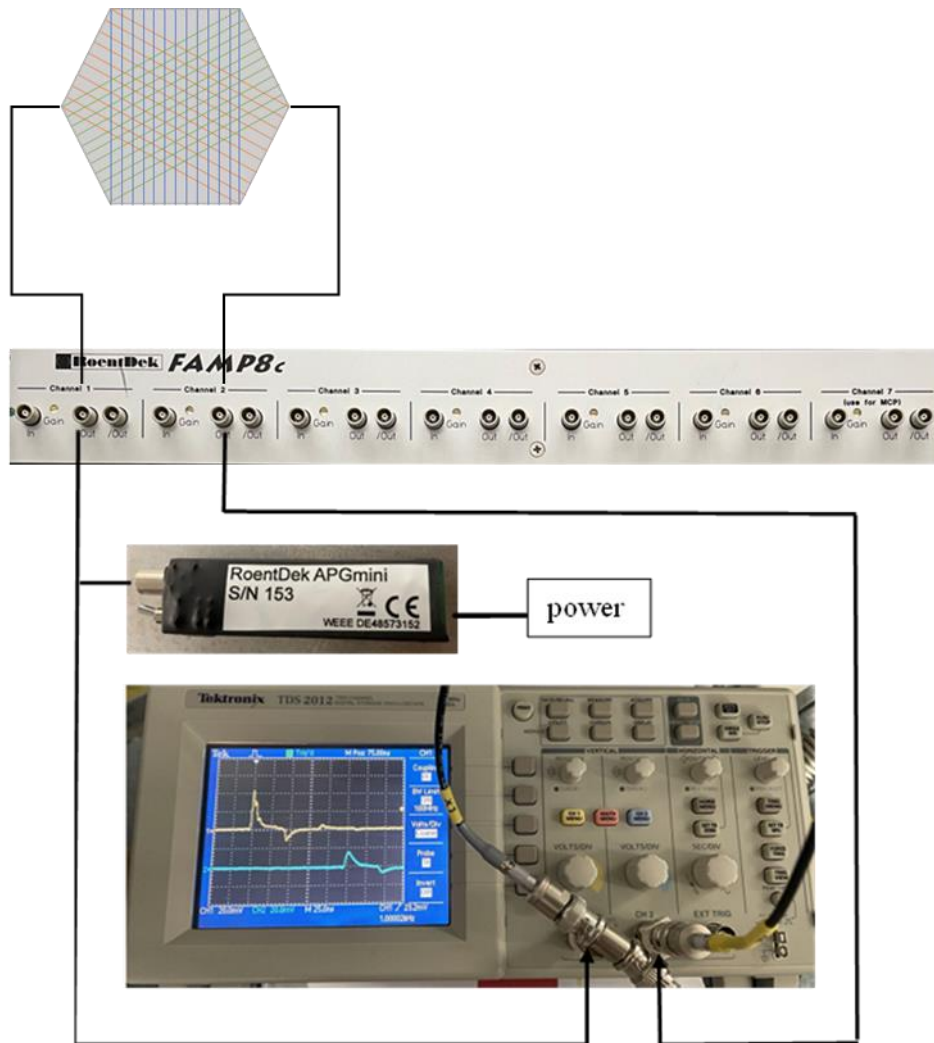


Figure 3.24: Diagram of a delay-line signal test.

Use the signal pulse generator to check the output pulse from the delay line; signals from the same layer should be identical. First, power on the signal generator and send the signal to the x1 channel on the FAMP and to the oscilloscope. Second, check the output signal from the x2 channel by oscilloscope. Since the x1 and x2 channels are from same layer, the x2 channel on the FAMP should output a delayed but larger pulse, and there should be no signal from other channels. By comparing the input and output signals on the oscilloscope, one can identify any issues with the delay line and determine which layer may have a problem.

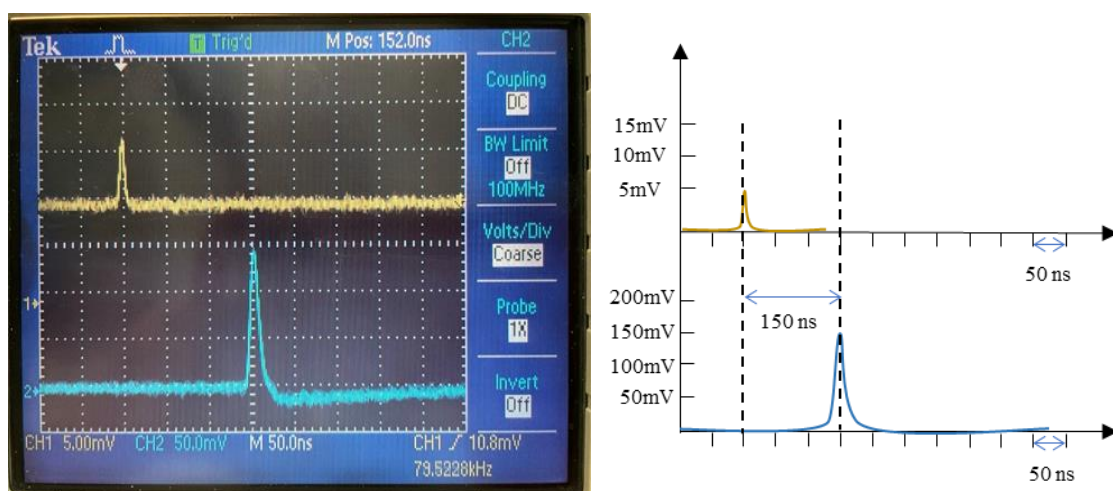


Figure 3.25: (left) yellow curve represents the input signal to x1 channel, and the blue curve represents the output signal from x2 channel. (right) the signal plot from the left plot. The signal has a delay of about 150 ns.

As shown in Figure 3.25, the input signal into the x1 channel is measured at 5mV. In contrast, the output signal from the x2 channel is amplified to 150mV, with an associated delay of about 150ns. The signal passes through a single layer in the hexanode, with the delay attributed to the resistance of the copper wire. Detailed procedures for checking MCP signal can be found in Appendix A.7.

3.9.3 Dark count test

In "ion mode," the MCP front is set to a negative potential, while the MCP back is maintained near zero voltage relative to ground. The anode bias is adjusted to a few hundred volts in the positive range. This configuration is used for the detecting positive ions. Dark count tests are conducted by applying ion mode voltages without activating the laser, which allows for data collection over approximately 30 minutes. In this test, the voltage at the MCP front is -2400V, HV-in is set to 300V and there is a 500V potential difference between the two meshes. The test includes checking the xy-image to ensure it captures a round image with abundant data points and no blackout areas. The dark count test should be performed for both detectors.

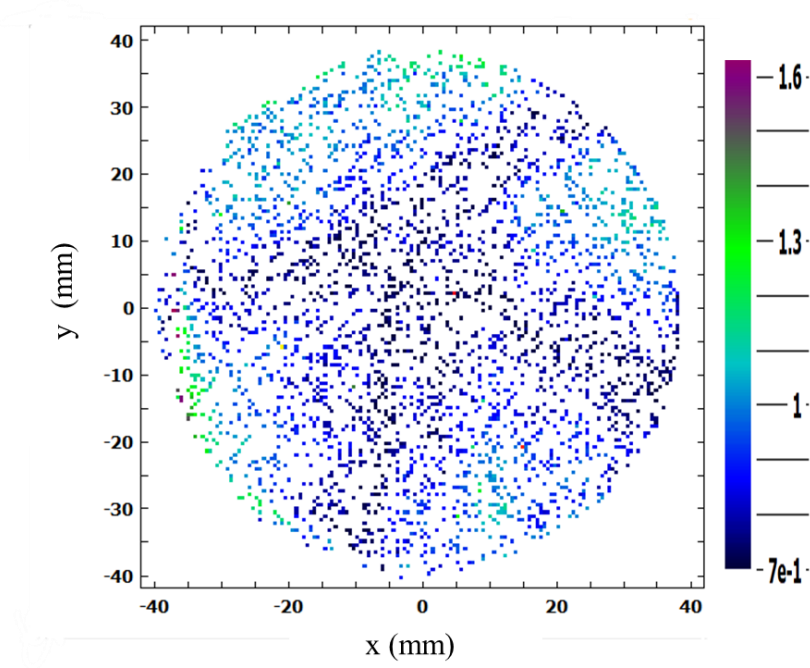


Figure 3.26: xy-image of a dark count test. Signal detection without laser source and gas jet.

3.10 Laser alignment

The incident beam, originating from the z-axis and reflected by a focusing mirror with focal length of 75mm, intersects the gas line that runs along the x-axis. The goal of the alignment process is to ensure the focal spot coincides with the gas line, as illustrated in Figure 3.27.

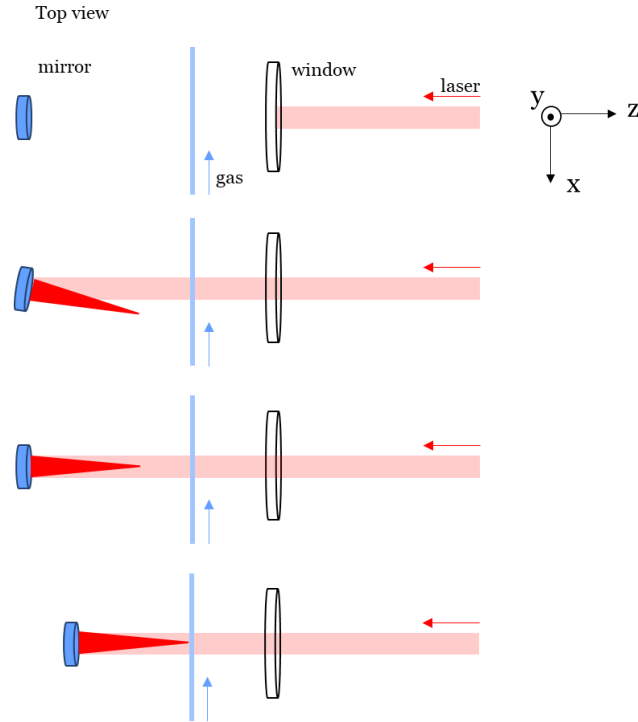


Figure 3.27: Laser alignment process. The laser is aligned along the z-axis, and the gas is along the x-axis.

Accurate positioning of the jet is essential in the experiment. The incident beam enters through the window and is subsequently reflected by a focusing mirror inside the main chamber. Our aim is to precisely align the gas jet with the focus point. Details of the alignment procedure are provided in Appendix A.6.

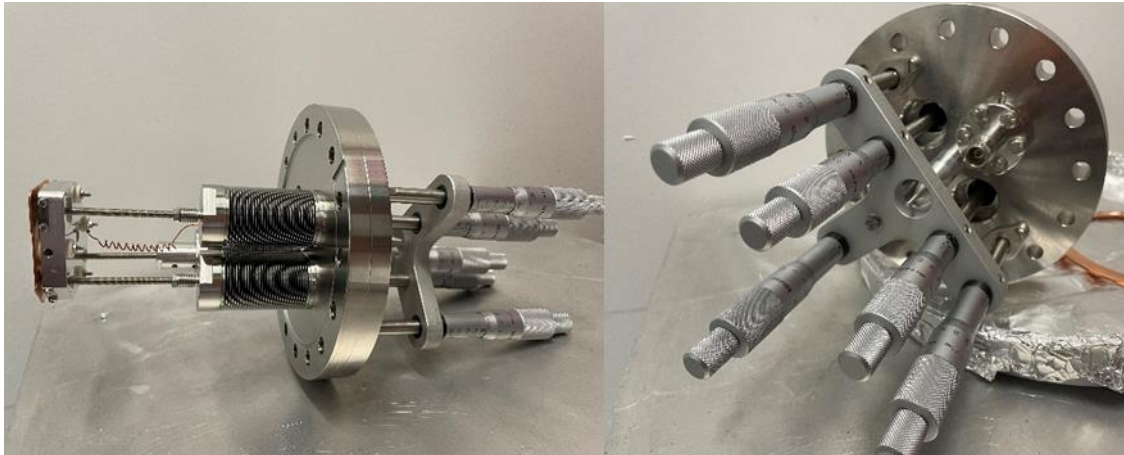


Figure 3.28: Focusing mirror with 75mm focal length.

The focusing mirror is mounted on a flange with a 5-micrometer controlled mount. To manipulate its position, rotating the outer three micrometers simultaneously changes the mirror's position in the z-direction. The inner two micrometers facilitate tilting of the mirror in

the x and y directions, where the x-direction aligns with the gas jet, the y-direction is perpendicular to the detectors, and the z-direction aligns with the laser beam. As illustrated in Figure 3.27, this method simplifies the complex task of locating the jet into several manageable steps, thereby enhancing the precision of jet localization. As shown in Figure 3.29, the xy image shows the successful adjustment of the laser focal spot and gas jet for the N₂ gas experiment. A key observation is the appearance of the densest spot, indicating that the gas jet molecules have interacted with the high-intensity region of the focal spot.

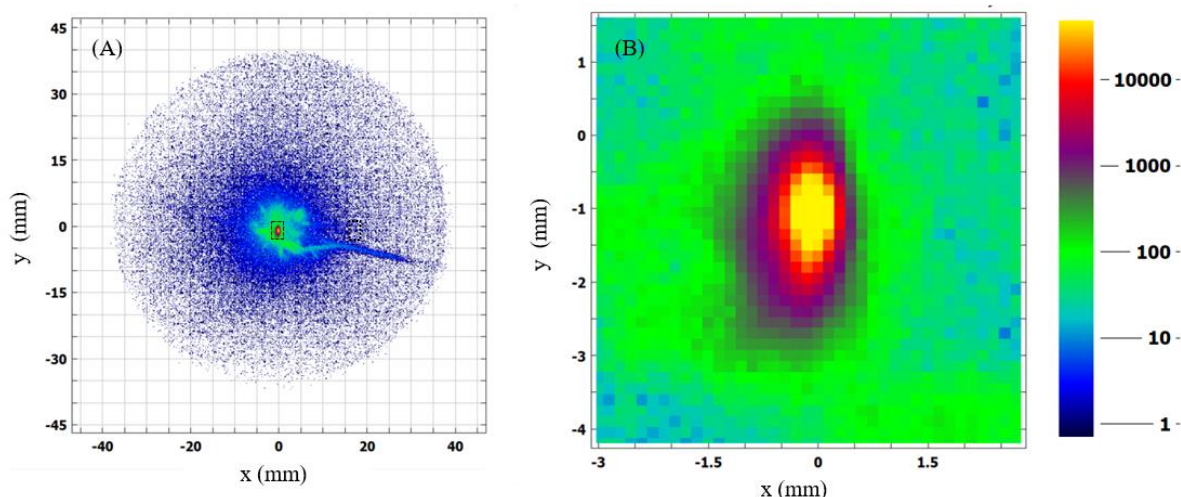


Figure 3.29: (A) The xy-image for N₂ gas. (B) Enlarged xy image plot of the densest area. The gas jet is along the y-axis from positive to negative, and the laser along the x-axis.

3.11 Data analysis

3.11.1 Calibration process

It is important to recognize that the real equipment may not precisely match the expected or theoretical values. For example, during the assembly of the spectrometer and its attachment to the flanges, measurement errors can occur, making it challenging to ensure the detector is perfectly parallel to the spectrometer. Similarly, when positioning the magnetic coils, ensuring its precise alignment with the spectrometer can be difficult. Ideally, we aim for the electric field to be vertical and the magnetic field to be horizontal. Additionally, during the experimental process, the exact electric field generated by applying voltage to the MCP and spectrometer, as well as the magnetic field produced by the current through the magnetic coil, remain uncertain due to the presence of multiple electronic components and resistances in the setup. And many other factors can influence the Time-of-Flight (TOF) and position data obtained from experiments. Therefore, a calibration process is required to determine the precise values of the

electric field strength (E field), magnetic field strength (B field) and all necessary experimental parameters.

The following test of N₂ gas was performed in the ALLS laboratory, utilizing a femtosecond laser with a pulse duration of 700 fs and a wavelength of 1030 nm.

Calibration of magnetic field

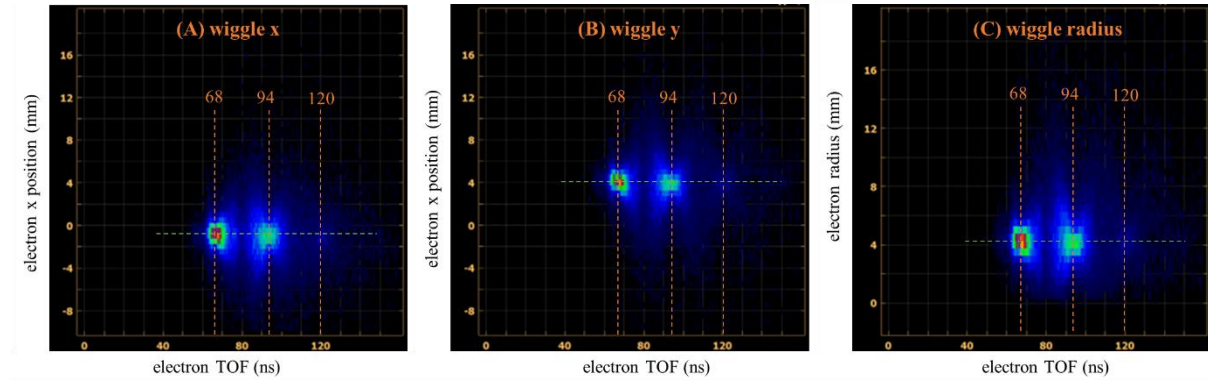


Figure 3.30: Wobble spectra for applied voltages ranging from 100V to 1800V, along with a plot of nodes. (A) Wobble x: electron TOF vs. x coordinate. (B) Wobble y: electron TOF vs. y coordinate. (C) Wobble radius: electron TOF vs. radius. x and y are the position on the detector, and radius is the $\sqrt{x^2 + y^2}$. The yellow dashed lines indicate the TOF for each node. The horizontal green dashed lines indicate that the magnetic field is set up parallel to the xy-plane.

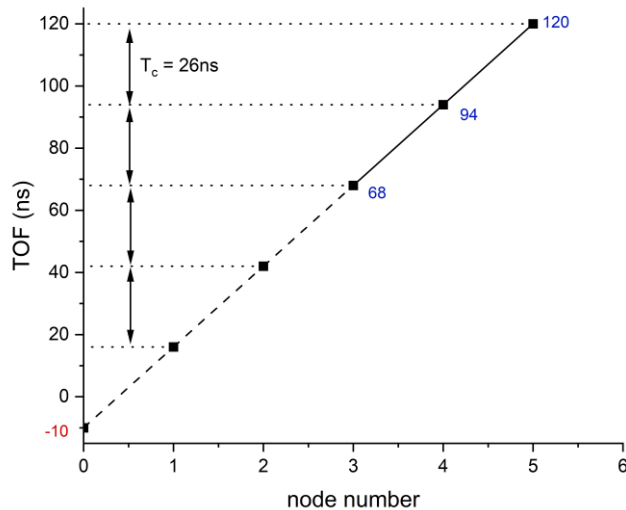


Figure 3.31: TOF vs node. The cyclotron period T_c is 26ns.

The wobble radius spectrum displays the electron TOF versus the corresponding distances of hit positions from the center of detector. It's generated by gradually changing the magnetic

field while maintaining a fixed electric field. The time offset is adjusted by shifting the TOF to the extrapolated value of the zeroth node. This spectrum is crucial for accurately determining TOF offset (t_0) and magnetic field strength. Additionally, it allows for precise position calculation by considering the offset from the zero position to the line passing through nodes in the wriggle x and wriggle y.

Figure 3.30 illustrates the identification of three nodes occurring at 68ns, 94ns, and 120ns. The spacing between any two successive nodes corresponds to the cyclotron period of an electron moving transversely in a magnetic field, and this spacing remains consistent throughout. Nodes closer to $t = 0$ represent electrons with higher initial kinetic energy, flying towards the detector. Conversely, nodes located farther away are associated with lower-energy electrons or those initially moving away from the electron detector but later change direction by the electric field. During this test, an increase in the voltage applied to the spectrometer resulted in a leftward shift of the nodes. This observation is consistent with the principle that a stronger electric field leads to a reduced detection time for electrons.

Four things need to be confirmed from the wriggle spectra. 1. The x and y position of each node in both wriggle x and wriggle y should be the same, indicating the magnetic coils are well-aligned in parallel with the spectrometer. 2. Determine the time zero offset of magnetic field. 3. Determine the exact strength of magnetic field. 4. Determine the strength of electric field to avoid nodes.

As shown in Figure 3.31, the nodes found in wriggle spectra are plotted and a straight line indicates the time zero off set t_0 is -10ns and the cyclotron period T_c is 26ns. Magnetic field strength B can be calculated by the equation $T_c = \frac{2\pi m}{Be}$, which is 13.7 G. In the following calibration test, a voltage of 500V is applied, and the resulting wriggle spectra are displayed in Figure 3.32. In this configuration, electrons are well positioned between two nodes.

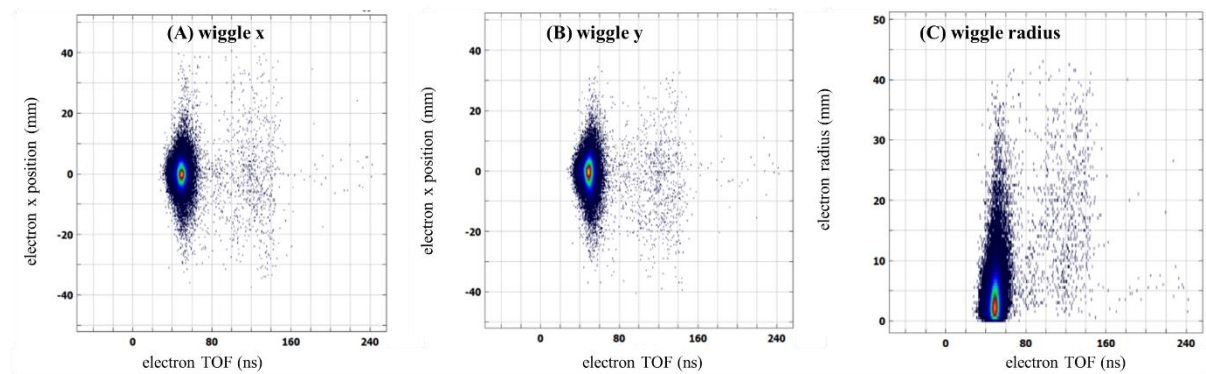


Figure 3.32: Wriggle spectra for an applied voltage of 500V. (A) Wriggle x: electron TOF vs. x coordinate. (B) Wriggle y: electron TOF vs. y coordinate. (C) Wriggle radius: electron TOF vs. radius.

Calibration of electric field

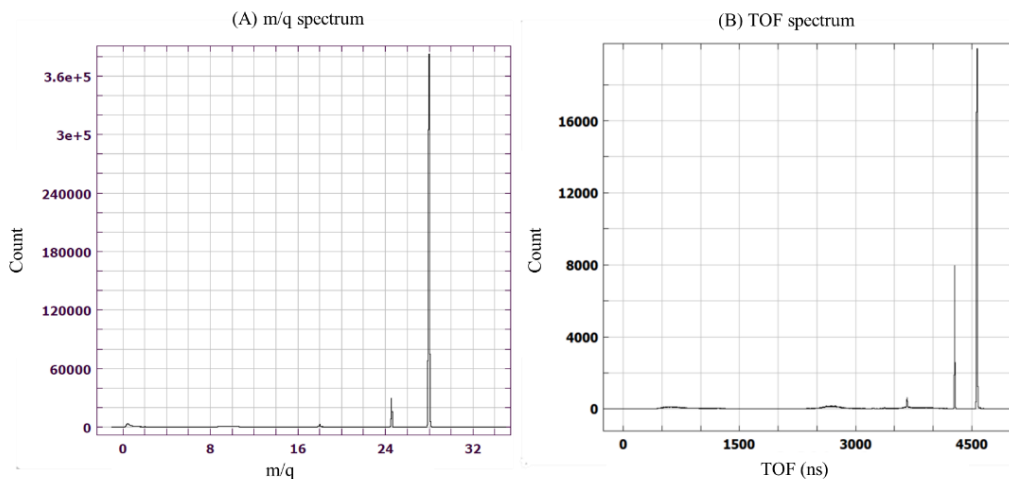


Figure 3.33: (A) m/q spectrum of ions. (B) TOF spectrum of ions.

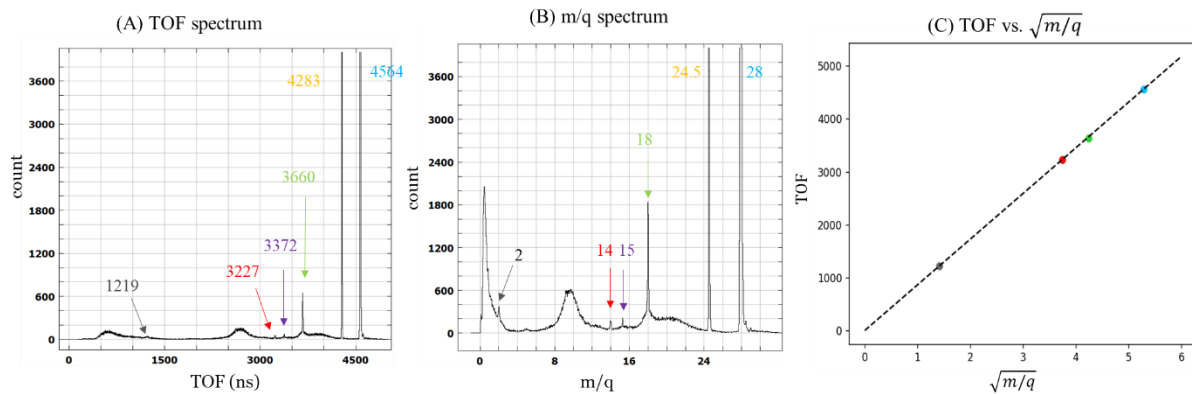


Figure 3.34: (A) enlarged TOF spectrum. (B) enlarged m/q spectrum. (C) TOF vs. $\sqrt{m/q}$

The m/q spectrum and TOF spectrum serve as the tools for calibrating the electric field. When dealing with ions with zero velocity in the z-direction (towards to detectors), the time of flight to detector, which is $TOF_0 = \sqrt{\frac{2d}{E}} \sqrt{\frac{m}{q}}$. Where d is the travel distance in z direction. Then TOF_0 for different ions are proportional to $\sqrt{\frac{m}{q}}$. The calibration process involves the following steps: 1. Identify at least two peaks in the m/q spectrum. 2. Recognize the corresponding peaks in TOF spectrum. 3. Compare the values of TOF then determine the time zero offset for electric field. For this test of N_2 , peaks for m/q at 14 for N_2^{++} , and 28 for N_2^+ can be chosen then time zero offset can be easily calculated. After calibration, can double check it with the peak of H^+ . As shown in Figure 3.34, TOF peaks of H_2^+ , N_2^{++} , H_2O^+ and N_2^+ can be determined. There are several peaks appear to be inconsistent with the expected results. The TOF peak at 4283ns, which has a m/q value 24.5. The TOF peak at 4283ns, which corresponds to an m/q value of

24.5, might be attributed to the presence of argon gas. This could be due to residual argon gas remaining in the gas line from a previous experiment. From the m/q spectrum, there is peak identified with an m/q of 0.5, which is incorrect. In the upcoming nitrogen experiment, it is essential to solve these questions.

3.11.2 Channel filtering

For molecules that break into two fragments, the coincidence channels can be determined by analyzing the correlation maps of the ion TOF. As shown in Figure 3.35 (B), the x axis shows the TOF of first detected ion, and the y axis shows the TOF of the second ion. In an ideal coincidence experiment, only one interaction event per laser shot, ensuring that the detected ions originate from the same molecule. The background of in PIPICO means the cases more than one event per laser shot. PIPICO can be plotted by m/q , as shown in Figure 3.35 (A). A distinct diagonal line with one end at (14,14), indicating the channel $N_2 \rightarrow N^+ + N^+$. To isolate this channel, the following steps are employed. Initially, data is filtered using TOF by examining the other end of the diagonal line on the PIPICO-TOF, resulting in Figure 3.35 (C). Then the data can be filtered based on the sum of momentum being less than 7 atomic units, as the Coulomb explosion channel results in nearly zero sum of momentum for all positively charged fragments. At the end, as demonstrated in Figure 3.35 (D), the channel is separated from the background.

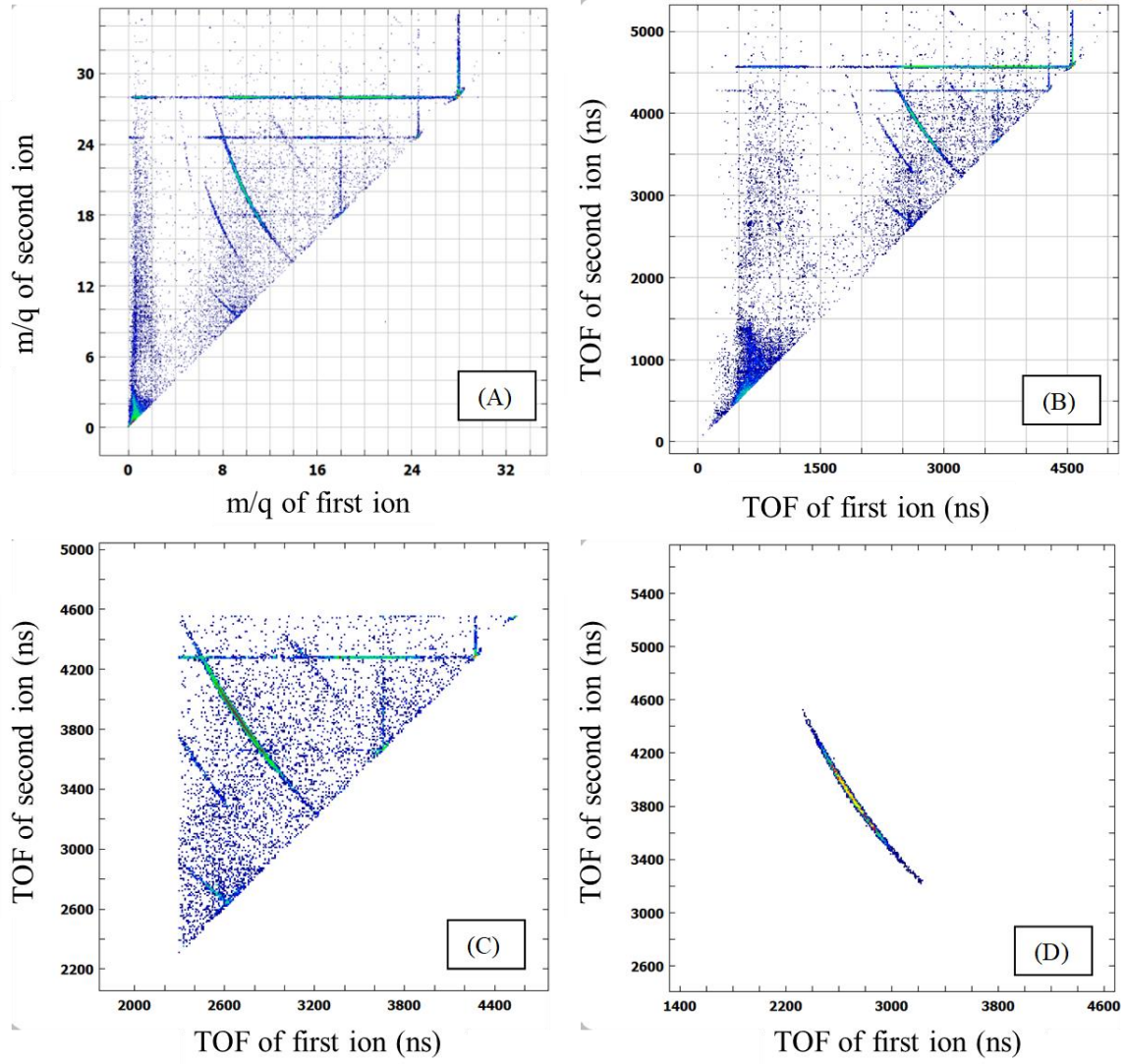


Figure 3.35: Photoion-Photoion Coincidence Map (PIPICO). (A) PIPICO for m/q . (B) PIPICO for TOF. (C) filtered by TOF. (D) PIPICO for $N^+ + N^+$ channel.

3.11.3 Channel analysis

From the previous section, a coulomb explosion channel: $N_2 \rightarrow N^+ + N^+$ has been identified.

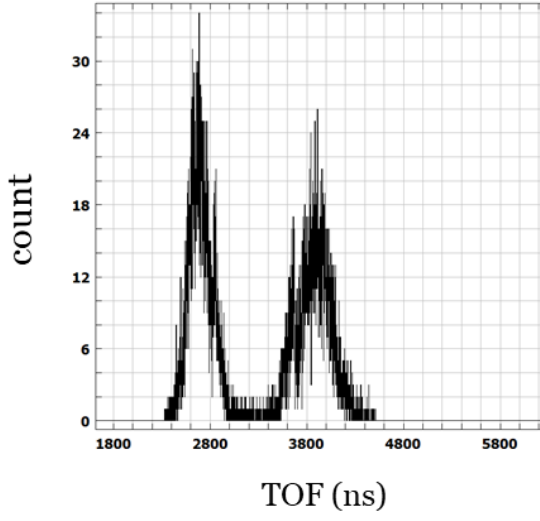


Figure 3.36: TOF spectrum for channel $N_2 \rightarrow N^+ + N^+$.

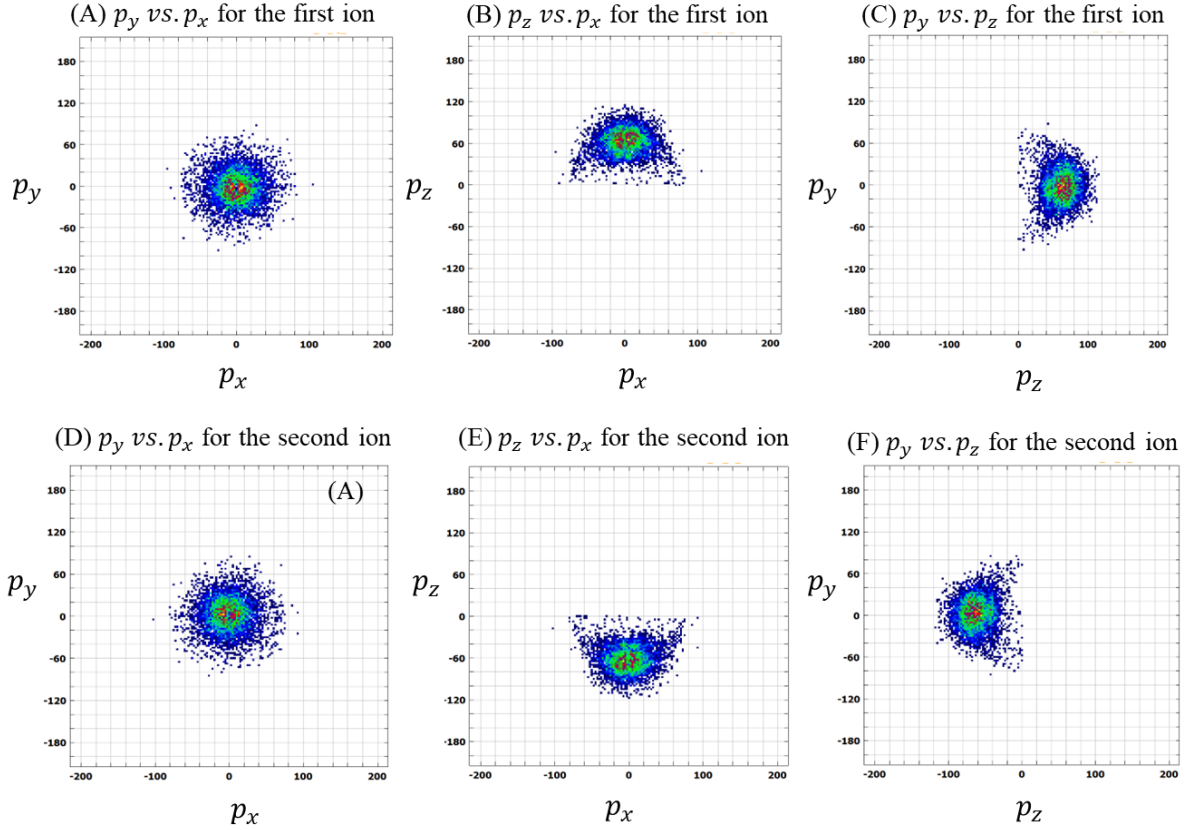


Figure 3.37: measured ion momentum of the first ion and second ion. (A), (B) and (C) represent the relationships of the x, y, and z components for the first ion. (D), (E) and (F) represent the relationships of the x, y, and z components for the second ion. The momentum is in atomic unit. The coordinate is the same as in Figure 3.18, laser is along the x-axis, gas jet is along the y-axis and spectrometer is along the z-axis.

As shown in Figure 3.36, the time-of-flight spectrum for the channel $N_2 \rightarrow N^+ + N^+$ shows two peaks. For two N^+ ions from same molecule, one N^+ first fly away from the ion detector, then due to the electric force finally comes back to the ion detector, for this type of N^+ takes more time to be detected. For the other one, N^+ flies direct to the ion detector, which has short time-of-flight. Same result can be observed by momenta for both the first ion and the second ion. As shown in Figure 3.37 (A), (B) and (C) represent the relationships of the x, y, and z components for the first ion. (D), (E) and (F) represent the relationships of the x, y, and z components for the second ion. (B) and (E) illustrate two N^+ ions flying in opposite directions along z-axis. Similarly, in (C) and (F), those first ions are flying towards the ion detector while those second ions are flying away from the ion detector initially. The momentum relation plots are like real images that can show where the ions are flying towards after the moment of interaction with a laser pulse.

3.4 Summary

In this chapter, an extensive overview of the five main components of UW-ALLS COLTRIMS is presented, along with detailed explanation regarding the cable connections and signal inspection procedures, jet-laser alignment, and data analysis for a sample calibration test. Additionally, the appendix section contains supplementary information about detailed operation procedures for starting and end an experiment, and heating steps.

Regarding the data analysis, the application of using N_2 as the target molecule is demonstrated, accompanied by thorough explanations of the crucial spectra employed. The N_2 experiment presented in this chapter serves as the initial trial in which a magnetic field was applied to our COLTRIMS at UW and ALLS. It was not a perfect experiment, and there are several questions that must be carried forward to the next experiment for resolution. For example, the appearance of the m/q value at 0.5 and 24.5, and the long tail in the xy-image need further investigation. Nonetheless, even with this imperfect data, the calibration process and data analysis have been validated.

Beamtime has been scheduled for experiments in 2024, focusing on the testing of H_2 and D_2 molecules at ALLS. These experiments are aimed at exploring coherent control using high repetition rate, carrier-envelop-phase controlled laser pulses.

Chapter 4 Experiment simulation and geometry reconstruction framework

4.1 Introduction

This chapter contains edited text from a publication, and the research builds upon the studies of Brichta [46] and Ramadhan [47]. Tian K, Ramadhan A, Nooijen M, Pantazi S, Karimi R and Sanderson J. *Approaches for Constraining Uncertainty and Degeneracy in Geometry Reconstruction of Molecules from Simulated Coulomb Explosion Data* [81].

Coulomb explosion imaging (CEI) [9] is a technique for studying the structure of small molecules in the gas phase. Essentially, the molecule is ionized, leading to fragmentation, during which the positively charged fragments repel each other due to the Coulomb force. The momentum vector of each fragment is measured, in coincidence, by a sophisticated detection apparatus [13], which incorporates time and position sensitive detection [48]. Information about the molecule's initial geometry is encoded in the recorded momentum vectors of the ions, but the relationship between momentum and geometry is not always one-to-one. Recent experimental work [49] has shown that a "forward" method, which employs a Monte Carlo approach to reproduce experimental data based on the initial nuclear distribution, can capture certain significant features. In principle, however, it is possible to reconstruct the molecular structure from only the final momentum vectors of the fragment ions, by employing an inversion or "backward" approach, provided there is knowledge of the interaction potential governing the initial repulsion. Here, the focus is on the challenge of reproducing molecules that are out of equilibrium as they respond to an excitation process [48], without prior knowledge of the nuclear distribution. However, this poses a non-linear problem, and the technique necessitates the use of an optimization method to find a solution.

Légaré et al. 2005 [50] were the first to use few cycles, femtosecond laser pulses (sub 7fs) and CEI to report on the molecular structure of small molecule (D_2O , SO_2). They employed the inversion process using Coulomb's law and compared with *ab initio* potential energy surfaces to reconstruct the equilibrium geometries of D_2O and SO_2 . J Gagnon et al. 2008 [51] also used the inversion method and reported the reconstruction of the five-atom molecule dichloromethane (CH_2Cl_2) using a unique stochastic-based simulated annealing algorithm that globally optimizes the molecular spatial configuration. Their work suggested that the major uncertainty in the geometry reconstruction was due to the uncertainty in the measurement of the velocity vectors. However, they were only able to obtain molecular geometries, for five sets

of measured velocity vectors, out of potentially hundreds of complete ion momentum measurements. Brichta et al. 2009 [52] proposed an inversion method for the reconstruction of small triatomic molecules using a simplex algorithm. They tested their method using the reconstruction of simulated geometries of carbon dioxide (CO₂) and formaldehyde (CH₂O). The simplex algorithm was originally developed for solving linear problems [53], and further improvements were therefore needed to solve the nonlinear problem that constitutes the challenge of a molecular reconstruction, with its large numbers of variables and constraints [54]. Since the simplex algorithm is a local search method and relies heavily on the starting guess geometry, for some cases, it is hard to distinguish a local minimum from the global minimum. Nevertheless, Bocharova et al. 2011 [55] analyzing the results of their few cycles laser initiated multiple ionization experiment, obtained the average CO bond distance and bend angle for CO₂ data employing the simplex code [52]. An interesting geometry reconstruction effort using CEI was performed by Kunitski et al. 2015 [56], they employed a reconstruction method by using a “look-up table” to return geometries of the Eflimov state of ⁴He₃. The method works, by matching experimental momenta to a set of predetermined, simulated, values stored in a three-dimensional array, defined by atomic separations (R₁, R₂, R₃). However, like most experimental work, they did not give details of their method or show the look-up table. The basic idea of the method is still a linear process, while the problem remains a non-linear problem, where a small change in the initial molecular structure will result in a large difference in the final momentum. Sayler et al. 2018 [57] showed that multiple initial configurations can result in identical momenta for a triatomic molecular explosion, even when focusing on the limited case of fixed total energy release. In a real Coulomb explosion experiment, the total released energy from a molecule would of course have a characteristic distribution, but these so called “degenerate” geometries could pose a fundamental obstacle to using the “backwards” approach to Coulomb explosion imaging in certain cases. Any successful reconstruction approach should have a process in place for identifying and if possible correcting errors that result from degeneracy.

This study focuses on the algorithm that involves mapping from momenta to geometry structures and identifying degeneracy cases. Geometry reconstruction is performed for simulated carbonyl sulfide (OCS) in the OCS → O²⁺ + C²⁺ + S²⁺ concerted Coulombic explosion process, using two approaches: a look-up table method, and a nonlinear constrained optimization method. OCS is a common target in CEI. OCS is selected due to its asymmetry and linearity, while also exhibiting slight bends caused by vibrational motion in its ground state, making it of interest to experimentalists. The 6⁺ state is chosen because all events in this state arise from concerted breakup processes. As detailed in study [60], the 3⁺ and 4⁺ states involve a combination of both concerted and stepwise processes. Two simulated initial geometry datasets are employed. To make the methods applicable to any unknown geometry, ground state

nuclear distributions for OCS are not used; instead, possibilities that might arise from electronic and vibrational excitation are considered. Then the final momentum vectors are calculated by the Coulomb explosion model as described in section 4.2.1, serving as our simulated experimental data. Each momentum vector is then fed into our reconstruction process, to find the reconstructed geometry. The known original geometries are used for comparing them with the reconstructed geometries and evaluating the ability of the two reconstruction methods. The evaluation is based on the number of events successfully reconstructed, speed, accuracy, and the ability to deal with degeneracy.

4.2 Preparation of simulated OCS geometries and momentum vectors

4.2.1 Coulomb explosion model

To simulate the Coulomb explosion of OCS^{6+} , similar simplifying assumptions are applied as in previous studies [46],[47],[50],[51],[52],[55]. 1. All six electrons are instantly removed, and there is no charge redistribution occurring afterward. Therefore, the interactions between electrons and nuclei are not considered in this model. 2. At $t = 0$, the bonds have already broken, and structural deformation has occurred. Therefore, the chemical bonding potential is negligible. 3. Ions behave as point-like charged particles, disregarding their size. The point like ion approach assumes that the motion of the ions is governed only by their mutual Coulomb repulsion. Therefore, only pure Coulomb potential is transferred into kinetic energy. 4. The impact of an external electric field on the structures is not considered. 5. Every ion starts with zero initial momentum. The final momentum is calculated at $t = T$ when the momentum components exhibit minimal further change within $0.0001\text{e-}22 \text{ kgm/s}$, considering it to be the asymptotic momentum.

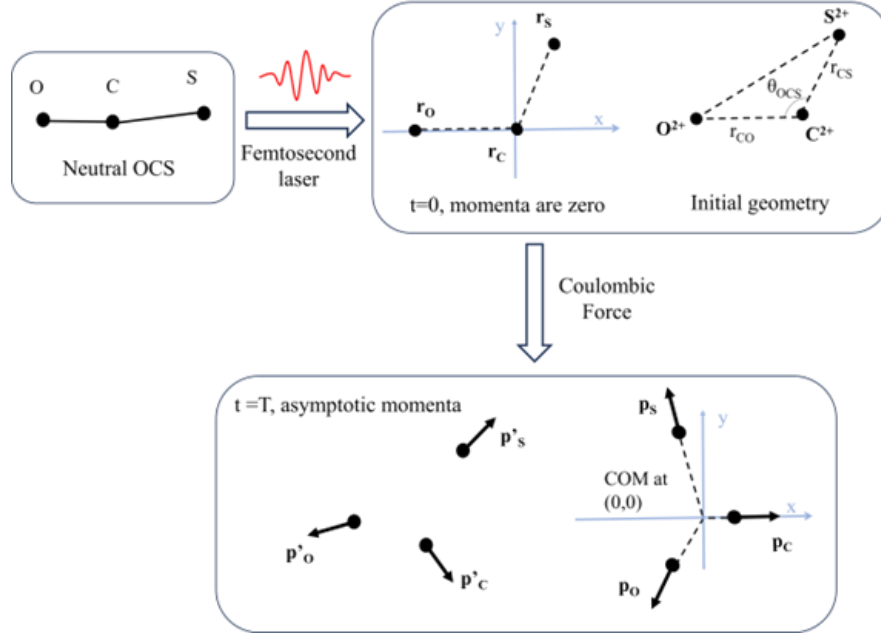


Figure 4.1: Structural evolution of OCS. The initial geometry is defined at $t=0$, with carbon at the origin (0,0) and oxygen along the negative x-axis and sulfur in the first quadrant. The final asymptotic momentum is defined at time T with $\mathbf{p}_C$ along the positive x-axis, $\mathbf{p}_O$ in the third quadrant and $\mathbf{p}_S$ in the second quadrant.

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i, i, j \in \{O, C, S\} \quad \text{Equation 4. 1}$$

$$H(\mathbf{r}_i, \mathbf{p}'_i, t) = \sum_{i=1}^n \frac{\mathbf{p}'_i{}^2}{2m_i} + \frac{1}{4\pi\epsilon_0} \sum_{\{i,j\}, j \neq i} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{Equation 4. 2}$$

$$\frac{d\mathbf{r}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}'_i} = \frac{\mathbf{p}'_i}{m_i} \quad \text{Equation 4. 3}$$

$$\frac{d\mathbf{p}'_i}{dt} = - \frac{\partial H}{\partial \mathbf{r}_i} = \frac{1}{4\pi\epsilon_0} \sum_{j, j \neq i} \frac{q_i q_j (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3} \quad \text{Equation 4. 4}$$

Consider the triatomic system as shown in Figure 4.1 where $\mathbf{r}_O$, $\mathbf{r}_C$, and $\mathbf{r}_S$ represent the position vectors and $\mathbf{p}'_O$, $\mathbf{p}'_C$ and $\mathbf{p}'_S$ are the momentum vectors. Under the above assumptions, at $t=0$, $\mathbf{p}'_O = \mathbf{p}'_C = \mathbf{p}'_S = \mathbf{0}$, and initial geometry $(\mathbf{r}_O, \mathbf{r}_C, \mathbf{r}_S)$. Since the CO and CS bond lengths, and bond angle θ_{OCS} are the key parameters of interest in our study, the initial geometry is described using $(r_{CO}, r_{CS}, \theta_{OCS})$ in the following discussions. In this way, the orientation of the geometry is no longer a factor since our focus is on studying the structure of each individual

molecule. Furthermore, to ensure produce a unique momentum for each geometry, carbon is positioned at the origin, the oxygen along the -x-axis, then the position of sulfur can be easily calculated in the xy-plane. At $t=T$, the final momentum ($\mathbf{p}'_O, \mathbf{p}'_C, \mathbf{p}'_S$) can be obtained from the Hamiltonian of the system, as detailed in Equation 4. 1Equation 4. 4. Additionally, to facilitate comparison with experimental data, the final momentum is adjusted to $\mathbf{p} = (\mathbf{p}_O, \mathbf{p}_C, \mathbf{p}_S)$ as shown in Figure 4.1. The center of mass is at the origin (0,0) with $\mathbf{p}_C$ along the positive x-axis, and structure remains in the xy-plane. The time $T=2\text{e-}13$ s is determined by the point when the momentum, in a simulation starting from the equilibrium geometry (116pm,156pm,175°) [55][59], reaches an asymptotic value. The equations are solved by *ode45* in Matlab.

4.2.2 Simulation of initial geometries

Two datasets of initial geometries are generated: the first one has geometries with bond lengths r_{CO} , r_{CS} and bond angle θ_{OCS} peaks at approximately 150pm,180pm and 160° respectively; and the second one with peaks at equilibrium structure (116pm,156pm,175°). Initially, the first dataset is the primary focus, as shown in Figure 4.2, which contains more molecules that stretched and bent compared to the equilibrium structure. The study [55] demonstrated the critical CO₂ geometry exhibiting stretching and bending. Based on this finding, we chose peak bond lengths exceeding equilibrium values and peak bond angle smaller than the equilibrium value. Flexibility in different molecular structures is achieved by allowing molecules to compress, stretch, and bend within defined ranges: $r_{CO} = (0,300\text{pm})$, $r_{CS} = (0,350\text{pm})$ and $\theta_{OCS} = (140^\circ, 180^\circ)$. Then, the corresponding momentum vectors can be obtained by applying the Coulomb explosion algorithm.

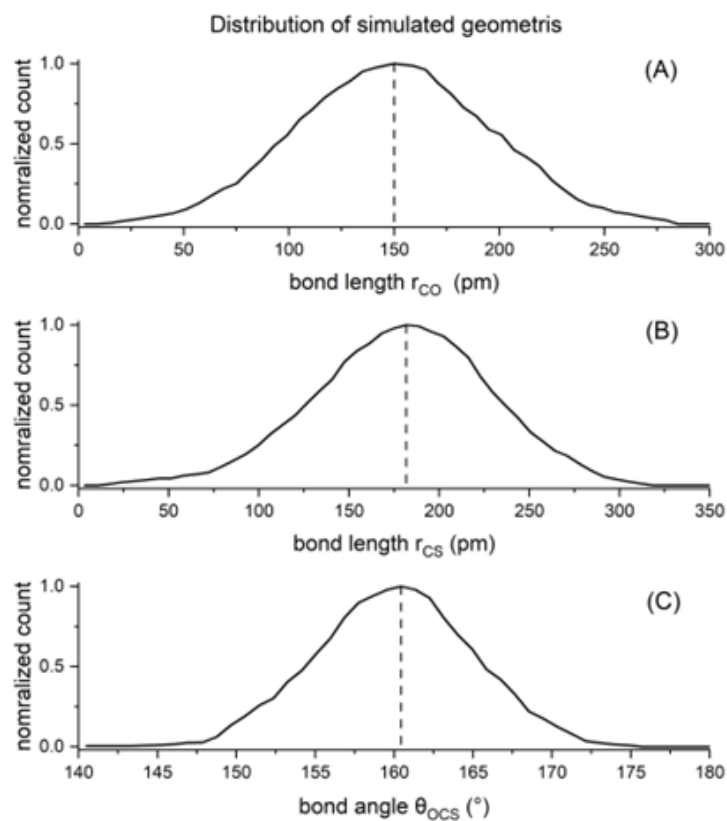


Figure 4.2: Distributions of r_{CO} , r_{CS} and θ_{OCS} from simulated OCS geometries.

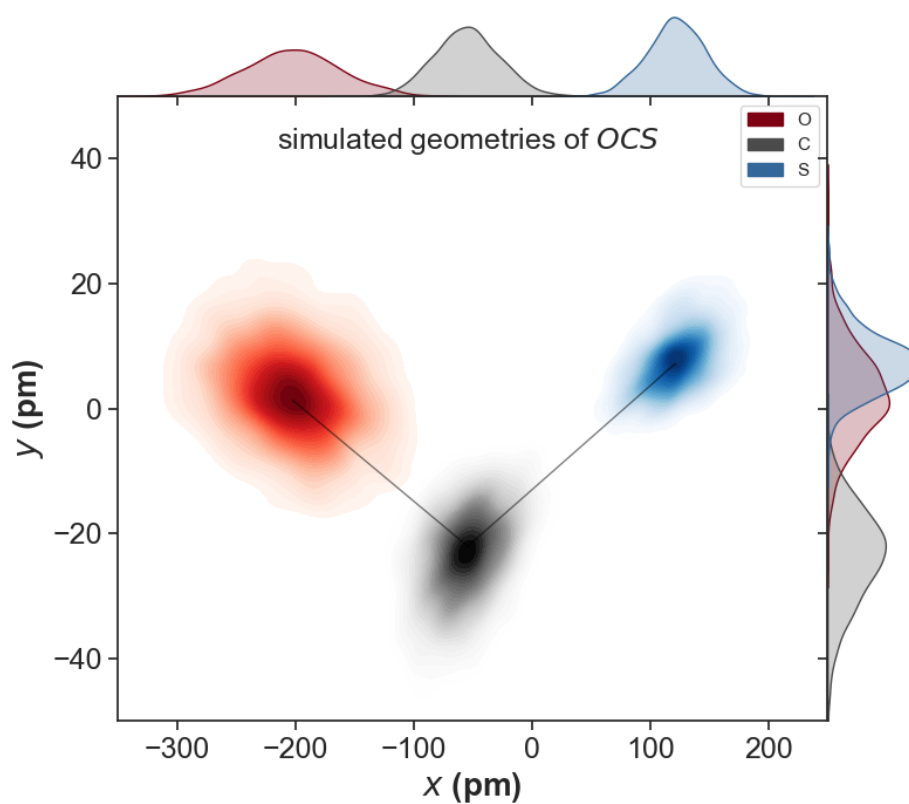


Figure 4.3: Geometry plot with marginal distributions for original simulated geometries. The red, black and blue area represent oxygen, carbon and sulfur respectively.

The peaks of the distributions for r_{co} , r_{cs} and θ_{ocs} are at 149.740 pm, 177.641 pm, and 161.565° respectively. The average values are 150.033pm, 179.484pm, and 159.915° . In Figure 4.3, the nuclear distribution of each atom is displayed intuitively in 2D. To generate this plot, first, position carbon atom at the origin (0,0). Then, position the oxygen atom and the sulfur atom in such a way that θ_{ocs} is evenly divided by the y-axis and the oxygen atom is placed in the second quadrant, while the sulfur is placed in the first quadrant. Finally, adjust the molecule's coordinates to ensure that the center of mass is at the origin.

4.3 Geometry reconstruction using a look-up table.

4.3.1 Look-up method

The concept behind a look-up table is relatively straightforward: it involves simulating a certain number of Coulomb explosions with a range of molecular structures. This creates a mapping from molecular structures to momentum vectors. As a result of storing results from numerous simulations, a look-up table of asymptotic momentum vectors is generated. This table can be correlated with any experimental measurement. To identify the structure corresponding to a particular set of observed momentum vectors, the table can be read in reverse. This involves searching for the momentum vectors that best match the observed set and subsequently deducing the corresponding structure. The degree of agreement is determined by calculating the squared norm between the observed and table vectors.

The look-up table has two parts: the table of original geometry values (r_{co} , r_{cs} , θ_{ocs}) and final momentum vectors $\mathbf{p} = (p_{ox}, p_{oy}, 0, p_{cx}, 0, 0, p_{sx}, p_{sy}, 0)$, expressed in the molecular frame. For effective comparison with this format, modifications are essential to the experimental momentum data. The sum of the momentum vectors of O, C and S from a single event has a very small number, less than $5 \cdot 10^{-23}$ kgm/s [60]. First, remove the motion of the center of mass, ensuring zero total momentum. Then, follow the same steps as mentioned in section 2 to rotate momentum vectors into xy-plane with the same orientation. This process reduces the momentum vector to 5-dimension without losing information of interest. To reconstruct the geometry corresponding to a set of molecular frame experimental momentum values the following steps are carried out.

Computational steps:

- (1) Generate a look-up table of 10,000,000 events, with (r_{co} , r_{cs} , θ_{ocs}) uniformly distributed within the ranges (10pm to 500pm, 10pm to 500pm, 140° to 180°).
- (2) Adjust the experimental momenta to match the format:
 $\mathbf{p}_{exp} = (p_{e_{ox}}, p_{e_{oy}}, 0, p_{e_{cx}}, 0, 0, p_{e_{sx}}, p_{e_{sy}}, 0)$, where $\mathbf{p}_{exp}$ represents the experimental data.

- (3) For each experimental momentum, compare it with every reference momentum, $\mathbf{p}$ from the look-up table. Calculate the square norm of the difference as $\|\mathbf{p}_{exp} - \mathbf{p}\|^2$.
- (4) Identify the smallest difference (error). If this error is below $1 \cdot 10^{-46} \text{ (kgm/s)}^2$, indicating an error for momentum component P_i within $\pm 0.1 \cdot 10^{-22} \text{ kgm/s}$, then recognize the corresponding geometry from the table as the reconstructed geometry.
- (5) If no matching geometry can be found, the reconstruction for this $\mathbf{p}_{exp}$ is unsuccessful and the algorithm moves to the next one.

4.3.2 Reconstruction result

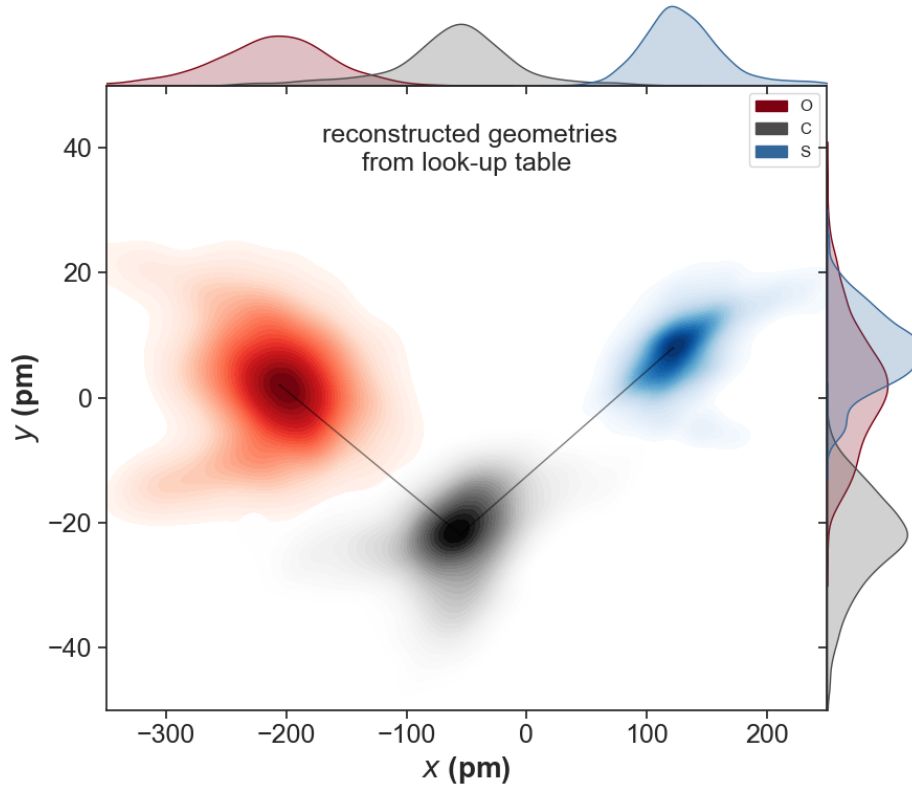


Figure 4. 4: Geometry plot with marginal distributions for reconstructed geometries by the look-up table method. The red, black and blue area represent oxygen, carbon and sulfur respectively.

Here, $\mathbf{p}_{exp}$ represents the momentum vectors that generated in section 4.2.2. For a total of 2000 momentum vectors, 1993 of them get reconstructed geometries, while 7 failed. Among the 1993 geometries, the peaks values for r_{co} , r_{cs} and θ_{ocs} are 152.286pm, 179.715pm, and 161.390° respectively. The average values are 155.687pm, 194.824pm, and 162.113° . Compared to the simulated geometries, the average bond length r_{cs} of 194.824pm is much larger than the expected value of 179.484pm, similarly, the average bond length r_{co} and θ_{ocs} also exhibit deviations from the anticipated values. As shown in Figure 4. 4, the shapes of the

distributions for O, C and S are different compared to the original distributions in Figure 4.3, with significant wings on the oxygen and sulfur distributions. Among these, only 376 geometries are reconstructed within a tolerance of $(\pm 1\text{pm}, \pm 1\text{pm}, \pm 1^\circ)$ when compared to the original geometries. This means that the remaining 1617 reconstructed geometries either have low accuracy or failed to produce the correct answer. The estimated time of reconstruction for each momentum vector set is around 4.98s.

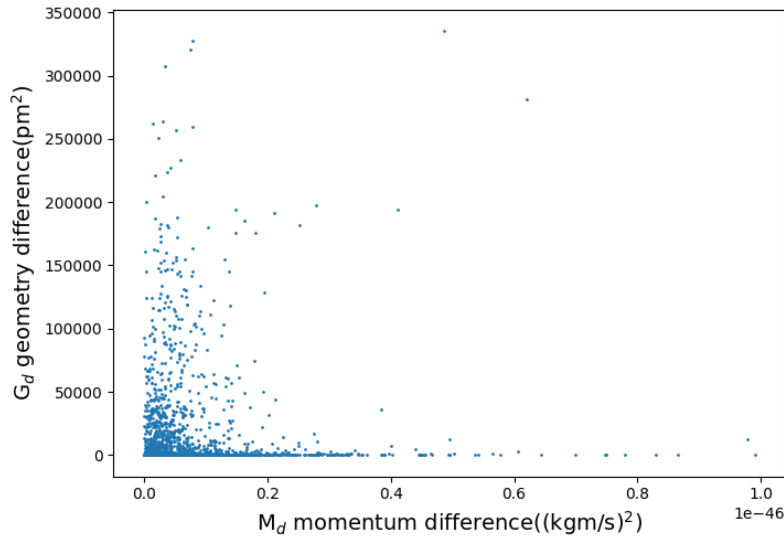


Figure 4.5: Scatter plot of momentum difference (M_d) and geometry difference (G_d).

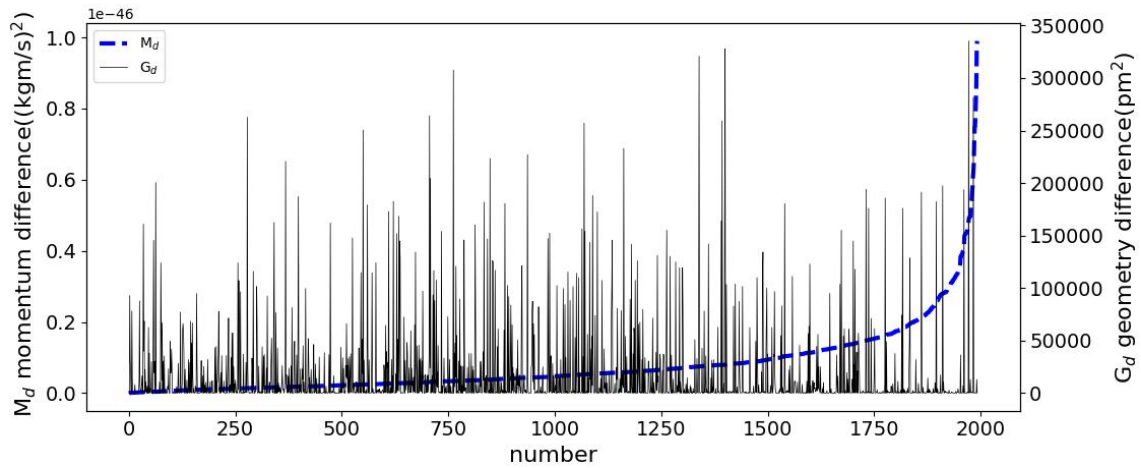


Figure 4.6: Momentum difference and geometry difference relation plot. The left y-axis shows momentum differences, the right y-axis shows geometry differences. The x-axis lists the event IDs in order of increasing momentum difference.

To understand the performance more quantitatively, the momentum difference M_d and the geometry difference G_d can be defined as:

$$M_d = \|\mathbf{p}_{exp} - \mathbf{p}_{solution}\|^2 = (\mathbf{p}_{e_o} - \mathbf{p}_{s_o})^2 + (\mathbf{p}_{e_c} - \mathbf{p}_{s_c})^2 + (\mathbf{p}_{e_s} - \mathbf{p}_{s_s})^2$$

$$G_d = \|G_{exp} - G_{solution}\|^2 = (r_{e_{co}} - r_{s_{co}})^2 + (r_{e_{cs}} - r_{s_{cs}})^2 + (r_{e_{so}} - r_{s_{so}})^2$$

M_d calculates the momentum difference in the same way as in the reconstruction process, while the G_d represents how far the reconstructed geometry deviates from the expected geometry. Figure 4.5 displays the relation between M_d and G_d of the 1993 events. Even though the momentum difference is close to zero, there are many points with a large geometry difference. In Figure 4.6, a similar idea is observed: when blue dashed line M_d is very low, some data still have a large value in G_d . That is, the look-up table, which is based on the linear concept, is not a reliable method to accurately determining the geometry structures.

4.4 Geometry reconstruction using an optimization method.

4.4.1 Optimization method

Setting up the optimization problem is an essential step in the reconstruction process. The standard form of an optimization problem [61] is to minimize (or maximize) the objective function $f(x)$, subject to constraint functions $g_i(x) \leq 0$, where $i \in \{1, \dots, m\}$, and $h_j(x) = 0$, where $j \in \{1, \dots, n\}$. For our geometry reconstruction, it is regarded as a non-linear optimization problem. The goal is to minimize the objective function defined as $f(x) = \|\mathbf{p}(x) - \mathbf{p}_{exp}\|^2$. Here, $\mathbf{p}(x)$ represents the momentum vectors iteratively calculated during the optimization process. The geometry structure $x = (r_{co}, r_{cs}, \theta_{ocs})$ and momentum $\mathbf{p}(x)$ satisfy the equality constraint functions $h_i(x)$, given by equations (1) - (4) in section 2. And $\mathbf{p}_{exp}$ ($\mathbf{p}_{experimental}$) represents the experimental momentum vectors. The inequality constraints, $g_i(x)$, define the box constraints ($a \leq r_{co} \leq b$, $c \leq r_{cs} \leq d$ and $e \leq \theta_{ocs} \leq f$). It is important to note that there are no restrictions on the dimensions of x and $\mathbf{p}$. For larger molecules, more variables can be incorporated using similar steps. In our calculations, the 'fmincon' function in Matlab is utilized, employing the 'interior-point' method. This algorithm is well-suited for constrained nonlinear optimization.

The optimization algorithm begins with an initial starting point $x_0 = (r_{co}, r_{cs}, \theta_{ocs})$ and evaluates the objective function and constraints at this point. Once the initial point is valid, the algorithm proceeds with iterative updates to improve the solution. During each iteration, the algorithm updates the current value of the momentum difference and the current point $(r_{co}, r_{cs}, \theta_{ocs})$ within the constrained region. Additionally, it calculates the gradient of the objective

function with respect to $(r_{co}, r_{cs}, \theta_{ocs})$, then determines the direction in which to search for the next point and computes an appropriate step size. The optimization process continues with iterations until convergence is achieved, with a convergence criterion set to a very small tolerance level of $1e-15$, or until the maximum number of iterations (3000) is reached. To ensure the optimized solutions and detect degenerate geometries, the entire process is repeated multiple times by a set of starting points within the constrained 3D space. These starting points can be uniformly distributed or follow any desired distribution, offering flexibility in the exploration of the solution space. In this case, there are a total of $125(5^3)$ starting points, which are uniformly selected from within the specified box range. To enhance the efficiency of the algorithm, iterations for each starting points are processed in a parallel fashion. If all starting points result in an identical solution, it indicates a unique solution, and the solution is considered fully optimized. However, if there are multiple solutions, it indicates there are multiple geometries corresponding to the same momentum vector.

Computational steps:

- (1) Set up the optimization problem:

Objective function: $f(x) = |\mathbf{p}(x) - \mathbf{p}_{exp}|^2$;

Coulomb explosion model functions as described in section 4.2.1.

Box constraints: $0 \leq r_{co} \leq 500\text{pm}$, $0 \leq r_{cs} \leq 500\text{pm}$ and $140^\circ \leq \theta_{ocs} \leq 180^\circ$.

- (2) Adjust the experimental momenta to match the format:

$\mathbf{p}_{exp} = (p_{e_{ox}}, p_{e_{oy}}, 0, p_{e_{cx}}, 0, 0, p_{e_{sx}}, p_{e_{sy}}, 0)$, where $\mathbf{p}_{exp}$ represents the experimental data.

- (3) Initial guess points:

Uniformly select 125 points within the constrained space as the starting points.

- (4) The preliminary result:

Each starting point undergoes the optimization algorithm independently, resulting in a solution.

- (5) The final result:

Classify the results based on the number of different solutions. Usually, results can be classified into one of three cases: unique solution, double degeneracy, or triple degeneracy.

4.4.2 Reconstruction result

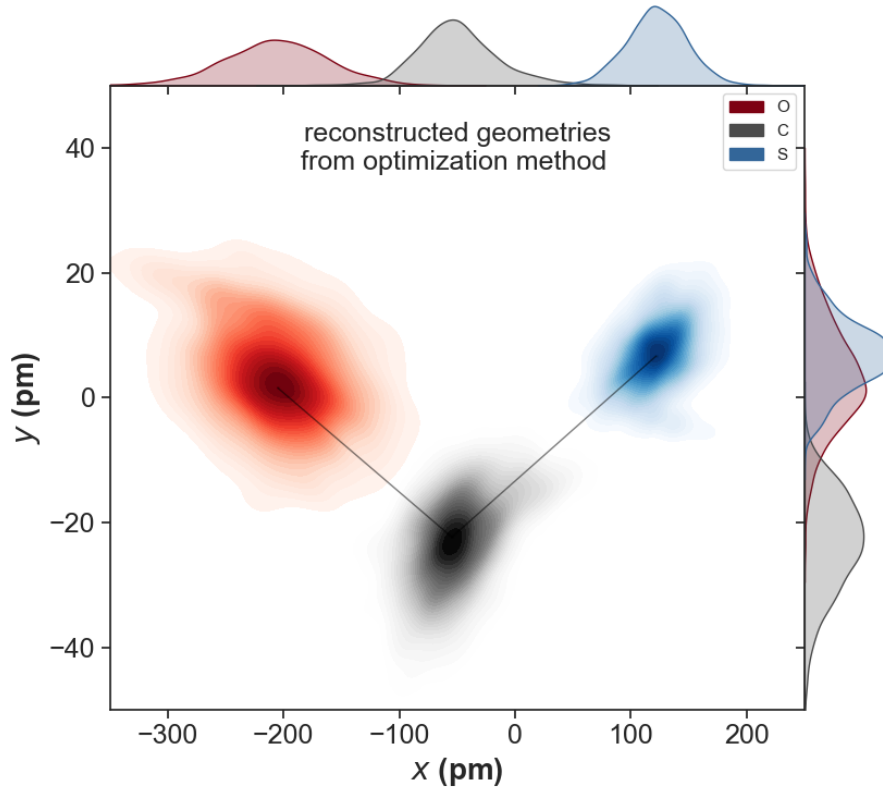


Figure 4.7: Geometry plot with marginal distributions for reconstructed geometries by the optimization method. The red, black and blue area represent oxygen, carbon and sulfur respectively.

Here, $\mathbf{p}_{exp}$ represents the momentum vectors that generated in section 4.2.2. For a total of 2000 momentum vectors, all of them produced reconstructed geometries. The peaks values for r_{co} , r_{cs} and θ_{ocs} are 152.336pm, 178.814pm, and 161.65° respectively. The average values are 160.011pm, 175.540pm, and $\theta = 160.473^\circ$. 1572 geometries are accurately reconstructed within a tolerance of (± 0.001 pm, ± 0.001 pm, $\pm 0.001^\circ$) when compared to the original geometries. And 650 of them are identified as having a unique solution, 718 of them have double solutions, 632 of them have triple solutions. Therefore, 67.5% of them are related to the degeneracy problem, 32.5% are non-degeneracy cases. The estimated time of reconstruction for each momentum vector set is around 2.04 seconds.

4.5 Degeneracy region

In this section, a degeneracy region is explored, where degeneracy is more likely and requiring further analysis of the results.

4.5.1 An example of triple degeneracy

Starting with a degeneracy case as shown below.

Table 4. 1: Comparison of reconstruction results between the look-up table method and the constrained non-linear optimization method for a single test.

	Geometry (r_{co} , r_{cs} , θ_{ocs}) (pm, pm, degree)	Error $f(x)$ (kgm/s) ²
Original geometry	(127.5295, 176.970, 162.9222)	
Look-up method	(217.8787, 108.9899, 164.6464)	10^{-48}
Optimization method	Geometry 1 = (127.5300, 176.9699, 162.9100)	$10^{-58.38}$
	Geometry 2 = (146.4786, 151.7719, 161.6963)	$10^{-58.03}$
	Geometry 3 = (213.0883, 111.0182, 164.3632)	$10^{-57.95}$

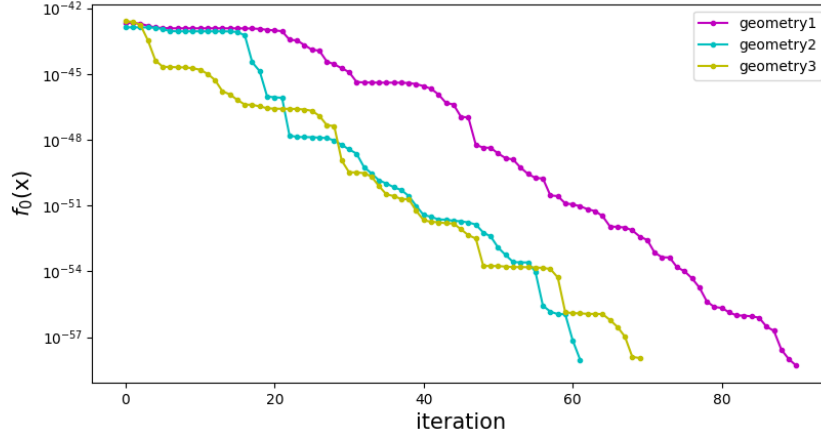


Figure 4. 8: Iteration plot (in log scale) for three initial starting geometries.

For the test, a stretched and bent geometry is selected. The bond lengths r_{co} and r_{cs} are stretched to 127.5295 pm and 176.9708 pm, respectively. While the bond angle θ_{ocs} bends to 162.9222° . The momentum is calculated, resulting in an asymptotic momentum vector $\mathbf{p}$ of $(-3.765393e-24, -6.34491e-22, 0, 3.47457e-22, 0, 0, -3.43691e-22, 6.34491e-22, 0)$ kgm/s.

By employing the look-up table method, the reconstructed geometry is (217.8787 pm, 108.9899 pm, 164.6464°). The corresponding error value $f(x)$, representing the squared norm of the difference momentum, is 10^{-48} . However, when employing the constrained non-linear optimization process, three solutions are discovered as shown in Table 4. 1. For a total of 125 starting points test, the most representative 3 calculations are selected to show the triple degeneracy. This indicates that for the given target momentum set, there exist three geometries, demonstrating a degeneracy of three. Notably, the error obtained from the optimization method is significantly smaller than that from the look-up table method. Additionally, the iteration plot Figure 4. 8 shows that the optimization process converges after 60-80 iterations, reaching an error of 10^{-58} . In our previous study that proposed the simplex approach [52], only three initial points were used, and an error of 10^{-52} was achieved.

4.5.2 Degeneracy region

All geometries related to the degeneracy problem are identified within the space $100\text{pm} \leq r_{\text{co}}$ and $r_{\text{cs}} \leq 500\text{pm}$ and $140^\circ \leq \theta \leq 180^\circ$. As shown in Figure 4. 9 (A), these geometries form a degeneracy region. This region is color-coded based on bond angle θ_{ocs} , where yellow represents more linear molecules, dark blue means more bent structures. From the degeneracy region, a geometry with a bond angle close to 160° is more likely to lead to a degeneracy problem. Also, if one bond is stretched much more than the other bond, it will also more likely to lead to the degeneracy. Moreover, by plotting the reconstruction results in this degeneracy region, we can understand how the degeneracy region correlates with the results presented in section 4. In Figure 4. 9 (B), blue points represent 32.5% non-degeneracy cases, as they are outside of the degeneracy region. In Figure 4. 9 (C), Red points represent those 67.5 % degeneracy cases, and they are located within the region.

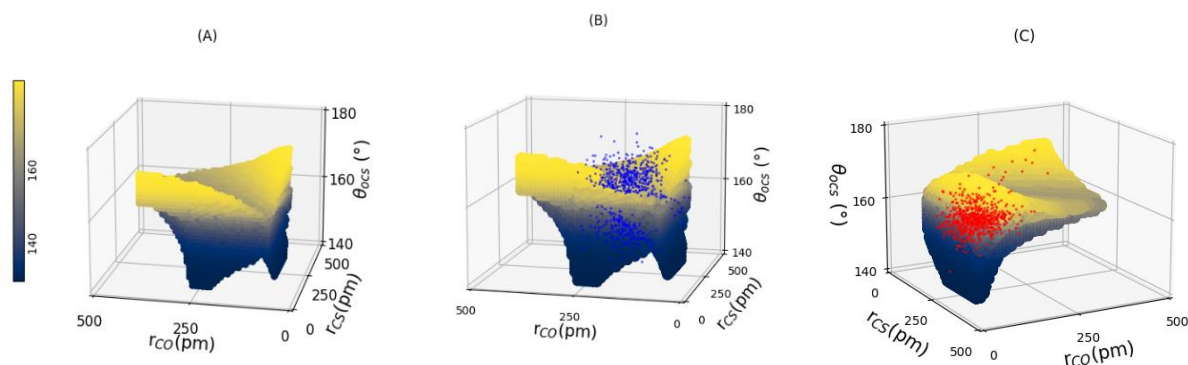


Figure 4. 9: A degeneracy region. Yellow represents more linear molecules, dark blue means more bent structures. (A) degeneracy region. (B) blue points are non-degeneracy cases from section 4. (c) red points are degeneracy cases in section 4.

4.6 Comparison of look-up table method and constrained optimization method

The reconstruction results from section 4.3.2 and 4.4.2 are analyzed. The table below presents a comparison of the reconstructed accuracy and speed between the look-up table method and the optimization method.

Table 4.2: Comparison of reconstruction accuracy and speed between two methods.

	Accuracy (pm, pm, degree)	Time per test	Identify degeneracy
Look-up table	$(\pm 1, \pm 1, \pm 1)$	4.98s	No
Optimization method	$(\pm 0.001, \pm 0.001, \pm 0.001)$	2.04s	Yes

As Table 4.2 shows, the optimization method outperforms the look-up table method in terms of both accuracy and speed for the tests in section 2 and 3. When considering the dataset of 2000 momentum vectors in section 2, only 18.8% of the cases are successfully reconstructed

within a tolerance of ($\pm 1\text{pm}$, $\pm 1\text{pm}$, $\pm 1^\circ$) using the look-up table method. The indication that a geometry is successful is typically an error less than 10^{-46} , but seldom lower than 10^{-49} . However, with the optimization method, results are obtained for 100% of the cases. Among them, 32.5% have a unique solution with a precision of ($\pm 0.001\text{pm}$, $\pm 0.001\text{pm}$, $\pm 0.001^\circ$), while the remaining 67.5% are degeneracy cases, where not only the solution found but other possible solutions are also discovered. Furthermore, the time required for each reconstruction using the look-up table method is more than twice that of the optimization method.

The precision of reconstruction is reliant on the resolution of the look-up table. To achieve greater precision, increasing the resolution is an option; however, that means a significant increase in storage space. As the resolution increases, the size of the table expands exponentially. This exponential growth in table size also occurs as the target molecule gets larger, meaning more atoms are involved. Furthermore, a very large table size, in turn, would likely result in a less efficient reconstruction. It is important to note that the result found through the look-up table is limited to the values present in the table itself. We can only reconstruct geometries that exist in the table, and, since the data in the table is discrete, it can not provide an exact solution to the reconstruction problem. The construction speed is influenced by multiple factors, including the size of look-up table, algorithms. The speed comparison provided here is only valid for the algorithms that implemented in this study. But for the look-up table method, generating a high-resolution table is obviously time-consuming. Overall, the constrained non-linear optimization method surpasses the look-up table method in aspects of accuracy, speed, precision, flexibility, and its ability to address the degeneracy cases and handle larger molecules.

4.7 Reconstruction for a second simulated dataset

A second dataset is generated with bond lengths r_{co} , r_{cs} and bond angle θ_{ocs} peaks at 115.710pm, 156.789pm, and $\theta_{\text{ocs}}=175.062^\circ$, close to the equilibrium structure. This dataset aims to capture the more typical behavior of molecules and avoids extreme cases of stretching, compression, or bend. This dataset is reconstructed using both the look-up table method and the optimization method. For a total of 200 momentum vectors, with the look-up table method, 57.6% of them get reconstructed geometries. However, only 21.5% of the cases are within the tolerance of ($\pm 1\text{pm}$, $\pm 1\text{pm}$, $\pm 1^\circ$). In contrast, when applying the constrained nonlinear optimization method, 100% of the geometries are reconstructed successfully, and all of them are within the stricter tolerance of ($\pm 0.001\text{pm}$, $\pm 0.001\text{pm}$, $\pm 0.001^\circ$).

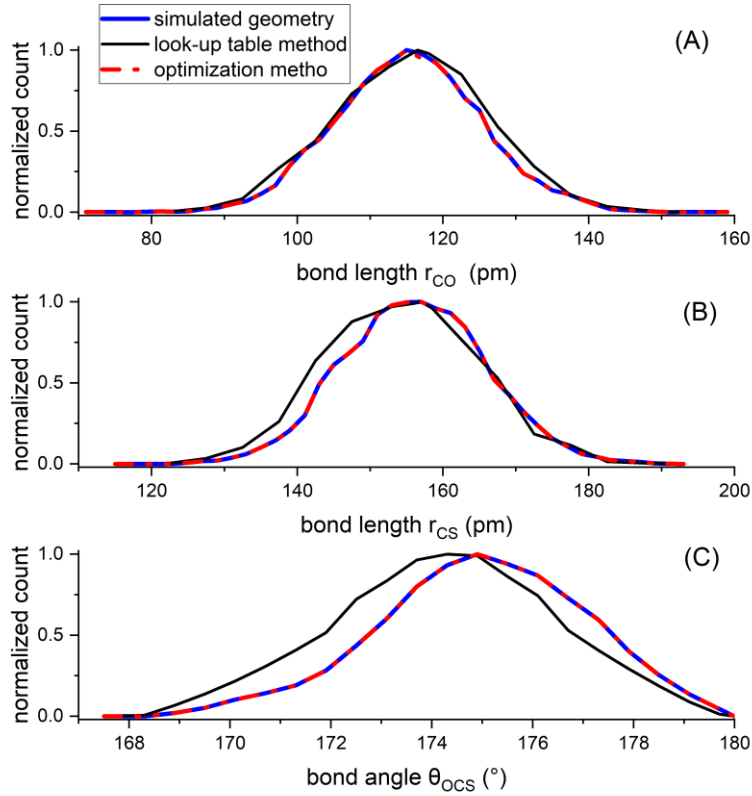


Figure 4.10: Bond length and bond angle distribution for original geometries and reconstructed results

Table 4. 3: Comparison of average values and peak values of distributions for original geometries and reconstructed results.

	Average geometry (unit in pm, degree)	Most likely geometry
Original geometry	$r_{CO} = 115.238$, $r_{CS} = 156.046$, $\theta = 174.989$	$r_{CO} = 115.710$, $r_{CS} = 156.789$, $\theta = 175.062$
Look-up table	$r_{CO} = 116.685$, $r_{CS} = 155.300$, $\theta = 174.300$	$r_{CO} = 116.277$, $r_{CS} = 156.392$, $\theta = 174.398$
Optimization method	$r_{CO} = 115.238$, $r_{CS} = 156.046$, $\theta = 174.989$	$r_{CO} = 115.710$, $r_{CS} = 156.789$, $\theta = 175.062$

Figure 4.10 illustrates the r_{CO} , r_{CS} and θ_{OCS} distributions obtained from both methods as well as the original geometries. And Table 4. 3 shows the average values and peak values of them. The distributions obtained from the optimization method closely match the original geometry distributions of r_{CO} , r_{CS} and θ_{OCS} , indicating high accuracy. However, the results from the look-up table method are different from the original geometries. The optimization method demonstrates its better accuracy in reconstructing geometries.

4.8 Conclusion

In this study, the comparison between the look-up table method and the constrained nonlinear optimization method have been conducted using simulated data from the asymmetric molecule OCS concerted explosion process. For the simple Coulomb model, it can be improved. The impact of the finite time during which sequential ionization occurs within the laser pulse should be considered. Although this time is short compared to molecular dissociation time scales, it is not negligible. Similarly, the non-zero effect of the laser field on ion trajectories should be considered. However, because previous studies with similar assumptions have been successful, it makes sense to focus on specific unanswered questions. The algorithm for mapping between initial geometries to final momenta has been demonstrated to be workable at least for the simulated data. The application to real experimental data is demonstrated in chapter 5.

The look up table method is simple to implement, relies on a predefined table and exhibits some ability to perform reconstruction for non-degeneracy cases. However, it would encounter challenges when applied to larger molecules, as the required storage space increases exponentially with the number of atoms in a molecule, making it a less efficient method. The optimization method performs better. By providing a large set of starting points as the initial guess solutions and carrying out the iteration processes in parallel to identify the multiple convergent results, solutions can be found quickly. One other notable benefit of the optimization method is that it can indicate if the given momentum vector set is related to more than one geometric structure. In addition, all possible molecular structures found by this method are accessible for further analysis to determine the most appropriate solution. For the triatomic molecule OCS, a degeneracy region in 3D space is defined, where degeneracies are most probable. This allows for instant feedback and visualization of whether a derived geometry distribution is trustworthy throughout or if certain results should potentially be rejected. Alternatively, this could be used as a starting point of the automated (e.g., AI driven) filtering process which could impose conditions on geometry variation between nondegenerate values, such as smoothly varying parameters, in order to choose the most likely molecular structure. These advantages make the constrained optimization geometry reconstruction method a valuable approach for studying and understanding molecular systems using Coulomb explosion.

Chapter 5 Geometry reconstruction for N₂O and OCS

The aim of this chapter is to demonstrate the implementation of the optimization geometry reconstruction method. Section 5.1 provides a detailed procedure for applying this method to real experimental data from N₂O. Section 5.2 presents the geometry reconstruction results of the experimental data for OCS. This chapter includes text edited from an in-process publication titled “Optimized geometry reconstruction on N₂O⁶⁺ 222 Coulomb explosion imaging data.”

5.1 Geometry reconstruction for N₂O

The asymmetric molecule N₂O, is a suitable candidate for the application of Coulomb explosion imaging (CEI). Several studies, conducted by Frasninski et al [62][63] using a laser with a wavelength of 600nm and a pulse length of 600 fs, relied on covariance mapping to indicate correlation without time and position-sensitive detection. Karimi et al [60], on the other hand, employed full coincidence and few cycle laser pulses, while Khan et al [64] explored various fragmentation channels up to N₂O⁷⁺ and investigated concerted and sequential processes in highly charged ion-induced Coulomb explosion(a process taking only a few femtoseconds for ionization). Previous studies [65][66] of the N₂O (1,1,1) channel revealed that as the bond lengths N-N and N-O stretch, the bond angle between them decrease. These studies utilized a 795nm, 100fs laser and collected data from a linear TOF mass spectrometer. These studies were analyzed using classical mechanical simulations, assuming that the N-N and N-O bonds stretch in the same proportion: $R_{NN} = \alpha_1 R_{eNN}$ and $R_{NO} = \alpha_2 R_{eNO}$, where r_e represents the equilibrium bond length. It was found that when $\alpha_1 = \alpha_2$, the produced momenta can cover the measured momentum range.

5.1.1 Experiment data from N₂O-(2,2,2)-7fs

In a recent study by Karimi, the kinetic energy released was calculated as a percentage of the energy expected from Coulomb explosion at the equilibrium geometry. The equilibrium geometry of N₂O is ($R_{NtNm} = 113\text{pm}$, $R_{NmO} = 119\text{pm}$, $\theta = 172^\circ$) [67]. As shown in Figure 5.1, the percentage is 86%, indicating the kinetic energy mostly comes from the Coulomb potential energy. This shows that 222-7fs channel is a suitable candidate for applying the Coulomb-based geometry reconstruction method.

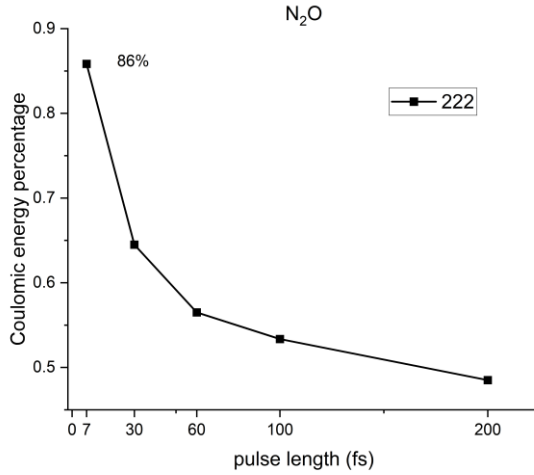


Figure 5.1: Kinetic energy released as a percentage of the Coulombic potential energy at the equilibrium geometry. A similar plot was originally published in the study by Karimi et al [60]. It has been recalculated and replotted.

The Coulombic energy percentage is calculated by dividing the kinetic energy released (KER) by the Coulombic potential energy at the equilibrium. The KER for a single event is given by $\frac{p_{Nt}^2}{2m_N} + \frac{p_{Nm}^2}{2m_N} + \frac{p_O^2}{2m_O}$ and the Coulombic potential energy is calculated as $\frac{kq_{Nt}q_{Nm}}{r_{NtNm}} + \frac{kq_{Nt}q_{Nm}}{r_{NtNm}} + \frac{kq_{Nm}q_O}{r_{NmO}}$. For N₂O-(2,2,2)-7s, the average KER for all events should be calculated first, and then it should be divided by the Coulombic potential energy. Assuming that at the initial point, the total energy of the molecule is initially obtained from the potential energy, and then after a time t, all the potential energy is transferred to the kinetic energy.

In the following sections, the experimental momentum data are analyzed first, followed by an explanation of the reconstruction procedure. Finally, the reconstruction results are discussed.

The experiment was conducted at the Advanced Laser Light Source using a kilohertz titanium-sapphire laser system with an output spectrum centered at 800nm, and the experimental setup is the same as described in previous studies [55][60]. Short 7-fs pulses with an intensity of $2 \times 10^{15} \text{ W/cm}^2$ were generated by directing the laser through a hollow fiber filled with argon gas, followed by compression by chirped mirrors. The laser pulses were focused by a parabolic mirror (f=10cm) onto a supersonic gas jet of N₂O in an ion imaging spectrometer (single electric field region), and a delay-line anode detector captured atomic fragments in coincidence. The events were stored by identifying triple coincidences in which the total momentum released from all of the ions was close to zero.

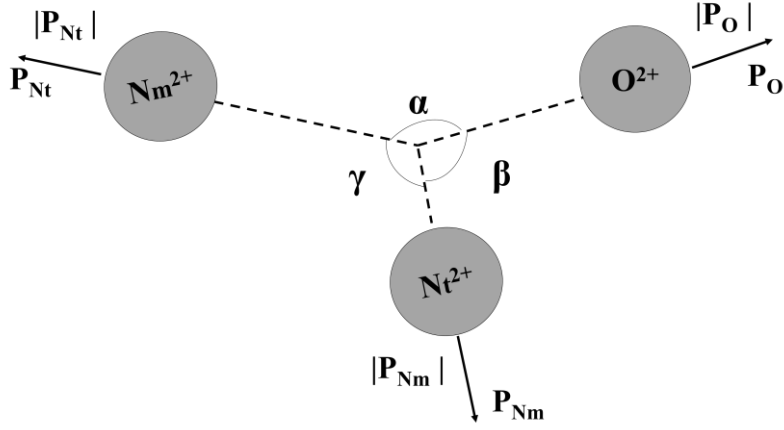


Figure 5.2: The diagram of momentum vectors and angles in N_2O structure.

In preparation for a more in-depth analysis, parameters are defined as shown in Figure 5.2. The N_2O (2,2,2) channel represents the dissociation process in which the N_2O molecule loses 6 electrons, resulting in each of the atoms becoming ionized and carrying two positive charges. $N_2O \rightarrow N_t^{2+} + N_m^{2+} + O^{2+}$. To distinguish between the two nitrogen atoms in one molecule, the terminal ion is defined as N_t , while the middle ion is defined as N_m . Each ion has a momentum vector: P_{Nt} , P_{Nm} , and P_O , together with their magnitude values $|P_{Nt}|$, $|P_{Nm}|$, and $|P_O|$. The angles between each pair of momentum vectors are denoted as α , β , and γ respectively.

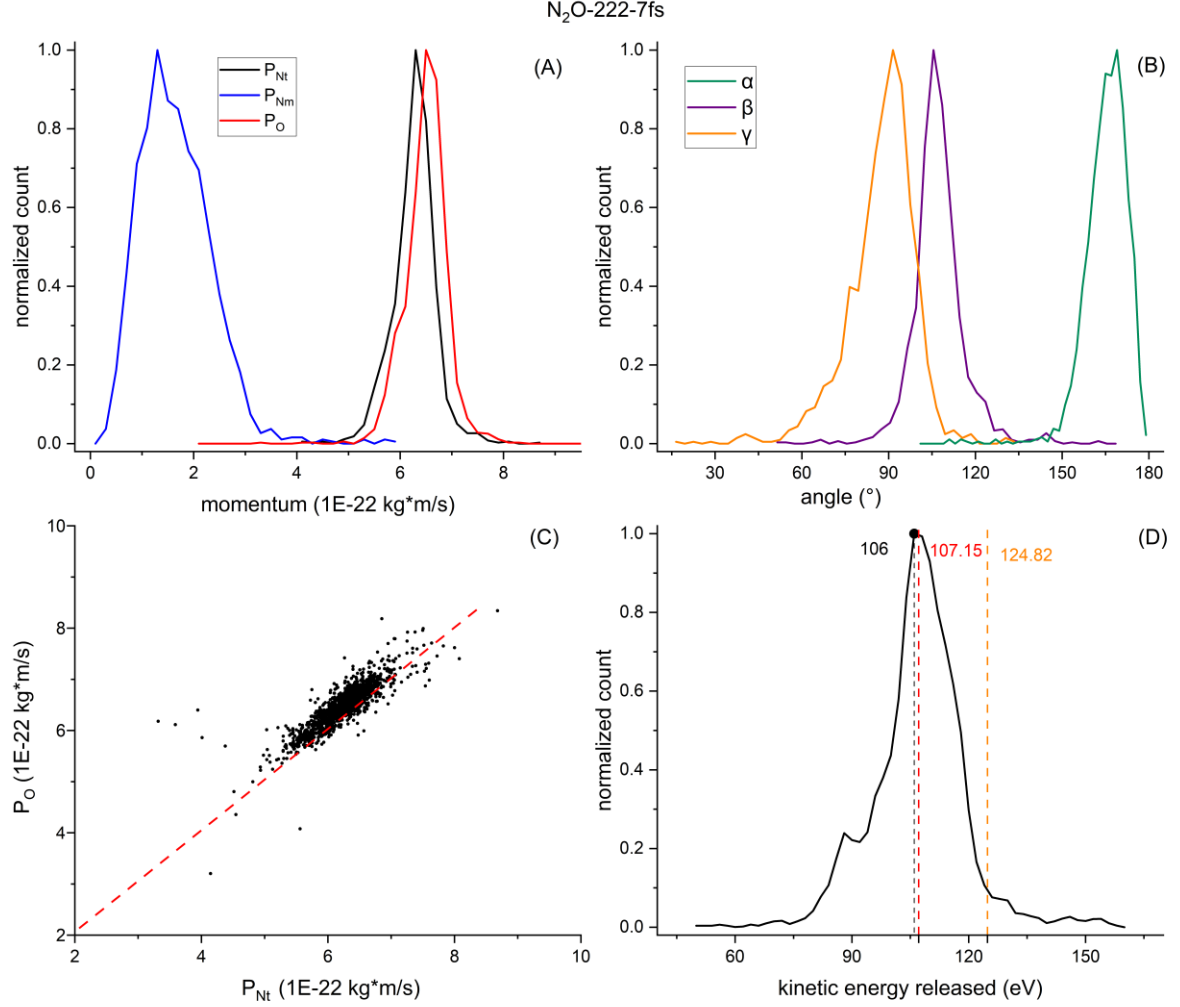


Figure 5.3: Momentum analysis of (2,2,2) of N₂O⁶⁺. (A) Distribution of momentum magnitudes for P_{Nt} , P_{Nm} , and P_O , colored in black, blue, and red respectively. (B) Distribution of angles between the three momentum vectors: α , β , and γ , colored in green, purple, and yellow respectively. (C) Correlation map showing the magnitude correlation between two terminal vectors P_{Nt} and P_O , and a 45° reference line. (D) Distribution of kinetic energy released for all events. The black reference line indicates the maximum value of KER, the red reference line indicates the average KER, and the yellow line indicates the expected KER for equilibrium structure.

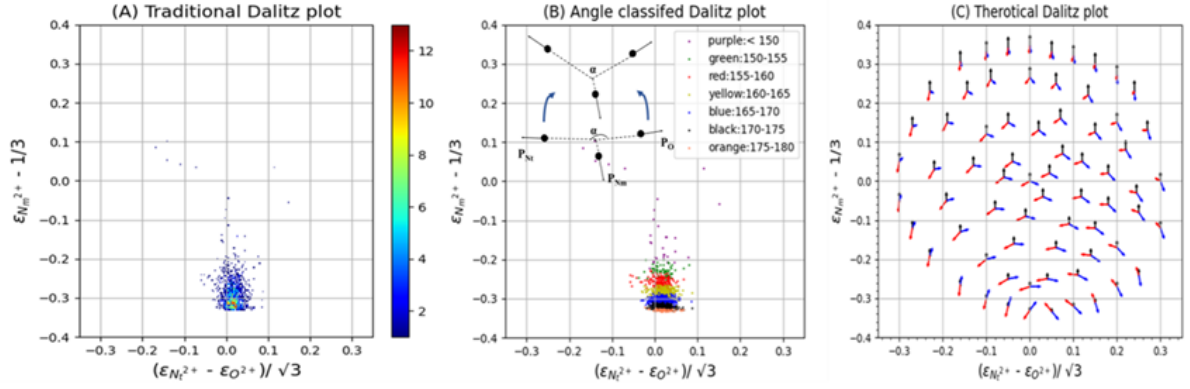


Figure 5.4: Dalitz plots for N₂O-(2,2,2)-7fs. (A) Traditional Dalitz plot. x-axis represents the energy differences between two terminal fragments N_t²⁺ and O²⁺, and y-axis represents the energy from middle fragment N_m²⁺. (B) Angle classified Dalitz plot. Event points are colored based on varying values of angle α from 0° to 180°. (C) Theoretical Dalitz plot: theoretical momentum structures for points on the Dalitz plot. Red arrows represent the momenta of N_t, black arrows represent the momenta of N_m, and blue arrows represent the momenta of O.

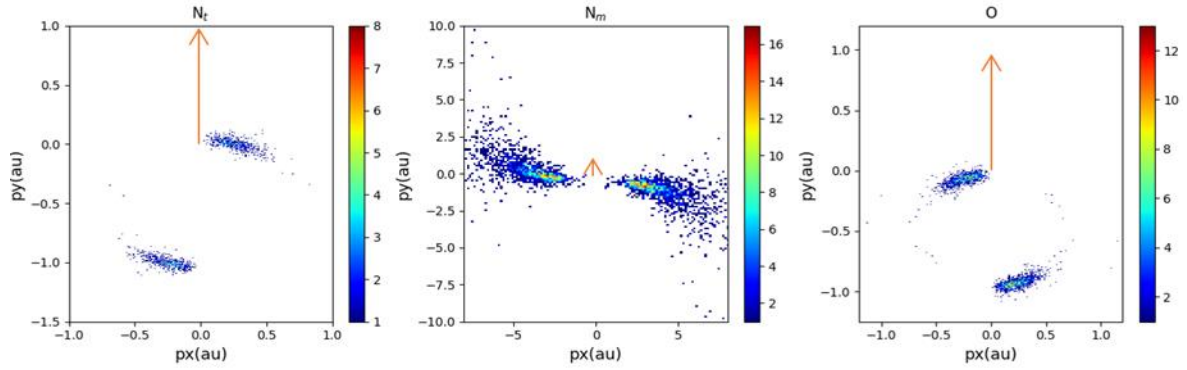


Figure 5.5: Newton plots for N₂O 222 7fs. From left to right, N_t, N_m and O as reference respectively. The orange arrows represent the reference ion momentum and (0,0) represent the center of mass. The first plot shows the normalized N_t²⁺ momentum vectors are fixed at (0,1), then the corresponding N_m²⁺ momentum vectors are placed at the left side of N_t²⁺ and O²⁺ momentum vectors are placed at right side.

In the initial stages of analysis, it is important to visualize the preliminary momentum data results. These visualizations provide a straightforward understanding without using any complicated methods. As shown in Figure 5.3, (A) and (C) illustrate that the middle N ion has the lowest momentum compared to the other two terminal ions. Since the masses of N and O are very similar, it is reasonable to expect similar momenta for them. (B) shows the distribution of angles between momentum vectors. Considering the equilibrium geometry of N₂O ($R_{N_t N_m} = 113\text{pm}$, $R_{N_m O} = 119\text{pm}$, $\theta = 172^\circ$) and the short 7fs pulse has been applied, the angle α is much larger than the β and γ . Given the asymmetric structure of N₂O, it is reasonable to observe that angles β and γ are different but still relatively close, reflecting the initial bonds are 113pm

compared to 119pm. And (D) shows the kinetic energy released is centered around 106eV. Figure 5.4 displays both the traditional Dalitz plot and the new type of Dalitz plot colored by angle α . The angle classified Dalitz plot can be color-coded to represent any desired information related to the event. In this plot, events are arranged from the bottom to the top, with the angle α decreasing from 180° downwards. For this N_2O data, the majority of events have α values greater than 150° and are located at the bottom of the plot, and the right of the origin. The geometries reflect the fact that energy released from the middle N is relatively small compared to the other atoms, while the energy released from N_t is mostly larger than that from O. Figure 5.5 shows the Newton plots using N_t , N_m and O as references. In the plots with N_t and O as references, the other two momenta form an off-centre ring shape, indicating that energy is not symmetrically shared, consistent with Figure 5.4(A). The plot with N_m as reference is centered at the origin, suggesting a more similar energy distribution between two terminal ions, this is consistent with the Figure 5.3(C). Additionally, the Dalitz plot and the Newton plot prove that the N_2O -(2,2,2)-7fs channel is not related to any stepwise process, only concerted process included.

5.1.2 Reconstruction process of N_2O

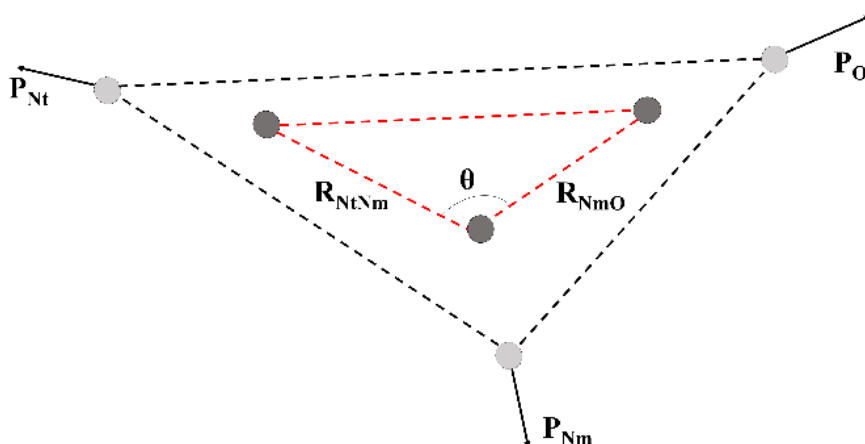


Figure 5.6: N_2O structure: Dashed red line initial structure at $t=0$ s (N_t = terminal Nitrogen ion, N_m = middle nitrogen ion and O oxygen ion), grey dashed line, instantaneous structure at some time t after the Coulomb explosion has started, showing momentum vectors of the three ions.

In preparation for the geometry reconstruction, parameters are defined as shown in Figure 5.6. The initial geometric structure, represented by red lines, form the central inquiry of this study. As N_2O is a triatomic molecule, its three points are always lying in a plane. Thus, it is straightforward to describe its geometry using two bond lengths and a bond angle, as illustrated in Figure 5.6. The momentum values for each ion, derived from our experiments, represent the state shortly after time t .

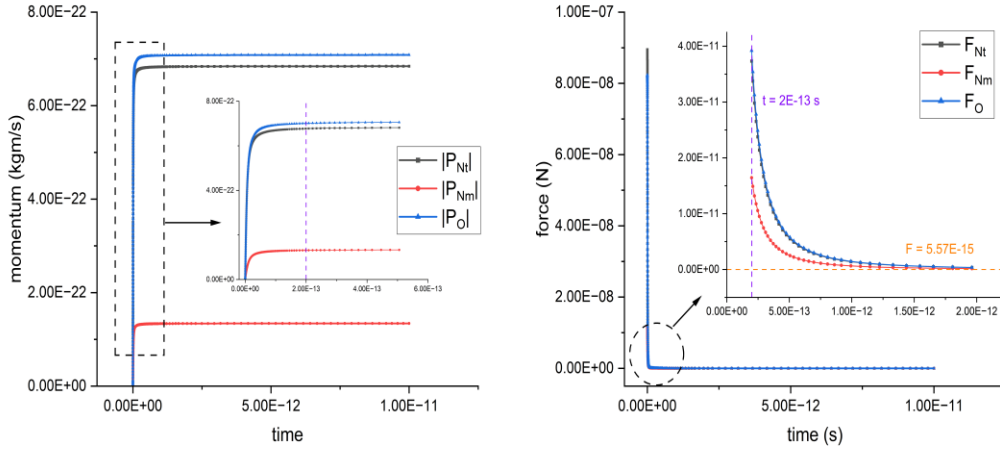


Figure 5.7: Momenta and forces evolution as time changes for geometric structure at equilibrium.

To apply the geometry method, some parameters need to be discussed. In our model, given the initial and final momenta, the initial geometry at $t=0$ is the target question. The parameter t represents the time at which the fragment ions reach to the asymptotic momentum condition. As illustrated in Figure 5.7 (left), this simulation is for the equilibrium geometric structure undergoing Coulomb explosion, with magnitude of momenta P_{Nt} , P_{Nm} , and P_O changing over time and colored in black, red and blue respectively. The magnified plot reveals the period over which the most significant change takes place. The time t is chosen at $2E-13$ s, where the momentum curves flatten, and the values exhibit minimal variation. In Figure 5.7 (right), it shows that Coulombic forces for each ion. At the time at $2E-13$ s, the electric force is $5.57E-15$, which is significantly smaller compared to the $E-11$ of the Coulombic forces.

“Constrained” refers to the box constraints that are applied to the algorithm. Constrains are defined as follows for N_2O : $50\text{pm} < R_{NtNm} < 350\text{pm}$, $50\text{pm} < R_{NmO} < 350\text{pm}$, $120^\circ < \theta < 180^\circ$, These ranges are significantly larger than the known equilibrium structure of the N_2O molecule, but reasonable in a case where significant laser induced deformation may have taken place. The algorithm uses MultiStart to search for points within the box constrain to ensure it finds the global minimum. The starting points are uniformly selected from within the box constraints.

“Optimization” refers to the algorithm minimizing an objective function: $f(x) = |p(x) - p_{exp}|^2$, where p_{exp} represents the experimental momenta measured at time t , and $p(x)$ represents the momentum iteratively calculated during the optimization process. To fit the measured momenta to the algorithm, the experimental momenta should be adjusted into the format as explained in section 4.4.1: $(p_{e_Ntx}, p_{e_Nty}, 0, p_{e_Nmx}, 0, 0, p_{e_Ox}, p_{e_Oy}, 0)$.

5.1.3 Reconstruction results

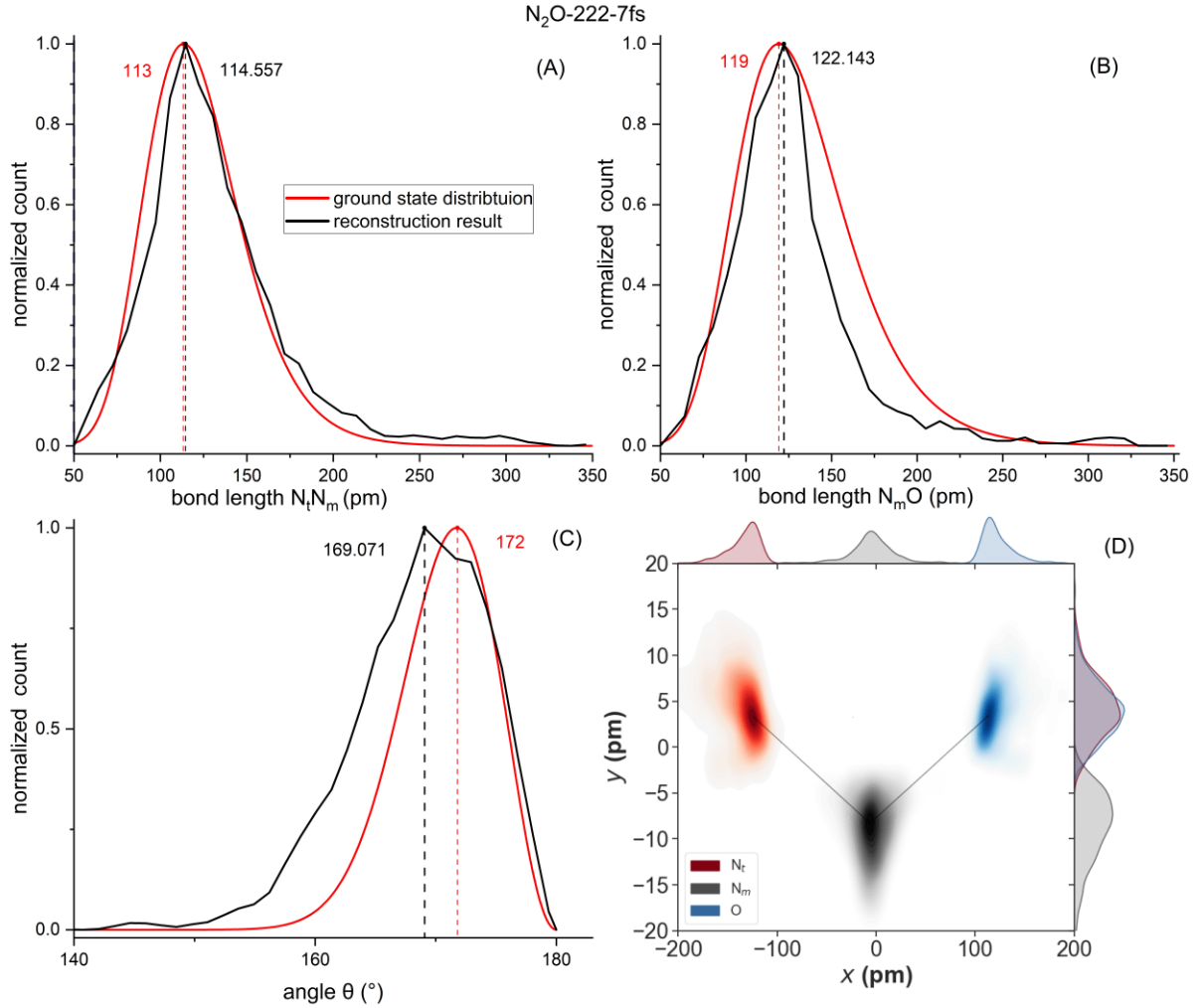


Figure 5.8: Bond lengths and bond angle distribution for reconstruction results and ground state of N_2O -222-7fs. (A) (B) and (C) are distributions for bond lengths $N_t N_m$, $N_m O$ and bond angle θ . Black lines represent the distributions of reconstruction results, and the red lines represent distributions of the ground state. (D) Geometry distribution on a xy position plot.

For a total of 1480 events from the N_2O (2,2,2) channel, 1263 were successfully reconstructed, resulting in a reconstruction rate of 83.33%. The objective function $f_0(x) = |p(x) - p_m|^2$ can be minimized to a value 10^{-58} , an improvement when compared to the 10^{-52} in our previous study [46]. Given that the momenta are measured in unit of $1e-22$ kgm/s, the error 10^{-58} makes the accuracy to $0.000001 \cdot e-22$ kgm/s for momenta. We find that there is no degenerate case in this test, which means all events are related to unique geometry structure. The reconstruction is not 100% reproduced, there are about 16.67% events that have no results, this might be because some of the molecules are sequential ionized. As shown in Figure 5.8 (A, B&C), the black curves represent the reconstructed distributions, and the most probable values

for R_{NtNm} , R_{NmO} and θ are 114.557pm, 122.143pm, 169.071° respectively. The red curves represent the ground state distributions, which are calculated based on the ground state of Morse potential using Density Functional Theory. When comparing the peak values, it is observed that the bond lengths R_{NtNm} and R_{NmO} have stretched by 1.38% and 2.64% respectively. Additionally, the bond angle is bent by 1.70%. In comparison to the method described in study [65], which assumed proportional stretching of bond length R_{NtNm} and R_{NmO} , our method allows for more structural freedom. Specifically, N_tN_m and N_mO bond lengths can be stretched in varying proportions, with no predefined restrictions on bond length or angle behaviours. This flexibility allows for a more accurate and realistic reconstruction of results. Figure 5.8 (D) displays the distribution of reconstructed structures in an xy-plot. To create this geometry plot, we first place all the N_m ions at the origin (0,0). Then place the N_t and the O in the second and first quadrant respectively. Then let the +y-axis separate the angle θ evenly. Finally, we shift the center of mass to the origin.

5.1.4 Geometry reconstruction for $\text{N}_2\text{O}-(2,2,1)$ -7fs

By following the procedure in the previous sections, the analysis and reconstruction results are presented below.

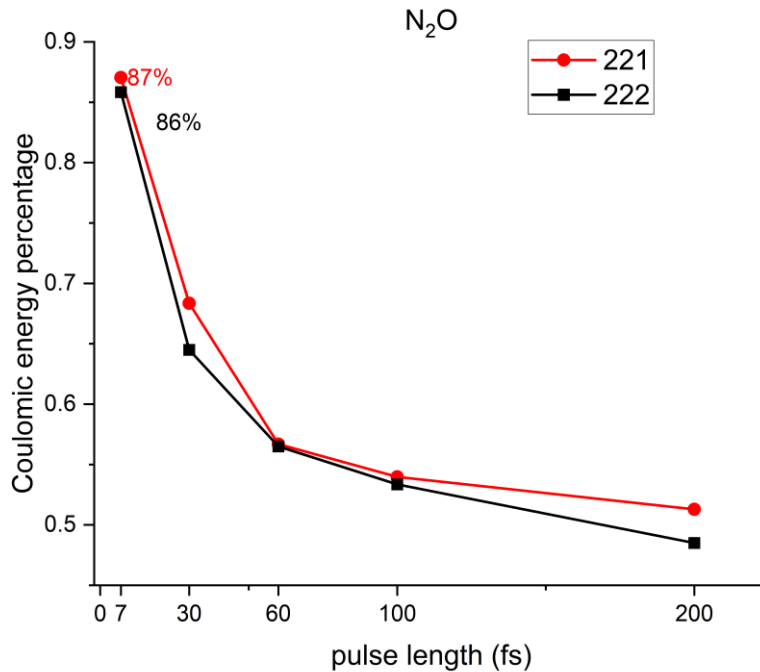
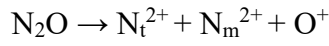


Figure 5.9: Kinetic energy released as a percentage of the Coulombic potential energy at the equilibrium geometry for channels $\text{N}_2\text{O}-(2,2,2)$ and $\text{N}_2\text{O}-(2,2,1)$.

As shown in Figure 5.9, the percentage value for channel (2,2,1)-7fs is 87%, which indicates it is possible to apply the geometry reconstruction method.

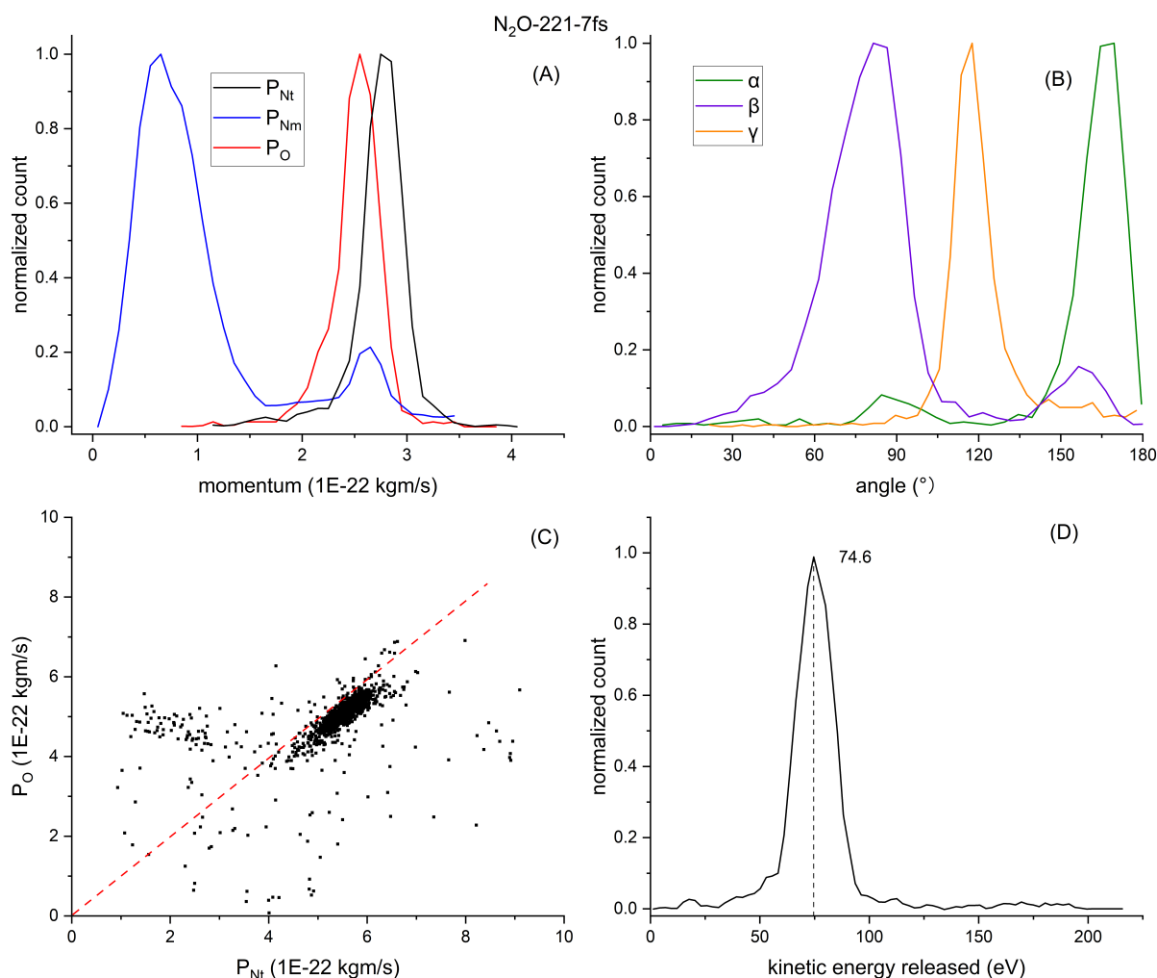


Figure 5.10: Momentum analysis of (2,2,1) of N_2O^{5+} . (A) Distribution of momentum magnitudes for P_{Nt} , P_{Nm} , and P_O , colored in black, blue, and red respectively. (B) Distribution of angles between the three momentum vectors: α , β , and γ , colored in green, purple, and yellow respectively. (C) Correlation map showing the magnitude correlation between two terminal vectors P_{Nt} and P_O , and a 45° reference line. (D) Distribution of kinetic energy released for all events. The black reference line indicates the maximum value of KER, the red reference line indicates the average KER, and the yellow line indicates the expected KER for equilibrium structure.

When comparing the momentum distributions in Figure 5.10 for (2,2,1) channel and in Figure 5.3 for the (2,2,2) channel, both channels exhibit lower momentum for the middle N. For a nearly linear triatomic molecule, it makes sense that the middle ion experiences forces from the two terminal ions in almost opposite directions. In the (2,2,1) channel, the momentum of O has a smaller peak value than the terminal N. In contrast, in the (2,2,2) channel, the P_O has a larger peak value than the P_{Nt} . Additionally, the (2,2,2) channel has a peak KER of 106eV, which is higher than the 74.6eV observed in the (2,2,1) channel.

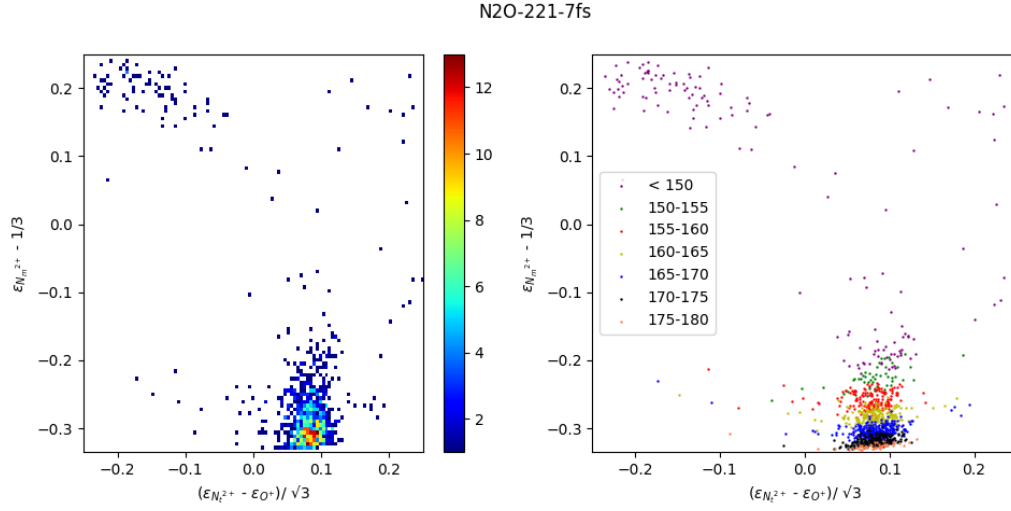


Figure 5.11: Dalitz plots for $\text{N}_2\text{O}-(2,2,1)\text{-7fs}$. (Left) Traditional Dalitz plot. (Right) Angle classified Dalitz plot. Event points are colored based on varying values of angle α from 0° to 180° .

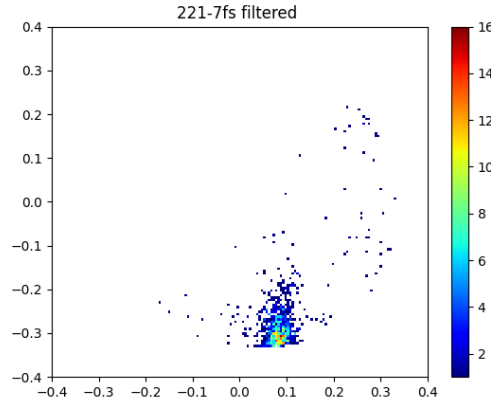


Figure 5. 12: Dalitz plot for $\text{N}_2\text{O}-(2,2,1)\text{-7fs}$ filtered data.

As shown in Figure 5.11, the Dalitz plot's left corner contains data points associated with stepwise process: $\text{N}_2\text{O} \rightarrow \text{N}_t\text{N}_m^{2+} + \text{O}^+ \rightarrow \text{N}_t^{2+} + \text{N}_m^{2+} + \text{O}^+$. However, the Coulomb model is applicable to concerted process. The momenta related to the concerted process can be filtered out, as shown in Figure 5. 12.

As shown in Figure 5.13, Coulomb forces and momenta change over time. At the time marked at $2\text{e-}13\text{s}$ to get asymptotic momenta. While the interesting thing is, the momentum of the middle N does not consistently increase. Within the time range $[4.27\text{e-}15\text{s}, 1.27\text{e-}14\text{s}]$ in Figure 5.13 (C), it shows a slight decrease followed by an increase. Similarly, in Figure 5.13 (D) the Coulomb force for terminal N is observed to rise slightly and then decrease again. The middle N experience a wiggle.

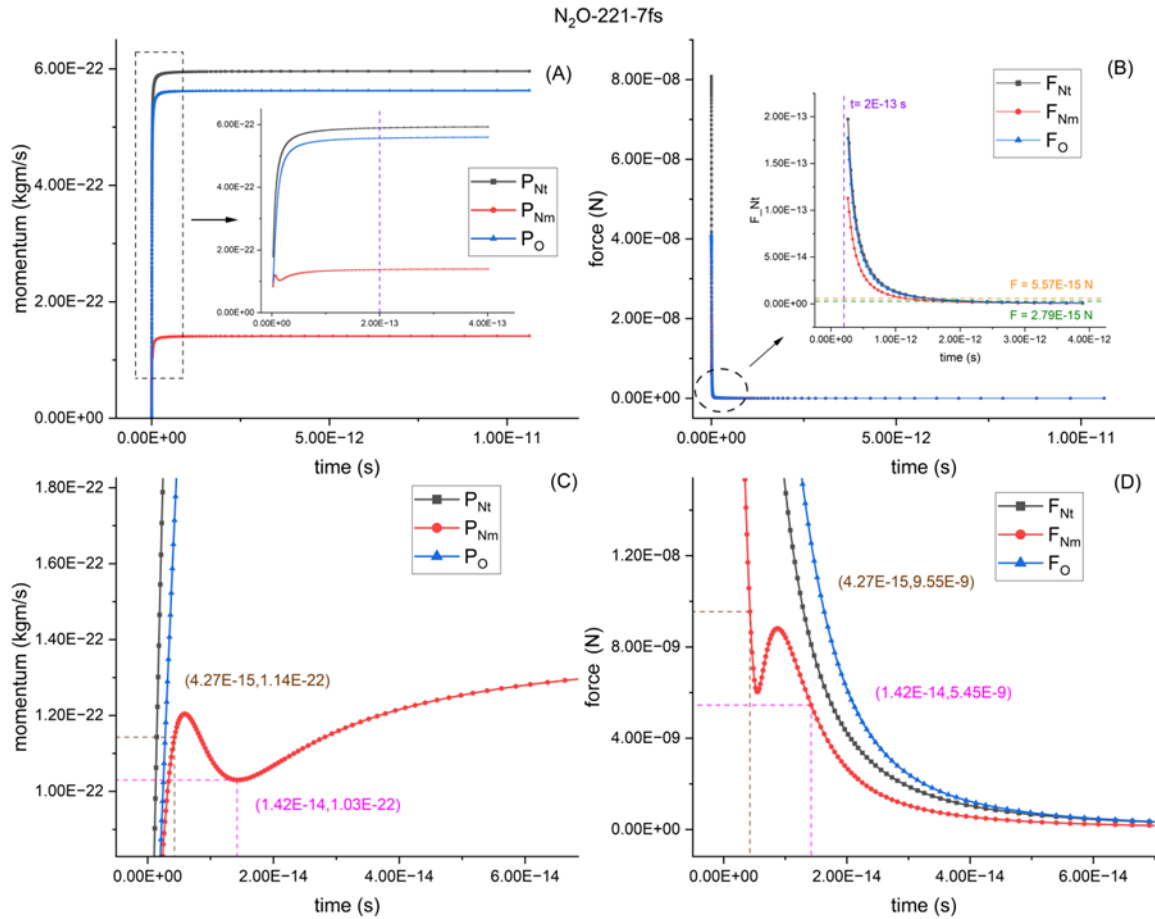


Figure 5.13: Momenta and forces evolution as time changes for geometric structure at equilibrium. (A) Momenta evolution as time changes. (B) Ion forces on evolution as time changes. (C) The magnified plot of momenta evolution for time interval $[0, 6\text{e-}14\text{s}]$. (D) The magnified plot of forces evolution for time interval $[0, 6\text{e-}14\text{s}]$.

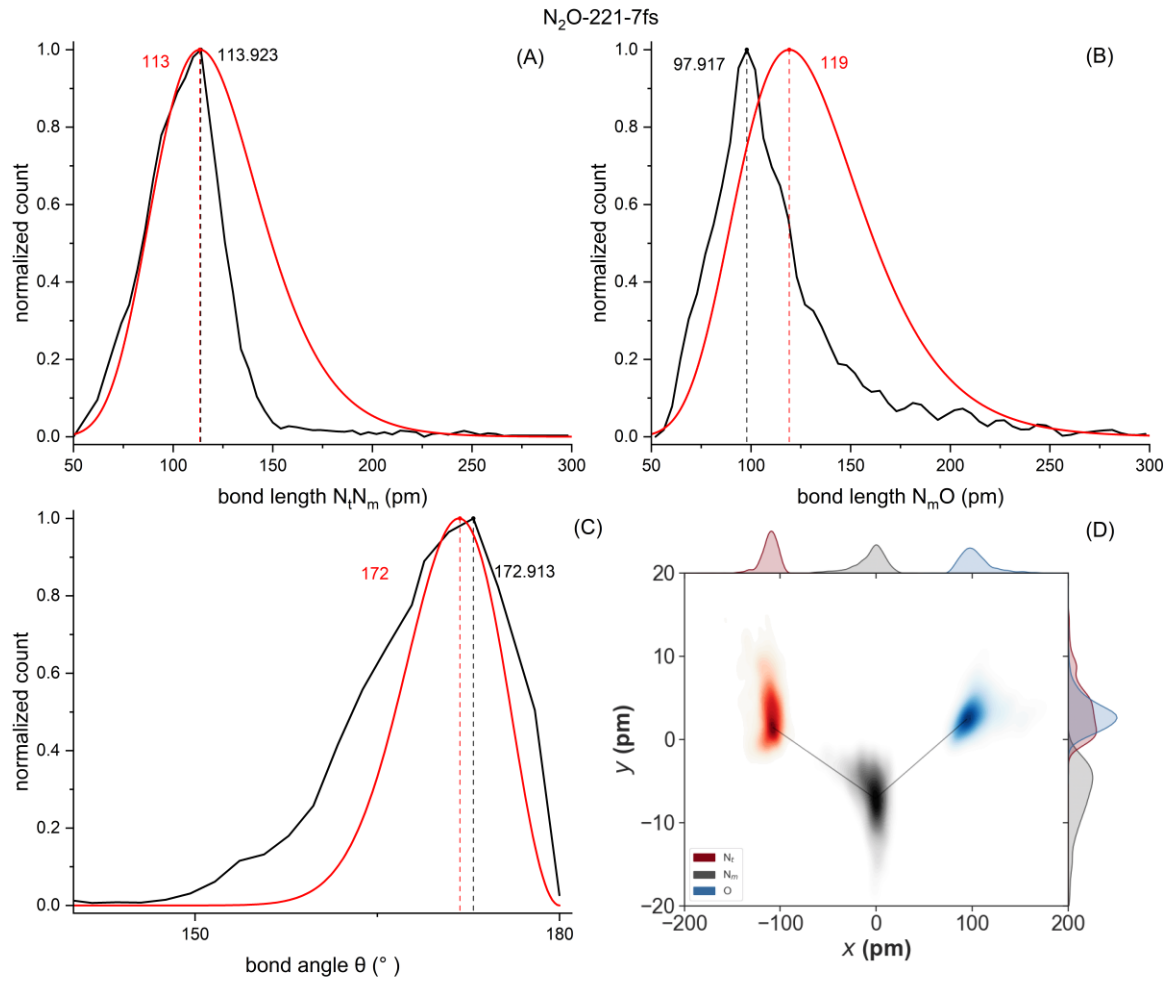


Figure 5.14: Bond lengths and bond angle distribution for reconstruction results and ground state of N_2O -221-7fs. (A) (B) and (C) are distributions for bond lengths N_tN_m , N_mO and bond angle θ . Black lines represent the distributions of reconstruction results, and the red lines represent distributions of the ground state. (D) Geometry distribution on a xy position plot.

For a total 1028 of events from the N_2O -(2,2,1)-7fs channel, 969 are identified as non-degeneracy cases, and 59 as double-degeneracy cases. The distributions take into account all possible geometries, where a unique solution is counted as 1 and a double solution counted as 0.5. As shown in Figure 5.14 (A, B&C), the most probable values for $R_{N_tN_m}$, R_{N_mO} and θ are 113.923pm, 97.917pm, 172.913° respectively. When compared to the equilibrium structure, the bonds $R_{N_tN_m}$ has stretched by 0.82% and R_{N_mO} has been compressed 17.72%. The bond angle is near the equilibrium value. Figure 5.8 (D) displays the distribution of reconstructed structures in an xy-plot. And the average values of bonds $R_{N_tN_m}$, R_{N_mO} and bond angle are 115.21pm, 113.54 pm and 168.53°.

5.2 Geometry reconstruction for OCS

In this section, the geometries reconstruction for OCS-(2,2,2) channel and OCS-(2,2,3) channel are detailed as follows.

The concerted processes for each channel are:

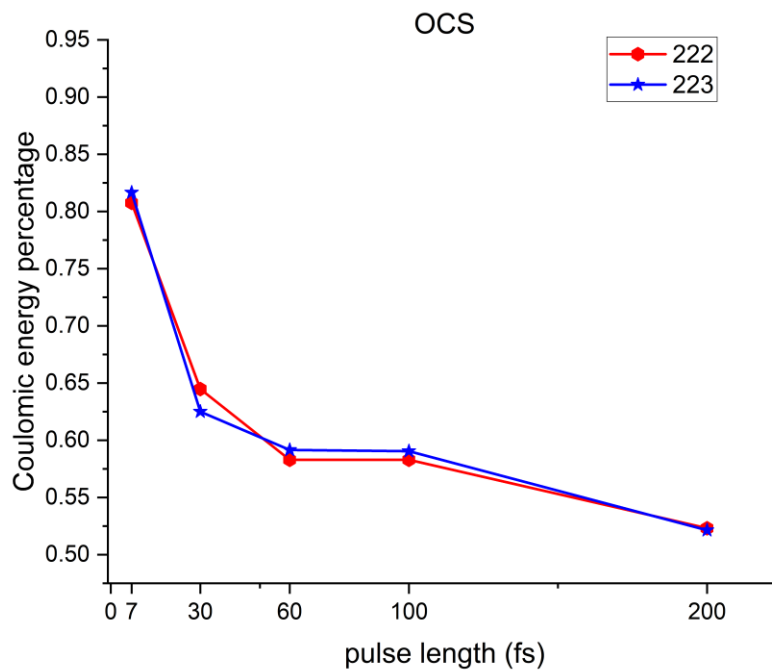
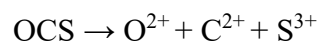
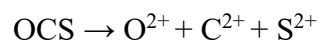


Figure 5.15: Kinetic energy released as a percentage of the expected coulomb potential energy for channels OCS-(2,2,2) and OCS-(2,2,3).

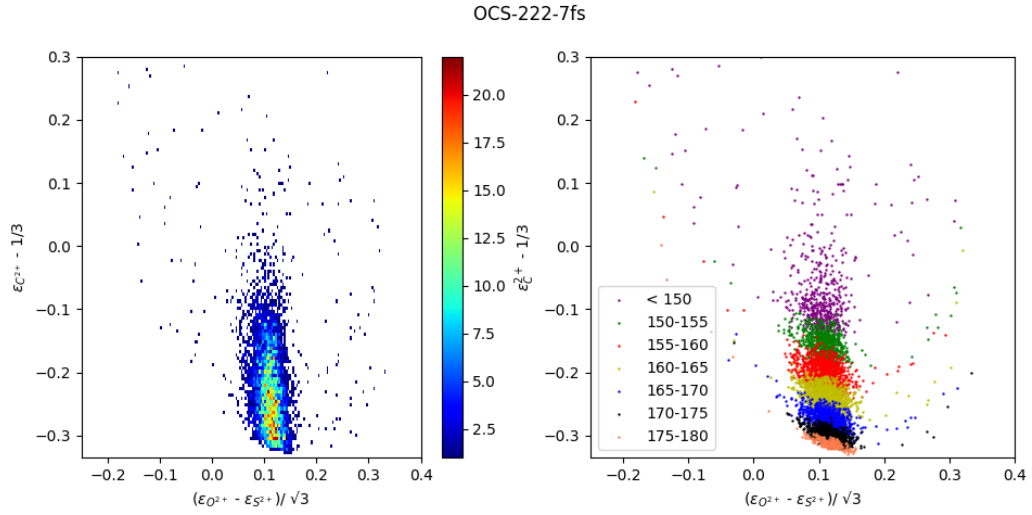


Figure 5.16: Dalitz plots for OCS-(2,2,2)-7fs. (Left) Traditional Dalitz plot. (Right) Angle classified Dalitz plot. Event points are colored based on varying values of angle α from 0° to 180° .

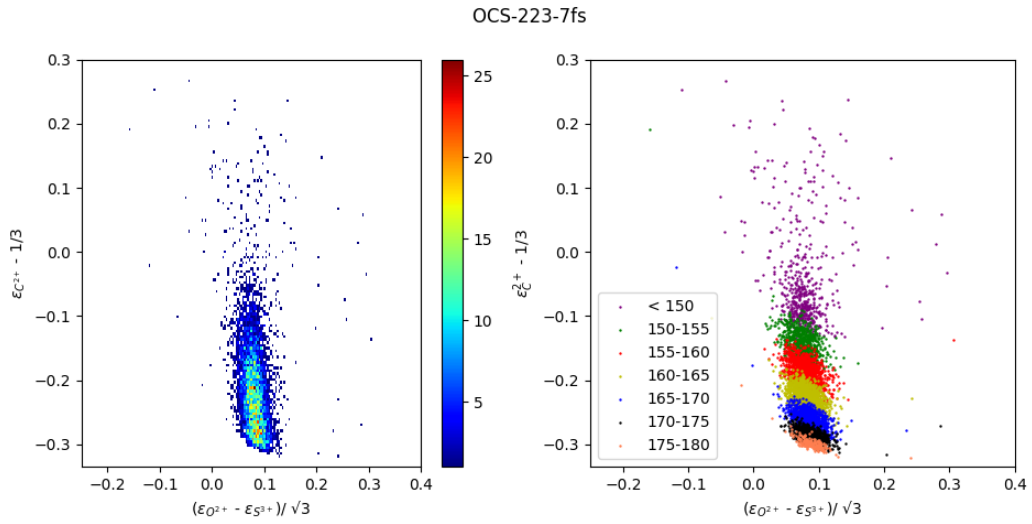


Figure 5.17: Dalitz plots for OCS-(2,2,3)-7fs. (Left) Traditional Dalitz plot. (Right) Angle classified Dalitz plot. Event points are colored based on varying values of angle α from 0° to 180° .

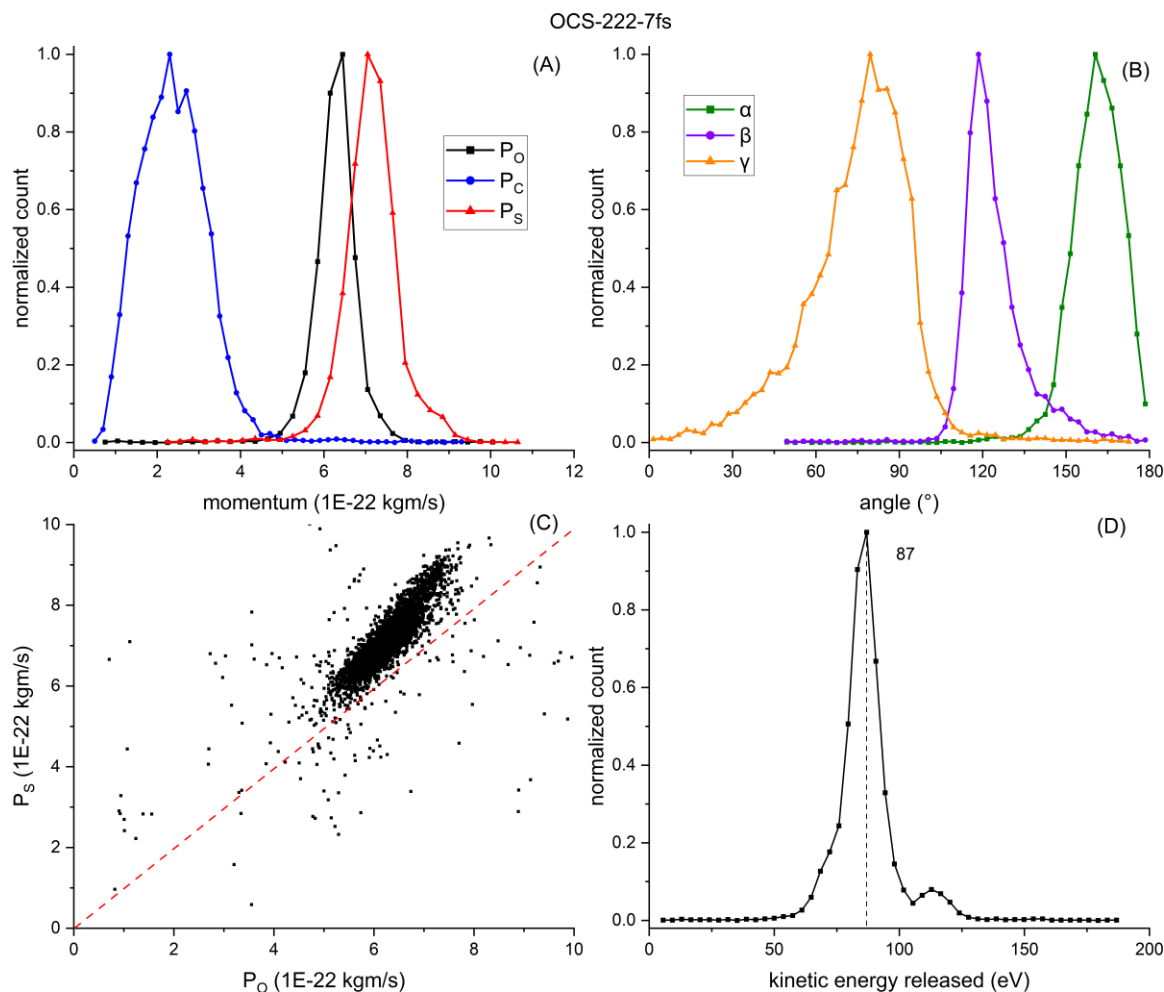


Figure 5.18: Momentum analysis of (2,2,2) of OCS^{6+} . (A) Distribution of momentum magnitudes for P_O , P_C , and P_S , colored in black, blue, and red respectively. (B) Distribution of angles between the three momentum vectors: α , β , and γ , colored in green, purple, and yellow respectively. (C) Correlation map showing the magnitude correlation between two terminal vectors P_O and P_S , and a 45° reference line. (D) Distribution of kinetic energy released for all events. The black reference line indicates the maximum value of KER, the red reference line indicates the average KER, and the yellow line indicates the expected KER for equilibrium structure.

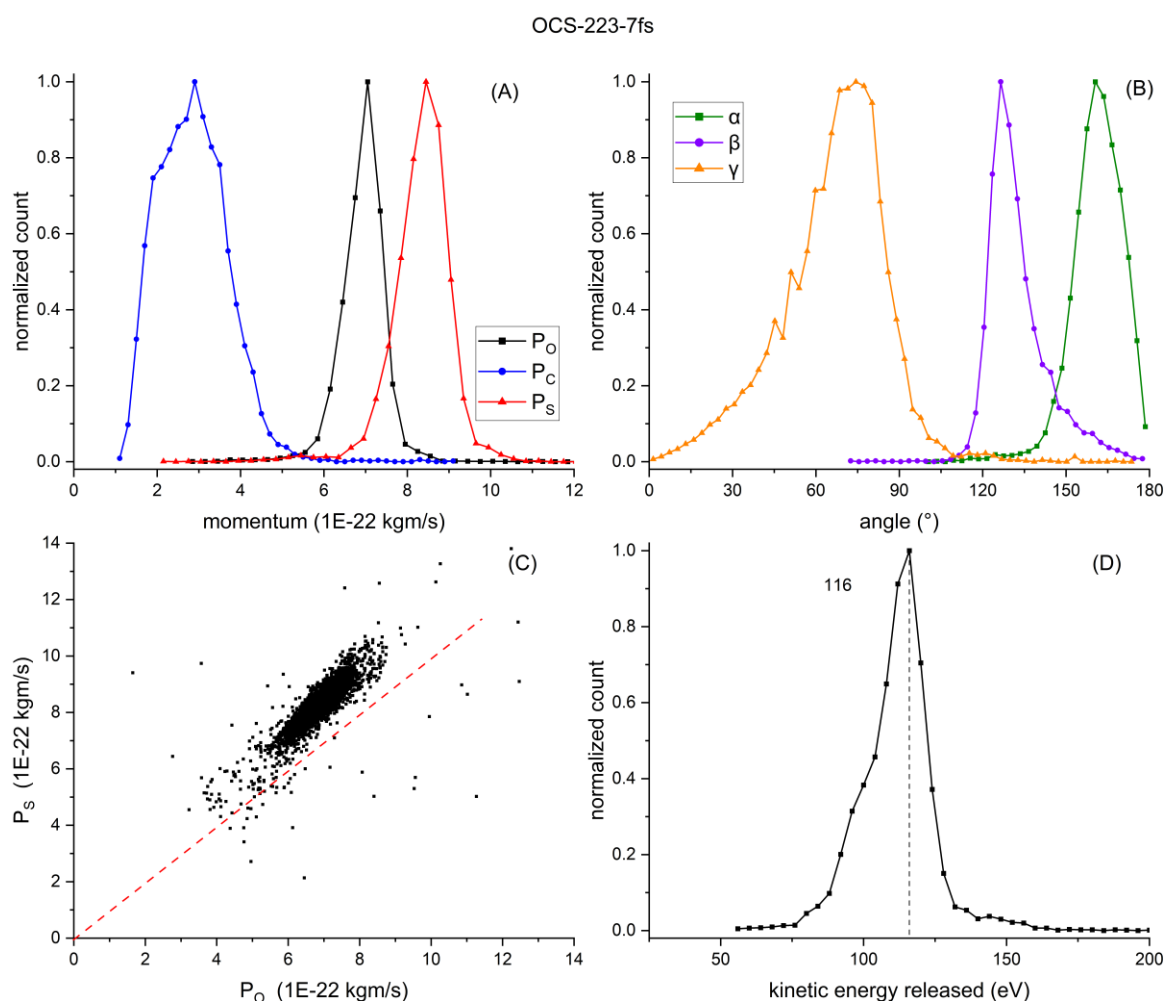


Figure 5.19: Momentum analysis of (2,2,3) of OCS⁷⁺. (A) Distribution of momentum magnitudes for P_O , P_C , and P_S , colored in black, blue, and red respectively. (B) Distribution of angles between the three momentum vectors: α , β , and γ , colored in green, purple, and yellow respectively. (C) Correlation map showing the magnitude correlation between two terminal vectors P_O and P_S , and a 45° reference line. (D) Distribution of kinetic energy released for all events. The black reference line indicates the maximum value of KER, the red reference line indicates the average KER, and the yellow line indicates the expected KER for equilibrium structure.

When comparing the momentum distributions in Figure 5.18 for (2,2,2) channel and in Figure 5.19 for the (2,2,3) channel, both channels exhibit lower momentum for the middle C. Same as the N₂O macular structure, OCS is also a nearly triatomic system. In both channels, the momentum of O has a smaller peak value than the S. Additionally, the (2,2,2) channel has a peak KER of 87eV, which is higher than the 116eV observed in the (2,2,3) channel.

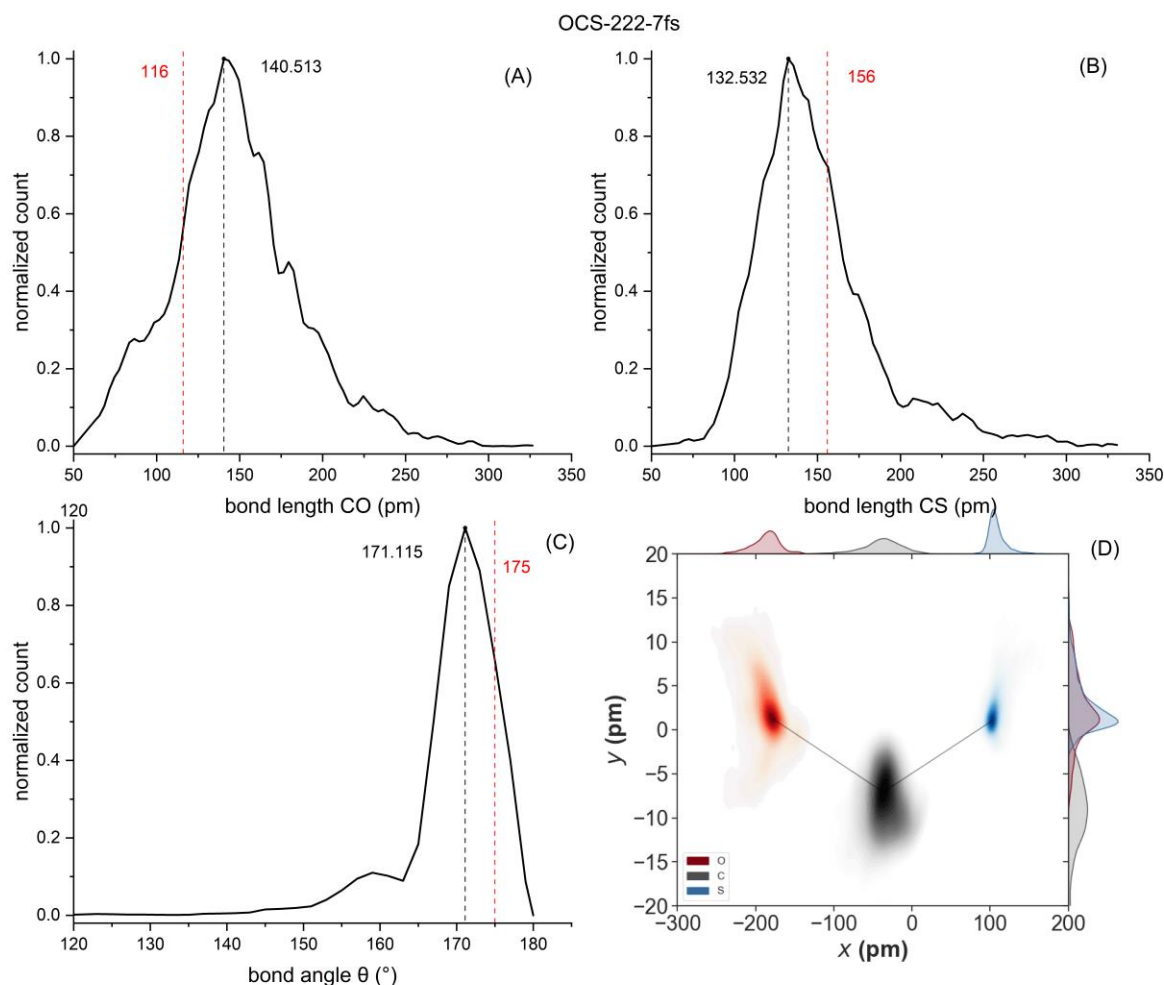


Figure 5.20: Bond lengths and bond angle distribution for OCS-222-7fs reconstruction results. (A) (B) and (C) are distributions for bonds R_{CO} , R_{CS} and bond angle θ . (D) Geometry distribution on a xy position plot.

For a total 5576 of events from the OCS-(2,2,2)-7fs channel, 4451(79.8%) are identified as non-degeneracy cases, 51(0.91%) as double-degeneracy cases, the rest are unsuccessful. The distributions take into account all possible geometries, where a unique solution is counted as 1 and a double solution counted as 0.5. As shown in Figure 5.20 (A, B&C), the most probable values for R_{CO} , R_{CS} and θ are 140.513pm, 132.532pm, 171.115° respectively. When compared to the equilibrium structure, the bonds R_{CO} has stretched by 21.13%, R_{CS} has been compressed 15.04% and the bond angle has been bent 2.22%. Figure 5.20 (D) displays the distribution of reconstructed structures in an xy-plot. And the average values of bonds R_{CO} , R_{CS} and bond angle are 147.58 pm, 151.28 pm and 169.51°.

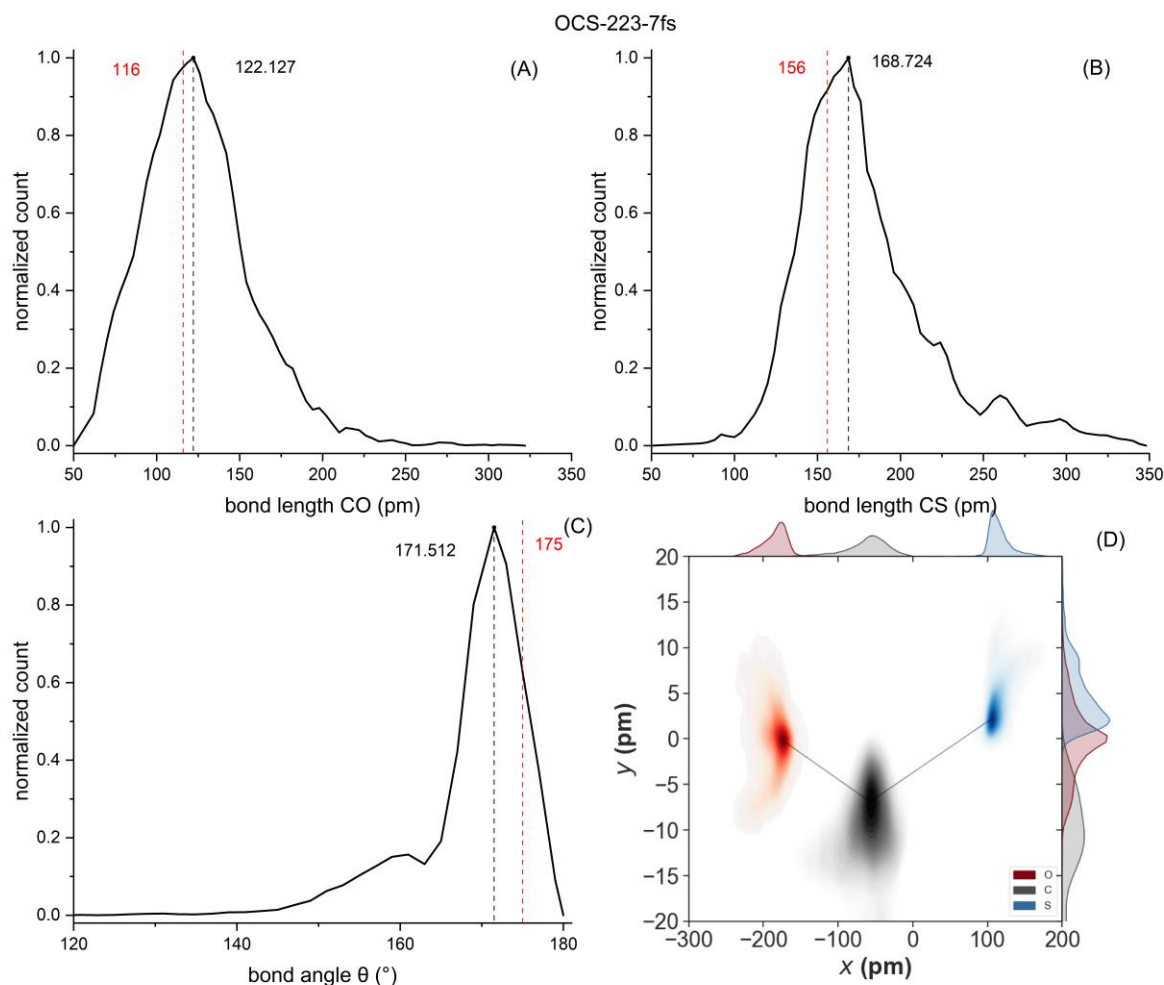


Figure 5.21: Bond lengths and bond angle distribution for OCS-223-7fs reconstruction results. (A) (B) and (C) are distributions for bonds R_{CO} , R_{CS} and bond angle θ . (D) Geometry distribution on a xy position plot.

For a total 6068 of events from the OCS-(2,2,3)-7fs channel, 4940 (81.41%) are identified as non-degeneracy cases, 17(0.28%) as double-degeneracy cases, the rest are unsuccessful. The distributions consider all possible geometries, where a unique solution is counted as 1 and a double solution counted as 0.5. As shown in Figure 5.21 (A, B&C), the most probable values for R_{CO} , R_{CS} and θ are 122.127 pm, 168.724 pm, 171.512° respectively. When compared to the equilibrium structure, the bonds R_{CO} has stretched by 5.28%, R_{CS} has been stretched 8.16% and the bond angle has been bent 2.00%. Figure 5.21 (D) displays the distribution of reconstructed structures in an xy-plot. And the average values of bonds R_{CO} , R_{CS} and bond angle are 124.51 pm, 180.18 pm and 168.32°.

5.3 Summary

This chapter begins by explaining the process of applying the optimization method to actual Coulomb explosion data. A crucial step in this process involves comparing the kinetic energy released to the Coulombic potential energy at equilibrium to assess the data's suitability for the Coulomb reconstruction model. The reconstruction results for data from N₂O-(222), N₂O-(221), OCS-(222), and OCS-(223) channels are reasonable in some respects. In most cases, they correspond to the bond stretching and angle bending, consistent with previous studies [55][66]. However, the resulting distributions of bond lengths are a little bit broad, which corresponds to the distribution of the kinetic energy released plot. In some cases, the KER is significantly high or low compared to the peak value leading to reconstructions showing highly compressed bond lengths. The presence of such a high degree of bond length compression is questionable. As discussed in the previous chapter, the Coulomb model simplifies the interaction between pulses and molecules. And when the value of kinetic energy released is close to the expected value, the energy might come from also the laser field or others. Therefore, further exploration will be required to address this question in the future.

Chapter 6 Summary and outlook

Having successfully assembled and tested the COLTRIMS, the next step is to conduct an actual experiment. We have selected H_2 and D_2 as target molecules [68], recognizing their important role in ultrafast molecular dynamics research. Their two-electron system allows for precise modeling and is suitable for experimental exploration. Additionally, with the addition of an extra neutron to its atoms, hydrogen exhibits a significant isotope effect. In our experiment, a distinguishing feature will be the application of a high repetition rate laser operating at 100 kHz and emitting at 2700 nm for 30fs, which utilizes a stabilized carrier envelope phase (CEP) [69] in the ALLS lab. We want to investigate the impact of manipulating the CEP of ultrafast laser pulses on the coherent control of molecular dynamics. The precise adjustment of CEP values offers the potential to influence and optimize specific quantum processes within molecules, enabling enhanced chemical reactions and electronic transitions in a controlled and coherent manner. Further, COLTRIMS will provide detailed analysis of electrons and ions, while our earlier studies focused only on ions. Insights from electron behaviors allow for correlating effects for individual molecules.

Regarding the COLTRIMS setup, the spectrometer was assembled with a shorter ion side of 4.65cm and an extended electron side of 27.5 cm. The detection of ions and electrons are affected by the spectrometer's dimensions, as well as the strength of the electric and magnetic fields. For experiments, adjusting electric and magnetic field is an essential step to ensure that most of the particles can be captured by detectors. Hence, predetermining the main research targets, understanding their interaction pathways, and predicting general released energy can help design a more reasonable spectrometer to meet the research requirements.

Regarding the geometry reconstruction, the reconstruction model can apply to the new experimental data from the UW-ALLS reaction microscope (COLTRIMS) and here are three main directions for further investigation. Firstly, while the classical Coulomb explosion model currently is limited to Coulomb explosion concerted process and has no consideration on electrons; therefore, a more precise model is needed. A semi-classical model that combines quantum interactions of laser fields with molecules and classical mechanics post-ionization could be developed. When the molecules interact with the laser field, they emit electrons and gain kinetic energies. This initial electron dynamics determine the initial conditions for the subsequent ion motion, which can be simulated. Once ionization occurs, the model transits to the classical mechanics as described in the classical model. Secondly, the determination of explosion time T can be improved. Currently, a fixed value derived from equilibrium structures is used for all data in one experiment. However, since T can vary depends on the initial

geometry. Modifying the algorithm to assign an independent T for each momentum would improve the precision of reconstruction results. Lastly, the exploration of larger molecule systems such as those with four or five atoms is also a direction for future investigation. Adapting the optimization method to experimental data from larger molecules is valuable for testing its efficiency.

Summary of Contributions

Approaches for Constraining Uncertainty and Degeneracy in Geometry Reconstruction of Molecules from Simulated Coulomb Explosion Data.

K Tian, A Ramadhan, M Nooijen, S Pantazi, R Karimi and J Sanderson.

Computer Physics Communications, vol. 297, 1 Apr. 2024, p. 109074,

Optimized geometry reconstruction on N_2O^{6+} 222 Coulomb explosion imaging data.

Kaili Tian, Reza Karimi, Samuel Beaulieu, Mathieu Giguère, Heide Ibrahim, François Légaré, Joseph H. Sanderson.

In process.

Waterloo/ ALLS Reaction Microscope Cold Target Recoil Ion Momentum Spectrometer Endstation.

K Tian, H Ibrahim, R Karimi, F Légaré, A Staudte and J Sanderson. 2023. *Journal of Physics: Conference Series*

Approaches for constraining uncertainty and degeneracy in geometry reconstruction of molecules from Coulomb Explosion Imaging data.

K Tian, A Ramadhan, M D Singh and J Sanderson. 2020. *Journal of Physics: Conference Series*. **1412** 13213.

One-Pot Synthesis of PEGylated MoSe_2 Nanomaterials with Limited Oxidation by Femtosecond Laser Ablation in Water.

Ye, Fan; Fruehwald, Holly; Tian, Kaili; Zandieh, Mohamad; Smith, Rodney; Sanderson, Joseph; Musselman, Kevin. *ACS Appl. Nano Mater.*

Geometrically reconstructing laser Coulomb-exploded molecules.

M D Singh, A Ramadhan, K Tian, J Sanderson, B Wales, R Karimi, S Beaulieu, W K Liu, J C Kieffer and F Légaré. 2020. *Journal of Physics: Conference Series*. **1412** 152084

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Appendices

A COLTRIMS instruction (Manual)

A.1 Vacuum system

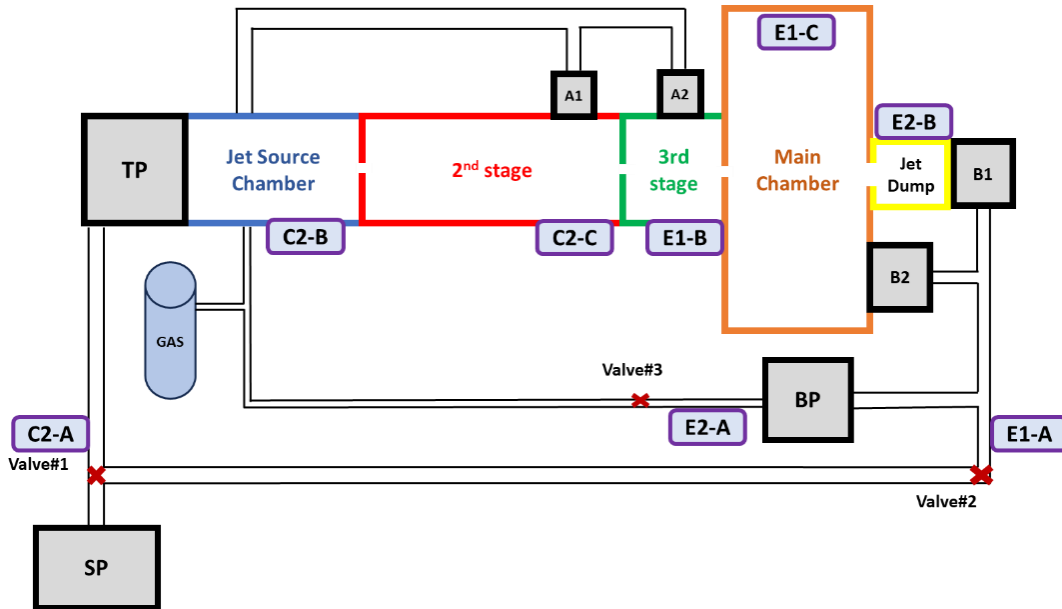


Figure A. 1: Vacuum system labeled with pressure measurement units. SP: scroll pump, TP: big turbo pump HiPace 1800, BP: back pump (EcoCube). A1, A2, B1, and B2 are small turbo pumps. The purple boxes represent pressure measurement components.



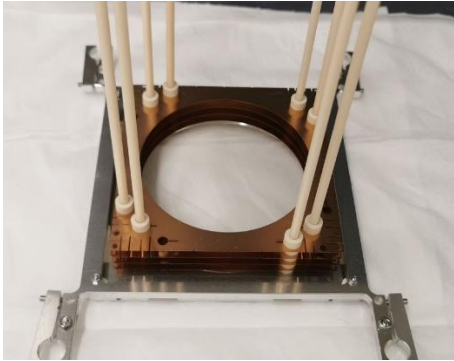
Figure A. 2: Picture of all DCU (display control unit) and VGC (vacuum gauge controller).

A.2 Assembly of spectrometer and detector including cables

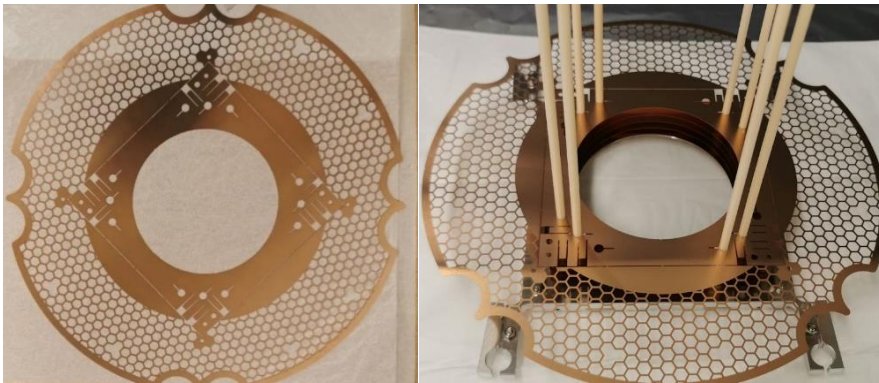
A.2.1 Assemble the spectrometer

- (1) Attach the mesh to the frame
- (2) Add 8 ceramic rods
- (3). Add copper electrodes.

Structure: 4 normal + cu-shield + 44 normal + 5 focus electrodes + 6 normal electrodes



- (4). Make sure the position of the hole and the electrodes.

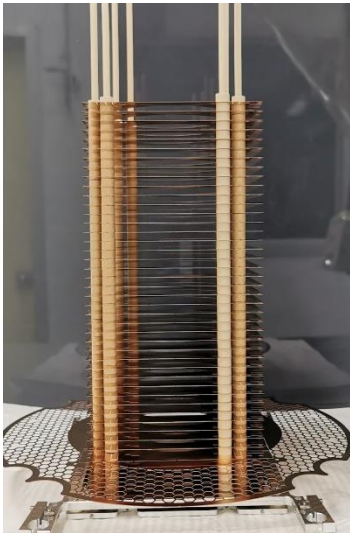


- (5). Focus region.

Add 5 special electrodes, start from 1 then 2, 3,4,5. To add them into the right position, need to check every hole with the normal electrodes.



- (6). Continue adding the normal copper electrodes.



(7). Add the other side with the frame and mesh.

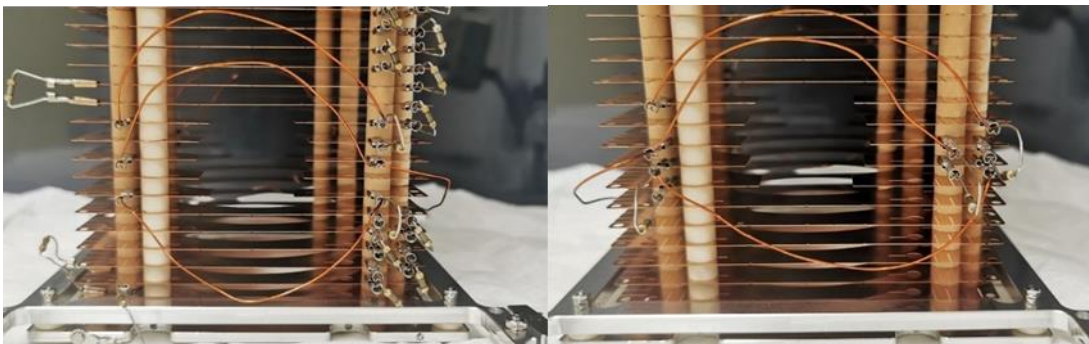
(8). Connect all copper electrodes with resistors.

(a). Connection between mesh and side electrode

Connecting the first electrode with the mesh is a little bit hard. We need to use the special resistor, bend it with a clamp. Connect the other side to the mesh with a screw. At the end, adjust the position to let the resistor chain away from the frame.



(b). Connection for focus region electrodes

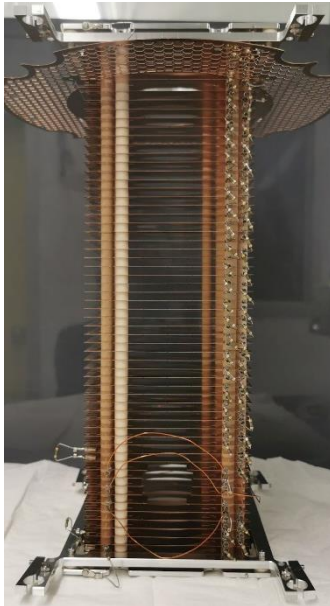


The focus region contains 5 special copper electrodes, since the copper wire cannot block the gas jet, 3 resistors are connected at one side, the other 2 are connected at the opposite side. So, give them enough space to avoid touching each other.

(c). Connection for normal region electrodes.



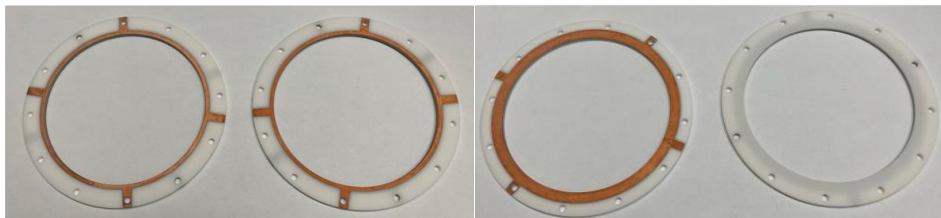
As shown in the pic, use a tweezer to bend into a 'U' shape, then twist it slightly. For other normal copper electrodes, just use the resistor to connect each one, then adjust the position at the end.



A.2.2 Assemble the MCP stack

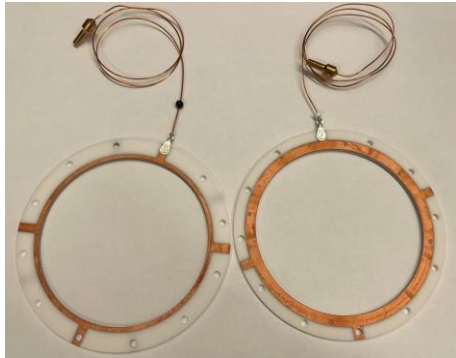
(1). Front ring and back ring

The front ceramic ring has copper on both sides, while the back ring only has copper on one side.



(2). Connect the cable for front ring and back ring.

The wire with black color is for the front ring, the white color is for the back ring. Check if the wire ends are tight enough.



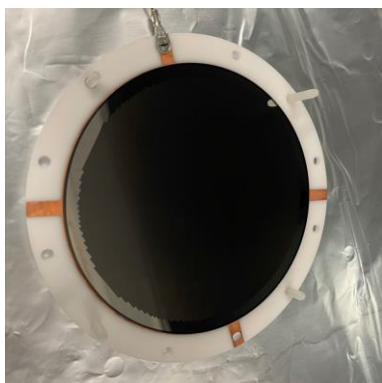
- (3). Insert four mounting screws on the front ceramic ring



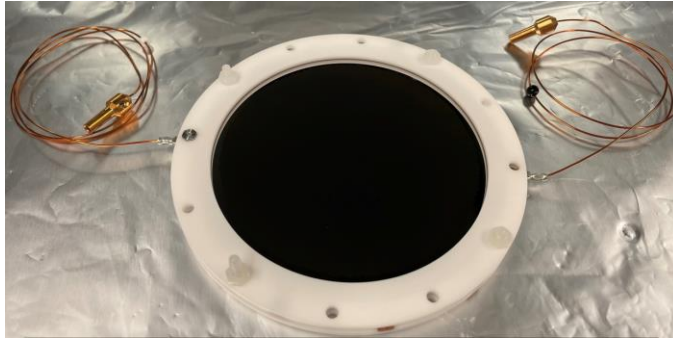
- (4). Find the front side of the MCP
The front side of the MCP has a 'V' shape at the edge.



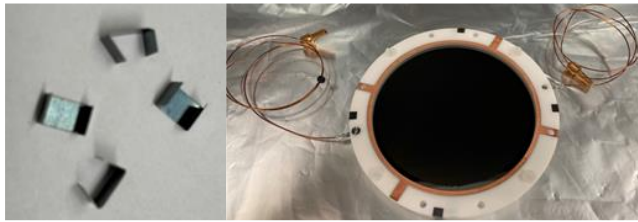
- (5). Put the two MCPs face down to the ring, mark o the outer rim of the pore. The pores of MCP should be in opposite direction. Blow by dry air for each MCP.



- (6). Put the back ring.
(7). Fix the stack by nuts, not to tight.



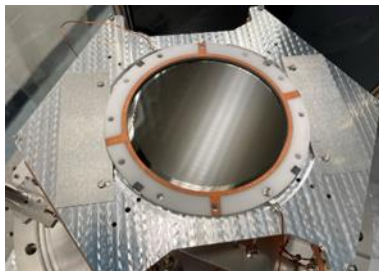
(8). Put the 4 spring clamps, one close to the cable of the back ring.



(9). Remove the nuts and screws.

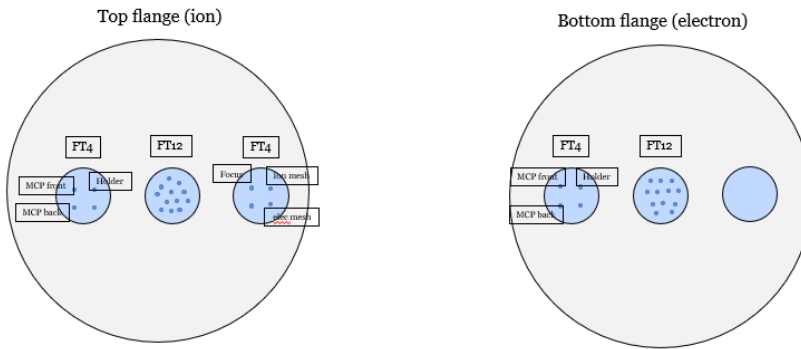


(10). Mount the MCP stack on the plate. Put the cable side of the back ring at the diagonal of the plate. Adjust the position of those 4 clamps, make sure none of them touch the plate, otherwise cause shortage.

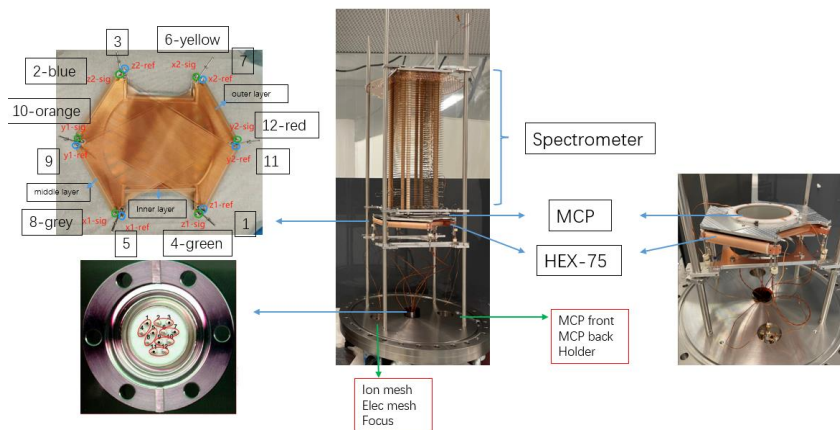


(11). use Ω meter check resistance between MCP back and front should be around $40M\Omega$.

A.2.3 Cable connection inside the chamber



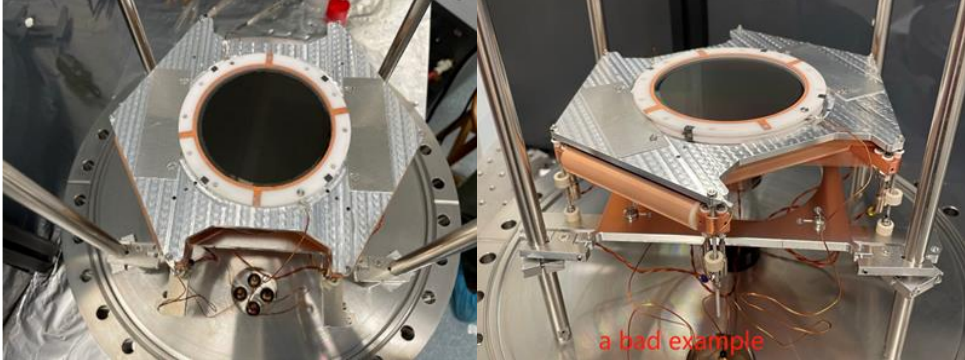
- (1) Top flange
 - a. 12-pin cable
 - b. Back ring cable
 - c. Front ring cable
 - d. Holder connection
- (2) Bottom flange
 - a. 12-pin cable
 - b. Back ring cable
 - c. Front ring cable
 - d. Holder cable
 - e. Top mesh & bottom mesh cable
 - f. Focus cable
- (3)



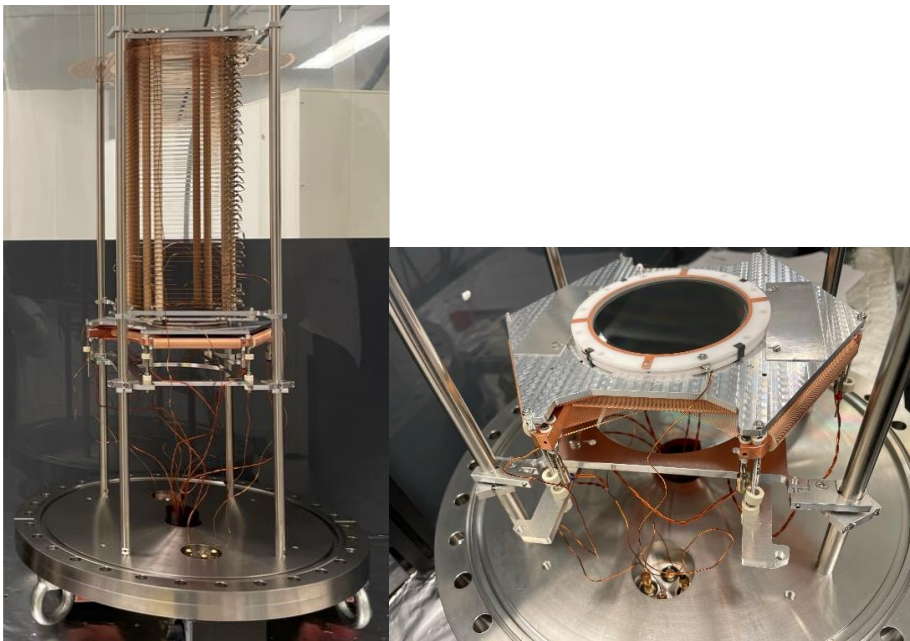
A.2.4 Mount the spectrometer and delay line detector

(1). Measure the position of the jet hat and center of the mirror window and record the height for each element. Set the center of the spectrometer to align with the center of the mirror window, then calculate the position of the delay line detectors. The distance from the surface of the MCP stack to the mesh should be maintained 3mm to 6mm.

(2). Mount the bottom delay line detector carefully. When attaching the holder frame to the delay line detector, select the symmetric 4 screws to ensure proper alignment. This precaution is necessary to prevent the jet hat from damaging the delay line detector when the flanges are reinstalled onto the chamber.

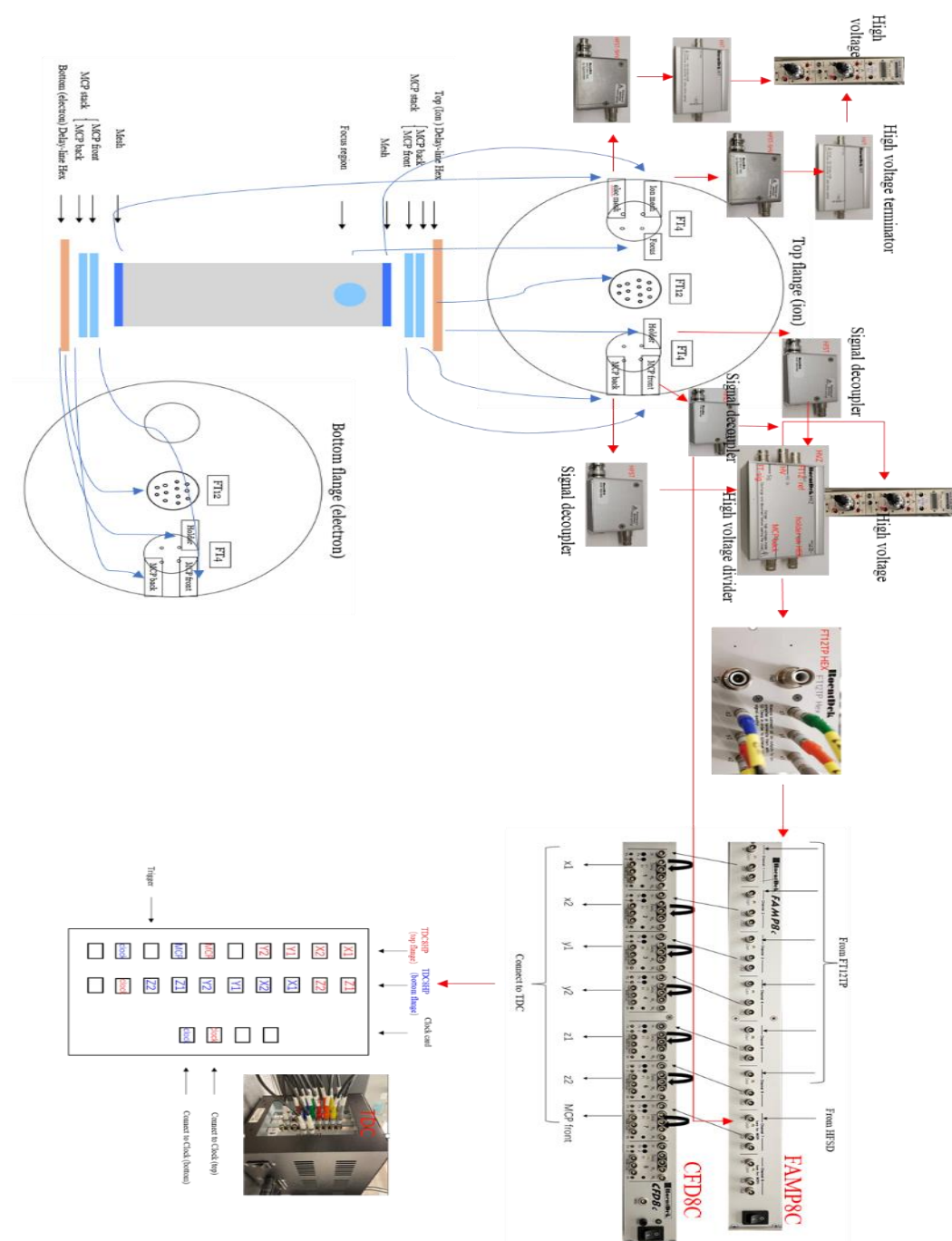


(3). Ready for put the flanges back to chamber



A.3 Cable connections for signal and high voltage

Cable connections for signal and high voltages.



A.4 Check list

Use an ohmmeter to check the continuity for all cables, and make sure no unexpected connections.

- (1) check the two ends of each wire, should be short
- (2) no shorts between any cable ends and the flange (body)
- (3) for the delay line detector, has the following resistance.

Pin number	1	2	3	4	5	6	7	8	9	10	11	12
position	Z1-ref	Z2-sig	Z2-ref	Z1-sig	X1-ref	X2-sig	X2-ref	X1-sig	Y1-ref	Y1-sig	Y2-ref	Y2-sig
color		blue		green		yellow		grey		orange		red

- a. 1&3, 2&4, 5&7, 6&8, 9&11, 10&12 should has some resistance 10-40 Ω , others have infinity resistance
- b. When connecting 12 cables, check again by ends, to make sure no mistake causing unexpected shorts or connection
- (4) The resistance between two meshes in our case is around 61*100k Ω .
- (5) The resistance between MCP front and back is around 40M Ω , (38M Ω for the top, 40M Ω for the bottom.)
- (6) Table list

Table 1: check the ends of each cable, also with flange.

Top	1	2	3	4	5	6	7	8	9	10	11	12
Ends												
Ground												
Bottom	1	2	3	4	5	6	7	8	9	10	11	12
Ends												
Ground												

Table 2: check the ends of each cable, also with the flange.

Top	MCP front	MCP back	holder	Ion mesh	Elec mesh
Ends					
Ground					
Bottom	MCP front	MCP back	holder		
Ends					
Ground					

Table 3: check the resistance of the delay line through the FT12 for both top and bottom.

Top FT12	1	2	3	4	5	6	7	8	9	10	11	12
1												
2												
3												

4												
5												
6												
7												
8												
9												
10												
11												
12												

Bot FT12	1	2	3	4	5	6	7	8	9	10	11	12
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												

	MCP front and back (ion)	MCP front and back (elec)	Two meshes	
Resistance				

A.5 Procedures of vacuum, baking and running experiments

A.5.1 start the vacuum system

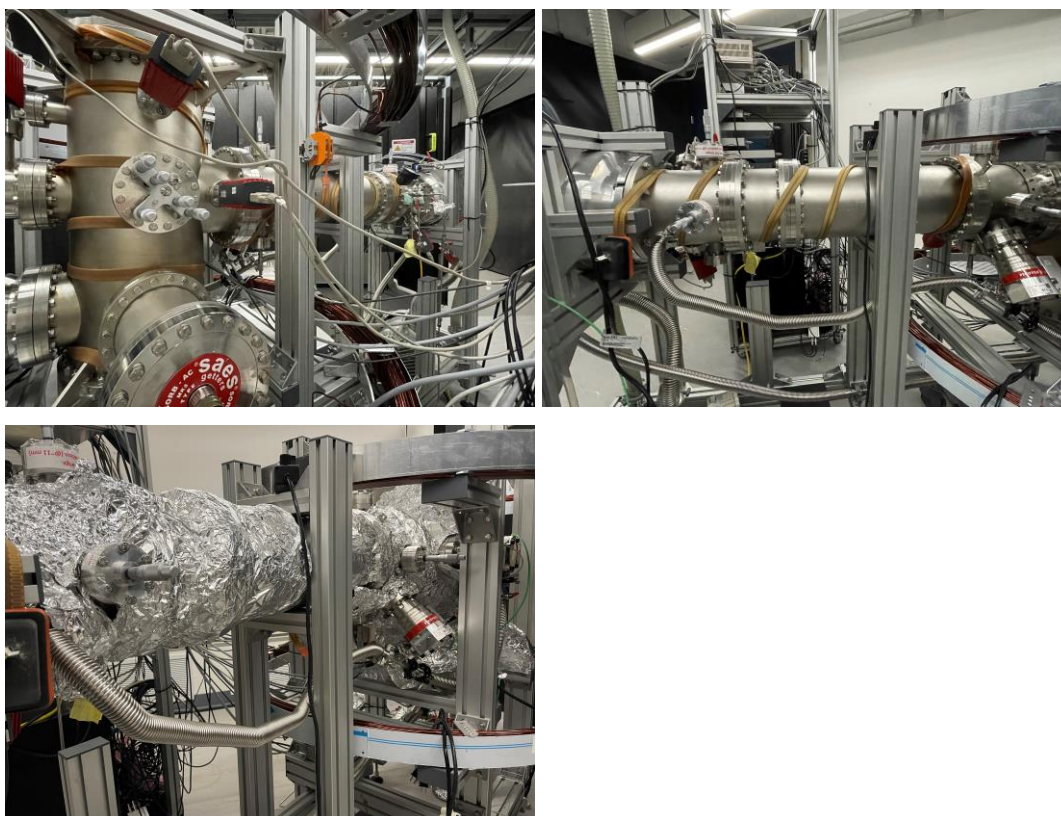
- (1) Verify that all vacuum gauges are correctly connected, ensure the cooling system is operational, and enable the power of the power control box.
- (2) Open valve No.2 and valve No.3
- (4) Close valve No.1 and start the scroll pump. There may be a 30s loud sound from the scroll pump. Then open valve No.1 after 1 min.
- (5) While pumping down, monitor the pressure gauges throughout the system to ensure they all show roughly the same pressure.
- (6) Close both No.1 and No.3 valves. If the pressure does not increase slowly, indicating a leak, it needs to be double-checked. If everything is in order, open both No.1 and No.3 valves and start EcoCube.

- (7) Check the pressure; if it is lower than $1\text{E-}1$ mbar and then start all the turbo pumps. The pressure in the main chamber should be around $1\text{E-}6$ mbar within several hours.
- (8) set the system into 'standby-mode': close No.1 and turn off the scroll pump. Then can start baking as shown in Appendix A.5.2.

A.5.2 Shut down the vacuum system

- (1) open valve No.2, close valve No.1
- (2) open scroll pump, open valve No.1
- (2) turn off 5 small pumps
- (3) send N₂ into the source chamber, within 0.5 bar
- (4) turn off big turbo pump, close valve No.1, turn off scroll pump
- (5) turn off EcoCube, close valve No.3

A.5.3 Baking



- (1) before baking, make sure the gas line is clean up.
- (2) warp the heater bands as indicated in the figures.
- (3) warp foil as indicated in the figures.
- (4) insert thermometer
- (5) set to 80°C , set heater to 3A
- (6) check temperature and pressure in the next 3 hours
- (7) after two days, increase heat band to 120°C , heater to 7A
- (8) after 6 days, decrease temperature to 80°C ,

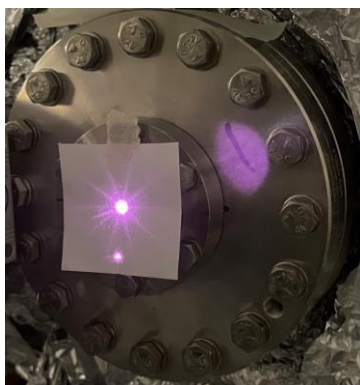
- (9) after 7 days, turn off heaters, let it cool down for 24 hours
- (9) check pressure in next 7 days

A.5.4 Running experiments

- (1) check the pressure is ok, open scroll pump and valve No.1
- (2) send gas into the chamber, check the pressure if ok and align the jet
- (3) align the laser perpendicular to the window
- (4) turn off ion gauges, then apply high voltages
- (5) adjust mirror to find the jet

A.6 Laser alignment

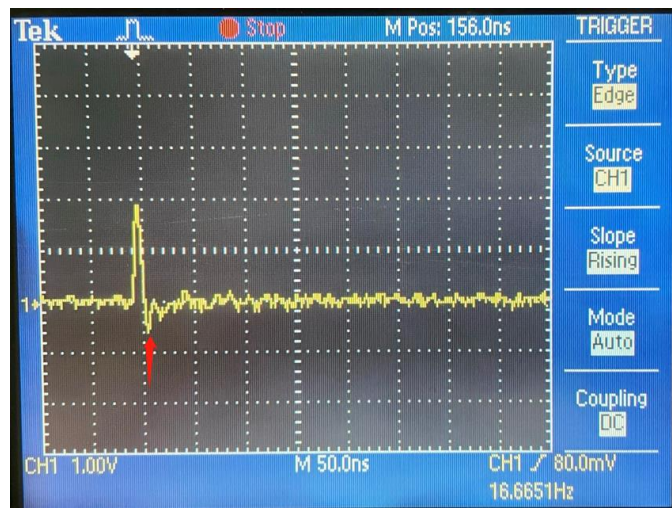
- (1) With ion gauges in operating and the 4-jaw slit fully open, introduce the target gas at around 1 bar. Adjust the xy-position micrometer screws to optimize the nozzle's position slightly. Monitor the pressure that in the jet source chamber, the second stage and the third stage.
- (2) Examine the focusing mirror through the window and ensure it is facing the window directly without a significant angle.
- (3) Run the laser and align the incident beam to be perpendicular to the center of the window by adjusting mirrors on optical bench. Check if the reflected beam from the window aligns with the incident beam.
- (4) Adjust the mirror in the x and y direction to ensure that the reflected beam from focusing mirror can go back to the center of the window. A piece of paper with a 1mm pinhole on it can help with the adjustment of focusing mirror.
- (5) Turn off all ion gauges, apply voltages to the detectors. Adjust the mirror to scan the z direction to find the jet. This step involves observing the xy-image in the software. Look for a dense, tiny spot near the center of the xy-image to confirm that the jet has been found.



An example of reflection from mirror is away from the incident beam.

A.7 check MCP signal

- Remove the output lemo cable from FAMP channel 7, then connect it to the oscilloscope.
- Apply the ion mode high voltages to the detector, increasing voltage gradually. (MCP front is -2400 V and holder is 300V.)
- A signal can be detected when the voltage of MCP front is around -1900V. when reach to -2400V, can get a signal as shown in the **Error! Reference source not found..**
- Adjust the signal decoupler to minimize the second peck (red arrow)

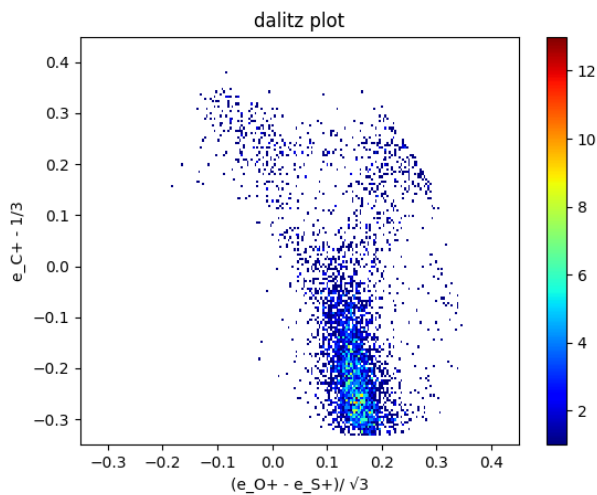


Signal from MCP front.

B Basic analysis plots code

B.1 Dalitz plot

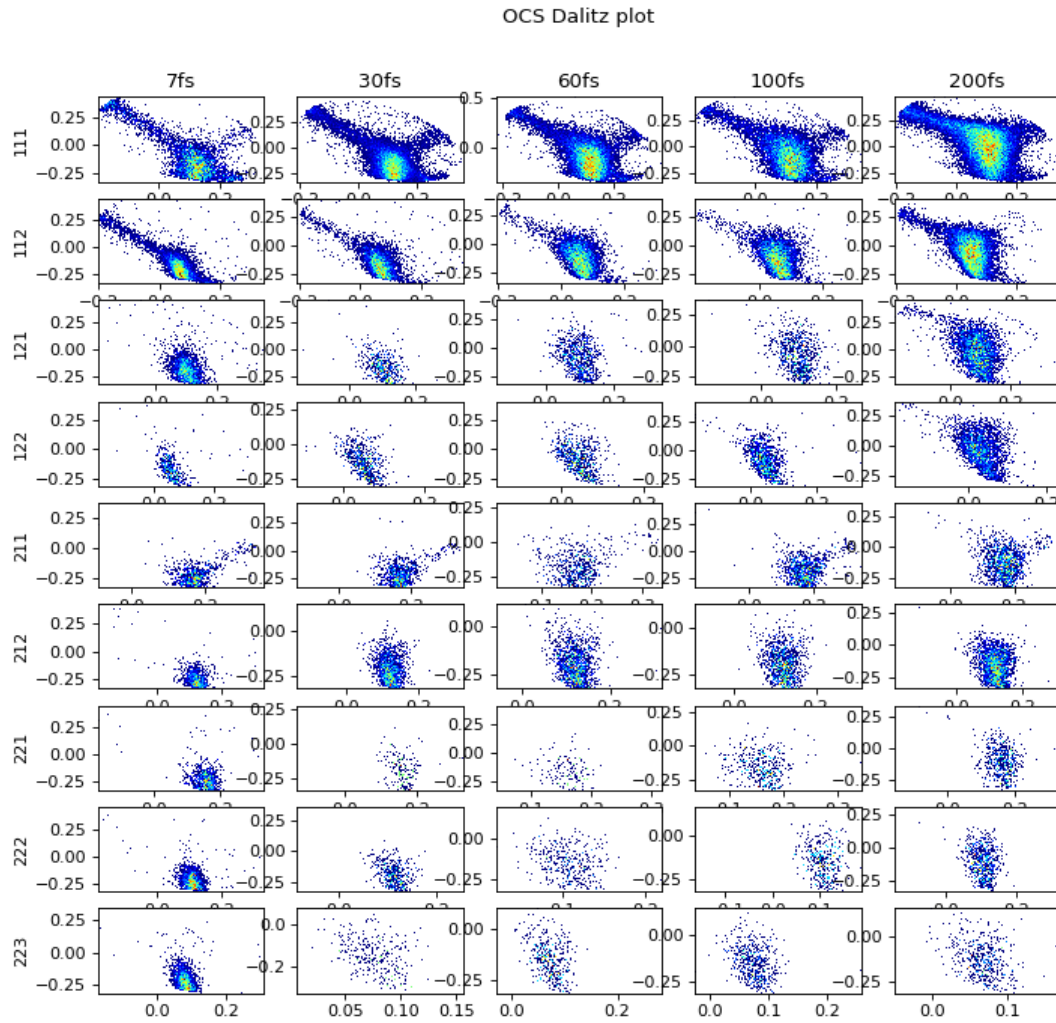
Code: Dalitz plot for OCS-111 channel 7fs



```

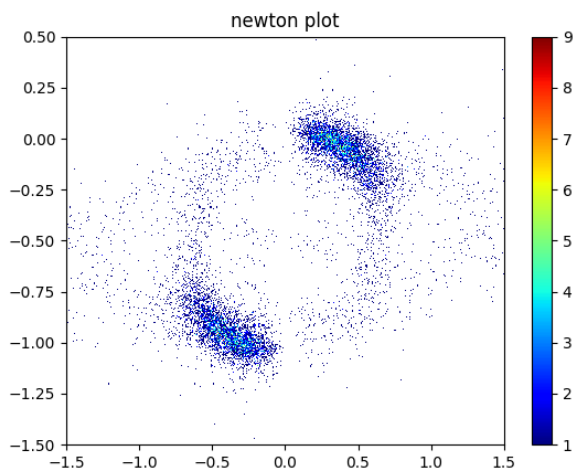
1 import matplotlib.pyplot as plt
2 import numpy as np
3
4 O = 16 * (1.66e-27)
5 C = 12 * (1.66e-27)
6 S = 32 * (1.66e-27)
7
8 data = np.loadtxt("E:111_007.txt")
9 # fraction number calculation
10 data2 = []
11 for p in data:
12     Eo = (p[0] * p[0] + p[1] * p[1] + p[2] * p[2]) / O / 2
13     Ec = (p[3] * p[3] + p[4] * p[4] + p[5] * p[5]) / C / 2
14     Es = (p[6] * p[6] + p[7] * p[7] + p[8] * p[8]) / S / 2
15     eoFr = Eo / (Eo + Ec + Es)
16     ecFr = Ec / (Eo + Ec + Es)
17     esFr = Es / (Eo + Ec + Es)
18     data2.append([ecFr, eoFr, esFr])
19 # set up x,y values
20 x = []
21 y = []
22 for e in data2:
23     x1 = (e[1] - e[2]) / (3 ** 0.5)
24     y1 = e[0] - 1 / 3
25     x.append(x1)
26     y.append(y1)
27 # plot
28 plt.figure()
29 plt.hist2d(x, y, 150, cmin=1, cmap='jet')
30 plt.colorbar()
31 plt.title('dalitz plot')
32 plt.xlabel('(e_0+ - e_S+)/ v3')
33 plt.ylabel('e_C+ - 1/3')
34 plt.ylim(-0.35, 0.45)
35 plt.xlim(-0.35, 0.45)
36 plt.show()

```



B.2 Newton plot

Code: Newton plot for OCS-111 channel 7fs



```

1 import matplotlib.pyplot as plt
2 import numpy as np
3 import math
4 import numpy.linalg as la
5
6 data = np.loadtxt("E:111_007.txt")
7 px1 = []
8 py1 = []
9 au = 1.9928e-24
10 for [x1, y1, z1, x2, y2, z2, x3, y3, z3] in data:
11     one00 = np.array([x1 / au, y1 / au, z1 / au])
12     one0C = np.array([x2 / au, y2 / au, z2 / au])
13     one0S = np.array([x3 / au, y3 / au, z3 / au])
14     nor00 = la.norm(one00, 2)
15     nor0C = la.norm(one0C, 2)
16     nor0S = la.norm(one0S, 2)
17     # 0 as reference
18     cosAng00_0C = (one0C.dot(one00)) / nor00 / nor0C
19     cosAng00_0S = (one0S.dot(one00)) / nor00 / nor0S
20     ang00_0C = math.acos(cosAng00_0C)
21     ang00_0S = math.acos(cosAng00_0S)
22     x0C = abs(nor0C * math.sin(ang00_0C)) / nor00
23     y0C = nor0C * cosAng00_0C / nor00
24     x0S = -abs(nor0S * math.sin(ang00_0S)) / nor00
25     y0S = nor0S * cosAng00_0S / nor00
26     px1.append(x0C)
27     py1.append(y0C)
28     px1.append(x0S)
29     py1.append(y0S)
30 plt.figure()
31 plt.title('newton plot')
32 plt.hist2d(px1, py1, 800, cmin=1, cmap='jet')
33 plt.colorbar()
34 plt.ylim(-1.5, 0.5)
35 plt.xlim(-1.5, 1.5)
36 plt.show()
37

```

C Potential surface

C.1 Optimized geometry of ground state in Orca:

Given that the entire Coulomb Explosion Imaging (CEI) process initiates from the ground state geometry, it is crucial to have precise knowledge of this initial geometry. Therefore, in the subsequent calculations, the determination of the ranges for R_{co} , R_{cs} , and θ must take this initial geometry into consideration.

Input:

```

1 !B3LYP def2-SVP Opt
2
3 * int 0 1
4 O 0 0 0 0.000 0.000 0.000
5 C 1 0 0 1.000 0.000 0.000
6 S 2 1 0 2.000 179.0 0.000
7 *

```

Output:

```

3009 -----
3010 INTERNAL COORDINATES (ANGSTROEM)
3011 -----
3012 O      0      0      0      0.000000      0.000      0.000
3013 C      1      0      0      1.160625      0.000      0.000
3014 S      2      1      0      1.569875      179.996      0.000
3015

```

C.2 CASSCF calculation in ORCA:

To obtain potential surfaces, CASSCF calculations are performed in ORCA, selecting Rco ranging from 1.0 Å to 2.1 Å, and Rcs from 1.1 Å to 2.5 Å. Once calculations for each geometry are complete, the CASSCF energies can be extracted.

For instance, in a CASSCF calculation for OCS^{2+} involving 9 orbitals, the parameters 'mult' and 'nroots' need to be determined. This requires multiple analyses of the output file to ascertain the appropriate values for these parameters. The primary objective is to identify the lowest energy state, thereby obtaining the ground-state potential energy surfaces.

Input:

```

1  !CASSCF cc-pvdz
2
3  * int 2 1
4  O      0      0      0      0.000000      0.000      0.000
5  C      1      0      0      1.300000      0.000      0.000
6  S      2      1      0      1.900000      180.0      0.000
7  *
8
9  %casscf
10 nel      8
11 norb     9
12 mult     3, 1
13 nroots   1, 3
14 end

```

Output:

```

6968 -----
6969 CASSCF RESULTS
6970 -----
6971
6972 Final CASSCF energy          : -509.292082993 Eh  -13858.5421 eV
6973
6974 -----
6975 ORBITAL ENERGIES
6976 -----
6977
6978 NO      OCC      E (Eh)      E (eV)
6979  0      2.0000    -92.741938    -2523.6364
6980  1      2.0000    -21.301087    -579.6320
6981  2      2.0000    -11.986240    -326.1622
6982  3      2.0000     -9.726405    -264.6689
6983  4      2.0000     -7.403502    -201.4595
6984  5      2.0000     -7.401941    -201.4171
6985  6      2.0000     -7.401941    -201.4171
6986  7      2.0000     -1.948372     -53.0179
6987  8      2.0000     -1.545355     -42.0513
6988  9      2.0000     -1.235499     -33.6196
6989 10      1.9627     -1.359001     -36.9803
6990 11      1.8748     -1.087449     -29.5910
6991 12      1.8748     -1.087447     -29.5909
6992 13      1.0073     -0.842886     -22.9361
6993 14      1.0073     -0.842885     -22.9361
6994 15      0.1192     -0.410911     -11.1815
6995 16      0.1192     -0.410906     -11.1813
6996 17      0.0332     -0.395643     -10.7660
6997 18      0.0016      0.374684      10.1957
6998 19      0.0000      0.027808       0.7567
6999 20      0.0000      0.085396       2.3237
7000 21      0.0000      0.093075       2.5327

7106 -----
7107 SA-CASSCF TRANSITION ENERGIES
7108 -----
7109
7110 LOWEST ROOT (ROOT 0 ,MULT 3) =  -509.327938595 Eh -13859.518 eV
7111
7112 STATE    ROOT  MULT  DE/a.u.    DE/eV    DE/cm**--1
7113  1:       0      1    0.054950    1.495    12060.1
7114  2:       1      1    0.054950    1.495    12060.1
7115  3:       2      1    0.105234    2.864    23096.2
7116

```

C.3 CASSCF and MRCI calculation in Molpro:

In Molpro, calculations require manual setting of additional parameters. At this stage, a comparison between two basis sets, cc-pvdz and cc-pvtz, is carried out. The cc-pvtz basis set is preferred over cc-pvdz because it yields lower energy results, indicating a more accurate approximation of the system.

An example of this process is the CASSCF and MRCI calculations for OCS^{3+} with 9 orbitals.

Input:

```
1  *** , OCS
2  symmetry, Z;
3  geometry={ANGSTROM;
4           O;
5           C,O,RCO(ind);
6           S,C,RCS(ind),O,Theta(ind)}
7
8  basis=cc-pvtz
9
10 RCOArray=[1.15];
11 RCSArray=[1.56];
12 ThetaArray=[179];
13
14 ind=0
15 do k=1,#ThetaArray
16   do j=1,#RCSArray
17     do i=1,#RCOArray
18       ind=ind+1
19
20       RCO(ind)=RCOArray(i)
21       RCS(ind)=RCSArray(j)
22       Theta(ind)=ThetaArray(k);
23
24       {rhf
25        WF,28,sym=2,spin=2;
26       }
27       escf(ind)=energy
28
29       {casscf;
30        OCC,15,4;
31        CLOSED,9,1;
32        WF,27,sym=2,spin=1,state,1;
33       }
34       ecasscf(ind)=energy
35
36       {mrci;
37        OCC,15,4;
38        CLOSED, 9, 1;
39        CORE, 6, 1;
40        WF,27,sym=2,spin=1;
41        }emrci_d(ind)=energd0(1)
42
43     enddo
44   enddo
45 enddo
```

The wavefunction parameters selected for the RHF (Restricted Hartree-Fock) calculation are determined to be (28, 2, 2). This configuration yields a much lower energy compared to (27, 2, 2), which makes it a preferable choice. Since the RHF calculation provides a preliminary estimate that serves as a starting point for subsequent CASSCF (Complete Active Space Self-Consistent Field) calculations, opting for 28 electrons in the RHF model is reasonable.

C.4 Results from ORCA of OCS^{2+} and OCS^{3+}

Finally, the potential energy surfaces (PES) for the ground state are obtained. Presented here are the PES for OCS^{2+} and OCS^{3+} at bond angles of 175° and 100° .

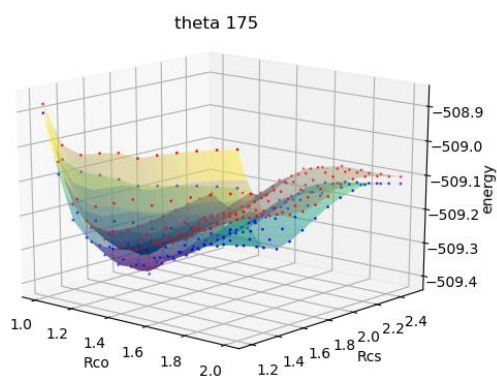


Fig3: Potential energy surface for OCS^{2+} , 175° , $R_{\text{co}} = [1 \text{ \AA}, 2.1 \text{ \AA}]$, $R_{\text{cs}} = [1.1 \text{ \AA}, 2.5 \text{ \AA}]$, low-lying triplet and low-lying singlet, the low-lying triplet is lower.

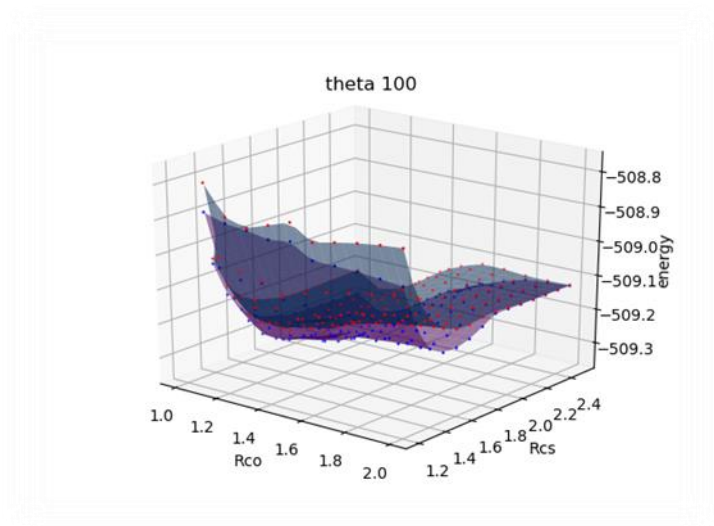


Fig4: Potential energy surface of OCS^{2+} , 100° , $R_{\text{co}} = [1 \text{ \AA}, 2.1 \text{ \AA}]$, $R_{\text{cs}} = [1.1 \text{ \AA}, 2.5 \text{ \AA}]$, for low-lying triplet and low-lying singlet, the low-lying triplet is lower.

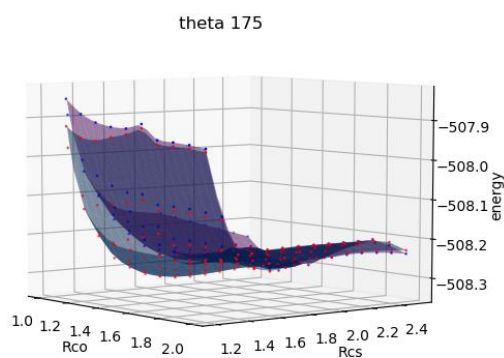


Fig5: Potential energy surface of OCS^{3+} , 175° , $R_{\text{co}} = [1 \text{ \AA}, 2.1 \text{ \AA}]$, $R_{\text{cs}} = [1.1 \text{ \AA}, 2.5 \text{ \AA}]$, for low-lying doublet and low-lying quadruplet, the low-lying doublet is lower.

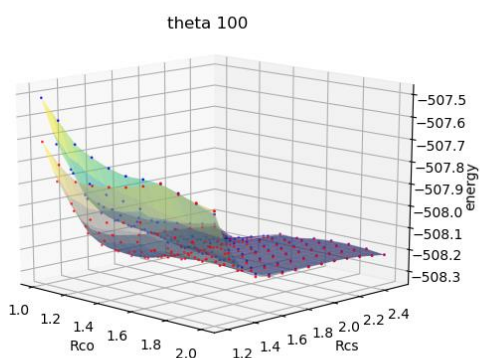


Fig6: Potential energy surface of OCS^{3+} , 100° , $R_{\text{co}} = [1 \text{ \AA}, 2.1 \text{ \AA}]$, $R_{\text{cs}} = [1.1 \text{ \AA}, 2.5 \text{ \AA}]$, for low-lying doublet and low-lying quadruplet, the low-lying doublet is lower.

3.3 Results from MOLPRO of OCS^{2+} and OCS^{3+}

In the MOLPRO, only ask the low-lying doublet PES for OCS^{3+} , and low-lying triplet PES for OCS^{2+} . Which is corresponding to the results from ORCA.

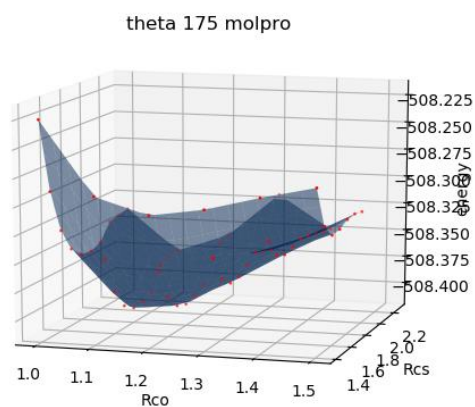


Fig7: Potential energy surface of OCS^{3+} , 175° , $R_{\text{co}} = [1.0 \text{ \AA}, 1.9 \text{ \AA}]$, $R_{\text{cs}} = [1.4 \text{ \AA}, 2.3 \text{ \AA}]$, for low-lying doublet.

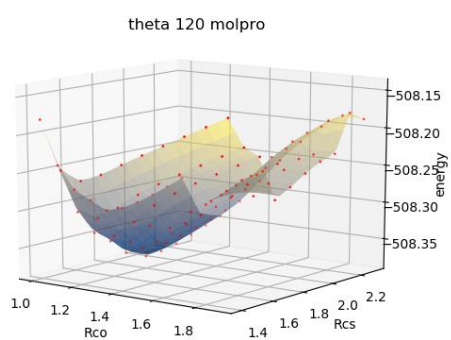


Fig8: Potential energy surface of OCS^{3+} , 120° , $R_{\text{co}} = [1.0 \text{ \AA}, 1.9 \text{ \AA}]$, $R_{\text{cs}} = [1.4 \text{ \AA}, 2.3 \text{ \AA}]$, for low-lying doublet.