
Ameyali Tapia

University of San Francisco, atapia5@usfca.edu

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A thesis presented to the faculty
of the Department of Chemistry
at the University of San Francisco
in partial fulfillment of the requirements for the degree of
Master of Science in Chemistry

Written by

Ameyali Tapia
Bachelor of Science in Chemistry
University of California, Santa Cruz

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Thesis Written by Ameyali Tapia

This thesis is written under the guidance of the Faculty Advisory Committee, and approved by all its members, has been accepted in partial fulfillment of the requirements for the degree of

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the University of San Francisco

Thesis Committee

Giovanni Meloni, Ph.D.                                      Date
Research Advisor

Michael Stevenson, Ph.D.                                      Date
Assistant Professor

Amrita Bhattacharyya, Ph.D.                                 Date
Assistant Professor

Jeffery Paris, Ph.D.                                         Date
Acting Dean, College of Arts and Sciences
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Abstract

This thesis presents the combustion study of 2-tertbutylfuran (2-TBF) in reaction with atomic oxygen (O($^{3}\text{P}$)). Data was collected at the Advanced Light Source (ALS) of the Lawrence Berkeley National Lab, using tunable vacuum ultraviolet radiation coupled with a multiplexed mass spectrometer to acquire the data. These data were taken at low pressures of 7 and 8 torr at temperatures of 550 K and 700 K, respectively. Primary products of the system were identified and characterized, while reaction pathways of the products are currently being studied to ensure thermodynamic feasibility. Branching fractions of the system were also calculated, to view the ratio of the concentration of products to the concentration of the reactants. The determination of the carbon-bromine (C-Br) single bond photoionization cross section using six different bromine species. This experiment also utilized the ALS, taking data at 298 K at various pressures. Using three sp$^2$ species and two sp$^3$ species, the HOMO molecular orbitals of both the neutral and cationic species were analyzed to determine whether hybridization made a difference in cross section. The cross sections of each of these six bromine species were also calculated, all at 11 eV, and subtracted from literatures values of the same non-brominated molecules to determine the single bond C-Br cross section.

Chapter one of the thesis goes over volatile organic compounds (VOCS) in the atmosphere along with the reactions they undergo in the environment. This chapter also discusses how these compounds contribute to global warming and other negative environmental impacts. Chapter 2 of the thesis presents the experimental methods used, while Chapter 3 explains the theoretical and computational methods used in these experiments. The combustion reaction of 2-TBF and its products are presented in Chapter 4, while the determination of the cross section of the C-Br bond and the absolute cross sections for brominated organic compounds are discussed in Chapter 5.
Chapter 1

1. Introduction

1.1 Fossil Fuels and Effects on Greenhouse Gas Emissions

1.2 Combustion

1.3 Biofuels and Biofuels Additives

1.4 Overview of Thesis

1.5 References
Chapter 1

1.1 Fossil Fuels and Effects on Greenhouse Gas Emissions

To this day, fossil fuels continue to dominate the energy sector, supplying about 80% of the world’s energy.¹ These fuels are mainly used in three forms: oil, coal, and natural gas. Though these fuels are efficient at providing energy for transportation, heating, and electricity, they have many major drawbacks. To begin, these fuels are a non-renewable resource, formed from the carbon-rich remains of animals and plants that were decomposed, compressed, and heated underground.² When these fuels are burned, they produce many harmful gases, also known as greenhouse gases (GHGs). Among these gases are methane (CH₄), nitrous oxide (N₂O), volatile organic compounds (VOCs), and carbon dioxide (CO₂). While all these gases are harmful to the environment, VOCs and CO₂ have been found to have the most emissions in the environment, which contribute heavily to global warming and climate change.³

In 2021, CO₂ emissions were calculated to be 6,340 million metric tons in the United States, about 79.4% of total greenhouse gas emissions, as shown in Figure 1.1.³ Although CO₂ is found naturally in the environment’s carbon cycle, the overabundance of this gas due to transportation, electricity, and industry has disturbed this cycle and influenced the ability of natural sinks, like forests and soil, to remove and store CO₂ from the atmosphere.
Volatile organic compounds (VOCs) are organic chemicals that evaporate into the atmosphere at room temperature. The main source of these chemicals are the burning of gasoline and natural gas. When VOCs react with sunlight and nitrogen oxides, tropospheric ozone is formed, which is another harmful air pollutant. Some examples of VOCs include benzene, polycyclic aromatic compounds (PAHs) and butadiene. Benzene is typically found in vehicle exhaust, PAHs are released when coal, oil, and gas are burned, and finally, butadiene is found in gasoline engine exhaust. Figure 1.2 shows the different sources of VOCs, from household emissions to the industry and energy sector. All these compounds are known to cause cancer, among other harmful effects.
As more and more gases are released into the atmosphere, a ‘blanket’ is formed over the earth, trapping heat from the sun, and thus increasing earth’s temperature. In a normal cycle, also known as the radiation balance, sunlight radiation is easily able to hit the earth’s surface and go back into the atmosphere, with greenhouse gases providing only a small amount of cover to allow the earth’s surface to stay warm. Due to the increased use of fossil fuels since the industrial revolution, this ‘blanket’ has only become thicker, trapping heat on the earth’s surface. Figure 1.3 shows the difference between the natural greenhouse effect and the human enhanced greenhouse effect. Researchers have found that the earth’s temperature has increased by as much as 1.1 °C from 1901 to 2020 as a result of increased greenhouse gas emissions. 

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**Figure 1.2 Sources of Volatile Organic Compounds**

![Image of VOC sources]
Climate change has many negative effects in the environment, including rising sea levels, melting glacier and ice caps, and deterioration of air quality throughout the world. Since 1880, the global sea levels have risen 8-9 inches, with the rate of rising sea levels accelerating from 0.06 inches throughout the 20th century to 0.14 inches per year from 2006 to 2015. Subsequently, this has contributed to the increased danger of flooding, shoreline erosion, and hazards from storms. Another factor caused by climate change is the melting glacier and ice caps. Compared to 1970 (0 meters of liquid water), it has been estimated that glaciers have lost the amount of ice equivalent to nearly 25 meters of liquid water, a factor that also contributes to the rising sea levels. Combustion contributes heavily to climate change, which will be discussed in the next section.
1.2 Combustion

Combustion of fossil fuels is an exothermic reaction between the fuel and an oxidizer to produce energy, heat, and various byproducts. In a perfect system, this combustion would ideally only produce CO$_2$, H$_2$O, and heat; however, these reactions form many other products, seen from the combustion of methane (CH$_4$) in Figure 1.4. Another product of combustion of these fuels is the release of nitrogen oxides into the atmosphere. These nitrogen oxides contribute to the formation of smog and acid rain. When these nitrogen oxides return to the land, they wash into nearby bodies of water, where they contribute to pollution, harmful algae blooms, and oxygen-deprived aquatic zones.

![Combustion Mechanism of Methane](image)

**Figure 1.4** Room Temperature (298 K) Combustion Mechanism of Methane$^{10,11}$

Combustion also varies depending on the type of engine being used, generally known as four-stroke cycle engines. These engines have four distinct processes: intake, compression, combustion and power stroke, and exhaust. Spark ignition (SI) engines use fuel mixed with air that is then inducted into the cylinder during the intake process. Once the piston compresses the fuel-air mixture, the spark ignites it, causing
In diesel or compression engines (CI), on the other hand, only air is inducted into the engine and then compressed. These engines then spray the fuel into the hot compressed air at certain rate, which causes it to ignite. Another notable type of engine is the homogeneous charge compression ignition engine (HCCI). This engine works by using diluted homogeneous charge and when the mixture reaches chemical activation of the precursor and the activating agents, auto-ignition takes place. A schematic of all three engines are shown in Figure 1.5.

**Figure 1.5** Schematic of Spark Ignition (SI), Compression Ignition (CI), and Homogenous Charge Compression Ignition (HCCI) Engines

There are many factors that contribute to the formation of unhealthy byproducts of combustion into the environment, most notably engine knocking. Engine knocking occurs when fuel is burned unevenly in the engine, causing erosion of the engine, an increase of air pollution, and, ultimately, limits the thermal efficiency of the engine. Among the gases that contribute to air pollution as a result of engine knocking are nitrogen oxides and unburned hydrocarbons. Between the three types of engines described, SI engines have the most knocking properties.
1.3 Biofuels and Biofuel Additives

Due to the aforementioned drawbacks of fossil fuels, both in the environment and in combustion, researchers have actively been on the hunt for a cleaner, more efficient fuel that is renewable and easily reproducible. Among these fuels are ethanol and biodiesel, both of which are considered first generation biofuels. Ethanol is made from plant material also known as biomass and is used as a blending agent with gasoline to increase octane numbers while reducing smog emissions.\textsuperscript{30} About 98% of U.S. gasoline contains ethanol, with a 10% ethanol to 90% gasoline blend, which slightly reduces air pollution. Because of the higher octane numbers this ethanol blend produces, the engine is less susceptible to engine knocking and ensures more efficient drivability.\textsuperscript{19}

Biodiesel is formed from new and used vegetable oils or animal fats and is biodegradable and nontoxic. The main advantage of this fuel is that it can be used in traditional diesel engines with little to no modifications, either as a blend of 20% biofuel and 80% diesel fuel (B20), or as B100, which is a 100% biodiesel fuel.\textsuperscript{20,21} According to the United States Department of Energy, this fuel has been shown to substantially reduce pollutant emissions, including unburned hydrocarbons (HCs), carbon monoxide (CO), sulfates, and particulate matter (PM).\textsuperscript{20,21} B20 specifically has been shown to reduce PM, CO, unburned HC, and carbon dioxide (CO\textsubscript{2}) emissions by 10%, 11%, 21%, and 15%, respectively.\textsuperscript{22}

More recently, second generation biofuels have been of more interest to researchers for their ability to be produced from residual and waste products, or unconsumable biomass. These biofuels include carbon-based fuels, such as furans like 2-methylfuran (2-MF). 2-MF has been studied extensively due to its similarities to fossil fuels, while still being able to run in conventional engines with little to no modification. A study done in 2021 by Hoang et al.\textsuperscript{23} shows the combustion behavior of 2-MF as a potential biofuel, while also discussing the feasibility of running in traditional engines. Because 2-MF has shown promising results as a potential biofuel, further studies for other furan derivatives are crucial to finding a cleaner, more efficient fuel for the future. This thesis studies a potential biofuel, 2-
tertbutylfuran, to help modelers understand the mechanisms of potential pollutant formation and under which experimental conditions these reactions become more or less relevant. Figure 1.6 shows production methods for first, second, and third generation biofuels.

Figure 1.6 Biofuel Generation and Production

1.4 Overview of Thesis

Chapter 2 of the thesis presents the experimental methods used in greater detail, while Chapter 3 explains the theoretical and computational methods used in these experiments.

Chapter 4 of this thesis studies the elementary combustion reaction of a potential biofuel, 2-TBF in reaction with atomic oxygen (O$^{(3)P}$). Data was collected at the Advanced Light Source (ALS) of the Lawrence Berkeley National Lab, using tunable vacuum ultraviolet radiation coupled with a multiplexed mass spectrometer to acquire the data. These data were taken at low pressures of 7 and 8 torr at temperatures of 550 K and 700 K, respectively. Primary products of the system were identified and
characterized, while reaction pathways of the products are currently being studied to ensure thermodynamic feasibility. Branching fractions of the system were also calculated, to view the ratio of the concentration of products to the concentration of the reactants.

Chapter 5 discusses the determination of the carbon-bromine single bond photoionization cross section using six different bromine species. This experiment also utilized the ALS, taking data at 298 K at various pressures. Using three sp² species and two sp³ species, the HOMO molecular orbitals of both the neutral and cationic species were analyzed to determine whether hybridization made a difference in cross section. The cross sections of each of these six bromine species were also calculated, all at 11 eV, and subtracted from literatures values of the same non-brominated molecules to determine the single bond C-Br cross section.
1.5 References


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Chapter 2

2.1 Experimental Methods

2.1.1 Sample Preparation

2.1.2 Details of Synchrotron-Based Measurements at the Advanced Light Source

2.1.3 Multiplexed Photoionization Mass Spectrometer

2.1.3.1 Excimer Laser

2.1.3.2 Time-of-Flight Mass Spectrometer

2.1.3.3 Microchannel Plates Detector

2.1.3.4 Vacuum Pumps

2.2 References
Chapter 2

This chapter focuses on the experimental setup used to obtain the data presented in this thesis. All data collection is conducted at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL), using tunable synchrotron radiation coupled with a multiplexed time-and-energy resolved mass spectrometer. Experimental details will be described within this chapter.

2.1 Experimental Methods

2.1.1 Sample Preparation

All reactants of interest (2-tertbutylfuran, bromobenzene, propargyl bromide, 1,3-dibromobenzene, 1,2-dibromoethylene, 2-bromobutane, and 2-bromopropane) are obtained from Sigma-Aldrich at known purities (97%, 99%, 80%, 97%, 98%, 98%, 99%, respectively) and are stored as liquids at room temperature. These compounds are prepared for experimentation using a freeze-pump-thaw purification method, which consists of a test tube, vacuum pump, and a gas cylinder, shown in Figure 2.1. The process begins when the bubbler, containing a small amount of the reactant is placed in a Dewar filled with liquid nitrogen until the sample is frozen. Next, the vacuum pump is opened to pump out any gaseous impurities that may have been in the sample. Once the vacuum pump is shut off, the sample is thawed to liquid form once again, and the process is repeated at least two more times to ensure complete purification of the compound. Before being placed into the gas cylinder, the gas lines must be flushed out with helium to remove any remaining gas molecules from previous experiments and pumped for several hours. Once this is done, the sample is then moved to the gas cylinder by opening the valves until the pressure is stabilized, and once this happens, helium is flowed through the gas cylinder to allow the sample to reach a molar fraction of ~1%, with total pressure around 2,000-2,500 torr. The pressures of the sample are monitored and recorded using two Baratron digital pressure readers, one of which measures high pressures up to
10,000 torr, while the other measures low pressures of 0.1-10 torr. Once this process has completed, the compounds are now ready to be run in the mass spectrometer.

**Figure 2.1** Chemical Sample Preparation Room at ALS, taken March 24\(^{th}\), 2023

### 2.1.2 Details of Synchrotron-Based Measurements at the Advanced Light Source

All reactions in this work have been analyzed using a multiplexed time-and-energy resolved mass spectrometer at the Advanced Light Source (ALS) of the LBNL (beamline 9.0.2). The purpose of the ALS is to provide a bright radiation in a wide energy range.\(^{1,3}\) This third-generation synchrotron at the ALS is composed of six parts: electron source, linear accelerator (linac), booster ring, storage ring, insertion devices called undulators and wigglers, and finally, beamlines (Figure 2.2).\(^{4}\) This section will go over the operating procedure of the ALS.
The process begins with the electron source, which consists of an electron gun and the electrons produced from that gun to be accelerated to nearly the speed of light. This electron gun consists of a cathode, a copper screen, and an anode. The barium aluminate cathode is first heated to release electrons from its surface. A voltage is then applied every 500 millionth of a second to create the pulsing anode, which allows for the electrons to move towards the copper screen. On the other side of this screen, there is a stronger anode that pulls the electrons through and into the buncher section of the linac (linear accelerator), which accelerates and increases the electron density of the electron bunches, where each electron bunch contains approximately $1.5 \times 10^{11}$ electrons. From there, the electron bunches are further accelerated and are moved further down the linac in wave patterns using microwave radiation from the klystron part of the radio frequency (RF) system, a system used throughout the ALS storage ring that provides energy to electrons (The RF system will be explained more in detail in the next paragraph of this section). Next, the electron bunches leave the buncher at about 60% the speed of light with 120 keV of kinetic energy. The RF system continues to provide energy to these electron bunches, which allows for the continuous acceleration and increase of electron density, while electromagnets lying along the length of the linac are used to maintain the electron density. At the end of this process, when the electrons are
fully through the linac, they are nearly at the speed of light, with an energy of 50MeV. Both the electron gun and the linac components are shown in Figure 2.3. This entire process is under vacuum, to ensure there are no accidental collisions between electrons and any other unwanted molecules.

The RF system provides continuous energy to the electrons. This system contains three components, klystrons, wave guides, and RF cavities. The klystron is a microwave amplifier, which moves wave pulses down the wave guides, which are coaxial cables connected to different RF cavities throughout the ALS. The RF cavities are responsible for carrying the resulting microwave radiation directly to the electrons, with a wavelength of 0.6 meters. A wave pattern is created from this radiation, allowing the electrons to be accelerated or decelerated based on their location on the wave, as shown in Figure 2.4.
The next sections of the ALS are the booster and storage ring, where the electron bunches are further accelerated using the booster ring and held at high energy in the storage ring.\textsuperscript{3,4} These electron bunches enter the booster ring as an electron beam, where they are circled around about 1.3 million times, reaching 1.5 GeV of kinetic energy, about $\sim$99\% the speed of light. Within the booster ring, there are quadrupole magnets, which ensure the electron beam is focused, and dipole magnets, which ensure the electron beam is being turned throughout the ring. Once reaching the necessary energy, the electron beam moves into the storage ring through an injection system. The storage ring, a dodecagonal-like shaped ring, allows for the energy of the electron beam to remain around 1.5-1.9 billion eV. The arc-shaped sections of the storage ring contain three precision electromagnets that help the electron beam focus and bend around the storage ring. The straight sections of the storage ring contain pieces known as undulators and wigglers, which form beams of light from emitted photons, which are then directed to the individual beamlines. These insertion devices contain a multitude of magnets, oriented in an alternating format, that move the electrons in a wave-like pattern and can be adjusted to reach the specific radiation energy needed for the experiment. While the undulators have over 100 magnetic poles and produce a more specific synchrotron radiation, the wigglers have less magnets and are able to produce synchrotron radiation with a broader spectrum.

Synchrotron radiation is then directed into several beamlines. The beamline used for the experiments described in this thesis is the Chemical Transformations (Vacuum Ultraviolet) Beamline 9.0.2. The radiation is first refined by an absorption cell filled with Argon (Ar) or Krypton (Kr) gas, which only allows harmonic radiation lower than the ionization energy of Ar or Kr to pass through.\textsuperscript{5} Next, the radiation is passed through an Eagle monochromator, which refines the light to a bandwidth of 10-50 meV. This monochromator allows for the bandwidth of the light beam’s photon energies to be narrowed, according to Bragg’s Law.\textsuperscript{7}

\[ n \lambda = 2 d \sin \theta, \text{ where } n \text{ is an integer (Equation 2.1) } \]
Bragg’s Law expresses that since the incident beam hits the reflecting plane of the monochromator at a specific angle (θ), only a specific wavelength (λ) can be reflected from the original beam (Figure 2.5). Because of this, different wavelengths can be measured by adjusting the angles of the incident beam and the reflecting plane. By the end of this process, the synchrotron radiation has been narrowed to a 2.5% bandwidth with a 7.2-25 eV range, however, data from 8-11 eV is the general light range considered for these experiments. This radiation is considered ‘quasi-continuous’ since the detection bandwidth is much smaller than the repetition rate of the pulsation of the light.

\[ m\lambda = d \sin \beta \pm d \sin \alpha \]

Figure 2.5 Mathematical Interpretation of Bragg’s Law

2.1.3 Multiplexed Photoionization Mass Spectrometer

This section will discuss the multiplexed photoionization mass spectrometer, which consists of an excimer laser, ionization chamber, microchannel plate (MCP) detector, and finally, the time-of-flight mass spectrometer (TOF-MS). This experimental set-up is shown in Figure 2.6, where a vacuum system is incorporated to maintain a low pressure throughout the apparatus. The gas mixtures previously described in Sec. 2.1.1, combined with the precursor gases, are flowed into a quartz reactor tube by calibrated mass flow controllers. This quartz reactor tube is a slow-flow reactor, with an 18 μm Nichrome tape wrapped around to prevent short circuits, maintain a constant temperature, and minimize any chance of radiating heat into the source chamber. The temperature is measured and maintained by a thermocouple on the centerline of the reactor. In addition, the pressure in the reactor is measured with a
capacitive manometer and maintained with a closed-loop feedback valve attached to the roots pump (the roots pump will be described in detail in Section 2.1.3.4). The tape is covered with a square-weave, ZYW-15 cloth, and a gold-plated copper sheath to further protect the apparatus. The combustion reaction of 2-tertbutylfuran with O(3\(P\)) presented in this work were completed at pressures of 7 and 8 torr, with temperatures 500 K and 700 K, respectively. The determination of the photoionization cross sections for a carbon-bromine single bond were completed at 298 K with various pressures.

![Experimental Set-up of the Multiplexed Mass Spectrometer](image)

**Figure 2.6** Experimental Set-up of the Multiplexed Mass Spectrometer

### 2.1.3.1 Excimer Laser

The first step in the process is the excimer laser, which photolyzes the selected precursor of the experiment to produce free radicals needed to react with the gas molecules to replicate a combustion-like reaction.

To understand how lasers function, population inversion and stimulated emission must be discussed. Population inversion explains the redistribution of atomic or molecular energy levels within a system. If a system is at thermal equilibrium, also known as ‘normal distribution’, there will be more atoms at the lower energy levels than at higher ones. However, with population inversion, the system’s equilibrium is disturbed, resulting in more of the atoms to be at higher energy levels rather than lower ones, as
demonstrated in Figure 2.7. These higher energy level atoms will eventually return to the lower energy states, resulting in the emission of energy as photons. To ensure all emitted photons have the same desired wavelength, these photons are stimulated with an incoming photon outside of the system. This incoming photon is considered a source of radiation, and becomes amplified, since the emitted photons in the system will move in the same direction as the incoming photon. This is known as light amplification by simulated emission of radiation, or LASER.

Figure 2.7 Energy Level Diagrams for Population Inversion and Equilibrium

This laser uses noble gases Kr, Ar, and Xe, that are mixed with halogens, F₂, Br₂, or Cl₂, to form excimers, or dimers that only exist in their electronic excited state. In this experiment, a xenon fluoride (XeF) excimer laser is used to produce the photons necessary for the photolysis of nitrogen dioxide (NO₂). To begin the process of population inversion that is needed to produce the laser, both xenon and fluorine gas are flowed through the gas chamber of the laser apparatus. Energy discharge will produce a spark, prompting the excitation of xenon atoms, which will then react with fluorine gas to form the following:

\[ \text{Xe}^* + \text{F}_2 \rightarrow (\text{XeF})^* + \text{F} \] (Equation 2.2)
The (XeF)* is now considered bound and will eventually drop to the ground state to form unbound XeF, which will emit photons at a wavelength of 351 nm. In this case, the (XeF)* compound is known as the excimer. The laser in this experiment is pulsed at 4 Hz with 160 mJ per pulse. In the experiments described in this thesis, the photolytic precursor used is NO\(_2\), which dissociates into NO and the O(\(^3\)P) radical to react with 2-tertbutylfuran, as shown below.

\[
\text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P}), \text{ with } h\nu = 351 \text{ nm (Equation 2.3)}
\]

### 2.1.3.2 Time-of-Flight Mass Spectrometer

This section will describe the multiplexed photoionization mass spectrometer used in this work. This mass spectrometer uses a Wiley-McLaren time-of-flight mass spectrometer design, which allows for continuous and simultaneous detection of ionic species at multiple mass-to-charge ratios (m/z), using high resolution maintained by electric fields.\(^{11}\) Using synchrotron radiation discussed in Sec. 2.1.2, the reaction species can be ionized into cations and are then directed to the time-of-flight analyzer by DC electric fields.\(^{12}\) These electric fields focus and align the cations of the reaction species to the end of the flight tube of the time-of-flight mass spectrometer. After this, the cations are guided to the detector by opposing repellers, positive electric fields, at 150 V, and pullers, negative electric fields, at -150 V. These accelerated ions are separated based on differing velocities as they travel down the flight tube. Because the velocity of an ion is only reflective of the specific m/z ratio, since the same electric field (U) is applied to all ions which result in the same initial kinetic energy (KE), the following equation can be used to describe the relationship between the specific velocities (v) and mass (m):

\[
v = \sqrt{\frac{2zeU}{m}} = \sqrt{\frac{2KE}{m}}, \text{ where } z = \text{ integer of the electron charge and } e = \text{ electron charge (Equation 2.4)}
\]
Based on this equation, ions that have lighter mass will have a faster velocity and vice versa, meaning heavier ions will reach the flight tube last. The cations will then be detected via a microchannel plates detector (MCP), which will be discussed in the next paragraph.

2.1.3.3 The Microchannel Plates Detector

The microchannel plates detector, located at the end of the field-free flight tube, collects data from the TOF-MS at varying masses. To do so, the MCP detector amplifies the signal of detected ions based on the arrival times to the plate. One MCP plate is composed of channel electron multiplier (CEM) tubes that are placed close together to increase the probability of ion collisions. Since these tubes are known semiconductors, any ion collision with the MCP plate can lead to the formation of secondary electrons that are then accelerated by an electric field. In this experimental apparatus, two MCP plates are stacked in a ‘V-stack’, or a chevron plate arrangement for plate-to-plate signal amplification, shown in Figure 2.8. This ‘V-stack’ reaches a capacity to generate $10^6$ electrons for each incoming cation that collides with the MCPs. Comparing this stack to the ‘Z-stack’ or a z-shaped arrangement of plates, the ‘Z-stack’ has a much more powerful signal amplification, reaching a capacity of generating $10^7$ electrons. This raw data is shown in a 3D block, which will further be discussed in the next chapter of data analysis.

**Figure 2.8** Diagram of various MCPs, from left to right: single MCP plate, chevron plate arrangement of 2 stacked MCPs, and z-stacked arrangement of 3 stacked MCPs.

25
2.1.3.4 Vacuum Pumps

The final important piece of the experimental apparatus are the vacuum pumps, used throughout the experiment to eliminate contamination from unwanted molecules in the system. The three different types of pumps used are turbomolecular, roots, and scroll pumps, all described in this section.

The first kind of vacuum pump is the turbomolecular pump, used with the source chamber, ionization chamber, and the detector, at speeds of 3,200 L/s, 1,600 L/s, and 600 L/s, respectively. This kind of pump is composed of circular blades layered on one another in a series of ‘stages’ and maintain a final pressure of $10^{-8}$ torr. Each of these stages has both a moving and stationary blade. The moving blade, also known as a rotor or turbine blade, gives momentum to gas molecules as they enter the vacuum and collide with the moving rotors. The molecules are then moved to the stationary blade, or the stator, where they are led to the next ‘stage’. As the molecules continue to move through ‘stages’, they increase in pressure until they are removed by a backing pump. A scheme of the turbomolecular pump is shown in Figure 3.9.

![Turbomolecular Pump Diagram](image)

**Figure 2.9** Diagram and Cross Section of Turbomolecular Pump

The next vacuum pump is known as the scroll pump, also known as the backing pump, previously mentioned. This pump connects to the source chamber underneath the quartz reactor tube and is in charge of removing the high-pressure gas from the turbomolecular pump. Much like the turbomolecular pump, the scroll pump has one rotating and one stationary scroll. Figure 2.10 shows how the scroll pump operates, with the red line representing the rotating scroll while the black line represents the stationary scroll. As the rotating scroll moves, the area between the two scrolls is continuously changing, leaving the...
gas molecules to become trapped and pushed into the vacant spaces of the pump, until they reach the center of the pump, or the outlet. This scroll pump has a pressure of $10^2$ torr and a pumping speed of 6-13 L/s².

![Diagram of Gas Molecules moving through Scroll Pump](image)

**Figure 2.10** Diagram of Gas Molecules moving through Scroll Pump

The final vacuum pump is the roots pump, which is connected to the quartz reactor and is composed of two rotors spinning in opposite directions to move the gas molecules to higher pressures. The two spinning rotors are synchronized with a rotation speed of 1,000-3,000 rpm². Figure 2.11 shows a diagram of the pump, where the gas molecules enter at the inlet of pump as low pressures and are then pushed towards the outlet where the pressure is increased. This pump works within the pressure range of $10^{-1}$ to $10^3$ mbar and a pumping speed of up to 8,333 L/s². The quartz reactor itself has a pressure range of 0.1 Pa to 3 MPa and a temperature range of room temperature to 1200 °C.

![Schematic of a Roots Pump](image)

**Figure 2.11** Schematic of a Roots Pump
2.2 References


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Chapter 3

3.1 Data Analysis

3.2 Theory

3.2.1 Ionization

3.2.2 Photoionization Cross-Sections and Overall Molar Yields

3.2.3 The Franck-Codon Principle and the Born-Oppenheimer Approximation

3.3 Computational Methods

3.3.1 Electronic Structure Calculations

3.3.2 Potential Energy Surface (PES) Scans utilizing Density Functional Theory (B3LYP)

3.4 References
3.1 Data Analysis

Once the experimental data is collected at the ALS, a three-dimensional data cube is produced where the relative ion signal (arbitrary units) is observed as a function of kinetic time (ms), mass-to-charge (m/z) ratio, and photon energy (eV). Using IGOR-09, the dimensionality of the data can be reduced by fixing one variable, such as time or energy. These two-dimensional images are reduced further to produce one-dimensional spectra, known as photoionization (PI) spectra, the mass spectrum, and times traces, as shown in Figure 3.1. To accurately view the data produced, it is background subtracted using IGOR64 to eliminate the pre-photolysis signal and to get rid of any ‘noise’ produced by the apparatus. This data is also normalized due to the variation in photon flux of the light by measuring the ALS photocurrent through a calibrated vacuum ultra-violet (VUV) sensitive photodiode. After this is done, the mass spectrum is generated to view the reactants and fragments depleting and the products of the system forming, as shown in Figure 3.2.
Figure 3.1 Example of Reduction of 3D Data Cube
Figure 3.2 Mass Spectrum of the 2TBF Reaction Project, where forming products are shown as positive signals and depleting reactants are shown as negative signals.

Time traces are then used to characterize between primary chemistry and other chemistry that may be crucial in the reaction. This is done by taking the vertical slices of ion signal vs. kinetic time at a fixed mass. Typically, the time of the reaction is 150 ms, however, for the 2-TBF project, time traces are plotted in the time range of 0-30 ms to account only for signal coming from the main reactions. By taking the inverse of the reactant and plotting it against any given product, primary chemistry can be identified when the slope of the product is similar or identical to the slope of the reactant. Conversely, other chemistry may have a smaller slope, depicting that the reaction is occurring slower than the primary chemistry. An example of a time trace of primary chemistry versus other chemistry is shown in Figure 3.3.
Finally, PI spectra are used to further analyze the products present in the reaction and characterize each signal to a specific compound. This is done by taking the vertical slice of ion signal vs. photon energy for each mass. By using literature spectra, specific products can be identified if the shape of the experimental...
curve matches that of the literature, as shown in Figure 3.4. These spectra are also used to determine the adiabatic ionization energy (AIE) by looking at the onset of the experimental curve. In some instances, there may be multiple products forming at the same mass. In this case, the summation of all products is used to fit the PI spectra, as shown in Figure 3.4. In the case that the literature spectrum of a species is not found, a simulation of the spectrum can be generated using the Franck-Codon (FC) principle and the CBS-QB3 method discussed in the next portions of this chapter.

Figure 3.4 The literature PI spectra of acetone$^2$ (blue) and propanal$^3$ (green) superimposed onto the experimental PI spectrum of m/z 58 (red open circles). The summation of the two fits the overall experimental curve.
3.2 Theory

3.2.1 Ionization

Adiabatic ionization energy is known as the minimum energy required to eject an electron out of a
gaseous molecule in its ground state.\(^4,5\) This energy is highly dependent on the electron configuration and
the number of lone electrons on a specific molecule. Because of this, noble gases have the highest
ionization energies due to their closed electron shells, while smaller molecules with lone pairs have outer
electrons that are more easily removed (ionization). Two common ways a molecule can ionize is either
through electron bombardment or photoionization. Both these methods result in the neutral molecule or
atom forming a cation, using a form of radiation. In the case of photoionization, light is used for the
process, as shown by Equation 3.1.

\[
M + h\nu \rightarrow M^+ + e^-, \text{ where } E = h\nu \text{ (Equation 3.1)}
\]

M is characterized as a neutral species in the gas phase, h is Planck’s constant, and \(\nu\) is the frequency of
light. \(M^+\) is the newly formed cation from ionization. In these experiments, the adiabatic ionization energy
(AIE) is the minimum amount of energy needed to remove an electron from a neutral species in the
ground electronic, vibrational, and rotational states.\(^4,5\)

3.2.2 Photoionization Cross-Sections and Overall Molar Yields

In general, cross-sections (\(\sigma\)) quantify the probability of a collision taking place between two or more
particles within a molecule.\(^6\) For the experiments discussed in this thesis, the particle refers to a photon,
and the cross-sections will be known as photoionization cross-sections (PICS). This photoionization cross
section can be visualized as the area (in cm\(^2\)) with the highest probability for the ionization to occur. This
quantity is measured in Megabarns, where 1 Mb = 1 \(\times 10^{18}\) cm\(^2\).
To calculate the $\sigma$ for any given molecule, the method used requires the cross-sections of well-known calibration gases. In this case, ethene, propene, and 1-butene are used in the experiments to calculate the unknown cross-section by flowing these calibration gases into the cell at a known concentration, along with the compound for which the photoionization cross section needs to be determined.\(^7\) Equation 3.2 shows how the ion signal ($S(E)$) is related to important quantities, such as the photoionization cross section ($\sigma(E)$). Because of the energy dependence of the ion signal and the photoionization cross section, they must be used at the same energy that is 11 eV in this work.

\[
S(E) = k\sigma(E)\delta C \quad \text{(Equation 3.2)}
\]

In this equation, ion signal ($S$), is the product of the instrumentation constant ($k$), the photoionization cross-section ($\sigma$), the mass discrimination factor ($\delta$) (equal to approximately the mass of the compound to the power of 0.64, as described by Savee et al.\(^7\)), and the concentration ($C$) of the species. By using this equation for both the experimental values of the given compound and the known values of the calibration gases, the unknown cross-section of the target molecule can be calculated, using Equation 3.3.

\[
\sigma_T(E) = \frac{S_T(E)\sigma_S(E)\delta_SC_s}{S_S(E)\delta_TC_T} \quad \text{(Equation 3.3)}
\]

The unknown cross-section of the target molecule ($\sigma_T$) is determined as a ratio of its signal intensity ($S_T$), cross-section of the standard ($\sigma_S$), mass discrimination factor of the standard ($\delta_S$), and concentration of the standard ($C_s$), all over the signal intensity of the standard ($S_s$), mass discrimination factor of the target molecule ($\delta_T$), and the concentration of the target molecule ($C_T$). For the experiments presented in this thesis, the absolute cross-sections of ethene and propene, taken by Cool et al.,\(^2\) and 1-butene, taken by Wang et al.\(^3\) are used. The photoionization cross section of ethene is found to be 7.67 Mb, 12.412 Mb for...
propene, both with uncertainties of ±25%, and for 1-butene it is found to be 11.1 Mb with an uncertainty of ±20%. All these values are taken at 11 eV.

Branching fractions (BF) are known as the ratio of concentration of products to the concentration of reactants in elementary reactions. For more complex/multiple reactions pathways we use the term overall molar yield. This calculation is integral to determining how much of each product is formed during the oxidation process. In this equation, the concentration of the product ($C_P$) is divided by the concentration of the reactant ($C_R$) and equated to the ratio of the ion signals (product: $S_P$, and reactant: $S_R$), the PI cross-sections (product: $\sigma_P$, and reactant: $\sigma_R$), and the mass discrimination factor (MDF).

\[
\frac{C_P}{C_R} = \frac{S_P \sigma_R \delta_R}{S_R \sigma_P \delta_P} = \frac{S_P \sigma_R (m_R)^{0.64}}{S_R \sigma_P (m_P)^{0.64}} = \frac{S_P \sigma_R}{S_R \sigma_P} \times MDF \quad \text{(Equation 3.4)}
\]

Once branching fractions or overall molar yields are calculated, they must be carbon normalized to be sure all masses are accounted for in the experiment, as close to 100% as possible. Equation 3.5 shows how to calculate this value for these experiments.

\[
\text{Carbon Normalization} = BF \times \frac{\# \text{ of C in product}}{\# \text{ of C in reactant}} \times 100\% \quad \text{(Equation 3.5)}
\]

**3.2.3 The Franck-Condon Principle and Born-Oppenheimer Approximation**

The Born-Oppenheimer approximation states that since the mass of the nuclei are much larger than that of the electron, nuclear motion can be separated by the electron motion.\textsuperscript{11} Essentially, the nuclei are considered stationary during ionization. By using Equation 3.6, any given molecule can be solved for energy and wavefunction as a whole.\textsuperscript{18}

\[
\Psi_{\text{molecule}} = \Psi_{\text{nucleus}} \times \Psi_{\text{electron}} \quad \text{(Equation 3.6)}
\]
The Franck-Condon principle states that when a molecule undergoes an electronic transition like ionization, the nuclear configuration of the molecule does not experience any significant change. This principle builds upon the Born-Oppenheimer approximation and adds that since the nuclei are stationary, it can be assumed that bond lengths, bond angles, and positions do not change during ionization. This electronic transition is also known as a vibronic transition, where an electron moves from one vibrational level to another. An example of this can be seen in Figure 3.5, where a vertical transition is shown beginning at the ground state and moving into different excited states, with no change to the nuclear geometry of the molecule in any way. This reflects the fact that the electronic transition is so fast that the nuclei do not have time (during the transition) to move. The intensity of the transition is regulated by the Franck-Condon factor, where the probability of a transition is higher when the overlap between two states is greater. This vertical transition depicts where the two wavefunctions have the greatest overlap, which is correlated to the most intense peak in the first electronic band of a photoelectron spectrum. 

![Figure 3.5 Franck-Condon Principle Diagram](image)
The Franck-Condon principle itself is derived from the transition dipole moment integral, which is an equation used to include the sum of all nuclear and electronic motions in a molecule, denoted by the operator, $\hat{\mu}$. Equation 3.7 shows this equation, where vectors $r_i$ and $R_I$ are the distances from the center of charge of the molecule, and $e$ and $Z_n$ are the electronic and nuclear components, respectively. This electronic transition is also known as a vibronic transition, where an electron moves from one vibrational level to another.

\[ \hat{\mu} = -e \sum r_i + e \sum Z_i R_i \]  
(Equation 3.7)

3.3 Computational Methods

3.3.1 Electronic Structure Calculations

In these experiments, computational methods are used to obtain important molecular parameters needed for the simulation of photoionization spectra, i.e., bond lengths and angles, and harmonic vibrational frequencies. All these computational methodologies are based on the solution of the Schrödinger equation with different levels of approximations. Basis sets are essentially the wavefunctions describing the atoms present in the molecular system under study. For our investigation we used the CBS-QB3 composite method within the Gaussian09 program and the results were visualized in the Avogadro program.

CBS-QB3 is known as the complete basis set method, an intermediate composite method (ab initio and density functional), used to first determine the geometry and the zero-point energy (ZPE) at a lower level of theory for the species, then performs a series of high-level single-point electronic energy calculations at the optimized geometry. In this method, the components of each model have been selected to be balanced so that no single component can dominate over the other, reducing the error from the truncation of the basis sets to only 1-1.5 kcal/mol. This method is split into four different parts, each contributing to the overall calculation of energies. The first is the B3LYP/CBSB7 level of theory, which performs the
optimization and frequency calculations, discussed in the next section. Next, the CCSD(T)/6-31+G(d') and the MP4SDQ/CBSB4 levels calculate the single point energies and finally, the MP2/CBSB3 level extrapolates the total energies to the infinite-basis-set limit with the additive correction to the CCSD(T) level.\(^{12}\)

This method also utilizes the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP) level of theory and the all-electron 6-311+G* basis set to optimize bond distances and harmonic vibrational frequencies.\(^ {13}\) To understand the B3LYP method in more detail, the density functional theory (DFT) must also be understood. DFT was originally hypothesized by Hohenberg and Kohn, who stated that the total electronic energy of an atom, molecule, or ion \((E_{\text{tot}}[n(r)])\), can be shown as a universal function, defined in terms of electron density \((n(r))\), and that the total electronic energy and other observable properties are a functional of \(n(r)\).\(^ {24,25}\) Based on this, they proved that inputting the exact ground state of the electron density into the universal functional yields the global minimum value of the energy functional.\(^ {24,25}\) The total electronic equation is shown in Equation 3.8, where each variable is dependent on \(n(r)\). In this equation, \(E_T\) is the total kinetic energy of the electrons, \(E_V\) total potential energy of the electrons, \(E_J\) is the total potential energy caused by the average Coulomb repulsion between pairs of electrons, \(E_X\) is the total quantum mechanical exchange energy of the electrons, and finally, \(E_C\) is the total correlation energy of the electrons.\(^ {24}\)

\[
E_{\text{tot}}[n] = E_T[n] + E_V[n] + E_J[n] + E_X[n] + E_C[n] \quad \text{(Equation 3.8)}
\]

To calculate the adiabatic ionization energy (AIE) of a molecule, the zero-point vibrational corrected energy \((E_0)\) of both the ground state of the neutral and cationic molecule is used. Equation 3.9 shows the calculation of this value. Once the AIE is computed, this value is used in the Franck-Condon spectral simulations. As mentioned in the previous section, when a spectrum is not available in literature, this method can be used to generate a photoelectron spectrum using Gaussian09. Through the calculation of
FC factors, the transitions of vibrational ground states of the neutral and cationic molecule are computed at various energies. The resulting output file includes the determination of the wavefunctions with the greatest overlap between the neutral and cationic molecule. This is visualized as the photoelectron spectra, and using IGOR64, this spectrum can be integrated to produce the simulated PI spectrum used to compare to the experimental PI curve of a species at a specific mass. An example of a simulated photoelectron spectrum and the integrated PI spectrum is shown in Figure 3.6. Generally speaking, the AIE predicts the onset of the curve, while the FC factors predict the general shape of the photoionization curve.

\[ AIE = E_{0\,(\text{cat})} - E_{0\,(\text{neut})} \] (Equation 3.9)
3.3.2 Potential Energy Surface (PES) Scans Utilizing Density Functional Theory (B3LYP)

Though the products of the reaction species have been characterized by unique PI spectra, they need to be further confirmed by having a formation pathway that is both thermodynamically and kinetically feasible. Potential energy surface (PES) scans use the optimized structure computed from the CBS-QB3 method to find a pathway that has barriers. This is done using the B3LYP method.\(^\text{14}\) For each predicted reaction, the reactant will endure hydrogen transfers, bond stretching or breaking to form the desired product.

PES scans have two distinct areas of interest, both pertinent to the formation of the desired product. The first is the saddle point, also known as the transition state of the dissociation. This is the highest point of the PES, and the highest energy species of the scan. This point is inputted using the CBS-QB3 method to calculate the correct thermodynamic energy. Once the species falls to its lowest possible vibrational electronic level, it is considered the global minimum of the reaction. This species occupies the ground
vibronic state \((\Psi'_{0})\) and is considered the most energetically favorable conformation of the resulting product. This point is also calculated using the CBS-QB3 method to find the exact thermodynamic energy. If transition states and global minima are below the thermochemical limit, i.e., the energy of the starting reactants, the pathway is considered thermodynamically feasible for the system. An example of a PES structure is shown in Figure 3.7, displaying the starting, transition state, and product (global minimum) of the scan. The final part of these calculations is the Intrinsic Reaction Coordinate (IRC) method, used to confirm that the calculated transition state is the correct one connecting a reactant to the expected product by determining the minimum energy pathway.\(^{26}\)
Figure 3.7 Example of a PES scan of 2-methylfuran from a B3LYP calculation. From top to bottom: starting point, saddle point, and global minima/ending structure.\textsuperscript{15}
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Chapter 4

4. Study of 2-Tertbutylfuran (2TBF) in Reaction with O(\^3P) at 550 K and 700 K Using Multiplexed Synchrotron Photoionization Mass Spectrometry

4.1 Abstract

4.2 Introduction

4.3 Experimental

4.4 Computational

4.5 Results

4.5.1 Product Identification

4.5.2 Overall Molar Yields

4.5.3 Future Work

4.6 Conclusion

4.7 Acknowledgements

4.8 Supporting Information
4.9 References


4. A Study of 2-Tertbutylfuran (2TBF) in Reaction with O(3P) at 550 K and 700 K Using Multiplexed Synchrotron Photoionization Mass Spectrometry

(Draft of manuscript in preparation for publication)

Ameyali Tapia and Giovanni Meloni

Department of Chemistry, University of San Francisco, San Francisco, California, 94117

4.1 Abstract

Vacuum-ultraviolet synchrotron radiation at the Advanced Light Source of the Lawrence Berkeley National Laboratory was used to examine the oxidation of 2-tertbutylfuran (2-TBF) with O(3P). The resulting reaction species were inspected using energy- and time- resolved multiplexed synchrotron photoionization mass spectrometry at the temperatures of 550 and 700 K. Using literature and simulated photoionization spectra, adiabatic ionization energies, and mass-to-charge ratios, preliminary products were identified at both temperatures. These potential energy surface scans will further validate the formation of these different products. Finally, overall molar yields for the system were calculated at the two temperatures. Preliminary products of the system at both temperatures include cyclopropanone at m/z 56, acetone at m/z 58, and 2-butenal at m/z 70. Future work includes electronic structure calculations to visualize the mechanistic pathways of these species.

4.2 Introduction

Fossil fuels currently supply about 80 percent of the world’s energy, releasing carbon and other greenhouse gases into the atmosphere.¹ These gases, also known as Volatile Organic Compounds (VOCs), are additionally found in a wide variety of indoor household products, like paints and cleaners.²³ These VOCs can have harmful effects on humans, such as irritation of the eyes, nose, and throat, and in the worst cases, can cause cancer.³ In the atmosphere, the greenhouse gases that are released contribute heavily to climate change. Since pre-industrial times it has been found that the global surface temperature has increased at least 1.1 °C.⁴ In 2015, it was estimated that the worldwide emissions from human
activities totaled nearly 47 billion metric tons of greenhouse gases.\(^5\) In addition to having harmful effects on the atmosphere, fossil fuels are a quickly depleting, non-renewable resource. For these reasons, biofuels and biofuel additives have been a key point of research in the recent years since they are both eco-friendly, easily reproducible, and do not release as many harmful VOCs, if any.

Two of the most notable biofuels today are ethanol and biodiesel. Ethanol, made from various plant materials known as “biomass”, is in about 98% of gasoline in the United States.\(^6\) Because ethanol has a higher-octane number than gasoline, by adding the two together, engine knocking can be prevented, ensuring fuel is burned evenly in the engine. Biodiesel is a renewable, biodegradable fuel produced from renewable feedstock, including vegetable oils and animal fats.\(^7,8\) In addition to these two fuels, alkyl furans, specifically 2-methylfuran (2-MF) and 2,5-dimethylfuran (2,5-DMF), have shown promising properties as novel biofuels.\(^9,10\) In a study done by Wang et al.,\(^11\) it was concluded that both these potential biofuels have better knock suppression than gasoline and produce a higher indicated thermal efficiency and less hydrocarbon emissions.

Because of the promising results of 2-MF and 2,5-DMF as novel biofuels, other alkyl furans, such as 2-tertbutylfuran (2-TBF), can be considered to study as a potential biofuel/biofuel additive. This work presents the findings of the simulated combustion reaction of 2-TBF initiated with the ground state oxygen atom, O(\(^3\)P), using a tunable synchrotron multiplexed photoionization mass spectrometer at 550 and 700 K temperatures. These results identify potential by-products of the reaction via photoionization spectra.

4.3 Experimental Methods

The experiments in this work were carried out at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. In summary, the ALS photoionization source produces tunable synchrotron radiation, coupled with a time-of-flight (TOF) multiplexed time- and energy-resolved mass
A spectrometer that can detect reaction species, intermediates, and products. Further detail about these experiments and the apparatus can be found in past works.\textsuperscript{12,13}

The vapors of 2-TBF (Sigma-Aldrich: purity 97\%) and helium gas were collected into a gas cylinder to create a 1\% reaction mixture. In this experiment, 2-TBF reacts with O\(^{(3)}\text{P}\) at 550 and 700 K, with pressures of 7 and 8 torr, respectively. NO\(_2\), the photolytic precursor, along with 2-TBF and helium are all flowed into a 62 cm long slow-flow reactor using calibrated mass flow controllers. The species effuse through a 650 \(\mu\)m pinhole on the side of the reactor, forming a molecular beam that is then flowed into a vacuumed ionization region. This reactor is also wrapped with an 18 \(\mu\)m nichrome tape to allow for the adjustment and stability of temperature. Finally, this reactor is connected to a roots pump, to allow for the pressure to be adjusted and maintained as needed. In this experiment, the photolytic precursor, NO\(_2\), is activated using a 4 Hz-pulsed unfocused 351 nm (XeF) excimer laser, shown below.

\[
\text{NO}_2 \rightarrow \text{NO} + \text{O}^{(3)}\text{P}, \text{ with } h\nu = 351 \text{ nm (Equation 4.1)}
\]

The concentrations of NO\(_2\) used in this work are calculated as 1.21 \times 10^{17} molecules/cm\(^3\) for the 550 K temperature, whereas for the 700 K temperature the concentration is 1.07 \times 10^{17} molecules/cm\(^3\). Once the reaction species are ionized, they are accelerated and detected by a 50 kHz pulse orthogonal acceleration time-of-flight mass spectrometer with a mass resolution of about 1,600. This results in a three-dimensional data block to be analyzed.

As previously mentioned, the three-dimensional data block produced from the reaction was analyzed using IGOR64.\textsuperscript{14} This block is broken down into one-dimensional slices that includes the ion signal (S), as a function of photon energy (eV), kinetic time (ms), and mass-to-charge ratio (m/z). The data is then background subtracted and normalized to account for the pre-photolysis signal. Firstly, the mass spectrum (ion signal (ab. units) vs. mass-to-charge (m/z)) is analyzed for the formation of products (shown as a
positive signal), and depletion of reactants (shown as a negative signal). Next, kinetic time traces (ion
signal (ab. units) vs. kinetic time (ms)) are looked through to interpret primary chemistry of the system, as
well as other chemistry that may be important to the system. Primary chemistry is identified as having the
same initial kinetic rise as the inverse kinetic time trace of the reactant (shown in Figure 4.3), while other
chemistry will show a slower kinetic rise than the reactant’s time trace.

Finally, the identified products are characterized using their photoionization (PI) spectra (ion signal (ab.
units) vs. photon energy (eV)) and their specific adiabatic ionization energies (AIE). AIEs are obtained by
taking the initial onset of the PI curve in the experiment. In addition to this, the data is integrated in the
time range 0-30 ms for both temperatures to eliminate signal contribution from slower chemistry of the
system. These species are identified by fitting their PI spectra with that of published data. Alternatively, if
literature data is not available, an integrated simulated Franck-Codon PI spectra is used, which will be
described in the computational methods section.

Once the characterization and identification of all reaction species are accomplished, the thermodynamic
feasibility of the pathways of formation must be determined. This is achieved using potential energy
surface (PES) scans, which will be discussed in the computational methods. The final step includes
product quantification by calculating the overall molar yields of the system, which are the ratio of
concentration of products to the concentration of reactants in the experiment. This calculation is integral
to determining how much of each product is formed during the oxidation reaction, shown by Equation
4.2. In this equation, the concentration of the product ($C_p$) is divided by the concentration of the reactant
($C_R$) and equated to the ratio of the ion signals (product: $S_P$, and reactant: $S_R$), the PI cross-sections
(product: $\sigma_p$, and reactant: $\sigma_R$), and the mass discrimination factor (MDF).

$$
\frac{C_p}{C_R} = \frac{S_P\sigma_R\delta_R}{S_R\sigma_P\delta_P} = \frac{S_P\sigma_R(m_R)^{0.64}}{S_R\sigma_P(m_P)^{0.64}} = \frac{S_P\sigma_R}{S_R\sigma_P} \star MDF \quad \text{(Equation 4.2)}
$$
Finally, once overall molar yields are calculated, they must be carbon normalized to be sure all masses are accounted for in the experiment, as close to 100% as possible. Equation 4.3 shows how to calculate this value for the experiment.

\[
\text{Carbon Normalization} = BF \times \frac{\# \text{ of } C \text{ in product}}{\# \text{ of } C \text{ in reactant}} \times 100\% \quad \text{(Equation 4.3)}
\]

### 4.4 Computational Methods

The products in this experiment were characterized using the complete basis set CBS-QB3 composite method, along with Gaussian-09.\(^{15}\) These calculations are used to obtain values for photoionization spectra, such as bond lengths, and harmonic vibrational frequencies using the B3LYP density functional level. By computing the zero-point vibrational corrected energy \((E_0)\) of both the ground state of the neutral and cationic molecule, the adiabatic ionization energy can be calculated. The equation of this calculation is shown in Equation 4.4.

\[
AIE = E_0(\text{cat}) - E_0(\text{neut}) \quad \text{(Equation 4.4)}
\]

Primary products can be identified by confirming both the AIE and experimental spectra match with the literature data. In some cases, literature spectra are not available for the given species. In this instance, a spectral simulation must be run using computational methods. This is achieved by using the optimized geometry of both the neutral and cationic species to simulate a photoelectron spectrum using the Franck-Condon (FC) factors through Gaussian-09. The resulting spectrum is vertically integrated in IGOR64 to produce the simulated photoionization curve.
Once the relevant products have been characterized, they must be further confirmed by having a formation pathway that is both thermodynamically and kinetically feasible. These calculations will be presented in a future work, however the process to compute these values will be explained below. Potential energy surface (PES) scans use the optimized structure computed from the CBS-QB3 method to find pathways of product formation with barriers. The B3LYP/6-31G(d) level of theory and basis set is used to compute these transitions, carried out as a function of bond lengths and bond angles. This calculation produces two key points of interest for the formation pathway, the saddle point (transition state) and the global minima (resulting product). For each transition state and product, a CBS-QB3 calculation is run to determine the zero-point energies. The last step to verifying a feasible formation pathway is by running intrinsic reaction coordinate (IRC) calculations. These calculations verify the forward and reverse steps of the PES scan, the transition states, and the global minima (products).

4.5 Results
As shown by previous research oxidation reactions have two main pathways, atomic oxygen addition to an unsaturated hydrocarbon or hydrogen abstraction. In this experiment, the oxidation of 2-TBF and O(\textsuperscript{3}P) only undergoes oxygen addition to form the products of the system. Four different adducts are formed from the oxygen addition, which then undergo intersystem crossing to form singlet epoxide species (Fig 4.1), which are in turn used to form products. The reaction enthalpy changes are also shown in Figure 4.1, calculated at 0 K. The singlet epoxide species are formed at -179 kJ/mol (A \rightarrow F), -259 kJ/mol (D \rightarrow F), -174 kJ/mol (B \rightarrow E), and -261 kJ/mol (C \rightarrow E). Of the four adducts formed from oxidation, A and B are most favorable with enthalpies of -127 kJ/mol and -129 kJ/mol, respectively. The other two adducts are considered less favorable with heats of formation of -43 kJ/mol for species C and -46 kJ/mol for species D.
Figure 4.1 The four adducts formed from the oxygen addition and the resulting singlet epoxide species, 2,3-epoxy-2-TBF (F) and 2,3-epoxy-5-TBF (E).

4.5.1 Product Identification

In these experiments, the same products are observed for both the 550 and 700 K temperatures. These products include m/z 56, 58, 70, 84, 112, and 140. At the 700 K temperature two additional products are formed, m/z 42 and 82. Both mass spectra can be seen in Figure 4.2. An additional peak at m/z 30 is seen in both these mass spectra, however, this peak is characterized as NO as a result of the photolysis of NO$_2$ to form O($^3$P). Characterization of reaction products was completed by comparing the kinetic time plots of the reactant to that of the desired product. In these experiments, it was found that all products have very similar kinetic rise as the inverse of the reactant. An example of this is shown in Figure 4.3.
For m/z 56, the species was identified as cyclopropanone. The time trace for this product is shown in Figure 4.3. Because there were no literature spectra available, a FC simulated spectra was created and fit.
to this product at both temperatures, shown in Figure 4.4. The initial onset of this product was found to be 9.10 ± 0.05 eV, matching the reference AIE of 9.10 ± 0.10 eV, and the CBS-QB3 calculated value of 9.11 eV.

![Figure 4.3 Time trace of m/z 56 taken at 700 K.](image)

**Figure 4.3** Time trace of m/z 56 taken at 700 K.
Figure 4.4 FC simulated PI spectrum of cyclopropanone (black line) fit to the experimental curve at 550 (pink open circles) and 700 K (red open circles).

For m/z 58, two species were identified as products. By using the summation of the PI spectra for propanal and acetone, it was confirmed that these products match very well with the experimental spectra, shown in Figure 4.5. The literature spectra taken by Cool et al.\textsuperscript{17} of acetone fits very well to the initial part of the experimental curve. The experimental AIE was found to be 9.65 ± 0.05 eV, which also agrees very well with the literature value of 9.62 ± 0.05 eV. At higher photon energy, it was found that the experimental spectrum matched that of propanal, taken by Wang et al.\textsuperscript{18} The ionization energy of this product is 9.94 ± 0.05 eV.
Figure 4.5 The summation (black line) of literature PI spectra of acetone (blue line) and propanal (green line) fit to the experimental spectra at 550 (pink open circles) and 700 K (red open circles).
For m/z 70, the species was identified as 2-butenal, as shown in Figure 4.6. This experimental spectrum was matched to that of Yang et al.,$^{19}$ with very similar ionization energies of $9.63 \pm 0.10$ eV for the experimental compared to Yang’s $9.70 \pm 0.05$ eV.

![Figure 4.6](image)

Figure 4.6 The literature PI spectra of 2-butenal (black line) fit to the experimental spectra at 550 (pink open circles) and 700 K (red open circles).
For m/z 84, the species was identified as 3-methyl-2-butenal. The experimental AIE was determined to be 9.16 eV ± 0.05 eV, which is similar to the literature value found by Yang et al. of 9.40 ± 0.05 eV. This value is also like the reference PI curve taken at the Advanced Light Source, which was determined to be 9.4 eV. For this product however, further research can be done to match the AIE of the experimental more closely to another known product, and potentially using the summation of these two products to match the experimental PI spectra more accurately. Figure 4.7 shows the preliminary PI spectrum for this species.
m/z 112 was identified as 2-methyl-4-hexen-3-one, shown in Figure 4.8. The AIE of this species was determined to be 9.05 ± 0.05 eV, which matches closely with the CBS-QB3 computed value of 9.06 eV. Since there was no literature spectrum available for this species, a FC simulated spectrum was created and fit to the experimental curve at both temperatures.
Figure 4.8 FC simulated PI spectrum of 2-methyl-4-hexen-3-one (black line) fit to the experimental curve at 550 (pink open circles) and 700 K (red open circles).

For m/z 140, the species was identified as 2,3-epoxy-5-tertbutylfuran or the singlet epoxide species E, shown in Figure 4.1. Typically, in these experiments the singlet epoxide is not seen as a product of the reaction, however, by creating a FC simulated spectrum, it was confirmed that this was in fact 2,3-epoxy-5TBF. Figure 4.9 shows this spectrum compared to the experimental spectrum. The AIE for the experimental curve was determined to be $8.75 \pm 0.05$ eV, which is similar to that of the CBS-QB3 computed value of 8.56 eV.
Figure 4.9 FC simulated PI spectrum of 2,3-epoxy-5-tertbutylfuran (black line, 550 K; blue line, 700 K) fit to the experimental curve at 550 (pink open circles) and 700 K (red open circles).
Two additional products were formed at the 700 K temperature, m/z 42 and m/z 82. For m/z 42, it was determined to be ketene, where the experimental curve was matched to that of Yang et al., 2008, shown in Figure 4.10. The experimental AIE for this product was determined to be $9.55 \pm 0.05$ eV, which matches the literature value of 9.58 eV. For m/z 82, it was determined that the species was 2-cyclopenten-1-one. Figure 4.10 shows the experimental curve matched to that of Yang. However, the AIE for the experimental was found to be $9.05 \pm 0.05$ eV, while the literature value is 9.32 eV. Based on this, another product could potentially be found to match the onset of the experimental PI curve more accurately. The two products can then be used as a summation to properly fit the entirety of the experimental curve.
Figure 4.10 The literature spectra of ketene and 2-cyclopenten-1-one (black line) fit to the experimental spectra at 700 K (red open circles).

4.5.2 Overall Molar Yields

Once the primary products are identified using their kinetic time traces and characterized by unique PI spectra, overall molar yields are calculated to know the relative concentrations of products with respect to the reactant. As described in the experimental section, overall molar yields are the ratio of the concentration of products to the concentration of the reactant. For these experiments, the cross section of 2-TBF used is 12.7 Mb at 11 eV. All additional values, photoionization signal and the remaining photoionization cross sections are also used at 11 eV. Table 1 shows the carbon normalized branching fractions for both temperatures.
Table 1 Branching fractions of preliminary products observed at 550 K and 700 K temperatures

<table>
<thead>
<tr>
<th>Signal</th>
<th>Identified Species</th>
<th>550 K</th>
<th>700 K</th>
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<tr>
<td>m/z 42</td>
<td>Ketene</td>
<td>N/A</td>
<td>0.8 ± 0.3</td>
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<tr>
<td>m/z 56</td>
<td>Cyclopropanone</td>
<td>12.3 ± 2.9</td>
<td>13.2 ± 2.4</td>
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<tr>
<td>m/z 58</td>
<td>Propanal</td>
<td>6.2 ± 1.6</td>
<td>4.6 ± 1.3</td>
</tr>
<tr>
<td>m/z 58</td>
<td>Acetone</td>
<td>6.2 ± 1.6</td>
<td>4.6 ± 1.3</td>
</tr>
<tr>
<td>m/z 70</td>
<td>2-butenal</td>
<td>7.3 ± 1.9</td>
<td>7.6 ± 0.9</td>
</tr>
<tr>
<td>m/z 82</td>
<td>2-cyclopenten-1-one</td>
<td>N/A</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>m/z 84</td>
<td>3-methyl-2-butenal</td>
<td>9.5 ± 2.0</td>
<td>10.1 ± 1.8</td>
</tr>
<tr>
<td>m/z 112</td>
<td>2-methyl-4-hexen-3-one</td>
<td>3.4 ± 0.8</td>
<td>3.1 ± 0.3</td>
</tr>
<tr>
<td>m/z 140</td>
<td>2,3-epoxy-5TBF</td>
<td>5.2 ± 2.0</td>
<td>2.8 ± 0.6</td>
</tr>
</tbody>
</table>

The largest contribution for both temperatures was cyclopropanone, where 12.3 ± 2.9% was calculated at 550 K and 13.2 ± 2.4% for 700 K. Mass 84, or 3-methyl-2-butenal follows closely with a 9.5 ± 2.0% contribution at 550 K and a 10.1 ± 1.8% contribution at the 700 K temperature. For 2-butenal, a 7.3 ± 1.9% contribution was determined for the 550 K temperature, while a 7.6 ± 0.9% contribution was found for 700 K. Interestingly, both m/z 58 species, m/z 112, and m/z 140 exhibit a decrease in contribution as the temperature increases from 550 K to 700 K. For propanal and acetone, the contribution was determined to be 6.2 ± 1.6% at 550 K, which then decreases to 4.6 ± 1.3% at the higher temperature. For 2-methyl-4-hexen-3-one, the contribution decreases from 3.4 ± 0.8% at 550 K to 3.1 ± 0.3% at the 700 K. Finally for 2,3-epoxy-5TBF, the contribution decreases from 5.2 ± 2.0% at 550 K to 2.8 ± 0.6% at 700 K. Lastly for the 700 K temperature, ketene was determined to have a 0.8 ± 0.3% contribution and 2-cyclopenten-1-one was determined to have a 1.5 ± 0.2% contribution.
4.5.3 Future Work
To ensure all preliminary products are true to the system, PES scans must be computed, as described in the computational methods section. This will be the last step to finalizing this project, to prove all products are thermodynamically feasible to form.

4.6 Conclusions
Synchrotron radiation was used at the Advanced Light Source of the Lawrence Berkeley National Laboratory to study the O(3P) initiated oxidation reaction of 2-TBF at both 500 K and 700 K. By using kinetic time traces and photoionization curves, preliminary products were able to be identified and characterized. The branching fractions for these products were then computed to view the overall contribution the reaction. Future work will be done to prove the thermodynamic feasibility of these species by running potential energy surface scans.

4.7 Acknowledgements
Thank you to Dr. Giovanni Meloni, for guiding and mentoring through this project, graduate students Lauren Lewellen, Lori Chen, Ed Buck, and former graduate student Sara Gallarati. Thank you to Dr. and Mrs. Whitehead for the Whitehead Summer Fellowship, the USF Faculty Development Fund, Sandia National Laboratories for use of their apparatus, and the ACS Bridge Travel Fund. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.
4.8 Supporting Information

Table S1. Optimized geometries for neutral epoxide species calculated in this work in Figure 4.9. All calculations were conducted using the CBS-QB3 model.

2,3-epoxy-5-tertbutylfuran

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4.9 References

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Chapter 5

5. Determination of the Absolute Photoionization Cross-Section of a Carbon-Bromine Bond and Absolute Photoionization Cross Sections of Brominated Organic Compounds

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5.3 Experimental

5.4 Computational

5.5 Results and Discussion

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5.5.2 Bromine Species with sp³ Hybridization

5.5.3 Determination of the C-Br Photoionization Cross Section

5.6 Conclusion

5.7 Acknowledgments

5.8 References
5. Determination of the Absolute Photoionization Cross-Section of a Carbon-Bromine Bond and Absolute Photoionization Cross Sections of Brominated Organic Compounds

(Draft of manuscript in preparation for publication)

Ameyali Tapia and Giovanni Meloni

Department of Chemistry, University of San Francisco, San Francisco, California, 94117

5.1 Abstract
The absolute photoionization cross sections of five different brominated species have been measured for the first time at the Advanced Light Source of Lawrence Berkeley National Laboratory using multiplexed synchrotron photoionization mass spectrometry. The measurement of these cross sections is vital in quantification of bromine-containing species, which are relevant to environmental studies and human use. In addition, the estimation of the C-Br photoionization cross section is performed. This work also presents calculated adiabatic ionization energies and thermochemical appearance energies, which agree with the experimental values. Lastly, bond dissociation energies are presented and discussed.

5.2 Introduction
Bromine is found in a variety of places, including the oceans, water treatment, and as a mercury emissions reducer.¹ Organobromine chemicals are produced naturally in many biological systems, most notably by marine creatures, which use these chemicals as hormones or as chemical defense.² This element exists in high concentrations of around 2,500-10,000 ppm in inland seas and on brine wells.³ This element is slightly toxic to humans, causing skin irritation or burns, gastrointestinal issues, and dizziness.⁴ When used as a water treatment aid, bromine oxidizes in water to form hypobromous acid (HBrO), which is known for its ability to kill known pathogens and bacteria.⁵ Coal burning and small-scale gold mining accounts for about 62% of the annual anthropogenic mercury emissions to air. When bromine is added to coal, the elemental mercury (metallic Hg) released is more easily captured by emission control equipment.⁶
Photoionization mass spectrometry is used widely in determining the cross sections of potential biofuels, such as the studies performed by Price et al., Smith et al., and Winfough et al., which identify the photoionization cross sections of furfural and other potential biofuels, as well as small organic molecules. The importance of these measurements can be seen in the development of quantitative kinetic modeling for bromine species reactions. Although there are several methods in determining photoionization cross sections such as Haddad and Samson’s method of using a dual ion beam in a dual ionization chamber, this work employs the method of Cool et al. This method involves using a photoionization mass spectrometer (PIMS) to determine photoionization cross sections based on values of known photoionization cross sections of ethene, propene, and butene.

In this study, five chemicals, bromobenzene (BB), 1,3-dibromobenzene (1,3-DBB), 1,2-dibromoethylene (1,2-DBE), 2-bromobutane (2-BB), and 2-bromopropane (2-BP), (shown below in Figure 5.1) were used to determine their absolute photoionization cross sections. This is the first time the cross sections for these brominated compounds have been reported. Using these newly determined values and the values of the non-brominated counterparts at 11 eV, the photoionization cross section of the C-Br bond has been determined showing almost identical values between C(sp³)-Br from 2-BB and 2-BP, and C(sp²)-Br bonds from BB, 1,3-BB, and 1,2-DBE.
5.3 Experimental Methods

The experiments presented in this work are performed at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL). The ALS photoionization source provides tunable synchrotron radiation, which is coupled with multiplexed time- and energy-resolved time-of-flight (TOF)
mass spectrometry. Further details about these experiments and the apparatus can be found in past works.  

Each of the bromine-containing species (Sigma-Aldrich: 2-BB: 98%; 2-BP: 99%; BB: 99%; 1,3-DBB: 97%; 1,2-DBE: 98%) are collected as vapor along with helium gas into a cylinder to create a ~1% reaction mixture. These mixtures are then flowed into a 62 cm long slow-flow reactor using calibrated mass controllers, along with a mixture of calibration gases: ethene, propene, and 1-butene, 1% each. After being pushed through a 650 μm pinhole on the side of the reactor, a molecular beam is formed that is then flowed into a vacuumed ionization region. The reactor itself is wrapped in an 18 μm nichrome tape to control the reaction temperature. It is also connected to a roots pump through a throttle valve to adjust and keep the pressure constant. For all experiments, the temperature is 298 K, and pressures of 1.5 torr for 2-bromobutane, 2 torr for bromobenzene and 2-bromopropane, 3 torr for 1,2-dibromoethylene, and 4 torr for 1,3-dibromobenzene are used. Once the reaction species are ionized, they are accelerated, collimated, and then focused into the detector of the TOF mass spectrometer, with a mass resolution of 1,600.

In analyzing the absolute data for photoionization cross section determination, the first step is to confirm the presence of the species, calibration gases and system to be analyzed, and any dissociative ionization fragments. Next, by comparing the PI curves of the three calibration gases to the system under investigation, equation 5.1 can be used. For these experiments, it is important to note that because relative ion signal and PI cross section are energy-dependent, the variables plugged into the equation must be taken at the same energy (E) for the cross section calculation, in this case, 11 eV.

\[
S(E) = k \sigma(E) \delta C \quad \text{(Equation 5.1)}
\]

In this equation, ion signal (S) is the product of the instrumentation constant (k), the photoionization cross section (\(\sigma\)), the mass discrimination factor (\(\delta\)), equal to approximately \(m^{0.64 \pm 0.08}\) (where \(m = \text{mass of the}\)
compound), as determined by Savee et al.,\textsuperscript{15} and concentration (C) of the compound. Relating this equation for both the bromine-containing species and the calibration gases, equation 5.2 can be used to calculate the unknown photoionization cross section of the target molecule.

$$\sigma_T(E) = \frac{S_T(E)\sigma_S(E)\delta_S C_S}{S_S(E)\delta_T C_T} \quad \text{(Equation 5.2)}$$

The unknown photoionization cross section of the target molecule ($\sigma_T$) is determined as a ratio of its signal intensity ($S_T$), photoionization cross section of the standard ($\sigma_S$), mass discrimination factor of the standard ($\delta_S$), and concentration of the standard ($C_S$), all over the signal intensity of the standard ($S_S$), mass discrimination factor ($\delta_T$), and concentration of the target molecule ($C_T$). In these experiments, the absolute photoionization cross-sections of ethene and propene, taken by Cool et al.\textsuperscript{11}, and 1-butene, taken by Wang et al.\textsuperscript{16} are used. The photoionization cross section of ethene is found to be 7.7 Mb, propene is found to be 12.4 Mb, and 1-butene is found to be 11.1 Mb, all with an uncertainty of ±10%. All these values are taken at 11 eV.

The uncertainties of the cross sections are calculated using the propagation of errors, which uses the uncertainty of the mass discrimination factor (approximately 8%), the uncertainties of the concentrations (2%), the uncertainties of the ion signal measurements (2%), and the uncertainties of the photoionization cross sections of the calibration gases (10%). Based on these values, the uncertainty for these experiments is around 16%.

### 5.4 Computational Methods

Utilizing the CBS-QB3\textsuperscript{17,18} composite method within Gaussian09\textsuperscript{19} program suite and Gaussview 6.0\textsuperscript{20} for visualization purposes, electronic structure calculations of all species are completed. To calculate the adiabatic ionization energy of any molecule, the zero-point vibrational energy corrected total electronic
energy ($E_0$) is needed from the optimizations of both the ground state of the neutral and cation of the molecule. The difference of the two is the calculated AIE, as shown by equation 5.3.

$$AIE = E_{0\text{ (cat)}} - E_{0\text{ (neut)}} \text{ (Equation 5.3)}$$

For those species presenting dissociative ionization fragments, bond dissociation energies (BDE) can be calculated as well. Equation 5.4 shows a sample reaction where the neutral parent (AB) acts as a reactant while the dissociative ionization fragment or daughter ion ($A^+$) and the neutral fragment (B) are products. Using this sample reaction along with the literature values for heat of formation, BDE are calculated using the equation 5.5.

$$AB \xrightarrow{hv} A^+ + B \text{ (Equation 5.4)}$$

$$D_0^0 (R - Br^+) = \Delta_f H_0^0 (R^+) + \Delta_f H_0^0 (Br) - \Delta_f H_0^0 (R - Br^+),$$

where $\Delta_f H_0^0 (R - Br^+) = AIE + \Delta_f H_0^0 (R - Br)$ (Equation 5.5)

5.5 Results and Discussion

Out of the five bromine-containing species studied, bromobenzene, 1,3-dibromobenzene, and 1,2-dibromoethylene have $C(sp^2)$-Br bonds, while 2-bromopropane and 2-bromobutane have $C(sp^3)$-Br bonds. By taking the difference of the photoionization cross section of these brominated species obtained in this study and the known literature photoionization cross section values of the same molecules without bromine, the carbon-bromine single bond photoionization cross section can be determined. It is calculated that on average the photoionization cross section for a C-Br single bond is 73.9 Mb, discussed in section 5.5.3. The following sections will discuss each of these species and their characteristics.
5.5.1 Bromine-containing species with C(sp³)-Br bonds

The PI spectrum of bromobenzene is shown in Figure 5.2, along with the determined photoionization cross-section values shown in Table 5.1. The data shows the AIE of bromobenzene as 8.95 ± 0.05 eV, which agrees with the value of 8.97 ± 0.02 eV, found by Baer, Tsai, et al., and the CBS-QB3 calculated value of 9.00 ± 0.05 eV. The initial ionization of this species is the result of the removal of the π-electron from the highest occupied molecular orbital (HOMO) localized on the benzene ring and the bromine substituent, showing a bonding (C₁=C₂ and C₃=C₄ bond distances) and antibonding character (C₅=C₆ and C-Br bond distances) (Figure 5.3). This can be further proved by looking at the changes in bond lengths upon ionization. The C₁=C₂ bond length is 1.394 Å for the neutral species, which increases to 1.428 Å for the cationic species. This is also seen in the C₃=C₄ bond length, where the neutral species is 1.394 Å, which extends to 1.420 Å when the first electron is removed. As for the C₅=C₆ bond length, the neutral species has a bond length of 1.396 Å, while the cationic species decreases to 1.376 Å. Finally, the C-Br bond length also sees a decrease from the neutral and cationic species, from 1.914 Å to 1.842 Å. Bond length and order are inversely proportional to each other: when the bond length is increased (as shown here), bond order is decreased, contributing to the weakening of chemical bonds (such as when an electron is removed from a bonding orbital). Using equation 5.2, the photoionization cross section for bromobenzene was calculated to be 112.8 Mb at 11 eV with an uncertainty of 16%.
Figure 5.2 Molecular photoionization cross section of bromobenzene
Table 5.1 The photoionization cross sections of bromobenzene, 1,3-dibromobenzene, and 1,2-dibromoethylene reported in megabarns (Mb) at different energies. (N/D: no data)

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Figure 5.3 Orbital Energy and electron distribution of bromobenzene (BB) obtained from CBS-QB3 orbital calculations

Figure 5.4 shows the photoionization spectrum of 1,3-dibromobenzene, with the photoionization cross-section values also found in Table 5.1. Its AIE is determined as 9.08 ± 0.05 eV. This value is similar to the literature value of 9.01 ± 0.02 eV, taken by Olesik, Baer, et al., \(^2\) and the calculated CBS-QB3 value of 9.15 ± 0.05 eV. Similar to bromobenzene, the ionization of the species is a result of the removal of the \(\pi\)-electron localized on the benzene ring and the two bromine substituents. The \(C_3=C_4\) bond for the neutral species is 1.394 Å, which extends to 1.436 Å for the cationic species. Both the \(C_1=C_2\) and \(C_5=C_6\) bond lengths slightly decrease from 1.394 Å in the neutral state to 1.392 Å in the cationic state. Both bromine substituents decrease from 1.911 Å in the neutral species to 1.858 Å for the cationic species (Figure 5.5). The photoionization cross section for this species is calculated to be 183.4 Mb at 11 eV with an uncertainty of 16\%.
Figure 5.4 Molecular photoionization cross section of 1,3-dibromobenzene

\[ \pi_{C=C} \]  
(HOMO)

Figure 5.5 Orbital energy and electron distribution of 1,3-dibromobenzene (1,3-DBB) obtained from CBS-QB3 orbital calculations
The experimental data of 1,2-dibromoethylene shows an AIE of $9.43 \pm 0.05$ eV, agreeing with the literature value of $9.46 \pm 0.02$ eV, found by Momigny$^{22}$, and the CBS-QB3 calculated value of 9.46 eV. The photoionization spectrum of this species is shown in Figure 5.6, with the corresponding photoionization cross section values found in Table 5.1. For this species, the ionization is a result of the double carbon bond, as visualized by Figure 5.7. The $C_1=\text{C}_2$ bond length increases from 1.327 Å in the neutral state to 1.382 Å in the cationic state. Conversely, the carbon-bromine single bond decreases between the neutral and cationic state. This value decreases from 1.902 Å to 1.826 Å, which is consistent with the antibonding character for this bond distance. The calculated photoionization cross section for this species is 154.2 Mb at 11 eV with an uncertainty of 16%.

![Figure 5.6 Molecular photoionization cross section of 1,2-dibromoethylene](image)

Figure 5.6 Molecular photoionization cross section of 1,2-dibromoethylene
Figure 5.7 Orbital energy and electron distribution of 1,2-dibromoethylene (1,2-DBE) obtained from CBS-QB3 orbital calculations

5.5.2 Bromine-containing species with C(sp³)-Br bonds

Based on the experimental data of 2-bromobutane, its AIE is determined as 9.93 ± 0.05 eV, consistent with the literature value of 9.98 ± 0.01 eV, found by Watanabe et al., and the CBS-QB3 calculated value of 10.07 ± 0.05 eV. The PI spectrum of this species is shown in Figure 5.10, along with the corresponding photoionization cross section values found in Table 5.3. The initial ionization of this species is the result of the carbon-bromine single bond, which has the most significant bond lengthening between the neutral and cationic species. For the neutral species, the bond length was found to be 2.010 Å, while it was determined to be 2.043 Å for the cationic species (Figure 5.11). This compound was also found to have a dissociative ionization fragment at m/z 57, with an experimental onset of 10.1 eV. Using Equation 5.5,
the theoretical bond dissociation energy was calculated and found to be 33 kJ/mol at 298 K. The total photoionization cross section for 2-BB is determined to be 83.5 Mb at 11 eV with an uncertainty of 16%.

**Figure 5.10** Molecular photoionization cross section of 2-bromobutane (blue circles), dissociative fragment (orange circles), and total photoionization cross section (black circles)

\[ \pi_{\text{C=O}} \]

(HOMO)

**Figure 5.11** Orbital energy and electron distribution of 2-bromobutane (2-BB) obtained from CBS-QB3 orbital calculations
Table 5.3 The total photoionization cross section of 2-bromobutane and its molecular and dissociative ionization fragments reported in Megabarns (Mb) at different energies (N/D: no data)

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The PI spectrum of 2-bromopropane is shown in Figure 5.12, with its photoionization cross section values shown in Table 5.4. As shown in the experimental data, the experimental AIE for 2-BP is 10.03 ± 0.05 eV, agreeing with the literature value of 10.08 ± 0.01 eV, as found by Watanabe, Nakayama, et al. For this molecule, the CBS-QB3 calculated AIE was found to be 10.28 ± 0.05 eV, which does not match with the experimental or literature value. The orbital energy diagram is shown in Figure 5.13. This species was also found to have a dissociative fragment at m/z 43, with an experimental onset of 10.42 eV. Using Equation 5.5, the theoretical bond dissociation energy for 2-BP was determined to be 60 kJ/mol at 298 K. Finally, the total photoionization cross section for this molecule was determined to be 75.3 Mb at 11 eV with an uncertainty of 16%.
\[ \sigma_{C=C} \] (HOMO)

**Figure 5.12** Molecular photoionization cross section of 2-bromopropane (blue circles), dissociative fragment (orange circles), and total photoionization cross section (black circles)

*Figure 5.13* Orbital energy and electron distribution of 2-bromopropane (2-BP) obtained from CBS-QB3 orbital calculations
Table 5.4 The total photoionization cross section of 2-bromopropane and its molecular and dissociative ionization fragments reported in Megabarns (Mb) at different energies. (N/D: no data)

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</table>

5.5.3 Determination of the C-Br photoionization cross section

In order to estimate the C-Br photoionization cross section, the additivity rule explained and expanded on by Bobeldijk, van der Zande, and Kistemaker\textsuperscript{27} is employed. This additivity model originally stated that molecular orbitals can be described by the sum of the valence orbitals of all atoms present in the molecule.\textsuperscript{27} Bobeldijk et al. expanded on this concept by stating that photoionization cross sections were able to be estimated by approximating the sum of cross sections for different ‘atom pairs’ in a molecule. In their paper, they tested various molecules at photon energies of 11.8 and 16.7 eV and presented the photoionization cross sections with a 20% error. In these experiments, the photoionization cross sections for the atom pair C-Br ($\sigma_{\text{C-Br}}$) are estimated at 11 eV. This is achieved by calculating the difference of the total photoionization cross section of the brominated molecule ($\sigma_{\text{total, halogenated}}$) and the non-brominated molecule ($\sigma_{\text{total, non-halogenated}}$), and dividing it by the number of C-Br bonds in the
brominated compound (n_{C-Br bonds}). Based on the Bobeldijk model, it is assumed that the C-H atom pair does not contribute to the photoionization cross section and thus Equation 5.6 can be applied to any organic compound with a halogen substitution.

\[ \sigma_{C-Br} = \frac{(\sigma_{total\,halogenated} - \sigma_{total\,non-halogenated})}{n_{C-Br\,bonds}} \]  (Equation 5.6)

Equation 5.7 shows an example of the calculation for the photoionization cross section of 1,3-dibromobenzene. The total cross section at 11 eV is used for all compounds to account for all brominated isotopes and fragments from the brominated parent molecules. The literature value for benzene (38.6 Mb at 11 eV) is taken from the photoionization experiments of Cool et al.\textsuperscript{11}

\[ \sigma_{C-Br} = \frac{(\sigma_{total\,1,3-DBB} - \sigma_{total\,benzene})}{n_{C-Br\,bonds}} = \frac{183.1 - 38.6}{2} = 72.3 \, Mb \]  (Equation 5.7)

Table 5.5 shows the estimations of the photoionization cross sections for the five brominated compounds, along with the averages for the respective C(sp\textsuperscript{2})-Br and C(sp\textsuperscript{3})-Br hybridized molecules. It is calculated that on average, the total C-Br photoionization cross section is 73.9 Mb. These values have an uncertainty of 16\%.
Table 5.5 Average estimations of sp² and sp³ hybridized C-Br photoionization cross sections at 11 eV (Mb).

<table>
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<tr>
<th>Brominated Molecule</th>
<th>Non-brominated Molecule</th>
<th>σ sp² C-Br</th>
<th>σ sp³ C-Br</th>
<th>Reference</th>
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<tbody>
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<td>Bromobenzene</td>
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<tr>
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<td>Benzene</td>
<td>72.3</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>10</td>
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<tr>
<td>2-Bromobutane</td>
<td>Butane</td>
<td>-</td>
<td>75.2</td>
<td>14</td>
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<td>2-Bromopropane</td>
<td>Propane</td>
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<tr>
<td>Average</td>
<td>-</td>
<td>73.3</td>
<td>74.9</td>
<td>-</td>
</tr>
</tbody>
</table>

5.6 Conclusion

The adiabatic ionization energies, bond dissociation energies, and photoionization cross sections of parent and dissociative fragments for five bromine products are presented to determine the C-Br single bond cross section. It was found that the experimental AIE values agree very well with the CBS-QB3 values, with the exception of 2-bromopropane. Since 2-bromopropane and 2-bromobutane have dissociative fragments, the theoretical bond dissociation energies were calculated at 0 K. Finally, using literature cross section values of similar molecules, the C-Br single bond cross section was determined by taking the difference of the calculated experimental cross section and the literature. It was determined that on average the photoionization cross section for a C-Br single bond is 73.9 Mb at 11 eV.
5.7 Acknowledgements

Thank you to Dr. Giovanni Meloni, for guiding and mentoring through this project, graduate students Lauren Lewellen, Lori Chen, Ed Buck, and former graduate student Sara Gallarati. Thank you to Dr. and Mrs. Whitehead for the Whitehead Summer Fellowship, the USF Faculty Development Fund, Sandia National Laboratories for use of their apparatus, and the ACS Bridge Travel Fund. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.
5.8 References


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