A New Three-Dimensional (3d) Particle Coincidence Imaging System And Its Applications In Strong Field Studies Of Reaction Dynamics In Atoms And Molecules

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A NEW THREE-DIMENSIONAL (3D) PARTICLE COINCIDENCE IMAGING SYSTEM AND ITS APPLICATIONS IN STRONG FIELD STUDIES OF REACTION DYNAMICS IN ATOMS AND MOLECULES

by

YUNFEI LIN

DISSERTATION

Submitted to the Graduate School
of Wayne State University,
Detroit, Michigan
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

2017

MAJOR: CHEMISTRY (Physical)

Approved By:

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Advisor Date

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DEDICATION

This work is dedicated to my parents for their unconditional support and love. I couldn’t imagine the sacrifice you have made all these years.

I also want to dedicate this to my grandfather. The happy memory will always be in my heart.
ACKNOWLEDGEMENTS

It has been a great experience in Professor Wen Li’s group at chemistry department of Wayne State University. During my six years of life here at United States, I have received tremendous help and support from many people. I would like to take this opportunity to express my sincere gratitude.

First and foremost, I want to acknowledge Dr. Wen Li’s tremendous support throughout the whole career of my graduate school. I can definitely say that I have become an improved person under his guidance. I could not image what it would be like if not for his support during personal hardship in my first and third year of graduate school. No word can express my deepest gratitude for his help in times of personal difficulties. I have learned in first hand his work ethic since I first joined his group. He has not only showed us his ability to conceive innovative scientific idea but also his persistence to implement these new ideas. When ran into bottleneck of our research, he demonstrated his swiftness in moving our research forward. He has also been a great mentor for his students. I have received unbelievable help from him in my research study. When I have questions, he always showed his patience and answered with clarity. When I reached difficulties in my research, he has always been very helpful, not only solving the problems but also making sure I learned something during the process. It is really fortunate of me to be a member of his group.

I own great debt to our three postdocs: Dr. Cunshun Huang, Dr. Qingbin Zhang and Dr. Suk Kyoung Lee, Dr. Huang’s expertise in vacuum chamber has made our research possible. Dr. Zhang’s expertise in ultrafast phenomena has been conspicuous. He has helped me a great deal whenever I had questions for him. Dr. Lee has always
been a major contributor in our research. Her expertise in LabVIEW program has been integral in our development of the new 3D particle imaging system. Her knowledge in atomic orbital alignment was crucial in our development of the new method to probe orbital alignment.

It’s been a great pleasure to work with other members of Li group. Dr. Thusani Herath, Alex, Pradip, Lin, Gihan and Duke, I want to thank you all for your help. My graduate school life has been more interesting with your presence. I also had the opportunities to work with several members of Suits group: Dr. Lu Yan, Steven and Chaya. I am very honored to work with you guys. Without your help, my research won’t be possible.

I also want to thank my dissertation committee members, Professor Vladimir Chernyak, Professor Mary Rodgers, Professor Erhard Rothe and former committee member Professor Arthur Suits. You have dedicated your time to help me and give me valuable guidance, which I greatly appreciate.

I also received tremendous help from many staffs of chemistry department. Melissa has helped me a great deal during the process of graduate school, from our orientation to the final steps of finishing my dissertation. Debbie, Diane, Nester and Kellie, thank you all for your support.

During these years, I have shared apartment with several graduate students from other departments of Wayne State University. I want to thank them all for the time we spent together and the help I received from them.

At last, I want to thank my parents back home. I haven’t been quite a son in traditional sense since I haven’t spent time with them for a long time. Yet, they have
always been loving me no matter the circumstances. Without their unconditional love and support, I wouldn’t become the person I am now. My brother has been taking care of my parents, relieving much of my duty, for which I am really grateful. I also want to express my gratitude to my relatives for their support and guidance.
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CHAPTER 1 INTRODUCTION

1.1 Time scale of electron dynamics in atoms and molecules

In 20th century, human’s understanding of electrons facilitated many scientific and technological inventions and applications. In 21st century, it’s expected that our knowledge of electrons will continue to improve so that more inventions and applications can be made to advance the society. Right now, what we still don’t understand about electron is its motion on the atomic scale.\(^1\)

The time scale of any dynamics in microcosm is inversely proportional to the spacing between energy levels:

\[
T = \frac{2\pi \hbar}{\Delta W},
\]

where \(\hbar\) is reduced Planck constant and \(\Delta W\) is the energy spacing between two quantum states. For example, the energy spacing of molecular vibrational states is in milli-eV range, which means that the time scale of molecular vibrational motion is on femtosecond scale. The invention of femtosecond (\(10^{-15}\) second) duration laser pulse has enabled the study of nuclear motion in atomic scale—femtochemistry.\(^2\) But the energy spacing of electrons in molecules and atoms ranges from less than 1 eV to tens of eV. This translates to the fact that the time scale of electron dynamics in atoms and molecules is in the attosecond (\(10^{-18}\) second) level.

To study this type of electron dynamics in attosecond time scale, we obviously would like to have laser pulses that have duration of attoseconds. Using femtosecond intense laser field, high harmonic generation (HHG)\(^3-5\) method can
produce attosecond extreme-ultraviolet (XUV) pulses. The shortest attosecond pulse achieved is about 67 attoseconds. The challenge this method faces right now is how to increase the intensity of the attosecond pulses. Nevertheless, high harmonic generation is currently the only established method to make attosecond pulses and it’s developing rapidly. Another approach is to use intense, controlled few-cycles pulse whose electromagnetic field consists of only a few cycle of oscillation. Both attosecond pulses and few-cycle pulses are made by the femtosecond laser beam coming out of Table-top Ti:sapphire laser system. The Ti:sapphire solid state laser system produces laser pulses with center wavelength of 800 nm, so the duration of single laser cycle is 2.6 femtosecond. If the Carrier Envelope Phase (CEP) of the few-cycle (typically two or three) 800 nm pulse is controlled, its interaction with atoms or molecules can be understood in attosecond time scale. The third approach is using another electron in the same atom or molecule for obvious reasons. All these tools will involve ionization of atoms and molecules in intense laser field.

1.2 Ultrafast Ti:sapphire laser system

The laser has been one of the most important inventions in the 20th century. Since the first laser was made in 1960, its development has been dramatic. The gain medium adopted includes almost all forms of matters: gas, liquid, solid and plasma. The duration of the pulsed laser has been reducing and the energy of the laser pulse increasing continuously. Laser technology itself is in fact one of the most vibrant subjects of research both in academic and industry settings. Laser as a tool has been used widely, for example, the laser printer and the scanner at
grocery store. It is used in cutting and machining hard material because of its incomparable precision and intensity. The intensity of laser used in industry cutting might be called strong but may not be the case in microscopic scale. To produce the electric field experienced by electron in hydrogen atom \((5.14 \times 10^9 \text{ V/cm})\), it will need a laser pulse that has intensity of \(3.51 \times 10^{16} \text{ W/cm}^2\). In microscopic world, a laser pulse of \(10^{13} \text{ W/cm}^2\) or more can be termed as strong or intense.

To produce high intensity laser pulse, one has to reduce the pulse duration and increase pulse energy:

\[
I = \frac{E}{\pi w_0^2 \Delta t},
\]

where \(I\) is the laser intensity, \(E\) the pulse energy, \(w_0\) the beam waist radius, \(\Delta t\) the pulse duration. Many solid state lasers can produce such pulses, for example, Ti:Al\(_2\)O\(_3\) (titanium-doped sapphire)\(^\text{11}\) and Nd:YAG (neodymium-doped yttrium aluminum garnet). KrF excimer laser can do this as well. The most widely used ultrafast femtosecond laser system is based on solid state Ti:sapphire crystal.

1.2.1 Ti:sapphire oscillator

Ultrafast femtosecond Ti:sapphire laser system usually consists of an oscillator and one or more stages of amplifier. To achieve wavelength tunability, an optical parametric amplification (OPA) system can be used.\(^\text{12}\)
Fig. 1 is the optical layout of one type of Ti:sapphire oscillator cavity. The green continuous wave (CW) laser beam is steered and focused on the Ti:sapphire crystal, providing pumping energy for the gain medium. The absorption band of Ti:sapphire crystal is from 400 nm to 600 nm. Usually the pumping laser beam are from argon-ion lasers or frequency-doubling Nd:YAG lasers. The emission band of the crystal ranges from 600 to 1100 nm, which is the widest gain bandwidth in all solid state gain medium. This is one of the major reason Ti:sapphire crystal is chosen to produce ultrafast pulse. Other reasons include its high conversion efficiencies and thermal conductivity, high damage threshold and large storage density.
In Fig. 1, the folding mirror and the output coupler enclose the oscillator cavity. The length of the pulse round trip within the laser cavity determines the spacing of the axial modes. When the axial modes are added up constructively, highest energy can be achieved. Mode-locking in this type of oscillator is achieved by way of Kerr lens effect.

![Diagram of Kerr lens effect of Ti:sapphire crystal](image)

**FIG. 2.** Kerr lens effect of Ti:sapphire crystal

The Ti:sapphire crystal's refractive index depends on the intensity of the laser beam:

\[ n(I) = n_0 + n_2 I, \tag{3} \]

where \( n(I) \) is the intensity dependent refractive index, \( n_0 \) the linear refractive index and \( n_2 \) the nonlinear refractive index. Usually the intensity of the beam is stronger towards the center (Gaussian beam for example), this intensity dependent index of refraction effectively induces the action of a lens. The cavity can be adjusted to
make those constructively added modes (higher intensity) gain energy in a single round trip whereas make other modes (lower intensity) lose energy, so the lens effect becomes stronger in the next round trip. During subsequent trips, the high-intensity phase-matched modes will extract more and more energy from the medium. This is the self-mode-locking mechanism that produce pulsed laser beam. Sometimes this self-mode-locked operation is spontaneous. In most cases, however, a small external perturbation applied to the cavity (prism for example) can induce the mode-lock operation and have the oscillator function in pulsed mode. Displacement of the Ti:sapphire crystal can lead to CW beam.

FIG. 3. (Color) Dispersion compensation by a pair of prism

This mechanism alone, however, will not produce gain-bandwidth limited pulse. The reason is group velocity dispersion (GVD) in the laser cavity. The two prisms inside the cavity (Fig. 4) are used to compensate the dispersion (Fig. 3). As a result, this oscillator can generate pulse as short as 15 fs. Some cavity design uses a combination of prism pair and chirped mirror (dispersion-compensating mirror), producing 5 fs pulse.
This type of oscillator can generate 70 MHz to 100 MHz repetition rates laser pulse depending on the cavity length. But it can only produce pulse of a few nJ ($10^{-9}$ J) energy. In order to increase the pulse energy, the pulse repetition rates are first reduced using a pulse picking system. Then one or more amplification stages are used to amplify the selected pulses.

1.2.2 Pulse amplification system

Most pulse amplification uses the method of chirped pulse amplification (CPA). The femtosecond pulse is first temporally stretched so in the amplification process the peak intensity is below the damage threshold of the gain medium.
After amplification, the pulse is compressed in the time domain (Fig. 5). The stretcher usually includes a grating pair, a telescope and a folding mirror. “Red” frequency component of the short pulse travels less distance than the “blue” component in the stretcher, i.e., the pulse is positive chirped. The pulse duration is greatly reduced. In this case, the 15 fs pulse coming out from oscillator is stretched to 150 ps by a factor of $10^4$.

After the stretcher and before the amplifier, a pulse picking system is utilized to reduce the repetition rate of the beam. There are various designs of the pulse picking systems, one of them is introduced here (Fig. 6). The seed pulse is horizontal (P) polarized, with ~80 MHz repetition rate. It passes through a polarizer which only allows horizontal polarized pulse to pass. (It also prevents the amplified vertical-polarized (S) light from sending back to the oscillator.)

![Fig. 6. Pulse picking system](image)

When the pockels cell is applied with high voltage, the polarization of the pulse is changed 90°. A second polarizer only allows passage of vertically polarized pulse. The pockels cell can function from 1 KHz to 10 MHz, but it is usually used between 1 KHz to 10 KHz, ensuring sufficient pulse amplification in the amplifier.

Now that the pulses with unwelcome polarization are cleaned up and the seed beam’s repetition rate is reduced, it’s ready for amplification. The most used
amplifiers are multi-pass amplifier\textsuperscript{16-17} and regenerative amplifier\textsuperscript{18}. These amplifiers can increase the pulse energy to 1 to 10 mJ at 1 KHz. If necessary, the mJ level pulse can be further amplified by “power amplifier” (mostly multi-pass design) to several joules at 10 Hz or even more at 0.2 Hz.\textsuperscript{19-20} All amplification stages use the Ti:sapphire crystal as the gain medium. The pumping laser (532 nm) has tens of watts of energy, which will be focused on the crystal. In order to prevent thermal damage and also to increase thermal conductivity, the crystal is cryogenically cooled below -175°C. The repetition rate of the pump laser is same as the pockels cells. The vertically polarized pump laser is adjusted to synchronize with the timing of the seed pulse.

The design of the regenerative amplifier is similar to the oscillator cavity. The seed beam (800 nm) will travel around 20 round trips within the cavity before being ejected. This many trips allow low-gain efficiency in each trip, which can prevent amplified spontaneous emission (ASE). This design also guarantees good overlap between the seed beam and the pump beam. The drawback of such long optical path is that it can increase high-order dispersion in the pulse. High-order dispersion is hard to compensate during the compression stage, limiting the duration of the pulse produced by this method to around 30 fs.\textsuperscript{21}

Multi-pass amplifier, however, does not require a cavity to have the beam passing through the Ti:sapphire crystal multiple times. Fig. 7 is a simple illustration of the multi-pass amplifier optical design. There are only 6 passes through the Ti:sapphire crystal in this illustration. The maximum number of passes can be as high as 15. All passes focus on the same area of the gain medium.\textsuperscript{21}
FIG. 7. (Color) Optical layout of a multi-pass amplifier.\textsuperscript{21} In another design only two curve mirrors are used, together with a long folding mirror.

An array of same-size apertures can be inserted in the optical system to reduce the size of each pass to optimize the spatial mode of the pulse. Compared with regenerative amplifier, multi-pass amplifier has higher gain per pass so that fewer passes are needed.

The energy of the amplified pulse can reach 10 mJ, but the pulse duration at this point is around 150 ps. It is then sent to a negative dispersion grating pair to be compressed. It should be noted that during the amplification process the center region of the spectrum gain more energy compared to the outer region—the gain-narrowing effect. As a result, the bandwidth of the laser spectrum is shortened and the pulse can no longer be recompressed to the duration before it’s stretched. The gain-narrowing effect limit the possible duration of the final compressed pulse to 25 fs.\textsuperscript{22} Some methods exist to shorten the pulse even more.
For example, one can send the 25 fs amplified pulse into hollow fiber filled with noble gas, the spectrum is broadened because of self-phase modulation; the pulse is also temporally chirped. The emitted pulse has to been recompressed. It is now possible to reduce the pulse to 5 fs with this method.23

1.2.3 Pulse characterization

To measure the pulse duration of the ultrafast pulse, frequency-resolved optical gating (FROG)24-25 is the simplest and most straightforward method. In this method, the ultrafast laser is sent into an autocorrelator setup and the two split beams are then overlapped on a second harmonic crystal. A spectrometer measures the second harmonic generation (SHG) as a function of the delay between two pulses. The femtosecond laser pulse can be fully reconstructed by an iterative algorithm.25 Another method to characterize ultrafast laser pulse is spectral phase interferometry for direct electric-field reconstruction (SPIDER).26 This technique split the beam into two beams first, which are then treated differently—one enters a Michelson interferometer, producing two temporally separated pulses; another enters a dispersive delay line, producing one chirped pulse. When the two beams are recombined on a doubling crystal, the two separated pulses in the first beam overlaps with different frequency components of the second beam (a stretched single pulse). The emerged two sheared pulses have different frequency component. They are dispersed even further and overlapped with each other. The spectrum of these two interfering pulses is measured and the interferogram can derive the shape of the original ultrafast pulse.22
One important character of few-cycle intense femtosecond pulse is the absolute phase $\varphi$, which hasn’t been a quantity of physical importance in optics.

$$E_L(t) = A_L(t) \cos(\omega_L t + \varphi)$$  \hspace{1cm} (4)

Here, $E_L(t)$ is the electric field within the pulse, $A_L(t)$ the time-dependent field amplitude, $\omega_L$ the carrier frequency. The subscript $L$ denotes linear polarized light. The absolute phase $\varphi$ can also be called carrier envelope phase (CEP). The importance of the absolute phase originates from its effect on the temporal evolution of the few-cycle pulse. The temporal evolution of strong electric field has dominant control over the electron’s movement when it’s unbound. When the field strength is close to the tunneling threshold (Fig. 8), $\varphi$ can determine whether tunneling ionization is possible.\textsuperscript{27}

![FIG. 8. Carrier envelop phase](image)

Normally the CEP of the pulses ejected from Ti:sapphire oscillator is not stabilized, i.e., different pulse has different $\varphi$. But the relative phase $\Delta \varphi$ between pulses can be measured by frequency domain detection.\textsuperscript{28} The measurement can provide feedback so the adjustment in the oscillator can be made to lock $\varphi$ (not
known) for all pulses. It is also possible to send the phase-stabilized pulse into amplification stage and produce intense CEP stabilized few-cycle pulse. The absolute phase can be measured by strong field ionization. Proper adjustment can be made to change $\varphi$ to a target value. This is one part of lightwave engineering. In order to approach single-cycle limit, the bandwidth of the pulse has to be much more than an octave. Self-phase-modulation (SPM) of intense laser pulse is one proven method to expand the spectrum. Wave mixing method can synthesize the waveform in sub-cycle scale.

1.3 Ionization in strong laser field

Ionization of molecules and atoms in intense laser field has different characters at different laser intensities. Keldysh parameter ($\gamma$) is used to identify these characters.

$$\gamma = \frac{|E_I|}{\sqrt{2U_p}}, \quad U_p = \left(\frac{F}{2\omega}\right)^2,$$  \hspace{1cm} (5)

where $E_I$ is the ionization potential, $F$ and $\omega$ are the amplitude and angular frequency of the laser field. $U_p$ is the ponderomotive energy, the average energy of oscillation of a free electron in the intense oscillating laser field. $U_p$ can also be expressed in term of laser wavelength and intensity:

$$U_p \, (eV) = 9.33 \times 10^{-20} \times \lambda (nm)^2 \times I \left(\frac{W}{cm^2}\right)$$ \hspace{1cm} (6)

When $U_p \ll E_I$ (or $\gamma \gg 1$), the ionization is in the multiphoton regime and can be explained by perturbation theory—the laser field does not significantly
change the coulomb potential. The electron can absorb the necessary number of photos to overcome the coulomb potential and be ionized. However, when $U_p$ approaches ionization potential of the molecule, the laser field strength is strong enough to change the shape of the potential experienced by the electron (Fig. 9) and the perturbation theory is not valid anymore.\textsuperscript{33} The observed high ionization rates in experiments are explained by tunneling theory: one side of coulomb potential is suppressed and the barrier is low enough for the electron to tunnel through, assuming zero or very short tunneling time compared with the laser period. If $U_p \gg E_I$ (or $\gamma \ll 1$), the barrier is suppressed even more and the electron is basically field ionized (over-the-barrier ionization).

![FIG. 9. Tunneling ionization (left) and over-the-barrier ionization (right)](image)

### 1.4 Electron-electron interaction

One important aspect of electron dynamics is the interactions between electrons, or so called electron correlation.\textsuperscript{34} To study this multielectron interaction, theorist proposed attosecond XUV pump—attosecond XUV probe method and measuring the momenta of each ejected electron in all three dimensions
coincidentally.\textsuperscript{35-36} But the method currently faces technical barriers as the probe pulse is not strong enough to ionize the second electron.

Another option is to use intense femtosecond laser field and induce electron correlation. It is realized in non-sequential double ionization (NSDI).\textsuperscript{37-38} This NSDI phenomena is used to explain the unusually high double ionization rate in strong laser field.

![Diagram of electron recollide with ionic core](image)

FIG. 10. Under the influence of oscillating electric field, electron recollide with ionic core after tunneling. At least five phenomena are confirmed to be related to this recollision mechanism. In this example, the electron tunnels out just after the laser electric field reaches the maximum. It returns to the ionic core about \(3/4\) cycle later.

The physical process of non-sequential double ionization consists of three distinct steps\textsuperscript{37} (also see Fig. 10): First the electron tunnels through the potential barrier; then the electron’s motion is dominated by the oscillating electric field. That is to say the coulomb force is ignored, which forms the principle of Strong Field Approximation (SFA).\textsuperscript{39} The electron may be returned to the ionic core depending on when the tunneling happens; in the third step, the electron with some gained energy (as high as \(3.2 \, U_p\)) will collide with the ionic core. The collision may be
in elastic: Some of the energy of the first electron will transfer to the system which becomes highly excited; or the first energetic electron directly knock off a second electron out of the system. There are other processes that can happen in this third step. The electron can elastically collide with the core and forward scatter or backscatter, which produce high-energy electron. It can also recombine with parent ionic core and emit photons. In fact, this is the process of high harmonic generation.

Because the tunneling happens in sub-fs scale (the electric field needs to be strong enough to modify the coulomb potential), the time scale of the electron wave packet that tunnels out is sub-fs. This has significant implications: By waveform control of a few-cycle pulse, the sub-fs electron wave packet can be steered and used as a tool to study electron dynamics in attosecond time scale. It is also the reason that when the recombination happens, the produced high harmonic pulse has attosecond duration. Multi-cycle intense laser field produces trains of such attosecond pulses: The tunneling threshold can be met twice every cycle and also in multiple cycles. It is now possible to generate isolated attosecond pulse with CEP stabilized few-cycle femtosecond pulse.

![Tunneling threshold](image)

**FIG. 11.** Tunneling threshold results in sub-cycle electron wave packet and sub-cycle electron dynamics
One way to avoid recollision in strong laser field is to use circularly polarized laser light. It has been experimentally proven that circularly polarized light can suppress the process of NSDI and HHG.\textsuperscript{41-42} The reason is that the transverse velocity initiated by circular light will move the electron away from the parent ion to avoid recollision effectively. This, of course, assumes that the electron tunnels out of the barrier will have no or very small initial transverse velocity, which is under further examination. So if the circularly polarized light can double ionize the atom or molecule—It must be sequential, as a result—the intrinsic electron correlation can be studied as well.\textsuperscript{43-45}

The aforementioned methods only deal with the realization of double ionization that produce two electrons whose interaction is of great interest. In order to find out whether the electron correlation exists and how the correlation manifests, another nontrivial task lies ahead of us: to measure the 3D momenta of both of the electrons ionized from the system coincidently. This dissertation revisits our journey of developing a new method to remove the existing technical barrier.
CHAPTER 2 THE PATH OF DEVELOPING A NEW 3D ELECTRON COINCIDENCE IMAGING SYSTEM

Generally, coincidence imaging technique allows simultaneous momentum measurement for multiple products produced from same molecule/atom in a process.\(^4\)\(^6\) 3D electron coincidence imaging needs to have the ability to measure the \((x, y)\) position (hence the velocity in these two dimensions) and time (hence the velocity in third dimension) of at least two electrons. We first review some of history of the particle imaging system, especially for ions and electrons.

2.1 Two-dimensional (2D) and three-dimensional (3D) particle imaging system

2.1.1 Components of an imaging system

Particle imaging method utilizes microchannel plate (MCP) combined with one type of anode designs. The MCP plate can detect not only electrons but also ions and photons with high detection efficiency. It is made from lead glass and there are about \(10^4\) to \(10^7\) channels in a single plate. The channel axis is biased to the surface at a small angle. The channel diameter is only around 10 micrometers, enabling superb spatial resolution. The channel walls are rendered with semiconducting capability.\(^4\)\(^7\) Each channel functions as an electron multiplier when applied with high voltage between front and back of the plate. The diameter of a MCP plate ranges from 20 mm to 120 mm, limited by fabrication technology. Usually at least two MCP plates are stacked together in a way to maximize the secondary electrons, for example, the chevron configuration. In some occasion three MCP plates are used. After amplification, the avalanche of electrons emitted
from back of the MCP plates is collected by various anode designs. The most used designs are phosphor screen and delay line anode. Other types of anode designs include multi-pixel detectors, crossed wire detectors, wedge-and-strip anode.

In the phosphor screen design, the high energy electron avalanche hits the phosphor screen and produces luminescence which is then recorded by a camera system. The position of the hit can be directly read out by the camera. Charge Couple Devices (CCD) camera is used when its data throughput speed is not limiting the data acquisition. But as the high-repetition rate (1 KHz to 10 KHz) femtosecond Ti:Sapphire laser comes along, complementary metal-oxide semiconductor (CMOS) camera is being used more frequently as it can match the laser repetition rate and still be able to provide sufficient spatial resolution. This anode design usually cannot offer precise arrival time of the particle, so it is tagged as a 2D imaging system.

But the delay line anode detector is a 3D imaging system because it can provide precise particle timing and 2D positional information. In its early design, a copper plate was surrounded by four ceramic rods, forming the base. There are two sets of copper wire winding helically around the base, perpendicular to each other. The electron avalanche impacts on the wires and produces electrical signal. In each wire set the signal transmits on two directions. The signals are amplified at both ends of the wire and then processed by constant fraction discriminator (CFD) and time-to-digital (TDC) units. The difference of arrival time of the signals at both ends of the wire set gives out the position on the dimension that is
perpendicular to this wire orientation. In such way, positions on both dimensions can be inferred. The time of the electron impact is the average of the timings of the four signals. More advanced delay line anode design (Hexanode) use three sets of wires. One of the wire is redundant but the overall design has an increased acceptance for multi-hit events.\textsuperscript{53}

2.1.2 Spectrometer design

While our goal is to measure the momenta of two electrons ejected from a system coincidently, it is also desirable and in some sense prerequisite to be able to achieve ion coincidence measurements.

The 2D ion imaging method was first developed by David W. Chandler and Paul I. Houston.\textsuperscript{54} The first application was to study the photodissociation of $CH_3I$. The photofragment $CH_3$ is state-selectively ionized via resonance-enhanced multiphoton ionization (REMPI) and the 3D velocity distribution of methyl ion is projected on 2D phosphor screen. Because the distribution has cylindrical symmetry along the polarization axis of the probe laser, the 3D distribution can be reconstructed (inverse abel transformation, for example).\textsuperscript{54} The authors pointed out the wind range of applicability of this imaging method in chemical dynamics study, for example reactive scattering in crossed beam experiments. The spectrometer design consisted of a repeller plate and a pair of grounded metal grids, similar to the Wiley and McLaren design used in mass spectrometer.\textsuperscript{55} The ions are born between the repeller plate and the first grid.
FIG. 12. Velocity mapping imaging spectrometer with four plate design. The ions that are born at different position on Y axis but with same velocity vector are focused by the ion optics onto same position on the detector plane. The same principle also applies on X dimension. Simulation is done in SIMION™

A major advancement of this spectrometer design in ion imaging is the velocity map imaging (Fig. 12). The first design uses three 70 mm diameter stainless steel plates with holes in the center. The repeller electrode has a 2 mm diameter hole whereas the other two electrodes (extract and ground electrode) have center holes of 20 mm diameter. These three electrostatic plates, when applied with suitable voltages, can focus ions with same initial velocity vector on the same spot on the detector—no matter where the ions are born within the overlapping region between the laser beam and the molecule beam. That's how the name “ion optics” for the set of three electrodes come from. This spectrometer design greatly improved the spatial quality of the image and reduced the distortion in the grid design as well.
Based on this design, Suits and coworkers developed direct current (DC) slicing imaging method where another electrode is added to the original three plate design.\textsuperscript{57} The extraction and acceleration field strength are also lowered for the purpose of extending the time-of-flight (TOF) spread of the ion cloud. The TOF spread of one fragment ion reached 500 ns, wide enough for time-slicing by applying 40 ns gate on the MCP detector. This method improved the image resolution even more. It’s also a 3D ion imaging method because it will not need mathematical reconstruction of 2D image any more. DC slicing imaging has been a powerful imaging method to study chemical dynamics and photodissociation process.

It is worth noting that velocity map imaging has one drawback: the electric field generated by the open electrodes is not homogenous. The cold target recoil-ion momentum spectrometer (COLTRIMS)\textsuperscript{58} design uses a weak homogenous electric field to direct the ion or electron and a weak homogenous magnetic field at the same time to confine the electron motion in order to maximize the collection efficiently on the MCP detectors. (The design can achieve $4\pi$ collection efficiency for ions without the help of magnetic field.)

2.1.3 The challenges of detecting two electrons coincidently

Measurement of photoelectron 3D velocity distribution is important to understand the process of photoionization. VMI and COLTRIMS are two essential tools to detect angle and kinetic energy resolved photoelectrons. MCP/Phosphor imaging system, when used to measure the momentum of photoelectron, is not a 3D imaging system. There has to be some mathematical transformation to
reconstruct the 3D velocity distribution.\textsuperscript{59} The DLD system have no trouble measuring 3D momentum of single electron with high efficiency. However, when it comes to measure the 3D momenta of two electrons coincidentally, all existing spectrometer design and detection system fall short. The source of the problems comes from the fact the electron is very light—the spectrometer design cannot separate two electrons long enough for the detection system to register both of them. Unlike ions (whose TOF spread can be tens of microsecond), the span of electron TOF is merely tens of nanosecond at most, limited by the vacuum chamber size and detector size. The separation between the two electrons can be a few nanoseconds, or less than one nanosecond when the two electrons’ velocity vectors on TOF axis are on the same direction when they are ejected.

One indirect way to get the momenta of the two electrons is to measure the momentum of the dication and one of the departing electron coincidently, then calculate the momentum of another electron assuming momentum conservation condition is met. This scheme has been adopted in numerous strong field double ionization studies.\textsuperscript{60-61} The uncertainty of the non-zero initial momentum of the molecule will affect the accuracy of the calculation.

The advanced three-layer DLD has a dead-time of around 10 ns and a position resolving power of 10 mm—the detector cannot distinguish the two electron hits when the arrival time are within 10 ns AND 10 mm, in other words, they are registered as one hit. However, when they arrive within 10 ns but are separated by more than 10 mm, they can be registered as two hits but the time of arrival of each electron cannot be distinguished—they are assigned with the same
The dead-time and dead-space of delay line detector come from the intrinsic dead-time of the high frequency electronics (for example the CFD and TDC units used for processing electric pulses coming from MCP and delay line anodes). A few variations of delay-line detectors have been developed to circumvent this issue with some success. Continetti and coworkers\textsuperscript{62} demonstrated a multi-quadrant delay line anode with independent four sets of processing electronics. Picard and coworkers\textsuperscript{63} incorporated a phosphor screen within the delay-line anode to provide positional information to aid the retrieval of multi-hit events. They also digitized the MCP signal and performed offline analysis to achieve a good temporal resolution and multi-hit capability. This detector achieved a dead-time of 2 ns and a dead-space of 2.4 mm and has been demonstrated in detecting coincident ions. A trend in the development of delay line detector is to abandon the CFD-TDC combination to avoid the dead-time restriction.\textsuperscript{64} A recent effort by Wallauer \textit{et al.}\textsuperscript{65}, is also along this line. Using a multichannel high-speed digitizer, they collect electric pulse waveforms from six delay lines and one MCP pick-off circuit. With sophisticated offline peak detection algorithms, they achieved an improved dead-time of 3 ns and a dead-space of 5 mm.

\textbf{2.1.4 Our approach towards 3D electron coincidence imaging}

We resort to MCP/phosphor screen coupled with camera system to achieve 3D electron coincidence imaging. Traditionally this method will not enable one to do this. DC slicing imaging method allows one to do 3D \textit{ion} imaging but not 3D \textit{electron} imaging. One scheme using a multi-anode photomultiplier tube (PMT) can
achieve 3D ion coincidence imaging: The multi-anode PMT can assist the association of arrival time (from PMT) and position (from CCD camera) of each ion. This method initially used CCD camera which has less than 100 Hz frame rate, limiting the scope of its applicability.

Our approach towards coincidence imaging utilizes one simple and important fact of the MCP/phosphor screen detector: Different particle spots on phosphor screen have different brightness. This neglected feature of MCP/phosphor screen detector will allow us to associate time and position of each particle in case of multi-hit event.

2.2 Coincidence ion imaging achieved with MCP/phosphor screen detector and fast frame camera

In typical experimental apparatus, ions can be separated by tens of nanosecond to few microsecond or even more. It will be much easier to achieve coincidence ion imaging than coincidence electron imaging. So it's natural to develop coincidence ion imaging first in order to achieve the ultimate goal of coincidence electron imaging.

2.2.1 Experiment setup

The experimental setup is illustrated in Fig. 13.

The continuous molecular beam (methyl iodide with carrier gas argon) bursting out of the nozzle (20 μm diameter) passes through the skimmer, which separates the source chamber and the main chamber. In the main chamber, there are four stainless steel plates with hollow circular center of different diameters. These four plates are applied with high voltages to form the VMI configuration.
Between the repeller (first plate on the right) and extractor (L1), the 780 nm, 1 kHz laser beam intersects the molecular beam at 90° at its focusing point.

![Experiment setup and principle of coincidence ion imaging](image)

**FIG. 13.** Experiment setup and principle of coincidence ion imaging

The intersection point, the center of the ion optics, the skimmer, and the nozzle are on the same line. After ionization/dissociation, the ions are extracted towards the multichannel plates. The MCPs are pulsed to detect slightly longer than TOF of iodine ion so that the majority of the ions produced (parent ion) are not detected. The count rate can be lowered to about 0.3 per laser shot and the false coincidence rate could be lowered dramatically. A photomultiplier tube (PMT) faces towards the phosphor screen. The transient of the PMT signal is recorded by a National Instrument (NI) digitizer as complete waveform. A fast frame CMOS camera records the position information of the ion hit.
In recent years, CMOS sensor technology has been gradually replacing CCD sensor technology in industry settings. For example, cell phones with camera and commercial digital cameras have been using CMOS sensor because its sensor speed, on-sensor imaging processing and noise reduction capabilities. We used a USB3 vision CMOS camera with a Sony IMX174 sensor. There are several reasons for this choice: (1) The maximum frame rate can reach 1 kHz at high resolution. (2) Position and amplitude of the camera spots are directly read out. (3) Low readout noise makes sure the accuracy of camera spot brightness. (4) It could be externally triggered with a TTL signal and has timing stamp on every frame, which is used to synchronize with the digitizer waveform. (5) Cost is low and implementation is relatively easy.

In the case of multi-hit event, the position of ion spot on the camera is associated with the peak timing on PMT waveform based on the order of intensity of that ion spot on the camera and the order of amplitude of the peak in the waveform. For example, in Fig. 13, the stronger spot on the camera frame is associated with the higher peak on the waveform. In this way, both position and time information of each and every ion are found out. This is the principle idea of this particle coincidence imaging system.

2.2.2 Computer algorithms

Although the hardware implementation is relatively easy compared with delay line detector, the software development is not. We developed the data acquisition and analysis programs under LabVIEW, a product of National Instruments as well. It will allow full control of the NI digitizers and also the CMOS
camera. The 1 kHz laser triggers both camera and digitizer to start acquisition. Each pulse can be seen as a trigger to an “event”, regardless whether it will initiate ionization or not.

FIG. 14. Acquisition algorithms flowchart

The camera will time stamp each frame in order to synchronize with the digitizer waveform. We adjust the exposure time to reduce dark noise of the camera. Thresholding method is used to remove the dark noise as well. The software can at the same time analyze the information coming out of the camera. The “center of mass” calculation algorithm is used to find the center of the ions spots. It is an “ion counting” method in reference to the earlier method of collecting all the overlapping image frames. Camera analysis produces the number of ion
counts, the positions and intensities of each ion spot. This method is timing critical so the code is first written in C language, compiled as dynamic link library (DLL) and then called by LabVIEW program. In some events, there may be multiple ions produced either through coulomb explosion or ionization of multiple molecules. As a result, the analysis will take longer time. To solve the problem of failing to keep up with the laser repetition rate, we used parallel computing algorithm, the ability rendered by multi-core CPU. In this way the data acquisition can be running smoothly even when the analysis is slow. The parallel computing algorithm is also applied on PMT waveform acquisition and analysis (Fig. 14).

The high-speed digitizer is properly configured to acquire the full waveform of PMT signal. Same as camera acquisition, digitizer will only acquire a bit further than the signal of heaviest ion needed in order to reduce the data size. At the same time, the peak detection method (peak of the first derivative of the waveform) produces number of peaks, the time and amplitude of each peak, which are then stored for further analysis.

After the data acquisition is finished, the counts of spots on camera and the peaks of the PMT waveform are first compared. If they are not the same, all the related information is discarded. If there is one ion spot on camera and one peak on PMT, the association of position and time is automatic. If there are two or more same amount of ion spots and peaks, the association of position and time of each ion is based on the brightness of the ion spots and the peak heights. After the association, we can calculate the momentum of each ion. If the momentum
conservation is met (the sum of momentum is restricted to less than $2 \times 10^{-23} \text{ kg} \cdot \text{m/s}$), we find ourselves a true coincidence event (Fig. 15).

![Data analysis algorithms flowchart](image)

**FIG. 15.** Data analysis algorithms flowchart

The innovation of this ion coincidence detection system includes the combination of the following: (1) Ion position and arrival time measurements are decoupled. This advantage will become more important in electron coincidence detection as it enables zero dead time detection. (2) High frame rate of the camera is utilized. Data acquisition time is a critical factor in molecular and electron dynamics study. In this setup, at $128 \times 128$ camera resolution, the camera frame rate can match the laser frequency at 1 kHz. (3) The computer algorithm performs real time image thresholding and center-of-mass calculation of ion spots. So only
the position and the intensity of the ion spots—not all the camera frame—are output for analysis. (4) High data-transfer rate of the digitizer is employed. At 1 kHz, 250 megasamples (MS) per second sampling rate, if only 4 microsecond TOF span is recorded, the data transfer rate will be one megabytes (MB) per second.

### 2.2.3 Single-hit and multi-hit performances

To validate this detection system, single-hit and multi-hit performances are tested. In a single hit event, only one ion spot is on the camera frame and only one peak will be detected in the waveform in theory. However, the detection efficiency of the camera and the PMT are different, i.e. in some occasion the PMT is able to detect the ion spot but the camera fails to register the hit. These cases only make up 5 percent of total events with our peak detection algorithm. For example, in Fig. 16 (a) two cases of non-matching are shown: in one case (red), the number of PMT peaks are larger than the number of ion spots on camera; in another case (blue) the situation is reversed. These kinds of events are discarded.

Fig. 16 (b) plots the correlation between camera ion spots intensity and PMT peak amplitude. In order to correctly assign time and position for each ion in a multi-hit event, the correlation coefficient $R^2$ of the linear fitting should be as close to one as possible. The rather large deviation of the correlation coefficient originates from the noise of the reactions of the MCP detector, camera and PMT between different laser pulses.
FIG. 16. (Color) (a) Initially registered ion counts by camera and PMT in data acquisition, about 500 laser shots are presented. (b) The correlation of ion spot intensity on camera and the amplitude of the peak on PMT waveform. The red line shows the linear fitting. (c) The correlation of such in three cases with more than five ions. The inset is the $R^2$ distribution of linear fittings for all multi-hit (more than two) events.

In Fig. 16 (c), 3 cases of more than 5 spots and peaks are shown. The inset shows the distributions of the correlation coefficient in all multi-hit (more than two) events. The majority of $R^2$ are larger than 0.95, which means the correlation is much better in a single shot.

The effective detector size in this experiment is $6\, cm \times 6\, cm$. With $128 \times 128$ camera pixel resolution, the spatial resolution is 0.47 mm. As a result, the dead space (the distance within which no more than one ion spot can be identified) is about 1 mm. The dead time of this detection system is about tens of nanoseconds,
mainly limited by the digitizer sampling rate and PMT peak resolving power. This dead time is comparable with that of delay line detector. In later development of electron coincidence imaging, the dead time of our detection system can surpass that of DLD.

2.2.4 Dissociative ionization of methyl iodide with this imaging system

We used this detection system to study dissociative ionization of methyl iodide. The laser intensity is $5 \times 10^{13} \text{ W/cm}^2$, which is in the range of previous study. At this laser power, both dissociative single ionization and dissociative double ionization are present. No previous experiments have performed coincidence ion imaging measurement of dissociate double ionization of methyl iodide.

![Image of ion momentum images and 2D ion TOF spectrum](image)

**FIG. 17.** (Top) Ion momentum images of sample mass: 15 ($CH_3^+$), 74, 80, and 127 ($I^+$). (Bottom) 2D ion TOF spectrum of all two-hit events. The inset is the enlargement of area that includes methyl cation and iodine cation.
Top part of Fig. 17 shows some momentum images of mass 15 ($CH_3^+$), 74, 80, and 127 ($I^+$). Apart from the expected methyl cation and iodine cation, there are other ions produced from residue gas in the vacuum chamber. Bottom of Fig. 17 is the two dimensional ion TOF spectrum for all two-hit events. If we inspect the area of both methyl and iodine cation, a line with -1 slope is clearly visible. This line translates to momentum conservation during dissociation of methyl iodide double ion.

FIG. 18. (a) Methyl iodide dissociative double ionization events. (b) Superposition images of methyl cation and iodine cation resulting from dissociative double ionization. (c) Total kinetic energy distribution of these events. (d) Angular distribution of the ions from dissociative double ionization of methyl iodide
After applying momentum conservation filter in this area, only events from dissociative double ionization are survived, resulting in Fig. 18 (a). Because methyl cations are lighter than iodine cations, they appear on the outer region of composite image Fig. 18 (b). The total kinetic energy distribution shows two distinct peaks at 4.37 eV and 5.11 eV, in agreement of previous study.\(^7\) The angular distribution is fitted with following equation:

\[
I(\theta) = 1 + \beta_2 P_2(\cos\theta) + \beta_4 P_4(\cos\theta)
\]  

(7)

Here \(P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)\) is the second Legendre polynomial and \(P_4(\cos\theta)\) the fourth Legendre polynomial. This yields to anisotropy parameters \(\beta_2 = 1.7\) and \(\beta_4 = 0.8\). \(\beta_4\) indicates that the ionization process is of multiphoton character.

2.3 Three dimensional (3D) velocity mapping electron imaging\(^7\)

The success of this detection system’s 3D coincidence ion imaging capability prompts us to continue with 3D coincidence electron imaging. Before that goal, it is necessary to achieve 3D electron imaging, or time- and space-slicing imaging.

In typical electron spectrometer setup, the TOF span of electron is in the range of few ns, which means that a few hundred picoseconds width (at least one tenth of total electron TOF) of slice is required. Fast pulsing the MCP detectors is not applicable because the inherent charging and discharging time is around tens of nanoseconds.

If we continue to use the previous setup of 3D ion imaging to detect electron, we will sure fail to achieve the goal of 3D electron slicing because the phosphor
screen alone has a rise time of a few nanoseconds and even longer decay time. PMT rise time (~10 ns) is also a limit. So instead we pick up the timing signal directly from the MCP lead (Fig. 19). 

2.3.1 Imaging system setup

![Image](image.png)

FIG. 19. Setup for 3D electron imaging

Between the MCP lead and high-speed digitizer, there is a signal decoupler and a pre-amplifier (not shown in Fig. 19). The signal decoupler removes the high voltage component. Off-line analysis will then be performed to obtain best timing resolution and accuracy. This scheme has been applied to delay line detector, in which 5 or 7 waveforms are need to be acquired and analyzed. In our setup, only one waveform is needed because the position information is decoupled from time measurement—done directly by fast frame camera. The pulse from MCP lead has a rise time of 1.5 ns and the width is about 3 ns. This enables better timing accuracy and smaller dead time in multi-hit events.

The highest sampling rate in this digitizer (NI, PXIe 5162) is 5 gigasamples per second (GS/s), which guarantees 200 ps temporal accuracy. But to be able to
carry out slicing for electron cloud with 1 ns TOF span, it’s still not enough. Quadratic polynomial interpolation is used to achieve better temporal resolution. This procedure is justified as the sampling rate of the digitizer is more than twice larger than the highest frequency component of the signal (1.5 GHz).

Another obstacle is the trigger timing jitter: Both the camera and digitizer are triggered by a photodiode placed in front of the chamber. Uncertainty of the trigger timing degrades the timing resolution. This obstacle is removed as we find out the TDC inside the digitizer can measure the trigger timing with 4 ps resolution. To test this function, we put one photodiode in front of the chamber (used as trigger) and another photodiode at the back of the chamber (used as signal). The distribution of laser pulse delay is shown in Fig. 20 (a). With trigger jitter correction, the standard deviation is only 18 ps, much better than the one without correction.

FIG. 20. (Color) (a) Laser pulse passing time from the front to the end of a vacuum chamber, red line is without trigger jitter correction, blue line is with correction. (b) TOF distribution of electrons from an area of 10 mm$^2$ in detector plane, only the forward electrons ($P_z > 0$) are selected.
2.3.2 Xenon strong field ionization

We test our systems by studying above threshold ionization (ATI) of Xenon with circularly polarized light. The laser intensity is $1 \times 10^{13} \ W/cm^2$. The wavelength of the laser is 800 nm. We select an area of 10 mm$^2$ on image plane and then plot the TOF distribution of all forward-ejected electrons ($P_z > 0$) within that area. The results Fig. 20 (b) indicates an electron TOF resolution of 32 ps can be achieved. (It is worth noting that the velocity mapping spectrometer configuration used in the chamber is able to focusing all electrons with same initial velocity on same area of MCP detector.)

Fig. 21 shows eight time-slicing images at different electron TOF. Each slice has a width of 32 ps. The resolution demonstrates the electron slicing capability of this imaging system.

![FIG. 21. Electron TOF from Xenon strong field ionization and 8 time-slicing with 32 ps width](image)

Also, this imaging technique removed the necessity of electron newton sphere having cylindrical symmetry to be able to get its 3D distribution through
inverse Abel transformation. When xenon is ionized by elliptically polarized light, even though the produced electron cloud does not have cylindrical symmetry, both time- and space-slicing are available (Fig. 22).

![Fig. 22. Slicing of electron newton sphere in all three plane.](image)

As can be seen, it is possible to achieve 3D electron imaging with traditional MCP/phosphor screen detector. The temporal resolution can reach as low as 32 ps, limited by MCP transit time spread (TTS)\textsuperscript{74} and residue digitizer trigger jitter. Nevertheless, the achieved temporal resolution is comparable with that of delay line detector. Moreover, the cost associated with this method is much cheaper than the delay line detector. It has great potential to be applied wherever 3D electron imaging is needed, for example, metal surface ionization experiments.

**2.4 Electron-electron coincidence measurement capability\textsuperscript{75}**

We then upgraded the digitizer (National Instruments, PXIe-5185). Its highest sampling rate is 12.5 gigasamples per second. This upgrade does not necessary improve TOF resolution, but it will provide 2.5 times more data points (compared to 5 GS/s digitizer) to help extract the overlapping pulses.
The ion counts from the camera will be the basis as of whether or not to initiate a global fitting algorithm on the digitizer waveform: If two spots are recognized on camera frame, the extraction process is started. The detailed fitting procedure is following: (1) All single-hit waveforms are averaged to produce a standard single-hit waveform (Fig. 23). (2) This single-hit waveform is then fitted with the sum of two Gaussian functions using the nonlinear Levenberg-Marquardt algorithm to construct the basis function. (3) A sum of two basis functions is used to fit the waveform to obtain the positions and amplitudes of each electrons hits. (4) Finally, by correlating the amplitude with the intensity of the camera spots, timings and positions of both electrons are obtained. The shortest dead time achieved by this algorithm is 0.64 ns.

For comparison, Fig. 24 (a) shows a digitizer waveform when two electrons arrive within 3 ns. It can be resolved by our algorithm as well as CFD (constant fraction discriminator) algorithm. However, when two electrons’ arrival times are within 1 ns, CFD algorithm will find it hard to extract two pulses out of the overall waveform. Our global fitting algorithm can accomplish this as shown in Fig. 24 (b).
Because of nonlinearity of two-pulse overlap, the assumption that the overall pulse is the sum of two single-hit waveform is not true anymore. We made small adjustments on basis function to retrieve correct timing information. As shown in inset picture of Fig. 25, before making adjustments there are distortion in the 2D electron TOF spectrum of electrons in coincidence with xenon single ions (all false coincidence).
The reason to choose false coincidence events is because TOF from single electron events can be used as a reference to optimize the basis function. After basis function adjustments, the distortions are removed in the main figure.

One important feature of this detection system’s coincidence detection ability is its zero dead-time detection. Because camera does not have dead time (it does have 1 mm dead space), electrons arriving less than 0.7 ns in between still can be seen, though they will have around 0.7 ns TOF ambiguity, which is an acceptable sacrifice. In Fig. 25, all these data points are moved to the diagonal
They are not discarded, all positional information on camera is kept, although with 0.7 ns TOF ambiguity. While the magnitude of the momentum of these electrons will have some uncertainties due to the TOF uncertainty, the directions of the momentum are completely accurate in the plane perpendicular to the TOF axis because it's measured by camera. There is potential issue with this approach: because the exposure time of the camera is generally much longer (~50 us) than the acquisition length of digitizer (30 ns), it tends to see more dark current and thus leads to a higher false coincidence rate. However, this can be mitigated by pulsing the high voltage of the MCP plate as has been shown in previous ion coincidence imaging.

To summarize, we have demonstrated an improved 3D imaging system to achieve highly efficient detection of two electrons in coincidence. With a new timing analysis algorithm, the system achieved an unprecedented dead-time of 0.64 ns while a true zero dead-time is possible when the width of the MCP pulses is further reduced and optimized.
CHAPTER 3 PHOTOELECTRON-PHOTOION COINCIDENCE IMAGING OF DISSOCIATIVE DOUBLE IONIZATION OF ETHANE

Until now, I have presented apparatus that can only detect either coincidence ions OR coincidence electrons. But there is also tremendous need in molecular and electron dynamics studies to measure 3D momenta of both ions AND electrons produced in a process. For example, in a non-dissociative double ionization event, it’s best to be able to detect the double ion and two electrons at the same time (triple coincidence). In a dissociative double ionization process, it’s necessary to measure 3D momenta of two single ions and two electrons simultaneously (quadruple coincidence). These abilities open the door for many interesting molecular reaction dynamics and electron dynamics studies. We constructed a photoion-photoelectron coincidence apparatus with the new imaging system which allows us to study these types of dynamics.

Photodissociation dynamics is one of the most important areas of laser-matter interaction studies. The photodissociation process can be complicated when the parent ion or dication have several electronic states that have similar energy. Combined with three dimensional energy- and angle-resolved imaging techniques, femtosecond pump-probe method can distinguish and identify the dissociation pathways. It is also interesting to the find correlation between total kinetic energy release (KER) of the recoil fragments and total kinetic energy of the coincident electrons. We use the new apparatus to study the dynamics of dissociative double ionization of ethane by intense femtosecond laser field.
3.1 Photoelectron-photoion coincidence imaging apparatus with the new imaging system

The vacuum chambers are formed by three differentially pumped chambers: the source chamber, pumped by a 1100 l/s magnetically levitated turbo pump; the buffer chamber, pumped by a 250 l/s turbo pump; and the main chamber (reaction chamber), which has a 1300 l/s pump.

In the source chamber, a 20 μm diameter nozzle produces supersonic gas beam. The backing pressure behind the nozzle ranges from 0.1 to 3 bar depending on experiments. The continuous gas beam first goes through a 1 mm diameter skimmer, which separates source chamber and buffer chamber. Another aperture with 1 mm diameter separates the buffer chamber and the main chamber. It will collimate the gas beam even further to prepare best supersonic gas beam for reactions. With molecule beam off, the gas pressure in the main chamber is $2 \times 10^{-9} \text{ mbar}$; with 1 bar behind the nozzle, the gas pressure is $5 \times 10^{-8} \text{ mbar}$.
In the main chamber, the ion optics are consisted of 6 electrostatic plates (lens). The center of each plate is open for electron and ion passage. The laser beam is sent through the front window of the chamber and focused by a concave reflective mirror which is mounted in the back and can be adjusted in three dimensions. At the focal point, it intersects with gas beam at right angle between plate 3 (L3) and plate 4 (L4), as shown in Fig. 26. After ionization/dissociation, the ejected electrons are extracted toward left and hit the electron detector. The produced ions instead are moved by the electric field toward right and eventually hit the ion detector. Outside the main chamber, there is a magnetic coil that generates field that counteracts earth magnetic field. This guarantees that majority of the electrons can be detected.

Other two major upgrades are made on this apparatus as well. The data acquisition program is developed to accommodate 3 kHz laser repetition rate, this reduces the acquisition time down to one third of that with 1 kHz repetition rate pulse. Both the ion camera and electron camera can operate with up to $450 \times 450$ pixels resolution if needed. These updates lead to 0.2 mm ion and electron spatial resolution (additional resolution can be gained through centroid algorithm).

### 3.2 Preliminary Results

We initially tried to find the correlations between the total kinetic energy of the two ejected electrons and KER of photofragments in a dissociative double ionization process in strong laser field. Along the way, we find one interesting dissociative double ionization channel—ejection of $H_3^+$. We then focused more on this channel.
3.2.1 One-dimensional and two-dimensional spectrums

**FIG. 27.** One dimensional ion spectrum in m/z domain, the inset is the enlargement of main figure from 0.5 to 4.2 m/z

In this experiment, we first use 1 kHz circularly polarized light. The acquisition time is 70 hrs. Fig. 27 is the one dimensional spectrum in m/z domain. Most interesting signal is $H_3^+$. $H_3^+$ has been found in early mass spectrometry.$^{81}$ Recent experimental study shows that $H_3^+$ could be produced efficiently from many hydrocarbon molecules irradiated by intense linear polarized femtosecond laser pulse.$^{82}$ Hydrogen migration mechanism is proposed because it is possible to produce $H_3^+$ from a molecule without methyl group, for example cyclohexane. Another combined theoretical and experimental study found that in the case of ethane the transition state is in the form of $[H_2 \leftrightarrow C_2H_4]^{2+}$ which then proceeds to $H_3^+$ and $C_2H_3^+$. All studies point to the precursor $C_2H_6^{2+}$ before dissociation to $H_3^+$. 
FIG. 28. 2D ion TOF

In the 2D ion spectrum (Fig. 28), there are two prominent dissociative double ionization channels:

I: \( C_2H_6 \rightarrow CH_3^+ + CH_3^+ + e + e \); (short-noted as \( CH_3^+ \) channel)

II: \( C_2H_6 \rightarrow H_3^+ + C_2H_3^+ + e + e \). (short-noted as \( H_3^+ \) channel)

It is more clear how \( H_3^+ \) is produced in the 2D ion spectrum.

The photoelectron-photoion kinetic energy spectrum (Fig. 29) shows no clear correlations between KER and total electron kinetic energy in both of the channels. Possible reasons are: different dication electronic states leading to same products; non-repulsive potential energy surface of dissociation channel; different amount of photons absorbed by the molecules.

The KER of \( H_3^+ \) and \( CH_3^+ \) channel range from 2.5 eV to 7.0 eV, and 2.8 eV to 7.5 eV respectively. Normally, this large kinetic energy release is a sign of
dissociative double ionization. The peak KER of $H_3^+$ channel is around 4.1 eV, which is similar to that of previous study. The peak KER of $CH_3^+$ is 4.5 eV, 0.4 eV higher than that of $H_3^+$ channel. Total electron kinetic energy peaks around 15 eV for both channel.

FIG. 29. Photoelectron-photoion energy spectrum (left column) and kinetic energy release distribution (right column) of two dissociative double ionization channels. Top row is for $C_2H_6 \rightarrow H_3^+ + C_2H_3^+ + e + e$ channel, bottom row is for $C_2H_6 \rightarrow CH_3^+ + CH_2^+ + e + e$ channel. The small tail at low KER of $CH_3^+$ channel comes from false coincidence events.
3.2.2 Angular distribution of photofragments of ethane produced in circularly polarized light

Angular distribution of photofragments is a valuable source of information to understand both the photoionization process and the dynamics of the dissociation. To construct the angular distribution, following procedure is performed: (1) Only the photofragments from dissociative double ionization are selected, i.e., momentum conservation is applied to two-ion events ($\text{CH}_3^+ + \text{CH}_3^+$ or $\text{H}_3^+ + \text{C}_2\text{H}_5^+$). (2) Center slice of 40 atomic units (a.u.) in momentum space is chosen, and only the outer ring in the momentum plane is selected. For example, to plot $\text{H}_3^+$ angular distribution in YZ plane, the range of $\text{H}_3^+$ momentum in X direction is limited to -20 a.u. to 20 a.u.; the range of $\text{H}_3^+$ momentum magnitude in YZ plane is 30 a.u. to 50 a.u.

![Diagram of laboratory-frame illustration](image)

FIG. 30. Laboratory-frame illustration

Fig. 30 illustrates how the axes in the laboratory frame are designated. X axis is given to the laser beam, Y axis to molecular beam, and Z axis is the time-of-flight axis. The polarization plane of the circularly polarized light is YZ plane.
FIG. 31. Momentum angular distribution of $CH_3^+$ from dissociative double ionization of ethane by circularly polarized intense laser field. Top: YZ plane (laser polarization plane), middle: XY plane, bottom: XZ plane. Left column is the momentum image. The vertical blank strip in momentum image in YZ and XZ plane is due to dead time of detecting two (same mass) methyl cation. Right column is the corresponding angular distribution.
FIG. 32. Momentum angular distribution of $H_3^+$ from dissociative double ionization of ethane by circularly polarized intense laser field. Top: YZ plane, middle: XY plane, bottom: XZ plane. Left column is the momentum image. Right column is the corresponding angular distribution $r_\alpha$. The angular distribution in YZ plane is isotropic. It should be noted that the blank vertical strip around $P_z =$
in the YZ momentum plane is due to dead time when detecting two same-mass ions ($CH_3^+$). The same situation happens in the XZ plane. In XY and XZ plane, the angular distribution is peaked around Y and Z axis respectively, which indicates parallel transition and axial dissociation.\(^{84}\)

$H_3^+$ angular distributions are shown in Fig. 32. The distribution in YZ plane is also isotropic. In XY and XZ planes, the distribution doesn’t peak around the Y or Z axis.

### 3.2.3 Effects of laser power and polarization

In pursuit of more evidence, we then study the effects of laser power and polarization on two dissociative double ionization channels of ethane. First, we try to find their effects on the channel ratio between $H_3^+$ channel and $CH_3^+$ channel.

**TABLE 1.** Laser power and polarization dependence of the ratio between $H_3^+$ channel and $CH_3^+$ channel

<table>
<thead>
<tr>
<th>Power</th>
<th>$N_{H_3^+}$</th>
<th>$N_{CH_3^+}$</th>
<th>$N_{H_3^+}/N_{CH_3^+}$</th>
<th>$N_{H_3^+}$</th>
<th>$N_{CH_3^+}$</th>
<th>$N_{H_3^+}/N_{CH_3^+}$</th>
<th>$1 - \frac{N_{H_3^+}/N_{CH_3^+}(C)}{N_{H_3^+}/N_{CH_3^+}(L)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45mW</td>
<td>26948</td>
<td>50361</td>
<td>53.51%</td>
<td>327</td>
<td>1026</td>
<td>31.9%</td>
<td>40.4%</td>
</tr>
<tr>
<td>60mW</td>
<td>41395</td>
<td>70509</td>
<td>58.71%</td>
<td>12119</td>
<td>29872</td>
<td>40.57%</td>
<td>30.9%</td>
</tr>
<tr>
<td>70mW</td>
<td>33113</td>
<td>50835</td>
<td>65.14%</td>
<td>7157</td>
<td>15444</td>
<td>46.34%</td>
<td>28.9%</td>
</tr>
</tbody>
</table>

**TABLE 1** lists the number of the events of $H_3^+$ ($N_{H_3^+}$) and $CH_3^+$ ($N_{CH_3^+}$) channels at different power and laser polarization and the calculated channel ratios. Last column is the double ionization suppression ratio by circularly polarized
light at different power. \( C \) and \( L \) refers to circularly and linearly polarized light, respectively.

**FIG. 33.** (Color) Laser power and polarization dependence of the ratio between \( H^+_3 \) channel and \( CH^+_3 \) channel. Star: Linear light. Square: Circular light

The trend (Fig. 33) is that higher laser power leads to more \( H^+_3 \) dissociation channel, which suggests that different ethane dication electronic states are responsible for two different dissociative double ionization channels. Linear light leads to more \( H^+_3 \) dissociation channel than circularly polarized light. Circular polarized light tends to suppress non-sequential double ionization so less ethane dication were available for dissociation.
FIG. 34. Channel suppression ratio ($H_3^+$ to $CH_3^+$ channel) by circularly polarized light.

It is also found that the higher the laser power, the less the circularly polarized light can suppress $H_3^+$ channel than it can suppress $CH_3^+$ channel (Fig. 34). This also confirms that different ionic states are needed to dissociate to $H_3^+$ channel and $CH_3^+$ channel, and that the electronic state of precursor ethane dication that leads to $H_3^+$ dissociation channel is at higher energy level than the other.

We then examine the effect of the laser ellipticity and laser power on the double ionization to single ionization ratio in strong laser field. The laser ellipticity is defined as $E_y/E_z$ and calculated as $\sqrt{I_y/I_z}$, where $I_y$ is the measured laser intensity in Y axis and $I_z$ the laser intensity in Z axis. Calculated double ionization events only consist of $CH_3^+$ channel and $H_3^+$ channel. There are other double ionization channels, for example, $C_2H_6 \rightarrow H + H_2^+ + C_2H_3^+ + e + e$, but these
channels are much weaker. Calculated single ionization events only consist of $C_2H_6^{1+}$. Ethane single ion dominates in the 1D ion spectrum.

**TABLE 2.** Effect of laser ellipticity on the ratio of double ionization to single ionization

<table>
<thead>
<tr>
<th>Ellipticity</th>
<th>$N_{C_2H_6^+}$</th>
<th>$N_{H_3^+}$</th>
<th>$N_{CH_3^+}$</th>
<th>$N_{H_3^+}/N_{C_2H_6^+}$</th>
<th>$N_{CH_3^+}/N_{C_2H_6^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>344429</td>
<td>15866</td>
<td>32201</td>
<td>4.606%</td>
<td>9.349%</td>
</tr>
<tr>
<td>0.27</td>
<td>636723</td>
<td>24261</td>
<td>50882</td>
<td>3.810%</td>
<td>7.991%</td>
</tr>
<tr>
<td>0.40</td>
<td>878012</td>
<td>16880</td>
<td>40620</td>
<td>1.923%</td>
<td>4.626%</td>
</tr>
<tr>
<td>0.59</td>
<td>639970</td>
<td>5853</td>
<td>15998</td>
<td>0.9146%</td>
<td>2.500%</td>
</tr>
<tr>
<td>0.73</td>
<td>755720</td>
<td>7862</td>
<td>17417</td>
<td>1.0409%</td>
<td>2.305%</td>
</tr>
<tr>
<td>0.85</td>
<td>953149</td>
<td>7157</td>
<td>15444</td>
<td>0.7509%</td>
<td>1.620%</td>
</tr>
</tbody>
</table>

TABLE 2 lists the number of the events of $H_3^+$ and $CH_3^+$ channels at different ellipticity and the calculated double ionization to single ionization ratio. $N_{C_2H_6^+}$ is the number of non-dissociative single ionization. The laser power is set at 70 mW. The effect of laser ellipticity (Fig. 35) follows the principle of suppression of double ionization by elliptical polarized light.65
FIG. 35. (Color) Effect of laser ellipticity on the ratio of double ionization to single ionization of ethane in intense laser field. The laser power is 70 mW. Circle: $H_3^+$ channel; Star: $CH_3^+$ channel; Square: Sum of $H_3^+$ and $CH_3^+$ channel.

The effect of laser power (TABLE 3 and Fig. 36) confirms the laser intensity dependence of double ionization to single ionization ratio.

TABLE 3. Effect of laser power on the double ionization to single ionization ratio

<table>
<thead>
<tr>
<th>Power (mW)</th>
<th>$N_{C_2H_6^+}$</th>
<th>$N_{H_3^+}$</th>
<th>$N_{CH_3^+}$</th>
<th>$N_{H_3^+}/N_{C_2H_6^+}$</th>
<th>$N_{CH_3^+}/N_{C_2H_6^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 (CP)</td>
<td>662634</td>
<td>327</td>
<td>1026</td>
<td>0.0493%</td>
<td>0.155%</td>
</tr>
<tr>
<td>60 (CP)</td>
<td>5617152</td>
<td>12119</td>
<td>29872</td>
<td>0.216%</td>
<td>0.532%</td>
</tr>
<tr>
<td>70 (CP)</td>
<td>953149</td>
<td>7157</td>
<td>15444</td>
<td>0.751%</td>
<td>1.62%</td>
</tr>
<tr>
<td>45 (LP)</td>
<td>941071</td>
<td>26948</td>
<td>50361</td>
<td>2.8635%</td>
<td>5.3515%</td>
</tr>
<tr>
<td>60 (LP)</td>
<td>1069967</td>
<td>41395</td>
<td>70509</td>
<td>3.8688%</td>
<td>6.5898%</td>
</tr>
<tr>
<td>70 (LP)</td>
<td>429867</td>
<td>33113</td>
<td>50835</td>
<td>7.7031%</td>
<td>11.826%</td>
</tr>
</tbody>
</table>
FIG. 36. (Color) Effect of laser power on the double ionization to single ionization ratio. Red: Linear polarized light; Purple: Circularly polarized light. Circle: $H_3^+$ channel; Star: $CH_3^+$ channel; Square: Sum of $H_3^+$ and $CH_3^+$ channel

### 3.3 Conclusions

Although we couldn’t find the correlation between photoelectron kinetic energy and photo-ion kinetic energy release in dissociative double ionization of ethane, we do result in finding out that $H_3^+$ channel and $CH_3^+$ channel originates from different ethane dication electronic states. The obtained angular distribution of $H_3^+$ and $CH_3^+$ also provides experimental references for further theoretical understanding of ejection of $H_3^+$ from ethane by intense laser field radiation.
CHAPTER 4 ORBITAL ALIGNMENT IN PHOTODISSOCIATION PROBED USING STRONG FIELD IONIZATION

The photodissociation of molecules often produces atomic fragments with polarized electronic angular momentum, and the atomic alignment, for example, can provide valuable information on the dynamical pathways of chemical reaction unavailable by other means. In this work, we demonstrate for the first time that orbital polarization in chemical reaction can be measured with great sensitivity using strong field ionization by exploiting its extreme nonlinearity.

4.1 Introduction

A non-statistical $m_l$ (magnetic quantum number) distribution in atoms (an aligned or oriented sample) can be produced in photodissociation process depending on the potential energy surfaces on which the dissociation evolves. This atomic orbital polarization reflects the excited state symmetry, coherence effects, and non-adiabatic transitions during the photodissociation process, which have been the research subject of great interest in many systems. Conventionally, they are measured using ion imaging techniques, core-sampled time-of-flight, fluorescence detection, Doppler spectroscopy and absorption spectroscopy, which are based on linear spectroscopy or low-order non-linear spectroscopy. Resonance enhanced multi-photon ionization (REMPI) in combination with ion imaging is the preferred method to probe orbital alignment and orientation. The sensitivity of REMPI probe arises from the density matrix dependence of the excitation function (for example, a 2-photon resonance
transition gives access to polarization moments up to rank 4). An extreme extension of REMPI detection is the strong field ionization (SFI), where the laser intensity reaches $10^{13} \, \text{W/cm}^2$. In the strong field ionization regime, the perturbative treatment, which was the foundation of the theory of REMPI, becomes invalid. However, the theory of tunneling ionization predicts a rather simple form of the ionization rate for atoms in a strong field:\textsuperscript{98-100}

$$w \propto \left( \frac{(2l + 1)(l + |m_l|)!}{2^{|m_l|}|m_l|!(l - |m_l|)!} \right) \left( \frac{3F_0}{\pi F} \right)^{1/2} \left( \frac{2F_0}{F} \right)^{2n-|m_l|-1} e^{-\frac{2F_0}{3F}},$$ \hspace{1cm} (7)

where $F$ is the laser electric field strength, $F_0 = (2E_l)^{3/2}$, $E_l$ is ionization potential, and $n, l, m_l$ is the principal quantum number, total orbital angular momentum quantum number and magnetic quantum number, respectively. It can be easily seen that the ionization rate is strongly dependent on the magnetic quantum number $m_l$. For example, with a laser intensity of $2 \times 10^{13} \, \text{W/cm}^2$ and ionization potential of 9.2 eV ($l = 2$), the ionization rate of $|m_l| = 0$ is 15 times higher than that of $|m_l| = 1$ and 723 times higher than that of $|m_l| = 2$. With such a high sensitivity to $m_l$, strong field ionization should be able to probe some weakly aligned or polarized atoms and thus provide new detailed information on the dynamics of photodissociation of molecules. Previously, this sensitivity has been utilized to produce noble gas cations with unequal $m_l$ distribution and then such alignment was probed by absorption spectroscopy.\textsuperscript{96-97, 101} van der Hart\textsuperscript{102} invoked this $m_l$ dependence of ionization rate to interpret the double photodetachment rate in negative ions. It is also worth pointing out that Eq. (7) will break down in an ultra-
strong laser field \((10^{16} - 10^{21} \, \text{W/cm}^2)\), due to \(m_l\) state scrambling by the laser field.\(^{103}\)

Previously, SFI probe has been exploited in the study of photodissociation of \(Br_2\) by monitoring the electron rearrangement.\(^{104-105}\) Here we demonstrate a new application of SFI by probing the atomic polarization in sulfur atoms produced in the photodissociation of ethylene sulfide (\(C_2H_4S\)) and carbonyl sulfide (\(OCS\)). By rotating the polarization of the probe laser electric field for photofragments recoiling with a particular velocity, we map out the shape of the electron density of the sulfur atoms. If orbital polarization or alignment is present, the electron cloud anisotropy will be revealed in the angular dependent ionization rate, and the degree of anisotropy reflects the \(m_l\) distribution.

### 4.2 Experiment section

The experimental setup is similar as the "raster imaging" method developed by Suits and co-workers.\(^{57}\) The technique was initially developed to record photofragment signals with selected recoil speed and angle employing REMPI probe. The setup is shown in Fig. 37 and the major components are described here. The photolysis laser (193 nm, \(~20\) ns) was generated by an ArF excimer system running at 100 Hz (GAM EX10/300), and the pulse energy was \(~0.2\) mJ. This beam was focused loosely onto the molecular target using an \(f = 50\) cm lens. We displaced the probe laser downstream from the photolysis laser about a few millimeters, and also off-axis from the molecular beam to avoid strong background from the parent molecules ionization and thus minimize the space charge effect. A pulsed supersonic molecular beam of gas sample seeded in helium was produced
by bubbling the carrier gas through ethylene sulfide (Sigma-Aldrich, 98%) in an ice bath and then expanded into the source chamber. Neat OCS sample was used without seeding.

FIG. 37. Schematic illustration of the experimental setup

After passing through a skimmer, the beam was intersected at right angles by the two counter-propagating laser pulses. The polarization of the photolysis light was horizontal and also parallel to the detection plane. The linear polarization of 193 nm laser was achieved by passing the polarized beam through a total of eight fused silica windows set at Brewster’s angle. For OCS, due to its very small absorption cross section at 193 nm, we used the unpolarized UV beam directly to
get enough signal level. This will effectively reduce the observed anisotropy of angular dependence ionization rate. A femtosecond Ti:sapphire amplified laser system (800 nm, 1 kHz, KMLabs, Wyvern 1000) producing 1 mJ pulse was used as the probe laser, and the pulse duration was 45 fs. The laser intensity at the focal spot was estimated to be around \(2 \times 10^{13} \text{ W/cm}^2\). After ionization by the strong field, the sulfur ions were extracted by the multi-lens velocity mapping electrode assembly and impacted upon a two-dimensional detector after flying through a 1-meter long time-of-flight tube. The resulting signal was recorded by a CCD camera in conjunction with the IMACQ acquisition program. We used a half-wave plate to rotate the polarization of the probe laser. We averaged over several datasets for each half-wave plate angle to minimize the effects of fluctuations in experimental conditions. We also calibrated the system using water background present in the chamber to further suppress the inherent systematic (windows and lens) anisotropy that could interfere with the measurement. In the experiment, we chose to probe the fastest sulfur atom recoiling along the polarization of the photolysis laser. This was easily implemented by moving the probe laser away from both the molecular beam and photolysis laser, as illustrated in Fig. 37. At fixed photolysis/probe time delay (typically a few microseconds), the spatial displacement of probe from photolysis region defined the laboratory-frame fragment velocities that could be detected. It was also straightforward to select the fragments with a different velocity vector (recoil angle and speed) by changing the distance between the photolysis and probe laser.
4.3 Results

The angular dependent ionization yield of sulfur atoms from photodissociation of \( C_2H_4S \) and \( OCS \) at 193 nm are shown in Fig. 38. It is clear that the sulfur atoms are indeed aligned in both cases.

![Graph](image)

**FIG. 38.** Angular dependent strong field ionization yield of sulfur atom produced from photodissociation of (a) ethylene sulfide (b) carbonyl sulfide at 193 nm. The red curves are the fitted results (see fitting method in the main text).

We note that in our setup, the strong field laser does not interact directly with the molecular beam and will not induce any alignment effect in the parent molecules.\(^{106}\) Therefore, the observed orbital alignment can only arise from the photodissociation process. In order to extract the population of each magnetic sublevel \( m_\ell \), the angular distribution of ion yield is fitted with "basis" function, which
are angular dependent ionization probabilities associated with each extreme population. For sulfur atom \((^1D_2, l = 2)\), there are three extreme cases, i.e.,

\[
P(|m_l| = 0) = 1; \sum P(|m_l| = 1) = 1; \sum P(|m_l| = 2) = 1
\]  
(8)

(where \(P\) is the population of a specific magnetic sublevel with respect to the recoil direction. In this study, the recoil direction is parallel to the polarization axis of the photolysis laser).

FIG. 39. Basis functions: the angular dependent ionization probabilities

Basis functions as a function of the angle between the polarization axes of photolysis and probe laser are computed by integrating the ionization rate of each \(m_l\) state (calculated from eq. 7) over the laser intensity envelop in time-domain and then transforming the density matrix using a rotation matrix. The overall fitting equation is written as

\[
l(\theta) = \sum_{|m_l|} a_{|m_l|} f_{|m_l|}(\theta),
\]  
(9)
\[ f_{|m_i|}(\theta) = D_{|m_i|}(\theta) \cdot \int w(F(t), l, |m_i|) dt , \]

where \( I(\theta) \) is the measured angular dependent ion yield, \( a_{|m_i|} \) is the population coefficient of each extreme case, \( F(t) \) is the time dependent laser electric field including a Gaussian envelop. \( D_{|m_i|}(\theta) \) is the density matrix at the angle \( \theta \) transformed with a rotational matrix. Volume integration is not performed because it does not affect the relative ion yield. It is also worth pointing out that the laser intensity should be kept relatively low in order to avoid ionization saturation and loss of sensitivity. In this study, the off-diagonal elements of the density matrix reflecting the coherence effect are ignored. This treatment is reasonable because the coherence effect is very small relative to the value of the population in most systems. The obtained \( m_i \) populations of ethylene sulfide and carbonyl sulfide are shown in Fig. 40. For both molecules, the population at \( m_i = 0 \) is dominant, which implies that the recoil velocity is perpendicular to the total orbital angular momentum.

FIG. 40. Extracted \( |m_i| \) distributions of sulfur atom \( ^1{D_2} \) from photodissociation of (a) ethylene sulfide (b) carbonyl sulfide. The right portion of each figure is the constructed electron charge cloud of the sulfur atom showing small degree of alignment along the pump laser polarization.
The non-equilibrium $m_l$ population can be used to construct the electron charge cloud,\textsuperscript{107} corresponding to the alignment of the total orbital angular momentum. It should be noted that the charge cloud obtained here always has cylindrical symmetry (a prolonged or oblate shape along the recoil axis) since the off-diagonal terms in the density matrix are not considered. The constructed electron clouds are shown in Fig. 40.

### 4.4 Discussion

#### 4.4.1 The photodissociation of ethylene sulfide

The photodissociation dynamics of ethylene sulfide at 193 nm has been studied previously using a vacuum ultraviolet (UHV) ionization probe.\textsuperscript{108-109} Reaction branching ratios between different product channels were measured and excited states were identified from these studies. The orbital alignment of sulfur atoms ($^1D_2$) has been investigated using DC slice imaging with a REMPI probe by Townsend et al.\textsuperscript{90} The polarization study revealed that sulfur atoms are dissociated from multiple potential surfaces with predominant parallel transition to a single potential surface of $^1A_1$ (transition to $4p_x$ Rydberg orbital). The measured degree of alignment was small. Our alignment results agree well with this: a preferable low $m_l$ state alignment indicating the involvement of the perpendicular transition to the vibrationally excited $4p_z$ Rydberg state. However, the magnitude of alignment signal (a strong modulation (~10\%) on the ionization rate) in our experiment is about 6 times higher than that in previous ion imaging studies. This illustrates the high sensitivity of this approach to orbital polarization of atomic photofragments.
The presence of another product channel $S(^3P) + C_2H_4(^1A_g)$ with the $S(^1D_2)$: $S(^3P)$ branching ratio of 1.4:1 could complicate the picture. Further experiments collecting the spectra of above threshold ionization electron will help identify which state is aligned, exploiting the different ionization potentials of $S(^1D_2)$ and $S(^3P)$.

### 4.4.2 Photodissociation dynamics of carbonyl sulfide

Carbonyl sulfide has been an interesting system for studying the dynamics and associated atomic orbital polarization in the dissociation process.\textsuperscript{110-113} Suzuki et al.\textsuperscript{110} reported that the excitation to the $2^1A'$ (parallel transition) and $1^1A''$ (perpendicular transition) states are both involved in the main dissociation process via conical intersections with $A'$ and $A'' (1\Pi)$ states, leading to rotationally hot CO and $S(^1D_2)$ asymptotic products. Lee et al.\textsuperscript{113} reported a thorough study of the orientation and alignment of sulfur atoms ($^1D_2$) at 193 nm employing high-resolution imaging technique. Using the reported alignment anisotropy parameters of the sulfur atom with the fastest velocity, we can construct the density matrix and compare it with ours. It appears that their studies measured a peak population at $|m_t|=1$. This discrepancy could be due to the following reasons: (1) As commented in their paper,\textsuperscript{113} it is possible that the higher order moment (hexadecapole moment) was overestimated. If only a quadruple moment was considered, the population distribution did show a peak at $|m_t|=0$, consistent with our results. The electron charge cloud shows a slight elongation along the recoil direction, as seen in Fig. 40. (2) It is known that the dominant channel at 222 nm is $S(^1D_2) + CO (^1\Sigma^+)$ with ~6% yield of $S(^3P)$.\textsuperscript{112} However, the production of $S(^3P)$ at 193 nm has not
been reported. A significant amount of $S(^3P)$ could cause the additional angular modulation in our results, even though we assume the negligible yield of $S(^3P)$ state in our analysis. (3) Another possible explanation for this discrepancy is polarization averaging by the unpolarized photolysis light we used instead of linearly polarized light. With unpolarized light, the higher order moment would more easily dissipate.

In this study, the SFI probe provides no information on coherence effects (off-diagonal matrix elements), which are also very important for understanding the underlying dynamics such as non-adiabatic transitions among multiple potential surfaces. Photoelectron angular distribution from aligned atoms might provide information on this.\textsuperscript{114} On the other hand, because of the intrinsic ultrashort pulse duration employed in SFI, it is possible to study time-resolved dynamical processes that affect polarization/depolarization of the atomic fragments. Traditionally with the ion imaging method, such information is inferred from the alignment/orientation measurement. A potential issue is the uncertainty of the laser intensity in the interaction region, which is essential to calculate the sensitivity matrix (basis functions). In this study, we estimated the laser intensity from the laser power and focal spot size. Methods\textsuperscript{115} do exist to measure the intensity very accurately so this would not be a major issue if quantitative analysis is needed.

4.5 Conclusions

We reported the first application of strong field ionization in the study of atomic alignment in photodissociation. Our results are in general agreement with previous measurements, showing that SFI is a sensitive probe of orbital
polarization. We believe SFI as a probe of atomic polarization will be a powerful tool for studying photodissociation dynamics due to its simplicity and high sensitivity relative to the conventional ion imaging method, which generally requires time-consuming measurement and complicated analysis. In addition, the ability of introducing radicals and short-lived species by photodissociation in our experiment also provides a new opportunity to study strong field dynamics in these chemically important species.
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Electron-electron interaction is an important and interesting research theme both in chemistry and physics. Experimental study of electron correlation is hindered by the long dead time (the time within which no more than two electrons can be detected) of electron detection system. We developed a new three-dimensional (3D) particle coincidence imaging system to remove this restriction. The detection system employs a new strategy: It uses a fast-frame camera to record positional information on 2D MCPs/phosphor detector (so the particle velocities in two dimensions can be measured); It utilizes a high-speed digitizer to pick up the signal from MCP lead, off-line analysis is performed on the waveform recorded by the digitizer to get time information (so the velocity in third dimension is measured) with best resolution and accuracy. This particle coincidence imaging system has three major breakthroughs: It achieved 0.64 ns dead time for electron detection; It’s also possible to have true zero dead with less than 1 ns TOF uncertainty; The best TOF resolution reaches 32 ps.
This detection system is then implemented in photoion-photoelectron coincidence detection apparatus to study electron correlation (the main goal) and dynamics in dissociative double ionization.

We also developed a new method to probe orbital alignment of atoms in photodissociation by strong field ionization.
AUTOBIOGRAPHICAL STATEMENT

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I was born to Guoping Lin and Huafang He in Changzhou City, Jiangsu Province, People’s Republic of China in 1987. I pursued my undergraduate study at University of Science and Technology of China (USTC) and received bachelor degree in chemistry in 2009. Then I continued science study in Dr. Wen Li’s research group in Department of Chemistry at Wayne State University in Detroit, United States. I have been a member of Dr. Li’s group since 2010 except the year of 2012.