Investigations of Two- and Three-Body Molecular Photodissociation Dynamics by Fast Beam Photofragment Translational Spectroscopy

by

Aaron Woods Harrison

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Committee in charge:

Professor Daniel M. Neumark, Chair
Professor Ronald C. Cohen
Professor Robert W. Dibble

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Investigations of Two- and Three-Body Molecular Photodissociation Dynamics
by Fast Beam Photofragment Translational Spectroscopy

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Abstract

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Fast beam photofragment translational spectroscopy is used to study the two- and three-body photodissociation dynamics of neutral molecules and molecular anions. With this method, a time- and position-sensitive coincident measurement of the dissociation products is made. This allows an accurate determination of the masses and populations of the available product channels as well as the corresponding translational energy release and photofragment angular distribution. This information provides insight into the branching ratios between the product channels and the potential energy surfaces involved in the dissociation mechanism. In addition, it is possible to elucidate three-body dissociation mechanisms (concerted vs. sequential) through the use of Dalitz plot analysis.

The details of the experimental apparatus are outlined in Chapter 2. Most importantly, the time- and position-sensitive detector utilized on the instrument has been recently upgraded to a delay-line detector from the previous CCD/PMT coincidence imaging detector. The principles of operation and the advantages of using this detector are discussed as well as the spatial and the translational energy resolution of the new detection system.

The photodissociation of the thiophenoxy radical (Chapter 3) was studied by preparing a fast beam of the thiophenoxide anion followed by threshold photodetachment to form the neutral radical. The fragmentation of thiophenoxy was investigated at 248, 193, and 157 nm. At each wavelength, this study revealed that following absorption to an excited state, there is internal conversion to the ground state potential energy surface followed by statistical dissociation. CS loss and SH loss are found to be the major dissociation pathways with a minor contribution from S loss. Electronic structure and RRKM calculations are employed to support the experimental data.
The three-body dissociation of ozone at 193 and 157 nm was investigated (Chapter 4). At 193 nm, this dissociation pathway is just barely accessible at this photon energy and is a relatively minor pathway (5.2(6)%). However at 157 nm, it is found that three-body dissociation constitutes 26(4)% of the total fragmentation. Dalitz plot analysis showed the three-body decay to occur through a concerted mechanism.

The three-body dissociation of the ion-molecule complex $\text{I}_2^-$(CO$_2$) was also examined (Chapter 5). Photodissociation of this complex is initiated by excitation of the $\text{I}_2^-$ chromophore to the repulsive A-state at 720 nm and B-state at 386 nm. The translational energy distributions showed excitation in the bending mode of CO$_2$ photofragment and provided an accurate measurement of the CO$_2$ binding energy ($218 \pm 10$ meV). An asynchronous-concerted three-body dissociation mechanism was evidenced through Dalitz plot analysis.
I dedicate this dissertation to the memory of my father.
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Chapter 1

Introduction

1.1. Photodissociation Dynamics

Photodissociation is a process by which a molecule absorbs a photon with energy in excess of one of the bond energies in the molecule and fragments in some way. These types of reactions are very important in gas phase chemistry including atmospheric and interstellar chemistry as well as the photochemistry of molecules in solution.

In addition, many chemical reactions occur by the collisional creation of an energized intermediate before going on to form new products i.e.,

\[ AB + C \rightarrow ABC^* \rightarrow A + BC, AC + B \quad (1.1) \]

As such, the photodissociation of ABC can represent a ‘half-reaction’ where there is formation of an excited molecular complex (ABC*) with a well-defined internal energy given by the photon energy. By investigating the photodissociation of ABC, information about the relative population of different product channels as well as the associated energetics and potential energy surfaces (PES) involved in the various reaction pathways can be obtained.\(^1\) Although, this analogy is most applicable to photodissociation reactions that involve internal conversion to the ground electronic state PES as most collisions don’t lead to formation of electronic excited states.

In general, photodissociation is initiated by excitation of a molecule to an excited state from its ground state conformation. The nature of the excited state PES will then determine the dynamics of the dissociation process and the ultimate products formed. In the simplest case, the excited PES is unbound with respect to one of the bonds in the molecule leading to an impulsive dissociation along this nuclear coordinate. This type of dissociation might be expected when exciting an electron from bonding to an anti-bonding orbital as is observed in the photodissociation of I\(_2^-\) described in Chapter 5.\(^2\)

A similar dissociation mechanism known as electronic predissociation also occurs along a repulsive reaction coordinate. However, in this case, absorption first occurs to an electronic state that is bound with respect to the dissociation coordinate (bound-bound transition) which is then followed by coupling to a repulsive state leading to dissociation. A textbook case of this type of dissociation is the predissociation of O\(_2\) (discussed further in Chapter 2) following excitation to the bound \(B^3\Sigma_u^-\) state\(^3\) and is one of the most important processes in the photochemistry of the Earth’s upper atmosphere.

While the previous two mechanisms involve dissociation along an excited state PES, it is also possible that following population of the excited state, there is internal conversion back to the ground state PES through a conical intersection. The excess energy is then funneled into the
vibrational degrees of freedom of the molecule leading to a highly, vibrationally excited molecule on the ground electronic state PES. The molecule can then dissociate in a statistical manner when enough energy accumulates in the reaction coordinate. Depending on the shape of the ground state PES, these reactions can be barrierless or there can be an exit barrier with respect to the formation of products. These types of dissociation mechanisms are characteristic of thiophenoxy photodissociation discussed in Chapter 3.

### 1.2 Photofragment Translational Spectroscopy

There have been many different experimental methods employed for studying molecular photodissociation such as laser-induced fluorescence, resonance-enhanced multiphoton ionization (REMPI), Doppler spectroscopy, etc. While these methods can provide product rotational and vibrational distribution as they have very high energy resolution and state-specificity, they often lack generality as many species cannot be conveniently probed in these ways.

A more general spectroscopic tool for investigating photodissociation dynamics is with the use of photofragment translational spectroscopy (PTS). To gain insight into the photodissociation dynamics of a given molecule, the translational energy of the photofragments \( E_T \) is measured which is given by the following conservation of energy relation:

\[
E_T = h\nu - E_{\text{int}}(\text{frag}) - D_o \quad (1.2)
\]

where \( h\nu \) is the photon energy, \( E_{\text{int}}(\text{frag}) \) is the internal energy of the photofragments, and \( D_o \) is the dissociation energy of the broken bond. Therefore, from a measurement of the translational energy, it is possible to determine thermodynamic quantities such as bond dissociation energies and heats of formation, as well as the product states for the photofragments from a given dissociation channel.

Furthermore, the appearance of the translational energy distribution is also directly related to the PES involved in the dissociation mechanism. First consider the case where dissociation occurs along a repulsive electronic excited state. Because these states are unbound along the reaction coordinate, there is very little redistribution of the available energy into the internal degrees of freedom of the energized molecule and instead almost all the excess energy is deposited into the translational energy of the products leading to a narrow \( P(E_T) \) distribution that peaks very near to the maximum available energy (Figure 1.1).
Figure 1.1. Potential energy surfaces for photodissociation on a repulsive excited state and the resulting translational energy distribution. Dashed line represents the maximum energy available for translation.

By contrast, if the dissociation occurs statistically on the ground state PES following internal conversion, there is substantial redistribution of the energy amongst the internal degrees of freedom of the molecule leading to deposition of much more energy into the internal energy of fragments. In turn, the $P(E_T)$ distribution is broader and peaks at an $E_T$ nearer to zero (Figure 1.2).

Figure 1.2. Potential energy surfaces for photodissociation following internal conversion to the ground state through a conical intersection (CI) and the resulting translational energy distribution. Dashed line represents the maximum energy available for translation.
Finally, angular distributions of the photofragments with respect to the dissociation laser polarization are also obtainable with this method. However, traditional PTS tends to be lower energy resolution than those methods mentioned above.

**1.2.1. Photofragment Translational Spectroscopy Techniques**

Experimentally, there are numerous ways in which PTS is performed. In two-particle fragmentation, it is only necessary measure the translational energy distribution of one of the fragments due conservation of momentum i.e.

\[ \sum_i m_i v_i = 0 \]  

Thus, if the fragment masses are known, it is sufficient to measure the velocity distribution of only one of the fragments for a complete picture of the photodissociation dynamics.

The original incarnation of PTS involved determining the translational energy release of the photofragments by measuring the time-of-flight (TOF) of one of the products using electron impact ionization mass spectrometry (EI-MS) at various scattering angles using a rotatable detector and/or molecular beam source. However, in recent years, photofragment imaging techniques have proven to be a very fruitful method for elucidating photodissociation dynamics. Here, one of the photofragments is ionized using REMPI (provided that the dissociation products are neutral) and is velocity-mapped (velocity map imaging; VMI) onto a 2D position-sensitive detector using ion optics. Analysis of the velocity-mapped images allows a straightforward determination of photofragment translational energy distributions as well as the angular distribution of the products.

While the other PTS methods involve the detection of a charged particle either with TOF-MS or VMI, the experiments detailed in this thesis make a coincident measurement of neutral particles arising from fragmentation. This is accomplished using a ‘fast beam’ (5-9 keV of kinetic energy) such that the high kinetic energy of the neutral particle is sufficient to cause an electron cascade on a microchannel plate (MCP). Laboratory frame energies of >1keV are necessary to obtain ~50% detection efficiency of the neutral particle.

In addition, our detection method makes use of a coincidence imaging technique where the relative position and arrival times from all particles arising from the photodissociation are detected using a time-and position-sensitive (TPS) detector. A schematic showing the laser-interaction region and the TPS detector (described in detail in Chapter 2) is shown in Figure 1.3.
As shown in Figure 1.3, a fast beam of some parent molecule, ABC, is intersected with a laser pulse, and those molecules that absorb and dissociate will recoil off the beam axis in accordance with conservation of momentum and strike the TPS detector while undissociated parent molecules are flagged with a beam block. With this type of detection scheme, it is possible to determine the fragment masses, translational energy release, and scattering angle for each dissociation event. This method also has the advantage that all dissociation channels can be investigated at once provided that the defect between the product masses is not too large. Mass ratios greater than ~10:1 lead to the light fragment scattering outside the field-of-view of the detector and the heavy fragment being flagged by the beam block. This constraint makes accurate measurements of hydrogen loss channels very difficult if not impossible.

1.3 Three-body Dissociation Dynamics

While the vast majority of photodissociation reactions involve fragmentation into two particles, there are some molecular systems that undergo three-body dissociation where there is cleavage two of the bonds in the molecule. This type of process was first observed in the photochemistry of acetone where the UV absorption can lead to the formation of CO and 2 methyl radicals. However, this has been observed in many common molecules such as sym-triazine, phosgene, and ozone.

A fundamental question with this type of fragmentation is whether both bonds break simultaneously or if there is cleavage of one bond leaving an excited intermediate that then undergoes a secondary dissociation step. As such, three-body dissociation mechanisms are divided into three types depending on the timescale between the bond breaking events: synchronous-concerted, asynchronous-concerted, and sequential.
In a synchronous-concerted dissociation, both bonds break simultaneously. Considering the simple example of atomization of a triatomic molecule, this would be akin to dissociating along a symmetric stretch coordinate. On the other hand, an asynchronous-concerted mechanism is characterized by breaking one bond followed by rapid cleavage of a second bond within a timescale on the order of a vibrational period ($10^{-15}$ s). Continuing with the example of a triatomic molecule, this would be similar to dissociating along an anti-symmetric stretching coordinate. Finally, there is the purely sequential dissociation mechanism. In this case, the first bond breaks leaving a long-lived intermediate that goes on to dissociate on the timescale of rotational period ($10^{-12}$ s).

Elucidating the mechanism by which three-body dissociation reactions is a difficult task experimentally. However, by making a coincident measurement of all three photofragments, we can gain insight into the three-body dissociation mechanism with the aid of Dalitz plot analysis. These plots represent the momentum partitioning between the three fragments i.e.,

$$f_i = \frac{|p_i|^2}{\sum |p_i|^2} \quad (1.4)$$

Each of three momenta can then be graphed in a ternary plot giving the diagram shown in Figure 1.4.

![Figure 1.4. Dalitz plot showing configurations of the momentum vectors in different regions of the plot.](image)

Figure 1.4 is the form of the Dalitz plot used in this dissertation, although, there are different methods of plotting these variables that may be encountered that are also referred to as Dalitz plots. Within the ternary plot, conservation of energy requires all point to lie within the triangle while conservation of momentum further requires all points to lie within the inscribed circle. The circle is centered at the point ($\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$) which is equal momentum.
partitioning between the three fragments and has a radius of $\frac{1}{3}$. Thus, the largest fraction of the momentum that one particle can carry is $\frac{2}{3}$, and other points along the edge of the inscribed circle correspond to collinear fragmentation in various geometries. Indicated within the inscribed circle in Figure 1.4 are pictures of the 3 momenta vectors in different regions of the Dalitz plots.

The populated regions and patterns within the Dalitz plot provide information about three-body decay and allow some classification of the dissociation mechanisms to one of the three possibilities described above. For instance, sequential decay is characterized by constant momentum in one of the fragment with randomization of the momentum between the other two fragments. This is due to the fact that the long-lived intermediate can rotate well away from the orientation of the first dissociation essentially decoupling the final two momenta vectors from the initial dissociation step. This type of dissociation mechanism appears as a line of constant momentum in the Dalitz plot and was observed in the three-body decay of the $I_2Br^-\bar{19}$ where there is first loss of $Br^-$ followed slow dissociation of the nascent $I_2$ fragment. Dalitz plots and the other possible dissociation mechanisms will be discussed in detail in Chapters 4 and 5 in the three-body dissociations of $O_3$ and $I_2^-(CO_2)$, respectively.

1.4. References

Chapter 2

Experimental Apparatus

2.1. Coincidence Imaging Fast Beam Photofragment Translational Spectrometer

In general, the goal of this project is to study the photochemistry of neutral radical species. This is accomplished by taking advantage of the fact that radicals, being open-shell molecules, will often form stable, valence-bound anions that can be mass-selected unlike neutral radicals (though O\(_3\) discussed in Chapter 4 has a singlet ground state, it is considered a diradical). The neutral radical of interest can then be formed by photodetaching the corresponding anion with a tunable dye laser and using a second laser to dissociate the neutral molecule i.e.,

\[
\text{ABC}^{-} \rightarrow h\nu_1 \rightarrow \text{ABC} \rightarrow h\nu_2 \rightarrow \text{AB+C} \quad (2.1)
\]

Ideally, the photon energy used for photodetachment is as close to the electron affinity as possible such that the neutral radical has is formed with very little internal energy. However for some molecules, such as O\(_3\), there are limitations that don’t allow near threshold detachment such as low detachment cross-section and/or direct photodissociation of the anion. In some cases, the species of interest is an anion rather than a neutral radical such as I\(_2\)(CO\(_2\)) (Chapter 5) making the detachment step unnecessary. These experiments are simpler in that they are one photon experiments.

The experiments described in this dissertation were performed using a fast beam photofragment translational spectrometer (often called ‘Fast Radical Beam Machine’ or simply FRBM). This instrument has been outlined in detail in previous publications\(^1,2\) and dissertations.\(^3,4\) A schematic of the instrument is shown in Figure 2.1.
Briefly, a sample precursor gas is introduced into the vacuum chamber using a pulsed valve (typical operating pressure $\sim 10^{-5}$ torr). The gas pulse then supersonically expands through a DC discharge assembly to generate anions. In addition, the gas pulse pulse may be intersected with $\sim 1$ keV electron beam from a home built electron gun to either increase or stabilize the amount of ion of interest produced. The resulting anion packet then passes through a 1 mm skimmer and enters the acceleration stack where the anions are accelerated to a high laboratory-frame energy (5-9 keV). Mass-selection of the anion of interest is achieved with a Bakker-type beam modulation mass spectrometer that imparts negligible kinetic energy spread to the ion beam. This is necessary as kinetic energy spread in the ion beam will degrade the ultimate translational energy resolution of the instrument.

From here, the mass-selected anion (corresponding to the neutral radical of interest) is photodetached with a laser pulse from a tunable dye laser, thereby generating a fast beam of the neutral radical species. Following detachment, a deflection plate with a constant voltage of $\sim 1$ kV is used to remove any residual anions from the beam. The neutral species then enter the dissociation region where they are intersected by a second laser pulse from an excimer laser or in some cases, the fundamental or frequency-doubled output from a dye laser. Photodissociated molecules recoil off the beam axis and travel $\sim 2$ m downstream and strike a time- and position-sensitive (TPS) detector. While undissociated parent molecules are flagged by a beam block and go undetected. The TPS detector is very important part of this instrument and will be discussed in detail in Section 2.4.

While much of the instrument remains unchanged from previous dissertations, there have been several changes and upgrades to the instrument that will be described here. Most importantly, FRBM has entered its third generation of time- and position-sensitive detectors with the replacement of the previous CCD/PMT detection scheme with a Roentdek Hexanode delay-line detector (DLD). The new DLD was used for the experiments described in Chapters 3 ($\text{O}_3$) and 4 ($\text{C}_6\text{H}_5\text{S}$), while the investigation of the three-body dissociation of $\text{I}_2$ ($\text{CO}_2$) (Chapter 5) were performed using the previous CCD/PMT setup. In addition, there have been
changes to the anion source as well as the laser system used for anion photodetachment.

2.2. Anion Source

Previously, this instrument made use of a piezoelectric valve to introduce the sample gas into the vacuum chamber. This valve functioned well but did suffer from some stability issues in the course of long, multi-hour experiments that are common with FRBM. This valve setup has now been upgraded to an Even-Lavie solenoid valve. This valve operates more reliably and also allows the use of higher stagnation pressures which leads to more effective cooling in the supersonic expansion of the gas. Typical backing pressures employed on our instrument range from 100-200 psi. Pulse widths for the valve can also be varied, but a pulse width of approximately 100 μs usually gives the best ion signal.

The new Even-Lavie valve is also equipped with a DC grid discharge assembly that was optimized on the slow electron velocity map imaging (SEVI) instrument in our research group. This setup consists of two stainless steel grids separated by a thin Teflon spacer (~1 mm) to keep them electrically isolated. One of the grids is grounded while a constant voltage of 500 – 1000V is applied to the other grid through a variable resistor such that when the gas pulse from the valve passes through the grids, a discharge occurs.

2.3. Laser Systems

Due to a flooding incident in our laboratory that ruined an excimer laser and the dye laser it pumped, we acquired a used SpectraPhysics Quanta Ray Nd:YAG laser from the liquid jet project in our group. Currently, the 532 nm second harmonic output of this laser (30 Hz, 250 mJ/pulse) is used to pump a Radiant Narrowscan dye laser which has a tunable range out to 900 nm. While this system doesn’t permit tunable output below 532 nm unlike the previous 308 nm excimer-pumped system (without second harmonic generation), this setup does give substantially better dye efficiency and output in the red and near-infrared part of the spectrum. This is very useful for photodetachment as many species of interest have electron affinities < 2 eV. In addition, there are plans to replace the QuantaRay laser with a Litron Nd:YAG laser (LPY 742-100) capable of producing 200 mJ/pulse at 100 Hz. This will allow faster data acquisition and reduce experimental runtime.

2.4. Roentdek Hexanode Delay-Line Detector

2.4.1. Time- and Position-Sensitive Detectors

The most significant change to instrument has been the replacement of the previous CCD/PMT setup for time- and position-sensitive particle detection with a Roentdek delay-line detector. This detector offers several improvements over the previous detection scheme.

With CCD/PMT setup, photofragments would strike a Z-stack of microchannel plates (MCPs) that were coupled to a phosphor screen. The resulting electron cascade leads to photoemission from the phosphor screen, and these photons would pass through a 50/50 beam splitter transmitting half the intensity to a CCD camera and reflecting half the intensity to 4x4 PMT anode array. The CCD camera would take a picture of the phosphor screen for accurate position measurement (~50 μm), while the PMT array would provide approximate position information and accurate timing information. Approximate position information from the PMT would then be used to place the appropriate PMT for the position of the photon. This setup has several issues such as the need for a high power laser and limited tunability. The Roentdek delay-line detector eliminates these issues by using a delay-line to position the photofragments on a single PMT, providing more accurate and detailed information.
array is necessary such that the correct arrival time is associated with the correct particle position. However, this introduces some limitations into this detection scheme. For a dissociation event to be analyzed, it is required that each spot recorded by the camera must uniquely correspond to the approximate position indicated by one of the 16 PMT anodes e.g. for a two-body dissociation event, each particle must correspond to a distinct PMT anode and be in agreement with the rough position information obtained from the PMT array. Events where the camera sees 2 particles but there is only one PMT anode activated must be discarded. This requirement enforces the limitation that 2 particles must be sufficiently separated for analysis.

While this requirement is virtually always satisfied for two body dissociation due to the equal and opposite momentum scattering of the two photofragments, this is certainly not the case for three-body dissociation where the kinematics are substantially different. In this case, it is required that three distinct anodes are activated that correspond to each of three particles seen by the camera. However, small inter-particle separations are far more common in three-body dissociation resulting in many more events being discarded. An example of such a situation is shown in Figure 2.2.

![Figure 2.2. Depiction of a) retained and b) discarded three-body dissociation event with the CCD/PMT detector.](image)

In addition to these restrictions, the CCD/PMT setup is much more complicated than the DLD requiring many more detection components and back-end electronics as well as a delicate alignment procedure for the camera and PMT for proper function. The DLD, on the other hand, is much simpler with both the position in the timing information being obtained from the detector assembly directly. A brief description of the principle of operation of delay-line
detectors and how the position and timing information are obtained will be provided herein. However, much more information can be found in the Roentdek Hexanode delay-line detector manual\textsuperscript{9} as well as numerous other publications.\textsuperscript{8,10,16,17} Interested parties are directed to those resources for a wealth of information on the operation of and data acquisition from these detectors.

2.4.2. Basic Operation Principles of Delay-Line Detectors

The basic principle of how the delay-lines make a position determination is by utilizing the fact that the end-to-end transit time for signal on a wire (the delay-line) is a constant which is referred to as the ‘time-sum’ ($T_{\text{sum}}$ varies slightly for the different layers but is \(\sim110\) ns). Thus, for electrons collected at some point along the delay-line, the relative arrival time for this signal at each end of the delay-line can be measured and used to determine the particle position along a given axis. And with this information from two delay-line layers, an (x,y) coordinate for the particle position can be determined. This principle is illustrated in Figure 2.3 using the simple case of a two-layered DLD where the two layers are oriented at 90° in the traditional Cartesian fashion.

![Pictorial representation of position determination with a delay-line (red circle represents charge cloud).](image)

In this configuration, the (x,y) position can be calculated with the following equations:

\[
X = (t_{x1} - t_{x2}) \cdot v_{x}^\perp \\
Y = (t_{y1} - t_{y2}) \cdot v_{y}^\perp
\]  

(2.2)  

(2.3)

where the $t_{x,y}$’s are the arrival times of the signal at each end of a given layer, and the $v_{x,y}^\perp$ are the perpendicular velocities for each layer. Because the velocity of the electrons along/parallel to the delay-line is virtually the speed of light, the velocity of interest is the rate at which the signal moves in the direction perpendicular to the winding direction of the delay-line i.e. in Figure 2.3a, this layer would provide the particle position in the vertical (y) dimension even though the wires are wound horizontally.
Figures 2.3 also indicates another important aspect of these detectors which is that the red circle representing the electron charge cloud is actually spread over adjacent parts of the wound delay-line. This is shown more explicitly in Figure 2.4:

![Diagram of charge cloud spread over delay-line](image)

**Figure 2.4** Schematic showing how different parts of the charge cloud are collected on the delay-line.

Although each part of the charge cloud that is collected on adjacent parts of the delay-line produces a signal pulse, there is dispersion of the electrons as they transit the delay-line such that the signals merge into a single, broader signal pulse when they reach the end of the delay-line. While it seems that this would severely impact the position resolution of the detector, this effect is largely cancelled out when taking the difference of the measured arrival time of the merged signal. This ‘center-of-mass’ averaging results in a position resolution (discussed further in Section 2.4.6) that is not dependent on the pitch distance (~ .5 mm) between the collecting tracks of the delay-line.\(^8,^{10}\)

### 2.4.3 Position Determination from Roentdek Hexanode

There are a few different flavors of delay-line detectors (also referred to as delay-line anodes). Our laboratory specifically makes use of the Roentdek Hexanode that consists of three layers of delay-lines staggered at 60° with respect to one another. In our setup, there is a Z-stack of MCPs (Hamamatsu, 75 mm diameter, L/d = 40:1) mounted on top of the three-layered hexanode. When an impinging particle strikes the MCP stack, there’s an electron cascade that produces a charge cloud that exits from the back MCP. This charge cloud then travels a very short distance (~ 1cm) where it is collected by the delay-lines. A schematic of the hexanode is shown in Figure 2.5.
Figure 2.5 Schematic of three-layered hexanode depicting axes for each the u, v, and w layers.

For the hexanode, the three layers are labelled u, v, and w, and the position along each axis is determined in the same manner as described for the two-layer anode i.e.

\[ u = (t_{u1} - t_{u2}) \cdot v_u \quad (2.4) \]
\[ v = (t_{v1} - t_{v2}) \cdot v_v \quad (2.5) \]
\[ w = (t_{w1} - t_{w2}) \cdot v_w + o \quad (2.6) \]

where o is an offset to ensure a common center for the three-layers.\(^8,9\)

In contrast to the two-layer example shown above, the hexanode uses a hexagonal coordinate system that can be transformed into Cartesian coordinates using the following equations:

\[ X_{uv} = u \quad (2.7) \]
\[ Y_{uv} = \frac{1}{\sqrt{3}}(u - 2v) \quad (2.8) \]
\[ X_{uw} = u \quad (2.9) \]
\[ Y_{uw} = \frac{1}{\sqrt{3}}(2w - u) \quad (2.10) \]
\[ X_{vw} = (v - w) \quad (2.11) \]
\[ Y_{vw} = \frac{1}{\sqrt{3}}(w - v) \quad (2.12) \]
While the hexanode uses a less intuitive coordinate system, it offers experimental redundancy in that any of the two layers can be used to make a (x,y) position-determination in instances where signal from one layer is lost for some reason or in the case where there are overlapping signals at the end of the delay line due to signal from two different particles propagating on the delay-line at once. This latter case is particularly important to consider for our experiment as it is a ‘coincident’ experiment where we require accurate position and timing information for all particles arising from a dissociation event to calculate the kinetic energy release of the dissociation. A diagram showing how this situation may arise is shown in Figure 2.6.

![Dissociation event](image)

**Figure 2.6** Dissociation event that would lead to overlapping signals at one end of the delay-line.

As the total signal transit time across an entire delay-line is ~ 110 ns (i.e. the $T_{\text{sum}}$), it is possible for particles whose relative arrival times are less than this value to have overlapped signals at one end of the delay-line as shown in Figure 2.6. In these cases, the redundant signal readout allows position determination from the other layers and reduces the ‘dead zone’ for these detectors.

### 2.4.4 Timing Information from Roentdek Hexanode

As of yet, how the relative arrival time of particles is determined has not been discussed, but this is much simpler conceptually than the position determination of the particles as the arrival time is just taken directly from the MCP stack. In our detection scheme, we gate the detection window (1 μs) using an external trigger, so the TOF is measured with respect to this trigger. The most important aspect here (as with CCD/PMT setup) is associating the correct particle arrival time with the correct position. In the case where the $\Delta t_{\text{pp}}$ (the relative arrival times of the particles) is greater than $T_{\text{sum}}$, there is no ambiguity and all signals corresponding to the first particle will arrive before any of the signals for the subsequent particle.

If the $T_{\text{sum}} > \Delta t_{\text{pp}}$, a consistency check is required for correct correspondence between the arrival time of the particle and its position. Since time zero is defined with respect to an external trigger, the TOF can also be calculated from:

$$\text{TOF} = T_{u1} + T_{u2} - T_{\text{sum}} = T_{v1} + T_{v2} - T_{\text{sum}} = T_{w1} + T_{w2} - T_{\text{sum}} \quad (2.13)$$

Here, the $T_{i,n}$ is the arrival time of the delay-line pulses with respect to the external trigger. As the TOF distribution is centered in the 1 μs detection window, these values would be in the range of 400 – 600 ns (typical time-of-flight distributions span a few hundred nanoseconds).
It’s worth noting here that there can be a terminology discrepancy depending on whom you talk to (for instance Roentdek technicians). From our point of view, we always consider our measurements as ‘coincident’ even if the relative arrival times are larger than $T_{\text{sum}}$ i.e. dissociation events where the particles relative arrival times is longer than the signal dwell time on the anode. Since there is only ever signal for one particle propagating on the detector in these cases, the detector is essentially operating in a ‘single-particle’ regime, and only instances where $\Delta t_{\text{pp}} < T_{\text{sum}}$ are considered truly coincident from that point of view.

2.4.5 Mask Calibration

For the Roentdek Hexanode DLD, the manual has recommended voltage settings for the MCP stack, the delay-line anode, and part of the detector referred to as the ‘holder’. To ensure proper propagation of the electron charge cloud from the back MCP to the hexanode, the holder must be biased at some intermediate voltage with respect to the back MCP potential ($+2400$ V) and the anode potential ($+2750$ V). This voltage needs to be optimized using a calibration mask such that the image linearity across the detector can be evaluated. If this voltage is not set properly, the charge clouds can be radially distorted resulting in an image that appears stretched or compressed.

To perform this calibration, the mask must be mounted over the front MCP. The mask patterning consists of many rows and columns of 400 $\mu$m holes separated by 1 mm (rows and columns are spaced every 5 mm). The ion gauge in the detector region of the instrument generates a sufficient number of particles to ‘illuminate’ the mask such that a distinct mask image can be collected in a relatively short amount of time (~30 min.). Two examples of such an image are shown in Figure 2.7 a) and b) at holder voltages of $+2550$ and $+2360$ V, respectively.

![Figure 2.7 Detector mask images at holder voltages of a) $+2550$ V and b) $+2360$ V.](image-url)
It’s clear from these images that when the holder voltage is set exactly intermediate between the back MCP and anode potential (Figure 2.7a), the image is radially distorted appearing compressed at the edges of the detector. However, when the holder potential is actually set at a slightly lower voltage than the back MCP (Figure 2.7b), the image looks much better is very linear across the entire field-of-view of the detector. Further mask experiments indicated that the image isn’t overly sensitive to the holder voltage but that it should be set in the range of +2350-2400 V to minimize the distortion of the image.

### 2.4.6 Electronics and Pulse Shapes for Roentdek Hexanode

Detailed descriptions of the signal processing electronics can be found Roentdek’s website where there are detailed manuals for all the components. Briefly, MCP and delay line signals are sent to a fast amplifier (FAMP8, Roentdek)\(^{18}\) and transformed to standard NIM pulses using a constant fraction discriminator (CFD8, Roentdek).\(^ {19}\) Finally, these NIM pulses are fed into a time-to-digital convertor (TDC8HP, Roentdek)\(^ {20}\) to be written into on-board memory.

The pulse shapes at each step of the signal processing can be easily monitored using an oscilloscope. A sample oscilloscope trace for one end of one of the delay-line layers is shown in Figure 2.8 for reference for future users.

![Figure 2.8 Sample oscilloscope trace for the signal processing from one end of a delay-line.](image)

The top trace is the output from the FAMP8 following amplification (~x55) and inversion of the signal from the delay-line. This signal is fed into CFD8 where a fraction of the signal (standard setting is 0.35) is split off from the rest of the signal and inverted. The main signal is then delayed (~5 ns) and added back to the inverted signal to give the bipolar signal in the second trace. The zero-crossing point of this signal can then be used to make a timing
determination that doesn’t jitter with varying input pulse heights (unlike leading-edge discrimination). The third trace is another intermediate signal from the CFD referred to as the digital monitor and indicates the zero crossing point of the bipolar signal. These signals lead to the production of the digital NIM pulse in bottom trace that is clocked by the TDC8HP for a timing determination. Roentdek estimates the overall timing resolution of this instrumentation to be 100 ps.

2.4.7. Position Resolution

There are a couple of ways in which to estimate the position resolution of our detection system. Since the position is ultimately determined from the accuracy of the \( T_{\text{sum}} \), the position resolution can be estimated from the width of the \( T_{\text{sum}} \) multiplied by the perpendicular velocity for the delay line. In Figure 2.9, a sample time-sum distribution (centered at zero) fitted to a Gaussian distribution is shown.

![Figure 2.9. Sample time sum spectrum (centered at zero) for delay-line anode (black) fitted with a Gaussian curve (red).](image)

From the Gaussian fit, the full-width half-max (FWHM) is found to be \( \sim .390 \) ns. Using this value and the perpendicular velocity for this layer, \( v = .3385 \) mm/ns (Note: the FWHM and \( v \) vary only slightly between the different layers), the spatial resolution is estimated to be \( \approx 130 \) \( \mu \)m.

Another way to estimate the spatial resolution is to consider the deviation between the three possible combinations in which the particle can be determined (uv, uw, and vw) defined as

\[
dR = \sqrt{\Delta x^2 + \Delta y^2} \quad (2.14)
\]

Where \( \Delta x \) and \( \Delta y \) are the deviation in the measured position for different combinations of the delay-line layers. This distribution is plotted in Figure 2.10.
From this plot, a FWHM \(\approx 75 \text{ \mu m}\) is obtained indicating a spatial resolution in good agreement with the time-sum method of finding the spatial resolution. Considering the two values, the position resolution of the detector is confidently estimated to be on the order of 100 \(\text{\mu m}\).

2.4.7. \(\text{O}_2\) Calibration and Energy Resolution

The predissociation of \(\text{O}_2(B^3\Sigma_u^-)\) is used as both a calibration system and to determine the translational energy resolution \((\Delta E_T/E_T)\) for this instrument.\(^{21}\) In this experiment, a specific vibrational level of the B-state of \(\text{O}_2\) is populated that then undergoes predissociation leading to the formation of 2 \(\text{O}(^3\text{P})\) in various combinations of spin-orbit states. These peaks allow both a calibration of the absolute translational energy release as well as a determination of the instrument’s ability resolve very closely spaced features in the translational energy release spectrum. As this experiment excites a specific vibrational transition, it removes the spectral broadening from the internal energy distribution of the \(\text{O}_2^-\) anions making it ideal for assessing the energy resolution of the instrument. Another important experimental aspect to consider is the kinetic energy spread of the parent beam as this will limit the ability to resolve closely spaced features. Since the ion compressor introduces kinetic energy spread into the parent ion beam, it is necessary that the compressor voltage is set to zero (or at the very least minimized). This leads to ion signal that is not very well collimated making this experiment more difficult.

For this experiment, \(\text{O}_2^-\) is photodetached well above its detachment threshold (\(E_A(\text{O}_2) = .45 \text{ eV}\)) such that you populate the entire Franck-Condon profile of the \(X^3\Sigma_g^-\) ground state of \(\text{O}_2\). There a few different transitions that can be used for this calibration experiment, but the \(v' = 2 \leftarrow v'' = 5\) at \(\lambda \approx 231.65 \text{ nm}\) was selected for ease (better doubled laser power and absorption cross-section). The most well-resolved translational energy distribution obtained from this experiment is shown in Figure 2.11.
Figure 2.11. Translational energy distribution resulting from predissociation of $\text{O}_2(B^3\Sigma_u^-) v' = 2$ with numbers in parentheses $(j_1,j_2)$ representing the spin-orbit states of the two $\text{O}(^3\text{P}_j)$ atoms.

In Figure 2.11, the peaks are labelled by the various combinations of spin-orbit states $(j_1,j_2)$ of the two resulting $\text{O}(^3\text{P}_j)$ atoms. Due to symmetry constraints the $(0,0)$ combination correlates to a gerade molecular state and is not populated in the predissociation of the $B^3\Sigma_u^-$ state. The two most intense peaks in the spectrum correspond to $j_1 = 2$ and $j_2 = 0,1$. The spacing of these two states is $\sim 8.5$ meV yielding a $\Delta E_T/E_T \sim .8\%$ under ideal conditions (i.e. very low or zero compressor voltage). This data was also collected using the longer, 2 m flight length for the photofragments, so this calibration must be re-done given the recent shortening of the instrument.
2.5. References

Chapter 3

Photodissociation Dynamics of the Thiophenoxy Radical at 248, 193, and 157 nm


3.1. Abstract

The photodissociation dynamics of the thiophenoxy radical (C₆H₅S) have been investigated using fast beam coincidence translational spectroscopy. Thiophenoxy radicals were produced by photodetachment of the thiophenoxide anion followed by photodissociation at 248 nm (5.0 eV), 193 nm (6.4 eV), and 157 nm (7.9 eV). Experimental results indicate two major competing dissociation channels leading to SH + C₆H₄ (o-benzyne) and CS + C₅H₅ (cyclopentadienyl) with a minor contribution of S + C₆H₅ (phenyl). Photofragment mass distributions and translational energy distributions were measured for at each dissociation wavelength. Transition states and minima for each reaction pathway were calculated using density functional theory to facilitate experimental interpretation. The proposed dissociation mechanism involves internal conversion from the initially prepared electronic excited state to the ground electronic state followed by statistical dissociation. Calculations show that SH loss involves a single isomerization step followed by simple bond fission. For both SH and S loss, C-S bond cleavage proceeds without an exit barrier. By contrast, the CS loss pathway entails multiple transition states and minima as it undergoes five membered ring formation and presents a small barrier with respect to products. The calculated reaction pathway is consistent with the experimental translational energy distributions in which the CS loss channel has a broader distribution peaking farther away from zero than the corresponding distributions for SH loss.
3.2. Introduction

Sulfur-containing molecules are a major constituent of both fossil fuels and biomass, and the combustion of these materials results in the emission of many sulfur oxide (SOₓ) pollutants. Gas phase reactions of sulfur-containing radicals are of particular importance as these highly reactive species can act as key intermediates in hydrocarbon combustion and have a major influence on the ultimate reaction products. It is thus of considerable interest to characterize the bond dissociation energies of these radicals and to identify the products from their unimolecular decomposition. Molecular beam photodissociation experiments provide a direct probe of the energetics and primary photochemistry of these species, thereby yielding a deeper understanding of their reactivity and their role in complex reaction mechanisms. Herein, we investigate the photodissociation of the thiophenoxy radical (C₆H₅S) using fast beam coincidence translational spectroscopy at 248, 193, and 157 nm.

This work is motivated in part by recent photodissociation experiments on the aromatic sulfur-containing compounds thiophenol (C₆H₅SH) and thioanisole (C₆H₅SCH₃). These species are important model systems for gaining a general understanding of the role played by conical intersections in dictating the photodissociation dynamics of aromatic molecules. Translational energy distributions for the H atom and CH₃ loss channels were determined using velocity map ion imaging and H-atom Rydberg tagging. From these distributions, one obtains the branching ratio between the ground state and first excited state of the thiophenoxy photofragment, thereby probing the non-adiabatic couplings among the parent electronic states as dissociation proceeds through various conical intersections.

While the kinetics and reaction mechanisms involved in the production of the thiophenoxy have been examined in some detail in the gas phase and in solution, the photochemistry of thiophenoxyl itself is less well-characterized. Experiments in solution have attributed two major absorption bands near 2.48 and 4.13 eV to thiophenoxyl with tentative assignments of the transitions involved. Further study of thiophenoxyl using laser-induced fluorescence following the photolysis of thiophenol and thioanisole found the origin of the first bright state to be 2.397 eV; this band was assigned to the B → A₂ − X → B₁ transition. Recently, slow electron velocity-map imaging of the thiophenoxyl anion has provided accurate values of both the adiabatic electron affinity (2.3542 eV) and the energy gap (0.3719 eV) between the A and X states of thiophenoxyl.

It is of interest to compare the thiophenoxyl radical to the more thoroughly studied phenoxy radical C₆H₅O. The thermal decomposition of phenoxy has been the subject of numerous experimental and theoretical studies owing to its central importance in the combustion of aromatic compounds. The only observed fragmentation pathway of phenoxy involves rearrangement of the ring system to form cyclopentadienyl radical (C₅H₅) and carbon monoxide (CO); it was determined that the mechanism for this reaction proceeds by initial formation of a bicyclic intermediate followed by the elimination of carbon monoxide from the remaining cyclopentadienyl ring. While this pathway presents a barrier to the formation of products, the thermodynamic stability of these products leads to a small ΔH° (~1 eV) for the overall reaction. Other possible dissociation channels such as hydroxyl radical and ortho-benzyn formation or oxygen loss to form phenyl radical and O
atom are substantially higher in energy (~ 5 eV) and do not compete with CO loss as a thermal decomposition channel.

The corresponding dissociation channels of thiophenoxy\(^{27,28}\) are much closer in energy:

\[
\begin{align*}
C_6H_5S & \rightarrow C_5H_5(\text{cyclopentadienyl}) + CS \quad D_o = 3.21 \pm 0.15 \text{ eV} \quad (3.1) \\
& \rightarrow C_6H_4(\text{o-benzyne}) + SH \quad D_o = 3.60 \pm 0.10 \text{ eV} \quad (3.2) \\
& \rightarrow C_6H_5 + S \quad D_o = 3.90 \pm 0.10 \text{ eV} \quad (3.3)
\end{align*}
\]

For cyclopentadienyl radical, the enthalpy of formation is still a topic of some controversy with a range of values from 2.5-2.8 eV reported in the last 30 years. More recent studies have favored the higher end of this range, and so to estimate the dissociation energy for equation 3.1, we used a value of 2.75 eV.\(^{29}\)

Herein, we report results on the photodissociation of the thiophenoxy radical at 248, 193, and 157 nm prepared by near-threshold photodetachment of the corresponding anion, thiophenoxide. We obtain translational energy and photofragment angular distributions, \(P(E_T, \theta)\), as well as branching ratios for the competing dissociation channels. These data indicate a statistical dissociation mechanism where absorption to an electronically excited state is followed by internal conversion to the ground state where dissociation occurs. In addition, we employ density functional theory (DFT) calculations and RRKM modeling to support our experimental findings.

### 3.3. Experimental

The fast beam coincidence translational spectrometer used in this study has been described in detail elsewhere,\(^{30,31}\) but a new detection system has been recently added and is discussed below. In this experiment, a fast beam of mass-selected thiophenoxide anions (\(C_6H_5S^-\)) is generated and photodetached to make thiophenoxy radicals. The radicals are dissociated by a second laser and the neutral fragments are detected in coincidence:

\[
C_6H_5S^- h\nu \rightarrow C_6H_5S \rightarrow \text{fragments} \quad (3.4)
\]

Here, a \(~0.1\%\) thiophenol/He mixture at 50 psi is expanded into the vacuum chamber through a pulsed molecular beam valve equipped with a DC discharge source to produce thiophenoxide anions. Resulting anions are then accelerated to a beam energy of 5 keV and mass-selected using a Bakker-type mass spectrometer\(^{32,33}\) that imparts negligible kinetic energy spread to the ion beam. Mass-selected thiophenoxide anions are then photodetached at 518 nm (2.394 eV) with an excimer-pumped dye laser (Lambda-Physik LPX-200 and Lambda-Physik FL 3002). This detachment energy is slightly above the electron affinity for thiophenoxo, 2.3542 eV,\(^{21}\) so as to minimize the production of vibrationally excited radicals. Those ions that remain are deflected from the beam, leaving behind a fast beam of neutral thiophenoxy radicals. This neutral packet is intersected by a UV pulse from a second excimer laser (GAM EX-50F) at 248 nm (5.0 eV), 193 nm (6.4 eV), or 157 nm (7.9 eV). Photofragments from dissociated radicals recoil off the beam axis and strike a time- and
position-sensitive (TPS) detector located 2 m downstream from the laser interaction region, while undissociated radicals are blocked by a 5 mm radius beam block in front of the detector.

We perform coincidence measurements in which the positions on the detector and differences of arrival times are determined for both photofragments from each dissociation event, thereby yielding the translational energy release, scattering angle, and photofragment mass ratio for each event.\textsuperscript{34,35} From these, we can construct the translational energy and photofragment angular distribution, $P(E_T, \theta)$, given by the following uncoupled relation

$$P(E_T, \theta) = P(E_T)[1 + \beta(E_T)P_2(\cos \theta)] \quad (3.5)$$

where $\beta$ is the energy-dependent anisotropy parameter and $P_2$ is the 2\textsuperscript{nd} order Legendre polynomial. For this experiment, $\theta$ is defined as the angle of the dissociation recoil axis with respect to the laser propagation direction as the unpolarized output from our GAM excimer laser was used for photodissociation. In this case, $\beta$ takes on the values between -1 and $\frac{1}{2}$ for parallel and perpendicular transitions, respectively.\textsuperscript{36}

We have recently upgraded our TPS detection scheme to a Roentdek Hex80 delay line anode detector.\textsuperscript{37} Our previous TPS detector involved a microchannel plate (MCP) assembly with a phosphor screen and a CCD camera for accurate position measurement and 4x4 multianode PMT array for accurate timing and rough position information.\textsuperscript{31} The delay-line anode has the advantage of much simpler data acquisition and read-out while requiring fewer detection components and less alignment for operation. The previous setup also had some limitations on timing recognition of neighboring particle hits that were encoded by the same PMT anode. While uncommon with traditional 2-body dissociation, dissociation into three (or more) fragments\textsuperscript{38,39} can result in two fragments read by the same PMT anode, resulting in a discarded data point. However, the delay line anode allows more efficient collection of events with small inter-fragment separation.

The Roentdek hexanode and the principles underlying delay line detection have been described in detail elsewhere.\textsuperscript{37,40,41} The detector comprises a $Z$-stack of three 75 mm diameter MCPs with a 40:1 aspect ratio mounted to a delay-line anode consisting of three layers of delay lines. When an incident particle strikes the front MCP, an electron cascade is produced and the resulting charge cloud that emerges from the MCP stack is collected by the three-layered anode. Each layer comprises one delay line along which the end-to-end signal transit time is constant ($T_{\text{sum}} = 100$ ns). Measuring the relative delay between the arrival times $t_1$ and $t_2$ of the counter-propagating signal pulse at each end of the wire yields one dimension of the particle position e.g. $x \propto t_1-t_2$. From any two of the layers, the 2D position of the article is determined. The third layer offers redundant position information, minimizing the ‘dead zone’ of the detector and allowing for reconstruction of data points when signal is lost or overlapped at the end of the delay line. MCP and delay line signals are sent to a fast amplifier (FAMP, Roentdek) and consecutively transformed to a standard NIM pulse using a constant fraction discriminator (CFD8, Roentdek). Finally, these NIM pulses are fed into a time-to-digital converor (TDC8, Roentdek) to be written into on-board memory. The position and time resolution are estimated to be 100 ps and 100 $\mu$m, respectively. Based on calibration experiments using the predissociation from the $B$ state of O$_2$,\textsuperscript{42} the kinetic energy resolution...
(ΔE/E) is measured to be ~ 0.8%.

In our experimental setup, the presence of the beam block and the finite radius of the detector lead to lower detection efficiency and larger error in the measured intensity for events with very low and high translational energies; this effect depends on the photofragment scattering angle as well. To account for these effects, the raw translational energy distributions are adjusted with a detector acceptance function (DAF). The P(E_T) distributions and branching ratios presented here have all been corrected using the DAF.

3.4. Results and analysis

3.4.1. Photofragment Mass and Translational Energy Distributions

Using conservation of momentum, the product mass ratio is determined from the measured distance of the two fragments from the dissociation center at the detector. This leads to a fragment mass resolution that is mainly dependent on the diameter of the parent beam at the detector. The radical beam is on the order of 1 mm at full width half maximum (FWHM) yielding a fragment mass resolution (m/Δm) of ~10.

Due to the relatively low mass resolution on the photofragments, we examined the photodissociation of both C6H5S and C6D5S to better differentiate between S and SH loss. Figure 3.1 shows product mass distributions at 248 nm (5.0 eV), 193 nm (6.4 eV), and 157 nm (7.9 eV) for both the undeuterated and deuterated species with Table 3.1 listing the corresponding contributions for each mass channel and dissociation wavelength. For the undeuterated species, these distributions have peak masses near 44 + 65 (mass channel B) corresponding to CS loss (equation 1) and 33 + 76 (mass channel A). Mass channel A is

![Figure 3.1](image_url)
Table 3.1. Relative contributions of mass channels A and B for C₆H₅S and C₆D₅S at each dissociation wavelength. Error in these values is estimated to be ± 1%.

closer in mass to the SH loss channel (equation 3.2) but could also be due to S loss (equation 3.3) or some mixture thereof. If SH loss is the major dissociation channel, the peak for the lightest photofragment in the mass distribution of the deuterated species should shift to slightly higher mass. However for S loss, this peak’s position should be relatively unchanged. In Figure 3.2, the mass distributions for the lighter photofragment of mass channels A and B are overlaid at each wavelength for C₆H₅S and C₆D₅S. We observe a small shift to higher mass for mass channel A, while for mass channel B the peak position is unchanged. This observation is consistent with SH/SD and CS formation. Furthermore, there is also a small isotope effect where deuteration leads to less population of mass channel A by comparison to the undeuterated species.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>C₆H₅S: Mass Channel A</th>
<th>C₆H₅S: Mass Channel B</th>
<th>C₆D₅S: Mass Channel A</th>
<th>C₆D₅S: Mass Channel B</th>
</tr>
</thead>
<tbody>
<tr>
<td>248 nm</td>
<td>23%</td>
<td>77%</td>
<td>18%</td>
<td>82%</td>
</tr>
<tr>
<td>193 nm</td>
<td>48%</td>
<td>52%</td>
<td>42%</td>
<td>58%</td>
</tr>
<tr>
<td>157 nm</td>
<td>59%</td>
<td>41%</td>
<td>53%</td>
<td>47%</td>
</tr>
</tbody>
</table>

Figure 3.2. Overlays of the mass spectra for the light photofragments of C₆H₅S (black) and C₆D₅S (red) at a) 248 nm, b) 193 nm, and c) 157 nm.

27
To gain more insight into the relative contributions of SH and S loss to mass channel A, the mass distributions at each wavelength were simulated using the experimental conditions and translational energy distributions (discussed below) with varying contributions of the possible product masses. At 248 and 193 nm, the best fit is obtained using mostly SH/SD, but the intensity of mass channel A is very low at 248 nm leading to more error in the simulation. At 157 nm, better fits are obtained when using approximately 2.5:1 of SH to S. A sample simulation is included in the Supporting Information (Sec. 3.9.1) with estimations of the branching ratios obtained from this method. In addition, kinetics calculations discussed in Section 3C further indicate that SH loss dominates over S loss at 248 and 193 nm and that S loss becomes more competitive at 157 nm.

It is clear that for both C₆H₅S and C₆D₅S, CS loss (mass channel B) dominates at 248 nm, but SH/SD loss (mass channel A) is much more prominent at 193 nm. At 157 nm, the combination of SH and S loss in mass channel A has more population than the CS loss channel. Based on the relative contributions of the two mass channels listed in Table 3.1, we find the branching ratio of mass channels A:B to be 0.30:1, 0.92:1, and 1.44:1 for dissociation at 248, 193, and 157 nm, respectively. While for C₆D₅S, the branching ratios are slightly smaller at every photon energy with values of 0.22:1, 0.72:1, and 1.13:1.

Figure 3.3 shows the corresponding translational energy distributions for each fragment mass channel and dissociation wavelength. From energy conservation, the translational energy release of the photofragments, Eₜ, is given by the following relationship:

$$E_T = h\nu - E_{\text{int}} - D_o$$  \hspace{1cm} (3.6)

where h\nu is the photon energy, E_{\text{int}} is the internal energy of fragments, and D_o is the bond dissociation energy. Eq. 3.6 assumes that the precursor radicals have no internal energy, a reasonable assumption since the anions are photodetached just above threshold (Section 3.3).

![Figure 3.3](image)

**Figure 3.3** Translational energy distributions (normalized) of (a) SH + C₆H₅⁻ and (b) CS + C₅H₅⁻ dissociation channels at 248 (red), 193 (black), and 157 nm (blue).
Because SH and S loss are unresolved in the mass distributions, we cannot make distinct translational energy distributions for the two product channels. As such, mass channel A is treated as SH loss for the following analysis, but there is also a small contribution from S loss especially at 157 nm. Also, the translational energy distributions for these dissociation channels are expected to be similar because both channels lack an exit barrier (Section 3.4.2) and have nearly equal available energy.

At 248 nm, the maximum kinetic energy available to the fragments is 1.4 and 1.8 eV for the SH loss and CS loss channels, respectively. The translational energy distribution for the CS loss channel peaks at 0.22 eV and extends out to approximately 1 eV. For SH loss, the P(E_T) distribution peaks closer to zero (0.10 eV) and is sharper with virtually all of its intensity below 0.5 eV. Similarly, at 193 and 157 nm, the translational energy distribution for the CS loss channel is broader than that of the SH loss channel, but at the higher photon energies, the distributions are broader and extend out to higher translational energy than the corresponding distributions at 248 nm. The maximum available energy (E_T^{Max}), peak translational energy (E_T^{Peak}), average translational energy release (<E_T>), and the corresponding fractional average energy release <f_T> for each channel and dissociation energy are listed in Table 3.2. The translational energy distributions for deuterated thiophenoxy have not been included as they very similar to the undeuterated species. Finally, all angular distributions were found to be isotropic, yielding β(E_T) values approximately equal to zero within the experimental uncertainties.

<table>
<thead>
<tr>
<th>Photon Energy</th>
<th>E_T^{Max}</th>
<th>E_T^{Peak}</th>
<th>&lt;E_T&gt;</th>
<th>&lt;f_T&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH loss</td>
<td>5.0</td>
<td>1.4</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>2.8</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>4.3</td>
<td>0.15</td>
<td>0.35</td>
</tr>
<tr>
<td>CS loss</td>
<td>5.0</td>
<td>1.8</td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>3.2</td>
<td>0.30</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>4.7</td>
<td>0.35</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 3.2. Maximum available, peak translational, and average translational energy release with the corresponding fractional average energy release for both product channels and dissociation energies of 5.0 eV (248 nm), 6.4 eV (193 nm), and 7.9 eV (157 nm). All energies are in eV.
3.4.2. Electronic Structure Calculations

To gain further insight into the dissociation dynamics of thiophenoxy, electronic structure calculations of the unimolecular reaction intermediates and products involved in each reaction pathway were performed. Previous theoretical studies on the thermal decomposition mechanism of the phenoxy radical indicated the importance of high level electron correlation methods in reliably predicting the energetics of the isomeric intermediates along the thermal decomposition pathway. However, the relative energies of the transition states and intermediates calculated using DFT with the B3LYP functional gave reasonable agreement with higher level methods (RCCSD(T) and CASPT2) for phenoxy decomposition and also performed reasonably well in a theoretical study of the ground and first excited state of thiophenoxy.

For this study, all equilibrium structures and transition states were optimized with DFT-B3LYP using the Dunning-type cc-pVDZ basis set augmented with diffuse functions in Gaussian 09. Minima and transition states were confirmed by frequency analysis and by following the intrinsic reaction coordinate (IRC) with DFT. These calculations were followed by single point energy calculations on the optimized structures using restricted open-shell MP2 (ROMP2) with the aug-cc-pVTZ basis set. Single point calculations at the ROMP2/aug-cc-pVTZ level theory with the DFT geometries were found to order the asymptotic dissociation energies better than DFT, so we chose this level of theory to calculate relative energies of the minima and transition states for each reaction pathway. Figure 3.4 shows the lowest energy reaction pathways and calculated energetics, including harmonic zero-point energies for both channels.

![Figure 3.4](image-url)

**Figure 3.4.** Schematic of the potential energy surfaces for C₆H₅S dissociation channels. Energies (eV) are relative to thiophenoxy ground state and calculated at ROMP2/aug-cc-pVDZ + ZPE (B3LYP/aug-cc-pVDZ) level of theory.
As is the case for CO loss from phenoxy, there are two possible routes for CS loss. The more energetically facile mechanism proceeds via the bicyclic isomerization pathway (shown in Fig. 3.4) where the β carbons approach to form a new bond. The optimized geometries with C-C and C-S bond lengths (Å) along with the point group symmetries for the transition states and minimum energy structures for this reaction pathway are presented in Figure 3.5. In both Figures 3.4 and 3.5, the primary nuclear motion corresponding to the imaginary frequency is represented by the dotted bond. The higher energy pathway (not shown) occurs by direct ring opening through homolytic cleavage of the C-C bond of C1 with one of the β carbons. Our calculations indicate the initial transition state for ring opening pathway to be approximately 1 eV higher in energy than the bicyclic pathway. Experimental kinetics data and RRKM calculations confirm the lower energy pathway to be the preferred mechanism for phenoxy, so this is the mechanism we focus on here.

The first step of the CS loss mechanism involves a pericyclic reaction where 1 passes through the first transition state, TS1, calculated to be 2.65 eV above the ground state of thiophenoxy, and then isomerizes to the bicyclic intermediate 2 (2.43 eV). This is followed by bond extension between C1 and one of the β carbons of 2 to form TS2 (2.64 eV) as the C1-C2-C6 ring system begins to open. Continuing along this path results in bond cleavage, leaving C1 bound to only one of the original β carbons to form 3 (2.32 eV). Finally, the highest energy barrier occurs at TS3 (3.58 eV) as the CS moiety departs from the 5-membered ring to yield CS + C5H5. The dissociation energy for CS loss was calculated to be 3.37 eV, in comparison to the experimental value of 3.2 eV.

Figure 3.5. Optimized geometries for the minima and transition states for the CS and SH loss channels (See Fig. 4 for labeling). For all structures, C-C and C-S bond lengths (Å) and point group symmetries are shown. Dotted bond for transition states indicates the primary nuclear motion corresponding to the imaginary frequency.
For SH loss, a hydrogen atom from one of the β carbons of 1 approaches sulfur to form TS4 (2.40 eV) then completes isomerization to the thiol radical intermediate 4 (1.44 eV). From 4, C-S bond cleavage proceeds without barrier to produce SH radical and ortho-benzene at calculated dissociation energy of 3.74 eV slightly larger than the experimental value of 3.6 eV. The optimized structures for this pathway are also shown in Figure 3.5. Finally, S loss proceeds through a pathway with no exit barrier to C₆H₅ + S. The dissociation energy was determined to be 4.00 eV in good agreement with the experimental value of 3.9 eV.

3.4.3. RRKM Calculations

RRKM theory was used to model the relative kinetics for the competing dissociation channels. The RRKM rate constant, k(E), is given by

\[ k(E) = \frac{W^* (E-E_o)}{h \rho(E)} \]  

(3.7)

Here W* is the sum of states at the critical configuration with E₀ representing the relative energy of this configuration with respect to the reactant whose density of states is ρ(E). The sum and densities of states were evaluated using the Beyer-Swinehart algorithm for calculation of the rate constants. All modes other than the reaction coordinate for both channels were treated as harmonic vibrations whose frequencies were taken from the electronic structure calculations.

To find the overall unimolecular rate constant for CS loss, we treated the following reaction mechanism

\[ \begin{align*}
1 & \xrightleftharpoons[k_1]{k_{-1}} 2 \\
2 & \xrightarrow[k_2]{k_{-2}} 3 \\
3 & \xrightarrow[k_3]{k_{-3}} D1
\end{align*} \]  

(3.8)

by applying a steady-state approximation to the intermediates 2 and 3 (Figure 3.3). This analysis results in the following expression for the rate constant for CS loss

\[ k_{CS loss} = \frac{k_1 k_2 k_3}{k_1 k_2 + k_1 k_3 + k_2 k_3} \]  

(3.9)

SH loss was also treated by applying a steady-state approximation to following reaction mechanism,

\[ \begin{align*}
1 & \xrightleftharpoons[k_4]{k_{-4}} 4 \\
4 & \xrightarrow[k_5]{k_{-5}} D2
\end{align*} \]  

(3.10)

which yields the following expression for SH loss

\[ k_{SH loss} = \frac{k_4 k_5}{k_4 + k_5} \]  

(3.11)

To calculate the rate constants for k₅ and S loss, variational transition state theory (VTST) was used as these reaction pathways lack saddle points. For these calculations, the geometry
was reoptimized with corresponding harmonic vibrational frequencies at defined C-S bond lengths up to 4 Å. For both of these C-S bond cleavage reactions, the minimum rate was found near 3.5 Å which is approximately 2\(r_{\text{eq}}\). Using the equations above, the rate constants for each dissociation channel were calculated as a function of photon energy from 4.5 to 8 eV and are plotted in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6** Unimolecular rate constants (s\(^{-1}\)) for each dissociation channel as a function of photon energy (eV).

The rate constants for each channel at the experimental dissociation energies are listed in Table 3.3 along with the RRKM and experimental branching ratios. Values for the individual rate constants can be found in the Supporting Information (Sec. 3.9.2).

<table>
<thead>
<tr>
<th>Photon Energy</th>
<th>(k_{\text{CS}})</th>
<th>(k_{\text{SH}})</th>
<th>(k_{\text{S}})</th>
<th>SH+S:CS (RRKM)</th>
<th>Mass Channel A:B (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>3.2 x 10(^6)</td>
<td>1.2 x 10(^6)</td>
<td>7.7 x 10(^4)</td>
<td>0.40:1</td>
<td>0.30:1</td>
</tr>
<tr>
<td>6.4</td>
<td>4.4 x 10(^8)</td>
<td>6.1 x 10(^8)</td>
<td>4.0 x 10(^7)</td>
<td>1.48:1</td>
<td>0.92:1</td>
</tr>
<tr>
<td>7.9</td>
<td>4.6 x 10(^9)</td>
<td>1.1 x 10(^10)</td>
<td>1.4 x 10(^9)</td>
<td>2.69:1</td>
<td>1.44:1</td>
</tr>
</tbody>
</table>

**Table 3.3** Calculated RRKM rate constants (s\(^{-1}\)) for both dissociation channels and photon energies (eV) with corresponding theoretical and experimental product branching ratios.

### 3.5. Discussion

A primary goal of this study is to determine whether the photodissociation of thiophenoxy results in dissociation on an excited state or by decay via non-adiabatic interactions to the ground state followed by statistical dissociation. This question can be addressed by comparing experimentally derived P(E\(_T\)) distributions and product branching ratios to those expected for statistical decay.
At both dissociation energies, the $P(E_T)$ distributions peak at low translational energy that is significantly less than the maximum allowed $E_T$ for a given channel. This is characteristic of ground state dissociation as opposed to dissociation on a repulsive excited state, which often results in much higher fractional translational energy release.\textsuperscript{48} To test more quantitatively for statistical dissociation, the barrierless SH and S loss channels (mass channel A) can be modeled with a prior distribution\textsuperscript{49,50} using the following equation

$$P(E_T | E_{av}) \propto E_T^2 \rho_{vr}(E_{av} - E_T)$$  \hspace{1cm} (3.12)

where $E_{av}$ is the available energy above the dissociation threshold and $\rho_{vr}(E_{av} - E_T)$ is rovibrational density of states of the fragments. For the simple model used here, the rotational density of states was treated as a constant. For the vibrational degrees of freedom, a semi-classical approximation of the vibrational density of states\textsuperscript{46} was used. Though the translational energy distributions for mass channel A have contributions from SH and S loss, the prior distributions illustrate that the two channels will have similar translational energy release within a statistical interpretation. The calculated distributions shown in Figure 3.7 are in reasonable agreement with the experimental translational energy distributions.

\textbf{Figure 3.7} Calculated Prior Distributions for SH loss (blue) and S loss (red) at a) 248, b) 193, and c) 157 nm
For CS loss, the P(E_T) distributions are consistent with the presence of an exit barrier to the formation of the C_5H_2 and CS products, resulting in more of the available energy going into translation. We find that the highest energy transition state is the final transition state TS3 where the CS moiety departs from the cyclopentadienyl ring. **TS3** presents a calculated barrier of 0.21 eV with respect to products. The P(E_T) distributions for CS loss would then suggest that much of this energy goes into translation as is expected for the late “product-like” transition state found in the calculations.

The product branching ratios provide additional insight into the dissociation mechanism. It can be readily calculated within a statistical model using the RRKM calculations discussed in Section 3.4.3. Within this framework, the branching ratios will be a function of both vibrational frequencies of the transition state and the available energy above the reaction barrier for each channel. For both the SH and S loss reaction pathways, C-S bond cleavage proceeds through a ‘loose’ transition state where the C-S bond lengthens. This is in contrast to CS loss pathway where passage through an initial ‘tight’ transition state is necessary for the formation of products. Though the reaction barrier for SH and S loss channels is higher than that of CS loss, the loose transition state for SH and S loss leads to a k(E) that increases more rapidly as a function of the available energy.**49** Indeed, we find experimentally that the relative population of the CS channel decreases significantly with photon energy from 248 to 157 nm, where SH/S loss (mass channel A) becomes more favorable than CS loss (mass channel B).

This trend is well-reproduced in the RRKM calculations. The calculations indicate that the branching ratios between mass channels A and B are largely determined by the relative rates of the SH and CS loss (Table 3.3) and that S loss should be minor at 248 and 193 nm. However at 157 nm, S loss should be more competitive. This result is consistent with our simulations of mass distributions which suggest that mass channel A is mostly SH loss at 248 and 193 nm but approximately 30% S loss at 157 nm. For the deuterated species, there is a consistent kinetic isotope effect where population of the SD loss channel is less than that of SH at each photon energy. Deuteration likely has the most significant impact on k_4 where H/D must migrate from one of the β carbons to the sulfur atom to form the radical thiol intermediate prior to SH/SD dissociation.

At each of the wavelengths studied, the RRKM rates underestimate the contribution from CS loss in the measured branching ratios. Discrepancies in the calculated rates are likely due to error in the asymptotic energetics and in part to our assumption of harmonic vibrational modes for each dissociation channel. This assumption can be particularly problematic for the loose transition states associated with SH and S loss, since some vibrational modes might be better treated as hindered rotors.**51** Nonetheless, the overall comparison of the experimental P(E_T) distributions and product branching ratios with expectations from statistical dissociation strongly suggest that the photodissociation of thiophenoxy proceeds via ground state statistical decay.

This conclusion then raises the question of how the photoexcited radical eventually finds its way to the ground electronic state. The excited states involved are still somewhat unclear. It is likely that at 248 nm (5.0 eV), there is population of the $^3\Sigma^+_1$ state with a vertical excitation energy calculated to be approximately 4.2 eV.**44** This state has strong oscillator strength and is believed to be responsible for the observed absorption of thiophenoxy near...
300 nm. Given that this is a highly excited electronic state of thiophenoxy with a manifold of lower-lying excited states, there are likely to be facile non-adiabatic pathways to the ground state via one or more conical intersections, leading to rapid internal conversion to the ground state. Population of the ground state prior to dissociation is further supported by the angular distributions which were found to be isotropic at each photon energy. Unfortunately, there are no electronic excited states above 5 eV known for thiophenoxy that can be assigned to excitation at 193 nm (6.4 eV) and 157 nm (7.9 eV).

3.6. Conclusions

We have studied the photodissociation dynamics of thiophenoxy at 248, 193, and 157 nm by the means of fast beam coincidence translational spectroscopy. Our experiment yields the primary photochemistry for thiophenoxy photodissociation including the product branching ratios and translational energy distributions. SH loss and CS loss channels were identified as the major dissociation channels at each dissociation energy with S loss becoming more competitive at 157 nm. Electronic structure calculations show that on the ground electronic state, SH and S loss have no exit barrier with respect to final products. In contrast, the CS loss pathway, which occurs through multiple reactive intermediates and transition states, has a small exit barrier (0.21 eV) between the final transition state and separated products. The measured translational energy distributions and product branching ratios are consistent with internal conversion to the ground electronic state followed by statistical dissociation.

3.7. Acknowledgements

This research was supported by the Director, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors would like to thank Thorsten Weber and Ottmar Jagutzki for their advice in setting up the delay-line detector and Hunter Shunatona for synthesizing deuterated thiophenol.
3.8 References

3.9 Supporting Information

3.9.1 Simulations of photofragment mass distributions

**Figure 3.8.** Sample simulation of photofragment mass spectra at 157nm for C$_6$D$_5$S.

**Figure 3.9.** Estimated branching ratios obtained from simulating experimental mass distributions.
3.9.2. Individual rate constants for CS and SH loss

<table>
<thead>
<tr>
<th>Photon Energy</th>
<th>$k_1$</th>
<th>$k_{-1}$</th>
<th>$k_2$</th>
<th>$k_{-2}$</th>
<th>$k_3$</th>
<th>Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 eV</td>
<td>$4.29 \times 10^7$</td>
<td>$1.47 \times 10^{12}$</td>
<td>$2.08 \times 10^{12}$</td>
<td>$2.72 \times 10^{11}$</td>
<td>$1.64 \times 10^{10}$</td>
<td>$3.19 \times 10^6$</td>
</tr>
<tr>
<td>6.4 eV</td>
<td>$1.16 \times 10^9$</td>
<td>$2.45 \times 10^{12}$</td>
<td>$3.40 \times 10^{12}$</td>
<td>$5.49 \times 10^{11}$</td>
<td>$4.22 \times 10^{11}$</td>
<td>$4.36 \times 10^8$</td>
</tr>
<tr>
<td>7.9 eV</td>
<td>$9.01 \times 10^9$</td>
<td>$3.09 \times 10^{12}$</td>
<td>$4.31 \times 10^{12}$</td>
<td>$7.87 \times 10^{11}$</td>
<td>$2.31 \times 10^{12}$</td>
<td>$4.58 \times 10^9$</td>
</tr>
</tbody>
</table>

Table 3.4. Rate constants ($s^{-1}$) for reaction steps involved in CS loss channel

<table>
<thead>
<tr>
<th>Photon Energy</th>
<th>$k_4$</th>
<th>$k_{-4}$</th>
<th>$k_5$</th>
<th>Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 eV</td>
<td>$1.86 \times 10^8$</td>
<td>$1.81 \times 10^{10}$</td>
<td>$1.12 \times 10^8$</td>
<td>$1.15 \times 10^6$</td>
</tr>
<tr>
<td>6.4 eV</td>
<td>$3.16 \times 10^9$</td>
<td>$7.67 \times 10^{10}$</td>
<td>$1.85 \times 10^{10}$</td>
<td>$6.14 \times 10^8$</td>
</tr>
<tr>
<td>7.9 eV</td>
<td>$1.84 \times 10^{10}$</td>
<td>$1.89 \times 10^{11}$</td>
<td>$2.84 \times 10^{11}$</td>
<td>$1.10 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Table 3.5. Rate constants ($s^{-1}$) for reaction steps involved in SH loss channel
3.9.3. 308 nm data contaminated with multiphoton dissociation

We also collected photodissociation data at 308 nm (4 eV), however this data appears to be strongly contaminated by multiphoton dissociation. We found that the photodissociation cross-section was very low at this wavelength requiring a large amount of laser power to obtain reasonable fragmentation signal. The branching ratios measured at this wavelength were very inconsistent varying from 20-40% contribution from mass channel A with broad translational energy distributions. For completeness, we’ve included some of this data here.

![Figure 3.10](image1.png)  
**Figure 3.10.** Sample mass distributions from 308 nm with approximately a) 20% mass channel A and b) 40% mass channel A.

![Figure 3.11](image2.png)  
**Figure 3.11.** Sample translational energy distributions at 308 nm for a) SH loss and b) CS loss.
Chapter 4

Investigation of 3-fragment Photodissociation of O$_3$ at 193.4 and 157.6 nm by Coincident Measurements


4.1. Abstract

Photodissociation of the ozone molecule at 193.4 nm (6.41 eV) and 157.6 nm (7.87 eV) is studied by fast-beam translational spectroscopy. Coincident detection of the dissociation products allows direct observation of the 3-fragment channel and determination of its kinematic parameters. The results indicate that at each wavelength, 3-fragment dissociation proceeds through synchronous concerted bond breaking, but the energy partitioning among the fragments is different. The branching fraction of the 3-fragment channel increases from 5.2(6)$\%$ at 193.4 nm to 26(4)$\%$ at 157.6 nm, in agreement with previous studies. It is shown that vibrational excitation of the symmetric stretch mode in O$_3$ molecules created by photodetachment of O$_3^{-}$ anion enhances the absorption efficiency, especially at 193.4 nm, but does not have a strong effect on the 3-fragment dissociation.
4.2. Introduction

The photodissociation of ozone is arguably the most important reaction in the photochemistry of Earth’s atmosphere, as it provides a protective shield against harmful ultraviolet radiation from the Sun.¹ ² This protection arises from efficient absorption by ozone at wavelengths between 200 and 300 nm known as the Hartley band. Radiation within this spectral range would otherwise reach the Earth’s surface with detrimental effects to life, causing damage to DNA and other biomolecules.³ While the photochemistry of ozone has been studied extensively in this spectral region, its photodissociation at higher photon energies is less well-characterized, owing to the lower solar flux, coupled with the high absorption cross-section of molecular oxygen at \( \lambda < 200 \) nm.⁴ ⁵ As such, ozone absorption is considered less important at these wavelengths, but ozone does have a weak, unnamed absorption band between 150 and 200 nm.⁶ ⁷ In this study, we investigate the photodissociation of O₃ at 193.4 and 157.6 nm, with the specific goal of characterizing the 3-fragment O₃ \( \rightarrow \) 3 O channel. The photodissociation of ozone at 193 nm (6.4 eV) has been the subject of several experimental studies,⁸ ¹³ mostly regarding the dominant O₃ \( \rightarrow \) O₂ + O process. Two of these studies are of particular importance for the present work. Measurements of the quantum yield of both O(\(^3P\)) and O(\(^1D\)) atoms reported in Ref. ¹⁴ revealed a quantum yield greater than unity (1.20 ± 0.15). This result was attributed to a small contribution (≈12%) from 3-fragment dissociation of O₃ to form three O(\(^3P\)) atoms. This dissociation pathway becomes energetically available at \( \sim 6.2 \) eV (\( \lambda \leq 200 \) nm) and is thus just barely accessible at 193 nm (6.4 eV). It was also observed by photofragment translational spectroscopy⁹ at 193 nm as a very sharp feature at low translational energy. In that work, 3-fragment dissociation was estimated to be \( \sim 2\% \) of the total fragmentation.

Ozone photodissociation at wavelengths shorter than 193 nm has received very little experimental attention. In measurements⁸ of the O atom quantum yield at 157 nm, the 3-fragment dissociation channel has been found much more prevalent than at 193 nm, constituting about half of the total fragmentation at this wavelength. It was speculated that this process occurs in two stages involving the initial formation of a triplet O₂ intermediate with internal energy higher than the O–O bond energy, which then undergoes secondary dissociation.

Theoretical work related to photoexcitation beyond the Hartley band is also very scarce.⁷ ¹⁵ It is mainly devoted to the absorption cross-section and only briefly touches on the 2-fragment dissociation dynamics. Although the electronic states of O₃ lying in the relevant energy range correlate to the 3O(\(^3P\)) fragments, the 3-fragment dissociation channel has not been considered so far.

Three-fragment dissociation resulting from photoexcitation, charge exchange, or collisions has been observed in other molecules, such as H₃⁶ ¹⁷ and sym-triazine,¹⁸ directly or deduced from product distributions (see Refs. ¹⁹–²³ ¹⁹ ²³ for some examples). A central question in such processes is whether the dissociation occurs through a concerted pathway, in which both bonds break simultaneously, or by a sequential process, in which one bond breaks first, leaving a highly excited intermediate fragment that dissociates after some delay.¹⁹ This question is difficult to address with conventional, noncoincidence, experimental methods, as 3-fragment dissociation is not observed directly but rather inferred from measurements of only one of the fragments. However, fast-beam photodissociation experiments capable of making a time- and position-sensitive measurement of all three fragments in coincidence have proven successful in gaining additional insight into 3-fragment dissociation mechanisms.¹⁶ ²⁴
Although coincident measurements have been used to investigate 3-fragment dissociative recombination of the $O_3^+$ cation\textsuperscript{25} and the Coulomb explosion of ozone $O_3 \rightarrow h\nu O_3^3+ \rightarrow 3O^+$,\textsuperscript{26} the present work is the first fast-beam coincident study of 3-fragment photodissociation of neutral $O_3$. We obtained kinetic energy distributions and branching ratios between 2-fragment and 3-fragment dissociation channels at both 193.4 and 157.6 nm. With the aid of Dalitz plot analysis,\textsuperscript{27} we provide evidence for a concerted 3-fragment dissociation mechanism.

4.3. Experimental

The fast beam coincidence translational spectrometer used in this study has been described elsewhere.\textsuperscript{28-30} Briefly, neat $O_2$ at 7 bar backing pressure is expanded into a vacuum chamber through an Even-Lavie pulsed solenoid valve\textsuperscript{31} equipped with a DC discharge source to produce $O_3^-$. At the nozzle exit, the molecular beam is also intersected by a 1 keV electron beam from a home-built electron gun to increase the amount of $O_3^-$. Resulting anions are then electrostatically accelerated to a beam energy of 8 keV and mass selected using a Bakker-type mass spectrometer\textsuperscript{32,33} that imparts negligible kinetic energy spread to the ion beam. Mass-selected ozonide is then detached at 400 nm (3.10 eV) with an excimer-pumped dye laser (Lambda-physik LPX-200 and Lambda-physik FL 3002).

Ideally, a detachment energy just above the corresponding electron affinity of ozone (2.10 eV\textsuperscript{34}) would be preferred in order to create neutral molecules with as little internal energy as possible. However, near the photodetachment threshold, the relatively weak anion photodetachment is overwhelmed by $O_3^-\text{photodissociation}$, which leads to $O_2 + O^- (and O_2^- + O$ at $h\nu \geq 2.7$ eV) fragments.\textsuperscript{35,36} that contaminate the studied $O_3$ photodissociation products. Therefore, a significantly higher energy (3.10 eV), at which the photodissociation cross-section drops and detachment becomes more favorable,\textsuperscript{36} was used in the present work. This higher photodetachment energy results in population of $O_3$ vibrational levels up to the dissociation limit (1.06 eV) with a distribution determined by the Franck-Condon factors between the anion and neutral, similar to the distribution seen in the photoelectron spectrum of $O_3^-$.\textsuperscript{34}

Following detachment, the remaining ions are deflected from the beam yielding a fast beam of neutral ozone molecules (with some amount of neutral $O_2$ and O fragments). This neutral packet is then intersected by an ultraviolet (UV) pulse from a second excimer laser (GAM EX-50F) at either 193.4 nm (6.41 eV) or 157.6 nm (7.87 eV). Fragments from $O_3$ dissociation ($O_2 + O or 3O$) recoil off the beam axis and strike a time- and position-sensitive (TPS) detector located \textasciitilde2 m downstream of the photodissociation region, while undissociated parent molecules are blocked by a beam block (4 mm radius) in front of the detector.

The position and arrival time of each fragment are measured in coincidence for each dissociation event with a Roentdek Hex80 delay-line anode detector.\textsuperscript{37} The detector consists of a Z-stack of microchannel plates (MCP) (75 mm diameter, 40:1 aspect ratio) mounted in front of an anode comprising three layers of delay lines. After an impinging particle strikes the MCP stack, the resulting electron cloud is collected by the delay lines. The difference between the arrival times of the signal pulse at the opposite ends of each line yields one dimension of the particle position, whereas the average arrival time yields the particle arrival time (delayed by a constant amount). Combining such measurements from the three layers yields the two-
dimensional position and arrival time for each particle, even if several fragments hit the detector within a short time interval. The time and position resolution are estimated to be 100 ps and 100 μm, respectively. Based on calibration experiments using the predissociation from the B state of O₂, the kinetic energy resolution (ΔE/E) is measured to be ~ 0.8 %.38

Due to the presence of the beam block and the finite size of the detector, some events with very low or high translational energies in at least one of the fragments cannot be detected, depending on their recoil directions relative to the detector. To account for these effects, all presented distributions were obtained by correcting the raw data with a detector acceptance function (DAF, see below).

4.4. Data Analysis

The time and position measurements yield laboratory frame velocities of all fragments in the dissociation event, which can be easily converted to center-of-mass (COM) velocities v_i. For 3-fragment dissociation, due to conservation of total momentum, the intensity distribution in the COM frame is 6-dimensional (6D) and can be considered as a function of velocity vectors of any two fragments. However, more insight into the dynamics can be gained by representing this distribution in another set of more symmetric variables. Namely, 3 degrees of freedom corresponding to COM kinetic energies

$$ E_i = m_i v_i^2 / 2 $$  (4.1)

of the fragments can be accounted for by 3 “energetic” variables: the kinetic energy release (KER)

$$ E = \sum_{i=1}^{3} E_i $$  (4.2)

describing the total kinetic energy of the fragments, and the 2-dimensional coordinates in the Dalitz plot,27 which is a convenient way to represent kinetic energy fractions

$$ \varepsilon_i = E_i / E $$  (4.3)

of each fragment. The remaining 3 degrees of freedom correspond to “orientational” variables and can be described by Euler angles (the rotation angle about the photon polarization axis, the angle between the axis and the dissociation plane, and the in-plane rotation angle).

Although a strong anisotropy has been observed previously in 2-fragment photodissociation of ozone (O₃ → O₂ + O) in the Hartley band (at ħν ≈ 5.5 eV)39 experiments at shorter wavelengths (down to 193 nm)9,13 have shown that at higher photon energies the anisotropy decreases and eventually changes its sign due to a contribution from a higher lying electronic state with a different symmetry. Moreover, in the case of an unpolarized laser excitation, as in our experiments, the observed distribution is averaged over polarizations, so that the apparent anisotropy in the laboratory frame is reduced.40 This suggests that even if the 2- and 3-fragment dissociation processes might be fairly anisotropic for each particular electronic state, the likely participation of several excited states (see below) producing different anisotropies in the dissociation and this effect of averaging over laser polarizations should lead to a relatively
isotropic distribution in the measured data. Analysis of 2-fragment dissociation data in our experiments did not reveal any significant anisotropy at either of the used photon energies, suggesting that the observed 3-fragment distributions are also likely to be relatively isotropic. In addition, the small amount of data collected in the experiments (≤ 2000 3-fragment events at each wavelength) is clearly insufficient to reliably determine the complete full-dimensional distribution and reconstruct the smeared and overlapping contributions from each particular vibrational level. Therefore, we decided to assume that the distribution is totally isotropic with respect to all “orientational” degrees of freedom, and analyzed only the 3D “energetic” distribution.

However, coincident detection of an event is possible if and only if all 3 fragments hit the sensitive area of the detector, and their trajectories depend on all the 6 kinematic parameters mentioned above. The detector acceptance function, therefore, was calculated by numerical integration in the full 6D space (using the actual geometric parameters of the setup) and over the parent beam distribution (obtained from analysis of the data) and then reduced to a 3D DAF under the assumptions of isotropic dissociation. The experimental data were binned to obtain a “raw” empirical distribution, which was then divided by this DAF to obtain an estimation of the underlying “true” (DAF-corrected) distribution.

By integrating over energy partitioning, the 3D distributions can be reduced to a kinetic energy release distribution (KED), which is 1-dimensional. In addition, the energy partitioning, either for particular KER or integrated over KERs, can be conveniently represented by 2-dimensional Dalitz plots. Since several somewhat different diagrams are currently referred to as “Dalitz plots,” it is necessary to define the convention used in the presented work. By Dalitz plot we mean the intensity distribution plotted in barycentric coordinates as a function of kinetic energy fractions $\varepsilon_i$. Since $0 \leq \varepsilon_i \leq 1$, all physically meaningful points lie inside the corresponding triangle (see Fig. 4.2). In addition, for fragments of equal masses, conservation of the total momentum limits the available area to the inscribed circle. For dissociation into indistinguishable fragments, as in our case, the plot must have $D3$ planar symmetry, which means that only one sixth part of it is unique. Nevertheless, we show the complete plots, so that all features can be seen in context, without artificial boundaries.

4.5. Experimental Results

Figure 4.1 shows the kinetic energy distributions obtained for 3-fragment dissociation at both excitation energies. These plots show two notable features. First, the spectra are extended and structured, even though all three fragments are atomic species. This result reflects the fact that the parent $O_3$ molecules are formed in a range of vibrational levels because the photodetachment energy lies well above the electron affinity of ozone. Photodissociation from each level results in a different kinetic energy release for the fragments:

$$E = h\nu - D_{0}(O_3 \rightarrow 3O) + E_{vib,rot}(O_3). \quad (4.4)$$

Hence, each peak in the spectrum can in principle be assigned to a specific vibrational level of $O_3$. 

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At each photoexcitation energy, the vertical dashed line at low KER in Fig. 4.1 corresponds to photodissociation of O₃ from its ground vibrational level, while the higher-energy dashed line is offset by the maximal possible O₃ vibrational energy. As expected, all the signal lies between these two limits. Positions of the origin peaks in the KEDs measured at both photoexcitation energies are also in good agreement with the values expected from the currently known value of the dissociation energy $D_0(O_3 \rightarrow O_2 + O)$.

Figure 4.1. Kinetic energy distributions in 3-fragment photodissociation of O₃ at 157.6 nm (top panel) and 193.4 nm (bottom panel). Bin size is 0.01 eV. Gray bands show ±1σ uncertainty estimates. Dashed lines mark the center of the origin band and the upper limit of KER for photodissociation of vibrationally excited parent O₃ (determined by its dissociation energy $D_0(O_3 \rightarrow O_2 + O)$).

is offset by the maximal possible O₃ vibrational energy. As expected, all the signal lies between these two limits. Positions of the origin peaks in the KEDs measured at both photoexcitation energies are also in good agreement with the values expected from the currently known value of the dissociation energy $D_0(O_3 \rightarrow 3O) = D_0(O_3 \rightarrow O_2 + O) + D_0(O_2) \approx 6.18$ eV (using $D_0(O_3 \rightarrow O_2 + O) \approx 1.06$ eV$^{41}$ and $D_0(O_2) \approx 5.12$ eV$^{42}$).

A second key observation is that the relative intensities of these peaks are different at 193.4 and 157.6 nm, even though the parent O₃ molecules were produced identically in all experiments and thus must have identical vibrational level populations. This demonstrates that the initial O₃ vibrational distribution is not the sole factor governing the intensities in the KEDs. One must also consider the relative transition probabilities for electronic excitation from each vibrational level at these photon energies and the possibility that the branching ratios between 3-fragment and 2-fragment dissociation depend on both the particular initial O₃ vibrational level.
and the photoexcitation energy. Therefore, the observed differences between the profiles of the KEDs indicate that at the two wavelengths, photoexcitation and subsequent dissociation proceed differently.

Figure 4.2 shows Dalitz plots integrated over the whole KER spectrum (0.1–1.4 eV for 193.4 nm data and 1.6–2.8 eV for 157.6 nm, see Fig. 4.1). Due to the relatively small amount of data, even these integrated distributions have considerable shot noise (with standard deviations of intensities no less than 15%). Also, as mentioned above, the presence of the beam block causes a significant decrease in the DAF for events with very small energy in one of the fragments. This effect is responsible for the high-intensity artifact in $\epsilon_i \approx 0$ regions in the 193.4 nm plot, which in fact comes from just 5 events, greatly amplified by DAF correction.

Figure 4.2. Dalitz plots for 3-fragment photodissociation of O$_3$ at 157.6 nm (top panel) and 193.4 nm (bottom panel) integrated over the whole KER range. Relative intensities are shown by shades of gray ranging from white (no signal) to black (maximal signal).

Nevertheless, the overall structure of the distributions is evident in the plots. Although these distributions are different for the two photoexcitation energies, they have some common properties: nonzero intensities are seen for all possible energy partitionings, but a large share of the intensity is concentrated in three spots corresponding to approximately equal fractions of energy in two of the fragments and slightly smaller (for 193.4 nm) or somewhat larger (for 157.6 nm) fraction in the other fragment.

The KEDs for 2-fragment dissociation O$_3$ $\rightarrow$ O$_2$ + O were also determined from corresponding coincident measurements; see Sec. 4.10.1. These distributions
cover a much wider KER range than the 3-fragment distributions, reflecting the much larger available energy for 2-fragment dissociation. They show no vibrational structure, owing to the combination of the initial broad distribution of O\textsubscript{3} vibrational levels with the presence of additional product degrees of freedom associated with the rovibrational states of the O\textsubscript{2} fragment. Moreover, the O\textsubscript{2} and O fragments are produced in multiple combinations of electronic states. No evidence of anisotropy above the noise level was observed in the distributions at either wavelength. The main utility of these data in the present work is for estimating the branching ratios between the 2- and 3-fragment channels, as discussed in Sec. 4.6.3.

4.6. Discussion

4.6.1. Kinetic Energy Distributions

Since the parent O\textsubscript{3} molecules are created by photodetachment of O\textsubscript{3}\textsuperscript{−}, their vibrational populations are determined by Franck–Condon factors (FCFs) for the photodetachment transition. Our experimental setup does not have the capability to measure photoelectron spectra, which would allow direct determination of the populations, but we can assume that the precursor vibrational distribution is similar to that in the previous experiments\textsuperscript{34} and use corresponding FCF simulations to infer the expected O\textsubscript{3} vibrational distribution. They show that the noticeably larger bond lengths and a slightly smaller bond angle in O\textsubscript{3}\textsuperscript{−} than in O\textsubscript{3} lead to a long progression in the symmetric stretch and some excitation of the bending mode upon detachment.

If all vibrational levels of O\textsubscript{3} produced by photodetachment exhibited the same 3-fragment dissociation efficiency, then the 3-fragment KEDs would be similar to the FC distribution of O\textsubscript{3} vibrational levels, and the KEDs at 193.4 and 157.6 nm would have identical profiles merely shifted in energy. As shown in Sec. 4.10.2, the KED at 157.6 nm is similar to the FC distribution but shows noticeably higher relative intensity in the range 1.8–2.0 eV, which corresponds to \(v_1 = 1, 2\) and combination levels with \(v_2 = 1\). The KED at 193.4 nm shows little resemblance to the FC distribution, having much higher intensity beyond 0.6 eV, which corresponds to vibrational levels with \(v_1 \geq 3\). The deviations of both KEDs, especially at 193.4 nm, from that expected based solely on the O\textsubscript{3} vibrational distribution means that we need to consider the details of the photodissociation mechanism.

Photodissociation of O\textsubscript{3} requires photoexcitation to one (or several) of its excited electronic states, with probabilities governed by corresponding FCFs, and subsequent break-up into three atomic fragments, which competes with 2-fragment break-up. These two factors could be separated if state-resolved branching ratios could be determined. Unfortunately, as mentioned above, in our case the 2-fragment KEDs are structureless, so that contributions from different O\textsubscript{3} levels overlap and cannot be resolved. On the other hand, the effect of FCFs on the photoexcitation probabilities can be estimated.

Although the potential energy surface (PES) and vibrational wavefunctions have been thoroughly studied for the ground electronic state of O\textsubscript{3},\textsuperscript{43,44} studies of the electronically excited states\textsuperscript{7,75,45-47} have been more limited. They are focused on dissociation of relatively cold molecules into O\textsubscript{2} + O, mostly at lower excitation energies that are relevant to the ozone UV absorption in the atmosphere. Thus, rigorous calculations of relevant FCFs from results available in the literature are impossible, and undertaking required electronic structure and vibrational computations is beyond the scope of the present work. Nevertheless, PES cuts along the symmetric stretch coordinate (which leads to 3-fragment dissociation)
for electronic states lying in the relevant energy range have been published\textsuperscript{7} and can be used for rough estimation of FCF behavior with respect to the \( \nu_1 \) mode. Specifically, the classical Franck–Condon principle, which states that electronic transitions are most likely to occur between classical turning points,\textsuperscript{48} allows us to determine the extent of vibrational excitation in the \( \nu_1 \) mode of the ground electronic state required to make vertical transitions to the excited electronic states possible for given photoexcitation energies.

This analysis (Sec. 4.10), which can be understood from Fig. 4.3, shows that while there are electronic states vertically accessible near both photodissociation energies (using notation from Ref. 7: \( 4^1A''(1B_1) \) for 193.4 nm (6.41 eV) and \( 6^1A''(1A_1) \) for 157.6 nm (7.87 eV)), their transition dipole moments are relatively small. For 157.6 nm, a stronger transition can occur to the \( 8^1A''(1B_2) \) state at a slightly stretched nuclear configuration, requiring \( \sim 0.1 \) eV of vibrational energy, which corresponds to \( \nu_1 \approx 1 \). For 193.4 nm, the situation is even more remarkable. Here, the vertical transition to the \( 3^1A''(1B_2) \) state, which is responsible for the strong absorption in the Hartley band, requires \( \sim 0.8 \) eV of vibrational energy, corresponding to \( \nu_1 \approx 6 \), and reduced bond lengths. These transitions are indicated in Fig. 3 by vertical arrows. Hence, excitation of the \( \nu_1 \) vibrational mode should enhance absorption at both wavelengths, and this effect should be particularly pronounced at 193.4 nm.

\[ \text{Figure 4.3.} \text{ PES cuts along the symmetric stretch coordinate (taken from Fig. 3 of Ref. 7) drawn with line widths proportional to vertical transition dipole moments from the ground state minimum (Table I of Ref. 7). The vertical solid line indicates the geometry of the ground state minimum, and the horizontal lines show the energies corresponding to photons with } \lambda = 193.4 \text{ and 157.6 nm. The red vertical arrows show the most intense transitions between classical turning points for vibrationally excited O}_3. \]
In order to account for the combined effect of photodetachment and photoexcitation probabilities on the relative intensities $I(v_1, v_2, v_3)$ in the KEDs, the $O_3$ populations $N(v_1, v_2, v_3)$ resulting from photodetachment must be multiplied by relative photoexcitation probabilities $f(v_1, v_2, v_3)$:

$$I(v_1, v_2, v_3) \sim N(v_1, v_2, v_3)f(v_1, v_2, v_3). \quad (4.5)$$

As a simple approximation, we assume that the photoexcitation FCF distributions for these strongest states can be described by Gaussian functions centered at the corresponding “vertical” $v_1$ values, and the overall photoexcitation probabilities to the multiple weaker states do not depend on the initial vibrational level. That is, the photoexcitation probabilities can be approximated as

$$f(v_1, v_2, v_3) = f_s \exp \left( \frac{(v_1 - v_c)^2}{2\omega^2} \right) + f_o, \quad (4.6)$$

where constants $f_s$ and $f_o$ describe respective contributions from the strongest and from all other electronic states, $v_c$ is the “vertical” $v_1$ value (6 for 193.4 nm and 1 for 157.6 nm), and $\omega$ accounts for the width of this approximated FCF distribution for the strongest state (see Sec 4.10). We also ignore here the effects of bending and antisymmetric stretch, since they are only weakly excited in the parent $O_3$. However, the bending mode might play an important role, as discussed later.

A comparison of the resulting distributions with the experimental spectra is shown in Fig. 4.4. As can be seen, this rough approximation is able to reproduce the overall trends in the intensities, although the intensities corresponding to combination levels ($v_1, 1, 0$) with one quantum in the bending mode are substantially underestimated, especially for the (3, 1, 0) and (4, 1, 0) levels in the 193.4 nm distribution. It is very unlikely that the observed excess in ($v_1, 1, 0$) intensities is caused by enhanced populations in $O_3$, since FCF simulations for the photodetachment step do not allow selective excitation of $v_2 = 1$ levels without also populating $v_2 = 2$ levels, which do not seem to be enhanced in the experimental spectra. Therefore, the levels with bending excitation might either have higher photoexcitation probabilities at these photon energies or higher probabilities to dissociate into three fragments. These two possibilities cannot be distinguished based on the available experimental data and calculations.

It should be noted that the observed peaks have halfwidths $\sim 60$ meV, almost independent of the kinetic energy, which is much broader than the experimental resolution ($\sim 20$ meV for the highest energies) and the photodissociation laser bandwidth (≤15 meV$^{49,50}$). This broadening cannot be explained by rotational excitation, since that would require an unlikely high rotational temperature $\sim 400$ K and produce appreciably asymmetric peak shapes with long tails towards higher KER that are not observed in the spectra (moreover, the peaks in the photoelectron spectrum$^{34}$ of $O_3^-$ produced in similar conditions were much narrower, suggesting a relatively low rotational temperature). However, if the electronically excited $O_3^*$ can dissociate into three $O(^3P_J)$ atoms with various combinations of spin-orbit states (each $J = 0, 1, 2$), the maximum KER difference between such channels (3O($^3P_2$) and 3O($^3P_0$)) should be about 84 meV, consistent with the observed halfwidths.

Unfortunately, the available theoretical studies of $O_3$ electronic states ignore the spin–orbit structure, and thus cannot provide any information (except very general constraints,
Figure 4.4. Comparison of simulated intensity distributions (see text) with experimental KEDs (Fig. 4.1). Experimental distributions are shown by black lines, simulations by red curves, and blue sticks indicate positions and simulated intensities corresponding to individual $O_3(X^1A_1)$ vibrational levels marked by vibrational quantum numbers $v_1, v_2, v_3$ (symmetric stretch, bending, antisymmetric stretch, respectively). Vibrational energies were taken from Ref. 44 (compilation of experimental data) and Ref. 50 (experimental data for high $v_1$ overtones), augmented with Ref. 45 (first-principle calculations) for experimentally unavailable data. Energies for several states missing in this collection were approximated by separable anharmonic extrapolation.

such as parity) about possible product state combinations and their relative contributions. In addition, even if such correlations can be determined for electronic states that are pure in some approximation, the actual branchings might be substantially different due to transitions among these “pure” states caused by various couplings taking place during the dissociation. These effects have been experimentally observed already for $O_2$ photodissociation$^{38}$ and can be expected to be much more complicated for $O_3$ with one more O atom and excitation of multiple electronic states.

Therefore, the observed broadening of the vibrational peaks is most likely due to dissociation into $O(^3P_J)$ atoms in multiple spin–orbit states. The experimental resolution, however, is not sufficient to see these contributions separately, and the limited amount of data does not allow deconvolution.
4.6.2. Dalitz plots

Three-fragment dissociation mechanisms are usually classified according to the timing between breaking of the bonds.\(^\text{19}\) In the synchronous concerted mechanism, the bonds break simultaneously, leading to symmetric energy partitioning. In asynchronous concerted dissociation, one bond breaks after the other with a delay comparable to the vibrational periods, producing an asymmetric but still correlated distribution. In sequential, stepwise dissociation, one fragment leaves first and the remaining part breaks into 2 fragments later on a timescale exceeding the rotational period, in which case the correlation between the 3 fragments is lost.

Dalitz plots provide a one-to-one representation of the energy partitioning and thus allow a direct visual examination of the correlations among the fragments, elucidating the underlying dissociation mechanism. Symmetric bond breaking should produce intensities on the symmetry lines of the plot, while asymmetric bond breaking generally partitions the energy unequally among all 3 fragments and thus should produce intensity off the symmetry lines. The loss of correlation in stepwise dissociation leads to intensities smeared along constant-\(\varepsilon_i\) lines, where the energy fraction \(\varepsilon_i\) of one of the fragments is determined at the first dissociation step.\(^\text{18,24,51}\)

As mentioned above, most of the intensity in the plots (Fig. 4.2) at both photoexcitation energies is concentrated in three spots. In neither case is the location of these spots very close to the partitioning corresponding to a sudden recoil along the bonds from the \(\text{O}_3\) equilibrium geometry, which would yield almost equal fractions for all three fragments:

\[
\varepsilon_{\text{terminal O}} = \frac{1}{2 + 4 \cos(\theta/2)^2} \approx 0.322, \quad \text{(4.7)}
\]

\[
\varepsilon_{\text{central O}} = 1 - 2\varepsilon_{\text{terminal O}} \approx 0.355, \quad \text{(4.8)}
\]

where \(\theta \approx 116.7^\circ\) is the bond angle.

Nevertheless, the distributions at both photoexcitation energies show only three spots, corresponding to equal energy fractions for two fragments, which suggests that the dissociation is synchronous concerted rather than asynchronous concerted, because in the latter case energy fractions for all three fragments are expected to be different, leading to six spots in the Dalitz plot. The asynchronous concerted mechanism can accidentally produce symmetric partitioning, but in the present experiment all three fragments are indistinguishable, and therefore these two cases cannot be clearly differentiated. This question can be investigated using \(\text{O}_3\) isotopomers (e.g., \(^{16}\text{O}^{18}\text{O}^{16}\text{O}\) and/or \(^{18}\text{O}^{16}\text{O}^{16}\text{O}\)), but would require much more elaborate experiments. More insight can be also gained from careful theoretical dynamics computations.

The difference in the location and size of the spots between the 193.4 and 157.6 nm data is likely due to participation of different electronic states in the dissociation. Namely, as indicated by FCF analysis above, photoexcitation at 193.4 nm occurs mostly to only one state, and PES plots\(^2\) show that this state does not interact with other states upon symmetric bond stretching and has only a small gradient in the bending coordinate. That is, the portion of the initial wavepacket that is not diverted towards 2-fragment dissociation should proceed roughly as symmetric dissociation along the bonds and resemble the sudden recoil approximation. On the one hand, the 157.6 nm photodissociation involves multiple electronic states, all of which have intersections accessible by symmetric bond stretching or bending. The dissociation dynamics therefore should be much more complicated and might be expected to result in larger deviations from the sudden recoil and a broader final distribution.
The absence of constant-εi lines corresponding to sequential dissociation is not surprising, since a stepwise process would require creation of metastable O2 fragments. In principle, the minimum of the lowest known metastable (B^3Σ_u^- state of O2 lies only ~1 eV higher than the O2 → 2O(^3P) dissociation limit, and this state predissociates to 2O(^3P) fragments through coupling with several repulsive states. Thus it should be energetically accessible in the 157.6 nm case. However, none of the studied O3 electronic states correlates to O2(B^3Σ_u^-) + O(^3P) fragments (the B^3Σ_u^- state itself correlates to O(^1D) + O(^3P), which is ~2 eV above 2O(^3P)), meaning that efficient excitation of such states probably requires much higher photon energies.

On the other hand, all excited states of O3 in the relevant energy range seem to correlate to 3O(^3P) fragments. Moreover, the dipole-accessible states have significant gradients along the symmetric stretch coordinate in the region of expected ground-state geometries (see Fig. 5 of Ref. 7), which means that at least immediately after photoexcitation the molecule should evolve towards symmetric 3-fragment dissociation. The potential energy surfaces, however, are not purely repulsive and have saddle points or conical intersections (appearing as avoided crossings in C_s symmetry) at sufficiently extended bond lengths. This severely complicates the subsequent dynamics, for example leading to preferential dissociation into O2 + O instead of 3O, especially at lower photoexcitation energies. Even if the dissociation proceeds to 3 fragments, the initially symmetric wavepacket, after passing symmetrically through the region of a saddle point or a conical intersection, can be split into a symmetrized combination of two asymmetric wavepackets, resulting in less symmetric energy partitioning.

The energy partitioning obtained in the present experiments at 193.4 nm is close to 2:1:2, which is somewhat different from the approximately 4:1:4 ratio previously inferred from analysis of non-coincident measurements at this wavelength. At the same time, a coincident study of dissociative recombination O3^+ + e^- → 3O(^3P), which corresponds to ~12.5 eV of excitation energy, exhibited almost 1:0:1 energy partitioning resulting from a practically linear recoil arrangement. This is an interesting result, given the initial O3^+ bent geometry, and differs significantly from the approximately 1:2:1 ratio obtained in the present work at 157.6 nm (~7.87 eV) excitation, reinforcing the conclusion that the dissociation process is very sensitive to the involved electronic states and is not straightforward.

Although the dynamics on the electronically excited PESs, and hence the energy partitioning among the fragments, can depend on the initial O3 vibrational level, the small amount of experimental data obtained in the present study does not permit a meaningful analysis of KER-dependent Dalitz plots. An examination of Dalitz plots integrated over KER intervals corresponding to distinct peaks in the KEDs (see Sec.4.10) shows only that the plots corresponding to the strongest peaks are more structured, and the plots for weaker peaks are more uniform. However, taking into account the amount of noise in these plots, such deviations from the overall Dalitz plots (Fig. 4.2) cannot be considered statistically significant. Another way to correlate the energy partitioning with the KER is to compare the overall KED with the KED corresponding to events lying within the three intense spots in the Dalitz plot. If these spots are due to dissociation starting from particular vibrational levels, then the associated KED should differ from the overall KED shown in Fig. 4.1. However, such comparisons (Sec. 4.10) also do not show any qualitative differences.
4.6.3. Branching ratios

The branching between the 2- and 3-fragment dissociation channels may also depend on the initial vibrational excitation, but this dependence cannot be discerned from the present experiments. Whereas vibrational structure in the 3-fragment data is partially resolved, the contributions from different initial O$_3$ vibrational levels are not distinguishable in the 2-fragment KEDs (see Sec. 4.10). Thus only the total branchings can be extracted from the data.

The total branching ratios were obtained by comparing the total intensities (KEDs integrated over all energies) of the 2- and 3-fragment channels. This procedure, however, is not straightforward. First, the DAF decreases significantly for high-energy fragments. For example, at the highest observed energies in 2-fragment dissociation, only the fragments recoiling in a relatively small solid angle with $\sim 60^\circ$ aperture around the beam axis reach the detector. This means that the anisotropy distribution for high KERs cannot be determined reliably. Therefore, since the anisotropy parameter estimated from the scarce data was randomly scattered in the full allowable range, we decided to DAF-correct the 2-fragment distributions as if they were isotropic. This may have led to some systematic errors in the total intensity, but considerably reduced the random noise propagated to KEDs from the anisotropy estimations. For the 157.6 nm photodissociation, which produced a weak 2-fragment signal, the noise remained quite large even with this assumption.

Another factor that must be accounted for is that imperfect detection efficiency of each particle hitting the detector leads to different probabilities of coincident detection for 2- and 3-fragment events. Namely, if the 1-particle detection probability is $p$, then the probability of coincident detection of 2-fragment event is $P_2 = p^2$, and that of 3-fragment event is $P_3 = p^3$. The probability $p$ can vary over a broad range (from $\sim 0.3$ to almost unity), depending on the speed, mass, and electronic state of the impacting particle, the particular type of the detector, its age and operating conditions. However, it can be estimated by comparing the detected number of 3-fragment coincidences with the number of events in which only 2 out of 3 fragments were detected (with probability $P_{2 of 3} = 3p^2(1 - p)$). Such events can be separated from genuine 2-fragment dissociation, since in the latter case the COM of the event must lie within the parent beam, whereas in the former case the COM of the 2 detected fragments is displaced, and the momentum of the undetected third fragment can be estimated such that the 3-fragment COM lies within the beam. Unfortunately, the COM spread in the parent beam is not negligible, leading to relatively poor accuracy of this reconstruction, so that it does not yield useful information for analysis of 3-fragment dissociation as in Ref. 16. Moreover, a relatively large number of false coincidences, especially in the 193.4 nm data, produce a noticeable background in the reconstructed distributions. Nevertheless, the structured parts of the distributions are consistent with the coincident 3-fragment data, and the comparison of their intensities yields the value of $p = 0.6 \pm 0.05$ for 1-particle detection probability.

The branching fractions for the 3-fragment channel obtained from the total DAF-corrected intensities and this 1-particle detection probability are 5.2(6)% at 193.4 nm and 26(4)% at 157.6 nm.

In a previous study of O$_3$ photodissociation at 157.6 nm, the branching between 2- and 3-fragment dissociation was inferred from indirect measurements (fluorescence in a gas cell). It was estimated that, on average, dissociation of each O$_3$ molecule produces approximately two O atoms, which means that the O + O$_2$ and 3O channels have approximately equal probabilities.
The 3-fragment fraction in photodissociation at 193 nm extracted from similar indirect measurements\(^\text{(14)}\) was \(\sim 12\%\) (with a large uncertainty). In a later molecular beam study,\(^\text{(9)}\) this fraction was estimated as \(\sim 2\%\) from fitting the O atom time-of-flight spectra with a simple model for the 3-fragment distribution.

Our results are consistent with previous work in that the 3-fragment branching fraction is higher at 157.6 nm than at 193.4 nm. However, the agreement among the numbers is quite poor (even between the previous 193 nm studies). In part, this can be explained by relatively low accuracies of all the estimations. Even though the present results were obtained from direct measurements of both channels and thus can be deemed more reliable, they can still have systematic errors, mostly from the isotropy assumption. Another issue is that while all previous studies used vibrationally cold \(\text{O}_3\), the branching ratios in the present work are essentially averaged over a very broad and peculiar vibrational distribution. Even though at 193.4 nm this averaged branching ratio is consistent with previous estimations for cold \(\text{O}_3\) (and actually lies between them), the possibility that the branching ratios are vibrationally dependent cannot be ruled out, and thus the present numbers should be used with due caution.

### 4.7. Conclusions

The work presented here is the first direct observation and dynamical characterization of 3-fragment photodissociation of the neutral ozone molecule. Although experimental evidence of this channel has been known for almost 30 years,\(^\text{(8)}\) it has received relatively little experimental and theoretical attention, despite being a very interesting case of 3-fragment dissociation into three atoms of a simple, stable molecule, directly related to real-world chemistry.

The Dalitz plots obtained here suggest that the dissociation proceeds by a concerted, and most probably symmetric, mechanism. It is also evident that excitation of the same vibrational ensemble of \(\text{O}_3\) at different wavelengths results in different kinetic energy distributions and branching ratios.

It should be noted that the photodissociation wavelengths 193.4 and 157.6 nm were used here only because they can be easily produced at sufficiently high intensities. However, these wavelengths actually lie close to the *minima* of the \(\text{O}_3\) absorption cross-section.\(^\text{(7)}\) Therefore, they correspond to a mixture of “hot bands” for several electronic transitions, which causes the observed enhancement of photodissociation probability for vibrationally excited ozone, especially at 193.4 nm. From this perspective, it would be very interesting to perform similar experiments at different wavelengths, corresponding to maxima of partial cross-sections, for example, at \(\sim 180\) nm (\(\sim 7\) eV) for the strongest absorption in this region, involving the \(5^1\text{A}''\) (\(^1\text{A}_1\)) state.

The analysis and interpretation of the present data was substantially complicated by a broad range of populated \(\text{O}_3\) vibrational levels in our experiment. Therefore, development of a method for producing a fast beam of vibrationally cold or, better, state-selected neutral \(\text{O}_3\) molecules is highly desirable. Since the precursor \(\text{O}_3^-\) anions in our experiment were sufficiently cold, near-threshold photodetachment coupled with some means to increase \(\text{O}_3^-\) production and to better separate \(\text{O}_3^-\) photodissociation byproducts from the \(\text{O}_3\) beam would be of interest. Alternatively, measuring the kinetic energy of the photodetached electron in coincidence with
photofragment detection\textsuperscript{55} would help in resolving contributions from different vibrational levels.

The indirect evidence for producing the O($^3P$) fragments in multiple spin–orbit substates motivates more detailed investigations of this issue. This question has been already studied for O\textsubscript{2} photodissociation\textsuperscript{38} using our experimental setup (with a slightly different detector). The peak separations in these experiments were somewhat larger due to a smaller number of possible combinations, and the signals were much stronger, allowing fitting of the contours. Nevertheless, optimization of conditions in the current experiment might make such measurements possible for O\textsubscript{3} photodissociation as well.

Finally, we hope that the experimental results reported in the present article will incite theoretical interest in the 3-fragment dissociation of ozone. The 193.4 nm case, involving one electronic state that is nearly isolated (at least along the symmetric dissociation route), should be amenable to computations using present-day methods. A reasonable description of 157.6 nm photodissociation with multiple interacting states might require a more complicated treatment with nonadiabatic effects, but can present an even better test case for non-trivial nuclear dynamics computations.

4.8. Acknowledgements

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4.9. References


4.10. Supplemental Information

4.10.1. 2-fragment KEDs

Figure 4.5 shows kinetic energy distributions in 2-fragment photodissociation of O\(_3\) obtained in the same experiments as the 3-fragment KEDs but, correspondingly, from coincidence events with two instead of three particles. Two-particle events corresponding to one missed particle from 3-fragment dissociation and to dissociation of O\(_2\) contaminant in the beam (see below) were discriminated based on conservation of momentum. The plotted data correspond to the O\(_3\) \rightarrow O\(_2\) + O process only, with the appropriate DAF-correction applied. The noticeable increase of the uncertainties toward higher KERs is due to the decreasing detector acceptance, as mentioned in the article.

The various possible channels are marked in the plots only for reference — they are energy- and spin-allowed but do not necessarily correlate to the participating O\(_3\) states and thus some of them probably make no contribution to the observed signal. Since our setup detects particles regardless of their type, we cannot distinguish different electronic states of the atomic O fragment. In addition, the parent O\(_3\) molecule has up to \(\sim 1\) eV internal energy, and the O\(_2\) fragments can have an even broader internal energy distribution, so that the marked origins are neither higher nor lower KER limits for the corresponding channels.

![Figure 4.5](image)

**Figure 4.5.** Kinetic energy distributions in 2-fragment photodissociation O\(_3\) \rightarrow O\(_2\) + O at 157.6 nm (top panel; bin size 0.1 eV) and 193.4 nm (bottom panel; bin size 0.02 eV). Gray bands show \(\pm 1\sigma\) uncertainty estimates. Origins of various spin-allowed channels (ignoring vibrations, rotations and spin–orbit splittings) are marked by dashed lines.
4.10.2. Franck–Condon simulations

Calculations of Franck–Condon factors (FCFs) for the photodetachment step were performed using the ezSpectrum package in the separable harmonic approximation. Although a more rigorous treatment including the Duschinsky effect could be used, previous studies indicate that the simple harmonic parallel-modes approximation (as in the original experimental study of the O$_3^-$ photoelectron spectra) is sufficient to reproduce the experimental intensities, which is the only goal in our case. The resulting intensity distribution, obtained as a sum of Gaussian peaks (simulating spin–orbit splittings, rotational envelopes and experimental broadening) with amplitudes corresponding to the resulting O$_3$ vibrational populations, is shown in Fig. 4.6. The overall intensity was scaled to match the “similar” part of the experimental distribution.

Since neither the full-dimensional potential energy surfaces (PESs) for O$_3$ electronically excited states nor parameters of their approximation are available in the literature, FCFs for the O$_3$ photoexcitation step cannot be calculated by usual methods. Moreover, most of the electronically excited states are repulsive and/or are excited above their dissociation limit. Therefore, we used the approximation that the maximal probability corresponds to a vertical transition between the classical turning points (classical Franck–Condon principle) and considered only the symmetric stretch mode, approximating it with pure symmetric stretching of the bonds (keeping the bond angle fixed).

The potential energy curves (one-dimensional PES cuts) were taken from [4] along with the transition dipole moments (TDMs) to estimate their relative contributions. It should be noted that these TDMs were calculated only for vertical transitions from the equilibrium geometry. Although the authors mention that for most states “the TDMs depend only weakly on the nuclear geometry around the Frank–Condon point”, the accuracy of the Condon approximation (geometry-independent TDM) for transitions from high vibrational states, important for the present work, is uncertain. The applicability of the harmonic parallel-modes approximation to the FCF calculations for these states is also unclear. Therefore, the obtained results can be, at best, only qualitative.

A diagram for estimation of the maxima in the FCF distributions for different electronic states is shown in Fig. 4.6. As can be seen, the states accessible vertically from the equilibrium geometry have very small TDMs. At the same time, the density of states is sufficient to allow nearly vertical transitions between classical turning points at any vibrational energy in the symmetric stretch.$^a$

However, two of the states ($3^1A'$ and $8^1A'$) have significantly higher TDMs than the rest. The graph indicates that the $3^1A'$ state can be accessed vertically from the ground electronic state with a 6.41 eV ($\lambda = 193.4$ nm) photon if the molecule has $\sim 0.8$ eV of vibrational energy in the symmetric stretch. This corresponds to $v_1 \sim 6$. For 7.87 eV ($\lambda = 157.6$ nm) photons, the strongest state $8^1A'$ is accessible with $\sim 0.15$ eV of vibrational energy, corresponding to $v_1 \sim 1$. The $v$-dependence of FCFs for these states can be approximated by Gaussian functions

$$e^{-\frac{(v_1 - v_c)^2}{2\sigma^2}}$$

(4.9)

$^a$ Note that the calculations in [4] were limited to only 8 states of each symmetry, and therefore they do not cover the whole energy range. Nevertheless, the kinks visible in the potential energy curves, resulting from avoided crossings with other states, suggest that the situation at higher energies is similar. The lower limit 2.2$a_0$ for the R range also causes the curves to end abruptly, but their behavior is clear from the plots and can be extrapolated “by eye”. 61
centered at the corresponding “vertical” $v_1 = v_c$ values. The width parameter $w$ should depend on the range of vibrational energies for which the transition is nearly vertical. As can be seen from the figure, it is relatively large for the $3^1A'$ state at 6.41 eV and significantly smaller for the $8^1A'$ state at 7.87 eV. The values that most closely fit the experimental distribution (see Fig. 4.2) are $\omega \sim 1.5$ for $\lambda = 193.4$ nm and $\omega \sim 0.2$ for $\lambda = 157.6$ nm, consistent with these considerations.

Figure 4.6. Comparison of intensity distributions simulated using only photodetachment FCFs with the experimental KEDs. Experimental distributions are shown by black lines, simulations by red curves, and blue sticks indicate positions and simulated intensities corresponding to individual $O_3(X^1A_1)$ vibrational levels marked by vibrational quantum numbers $v_1, v_2, v_3$ (symmetric stretch, bending, antisymmetric stretch, respectively).

The relative intensities of the strongest state and the uniform “background” weak states were also adjusted to best fit the experimental distributions. As noted in the article, there is noticeable disagreement for intensities corresponding to combination levels with one quantum in the bending mode. However, extension of this rough FCF model to include bending does not seem to be justified since provides PES cuts along the bond angle only at the equilibrium bond length, and the angular energy dependence is very likely to be sufficiently different at the reduced and extended bond lengths, at which the strongest transitions occur. In addition, the
actual symmetric stretch mode is not a pure change in the bond lengths but also involves the angle, and at \( v_1 \sim 6 \) this deviation can be large enough to preclude a simplistic analysis of the effect of bending vibrations on the FCFs.

Figure 4.7. The top panels show PES cuts along the symmetric stretch coordinate (taken from Fig. 3 in [4]) with line widths proportional to TDMs from the ground state (Table. 1 in [4]). The vertical solid line indicates the geometry of the ground state minimum, and the horizontal lines show the energies corresponding to photons with \( \lambda = 193.4 \) and 157.6 nm. The red arrows show the most intense transitions between classical turning points for vibrationally excited \( O_3 \). The bottom panel shows the vibrational energy in the ground electronic state required for vertical transitions between the classical turning points as a function of the electronic energy difference. The vertical lines show the photon energies at the corresponding wavelengths. The most intense transitions are marked by red circles.
4.10.3. Possibility of using isotopomers

Since $^{16}\text{O}_3$ dissociates into 3 indistinguishable $^{16}\text{O}$ fragments, the cases of symmetric dissociation and asymmetric dissociation with accidentally equal energy partitioning among 2 fragments cannot be distinguished. However, if one of the $^{16}\text{O}$ atoms is replaced by the heavier isotope $^{18}\text{O}$, the fragments become (partially) distinguishable.

It should be noted that $^{18}\text{O}$-substituted ozone can have two different isotopomers: symmetric $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and asymmetric $^{18}\text{O}^{16}\text{O}^{16}\text{O}$. Although they cannot be selected mass-spectroscopically, they have different vibrational spectra, and thus their relative concentrations can be determined. Since $^{16}\text{O}_3$ has $C_2v$ symmetry, it would be preferable to use exclusively the $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ isotopomer, which has the same symmetry. However, it is difficult to devise a practical method for its selective production. On the other hand, the asymmetric isotopomer $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ is produced by the $^{18}\text{O} + ^{16}\text{O}_2 \rightarrow ^{18}\text{O}^{16}\text{O}^{16}\text{O}$ reaction almost exclusively. Thus careful selection of conditions for $\text{O}_3^-$ production (maybe with $\text{O}_3$ produced before expansion through the nozzle) should allow to control the isotopomer ratio.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.8.png}
\caption{Intensity distributions expected in symmetric and asymmetric dissociation mechanisms for symmetric and asymmetric isotopomers. The axes are marked as 'F' and 'S' for fast and slow light fragments and 'H' for the heavy fragment. The atoms in the momenta diagrams are colored correspondingly (dark yellow means that both light atoms have equal energies). The full Dalitz plot has reflection symmetry with respect to the light fragments, so the part with interchanged fast and slow fragments is shown shaded.}
\end{figure}

\textsuperscript{b} See [5]. Attachment of $^{16}\text{O}$ to $^{16}\text{O}_2$ is almost barrierless, whereas isomerization to $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ or direct insertion of $^{18}\text{O}$ between two $^{16}\text{O}$ atoms involves the cyclic ozone structure, which lies \~0.3 eV above the dissociation limit and is additionally surrounded by \~1 eV barrier [6]. Interestingly enough, even in presence of isotope scrambling, the reaction $^{16}\text{O} + ^{16}\text{O}^{18}\text{O}$ yields more $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ than $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ [5].
In principle, isotopic substitution might have some effect on the dissociation dynamics, and this effect is likely to be different for the symmetric and asymmetric mechanisms. Dynamics calculations are required to predict the outcomes, and if they turn out to be different, comparison of experimental distributions for substituted and unsubstituted molecules could validate these findings. But even if the dynamics do not depend noticeably on the fragment masses, the intensity distributions in the Dalitz plots should be different for the two mechanisms, as schematically shown in Fig. 4.8. The figure illustrates the situation where one of the fragments has a larger energy fraction than the other two, as in the 157.6 nm case, but similar diagrams can also be drawn for the opposite situation, as in the 193.4 nm case.

As can be seen, if only the symmetric or only the asymmetric isotopomer is present, the symmetric and antisymmetric dissociation mechanisms lead to clearly different intensity distributions in the Dalitz plot. If symmetric and asymmetric isotopomers are mixed, the patterns overlap, producing the same spot configuration, but the relative intensities of these spots are still different for the two mechanisms. Therefore, unless the ratio $a:s$ of asymmetric to symmetric molecules in the mixture is exactly $2:1$, the dissociation mechanisms can be distinguished by comparing the relative intensities of the spots.

4.10.4. Analysis of correlations between KER and energy partitioning

Although the amount of data is not sufficient to examine the 3-dimensional distributions (in “energetic” variables, even assuming complete isotropy in “orientations”), if the dissociation dynamics strongly depends on the initial vibrational state, this could be revealed by comparing Dalitz plots for events with KERs in several sufficiently narrow ranges corresponding to different vibrational states. Unfortunately, the KED peaks corresponding to combination levels with bending excitation ($v_1,1,0$) overlap with ($v_1 + 1,0,0$) peaks, and thus the effect of bending cannot be examined easily.

Nevertheless, the KEDs show several pronounced peaks, and Dalitz plots for them, each limited to a small number of vibrational states, can be compared. Figures 4.9 and 4.10 show such “partial” plots together with the “total” Dalitz plots for the whole KER ranges. As can be seen, all partial plots are much noisier than the total plots. The plots corresponding to the most intense KED peaks exhibit distributions very similar to those in the total plots, except the 2.05–2.80 eV plot for the 157.6 nm data, which has a significantly more uniform distribution. However, this region covers the long tail of the KED and corresponds to a large number of different vibrational states. The plots corresponding to weak KED peaks also appear more uniform, but they have very low signal-to-noise ratios (SNR), and therefore these differences could be due to statistical fluctuations. (It should be noted that $1\sigma$ uncertainties presented in the figures were estimated from the event counts in the available data. Since rigorous uncertainty estimation is impossible without a reasonable model for the intensity distribution, which we do not have yet, the bins without events have no uncertainty estimates at all, and the uncertainties for the bins with events are most likely underestimated.)
Figure 4.9. Dalitz plots by kinetic energy ranges for photodissociation at 157.6 nm. Plots on the left show normalized intensity distributions, and those on the right show 1σ uncertainty estimates for the left plots in the same scale. Each label indicates the KER range for the plot, the total number of unique events after DAF correction (“tot”), and the maximal intensity per bin (“max”).
Figure 4.10. Dalitz plots by kinetic energy ranges for photodissociation at 193.4 nm. In each column, the left plot shows normalized intensity distribution, and the right one shows 1σ uncertainty estimates for the left plot in the same scale. Each label indicates the KER range for the plot, the total number of unique events after DAF correction (“tot”), and the maximal intensity per bin (“max”).

In addition to reducing the 3-dimensional distributions to a set of 2-dimensional Dalitz plots by KER ranges, these distributions can also be reduced to a set 1-dimensional KED plots for events with specific energy partitioning patterns (corresponding to different regions in Dalitz plots). Figure 4.11 shows a comparison of such “partial” KEDs corresponding to the events in the most intense spots of the Dalitz plot at both wavelengths with the “total” KEDs.
As can be seen, the events in the spots have KEDs very similar to the total KEDs and account for about half of all 3-fragment dissociation events at any KER. The only noticeable deviation is in the low-KER part of the 193.4 nm data, where the “spot” intensities are apparently lower than half of the total intensities. However, even the overall intensities in that range are very small, so that the SNR is also very poor. In fact, the observed difference is comparable to the estimated standard deviations ($\sigma$) and therefore cannot be claimed statistically significant at any reasonable level.

Thus, even if different initial vibrational states, or at least some of them, lead to substantially different 3-fragment dissociation routes, we cannot discern this from the available experimental data.

**4.10.5. Reconstruction of 3-fragment data from 2 detected fragments**

As explained in the article, due to momentum conservation, products in 3-fragment dissociation have only 6 degrees of freedom instead of 9. Therefore, in principle, coincident detection of any 2 of the 3 fragments is sufficient to determine the complete picture. In practice, however, the parent beam has finite dimensions and velocity spread, which means that dissociation events have some distribution of their COM parameters. This distribution is easily determined if all 3 fragments are detected, but if one of the fragments is lost, the position and
velocity of the event COM remain unknown. Using the center of the COM distribution as an approximation for the actual COM parameters, the KER and energy partitioning can be extracted from 2 detected fragments, but only with the corresponding uncertainty. Figure 4.12 shows the results obtained in this way.

It should be noted that most events in which 2-particles are detected in coincidence correspond to actual 2-fragment dissociation $O_3 \rightarrow O_2 + O$ (especially at 193.4 nm) or some (minor) contamination from $O_2 \rightarrow O + O$ dissociation of $O_2$ produced in the $O_3 \rightarrow O^- + O_2$ process that competes with the $O_3^- \text{photodetachment}$. However, these events, being analyzed as 3-fragment dissociation, produce distinct features in the Dalitz plot.

![Figure 4.12](image)

**Figure 4.12.** Comparison of kinetic energy distributions (left) in 3-fragment dissociation of $O_3$ at 157.6 nm (top) and 193.4 nm (bottom): black curves—from coincident data, blue curves—reconstructed from 2 detected fragments, thin red curves—broadened coincident data distribution, thick red curves—same but scaled to match the blue curves. Dalitz plots (right) show the corresponding energy partitioning distributions. The parts near the limiting circle, corresponding to nearly linear recoil configurations, are heavily contaminated by 2-fragment dissociation products (especially in the 193.4 nm data) and thus were removed.

Namely, $O_2 \rightarrow O$ appears as $(O + O) + O$ with two of the fragments having almost equal momenta, as if the $O_2$ molecule were considered as two separate $O$ atoms, one of which is not detected. Clearly, the momenta of the 3 “reconstructed” fragments are related as $1 : 1 : -2$, hence the energy fractions are $\{1/6, 1/6, 4/6\}$, which corresponds to points in the Dalitz plot located at intersections of the momentum-limiting circle with the axes. Similarly, for $O+O$ events from $O_2$ dissociation the “reconstructed” third fragment has zero momentum and, accordingly, the energy fractions are $\{1/2, 1/2, 0\}$, corresponding to points at which the momentum-limiting circle touches the energy-limiting triangle.

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<sup>c</sup> Basically, the “remaining” 3 out of 9 degrees of freedom are associated with the COM. Without knowing them, the measured laboratory picture of the dissociation cannot be converted to the COM picture.
Thus, all 2-particle events wrongly attributed to 3-fragment dissociation should lie on the momentum-limiting circle in the Dalitz plot. Ideally, they correspond to only 6 points on this circle, but due to the mentioned uncertainty in the reconstruction, some area along the circle becomes occupied. Since the coincident 3-fragment data has most of the intensity (and structure) near the center of the plot, removal of events lying in the peripheral part of the plot allows a more meaningful analysis of the reconstructed data. For a direct comparison with the coincident data, the reconstructed events that could not be detected in coincidence (because the third fragment misses the detector or hits the beam block) were also discarded.

The distributions reconstructed from 2-particle events, shown in Fig. 4.12, are similar to those obtained from 3-particle events, but are less structured. In addition to a blurring due to the mentioned COM uncertainty, the reconstructed distributions show a relatively uniform background, which is especially pronounced in the 193.4 nm case. This background is associated with false coincidences—detection of 2 fragments from different dissociation events.

Namely, in 193.4 nm experiments, ~95% of photodissociation events produce 2 fragments (O$_2$ + O). If two such events occur during one laser pulse, and only 1 fragment of each is detected (either because the other fragments miss the detector or do not trigger the MCP), this is recorded as a 2-particle event. Obviously, the particles in such events are not correlated and hence produce broad unstructured distributions in the analysis.$^d$

In order to compare the overall intensities, the KEDs from coincident data were broadened by convolution with a Gaussian contour simulating the reconstruction uncertainty, such that the resulting shape matches the reconstructed KEDs, and then shifted to account for the background and scaled to match the intensities of the reconstructed KEDs.$^e$ The resulting intensity scaling factors are 1/0.6 for the 157.6 nm data and 1/0.43 for the 193.4 nm data. As explained in the article, the ratio of the intensities for coincident 3-fragment detection and detection of 2 out of 3 fragments is

$$I_3/I_2 = \frac{p}{3(1-p)}, \quad (4.10)$$

where p is the 1-particle detection probability of the detector. Therefore, this probability can be estimated from the measured intensity ratios as

$$p = \frac{I_3/I_2}{I_3/I_2 + 1/3} \quad (4.11)$$

The ratios from above ($I_3/I_2 = 0.6$ and 0.43) yield estimations $p \sim 0.64$ and $p \sim 0.56$ from 157.6 nm and 193.4 nm data respectively. The difference between these values, despite identical detector operating conditions in all experiments, is probably caused by an incomplete treatment of the background, which was assumed KER-independent. Nevertheless, taking into account the magnitude of other uncertainties in the estimation of branchings between the 2- and 3-fragment channels (for which this determination of 1-particle detection probability was needed), the ~10% accuracy is sufficient.

$^d$ Such false coincidences do not affect 2-fragment distributions and 3-fragment distributions obtained from 3-particle events, since they are easily rejected as violating momentum conservation.

$^e$ For better matching, the KEDs were also slightly shifted to higher energies. This is an expected effect, since KER is quadratic in the momenta, and thus uncertainty in reconstructed KERs due to momenta uncertainties should have a positive bias.
4.11 References

Chapter 5

Three-body Photodissociation Dynamics of I$_2^-$ (CO$_2$)


5.1. Abstract

The three-body dissociation of I$_2^-$ (CO$_2$) following excitation of the I$_2^-$ chromophore to the repulsive $A^2 \Pi_{g,1/2}$ and $B^2 \Sigma_{g,1/2}^+$ electronic states at 1.72 and 3.21 eV has been investigated using fast beam photofragment translational spectroscopy. The translational energy distributions for three-body dissociation provide a direct measurement of the CO$_2$ binding energy, yielding a value of 218±10 meV. These distributions are vibrationally resolved and show that some CO$_2$ is produced with bend excitation. Dalitz plots show that the dominant three-body decay mechanism is asynchronous–concerted decay, in which the two bond cleavages are distinct but nearly simultaneous events.
5.2. Introduction

The formation and cleavage of molecular bonds in chemical reactions is one of the most fundamental concepts in all of science. Scattering measurements such as crossed molecular beams experiments probe this process in exquisite detail in bimolecular reactive collisions. Complementary information on unimolecular dynamics is obtained from photodissociation experiments, in which absorption of a single photon with well-defined energy results in the rupturing of one or more chemical bonds, thereby providing invaluable insights into the mechanism by which vibrational or electronic excitation is coupled to molecular dissociation. The vast majority of these studies have focused on two-body dissociation; photodissociation into three fragments remains less explored largely owing to the difficulty of obtaining a complete picture of these complex decay pathways. However, photofragmentation into three (or more) fragments has been inferred in species such as H$_3$COCl$^-$, and glyoxal; three-body dissociation is also seen in collision-induced dissociation, dissociative photodetachment, and dissociative charge exchange. The mechanism by which these three-body dissociation reactions occur (concerted vs. sequential) is a topic of much interest in reaction dynamics. It is particularly fruitful to study these dynamics using fast beam dissociation experiments that are capable of making time- and position sensitive measurement of all coincident photofragments. This methodology offers a complete picture of the fragmentation and allows elucidation of both energetic and mechanistic information.

In this paper, the three-body photodissociation of the ion-molecule complex I$_2$CO$^-$ is investigated. Photodissociation of I$_2$CO$^-$ following excitation into the repulsive $A^+$ electronic states has been studied extensively, not only as an isolated species in the gas phase, but also in charged clusters with various solvating species and in bulk solution. As such, the ease of formation and mass selection of I$_2$CO$^-$ clusters in the gas phase coupled with the energetic accessibility of the three-body dissociation limit makes I$_2$CO$^-$ an excellent model system for the study of three-body decay. Prior to dissociation, the I$_2$CO$^-$ chromophore is largely unperturbed by the presence of CO$_2$, but the addition of just one solvent molecule can be sufficient to alter the dissociation dynamics. For example, Lineberger and co-workers have shown that in the photodissociation of a very similar system, IBr$^-$(CO$_2$), the CO$_2$ molecule mediates a long-range electron transfer between the separating halogens. This interaction results in a small amount of Br$^-+$I products upon excitation of the $A''$ state of IBr$^-$(CO$_2$), whereas in the bare diatomic the $A'$ state dissociates solely to I$^-+$Br.

Anion photoelectron spectroscopy of I$_2$CO$^-$ reveals a progression in the CO$_2$ bending mode, indicating that the CO$_2$ is slightly bent in the anion. As part of that study, electronic structure calculations and Franck-Condon analysis determined that the ground-state geometry is of C$_2v$ symmetry in which the CO$_2$ is bound at the I$_2$ waist with an OCO bond angle of approximately 177.5$^\circ$; the CO$_2$ lies in a plane that perpendicularly bisects the I-I internuclear axis. Population analysis showed some charge transfer into the $\pi^*$ LUMO of CO$_2$, which would favor a bent geometry, but the distortion can also result from electrostatic interactions. The strong charge-quadrupole interaction of the electropositive carbon and the negatively charged I$_2$$^-$ leads to relatively large solvation energies in these clusters. Cluster calorimetry was used to determine these energies over a range of cluster sizes and yielded a binding energy of 234±21 meV for the first CO$_2$. 

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In this method, the anion binding energy is extrapolated by measuring the shift in vertical detachment energy of I$_2^-$ over a range of I$_2^-$ (CO$_2$)$_n$ cluster sizes. Recent electronic calculations on the microsolvation of I$_2^-$ (CO$_2$)$_n$ clusters$^{26}$ are in substantial agreement with the experimental binding energy, finding values of 224 and 232 meV at the MP2 and CCSD(T) level of theory, respectively.

Herein, we report a kinematically complete study of the three-body photodissociation of I$_2^-$ (CO$_2$) by coincidence imaging of the recoiling photofragments following dissociation of a fast beam of parent ions. Results are presented for dissociation of I$_2^-$ (CO$_2$) following excitation of the I$_2^-$ chromophore into the $A'$ $^2$Π$_{g,1/2}$ state at 720 nm and the $B'$ $^2$Σ$_{g,1/2}$ state at 386 nm. The three-body translational energy distributions show resolved structure resulting from vibrational excitation of the CO$_2$ fragment and directly yield the I$_2^-$·CO$_2$ binding energy. Analysis using Dalitz plots probes the detailed three-body decay mechanism. Differences in the CO$_2$ vibrational distribution and Dalitz plots at the two wavelengths are observed and discussed.

5.3. Experiment

The current study was performed on our fast beam photofragment translational spectrometer that has been described in detail elsewhere.$^{28,29}$ Briefly, I$_2^-$ (CO$_2$) cluster ions are produced by flowing a mixture of 10% CO$_2$ seeded in O$_2$ (25 psig) over iodine crystals (neat O$_2$ for bare I$_2^-$) and subsequently expanding this mixture into a vacuum chamber through a pulsed piezoelectric valve operating at 60 Hz. This free jet expansion is intersected downstream by a continuous 1 keV electron beam, and the resulting ions are accelerated to a laboratory frame beam energy of 8 keV. Mass selection is achieved by a Bakker time-of-flight mass spectrometer$^{30,31}$ that imparts negligible kinetic energy spread to the ion beam. The ion packet of interest is then intersected with a pulse from a Lambda-Physik XeCl excimer-pumped dye laser system (FL 3002 and Scanmate at 720 and 386 nm, respectively) polarized in the plane of the detector. The recoiling photofragments are detected 2.15m downstream by a time- and position-sensitive (TPS) detector, while undisassociated parent ions are intercepted by a 5mm diameter beam block.

The TPS detector comprises three 75 mm diameter microchannel plates in a Z-stack and coupled to a phosphor screen. The image from the phosphor screen is split by a dichroic beam splitter to a photomultiplier tube and CCD camera for relative timing and position information, respectively.$^{32}$ Analysis of this data yields the photofragment masses, the center-of-mass translational energy release $E_T$, and the recoil angle with respect to the polarization of the laser beam for two-body dissociation. In the case of the three-body dissociation, the center of mass momenta of each fragment are calculated providing additional mechanistic information about the fragmentation through the use of Dalitz plot analysis.$^{33}$
5.4. Results and Discussion

5.4.1. Translational Energy Distributions

Figure 5.1 shows the photofragment translational energy dissociation for the two-body dissociation of $I_2^-$ and the three-body dissociation of $I_2^-(CO_2)$ following excitation of the $A^2\Pi_{g,1/2} - X^2\Sigma^+_{u,1/2}$ transition of $I_2^-$ at 720 nm (1.722 eV). Figure 5.2 shows the analogous results from excitation of the $B^2\Sigma^+_{g,1/2}$ state at 386 nm (3.212 eV). In both cases, the excited $I_2^-$ state is repulsive in the Franck-Condon region, the $A^2\Pi_{g,1/2}$ state correlates to $I^- + I(2P_{3/2})$ products, while the $B^2\Sigma^+_{g,1/2}$ state correlates to $I^- + I^*(2P_{1/2})$ products, lying 0.943 eV higher in energy. The two- and three-body distributions are shown as dotted and solid lines, respectively, and the dashed vertical lines indicate the peak position for each feature.

![Figure 5.1. Translational energy distributions for the dissociation of both bare $I_2^-$ (red, dotted line) and $I_2^-(CO_2)$ (solid, black line) following the $A^2\Pi_{g,1/2} - X^2\Sigma^+_{u,1/2}$ transition at $E_{hv} = 1.722$ eV.](image)
Figure 5.2. Translational energy distributions for the dissociation of both bare I$_2$ (red, dotted line) and I$_2^-$ (CO$_2$) (solid, black line) following the $B^2\Sigma^+_{g,1/2} \rightarrow X^2\Sigma^+_{u,1/2}$ transition at $E_{hv} = 3.212$ eV.

At both wavelengths, dissociation of I$_2^-$ produces a single peak whose translational energy is determined by

$$E_T = h\nu - D_0(I^-),$$

(5.1)

where $D_0(I^-)$ is the bond dissociation energy for the relevant dissociation channel: 1.007±0.005 eV and 1.950±0.005 eV for production of I($^3P_{3/2}$) and I*($^2P_{1/2}$), respectively.\textsuperscript{35} The experimental peak positions at the two wavelengths, $E_T$=0.72 eV (720 nm) and 1.26 eV (386 nm), conform to the expected values. The full-width-at-half-maximum peak widths of ~50 meV and the tail toward higher $E_T$ reflect the internal energy of the parent I$_2^-$ anion.

The three-body distributions for I$_2^-$ (CO$_2$) at both wavelengths are shifted toward lower $E_T$, and each distribution comprises two peaks. The dominant peaks are at 0.51 eV and 1.05 eV at 720 and 386 nm, respectively, so each lies ~0.21 eV below the corresponding I$_2^-$ peak. At each wavelength, the smaller peak is shifted to lower $E_T$ by 80 meV with respect to the larger peak, an energy interval equal to the fundamental bending vibrational frequency in CO$_2$ (667 cm$^{-1}$). Based on the peak heights, the relative intensity of the smaller peak with the respect to the higher energy peak is approximately 16% at 720 nm and 59% at 386 nm.
5.4.2. Dalitz Plot Analysis

To gain further insight into the three-body dissociation dynamics, the momentum partitioning among the photofragments in the decay process, \( f_i = \frac{p_i^2}{\sum p_j^2} \), can be represented in a Dalitz plot\(^{33}\) as shown in Figure 5.3.

![Dalitz plots for \( A' \) and \( B \) states](attachment:image.png)

**Figure 5.3.** Dalitz plots of momentum partitioning (\( f_i = \frac{p_i^2}{\sum p_j^2} \)) between the fragments in three-body dissociation of \( \text{I}_2^- (\text{CO}_2) \) for both transitions studied. a) \( A' \)-state b) \( B \)-state.

*The line AB corresponds to equal iodine momenta.

Conservation of energy requires that all points representing a three-body dissociation event lie within the triangle, while conservation of momentum further requires all points to lie within the inscribed circle\(^8\). With unit triangle height, the radius of the inscribed circle is \( \frac{1}{\sqrt{3}} \) with its center at \( \left( \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \). Points along the edge of this circle correspond to events in which the three momentum vectors are collinear, while points near the center originate from more symmetric, non-collinear fragmentation\(^6\). Given that the iodine atoms are indistinguishable in terms of their mass, these plots are two-fold symmetric for this system about the line AB (equal iodine momenta) indicated in Figure 3. To take advantage of this symmetry, we apply a convention of plotting the iodine fragments receiving more (less) of the center of mass momentum on one axis labeled \( I_{\text{fast}} \) \( (I_{\text{slow}}) \). This convention allows the Dalitz plot to be ‘folded over’ with all points now confined to half of the inscribed circle\(^8\).

Dalitz plots for dissociation from excitation to the \( A' \) and \( B \) states are shown in Figure 5.3a) and b), respectively. These plots are similar in appearance with pronounced intensity in the region corresponding to low \( \text{CO}_2 \) momentum \( (f_{\text{CO}_2} \leq 0.1) \), indicating that most of the available momentum is taken up by the recoiling I atoms. The points are noticeably more confined near the radius of the inscribed circle in Fig. 5.3b. These plots are discussed in more detail in Section 5.4.4.
5.4.3. Dissociation Energies

In the three-body dissociation of $I_2^-(CO_2)$, the translational energy for a photodissociation event will be

$$E_T = h\nu + E_{int} [I_2^-(CO_2)] - [D_0(I^-_2) + D_0(I^+_2\cdot CO_2) + E_{int}(CO_2)], \quad (5.2)$$

where $E_{int}$ refers to vibrational and rotational energy of either the parent ion or CO$_2$ fragment, and $D_0(I^-_2\cdot CO_2)$ is the binding energy of CO$_2$ to $I_2^-$. By comparison to Eq. (5.1), if the parent ion and CO$_2$ fragment have no internal energy, then the shift of the three-body peaks in Figs. 5.1 and 5.2 compared to the two-body peaks directly yields the CO$_2$ binding energy.

Given that the two three-body peaks at each wavelength are separated by the CO$_2$ bending frequency, we assign the dominant peak to $\Gamma^- + I^+ + CO_2(v_2 = 0)$, and the smaller peak to $\Gamma^- + I^+ + CO_2(v_2 = 1)$, with the I atom in its $^2P_{3/2}$ or $^2P_{1/2}$ state depending on the excitation wavelength. The peak widths for the three-body features in Figs. 5.1 and 5.2 are similar to those for the two-body features, indicating that the contribution from additional degrees of freedom such as CO$_2$ rotational energy to the three-body widths is negligible. Since the peak maxima in the two-body features give the correct $I_2^-$ bond dissociation energy, it is reasonable to attribute the maximum of the $\Gamma^- + I^+ + CO_2 (v_2 = 0)$ peak to dissociation from ground state parent ions to ground state products. Hence, the difference between the maximum of this feature and that of the two-body feature is an appropriate measure of the CO$_2$ binding energy. Averaging this difference from data taken at both excitation energies, we obtain an average value for the binding energy of $218 \pm 10$ meV.

This value lies within the error of the previous cluster calorimetry measurement of $234 \pm 21$ meV$^{27}$. However, the calorimetry method only measures the shift in electron affinity as a function of cluster size, providing the energy gap between the neutral and anionic cluster rather than the anion solvent binding energies. Thus, that value requires an estimate of the neutral binding energy, whereas the method described herein does not. Fitting the calorimetry data over a range of cluster sizes yielded a value of $95(\pm 16)$ meV for the neutral binding energy. With the $I_2^-(CO_2)$ binding energy obtained here $S^-(1)$, and the previous measurement of the increased electron affinity of $I_2^-(CO_2)$ with respect to bare $I_2^-$, $\Delta E_a = 139$ meV$^{24}$, the neutral binding energy is given by

$$S^0(1) = S^-(1) - \Delta E_a, \quad (5.3)$$

and found to be $80 \pm 15$ meV for I$_2$(CO$_2$).

5.4.4. Three-body Dissociation Dynamics

From fitting and integrating the two peaks in each three-body distribution, we find that dissociation from the $B$ state produces vibrationally excited CO$_2$ in approximately 34% of the three-body dissociation events as opposed to only 13% from $A'$ state dissociation. This dependence upon excitation energy deviates from a strictly Franck-Condon (FC) model of photodissociation$^{36}$, in which the CO$_2$ vibrational distribution is
determined by the projection of the distorted, anion-bound CO$_2$ geometry onto the vibrational states of linear, isolated CO$_2$, yielding the same vibrational distribution for dissociation from either the A' or B state. Hence, it appears that final state interactions as the CO$_2$ separates from the dissociating I$_2^-$ differ for excitation into the two I$_2^-$ states. One can attribute these differences at least in part to the greater translational energy available to the fragments upon excitation to the B state, about 1 eV vs. 0.5 eV, as shown in Figs. 5.1 and 5.2, but additional insights into the mechanistic origin of this effect can be gleaned from comparison with other data.

For example, the photoelectron spectrum$^{24}$ of I$_2^-$ (CO$_2$) shows bend excitation in the CO$_2$ moiety of the neutral complex comparable to that seen here in the CO$_2$ fragment upon excitation to the A' state. As the extent of vibrational excitation in the photoelectron spectrum is determined by the FC overlap of the bent CO$_2$ in I$_2^-$ (CO$_2$) with the linear CO$_2$ in neutral I$_2$(CO$_2$), it appears that the simple FC picture does apply to photodissociation of I$_2$(CO$_2$) via the A' state. In contrast, the CO$_2$ distribution from excitation of the B state is closer to the extent of bend excitation seen in the photoelectron spectrum of I$^{-}$(CO$_2$),$^{25}$ where the CO$_2$ is more strongly bent than in I$_2^-$ (CO$_2$). These comparisons suggest that the CO$_2$ from A' state excitation is leaving from an approximately intact I$_2^-$ moiety, while the CO$_2$ vibrational distribution from B state dissociation is determined more by the I$^{-}$(CO$_2$) interaction than by the I$_2^-$ (CO$_2$) interaction. Such a result might indicate sequential three-body decay upon B state excitation in which the iodine bond breaks first, followed by dissociation of the I$^{-}$(CO$_2$) fragment.

These somewhat speculative arguments can be tested by examining the Dalitz plots in Fig.5.3. The limiting three-body decay mechanisms inferred from these plots, which have been discussed in detail previously$^{4,5}$, can be summarized as follows. Points along the line AB represent events in which the I atoms recoil with equal and opposite momentum, with the remainder appearing as CO$_2$ recoil. Events at point A represent those in which zero momentum is imparted to the CO$_2$ fragment, which essentially acts as a spectator. As one moves away from point A along AB, there is increasing momentum taken up by the CO$_2$, with the three momentum vectors forming a "T" with C$_{2v}$ symmetry. Events along this line correspond to synchronous-concerted dissociation, in which the I-I and I$_2$-CO$_2$ bonds break simultaneously.

Points along the circumference of the inscribed circle correspond to collinear events in which all three momentum vectors are parallel; moving away from point A along the circumference corresponds to increasingly asymmetric partitioning of the momentum between the two I atoms, with the CO$_2$ making up the difference. This partitioning indicates an asynchronous-concerted decay mechanism, in which the second bond breaking event occurs within a vibrational period of the first. This type of decay confines both bonds to break within the original plane of the parent molecule that contains the two dissociating bonds and results in intensity along the edge of the allowed circular region. Asynchronous concerted decay is distinct from asynchronous sequential decay, in which the intermediate formed after the first bond cleavage lives on the order of a rotational period prior to dissociation. Asynchronous sequential decay leads to a constant fraction of the momentum in one fragment, as evidenced by a line segment parallel to one side of the triangle in the Dalitz plots.$^{12,37}$
In a previous study of $I_2^-(Ar)$ on our instrument \(^{29}\), the dominant mechanism was synchronous-concerted dissociation with nearly zero momentum imparted to the Ar atom, i.e. events clustered around point A on the Dalitz plot. While the Dalitz plots for $I_2^-(CO_2)$ do show contributions at point A and along AB, there are considerably more dissociation events with unequal partitioning of the momenta between the iodine atoms and non-zero CO\(_2\) momentum at both excitation energies. As with $I_2^-(Ar)$, deviations in the initial cluster geometry from strict $C_{2v}$ symmetry owing to large amplitude vibrational motion can also result in a small number of dissociation events with unequal iodine momenta even though the dissociation remains synchronous. This mechanism should contribute to some of points lying off the line AB in the Dalitz plots for $I_2^-(CO_2)$. However, compared to $I_2^-(Ar)$, most of the signal lies well away from the AB line and there is significantly more intensity along the edge of the inscribed circle, the signature of asynchronous-concerted decay. There is no evidence for asynchronous-sequential decay.

Comparing the plots at the two wavelengths, the dissociation events from $B$ state excitation are more confined to the diameter of the inscribed circle than those from $A'$ state excitation. Hence, while both wavelengths are dominated by asynchronous rather than synchronous decay, the $B$ state represents a purer case of the asynchronous-concerted mechanism, in which a short-lived $I^-(CO_2)$ fragment promptly dissociates following the initial I-I bond cleavage. This distinction may reflect the more repulsive interaction between the two I atoms in the $B$ state than in the $A'$ state; in the $B$ state, the two I atoms separate rapidly, leaving the CO\(_2\) attached to the $I^-$ fragment, whereas in the $A'$ state, the separation between the two bond cleavages is not as clean.

It thus appears that the distinction between the Dalitz plots at the two wavelengths is consistent with the origin of the differing CO\(_2\) vibrational distributions that was suggested at the beginning of this section. Upon excitation of the $A'$ state, the departing CO\(_2\) is interacting with a dissociating $I_2^-$ moiety, whereas $B$ state dissociation involves a more distinct passage through a short-lived $I^-(CO_2)$ intermediate. Based on the Franck-Condon picture outlined above, these dynamics would result in more bend excitation in the CO\(_2\) fragment from $B$ state dissociation, consistent with the results seen in Figs. 1 and 2. It would certainly be of interest to perform molecular dynamics calculations on the two excited states of the cluster to test these ideas more rigorously.

5.5. Conclusions

The three-body photodissociation of $I_2^-(CO_2)$ has been studied following excitation to both the $A'^2\Pi_{g,1/2}$ state at 720 nm and the $B^2\Sigma^+_{g,1/2}$ state at 386 nm of the $I_2^-$ chromophore. The three-body translational energy distributions directly yield $D_0(I_2^- \cdot CO_2)=218\pm10$ meV. These distributions are vibrationally resolved and show short progressions in the CO\(_2\) bending mode, with more bend excitation resulting from excitation of the $B$ state. Dalitz plots of the three-body events indicate that dissociation at both wavelengths is primarily asynchronous-concerted, although the results for the $B$ state conform to this limit more than those for the $A'$ state, suggesting the formation of a transient $I^-(CO_2)$ intermediate at 386 nm excitation. These differences in mechanism are proposed as the origin of the differing vibrational distributions at the two wavelengths, since the formation and dissociation of such an intermediate is likely to result in more CO\(_2\) bend excitation than a less asynchronous mechanism.
5.6. Acknowledgments

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5.7. References

Appendix 1

A.1. Data Acquisition on FRBM

In this section, details about actually running this experiment will be provided such that new users will have some sort of guide on how to effectively collect data using the instrument. These types of details have been omitted from many of the previous theses on this project, and as well, the instrument has undergone numerous changes making this more necessary.

Firstly, the most important bottleneck of this experiment is usually generating sufficient amount and stability of the ion signal of interest to make the acquisition of enough data to build a kinetic energy release spectrum possible. This is highly dependent on the species of interest, and conditions that work well for one anion won’t for another. This aspect of the experiment is typically worked out through trial and error. The most crucial experimental timing to consider here is the ‘reference to ground’ timing when the reference to ground cylinder is rapidly pulsed from the beam energy to ground. This timing with the new valve setup is most often in the range of 150-250 μs after the valve opens. Optimum signal well outside this range (< 100 μs or > 300 μs) is rarely encountered.

Once ion signal has been found, the ion throughput through the pinholes dividing the differentially pumped regions of the instrument should be maximized. This is done by both adjusting the voltages of the vertical and horizontal steering plates as well as the einzel lens voltage. Steering voltages can vary, however the einzel lens voltage is often best at less than half of the beam acceleration voltage i.e. ~4 kV would be a typical setting for a final beam voltage of 9 kV.

From here, the ion signal can be further improved by first adjusting the mass spectrometer timing (the time at which the voltage is reversed between the two mass spectrometer plates). However, the ion signal is generally not very sensitive to this timing, so scanning in steps of 100 ns in the range of 800-2000 ns after the reference to ground trigger is recommended. Some fine tuning can then be done in steps of ±10 ns but will unlikely have a large impact. Finally, the mass spectrometer is almost always operated at ~30 V as lower voltages lead to broader ion signal while higher voltages often give less signal amplitude. One case in which it can be useful to run the mass spec at higher voltage is when you wish to minimize the kinetic energy spread of the ion packet by reducing the ion compressor voltage.

Optimizing both the ion compressor voltage and timing is critical for the ion signal quality. If the ion compressor trigger timing is inappropriately set, this results in ion signal that has a broad, gradual leading edge. Unlike the mass spectrometer timing, ion signal is very sensitive to the ion compressor such that this timing should be adjusted in steps of ±10 ns until the leading edge of the signal is very sharp/steep. This will help maximize the amount of anion photodetachment. The ion compressor voltage should then be tweaked to increase signal amplitude and shape. It is most closely related to the beam voltage where beam acceleration voltages of 7-9 kV usually require ion compressor voltage in the range of 150-250 V, while 50-150 V is typical of beam voltages of 5-7 kV. If the ion compressor voltage is too low, the ion signal will also appear broad (i.e. less compressed). Running the ion compressor voltage too high
doesn’t degrade the signal quality nor does it really improve it (there’s some limit to the compression of the ion packet), but it will introduce an unnecessary amount of kinetic energy spread into the ion packet which is undesirable. FWHM of the ion packet should be ~ 20 ns with optimal settings.

Now that the ion signal has been optimized, the detachment and dissociation laser trigger timings need to be found. For the detachment laser, this is done by using the deflection plates in the third differential region of the instrument. A constant bias is applied between these plates such that the ions are deflected and unable to pass through the pinhole separating the third differential region and the detector region of the instrument where the retractable MCP setup is located. Assuming that the detachment laser has been aligned through the detachment window, we can scan this timing until signal reappears on the oscilloscope from the retractable MCP setup at the expected arrival time of the ion of interest. As the detachment laser leads to the formation of a neutral species, the now neutral packet will be unaffected by the deflection plate and will pass through the pinhole and be detected on the MCPs. For this procedure, initially scan the laser trigger in steps of 10 ns then fine tune in steps of 1 ns to maximize signal. While looking at the oscilloscope, it is also important to finely adjust the vertical alignment of the laser beam using the focusing lens to increase the spatial overlap of laser beam and ion packet such that peak signal is achieved. The laser trigger timing is obviously dependent on the anion’s time-of-flight which is in turn dependent on its mass and the beam acceleration voltage. Photodetachment timings for different anions, beam voltages, and detachment lasers have been noted in detail in the laboratory notebooks.

The final step before beginning to acquire data with the DLD is determining the trigger timing for the photodissociation laser. Much of this procedure is similar to the procedure for the photodetachment laser except that the deflection plates in the third differential region cannot be used. However, in the detector region, there is another set of deflection plates (called ‘the flipper’) that is used to steer the ions onto a blocking strip on the retractable MCP setup (see Doug Cyr’s thesis). In contrast to the deflection plates in the third differential region, the flipper voltage is pulsed for a microsecond which is relatively long with respect to the time-of-flight of the anions. As such, it is usually quite easy to find an appropriate flipper timing. In addition, the flipper can be tuned from 0-300 V, so the pulse timing and the voltage of flipper should be set so that the ions have been effectively steered onto the blocking strip and the signal on the oscilloscope has been removed. Now, as with the detachment laser, the photodissociation laser should be scanned in steps of 10 ns until signal reappears on the oscilloscope. Given the higher photon energy of the photodissociation laser, the signal that reappears will sometimes include direct photodissociation of the anion leading to signal that is more spread out in time than the anion signal. Often though, it will simply be anion photodetachment that is observed when the dissociation laser is temporally overlapped with the anion of interest. Again, adjust the vertical alignment of the photodissociation laser to maximize spatial overlap with ion packet. With the two laser timings known, it is now possible to begin collecting photodissociation with the DLD.

As mentioned before, the calibrated voltages to run the detector are +2400, 2360, and 2750 V for the back MCP, holder, and hexanode, respectively (the front MCP is grounded). In rare cases, if the detector voltages are ramped up too quickly arcing will occur. This has only ever been observed at voltages over 2 kV, so it is recommended to increase the voltage more slowly in this range (~100-200 V every 5-10 minutes) to prevent arcing.
The data acquisition program provided with Roentdek hexanode is called Cobold, and a user manual is provided on Roentdek’s website that provides much more information about the program than will be discussed here. To begin data acquisition on the computer, there are three files required in the data folder:

File 1: Cobold2008R2_32bit_TDC8HP-Pro-DAq-part1.ccf

File 2: Pro_DAn-part2.ccf

File 3: correction_table_i_det_part3.ccf

Most importantly, File 1 contains information concerning how the detector is triggered and the length of the detection window. Open Cobold and type ‘exe’ into the command line and select File 1 (in the folder you wish to save your data), then entitle the data file which has a .lmf extension (list-mode file) and click OK.

Now, the detector is acquiring data and it is necessary to find the appropriate external trigger timing (if this is already set properly these next steps are unnecessary). First, type “update 1s” into the command line of Cobold so that it updates the data in real time. Because in most cases, the data collection rate for the photofragments is relatively slow, it is easiest to find the timing window using the detachment signal. To do this, lift the beam block out of its blocking position so that the neutral parent beam hits the detector. Then, the external trigger can be more quickly and easily scanned until a significant amount of signal is seen in the center of the detector, Using the TOF distribution, center the arrival of the parent beam in the detection window around 500 ns. Move the beam block back into blocking position and restart the data acquisition by typing ‘stop’ into the command line and following the steps above regarding executing and saving the data acquisition.