Spring 5-19-2017

Investigation of Absolute Photoionization Cross Sections of Cyclic Ketones, Low Temperature Combustion of Propargylamine by Synchrotron Photoionization Mass Spectrometry, and Computational Study of Hypersalts

Chelsea Liliana Price
cprice4@dons.usfca.edu

Follow this and additional works at: https://repository.usfca.edu/thes

Recommended Citation
https://repository.usfca.edu/thes/246

This Thesis is brought to you for free and open access by the Theses, Dissertations, Capstones and Projects at USF Scholarship: a digital repository @ Gleeson Library | Geschke Center. It has been accepted for inclusion in Master's Theses by an authorized administrator of USF Scholarship: a digital repository @ Gleeson Library | Geschke Center. For more information, please contact repository@usfca.edu.
Investigation of Absolute Photoionization Cross Sections of Cyclic Ketones, Low Temperature Combustion of Propargylamine by Synchrotron Photoionization Mass Spectrometry, and Computational Study of Hypersalts

Thesis written by Chelsea L. Price

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

Masters of Science in Chemistry
at
the University of San Francisco

Thesis Committee

Giovanni Meloni, PhD. Research Director

Janet Yang, PhD. Assistant Professor

William Melaugh, PhD. Professor

Marcelo Camperi, PhD. Dean, College of Art and Sciences
Investigation of Absolute Photoionization Cross Sections of Cyclic Ketones, Low Temperature Combustion of Propargylamine by Synchrotron Photoionization Mass Spectrometry, and Computational Study of Hypersalts

A Thesis Presented to the Faculty of the Department of Chemistry at the University of San Francisco in partial fulfillment of the requirements of the Degree of Master of Science in Chemistry

Written by

Chelsea L. Price
Bachelor of Science in Biochemistry
Wake Forest University, Winston-Salem, NC
5/15/2015
Table of Contents

1. Introduction

1.1. Demand for Sustainable Energy and Pollution Reduction 1
1.2. Overview of Combustion 1
1.3. Internal Combustion Engines 4
1.4. Production and Security of Biofuels 6
1.5. Pitfalls of Biofuels 7
1.6. Biofuels from Feedstock 8
1.7. Purpose of this Work 9
1.8. References 10

2. Theoretical Concepts

2.1. Mass Spectrometry 14
2.2. Ion Sources and Techniques 16
2.3. Mass Analysis 19
2.4. Detection of Ions 26
2.5. Data Acquisition 30
2.6. Multiplexed Technique 32
2.7. Photoionization 34
   2.7.1. Photoionization Cross Sections 37
2.8. Lasers 40
   2.8.1. Types of Lasers 47
2.9. Franck-Condon Principle 51
2.10 Photoionization Spectra 55
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.11</td>
<td>Computational Tools</td>
<td></td>
</tr>
<tr>
<td>2.11.1</td>
<td>CBS-QB3</td>
<td>57</td>
</tr>
<tr>
<td>2.11.2</td>
<td>Density Functional Theory</td>
<td>58</td>
</tr>
<tr>
<td>2.11.3</td>
<td>Coupled Clustered Method</td>
<td>59</td>
</tr>
<tr>
<td>2.11.4</td>
<td>B3LYP</td>
<td>60</td>
</tr>
<tr>
<td>2.11.5</td>
<td>Basis Sets</td>
<td>61</td>
</tr>
<tr>
<td>2.12</td>
<td>References</td>
<td>63</td>
</tr>
<tr>
<td>3.0</td>
<td>Experimentation</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Sample Preparation</td>
<td>66</td>
</tr>
<tr>
<td>3.2</td>
<td>Experimental Apparatus</td>
<td>67</td>
</tr>
<tr>
<td>3.3</td>
<td>Initial Setup</td>
<td>68</td>
</tr>
<tr>
<td>3.4</td>
<td>Slow Flow Tube</td>
<td>69</td>
</tr>
<tr>
<td>3.5</td>
<td>Lasers</td>
<td>71</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Excimer Laser</td>
<td>71</td>
</tr>
<tr>
<td>3.6</td>
<td>Vacuum</td>
<td>73</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Roots Pumps</td>
<td>73</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Turbomolecular Pumps</td>
<td>75</td>
</tr>
<tr>
<td>3.6.3</td>
<td>Scroll Pumps</td>
<td>75</td>
</tr>
<tr>
<td>3.7</td>
<td>Linear Accelerator</td>
<td>77</td>
</tr>
<tr>
<td>3.8</td>
<td>Beamline</td>
<td>80</td>
</tr>
<tr>
<td>3.8.1</td>
<td>Orthogonal Accelerator Time-of-Flight Mass Spectrometer</td>
<td>82</td>
</tr>
<tr>
<td>3.8.2</td>
<td>Detector</td>
<td>84</td>
</tr>
<tr>
<td>3.8.3</td>
<td>Data Acquisition</td>
<td>85</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>3.9. Data Representation</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>3.10 Data Analysis</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>3.11 References</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>4. Absolute Photoionization Cross Sections of Two Cyclic Ketones:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentanone and Cyclohexanone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1. Abstract</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>4.2. Introduction</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>4.3. Experimental Methodology</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>4.3.1. Apparatus</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>4.4. Measurement</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>4.5. Computational</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>4.6. Results and Analysis</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>4.6.1. Cyclopentanone</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>4.6.2. Cyclohexanone</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>4.7. Conclusions</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>4.8. Acknowledgements</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>4.9. References</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>5. Cl-initiated oxidation of propargylamine via synchrotron multiplexed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>photoionization mass spectrometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1. Abstract</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>5.2. Introduction</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>5.3. Experimental Methodology</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>5.3.1. Apparatus</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>5.3.2. Computational Methods</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>
5.4. Results and Analysis

5.5. Conclusions

5.6. References

6. Computational Investigation of LiF Containing Hypersalts

6.1. Introduction

6.2. Theoretical Methods

   6.2.1. Computational Methodology

6.3. Results and Discussion

   6.3.1. Superalkali

   6.3.2. Hyperalkali

   6.3.3. Superhalogen

   6.3.4. Hyperhalogen

   6.3.5. Hypersalts designed using hyperhalogen and metal cation

   6.3.6. Hypersalts designed using hyperalkali and halogen

6.4. Conclusions

6.5. Acknowledgements

6.6. References
Chapter 1: Introduction

1.1 Demand for Sustainable Energy and Pollution Reduction

A demand for both sustainable energy and fuel has risen globally in the 21st century due to increasing population and transport. Conventional fuel, derived from fossil fuel, is both in limited quantity and releases a substantial amount of greenhouse gases (GHGs) that affect Earth’s climate. There is a consensus among scientists that Earth’s climate is warming because of the accretion of GHG emissions generated by burning fossil fuel for energy. GHG emissions must be reduced before a dramatic change to the environment cannot be reversed. A suitable alternative energy source may be biofuels; a sustainable alternative energy source that lowers GHG emissions, mends air quality in urban areas, improves overall health, and provides fuel security.¹

The Environmental Protection Agency (EPA) indicated common air pollutants that have detrimental effects on human and animal health: (1) ozone (O₃), (2) particulate matter (PM), (3) carbon monoxide (CO), (4) nitrogen oxides (NOₓ), (5) sulfur dioxide (SO₂), and lead.²⁻³ Researchers investigate ways to reduce pollutants produced through automotive combustion.

1.2 Overview of Combustion

Combustion of fossil fuels powers our cars and heats our homes, making it an integral part of our daily lives. The limited availability of oil and increase of air pollutants from combustion drives investigation into alternative energy sources, but all possibilities rely on the understanding of their combustion. Manufacturers who developed combustion engines in the early 20th century barely had knowledge of the mechanisms involved⁴ and were not concerned about the intermediate steps. Their understanding followed the simple equation:

\[ \text{Fuel} + \text{Air} \rightarrow \text{Heat} + \text{CO}_2 + \text{Water} \]
Research interests also extend to the combustion mechanisms of engines and improvement of their efficiency. Engines create power by consuming large amounts of fuel, which in turn emits pollutants. During an engine’s acceleration, incomplete combustion of fuel converts pollutants like NO to NO$_2$, which are then released into the atmosphere and react with hydrocarbons. This increases the concentration of ozone, especially in urban areas.

These pollutants harm human health in various ways. Ozone irritates the mucous membrane of the respiratory system leading to coughing and clogging. Particulate matter (PM) that results from toxic emissions is full of carcinogens and causes increased probability of asthma and other respiratory issues. PM derives from soot from engines exhaust. It can be differentiated into three categories depending on the size of its particles: coarse particles (> 2.5 $\mu$m), fine particles (< 2.5 $\mu$m), and ultrafine particles (< 100 $\mu$m). Aerosols present in gas and composing most PM in the atmosphere are made of ultrafine particles. Substantial amounts of NO$_2$ also causes adverse effects such as: increased viral infections (like influenza), lung irritation, edemas of lungs, bronchitis, allergies, and decreased pulmonary function. Likewise, SO$_2$ debilitates lungs.
by constricting air-ways and damaging lung tissues. Collectively, these pollutants increase the likelihood of emphysema and suffocation.\textsuperscript{3,13}

\textbf{1.3 Internal Combustion Engines}

Biofuels show promise as a main source of alternative energy that lowers both the probability of pollutant emissions and impairment to health. Internal combustion (IC) are the primary engines used in the automotive industry and it is imperative to develop IC engines that use biofuels as the main source of energy.\textsuperscript{13} Recent attention is placed on the combustion of premixed fuels, specifically within the spark ignition (SI), compression ignition (CI), and homogenous charge compression ignition (HCCI) engines. Figure 2 depicts the differences between the three types of engine.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ic_engines.png}
\caption{Comparison of fundamentals of various IC engines; SI and CI engines are ignited at single points with an external ignition source, whereas HCCI engines are ignited at multiple points by autoignition. HCCI engine is a hybrid of the SI and CI engine.}
\end{figure}

Combustion of the SI engine takes place using flame propagation through a homogenous mixture of air and fuel while a compression ignition (CI) engine’s combustion depends upon diffusion of the mixture. In a HCCI engine, a homogenous flammable mixture of fuel and air is prepared before ignition and is autoignited because of the increase in temperature in the
compression stroke; combustion is spontaneous and takes place in absence of a flame. Researchers determined that hydrogen peroxide (H2O2) is necessary for autoignition and thermally decomposes to hydroxyl radicals (·OH) that ignite the reaction with the fuel-air blend. HCCI engines depend on the autoignition temperature and are limited to temperatures below 1800 K. This upper limit minimizes formation of exhaust emissions (NOx and soot), as shown in Figure 3. SI and CI engines are ignited at single points while HCCI engines are ignited at multiple points. HCCI engine is a hybrid of the SI and CI engine.13-14

![Figure 3. HCCI combustion: reduction of NOx and soot (PM).](image)

The presence of excess air and use of low temperature flames within the HCCI engine results in enhanced fuel combustion and reduces soot, CO, NO, and hydrocarbon emission.13 HCCI engines show promise for future transportation because they can utilize various fuels, have higher efficiencies (the fuels are more efficiently burned), and lower exhaust emissions more than other engines on the market.13,18-20 HCCI engines, however, do have drawbacks. The ignition is controlled by fuel composition, which affects the chemical kinetics and requires in depth knowledge of the combustion process in order to complete the kinetics and design the correct
mixtures. Incorporating potential biofuels into HCCI requires further investigation, but may facilitate reduction of pollutants.

1.4 Production and Security of Biofuels

Biofuels are propitious renewable alternative energy sources because they are non-toxic, biodegradable, and sulphur free. Biofuels are categorized as first, second, and third generation. The source from which a biofuel is derived determines the generation. First generation biofuels are developed from plant oils, cooking oils, and animal fat. Plant oils are produced from sunlight and air, while animal fat is produced from an animal’s consumption of plants and other animals. Cooking oil may be a mix of the previous two. These oils and fats are subsequently converted to fatty acid methyl esters (FAMEs) through transesterification. This process increases the carbon chain length (C15-C18) and number of carbon double bonds. The mixture of these esters have different biofuel properties. Second generation biofuels are derived from biomass, composed of woodland residue and lignocellulose. Researchers have been exploring biofuels obtained from algae, termed third generation biofuels. Since biofuels are obtained from an array of natural sources, when they are burned they do not give off additional CO₂, as a result of plant growth. Plants use CO₂ from the atmosphere as they grow to make stems, roots, and leaves. After oil from plants is extracted, converted to biofuel, and burned, CO₂ is released and returned to the atmosphere. This released CO₂ does not add to the net concentration of CO₂ in the air because the next crop of plants will use the same CO₂ as it matures.

Conventional gasoline releases GHGs (including CO₂) into the atmosphere upon combustion and its exhaust produces toxic emissions. Biofuels are a possible solution to diminish both. Second generation biofuels composed of oxygenated hydrocarbons have higher oxygen content (10 – 45%) than traditional fuel and are proven to increase the oxygen content of fuel, which in turn decreases GHG, CO, and NOₓ emissions. It is possible that second generation
biofuels possess higher cetane numbers due to particularly saturated esters. The greater the cetane number, the shorter the ignition delay. One study showed GHG, carbon monoxide, and PM emissions were reduced by 41% if second generation biofuels were used as fuels.

The use of biofuels also provides security of both price and availability. Oil prices vary dramatically over time, reaching $125 per barrel in 2008, and prices collapsed towards the end of 2014. In early 2016 price per barrel fell below 30 dollars, but steadily rose to over 50 dollars by the end of the year. This fluctuation makes conventional oil an unpredictable and unsustainable source for energy and fuel.

1.5 Pitfalls of Biofuels

Although the production of biofuels seems all-around beneficial, there are downfalls. There is a dilemma for what land should be used for fuel or food. First generation biofuel producers have limited access to raw materials and the cost of crude vegetable oil from crops is variable. Producers are worried since the price of feedstock is a major portion (~70-90%) of the total manufacturing cost. Biofuel producers are also competing with the food and livestock industry for land to grow crops. The price of corn doubled in the USA from 2006-2007 in addition to the increase in price of milk, eggs, and chicken in response to the fight for land. As manufacturing of biofuels increases, there will be a struggle between food and feed grain for humans and livestock and grain for fuel; this will cause the price of grain to increase. Price will also escalate in presence of a drought. Importation of grains would be necessary to fulfill needs, which would raise the price of food and fuel. The environmental impact of biofuels stretches beyond GHG emissions and carbon balance.

In addition to the aforementioned, consideration must be placed towards water usage, eutrophication, and impact on ecosystems. The palm oil industry expanded rapidly since the 1990’s with oil cultivation boosting by 43%, made possible by clearing rainforests. Fuel crops
also replaced tropical rainforests in Malaysia and have caused the elimination of savannas and grasslands.\textsuperscript{36} Deforestation both endangers biodiversity and releases large amounts of carbon, which is the exact dilemma biofuels try to remedy. This encourages researchers to synthesize biofuels from feedstock that have minimal to no competition with food production and that do not endanger the ecosystem of an area.

1.6 Biofuels from Feedstock

Feedstock that has little competition with food production includes (1) plants grown on abandoned lands used for agriculture, (2) crop residues, (3) harvested wood and forest residues, (4) mixed cropping systems, and (5) municipal and industrial waste.\textsuperscript{37}

(1) Plants grown on abandoned land does not allow competition with food crops, reduces the potential for land clearing, which also reduces the impact on biodiversity of the area. The proper use of these degraded lands can also improve water quality.\textsuperscript{37-41}

(2) Crop residues from rice and wheat are produced in such great quantity that they are abundant in carbon (C) and nitrogen (N) which maintain soil fertility and minimizes soil erosion.\textsuperscript{37,42} This also provides the same amount of biomass as degraded lands, which increases the prospect for harvesting biofuels.

(3) Sustainably harvested wood includes tree branches that are discarded and cleared to prevent forest fires. Sustainably harvested wood includes tree branches that are discarded and cleared to prevent forest fires.\textsuperscript{43}

(4) Double crops aid in the competition between growing crops for food and for fuel. Fuel crops are grown in the summer while food crops are grown during the conventional season on the same land.\textsuperscript{37,44} Mixing crops is the same concept, but fuel and food crops are grown and harvested simultaneously.\textsuperscript{37,45-46}
(5) Using industrial waste from rural and urban allows the organic matter from paper and plastics to be converted to liquid fuels.\textsuperscript{47-48}

1.7 Purpose of this Work

The focus and importance of this Master’s project is to identify mechanisms of OH-initiated oxidation reactions that are relevant to HCCI engines as a model for combustion. Many combustion mechanisms of potential biofuels have been studied,\textsuperscript{49-52} but this work will focus on the OH- and HO\textsubscript{2} elimination pathways of propargylamine (PAM) to gain insight for its potential as a biofuel. In addition to the bimolecular combustion reaction of PAM, the absolute photoionization cross sections of cyclopentanone and cyclohexanone are studied to help quantify and identify possible products in combustion reactions.

The final investigation is purely computational and focuses on the possible synthesis of hypersalts. Building blocks used to create hypersalts are superalkalis, superhalogens, and hyperhalogens. Superalkalis contain a smaller ionization potential than alkalis while superhalogens have a larger electron affinity than halogens. These have great reducing properties, and when combined with superhalogens they form supersalts which show potential in the design of energy storage materials. This concept can be extended to hypersalts, which could create better energy storage materials than supersalts. The atoms used to design these various species are lithium and fluorine. Further exploration will go into the composition of hyperalkalis to possibly build hypersalts using the former in conjunction with hyperhalogens.
1.8 References


35. Lovett, J. C., Biofuels and ecology.


Chapter 2: Theoretical Concepts

This chapter covers the theory and applications of techniques used in gas phase reactions studied in this work. Topics include: mass spectrometry, photoionization, lasers, Franck-Condon principle, and computational techniques.

2.1 Mass Spectrometry

Mass spectrometry (MS) is a technique that can quantify known compounds, identifies unknown species in a sample, and reveals the structure and chemical properties of different molecules. In “normal” MS, a sample is converted into gaseous species and ionized, with or without fragmentation. Then, they are separated according to their mass-to-charge ratio, and detected based on various components, depending on the type of detector and the relative abundance of each ion. Mass spectrometry focuses on the effect that ionizing energy has on a molecule and might determine thermodynamic properties of a reaction. Ions are preferred to neutral species because their motion and direction are easily manipulated and allow for better detection. A mass spectrum of the sample is then produced as a plot of ion abundance versus mass-to-charge ratio. Figure 1 shows the basic path of ion formation, separation, and detection.

A mass spectrometer needs three components: (1) an ion source to produce a beam of gaseous ions from the studied component. Any excess energy produced by this process may break the compound into fragments. There are different ion sources used to form ions. These will be discussed in the section titled “Ionization Techniques.” (2) In a mass analyzer the ions and fragments are separated based on their mass-to-charge ratio. The separation of ions of different masses is based on the principle that all ions are given equal energy.1 Further discussion on mass analyzers is in the section titled “Mass Analysis.” (3) In a detector, ion current is measured, amplified, and displayed as a mass spectrum. The second two components operate under vacuum so ions
move freely without colliding into other species.\cite{2} Collisions lead to unwanted fragmentation of molecular ions, reduce sensitivity, increase ambiguity in measurement, and decrease resolution in the mass spectrometer.\cite{2} The ion source is also most frequently operated under vacuum, but there are examples of ion sources working under ambient conditions, one of which is electrospray ionization (described later). The regular ion source region works at a pressure of around $10^{-4}$-$10^{-8}$ Torr while the mass analyzer is kept around $10^{-8}$ Torr.\cite{2} Detectors are further discussed in the section titled “Ion Detection.”

\begin{align}
M + e^- \rightarrow M^+ + 2e^- \quad (1)
\end{align}

The electron leaves the compound in a short amount of time in the ground vibrational state. This causes little change in the position of the nuclei during an electronic transition. Since the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Progression of ion through a mass spectrometer.\cite{3}}
\end{figure}
change in nuclear separation is negligible, it follows the Franck-Condon principle.\textsuperscript{1} If the applied ionizing energy is higher than the ionization energy of the specific species, greater fragmentation of the species occurs. Fragmentation may be so severe that the parent ion does not “survive.” This can cause many problems so the use of lower ionizing energies might be necessary. Once the mass-to-charge ratio of a parent ion is determined by the mass spectrum, the molecular weights of samples can be found. As the size and complexity of a molecule is increased, fragmentation also increases. This process reduces the abundance of the parent ion and its level of fragmentation depends on the ionization energy used (i.e., different ionization energies correlate to different levels of fragmentation).\textsuperscript{1}

The second type of ions seen are fragment ions, also known as daughter ions. Fragment ions are produced by a parent ion through bond cleavage. These ions are dependent upon bond dissociation energies and the relative stability of the neutral fragment.\textsuperscript{2}

\section*{2.2 Ion Sources and Techniques}

An ion source is an essential element of mass spectrometers and is needed to produce a beam of gaseous ions composed of the compound of interest. The ion source should have high ionization efficiency, low energy spread, and minimum contamination between entries of samples.\textsuperscript{2} Ionization techniques can range from very harsh (causing fragmentation) to soft (producing only ions of specific species since a small amount of energy is transferred to species during ionization). There are various techniques available, those discussed are: (1) Electrospray Ionization (ESI), (2) Matrix Assisted Laser Desorption (MALDI), (3) Electron Impact Ionization (EI), and (4) Photoionization.

(1) Samples used in electrospray ionization (Figure 2) are dissolved in a polar solvent and introduced into a mass spectrometer as an aerosol spray.\textsuperscript{4} This is achieved through a thin needle and a strong electric field is applied to the liquid under atmospheric pressure and
pushed out of the capillary tube. This process creates finely charged droplets (aerosol) due to the charge build up at the end of the capillary. The droplets are then passed through a desolvating capillary and kept under high pressure. Here the droplets are vaporized with the aid of an inert gas, usually nitrogen, to remove the remaining solvent particles. The droplets break down further and become unstable as charged molecules move closer together. The drops elongate due to the growth of charge and produce a Taylor cone where smaller droplets are released and explode (coulombic fission). This cycle is repeated until the analyte is free from the solvent and becomes an ion that can pass through the mass analyzer.

![Diagram](image)

**Figure 2.** Electrospray Ionization technique diagram.

(2) In Matrix Assisted Laser Desorption (MALDI) (Figure 3) a sample is dissolved in a solvent that contains an excess of a matrix. The matrix absorbs laser energy and prevents the analyte from being destroyed by the laser. It is then placed onto a MALDI plate and dried under vacuum and co-crystallized with the matrix. A laser is used to desorb and ionize the analyte molecules within the matrix. These ions are then accelerated towards the mass analyzer. The origin of ions produced in MALDI, however, is not fully understood.
(3) Electron Impact (EI) ionization (Figure 4) is a common and reliable source due to its low energy spread and steady ionizing electron beam. Solids, liquids, and gases can be used in this method if they can withstand vaporization without decomposing. A heated metal filament (the cathode ~ 1500-2000 K) produces electrons, which are subsequently accelerated towards the anode. Meanwhile, the sample is vaporized into a vacuum and the gaseous species are bombarded with the electrons. The ionizing chamber is kept at a constant pressure around 0.0005 Torr. Positive ions form from the exchange of energy during these collisions expelling electrons. The positive ions leave the chamber due to the potential difference between two oppositely charged plates, which accelerate the ions according to their masses. The energy of the electron beam is controlled; if the energy is greater than the ionization potential of the gas, the electrons may cause fragmentation of the sample.
(4) Another ion source of interest is photoionization, which will be discussed more in depth in the section titled “Photoionization.” In short, a gaseous molecule is hit with a beam of photons of a known energy. The photon beam typically comes from a vacuum ultraviolet (VUV) radiation source. Photons of a desired wavelength at a known energy can be selected and the degree of fragmentation is controlled to some extent.

2.3 Mass Analysis

Mass spectrometers depend heavily on mass analyzers, which are needed to separate ionized masses based on their mass-to-charge ratio and output them to the detector. A mass analyzer performs two functions: (1) disperses all ions based on their mass-to-charge ratio and (2) focuses all mass-resolved ions to a single focal point. A moving particle of interest can be distinguished based on differences in momentum, kinetic energy, and velocity. A mass analyzer can make use of one of these attributes to mass-resolve ions. Mass range, resolution, and sensitivity are preferred features in a mass analyzer. Mass range allows species with higher masses to be analyzed and resolution provides the ability to separate neighboring ions. Sensitivity allows the
smallest amount of a species to be detected. A few mass analyzers of interest include: (1) Quadrupole mass analyzer, (2) Magnetic sector mass analyzer, and (3) Time-of-Flight mass analyzer.

(1) The quadrupole mass analyzer (Figure 5) uses the stability of trajectories in oscillating electric fields to separate ions according to their mass-to-charge ratios. The mass analyzer is made up of four parallel rods. Radio Frequency (RF) and Direct Current (DC) voltages compose the parallel beams; the application of the voltages determines the trajectories of ions of a given mass-to-charge ratio. Ions with stable trajectories reach the detector, while those with unstable trajectories are neutralized when they strike the electrodes.

![Quadrupole mass analyzer](image)

**Figure 5.** Quadrupole mass analyzer consisting of the source, focusing lens, cylindrical rods, and detector.

(2) A Magnetic Sector mass analyzer (Figure 6) uses magnetic fields to separate ions (Figure 7 shows the path and deflection of incoming ions).
Figure 6. Components of a magnetic mass sector mass analyzer.\textsuperscript{10}

Figure 7. Schematic of the process of mass-to-ratio ion separation.\textsuperscript{10}
Once ions are accelerated from the ion source, magnetic sectors bend the trajectories of ions into circular paths and separate ions of different mass-to-charge ratio based on their momentum and direction. When ions of different mass-to-charge ratio, as well as equal kinetic energy, enter the magnetic field they travel in different paths (larger ions have larger paths while smaller ions follow a smaller path). The magnetic field of strength B, ion charge (q), and velocity (v) experiences a force (F) that is perpendicular to the direction of the magnetic field:

\[ F_B = Bqv \]  

Since the ion follows a circular trajectory with radius, r, the centrifugal force equals the magnetic force:

\[ qvB = \left( \frac{mv^2}{r} \right) \]  

where \( qvB \) is the centrifugal force with m being the mass of a moving ion, q is the charge, v is the velocity at which the ion flies into the constant magnetic field, and the left is the homogenous magnetic field with magnetic force, B.

The velocity of the ion is determined by its kinetic energy, \( \frac{mv^2}{2} \), which the ions gain during their acceleration at an accelerating voltage, V.

Therefore, the equation becomes:

\[ \frac{m}{q} = \frac{r^2B^2}{2v} \]  

In a fixed magnetic field strength, ions that have the same mass-to-charge ratio, which initially had different paths, are focused so that ions all follow the same path to the ion detector. In this way, when the magnetic field strength is scanned, ions of different mass-to-charge ratios are separated before detection.
A Time of Flight mass analyzer (TOF), (Figure 8), accelerates an ionized sample and finds the mass-to-charge ratio based on how long each ion is “in flight” to reach the detector.

Figure 8. Time-of-Flight mass analyzer; sample is ionized by electron bombardment and then accelerated by an electromagnetic field. The ions travel through a vacuum before being detected. Here the analysis of all produced ions from a pulsed source is seen. There is no magnetic field for the separation of ions of different mass-to-charge ratios. Instead, the TOF mass analyzer determines how long it takes the ions to reach the detector. This flight time depends on the mass-to-charge ratio. The flight time is related to the kinetic energy, $T$, that when subjected to a proper potential, $V$, is equal to

$$ T = \left( \frac{m \nu^2}{2} \right) = eV $$

(6)

This equation can be rearranged to separate the ion velocity:

$$ \nu = \sqrt{\frac{2eV}{m}} $$

(7)
\[
TOF = d \sqrt{\frac{m}{2eV}}
\]

where path length (d) and potential (V) are constant. The TOF can then be rewritten as

\[
TOF = K\sqrt{m/z}
\]

Therefore, the time of flight of various ions is proportional to the square root of the mass-to-charge ratios of ions causing ions of a lower m/z to reach the detector first with their arrival time following the equation:

The measured arrival times of all ions gives a time spectrum that is converted into a mass spectrum by calibrating the instrument. A general calibration equation is:

\[
\frac{m}{q} = \alpha t^2 + \beta
\]

where alpha is the constant of proportionality between an ion’s arrival time and its mass-to-charge ratio, and beta is the time offset that comes from the difference in time between ion extraction and data acquisition start.

Mass calibration in these experiments is conducted through the calibration of calgas (consisting of ethene, propene, and butene). The TOF of each peak (from the TOF mass spectrum), representing the components of the calgas, is recorded to acquire alpha and beta values. These values calibrate the graph of a specific mass. Knowing these values allows all obtained mass peaks to be properly correlated to the right mass values.

An advancement made in time-of-flight mass analysis has been the creation of orthogonal acceleration to couple to continuous ionization sources. A continuous ion source fills an acceleration region. Once full, an orthogonal acceleration process sends ions into the time-of-flight drift. While ions are separated in the drift region, new ions fill the acceleration region.
When the ions leave the acceleration region they move in a particular direction. Once an injection pulse voltage is applied, the ions are pushed by an electric field in a direction orthogonal to their original trajectory and “fly” towards the analyzer. Once ions reach the drift region, a new sample of ions fills the orthogonal accelerator. One flight cycle is complete when the heaviest ion reaches the detector and another begins when a voltage is applied.

Since orthogonal acceleration gives a new component of velocity to the ions, this component is independent of the velocity of the ions in the ion beam. If ions do not have the same kinetic energy as they did in the ion beam on their way to the detector, a divergence in trajectory is seen. Figure 9 shows a schematic of orthogonal acceleration with a linear mass analyzer.

![Figure 9. Schematic of oa-TOF](image)

### 2.4 Detection of ions

After the ions pass through the mass analyzer they are detected and transformed into a usable signal. The detector can create an electric current from the ion that is proportional to its abundance. There are many detectors available, but all detect ions based on charge, mass, or
velocity. On average, about 10 incident ions per second will reach a detector and produces an electric current of $1.6 \times 10^{-18}$ A. Amplification is therefore required to increase the signal. Most detectors multiply the intensity of the signal through a cascade effect. Other desirable detector properties include fast time response, low noise, high collection efficiency, and an equivalent response to all masses. There are two classes of detectors available: (1) point ion collectors and (2) array collectors. Point ion collectors detect all ions of a single mass at one time. Array collectors count multiple masses and their respective ions at once along a plane. A few of interest may be: (1) Faraday Cups, (2) Electron Multipliers, and (3) Microchannel Plates (MCP).

1. A Faraday cup (Figure 10) is composed of a metal cup with a small entrance. As ions enter the cup they are neutralized as they strike the wall (gain or lose electrons), which leads to a current through the resistor. The DC is amplified and detected, which provides a measure of ion abundance. If entering ions have higher energies than the material of the cup, secondary electrons are formed when ions strike the walls (this is a source of error). If a secondary electron leaves the cup, it may appear as if an additional ion has entered because the charge of an electron leaving the wall of the detector is equal to the arrival of a positive ion. Therefore, accuracy of this detector is compromised, but can be improved by preventing the generation of secondary electrons. This simple detector has low sensitivity and slow response time. The sensitivity of Faraday cups is limited by the noise of the amplifier.
(2) Electron Multipliers (Figure 11) are the most common ion detector used in mass spectrometry. Ions from the analyzer are accelerated to enhance efficiency. An electrode, conversion dynode, is held at a high potential that is opposite to the charge on the ions. When an ion (positive or negative) hits the conversion dynode, secondary electrons form. As electrons progress through the tube, they strike other dynodes that cause an amplification of secondary electrons. The cascade of electric current (Figure 11) that arrives at the anode is amplified to provide a gain of approximately $10^7$ electrons for each incident ion.

(3) Microchannel plates (Figure 12) are a type of continuous dynode electron multiplier. These plates have drilled parallel cylindrical channels termed channel electron multiplier (CEM) tubes, depicted in Figure 12. The plate input side is kept at a negative potential compared
with the output side. Each tube is made from semiconducting lead glass and a high voltage is applied between the ends. The CEM tube is about 12 µm in diameter and each channel is separated by 10 µm. These channels are tilted with respect to the plate surface so that the incident ion beam does not pass through linearly (Figure 12). When an incident ion hits the surface of the microchannel plate, secondary electrons are produced and are then accelerated towards the positive voltage hitting channel walls along the way. With each strike, electrons are reflected back and forth throughout the length of the tube and have the opportunity to strike other electrons, which in turn generates more secondary electrons (cascade effect). Different connections between plates are possible and allow acceleration of ions to the output side as seen in Figure 13. Connections include simple channels, curved channels, chevron assembly, and z-configuration. The apparatus used in the Advanced Light Source uses plates with a chevron assembly to increase the total electron gain, which results in a greater gain than using simple channels or curved channels alone. Figure 14 shows how the arranged plates cause an amplification of secondary electron generation. The cascade effect in a channel can multiply electrons by 10^5. One plate can amplify to about 10^4, while using many plates can increase amplification to 10^8. Since the electron path in the channel is short, there is a fast response time, which allows MCP to be of great use in time-of-flight mass analyzers.
Figure 12. Top: MCP with each whole representing a single channel detector. Bottom: Electron multiplication within a CEM tube of a MCP.\textsuperscript{24}

Figure 13. Different connections of CEMs within MCPs.\textsuperscript{9}
2.5 Data Acquisition

Electrical signals from the detector are visualized by a computer through a process called data acquisition. Detectors can either operate in the analogue mode or the pulsed counting mode, which allows for different types of data acquisition systems. The data acquisition system converts the signal from the amplifier to a digital value, which can then be visualized. When a detector produces an analogue electrical signal that is amplified, background noise is reduced by a filter that cuts off high frequencies. If a higher resolution is required, then sampling frequency must increase since the number of data points per unit time increases as well. One type of detection system used in the time-of-flight mass spectrometer operates in the pulse counting mode that is coupled to a time-to-digital converter (TDC). The pulse from the detector is amplified and sent to the discriminator. The discriminator sends a timing pulse to the TDC, which then counts the time from start to stop of each pulse and records this in the histogram memory (Figure 15). The cycle continues over the course of the acquisition period and data is sent to the system as a spectrum. Figure 16 shows the incident ion beam traveling to the time-to-digital converter.
A time-to-digital convertor measures ion arrival times and converts times into mass-to-charge ratio values. The number of ions arriving at a specific mass-to-charge ratio is the same as the number of events recorded. Since the recording time lasts only a few microseconds, many ions will not arrive to the detector at the same time, even when there is an abundance of ions. If two ions arrive at the MCP detector at the same time at a specific mass-to-charge ratio, the time-to-
digital convertor cannot distinguish the two. A difference is created between the true number of ions and the number given by the time-to-digital convertor, termed “blindness” (dead time). In order to correct dead time an algorithm is implemented to increase the given ion yield. The number of events is increased in proportion to the recorded number of events and creates a more accurate mass spectrum.

Mass-to-charge ratio plotted as a function of the ionizing energy is called an ionization efficiency curve. From this curve it is possible to obtain the ionization and appearance energies. The appearance energy is the minimum amount of energy required to produce a fragment ion (daughter ion) and its neutral fragments. The ionization energy is the minimum amount of energy required to remove an electron from a neutral molecule. Here the reference states are ground vibronic states of both the neutral and the ion. In such case, the ionization is called adiabatic ionization energy (AIE).

2.6 Multiplexed Technique

All molecules and atoms can be ionized and detected by any technique that uses mass spectrometry. Multiplexed detection means that multiple species and their properties can be detected simultaneously, which is a great benefit when studying gas phase kinetics.

Before there was a multiplexed mass spectrometer, isomeric products that formed following reactions could not be distinguished. Reactions were interwoven and made analyses problematic. In order to resolve the issues an experimental apparatus needed to meet the following requirements: (1) detection that would be applicable to all atoms and molecules, (2) detection of all species simultaneously (multiplexed), (3) resolution of isomers, (4) detection of low concentrations of species, (5) and temperature and pressure variation over a wide range of experimental conditions.
The instrument that solves these problems is based on the Photoionization Mass Spectrometer (PIMS) created by Slagle and Gutman.\textsuperscript{15-16} PIMS used fixed frequency VUV radiation from microwave discharge lamps to form photoions.\textsuperscript{14} The instrument’s design utilized in our research differs in two ways from the original PIMS described above. The photoionization source uses radiation from the beamline located at the Advanced Light Source (ALS) Synchrotron in the Lawrence Berkeley National Laboratory.\textsuperscript{14} The ALS radiation is bright and increases in sensitivity while tunability provides selectivity. The two allow minimization of fragmentation and sort structural isomers based on their ionization energies and photoionization spectrum shape, which depends on Franck-Condon factors (discussed later).\textsuperscript{14}

The second innovation is a multiplexed mass spectrometer that can detect multiple masses simultaneously, which is more efficient and provides the ability to measure the time dependence of all species concurrently.

Time and photon energy resolved mass spectra are collected from the use of the multiplexed, time- and energy-resolved PIMS instrument and a three-dimensional data block results. Cool and co-workers\textsuperscript{17} calibrate the ion signal in the photoionization spectrum against a species with a known photoionization cross-section and concentration, like propene. The ion signal is dependent on how many counts are present in a resulting peak after detection. The counts refer to the intensity of a peak. These counts form the y-axis (counts per second) in a photoionization cross section graph while the x-axis represents the mass-to-charge ratio. The cross section is the relative area in which a photon must strike to ionize the compound. From the time-resolved plots, the formation and depletion of a species during a photolytic reaction can be monitored.\textsuperscript{18} Theses curves yield rate coefficients and isomer-resolved product branching ratios as a function of pressure and temperature.
Overall, the data obtained is represented as the ion signal, S, which is proportional to the concentration of neutral molecules in the reactor, the mass-to-charge ratio of the detected ion, reaction time, and photoionization energy.\textsuperscript{14}

2.7 Photoionization

The formation of ions in a mass spectrum can occur in many ways. One method that will be examined more in depth is photoionization. The photoionization of a molecule requires the absorption of a vacuum ultraviolet photon.\textsuperscript{19}

Mass and energy are described by,

\[ E = h \nu \]

also, known as the quantum of radiation. One quantum of radiation is called a photon. Einstein stated that light travels in the form of photons and its energy is found through Einstein’s equation:

\[ E = mc^2 \]

where m is the photon mass and c is the velocity of light in a vacuum. This equation is rearranged to give the momentum of a photon\textsuperscript{20}

\[ \overline{m} = \frac{h \nu}{c} \]

While the energy of a photon is given through the Planck-Einstein relation:

\[ E (eV) = \frac{hc}{\lambda (nm)} \] \textsuperscript{(14)}

Depending on the wavelength of a photon, whose energy is found by using equation (14), both ionization and fragmentation of the ionized compound can occur.\textsuperscript{19} Fragmentation of an ionized compound can also occur through the absorption of a photon, termed photodissociation.

Photoexcitation occurs when a compound absorbs a photon and the radiation can be transferred from a ground state to an excited state. If the photon involved has an energy greater
than the adiabatic ionization energy, the absorption of radiation of a molecule allows an electron to be ejected from the outermost orbital.\textsuperscript{21} Figure 17 shows the energy levels of an atom.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig17.png}
\caption{Energy levels of an atom showing the ejection of an electron if ionization threshold is exceeded in the absorption of light.\textsuperscript{21}}
\end{figure}

Adiabatic is used to describe the energy difference between the ground vibrational states of a neutral molecule and its cation, as depicted in Figure 17. This adiabatic ionization energy also refers to the minimum amount of energy required to remove an electron. When a molecular species absorbs a photon with enough energy to exceed this energy gap, it gets rid of the excess energy in the form of kinetic energy that is used in the separation of an electron from an ion (equation 16). In order to conserve momentum, an electron must be given kinetic energy since it is much lighter than an ion.\textsuperscript{21}
The absorption lines corresponding to this energetic transition from a spectral series and beyond the limit of the spectral series there is continuous absorption, which corresponds to the photoionization of a compound. The absorption is considered continuous because excess energy is removed as kinetic energy. That is:

\[ h\nu = (v_i + k^2)e^- \]  \hspace{1cm} (15)

where \( v_i \) is the ionization potential (ionization threshold energy) of a compound in eV and \( k^2 \) is the \( \Sigma \) (sum) of kinetic energy of the electron.

When there is an interaction between a photon and compound, either photodissociation or photoionization of that compound can occur. When a light source emits a photon that is subsequently absorbed by a molecular species, energy is distributed within the molecule. An electron is ejected and the excited molecule causes various degrees of vibrational motion. This process of photoionization is used to study the energetics, kinetics, and structure of a particular compound. It is essential to carry out photoionization experiments in a high vacuum so that ions move freely and do not collide into other species.

To fully grasp the concept of photoionization, one must also understand a molecule’s environment in terms of orbitals. Orbitals are used to show the distribution and properties of electrons within a molecule or atom. Each orbital has an energy, \( E_n \), where \( n \) determines the type of orbital. To move an electron from one orbital to another it absorbs an energy equal to the difference between the two orbitals in play (\( \Delta E \)):

\[ \Delta E = E_f - E_i \]  \hspace{1cm} (16)

where \( E_i \) and \( E_f \) are the orbitals involved in the electronic transition.

As mentioned before, when the compound absorbs a photon with enough energy to surpass this energy gap, the excess energy is released as kinetic energy. Here, the electron escapes all the
bound orbitals; it is freed from the binding forces in the molecule. Photoionization takes place since the electron absorbed enough incident radiation energy to surpass its ionization limit.

This process of photoionization follows the principle of the conservation of energy. An electron gains energy, which in this case is the difference between photon energy \((h\nu)\) and ionization energy \((E_i)\), in the form of kinetic energy \((KE)\).\(^{22}\)

\[
M + h\nu \rightarrow M^+ + e^- + KE
\]

where \(M\) is the compound of interest

In equation 12 the threshold of ionization is produced by a small amount of excess energy that is given to an electron so it can separate from the ion. The electron is now termed a threshold electron with nearly zero kinetic energy.\(^{22}\) When the electron is not ejected, the molecule vibrates to remove energy as the electron goes back to the electronic ground state of the neutral molecule. This is explained with the Franck-Condon principle, which will be further described in a later section. Photoionization strictly follows this principle and shows that the most probable process will contain a vertical transition.\(^{19}\)

Photoionization also results in a small cross section at the threshold, which makes it easier to detect the start of ionization.

### 2.7.1 Photoionization Cross Sections

Photoionization Mass Spectrometry (PIMS) may be used to determine the cross sections for molecules.\(^{17}\)

The cross section is related to the collision area of a photon with an atom or molecule. When one photon is involved with a single ionization followed by fragmentation, it can be written as:

\[
M + h\nu \rightarrow [M^+] + e^-
\]

\(^{(18)}\)
or

\[
[AB^+] \rightarrow AB' \text{ or } A+B^\text{+}
\]  \hspace{1cm} (19)

where \( h\nu \) is the incident photon energy, \( M \) is the target compound in the ground vibrational state, \([AB^+]\) is a molecular ion in the excited state, \( j \), and \( e^- \) is the lost electron with kinetic energy.  

In equation 19, the electron is released much faster \( (\tau_e \sim 10^{-17} \text{ s}) \) than the molecular ion relaxation process in equation 20 \( (\tau_m \sim 10^{-13} \text{ s}) \). From the two equations one can find that the cross sections are functions of the energy, \( h\nu \). Therefore, the cross section \( (\sigma) \) is defined as the area of a gaseous molecule that interacts with light during an ionizing event.  

Knowing that the cross sections are a function of energy, \( h\nu \), the cross section at a specific frequency, \( \nu \), is:  

\[
\sigma_{p,\nu} = \frac{\pi e^2}{mc^2} \cdot \frac{df}{d\nu}
\]  \hspace{1cm} (20)

or

\[
\sigma_{p,\nu} = \frac{8\pi^3 e^2 v}{3e g_i h\nu'} |M_{if}|^2
\]  \hspace{1cm} (21)

where \( h\nu' \) is the photon energy past the ionization threshold and \( g_i \) is the number of degenerate sublevels at the energy of the initial state and

\[
|M_{if}|^2 = \sum_i \sum_f | \int \psi_i^* \sum_{\mu} r_{\mu i} \psi_f |^2
\]  \hspace{1cm} (22)

where \( M_{if} \) is the matrix element of the interacting light with a molecule with continuous wave functions.  

Cross sections are of importance because they determine product concentration and give branching ratios of a certain product mass and that mass’ isomers. The cross sections are expressed in units of \( \text{cm}^2 \) or in megabarns \( \text{(Mb} = 10^{-18} \text{ cm}^2 \text{)} \).
The ion signal ($S_E$) in the experiments presented in this thesis at a specific photon energy (E) is related to the cross section ($\sigma_E$) by:

$$S_E = k\sigma_E\delta_p C$$

(23)

where $k$ is the instrument constant, $C$ is the concentration of the molecule, and $\delta$ is the mass discrimination factor, which has been determined experimentally to be equal to $(mass \ of \ species)^{0.67}$. Here the ion signal correlates to the concentration of the species.

The ion signal of the product ($S_p$) must be converted to its photoionization cross section ($\sigma_T$) through the use of the following equation adapted from Cool et al$^{17}$ and Welz et al$^{27}$:

$$\sigma_T(E) = \frac{\sigma_R(E)S_p(E)m_p^{0.67}C_R}{S_R(E)m_p^{0.67}C_p}$$

(24)

where $C_p$ and $C_R$ are the concentrations of the product and calibrant, respectively, and $m_R$ and $m_p$ are the masses of calibrant and product, respectively, and $S_R$ is the reference signal of the calibrant, and $\sigma_R$ is the calibrant cross section. When a reactant replaces the calibrant in equation 25, information on the concentration of the product relative to the reactant is obtained. The ratio of the two provides a branching fraction (BF).

The BF is calculated by using the ion signals of the product (P) and the reactant (R) at a specific photon energy (E). The photon energy is chosen at a constant ion signal of the spectrum to minimize error.$^{17,27-28}$

$$BF_p = \frac{C_p}{C_R} = \frac{S_{p,E}}{\sigma_{p,E}\delta_p} = \frac{S_{p,E}\sigma_{R,E}\delta_R}{S_{R,E}\sigma_{p,E}\delta_p} \left(\frac{m_R}{m_p}\right)^{0.67} = \left(\frac{S_{p,R}}{S_{R,p}}\right)MDF$$

(25)

One potential problem in this scenario is the appearance of more than one isomer in a photoionization spectrum. The total cross section of the observed signal can be found from the sum of individual isomer cross sections.$^{27}$
\[ \sigma_T = \sum_{i=1}^{n} X_i \sigma_i \]  

(26)

and

\[ \sum_{i=1}^{n} X_i = 1 \]  

(27)

where \( X_i \) and \( \sigma_i \) are the mole fraction and photoionization cross section, respectively, of the isomer. This will help in analyzing combustion data since products may have the same mass.

PIMS is of great importance when it comes to the study of small hydrocarbon combustion. When discussing small hydrocarbons, their appearance energy for dissociative ionization are within 1-2 eV of the adiabatic ionization energy of the parent so mass-resolved ion detection is used to tell the difference between a partial contribution to the total cross section made by the ion.\(^{10}\) Ion fragments with same mass-to-charge ratio as a species may interfere with the detection of a parent ion. In this case, if the unwanted dissociative ionization fragment’s photoionization cross section is known then it is appended to the experimental cross section within the IGOR\(^{20}\) program. The unwanted structure’s cross section is subsequently subtracted from the experiential cross section and the remaining cross section is used for identification.

2.8 Lasers

The acronym LASER stands for “Light Amplification by Stimulated Emission.” Lasers produce a focused source of intense heat, which does not lose power as it moves away from the source.

Lasers are different from ordinary light sources. Some uses for lasers are to characterize matter by measuring properties and composition of compounds and to initiate/control chemical changes in a system. They have unique properties that will be discussed below:

(1) Lasers are brighter than normal light sources providing a better signal-to-noise ratio. The brightness (related to the output power and beam quality of the laser) also allows lasers to
probe and record small concentrations of reaction intermediates and photodissociation fragments.\(^3\)

(2) Being highly monochromatic (consisting of one specific wavelength or color of light) provides the basis for high resolution spectroscopy. The interaction between the radiation and molecules is very selective, which helps in photochemical processes because there is sufficient control.\(^3\)

(3) Being uniformly polarized means that all photons share the same polarization\(^3\)

(4) Lasers can probe molecules on the femtosecond \((10^{15}s)\) time scale. This allows one to observe fast reactions in real time.

(5) Coherence is the interaction of two electromagnetic waves that have slightly different frequencies, and all photons remain in the same phase.\(^3\) This arises from the stimulated emission process, which provides amplification.

(6) Being collimated means that all photons are parallel and little light diverges in contrast to a point source\(^3\)

A laser consists of three parts:\(^3\)

(1) A source of energy, usually a pump: This can be an electric current, flash lamp, light from another laser, or a chemical reaction. Pumping is necessary for laser action and is a process by which a species is excited. During pumping, several of the higher electronic and vibrational energy levels are populated by the active species.

(2) A lasing medium (gain medium) usually a solid, liquid, or gas: The gain medium will determine which type of pump is needed and the wavelength of resulting light.

(3) An optical resonator: This consists of two parallel mirrors, a reflective mirror and a partially reflective mirror.
When energy is applied to an atom the energy is absorbed and an electron moves from a low energy orbital (the lowest energy state is called the ground state, \( E_1 \)) close to the nucleus to a higher energy orbital (termed an excited state, \( E_2 \)) away from the nucleus. When an electron falls back to ground state it releases the difference in energy as a photon, which causes light. This process is termed spontaneous emission (Figure 18). As mentioned before, a photon has frequency, \( \nu \), energy, \( h\nu \), (equal to \( E_2 - E_1 \)), and has random phase and direction. The wavelength of light produced is found by using the energy released when the electron moves from a higher state to a lower one.

Figure 18. The movement of an electron from ground state to excited state that results in emission.31

If a photon hits an excited electron in a gain medium, a second photon is released that is identical to the first photon in direction, phase (coherence), polarization, and energy. This process is termed stimulated emission.31 As more photons stimulate the emission of other photons a cascade effect occurs, shown in Figure 19, and results in amplification (optical gain), which produces light.
Figure 19. The cascade effect of photons that results in stimulated emission.\textsuperscript{31}

During this cascade, some photons may differ in direction, but as stimulated emission progresses the photons are reflected between two mirrors and they release light along the same axis. When a small number of photons escape the gain medium, laser light is produced and aimed at the target through a delivery system.\textsuperscript{31} Since the cascade is caused by a common stimulus, the emitted photons are in step with one another so they have a definite phase in relation to each other. This coherence is described in terms of spatial coherence and temporal coherence, which are important in producing interference. Spatial coherence is the degree to which a beam of light appears to have originated from a single source and is inversely proportional to the diameter of the
source. Temporal coherence is the extent to which all the photons in a light beam are of the same frequency or wavelength.

To create a sustained laser most of the atoms or molecules must remain in the excited state. The probability for an atom or molecule to absorb a photon is the same as an excited atom or molecule emitting a photon through stimulated emission. The probability of stimulated emission is low since not all atoms or molecules are usually in the excited state. If there are more atoms or molecules in the upper level than in the lower level the system is not at equilibrium. According to the Boltzmann principle, the relative population of two energy levels is:

\[ \frac{N_2}{N_1} = \exp \left( -\frac{E_2 - E_1}{kT} \right) \]  

where \( N_2 \) and \( N_1 \) are the populations of the upper and lower energy states, respectively, \( T \) is the equilibrium temperature, and \( k \) is the Boltzmann’s constant.

Substituting \( hv \) for \( E_2 - E_1 \) gives:

\[ \Delta N = N_1 - N_2 = \left( 1 - e^{\frac{hv}{kT}} \right) N_1 \]  

This shows that for a normal population of atoms or molecules, most will be in a lower energy level than an upper one. To create a system not at equilibrium, energy must be added via a process known as pumping; this will raise enough atoms or molecules to the upper level. This is called population inversion and is given by \( \Delta N = N_1 - N_2 \). Light is amplified when population inversion is positive.

Atomic and molecular energy states contain many energy levels, each one with a unique time for decay. Figure 20 represents a four-level energy diagram that applies to certain lasers.
Figure 20. Energy diagram representative of 4-level lasers.³³

Considering Figure 20, an electron is pumped (excited) to the upper level, E₄, and decays to E₃ followed by E₂, and then to the ground state E₁. Assume in a large population of atoms or molecules at equilibrium with a pumping process, that the decay from E₃ to E₂ is longer than the decay from E₂ to E₁. A population inversion would occur between E₃ and E₂ and a photon entering the population would be amplified coherently.³³ This population inversion is capable through the continuous input of energy from the pump, which excites electrons and gives the ability to amplify a signal via stimulated emission.³¹ The actual gain is small and most of the atoms or molecules in the population emit spontaneously.
To create a laser, the majority of the atoms or molecules in the population need to contribute to the coherent output.\textsuperscript{33} This is solved by a resonator; a system of mirrors that reflect off-axis photons out of the system and on-axis photons back into the excited population where they can be further amplified. Considering Figure 21, the lasing medium is continuously pumped to create a population inversion. Excited atoms or molecules start to decay and spontaneously emit photons; some along the axis of the lasing medium and most are directed out the sides. Those along the axis can stimulate other atoms or molecules in their path so that they emit photons. Photons traveling parallel to the axis are reflected back into the lasing medium and can possibly stimulate more excited atoms or molecules.\textsuperscript{33} This creates a laser. To remove the light from the system, one of the mirrors is partially reflective and allows a small percentage of photons to escape and create light.

Knowing that stimulated emission increases with the number of excited state atoms or molecules and incident photons, there needs to be a method to ensure emission is sustained. This is done by either raising the number of excited state atoms or molecules or by raising the number

**Figure 21.** Basic diagram of a generic laser.\textsuperscript{33}
of incident photons. To achieve a temporal concentration, stimulated emission must be triggered when there is a large number of atoms or molecules in the upper level, known as Q-switching.\textsuperscript{32} To achieve the second method, the photons in the optical cavity are condensed into a pulse that will bounce back and forth between the mirrors, known as mode-locking.

In Q-switching, many atoms or molecules must remain in an upper level, so the decay to a lower level must be limited. An attenuator is placed in the cavity to stop light from traveling back and forth, so the only decay is due to spontaneous emission.\textsuperscript{32} When the pumping system supplies more atoms or molecules per second than lost by spontaneous emission, the population in the upper level increases.

Mode-locking is very different from Q-switching. In mode-locking, the laser oscillator reaches a steady state and the oscillation cavity is kept clear, but is prevented from filling with photons.\textsuperscript{32} Only a “packet” of photons is allowed to fill the cavity at a time. This pulse is shorter than the length of the cavity. This is done by using a rapid light modulator that can “chop” the light in the cavity into periods of the same length of the cavity. Photons allowed to pass through the modulator in its on-state will be amplified and will always find the modulator in this state after each roundtrip of the cavity while other photons in the cavity may be lost.\textsuperscript{31}

### 2.8.1 Types of Lasers

Although there are different classes of lasers, this paper will focus on two types of gas lasers.
A common design of a gas laser, as seen in Figure 22, consists of a gas held within a tube with mirrors at each end. One mirror is reflecting and the other transmits light from the output beam. These lasers are excited by passing an electric current through the gas. The discharge is longitudinal, Figure 22, but some may be transversal. Electrons in the discharge transfer their energy to the laser gas to create a population inversion and the cascade of stimulated emission produces light.

The Helium-Neon laser (He-Ne) is widely used due to its coherence and visible beam. Electrons pass through the 5:1 helium-neon gas and excite both to high energy states, yet the helium atoms gain more energy. The energy levels in the He-Ne laser are depicted in Figure 23 while the He-Ne laser schematic is shown in Figure 24. When the species collide, energy is passed from the helium atoms to neon atoms, which are then excited to a higher energy level where they are metastable (neon atoms have a larger lifetime), which produces a population inversion.
Figure 23. Energy levels and transitions in He-Ne laser.\textsuperscript{35} Neon atoms eventually fall to a lower energy level until they reach ground state. If helium atoms transfer energy to neon atoms during their fall, neon atoms may be raised up to an upper energy level.

Figure 24. Schematic design of a typical He-Ne laser.\textsuperscript{35}
Discharge from the He-Ne laser passes between electrodes at opposites ends of the tube and is concentrated in a narrow passage, a bore. This concentration raises the laser efficiency and controls beam quality. There are two mirrors in the design: the rear cavity is totally reflective and output mirror partially transmits light. The mirrors must have low losses to make up for the low gain of the laser. The laser is focused in the cavity through the concave quality of the mirrors.

Another type of gas laser available is an excimer laser. Light is emitted by short-lived molecules that are made up of a rare gas atom (argon, krypton, xenon) and one halogen. The energy levels of an excimer laser are depicted in Figure 25. These lasers create high power ultraviolet pulses and are becoming widely popular even though they are complex and expensive. These “excimers” are diatomic molecules bound together in an electronically excited state.

**Figure 25.** Energy level of a typical excimer laser, where R is the rare gas an H is the halogen.

The laser is excited by passing a short and intense electrical pulse through an active medium, such as a rare gas halide, that is not involved in the reaction. The rare gas and the
halogen make up a small portion of the entire gas the laser is excited through. The resulting discharge splits the halogen molecules freeing excited halogens, which are electronically excited and will react with the rare gas to produce an excited dimer (“excimer”). This produces population inversion and as the molecules fall to ground state and separate, ultraviolet radiation is emitted.

The dimer, in this method, is bound only in the excited state and falls apart as it transition back to the ground state. This process, however, quickly empties the lower laser level, which sustains a population inversion. The region in the excited state with a “dip” (Figure 25) shows where the rare gas and halogen have a minimum energy and binds the two to form a dimer. The excited molecule can occupy various excited vibrational levels. One must remember that because halogens are used, the tube must be made up of halogen resistant materials. These tubes are sealed and used until laser power decreases and the gas must be replaced.

2.9 Franck-Condon Principle

To discuss the Franck-Condon principle, one must first understand the Born-Oppenheimer (BO) approximation. An electron’s mass is much lighter than that of a proton or neutron. The nuclei travel rapidly, but an electron travels at a much faster rate (about 1,850 times faster). Because of this, when electronic distributions are studied from a nuclei’s perspective the nucleus seems static and maintains the same position and velocity before the transition takes place; nuclei rearrangement occurs after an electronic transition. Nuclei move in response to electronic transitions for a specific reason; when a molecule absorbs a photon, an electron travels from its HOMO to its excited MO state. Due to this excitation, the bonds of a molecule are changed and the nuclei must rearrange according to the new electronic configuration and results in a molecular vibration. Because of this, electronic transitions cannot occur without vibrational dynamics.
Since the transition between molecular quantum states is caused by a photon, the transition dipole matrix is non-zero (discussed later).

Since nuclei rearrangement occurs after an electronic transition, it makes it possible to visualize molecular energy changes as potential energy curves (PEC), (Figure 26). Figure 26 depicts two potential energy curves.\(^{11}\) When a transition contains electronic and vibrational transitions, it is called a vibronic transition and the bands are referred to as vibronic bands.

**Figure 26.** Two potential energy curves depicting the three types of transitions.\(^{11}\)

In Figure 26, the vertical arrows show vertical transitions that occur when a molecule is excited by a photon and undergoes vertical transitions to its cationic state. This is done according to the Franck-Condon principle and Born-Oppenheimer approximation.\(^{11}\) Figure 26 also depicts two other types of transitions: adiabatic and dissociation. The adiabatic transition is the electronic
transition from the neutral vibronic ground state to the vibronic ground state of the cation. The energy difference between the two states is known as the “adiabatic ionization energy (AIE). The dissociative transition occurs when a cationic molecule in the excited vibronic is unbound. When a molecule receives more energy (AIE plus the cation dissociative energy), the molecule dissociatively ionizes (fragmentation), creating cation fragments. The appearance energy of a specific fragment is the energy at which it appears. This is found through the sum of the AIE of the molecule and the cation dissociation energy, when there is no dissociation barrier.

For a diatomic molecule, the PEC is simple; a plot of energy versus bond length. For a polyatomic molecule, the PEC results as a potential energy surface (PES) diagram. The energy is described as “potential” because if the molecule is released from a non-equilibrium state it will attempt to return to an equilibrium state by vibrating around the equilibrium point. The energy rises as the nucleus rearranges and corresponds to the potential energy gained by the molecule.

When James Franck and R. Condon applied the Born-Oppenheimer approximation to transitions between electronic energy levels, the Franck-Condon principle resulted. The principle explains the spectral intensity distribution for vibrational transitions between electronic states. In summary, the principle states that electronic transitions occur faster than nuclei can respond; the electronic transitions occur faster than the vibrational motion.

The Franck-Condon factor, itself, shows the probability of these electronic transitions and results in spectral line intensity. The extent of overlap between the vibrational wave functions and electronic states gives the probability of electronic transitions. For a strong electronic transition (large absorption cross section) there will be a large overlap between vibrational states in initial and final electronic states.

The spectral line intensity (transition probability) is shown as:
\[ I_{em,v'v''} = \frac{64}{3} \pi^4 c N_{v'v''} R_e^2 \left[ \int \psi_{v'} \psi_{v''} dr \right]^2 \]  

(30)

where \( \psi_{v'} \) and \( \psi_{v''} \) are wave functions of upper and lower electronic states, respectively, \( dr \) is the volume element, \( R_e \) is the average electronic transition moment, \( v \) is the frequency of light emitted in the transition, \( N_v \) is the population of light (following equations 28 and 29), and \( c \) is the speed of light (3.0 x 10⁸ m/s). The transition probability is proportional to squared term in the equation. This overlap is referred to as the Franck-Condon factor.³⁶

The Franck-Condon principle discussed mathematically is more complicated than discussed qualitatively. The transition dipole matrix must be calculated by using:\³⁸

\[ \mu_{final,initial} = < \psi_{total,final} | \mu | \psi_{total,initial} > \]  

(31)

The total wave function (\( \Psi \)) is a product of four motions:

\[ \psi_{total} = \psi_{translational} * \psi_{rotational} * \psi_{vibrational} * \psi_{electronic} \]  

(32)

where \( \psi_{electronic} \) follows the Born-Oppenheimer approximation, so the nucleus remains “static” during the electronic transition.

To simplify Franck-Condon Factors only the electronic and vibrational wave functions are considered because they relate to the degrees of freedom with the largest energy.³⁹ The equation for the Franck-Condon principle now becomes:\³⁸

\[ \psi_{total,final} | \mu | \psi_{total,initial} \]  

(33)

Only considering electronic and vibrational wave functions:

\[ \psi_{electronic,final} * \psi_{vibrational,final} | \mu | \psi_{electronic,initial} * \psi_{vibrational,initial} \]  

(34)

where \( \mu \) is the total molecular dipole, which includes charges and positions of electrons and nuclei:\³⁹-⁴⁰

\[ \mu = -e \sum_i r_i + e \sum_j Z_j R_j \]  

(35)
where \( r_i \) is the electronic coordinate of the species, \( Z_j \) is the nuclear charge of the species, and \( R_j \) is the nuclear coordinate of the species.

Combining equations 34 and 35 gives:

\[
\psi_{\text{electronic, final}} * \psi_{\text{vibrational, final}} \left| -e \sum_i r_i + e \sum_j Z_j R_j \right| \psi_{\text{electronic, initial}} * \\
\psi_{\text{vibrational, initial}}
\]

simplifying above:\textsuperscript{38,40}

\[
-e < \psi_{\text{electronic, final}} \left| \sum_i r_i \right| \psi_{\text{electronic, initial}} > < \psi_{\text{vibrational, final}} * \psi_{\text{vibrational, initial}}
\]

\[
+ e \sum_j Z_j < \psi_{\text{electronic, final}} * \psi_{\text{electronic, initial}} > < \psi_{\text{vibrational, final}} \left| \sum_j R_j \right| \psi_{\text{vibrational, initial}}>
\]

Since the nuclei move slower than electrons (Born-Oppenheimer), \( R_j \) wave function for vibrations factors out from the first term.

The second term is zero since the overlap between different electronic states is zero due to orthogonality.\textsuperscript{38,39}

Equation 38 becomes:

\[
-e < \psi_{\text{electronic, final}} \left| \sum_i r_i \right| \psi_{\text{electronic, initial}} > * S_{\text{final, initial}}
\]

where\textsuperscript{39}

\[
S_{\text{final, initial}} = < \psi_{\text{vibrational, final}} * \psi_{\text{vibrational, initial}} > \text{Franck – Condon principle}
\]

2.10 Photoionization Spectra

Photoionization (PI) spectra are used to identify oxidation reactions products in the gas phase. Each molecule is unique and has its own ionization energy, geometry, and vibrational modes (Franck-Condon factors) and should result in an exclusive PI spectrum. According to the Franck-Condon principle the better overlap between the neutral and cationic vibronic states results in higher intensity of the electronic transition and steeper onset slope of the PI spectrum. Therefore, the photoionization signal of a specific mass can be assigned based on the shape of the
photoionization spectrum and mass-to-charge ratio. This can be applied to isomers of a specific molecule since they have distinctive ionization energies.

A PI spectrum can be determined for each mass by plotting ion intensity versus the corresponding photon energy. The ion signal of a specific mass peak will rise from the baseline as ionization occurs. The onset of the PI spectrum corresponds to the ionization energy of the species. Knowing the ion signal at a specific photon energy can relate to a photoionization cross section (discussed earlier).

2.10 Computational Tools

The ab initio prediction of molecular structure and energy is of importance in molecular electronic calculations and has led to the development of methods for those calculations with chemical accuracy. Ab initio calculations are those without experimental data and rely on quantum mechanical means. A computational method of interest is CBS-QB3, which is a composite method combining ab initio and density functional calculations. Density-functional theory (DFT) calculations provide reliable molecular parameters. The CBS-QB3 composite model is used to optimize bond lengths and angles, harmonic vibrational frequencies, and force constants of a particular molecule. This method is chosen because it provides accurate energy calculations at a low computational cost.

The Schrödinger equation is key in the calculation of electronic structure and helps describe particle behavior.

\[ \hat{H} \psi(x, y, z) = E \psi(x, y, z) \]  

where \( \hat{H} \) is the Hamiltonian operator (kinetic and potential energy operators), \( \Psi \) is the multi-electron wave function for the system, and \( E \) is the total electronic energy. Here, the Hamiltonian
operates on the wave function and generates energy (eigenvalue) that is multiplied by the wave function (eigenfunction).

2.10.1 CBS-QB3

The CBS-QB3\(^{43-44, 54}\) method is used extensively in our research to provide accurate chemical predictions for thermochemical parameters and uses different levels of theory like those previously discussed. This complete basis set (CBS) model uses a series of calculations based on a specific molecular geometry and includes corrections for basis set truncation errors as mentioned in the coupled cluster method.\(^{45}\) Extrapolation at the CBS is worthwhile because smaller basis sets are used to find the total electronic energy and computation time is decreased.

The CBS-QB3 model uses a coupled cluster calculation with triple excitations for the highest level of calculation, unlike the CBS-APNO model, which uses quadratic configuration interaction.\(^{54}\) Models need geometric accuracy and energetics must converge in basis set size and degree of correlation, yet increasing the two adds to the computational cost of the calculation.\(^{54}\)

The structure and energy of the molecule is obtained at the HF or B3LYP, but smaller corrections to both can be found with less accuracy than at lower levels of theory.\(^{43-44, 49}\) The CBS-QB3 model does not correct the initial B3LYP structure, therefore it uses a larger basis set for the structure and first-order HF calculation, a medium sized basis set for the second order correlation correction, and a small basis set for higher order correlation corrections.\(^{54}\)

There are five steps in calculations of the CBS-QB3 model. The first is geometry optimization of the structure at the B3LYP level with CBSB7 basis set, which includes 6-311G(2d, d, p).\(^{43-44}\) The basis set 6-311G(2d, d, p) gives another d polarization function for second row elements.\(^{49}\) The second step is the frequency calculation for thermal corrections, zero-point vibrational energy (ZPE), and entropic information. The last three steps are single point energy
calculations (SPC’s) at the Coupled Cluster Singles and Doubles including Triples (CCSD(T)/6-31+G(d’)), MP4SDQ/CBSB4, and MP4 levels.\textsuperscript{48,55} The CCSD(T) adds singles, doubles, and triples to the coupled cluster method to enhance inclusivity. MP4, fourth-order Møller-Plesset theory, introduces correlation to geometry and frequency calculations, but MP4 frequencies are expensive so MP4SDA/CBSB4 level is implemented to correct this.\textsuperscript{43-44,54} Finally, extrapolation of the total electronic energy to the Complete Basis Set (infinite limit) finds the final energies.\textsuperscript{54} Overall, the CBS-QB3 model offers high accuracy at a relatively low computational cost.

As mentioned before, CBS-QB3 calculations can be used to analyze gas phase reactions. It can help when literature values of ionization energies and photoionization cross sections are not known. CBS-QB3 can perform a Franck-Condon simulation to provide a photoionization spectrum. Recalling the process of photoionization, the adiabatic ionization energy is found by the difference between the zero-point energy (ZPE) corrected total electronic energies of the cationic (i) molecule and neutral molecule (n):\textsuperscript{49}

\begin{equation}
AIE = ZPE_{i}^{CBS-QB3} - ZPE_{n}^{CBS-QB3}
\end{equation}

The corrected electronic energy can be used to find other thermodynamic quantities, such as enthalpy.\textsuperscript{43-44}

\begin{equation}
\Delta H_{rxn} = \sum ZPE_{products}^{CBS-QB3} - \sum ZPE_{reactants}^{CBS-QB3}
\end{equation}

Above, based on Hess’ law: summation of formation of products minus reactants gives reaction enthalpy.

Another application uses optimized geometries found through CBS-QB3 calculations to predict photoionization spectra in the program \textit{Gaussian}.\textsuperscript{56}
2.10.2 Density Functional Theory

Density functional theory (DFT) uses the Kohn-Sham theorem; though other explanations for DFT are available. The theory calculates varying properties of a molecule based on the molecular electron density (a physical characteristic). The theory uses a simple reference system: independent non-interacting electrons in a common one-body potential \( V_{KS} \) that yields the same density as a “real” interacting system. This is used to calculate the density function exchange correlation \( E_{XC} \). A set of reference orbitals \( \Psi_i \) satisfies the independent-particle Schrödinger equation:

\[
-\frac{1}{2} \nabla^2 \psi_i + V_{KS} \psi_i = e_i \psi_i
\]  

where \( \Psi_i \), the non-interacting density, is:

\[
\rho = \sum_i^N |\psi_i|^2 
\]  

The total electronic energy of the real interacting system is the following:

\[
E_{Total} = T_0 + \int \rho V_{nuc} d^3r + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} d^3r_1 d^3r_2 + E_{XC}
\]  

where \( T_0 \) is the kinetic energy of the non-interacting reference system, the second term is the nuclear interaction energy, the third term is the classical Coulomb self-energy.

2.10.3 Coupled Cluster Method

As mentioned before, the Kohn-Sham theory states that electrons do not interact with each other, but as seen in equation 45 the distance between electrons and the nucleus is considered. This limits the equation that uses Kohn-Sham theory since electrons do not interact. To fix this deficiency, the perturbation method, Møller-Plesset (MP) theory, is implemented. At the Hartree-Fock (HF) level, bond dissociation energies are poorly described if there is no correction in the electron energy correlation. This correction is handled by the perturbation method of MP theory and is useful up to the fourth level (MP4). MP expresses \( \hat{H} \) as the sum of an unperturbed
Hamiltonian that operates on HF wave functions for the electrons in the molecule.\textsuperscript{51} To further correct the electron correlation, the coupled cluster (CC) method applies \textit{Slater determinants} (anti-symmetric wave functions that can be excited orbitals).\textsuperscript{50} Determinants replace an occupied molecular orbital with unoccupied orbitals and leads to singly, doubly, and so on, excitation:\textsuperscript{50}

\[
\psi_{cc} = e^\Psi_0
\]  \hspace{1cm} (46)

Coupled cluster correction where wave function “cc” is the ground state wave function, \( \phi \) is the normalized HF wave function and\textsuperscript{50}

\[
e^T = 1 + T + \frac{1}{2} T^2 + \frac{1}{6} T^3 + \cdots = \sum_{k=0}^{\infty} \frac{1}{k} T^k
\]  \hspace{1cm} (47)

where

\[
T = T_1 + T_2 + T_3 + \cdots T_n
\]  \hspace{1cm} (48)

in the equation above, \( T \) represents excitation operators that can promote electrons into spin orbitals.\textsuperscript{50,18}

Including all \( T \) operators applies to smaller systems and to make it applicable to larger systems \( T \) must be truncated. When \( T_2 \) is the only operator coupled cluster doubles is implemented and is the lowest approximation in coupled cluster methods. When coupled cluster singles, doubles, and perturbative triples energy are included the approximation and reliability increases but comes with a higher computational cost.\textsuperscript{52}

\textbf{2.10.4 B3LYP}

A specific DFT method is B3LYP\textsuperscript{46-47} (Becke 3-parameter hybrid functional level) and is used in the CBS-QB3\textsuperscript{45-47} model, discussed later. \textit{LYP} is a functional of Lee, Yang, and Par.\textsuperscript{43-44} A \textit{functional} is a function of a function and the energy of a molecule is a functional of the electron density. This is a \textit{gradient-corrected} functional, which considers the non-uniformity of electron density and their gradients.\textsuperscript{43-45} Where the electron density is a function of three variables \((x, y, z)\)
position of the electrons, but is independent of the number of electrons, unlike wave-functions.\(^{43-44}\)

B3LYP was introduced in 1993 by Axel Becke to improve results from the gradient-corrected functional. \(B3LYP\), specifically, is a \(\text{hybrid functional}\), which defines the exchange functional as a linear combination of HF, local, and gradient corrected exchange terms (\(E_x^{\text{HF}}\)). This \(\text{hybrid}\) method tries to incorporate \(\text{ab initio}\) methods (like HF) with improvements to DFT and is the top choice for reaction calculations.\(^{43-44}\) This method gives accurate vibrational frequencies.

### 2.10.5 Basis Sets

A \(\text{basis set}\) is a set of wave functions that describes the best possible orbitals. The components of basis sets are used to solve the Schrödinger equation using various approximations. The basis set used for CBS-QB3 in this investigation is an all-electron triplet valence. The basis set \(6-311+G^*\) it includes a set of Gaussian type orbitals shown in terms of Cartesian coordinates:\(^{46-49}\)

\[
X\xi l_x l_y l_z (x, y, z) = N x^{l_x} y^{l_y} z^{l_z} e^{-\xi r^2}
\]  
(49)

where \(N\) is a normalization constant, \(x, y, z\) are Cartesian coordinates, and the sum of \(l_x, l_y, l_z\) determines the orbital (\(s, p, d, f\))

The “6-311+G*” set is defined as follows:\(^{53}\)

(1) 6: there are six types of Gaussian orbitals (\(X(PGTO)\)) used to find the core atomic orbitals

(2) 3: inner valence atomic orbitals with three contracted PGTO (\(X(CTGO)\))

\[
X(CTGO) = \sum_k a_i X_i(PGTO)
\]  
(50)

where “\(a\)” is a contraction coefficient and \(k\) is the degree contraction

(3) 1: only one Gaussian function is used for outer valence component

(4) +: accounts for electron density distance from nuclei, lone pairs…
(5) *: set of polarization functions of d and p types

For polarization, one mixes one orbital with another to bend the shape of the first orbital to account for uneven shape\textsuperscript{53}
2.11 References


Chapter 3: Experimentation

This research focuses on experiments conducted at the Advanced Light Source (ALS) in the Lawrence Berkeley National Laboratory. The 3rd generation synchrotron provides the ionizing energy used for detection in the multiplexed mass spectrometer. The ALS produces high brightness \(10^{21}\) photons cm\(^{-2}\) s\(^{-1}\), tunable (7.2-25.4 eV at the Chemical Dynamics Beamline) vacuum ultraviolet (VUV) radiation with medium resolution \(E/\Delta E \sim 1000\); this serves as the photoionization source for the systems under study.\(^1\) This chapter discusses the apparatus used at the Chemical Dynamics beamline of the ALS.

3.1 Sample Preparation

The compounds used in the experiments first need to be purified through a process called freeze-pump-thaw (Figure 1) to remove impurities within the compound.

![Figure 1. Freeze-pump-thaw set-up.](image)

In general, the compound studied must have a pressure greater than 5 Torr so it can be measured by the pressure gauges. In the current set-up, two pressure gauges are used, one for high
pressures up to 10,000 Torr and one for low pressures from 1-10 Torr. The compound is placed into a glass bubbler that is attached to a steel vacuum line, connected to an empty steel gas cylinder (tank) used for sample preparation. The compound should make up about 1% of the total pressure in the tank. The liquid compound in the bubbler is frozen using liquid nitrogen and while it is thawing gas impurities are pumped out of the sample by opening the steel vacuum line. A pressure gauge reader monitors the pressure within the bubbler. The steel line is connected to MKS transducers and Baratron® digital pressure readers. Two baratron digital pressure readers are used. Each is connected to a MKS transducer of different scales: a sensitive low pressure (1-10 Torr) MKS transducer with high accuracy (~ 0.05 % from reading) and a high pressure (10,000 Torr) MKS transducer. Once thawed, the cycle is repeated two more times. The vapor of the pure compound then flows into the steel vacuumed gas cylinder and equilibrates. Helium flows into the cylinder until the sample composes about 1% of the total pressure within the cylinder. The total pressure in the cylinder must not be too low, otherwise the sample concentration in the cylinder will not be sufficient to carry out a proper experiment (the sample should last for the whole duration of the experiment). The gas percent purity is calculated by:

\[
\text{\%purity}_{\text{gas}} = \frac{P_{\text{gas}}}{P_{\text{tot}}} \times 100
\]

where \(P_{\text{gas}}\) is the partial pressure of the sample and \(P_{\text{tot}}\) is the total pressure in the steel gas cylinder.

3.2 Experimental Apparatus

A slow-flow reaction cell, an excimer laser, an ionization chamber, a time-of-flight mass spectrometer, and microchannel plates ion detector make up the experimental apparatus at the ALS. Components are under vacuum maintained by vacuum pumps (Figure 2).
3.3 Initial Setup

Before the experiment begins, the apparatus must be aligned with the synchrotron radiation from the beamline. Then, the desired energy used for the experiment is selected by the monochromator and the photolysis laser is aligned to ensure that it goes through the slow flow reactor. A polynomial is then generated to assure that the energy from the undulators matches the energy delivered by the monochromator to the ionization region of the apparatus. After this is complete, one needs to check to make sure that a time-dependent signal is measured. The energy resolution of is also measured by scanning an argon ionization resonance transition in the possible energy range of 7.4-24.6 eV. The higher harmonics radiation larger than the ionization energy of argon (15.76 eV) is removed. Finally, the mass calibration is achieved by determining the alpha
and beta values, which relate the mass-to-charge ratio to the time-of-flight. Knowing the alpha and beta values allows peaks from the time-of-flight spectrum to be correlated to the correct mass values. Calibration is completed through the empirical determination of the times-of-flight of known masses; in this experiment, a calgas mixture (ethene, propene, and butene) is used as the reference. The mass calibration equation follows:\(^2\)

\[
\frac{m}{z} = \alpha t^2 + \beta \tag{2}
\]

where \(\alpha\) is the constant of proportionality between an ion’s arrival time and its mass-to-charge ratio and \(\beta\) is the difference in time between ion extraction and the data acquisition start.\(^2\) From this, any experimental time-of-flight can be converted to a mass-to-charge ratio, which will identify the correct mass of ions.

Since this experiment uses calgas for the mass calibration it follows a sample equation:

\[
t = \alpha + \beta \sqrt{m/z} \tag{3}
\]

where \(t\) represents the time-of-flight of an ion, which is linearly related to the square root to the mass-to-charge ratio of a species, \(\alpha\) is the slope, and the \(\beta\) corresponds to the y-intercept.

### 3.4 Slow Flow Tube

The flow rates of the reactant gases are setup in LabView (flows range from 10 to 200 sccm) and controlled by calibrated mass flow controllers. The gas sample from the steel cylinder and the reactant gases (in our case Cl\(_2\) and O\(_2\)) flow into the 62 cm long quartz reaction tube with an outer diameter of 1.27 cm and inner diameter of 1.05 cm.\(^1\) Reactions carried out at room temperature require the pressure within the reaction chamber to be 4 Torr, and is monitored by a capacitive manometer and controlled by gas removal from the reactor.\(^1\) The pressure in the reaction chamber is kept low throughout these experiments to assure a uniform initial radical density; gaseous diffusion smooths any inhomomogenous radicals on a rather short time scale. Gas removal
from the reactor is obtained through a closed-loop feedback throttle valve connected to a Roots pump. The rest of the reaction chamber is evacuated by a 3200 Ls$^{-1}$ oil-free turbomolecular pump.

The temperature of the reaction chamber ranges anywhere from room temperature to 1050 K. Increase in temperature is achieved by resistive heating using 18 µm thick nichrome heating tape wrapped around the length of the reaction tube. The heating tape maintains temperature uniformity because it is insulated with square weave yttria-stabilized zirconia cloth encapsulated by a gold plated copper sheath and reduces the transfer of heat to the vacuum chamber. As the temperature increases so should the pressure of the reaction chamber, due to manipulation of the gas flow rate and concentration of the molecules (cm$^{-3}$). The total gas flow rate must maintain a relatively constant flow rate throughout the experiment because it is related to the total flow and pressure. The flow rate follows the equation:

$$v \left( \frac{m}{s} \right) = 0.127 \left( \frac{f_{low\text{scm}}}{\pi R^2 (cm^2) p(\text{Torr})} \right)$$

(4)

where R is the reaction tube radius and p is the pressure in the reaction tube.

The concentration of molecules must also be calculated from the flow rate to find the concentration of the starting molecules. Found using:

$$Concentration = (3.24 \times 10^{16}) (P) \left( \frac{F_R}{F_T} \right) \left( \frac{T}{298.15} \right)^{-1}$$

(5)

where P is the pressure maintained inside the chemical reactor, $F_R$ is the flow rate of the reactant (assuming 100% purity), $F_T$ is the total flow rate of all components, and T is the temperature of the reactor. Since equation 3 assumes that 100% of the reactant gas flows into the reactor, equation 1 must be used to find the actual gas purity.

Photolysis initiates the reaction via an excimer laser (XeF, wavelengths of 193, 248, or 351 nm, depending on the photolytic precursor) creating free radicals, exemplified below.

$$Cl_2 \rightarrow 2Cl \cdot$$

(6)
The radicals move down the length of the reaction tube with a fresh sample of gas used for each laser pulse. About 35 cm downstream from the reaction tube top, a small orifice (400-650 µm) in the side allows gases to flow into the source chamber.\textsuperscript{1,4} Gas flow rate in the reactor tube is constant (~ 400 cm s\textsuperscript{-1}) and gases are skimmed into the vacuumed ionization chamber where continuous tunable VUV synchrotron radiation photoionizes the gaseous species. A 1600 Ls\textsuperscript{-1} turbomolecular pump, backed by oil free scroll pumps, evacuates the photoionization chamber.\textsuperscript{1} The ions are then accelerated, focused, and collimated towards the orthogonal time-of-flight mass spectrometer and detected by multichannel plates (MCP).

### 3.5 Lasers

As mentioned above, the reactions are photolytically initiated by using an excimer laser. Laser is an acronym that stands for \textit{Light Amplification by Stimulated Emission}. In short, when energy is applied to an atom or molecule, energy is absorbed causing an electron to jump from the ground state energy level to a higher energy state. When the electron falls back to ground state, energy is released in the form of a photon. This process is called spontaneous emission.\textsuperscript{5} To achieve stimulated emission, a photon must hit an excited electron in the gain medium. When this occurs, a second photon is released that is identical to the first photon in direction, coherence, polarization, and energy.\textsuperscript{5} As more photons stimulate emission of other photons, the result is a cascade effect and this amplification eventually produces light. Electrons must remain in the excited state so the result of the cascade effect is amplified to a larger degree. This is called population inversion.\textsuperscript{6} In order to achieve this, a pump must provide a continuous input of energy, which excites more electrons.

#### 3.5.1 Excimer Laser

There are several types of lasers. Excimer lasers function based on the presence of excimers, diatomic molecules (dimers) bound in an excited electronic state. In the following
experiment, a mixture of Xe and F\textsubscript{2} molecules is pumped into the laser gas chamber and an electrical discharge ionizes and simultaneously excites Xe atoms (Xe\textsuperscript{*}), which react with F\textsubscript{2} to form (XeF\textsuperscript{*}).

\[ \text{Xe}^* + \text{F}_2 \rightarrow (\text{XeF})^* + \text{F} \]  \hspace{1cm} (7)

These excited dimers must be generated to relax to the unbound ground state and emit a photon with a wavelength of 351 nm. This achieves population inversion and causes photons to be emitted (lasing).\textsuperscript{7} Lasing generates energy that is released between the excited state and ground state in the form of a photon and follows the course of population inversion.

An excimer laser has a lasing medium made up of two atoms and when combined only exist in the excited state and excitation energy is released once the atoms dissociate (figure 3).\textsuperscript{6-7} In these experiments, the lasing medium consists of a mixed gas: 1\% fluorine, xenon, and helium (buffer gas).

![Potential energy diagram](image)

**Figure 3.** Potential energy diagram of the bound excited state and unbound ground state for an excimer laser.\textsuperscript{7}

Following Figure 3, when molecules are in the excited state they are bound and as they fall to the ground state they become unbound. The absence of any dip in the energy level means that
the atoms are not bound to each other and that their energy decreases as the inter-atomic space increases. The well in the excited electronic state demonstrates that the species has a minimum in energy.

The pulse of the excimer laser used in the experiment has a fluence of about 10-60 mJ cm⁻², a pulse width of 20 ns, repetition rate of 4 Hz, and wavelength of 193, 248, or 351 nm. An XeF excimer laser gives off enough radiation (photons) to break Cl₂ to produce Cl atoms that initiate the oxidation reactions.

3.6 Vacuum

The whole apparatus is kept under vacuum using turbomolecular pumps (3200 L s⁻¹). The other pump used are the Roots pump (1600 L s⁻¹), which evacuates the reaction tube and scroll pumps (700 L s⁻¹), which are backing pumps for the turbomolecular pump. The lowest pressure achieved can be about 10⁻⁹ Torr when TMPs are used in tandem. The three pumps are considered clean because the pumped gas does not encounter any oil. This means that there is no risk that oil vapor can enter the chamber that is pumped.

3.6.1 Roots Pumps

Roots pumps’ pumping speed (~250 m³h⁻¹) depends on the inlet pressure and its purpose during these experiments is to evacuate the reaction tube. Higher pressures involve lower speeds to prevent the pump from overheating. The ultimate pressure achieved by a Roots pump is near 20 x 10⁻⁴ Torr and the lowest pressure (10⁻⁴ Torr) requires the backing of a scroll pump. Roots pumps have two symmetrical rotors (0.05-0.25 mm apart) that rotate (speed of 500-3500 rpm) in opposite directions (Figures 4 and 5). The gap between the rotors ensures that they do not come into contact with each other or with the wall, which provides higher rotation speeds.
Figure 4. Roots pump cross section.\textsuperscript{9}

Figure 5. Illustration of Roots type pump.\textsuperscript{10}

The theoretical pumping speed of a Roots pump follows the equation:\textsuperscript{9}

\[ S_{th} = 4 \times n \times V' \]  \hspace{1cm} (8)

where \( n \) is the rotational speed of the rotors and \( V' \) is the volume of gas from the inlet. The net pumping speed, however, is found using the expression:\textsuperscript{9-10}

\[ S_{eff, Roots} = S_{th} \frac{k_0 p_{out}}{k_0 p_{out} + \left( \frac{S_{th}}{S_{back}} \right) - 1} \]  \hspace{1cm} (9)
where \( p \) is the pressure at the inlet and outlet, \( \frac{S_{\text{eff Roots}}}{S_{\text{th}}} \) is the mechanical efficiency, \( p_{\text{back}} \) is the pressure of the backing pump, \( S_{\text{back}} \) is pumping speed of the backing pump, and \( k_0 \) depends on the shape and space between the rotors and is dependent of the gas type and found by:

\[
k_0 = \left( \frac{p_{\text{out}}}{p_{\text{in}}} \right)_{0}
\]

(10)

### 3.6.2 Turbomolecular Pumps (TMP)

The turbomolecular pump (TMP) compresses gas using the momentum transfer from high-speed (24,000-80,000 rpm) rotating blades (stator and rotor) to the gas molecules. The two blades are placed at an angle so that the momentum transfers to gas molecules traveling from the inlet to outlet increasing the number of gas molecules that reach the outlet. Figure 6 represents a single blade used in a TMP while figure 7 shows the cross section of the stator and orbiting rotator. The pumping speed (S) of the TMP depends on molecular mass of the gas pumped and the rotating blade angles:

\[
S_0 = \pi/(2k * \sin \alpha \cos \alpha (R_0^2 - R_i^2) v)
\]

(11)

where \( \alpha \) is the blade angle, \( R_0 \) is the disk radius, \( R_i \) is the radius of the blade base, \( v \) is the speed of the gas molecules, and \( 2K \) is the part of the incoming gas which is pumped.

![Figure 6. Turbomolecular pump blade.](image)
Figure 7. Cross section of a TMP. Roughing pump is a term for scroll pump.\textsuperscript{9}

The lowest pressure that can be achieved using TMPs is $\sim 10^{-9}$ Torr with pumping speed range of $70 \text{ l s}^{-1} - 6000 \text{ l s}^{-1}$.\textsuperscript{10}

### 3.6.3 Scroll Pumps

The turbomolecular pump must be backed by a scroll pump (Figure 8) to work satisfactorily. One scroll of this pump is fixed (stator) while the other is moving (rotor). Gas enters the chambers and goes around the spiral helical path until it exits.\textsuperscript{8} The final pressure that can be achieved is $10^{-2}$ Torr and the capacity is about $15$-$40 \text{ m}^3 \text{ h}^{-1}$.

Figure 8. Diagram of a scroll pump. Right: moving scroll. Left: cross section of stator (stationary) and orbiting rotor.\textsuperscript{8}
Photoionization Source

The synchrotron in the ALS at Lawrence National Laboratory consists of an electron generator, linear accelerator (linac), booster ring, storage ring, and beamlines (Figure 9) and its light in these experiments at the Chemical Dynamics Beamline is used to ionize species in the VUV region (7.2-25 eV) for detection by mass spectrometry.\textsuperscript{11}

![Figure 9. Floor plan of Advanced Light Source: electron generation, storage, and light production.\textsuperscript{11}](image)

3.7 Linear Accelerator (Linac)

Electron generation consists of an electron gun followed by a buncher and linear accelerator called linac (approximately 4 m long) (Figure 10).
An electron beam results from the thermionic emission of electrons arising from a heated barium aluminate cathode. Electrons are drawn to a gate with a positive charge at a frequency of 500 MHz and subsequently pass through the main doughnut-shaped anode and flow to the buncher, which packs electrons into bunches and accelerates them towards the linear accelerator (linac) with help from the klystron (microwave amplifier). The linac continues to accelerate and bunch electrons as they proceed towards the booster ring.

Each time electrons circle around the booster ring (~1,300,00 revolutions in less than 1s) a “boost” is given through an accelerating chamber (RF cavity). Through this process, electrons reach about 99.999994% the speed of light with an energy of 1.5 or 1.9 MeV. Quadrupole magnets guarantee the electron beam stays focused while they continue towards the storage ring (diameter of about 63 m) where they circulate and emit the electromagnetic radiation used for the experiments.

The storage ring is composed of 12 arc shaped sections and in-between each arc is a straight section that ensures electrons do not collide with walls to maintain a constant speed. As electrons pass through arc shaped sections, they are bent and focused by bending magnets, which also emit synchrotron radiation with a broader electromagnetic range, and proceed to undulators and wigglers (straight sections; Figure 11) where they “wiggle” the electrons to form a very bright, narrow beam of light. Undulators, the linear portion of the storage ring, consist of alternating

![Figure 10. Components of the linac.](image)
magnetic poles that force electrons to wiggle and change trajectory to make the synchrotron radiation tunable. The alternating parallel magnetic fields cause sinusoidal oscillations in the trajectory of electrons perpendicular to magnetic fields. Figure 11 demonstrates when the electron beam passes through the undulators the trajectory changes curves and light emitted from each curved trajectory is added together to form a narrow, bright beam (synchrotron radiation). Undulators in the ALS are 4.5 meters long and weigh approximately 20 Tons. Wigglers are similar to undulators, but have fewer magnetic poles and produce radiation with a broader spectrum.

Synchrotron radiation is the electromagnetic radiation given off by electrons while they travel in a curved path at extreme velocities. When an electron passes through a magnetic field, like undulators, a magnetic force is applied perpendicular to the plane of velocity, causing synchrotron radiation to emit. This is shown by:

$$\rho = \frac{CE}{B}$$

(12)

Where $\rho$ is the radius of curvature, $B$ is the magnetic field, $C$ is a constant, and $E$ is the electron energy. The strength of an undulator’s magnetic fields is determined by the spacing between the planes of the magnets, proportional to the radius of the electrons’ path. Since the electron beam is sinusoidal, synchrotron emissions accumulate, cause a high intensity.

The photon energy of the undulator is found through the equation:

$$h\omega \equiv \left(\frac{4\pi c^2 \gamma^2}{\lambda_L}\right)^{1 \over 2} \left(1 + \frac{1}{2} K^2 + \theta_L^2 \gamma^2 \right)^{-1}$$

(13)

Where $h$ is Planck’s constant, $c$ is the speed of light, $\lambda_L$ is the spacing between the magnets, $K$ is the parameter of the wiggler strength, $\theta_L$ is the direction of emitted light, and $\gamma$ is the beam energy which can be written as:

$$\gamma = \left(\frac{E}{m_0 c^2}\right)$$

(14)
In equation (14), \( m_0 \) is the resting mass of an electron, \( E \) is the electron energy, and \( K \) is expressed as:

\[
\kappa = \frac{eB_L\lambda_T}{2\pi cm_0}
\]  

(15)

where \( e \) is the electron charge and \( B_L \) represents the magnetic field strength. These equations reveal that the smaller the spacing between magnets, the higher the energy produced.

Emitted radiation from electrons is contained by large concrete and lead blocks that surround the storage ring. Electrons are consistently supplied into the storage ring (top-off mode) so that the photon density remains constant throughout the experiment.\(^{11}\)

![Figure 11. Electron beam passing through wiggler and undulator. Wigglers contain fewer magnetic poles and produce a broader spectrum of radiation than undulators.](image)

### 3.8 Beamline

Synchrotron radiation is delivered to beamlines that branch tangentially from each of the bending magnet sections and the undulators (explained in section c) also creates synchrotron radiation.\(^{15}\) Experiments are performed at the Chemical Dynamics Beamline 9.0.2, where light from the storage ring first passes through a gas filter. The gas filter is a windowless absorption cell filled with 30 Torr of either Ar or Kr gas whose purpose is to remove harmonic radiation from the undulator greater than the ionization energies than the gases mentioned; 15.76 eV for Ar and 14.00
eV for Kr.\textsuperscript{1} A 3 m off-plane Eagle monochromator (Figure 12) separates and transmits (filters) a narrow portion of the synchrotron radiation from a relatively broad range of wavelengths coming from the undulator.\textsuperscript{1} The specific wavelength, corresponding to an energy in the range of 7.2 – 25.4 eV, chosen by the monochromator follows Bragg’s Law:\textsuperscript{16}

\[ n\lambda = 2dsin\theta \]

where \( \theta \) is the incoming angle produced when a beam of light hits the diffraction grating and is reflected, d is the distance between the groves of the diffraction gratings, n is the order number of diffraction, and \( \lambda \) is the diffracted wavelength that corresponds to the desired photon energy. According to equation 13, when a beam of light hits the diffraction grating at a certain angle (\( \theta \)) only a specific wavelength can be reflected. When this is applied to the ALS apparatus, the incident synchrotron radiation hits the monochromator surface at varying angles, and narrows the bandwidth of radiation and is then directed into the ionization chamber.

*Figure 12. Depiction of the monochromator used at the ALS.*
The experimental apparatus is made up of an orthogonal-acceleration time-of-flight mass spectrometer (oa-TOF-MS) (Figure 13) connected to the ALS.

**Figure 13.** Simplified overview of orthogonal acceleration time-of-flight mass spectrometer.\(^{17}\)

### 3.8.1 Orthogonal Accelerator Time-of-Flight Mass Spectrometer (oa-TOF-MS)

Figure 13 shows a schematic of the oa-TOF-MF used in these experiments. All molecules are ionized in the ionization chamber when hit by an energy higher than a molecule’s ionization energy. The light used is a result of synchrotron radiation. Ions are collimated by a series of electric fields so that they do not spread out and get lost in the acceleration region and are focused so that they can be re-accelerated in a direction orthogonal to their initial trajectories.\(^{18}\) For all ions to have the same inclination (towards the mass analyzer and detector) they must have the same kinetic energy in the ion beam direction when they are introduced.\(^{18}\)
A time-of-flight mass spectrometer separates ions of different mass-to-charge ratios based on the idea that all ions receive equal energy. Therefore, ions of different masses will have different velocities. If there is a set distance of travel, the time of each ion’s travel will depend on its mass; a lighter mass will travel faster and reach the detector first. The kinetic energy (K) gained by the ions, when subjected to a proper potential (V) is:

\[ K = \frac{1}{2} m v^2 = eV \]  

(17)

In the case of a TOF-MS, the time it takes an ion to reach the detector depends on its mass-to-charge ratio:

\[ TOF = time = \frac{d}{v} \text{ in seconds} \]

where d is the path length of the ion and v is the velocity:

\[ v = \sqrt{\frac{2eV}{m}} \]  

(18)

Therefore,

\[ Time \ of \ Flight \ (t_f) = d \frac{m}{\sqrt{2eV}} \]  

(19)

If the path length and energy are constant (as in these experiments), the time of flight becomes proportional to the square root of the mass-to-charge ratio of the ions.

\[ t_f \propto \sqrt{m/z} \]  

(20)

After the gaseous reaction species flow through the reactor tube, VUV radiation ionizes the species. In the ionization chamber, within the time-of-flight analyzer, ions are extracted at a repetition rate of 50 kHz, repeating once the heaviest ions reach the detector. The ions are then focused into an ion beam that enters the orthogonal accelerator. Once the heaviest ions (those that travel the slowest) have reached the detector, new ions are injected into the orthogonal accelerator; ions are analyzed while new ions are pulsed into the accelerator. For these
experiments, microchannel plates are used as the detector and are linked to time-to-flight digital converters (TDC) to increase resolution for data acquisition and representation.

3.8.2 Detector

The detector used are microchannel plates (Figures 13 and 14) that contain chevron style connections and are stacked in pairs of two.

![Diagram](image1.png)

**Figure 14.** Side view of a single linear electron multiplier.²⁰

![Diagram](image2.png)

**Figure 15.** Various multichannel plate arrangements: Single, Chevron, and z-stack.²⁰
The function of the microchannel plates detector is described in detail in the theoretical chapter. The final electron gain, however, is about $10^6$-$10^7$. Once all the cations reach the detector they are sent to the time-to-digital converter.

### 3.8.3 Data Acquisition: Time-to-Digital Converter (TDC)

Because the apparatus is multiplexed, the ion signal is a function of the mass-to-charge ratio, reaction time ($t$), and photon energy ($h\nu$). Ions in a time-of-flight analyzer arrive at times that are proportional to their mass-to-charge ratio (equation 11). The photolysis laser is fired (at time $t_0$) to start an oxidation reaction in the reactor tube by photolyzing radical precursors. The species from the reaction that is ionized has a lifetime of at least few ms to reach the microchannel plates (detector). Microchannel plate detectors record total ion arrivals. The resulting ion pulse of each mass-to-charge ratio is detected as an electrical current and sent to a recording device, time-to-digital converter (TDC). It is important that the time-to-digital converter measures the number of ions at each mass-to-ratio so it obtains ion abundances. The addition of all mass spectra from all ions at a specific mass-to-charge-ratio makes the final mass spectrum, which is time- and energy-resolved.

### 3.9 Data Representation

As the reaction species proceeds to the ionization chamber, the photon energy is increased in chosen increments (usually stepsize of 0.025 eV) along the range of 8.0-11 eV. At each photon energy step, the laser pulses about 200-250 times and the energy, reaction time, mass-to-charge ratio, and ion signal are recorded and added to improve the signal-to-noise ratio.

The time-independent signal must be removed through background subtraction, completed in the IGOR program using specific procedures written ad hoc for these experiments called ALS Kinetic Tools. The ion signal is subsequently normalized by the ALS photocurrent (measured using a calibrated photodiode) to account for the changes in photon flux from the ALS light. The
data collected is represented as a three-dimensional data block, as shown in Figure 18, by plotting the ion signal against mass-to-charge-ratio, time, and photon energy.

The 3D block is challenging to visualize because there are three variables involved. Therefore, the data block is simplified to 2D images and reduced to a 1D plot. This is accomplished by fixing one of the variables (mass-to-charge ratio, ion signal, or photon energy) and plotting the other two. The two plots focused in this research are time-dependent and energy-dependent mass spectra.

For each mass-to-charge ratio, a photoionization (PI) spectrum and time-trace can be obtained; referred to as 1D slices. These two slices are depicted in the top corners of Figure 18 with the PI spectrum on the left and time-trace on the right. The time-trace gives visual information
on the temporal behavior of the detected compound at a specific mass and the PI spectrum gives the ionization energy, among other information, of the compound. These two plots can give insight to determine if a compound is a primary product, radical, fragment, or depleting reactant.

For example, in figure 18, the top left corner shows the PI spectrum of species A and B. Once the signal is normalized for the known photoionization cross sections, the actual concentrations can be derived. Species A now has a higher signal than species B. The top right corner shows the time-trace of the two species. Species A forms quickly and hastily depletes, a characteristic of a possible radical. Species B forms quickly, but remains constant, characteristic of a stable product. Considering both sets of information, species A would have a noisier PI spectrum due to its rapid formation and depletion, seen in the time-trace. The time-trace of the possible product should also be compared to the time-trace of the parent. If the rate of formation of the product matches the rate of depletion of the parent, the product would be primary. If the product forms at a slower rate, then it may be a secondary product. If the species is determined to be a primary product, a mechanism is needed to explain its formation.

3.10 Data Analysis

The energy at the onset of a PI spectrum is the adiabatic ionization energy (AIE) of a molecule. The shape of a PI spectrum and ionization energy are unique to every molecule. In an experiment this can help identifying an unknown species. When there is an idea of what the unknown species may be, the literature photoionization spectrum may be superimposed onto the experimental PI spectrum of the species. If the two match, the unknown species is determined. If there is an idea of what the unknown species may be, and no literature PI spectrum is available, a Franck-Condon simulation can be performed to provide a photoionization spectrum. This Franck-Condon simulation is also applicable to identification of multiple isomers at a certain mass, since each isomer has unique FC factors for ionization transitions. To simulate a photoionization
spectrum, the CBS-QB3$^{23-25}$ composite model is used within the Gaussian 09$^{26}$ program. For a possible unknown compound, the neutral and cationic states are optimized to obtain the adiabatic ionization energy and the optimized geometrical parameters to simulate a PI spectrum. The optimization of each structure, done in the Gaussian 09$^{26}$ program using the CBS-QB3$^{23-25}$ composite model, provides information about bond lengths, bond angles, ionization energies, vibrational frequencies, and force constants. This composite model is chosen due to its high accuracy at a low computational cost, and its mean average deviation (MAD) of 4-5 kJ mol$^{-1}$. The zero-point vibrational corrected total electronic energy ($E_0$) is obtained from the optimized neutral and cationic state. When the two energies are subtracted, the AIE is found:

$$AIE = E_{cat} - E_{neu}$$  \hspace{1cm} (21)

The AIE is applicable in generating Franck-Condon simulations of the photoelectron spectrum (PE). To do this, a second calculation is run, in addition to the AIE, but this calculation does not use a basis set, instead it uses the neutral’s and cation’s Franck-Condon factors to create a photoelectron spectrum.$^4$ Photoelectron spectra are simulated using Franck-Condon (FC)$^{27-29}$ and Franck-Condon-Herzberg-Teller (FCHT)$^{29}$ methods in the Gaussian 09$^{26}$ program, which approximates the FC factors for vibronic transitions of the neutral to cationic state of a species. In addition, the FCHT method determines the vibrational normal modes using the Duschinsky rotation matrix.$^{30}$ Afterwards, a set of recursive formulas, created by Ruhoff,$^{31}$ is used to calculate the FC overlap integrals. Resulting photoelectron spectra are then integrated to give the photoionization spectra, which are compared to experimental PI spectra. The photoionization spectra will be used to determine the species at specific masses. The Franck-Condon factors determine the shape of the photoionization spectra while the adiabatic ionization energy determines the onset of the curve in the photoionization spectra.$^{26}$
The ZPE corrected electronic energy can also be used to find other thermodynamic quantities, such as reaction enthalpies based on Hess’ law:

$$\Delta H_{\text{rxn}} = \sum ZPE_{\text{products}}^{\text{CBS-QB3}} - \sum ZPE_{\text{reactants}}^{\text{CBS-QB3}}$$ (22)

The heat of the reaction is used to show if a proposed reaction mechanism is thermodynamically feasible. Proving a reaction mechanism is also aided using potential energy surface (PES) scans at the B3LYP level (a level used in CBS-QB3 optimizations). Transition states (saddle points) are found from the maximum energy in the scans and must contain one imaginary vibrational frequency. Transition states are optimized using the CBS-QB3 method, with the respect to the imaginary frequency. To further prove the transition state, Intrinsic reaction coordinate (IRC) calculations (forward and reverse) are used to validate the minima on both sides of the transition state. Using all these values determines the enthalpy change (kJ mol$^{-1}$) of proposed mechanisms, which also determines the exothermicity of a reaction.
3.11 References


Chapter 4: Absolute Photoionization Cross Sections of Two Cyclic Ketones: Cyclopentanone & Cyclohexanone

4.1 Abstract

Absolute photoionization cross sections for cyclopentanone and cyclohexanone, as well as partial ionization cross sections for the dissociative ionized fragments, are presented in this investigation. Experiments are performed via a multiplexed photoionization mass spectrometer utilizing VUV synchrotron radiation supplied by the Advanced Light Source of Lawrence Berkeley National Laboratory. These results allow the quantification of these species that is relevant to investigate the kinetics and combustion reaction of potential biofuels. The CBS-QB3 calculations agree with the experimental results and the identification of possible fragments is proposed.

4.2 Introduction

With the population expected to grow to over nine billion by the year 2050,[1] demands for alternative fuels other than fossil fuels has increased. Formed over 300 million years ago, fossil fuels used today are in limited quantities and when burnt emit greenhouse gases (GHG), which affect climate change. These problems can be attenuated with a renewable energy source such as biofuels. Biofuels are categorized into three types: first, second, and third generation. The main difference between the three generations is the source from which the fuel is procured. First generation biofuels are developed from components found in crops, whereas second generation biofuels are derived from biomass. Third generation biofuels, however, are obtained from algae. [2] Research, development, and production of new biofuels is ongoing and even surpassing first generation biofuels.[3-5]
Microorganisms and plants are being explored as potential sources for producing biofuels. These biomass sources may be used as “drop-in” fuels in transport, without the need to modify existing engines. Second generation biofuels produced from lignocellulosic material are expected to reduce GHG emissions more than first generation biofuels. Lignocellulosic material consists of carbohydrates, with an excess of oxygenated groups, used in the conversion process into fuels through different reactions. Linear and branched alkanes have been studied for the use of renewable fuels, but these must be mixed with conventional jet-fuels to increase their density in order to be used for air transportation. Conversely, cyclic hydrocarbons have higher energy densities, due to ring strain, and are preferred to be mixed into conventional jet-fuel to increase its density. Past investigations have also found that the addition of oxygenates to fuel, in which the oxygen is bonded to two carbons as with ethers and esters, yield the lowest soot emissions of particulate matter and emissions decline as the oxygen content is increased. In addition, it has been found that when a cyclic ketone is added at a constant concentration to a heavy-duty direct injection diesel engine the smoke opacity and soot emissions are lowered. These findings have led to interest in cyclic ketones, two of which are presented in this investigation: cyclopentanone (CPO) and cyclohexanone (CXO).

From the 1930s to the 1960s, the photochemical decomposition mechanisms of both cyclohexanone and cyclopentanone were studied, and recently gained attention, again, due to their potential as biofuel sources. The mechanisms of combustion for the two ketones have been explored, but to our knowledge their absolute photoionization cross sections have yet to be investigated.

Cyclopentanone has raised interest in the alternative fuel industry because of its conversion from furfural through a one-step hydrogenation process. This method provides a cost-effective
way to produce diesel or jet-fuels from lignocellulosic materials.\textsuperscript{[7]} Because of cyclopentanone’s cyclic structure, it could be used as a potential source for the synthesis of jet fuels.\textsuperscript{[9]} One particular renewable high energy density fuel and “drop in” fuel that is created from the self-condensation and hydrodeoxygenation of cyclopentanone is bicyclopentane,\textsuperscript{[9,26]} which establishes CPO as a platform compound for the production of high-density fuels.

Cyclohexanone is another potential biofuel of interest derived from lignin.\textsuperscript{[26,27]} Compared to cyclopentanone, cyclohexanone can produce hydrocarbons with higher energy densities through a hydroxyalkylation/alkylation process with 2-methylfuran, such as pentylcyclohexane and naphthene.\textsuperscript{[28]} It can also be converted to bi-cyclic fuels, like bi-cyclohexane, through self-aldol condensation followed by hydrodeoxygenation.\textsuperscript{[26]}

Cool \textit{et al.}\textsuperscript{[29,30]} developed a technique that uses photoionization mass spectrometry (PIMS) to determine the photoionization cross sections of molecules by comparison with a known standard, such as ethene, butene, or propene. This technique has been used to study the cross sections of biofuels,\textsuperscript{[29-35]} but is difficult to apply when used with compounds that have low vapor pressures (\(< 5 \text{ Torr} \text{ at } 25^\circ\text{C}\)), as it is hard to quantify such compounds in the gas phase. Before PIMS, cross sections were determined by employing a double ion beam in a dual ionization chamber as used by Haddad \textit{et al.} to measure the cross section of water.\textsuperscript{[36-37]}

In this study, the PIMS technique is used to investigate the photoionization cross sections (PICS) of two cyclic ketones: cyclopentanone and cyclohexanone (Figure 1). The absolute cross sections of these species relate the observed ion signal to their concentrations that allow for quantification through PIMS. The absolute concentrations of each reactant in an experiment is important to both the kinetics and analysis of a combustion reaction.\textsuperscript{[38]}
4.3 Experimental Methodology

4.3.1 Apparatus

Experiments were performed using the third-generation synchrotron Advanced Light Source (ALS) of the Ernest Orlando Lawrence Berkeley National Laboratory in Berkeley, CA. Only a brief overview of the experimental setup is given here, but a more detailed description of the design and implementation can be found elsewhere. Helium gas, calibration mixture gas, and the molecules under investigation are introduced into the reactor using calibrated mass flow controllers. The reaction tube is a 62 cm quartz slow flow reactor and is held at a pressure of 4 Torr, temperature of 298 K, and total flow of 100 sccm. The species flow through a 650 µm hole into a source chamber, evacuated by a turbomolecular pump, and skimmed into the ionization region. The molecular beam is then orthogonally intersected by the continuous tunable vacuum ultraviolet synchrotron radiation, which is generated by an undulator and filtered through a beamline windowless gas filter filled with 30 Torr of argon gas. The resulting ions from the intersection of the molecular beam and ALS radiation are accelerated, collimated, and focused towards the detector of an orthogonal time-of-flight mass spectrometer. The resulting species are analyzed based on their mass-to-charge ratio and ion signal intensity in the 8-11 eV photon energy range. The mass resolution for these experiments is about 1600 under the current conditions. After the signal is detected, it is normalized at each photon energy for the photon current of the ALS measured using a vacuum ultraviolet calibrated photodiode. Both cyclopentanone and cyclohexanone are purchased from Sigma-Aldrich (≥99% purity), and impurities from both samples are removed through the freeze-pump-thaw technique. Once purified, the sample is flowed into a steel vacuumed gas cylinder and equilibrates. Helium is then flowed into the gas cylinder until the sample composes about 1% of the total pressure within the cylinder. The
sample’s vapor pressure is measured using a low-pressure transducer (0.5 % accuracy of stated reading). The samples are then stored under vacuum until needed.

4.4 Measurement

Ruscic and Berkowitz\textsuperscript{[43]} developed the procedure used in this study to extrapolate the adiabatic ionization energies (AIEs) and the experimental appearance energies (AEs). They convoluted the thermal distribution function described by Haarhoff\textsuperscript{[44]} using three different kernel functions (linear, square root, and exponential) and then simulated the photoion yield curves. They found that exponential functions produced the best fit and that AIEs and AE’s can be extrapolated by adding twice the thermal energy term, kT, to the threshold energy used. Experimental AIEs are obtained by extrapolating initial onsets of the photoionization energy curves using the exponential function: $1-e^{-bE}$\textsuperscript{[43]} where b represents an arbitrary constant and E represents the energy in eV. The AE of the dissociative ionization fragments are found in the same manner but uses a pre-threshold exponential function and a post-threshold exponential function, as outlined by Ruscic and Berkowitz.\textsuperscript{[43]} Both AIEs and AEs are obtained with an uncertainty of ± 0.05 eV to account for photon energy calibration and possible presence of hot bands.\textsuperscript{[42,43]}

The absolute photoionization spectrum of a molecule is found through the comparison of experimental data with the known absolute photoionization cross section of a reference compound. The reference compounds for this study are ethene, propene, and 1-butene, which compose the calibration gas (cal-gas). In this investigation, the absolute photoionization cross section of propene of 12.4 Mb at 11.0 eV, with an evaluated error of 10\%, measured by Person and Nicole,\textsuperscript{[45]} is used as a reference in the photon energy range of 8-11 eV.

Equation (1) shows the relationship of a species’ factors, where the relative ion signal (S) and compound’s photoionization cross section (σ) are energy dependent and should be found for the same energy (E) throughout the calculations. The remaining variables in equation (1) are
defined as: instrument constant (k), the mass discrimination factor (δ), and the concentration (C) of the compound. The mass discrimination factor, experimentally determined and described in detail by Savee et al.\textsuperscript{46} is equal to \(m^{0.67}\) where m is the mass of the compound.

\[ S(E) = k\sigma(E)\delta \]  \hspace{1cm} (1)

Using equation (2) in conjunction with a known standard, the unknown cross section of the target compound (\(\sigma_T\)) can be found as the ratio of its ion signal intensity (\(S_T\)), photoionization cross section of the standard (\(\sigma_s\), propene), mass discrimination factor of the standard (\(\delta_s\)), and concentration of the standard (\(C_S\)), to the ion signal intensity of the standard (\(S_S\)), mass discrimination factor of the target (\(\delta_T\)), and the concentration of the target (\(C_T\)).

\[ \sigma_T = \left( \frac{S_T(E)\sigma_S(E)\delta_S C_S}{S_S(E)\delta_T C_T} \right) \]  \hspace{1cm} (2)

Utilizing the uncertainties for the concentration (1.00%), ion signal measurements (1.00% for both \(S_T\) and \(S_S\)), mass discrimination factor (13%), with the uncertainty for the photoionization cross section of propene (10%), the uncertainty measured for the cross sections attained using this mass spectrometer is ± 17%.

\textbf{4.5 Computational}

Figure 1 presents the structures of cyclopentanone and cyclohexanone. Optimized molecular parameters, including bond lengths, harmonic vibrational frequencies, rotational constants, and energetics for neutral and cation species are calculated using the CBS-QB3 composite model, which provides accurate energy calculations at a low computational cost.\textsuperscript{47-49}
All ab initio quantum chemical calculations are carried out using the Gaussian09\textsuperscript{[50]} suite of programs and all molecules are visualized using Gauss View.\textsuperscript{[50-52]} The CBS-QB3 composite method has a reported mean average deviation (MAD) of ± 0.05 eV, i.e., 4-5 kJ mol\textsuperscript{-1}.\textsuperscript{[49]} The adiabatic ionization energy of a molecule is calculated by the difference in the zero-point corrected energies (E\textsubscript{0}) between a molecule’s neutral and cationic states, as shown in equation (3):

\[
AIE = E_{0\text{cat}} - E_{0\text{neu}}
\]  

(3)

The appearance energy at 0 K of dissociative fragment ions is found through the difference in CBS-QB3 calculated energies by:

\[
AE = AB \rightarrow A^+ + e^- + B
\]

(4)

where A\textsuperscript{+} is the dissociative ionization fragment or daughter ion, B is the neutral fragment, and AB is the neutral parent molecule, assuming no barrier for dissociation is present (thermochemical limit).

4.6 Results and Analysis

4.6.1 Cyclopentanone

Cyclopentanone is stored as a 0.33\% mixture (8 Torr of CPO in 2408 Torr total in helium) and is flowed at a rate of 2.08 sccm, resulting in a concentration of 8.75x10\textsuperscript{12} molecules cm\textsuperscript{-3} in
the reactor. Table 1 shows the variation of bond lengths from the neutral to cation molecular structure of cyclopentanone.

**Table 1.** Optimized neutral and cation bond lengths of CPO using the CBS-QB3 composite model.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Neutral (Å)</th>
<th>Cation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁O</td>
<td>1.204</td>
<td>1.183</td>
</tr>
<tr>
<td>C₁C₂</td>
<td>1.532</td>
<td>1.563</td>
</tr>
<tr>
<td>C₂C₃</td>
<td>1.535</td>
<td>1.536</td>
</tr>
<tr>
<td>C₃C₄</td>
<td>1.546</td>
<td>1.529</td>
</tr>
<tr>
<td>C₄C₅</td>
<td>1.535</td>
<td>1.536</td>
</tr>
<tr>
<td>C₅C₁</td>
<td>1.532</td>
<td>1.563</td>
</tr>
</tbody>
</table>

These bond length changes provide information about the character of the molecular orbital from where the electron is removed. Koopmans’ Theorem \[^{53}\] may be used with Hartree-Fock orbital energies to directly calculate ionization energies by taking the absolute value of the HOMO energy. In this study, however, the absolute value of orbital energies is not used, but instead the difference between orbital energies is applied to provide excitation energies (term energies), as successfully completed by other studies. \[^{54-56}\] The HOMO and HOMO-1 of cyclopentanone are showed in figure 2.

**Difference of Orbital Energies**

2.26 eV

![HOMO and HOMO-1](image)

**Figure 2.** Electron distribution and orbital energy of cyclopentanone at the B3LYP/6-311G(2d,d,p) level of theory.
The most evident elongation in bond length occurs with the $\alpha$ and $\alpha'$ carbons ($C_1-C_2$ and $C_1-C_5$) bonded to the carbonyl group. Both bonds extend from 1.532 Å, in the neutral state, to 1.563 Å in the cation state. At the same time, the $C_1-O$ bond is shortened upon ionization by 0.021 Å. Therefore, the initial ionization is the result of the removal of an electron from a bonding orbital localized on the $\sigma$ bonds of both the $\alpha$ and $\alpha'$ carbon and the antibonding $C_1-O$ $\pi$ orbital. This finding is also sustained by other investigations\textsuperscript{[57,58]} in which the first ionization energy is a result of the removal of an electron from the $\sigma$ network of the ring. Separate studies found that the ionization energy associated with this electron removal is $9.25 \pm 0.02$ eV,\textsuperscript{[57,58]} while another study\textsuperscript{[59]} found the ionization energy to be $9.28 \pm 0.01$ eV. Both are comparable to this study’s experimental ionization energy of $9.30 \pm 0.05$ eV with a CBS-QB3 calculated AIE of $9.29 \pm 0.05$ eV.

With the use of Koopmans’ Theorem,\textsuperscript{[53]} it is estimated that a second spectral band should appear at $11.5$ eV ($\text{AIE} + \Delta (E_{\text{HOMO}-1} - E_{\text{HOMO}})$), corresponding to the first excited state of the cyclopentanone cation. This value is outside this experiment’s energy range, but coincides with another experiment’s finding\textsuperscript{[58]} of $11.30 \pm 0.02$ eV. Figure 3 depicts the absolute photoionization spectrum of cyclopentanone with the corresponding photoionization cross section values listed in Table 2. Figure 3 also presents two dissociative fragments, $m/z = 54$ and 56 (magnified in fig 4).
Table 2. Cross section values of cyclopentanone and dissociative fragments in Megabarnes (Mb).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>CPO</th>
<th>$m/z = 54$</th>
<th>$m/z = 56$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.15</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.2</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.25</td>
<td>1.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.3</td>
<td>3.47</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.35</td>
<td>4.44</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.4</td>
<td>5.92</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.45</td>
<td>7.71</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.5</td>
<td>8.65</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.55</td>
<td>9.84</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.6</td>
<td>10.63</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.65</td>
<td>11.44</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>9.7</td>
<td>12.10</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>9.75</td>
<td>12.91</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>9.8</td>
<td>13.88</td>
<td>0.09</td>
<td>0.53</td>
</tr>
<tr>
<td>9.85</td>
<td>14.25</td>
<td>0.16</td>
<td>0.80</td>
</tr>
<tr>
<td>9.9</td>
<td>15.13</td>
<td>0.23</td>
<td>1.21</td>
</tr>
<tr>
<td>9.95</td>
<td>15.38</td>
<td>0.30</td>
<td>1.41</td>
</tr>
<tr>
<td>10</td>
<td>16.38</td>
<td>0.38</td>
<td>2.07</td>
</tr>
<tr>
<td>10.05</td>
<td>16.75</td>
<td>0.41</td>
<td>2.02</td>
</tr>
<tr>
<td>10.1</td>
<td>17.54</td>
<td>0.54</td>
<td>2.43</td>
</tr>
<tr>
<td>10.15</td>
<td>17.89</td>
<td>0.53</td>
<td>2.80</td>
</tr>
<tr>
<td>10.2</td>
<td>18.41</td>
<td>0.61</td>
<td>2.84</td>
</tr>
<tr>
<td>10.25</td>
<td>18.99</td>
<td>0.64</td>
<td>2.91</td>
</tr>
<tr>
<td>10.3</td>
<td>19.41</td>
<td>0.72</td>
<td>3.06</td>
</tr>
<tr>
<td>10.35</td>
<td>19.51</td>
<td>0.69</td>
<td>3.38</td>
</tr>
<tr>
<td>10.4</td>
<td>19.91</td>
<td>0.82</td>
<td>3.16</td>
</tr>
<tr>
<td>10.45</td>
<td>20.37</td>
<td>0.97</td>
<td>3.66</td>
</tr>
<tr>
<td>10.5</td>
<td>20.40</td>
<td>1.08</td>
<td>3.76</td>
</tr>
<tr>
<td>10.55</td>
<td>20.56</td>
<td>1.10</td>
<td>3.44</td>
</tr>
<tr>
<td>10.6</td>
<td>20.85</td>
<td>1.26</td>
<td>3.75</td>
</tr>
<tr>
<td>10.65</td>
<td>20.92</td>
<td>1.23</td>
<td>3.69</td>
</tr>
<tr>
<td>10.7</td>
<td>21.23</td>
<td>1.36</td>
<td>3.81</td>
</tr>
<tr>
<td>10.75</td>
<td>21.87</td>
<td>1.45</td>
<td>3.88</td>
</tr>
<tr>
<td>10.8</td>
<td>22.07</td>
<td>1.53</td>
<td>3.85</td>
</tr>
<tr>
<td>10.85</td>
<td>22.76</td>
<td>1.54</td>
<td>4.71</td>
</tr>
<tr>
<td>10.9</td>
<td>23.33</td>
<td>1.67</td>
<td>4.42</td>
</tr>
<tr>
<td>10.95</td>
<td>23.97</td>
<td>1.63</td>
<td>5.02</td>
</tr>
<tr>
<td>11</td>
<td>24.71</td>
<td>1.79</td>
<td>5.26</td>
</tr>
<tr>
<td>11.05</td>
<td>24.84</td>
<td>1.81</td>
<td>5.25</td>
</tr>
<tr>
<td>11.1</td>
<td>25.20</td>
<td>1.76</td>
<td>5.82</td>
</tr>
</tbody>
</table>
Figure 3. Molecular photoionization cross section for cyclopentanone (red crosses) with its dissociative photoionization fragments at $m/z = 54$ and 56.

Other dissociative fragments detected include $m/z = 58$, 74, and 80, but their intensities are approximately 99% smaller than CPO’s and 56 times smaller than $m/z = 56$ and 54. The experimental AE for $m/z = 56$ is approximately $9.75 \pm 0.05$ eV, while that of $m/z = 54$ is $9.70 \pm 0.05$ eV (Figure 4).

Figure 4. Appearance energies, extrapolated following Berkowitz\textsuperscript{[43]} procedure, of CPO’s two dissociative ionization fragments.
Possible identifications for the two dissociative fragments are calculated through appearance energies of numerous structures. For \( m/z = 54 \), two neutral \( m/z = 30 \) fragments are possible: formaldehyde (CH\(_2\)O\(^\text{\textsuperscript{n}}\)) and ethane (C\(_2\)H\(_6\)\(^\text{\textsuperscript{n}}\)). Possible dissociative fragment structures are shown in Table 3, yet their appearance energies are too high (>11 eV) to be considered as a possible match for this study.

**Table 3.** Possible calculated dissociative fragments for cyclopentanone with their respective appearance energies in eV.

<table>
<thead>
<tr>
<th>( m/z ) 56</th>
<th>Neutral Fragment ( m/z 28 )</th>
<th>Structure</th>
<th>Appearance Energy ( \text{eV}\pm0.05 )</th>
<th>( m/z ) 54</th>
<th>Neutral Fragment</th>
<th>Structure</th>
<th>Appearance Energy ( \text{eV}\pm0.05 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td>CH(_2)O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclobutane</td>
<td></td>
<td>10.91</td>
<td>methylcyclopropane</td>
<td></td>
<td></td>
<td>12.30</td>
</tr>
<tr>
<td></td>
<td>but-1-ene</td>
<td></td>
<td>10.45</td>
<td>but-2-yne</td>
<td></td>
<td></td>
<td>11.88</td>
</tr>
<tr>
<td></td>
<td>(E)-but-2-ene</td>
<td></td>
<td>9.91</td>
<td>buta-1,3-diene</td>
<td></td>
<td></td>
<td>11.02</td>
</tr>
<tr>
<td></td>
<td>methylcyclopropane</td>
<td></td>
<td>10.40</td>
<td>but-1-yne</td>
<td></td>
<td></td>
<td>12.76</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td></td>
<td></td>
<td>12.04</td>
<td>buta-1,2-diene</td>
<td></td>
<td></td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td>acrylaldehyde</td>
<td></td>
<td>11.92</td>
<td></td>
<td>cyclobutene</td>
<td></td>
<td>11.99</td>
</tr>
<tr>
<td></td>
<td>cyclopropanone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>prop-2-yn-1-ol</td>
<td></td>
<td>13.55</td>
<td>propa-1,2-dien-1-one</td>
<td></td>
<td></td>
<td>11.52</td>
</tr>
<tr>
<td></td>
<td>propa-1,2-dien-1-ol</td>
<td></td>
<td>11.89</td>
<td>propiolaldehyde</td>
<td></td>
<td></td>
<td>13.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cycloprop-2-enone</td>
<td></td>
<td></td>
<td>12.23</td>
</tr>
</tbody>
</table>
An investigation conducted in 1960\cite{60} displayed a peak at $m/z = 54$ in the mass spectrum of CPO that consisted of a mixture of $C_3H_2O$ and $C_4H_6$. Also, previous studies\cite{16,17,62} determined cyclopentanone decomposes into two ethylene molecules, cyclobutane, and carbon monoxide, and can even rearrange to form 4-pentanal through the bi-radical.

For $m/z = 56$, 1-butene is removed from the experimental data since it is a component of the calibration gas mixture. A neutral fragment of $m/z = 28$ would match the loss of carbon monoxide or ethylene; the only appearance energies that is close to the observed $m/z = 56$ onset is 2-butene with a calculated appearance energy of 9.9 eV. A loss of ethylene, however, resulted in appearance energies that were too high to be considered in this investigation. Another investigation by Norrish et al.\cite{14} found that the irradiation of cyclopentanone in the gas phase resulted in cis and trans-2-butene, which made up 50\% of the product, $m/z = 56$, while the other 50\% were two ethylene molecules. These products were identified using three fractions and pumping off the gas: one of liquid nitrogen, which resulted in carbon monoxide, the second of solid carbon monoxide and ether, which resulted in olefins, and the last of hydrochloric acid, which resulted in volatile gases. The three fractions were analyzed and identified separately through the determination of vapor pressure, boiling and freezing point, and molecular weight.\cite{14,61} A later study conducted by Benson et al.\cite{16} however, corrected these previous findings\cite{14,15} since part of the reaction occurred in the liquid phase, causing errors in the results. For this reason, Benson et al.\cite{16} used microtechniques\cite{62} in the gas phase and physical properties to determine products of photochemical decomposition. This new investigation suggested that $m/z = 56$ was, in fact, composed of cyclobutane. In addition, another study\cite{60} revealed that from the mass spectrum of CPO $m/z = 56$ was both $C_4H_8$ and $C_3H_4O$, the former of which composed a larger percentage of the peak. The mass resolution used in this investigation shows that single species peaks are rather
narrow. For \( m/z = 56 \) the mass spectrum obtained in this investigation shows that this mass’ peak (Figure 5) is not as narrow as others since the peak is composed of \( m/z = 55.93 \) and \( m/z = 56.08 \) supporting the previous finding \cite{60} that \( m/z = 56 \) is composed of two species, \( \text{C}_3\text{H}_4\text{O} \) and \( \text{C}_4\text{H}_8 \), respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mass_spectrum_for_CPO}
\caption{High resolution mass spectrum for CPO; \( m/z = 56 \) is displayed in the inset.}
\end{figure}

\subsection{4.6.2 Cyclohexanone}

Cyclohexanone (CXO) is stored as a 0.0976\% mixture (2.189 Torr of CXO in 2242 Torr total in helium) and is flowed into the system at a rate of 3.15 sccm. This resulted in a concentration of \( 7.81 \times 10^{12} \text{ molecules cm}^{-3} \) in the cell.

Through CBS-QB3 calculations, it is found that the chair conformation of cyclohexanone is lower in energy than the boat conformation, Figure 6, with an energy difference of about 16 kJ mol\(^{-1}\). The eclipsing interactions present in the boat conformation cause steric strain making this conformation higher in energy than the chair. The chair’s staggered placement of hydrogen atoms “relaxes” this molecule to a lower energy state.
The band gap between HOMO and LUMO (lowest unoccupied molecular orbital) gives insights into the stability of a structure; a larger gap results in a more stable structure.\textsuperscript{[61]} The band gap, calculated at the B3LYP level within the CBS-QB3 composite model, for the boat conformation is 9.72 eV, whereas that of the chair is 9.77 eV, a difference of 131 kJ mol\textsuperscript{-1}, further demonstrating that the chair conformation is more stable than the boat.

The change in bond lengths between the neutral and molecular cation of CXO is shown in Table 4.

\textbf{Table 4.} Optimized neutral and cation bond lengths of CXO using the CBS-QB3 composite model.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Neutral Chair (Å)</th>
<th>Cation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{1}O</td>
<td>1.210</td>
<td>1.183</td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}</td>
<td>1.522</td>
<td>1.567</td>
</tr>
<tr>
<td>C\textsubscript{2}C\textsubscript{3}</td>
<td>1.542</td>
<td>1.526</td>
</tr>
<tr>
<td>C\textsubscript{3}C\textsubscript{4}</td>
<td>1.534</td>
<td>1.532</td>
</tr>
<tr>
<td>C\textsubscript{4}C\textsubscript{5}</td>
<td>1.534</td>
<td>1.532</td>
</tr>
<tr>
<td>C\textsubscript{5}C\textsubscript{6}</td>
<td>1.542</td>
<td>1.526</td>
</tr>
<tr>
<td>C\textsubscript{6}C\textsubscript{1}</td>
<td>1.522</td>
<td>1.567</td>
</tr>
</tbody>
</table>

The α and α’ (C\textsubscript{1}-C\textsubscript{2} and C\textsubscript{1}-C\textsubscript{6}) carbons bonded to the carbonyl group show noticeable changes in bond length. The α and α’ carbon’s length is initially 1.522 Å and upon ionization it extends to 1.567 Å, while the carbonyl group decreases by 0.027 Å. The bond elongations and compression reveal that the initial ionization is a consequence of the removal of an electron from a bonding orbital localized on the α and α’ carbon’s σ bonds and antibonding C\textsubscript{1}-O π orbital (Figure 7).
Another investigation conducted by Chadwick *et al.*\(^{[58]}\) also found that the initial ionization is caused by the removal of an electron from an orbital localized on the $\sigma$ network of the ring. Figure 8 depicts the experimental photoionization spectrum of cyclohexanone with the corresponding photoionization cross section values listed in Table 5.
Table 5. Cross section values of cyclohexanone and its dissociative fragments in Megabarns (Mb).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>CXO</th>
<th>( m/z = 80 )</th>
<th>( m/z = 70 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.09</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.05</td>
<td>0.22</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.1</td>
<td>0.65</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.15</td>
<td>2.77</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.2</td>
<td>4.15</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>9.25</td>
<td>5.35</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>9.3</td>
<td>7.12</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>9.35</td>
<td>8.54</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>9.4</td>
<td>9.42</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>9.45</td>
<td>10.39</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>9.5</td>
<td>11.02</td>
<td>0.07</td>
<td>0.00</td>
</tr>
<tr>
<td>9.55</td>
<td>11.81</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>9.6</td>
<td>13.30</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>9.65</td>
<td>13.33</td>
<td>0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>9.7</td>
<td>14.51</td>
<td>0.17</td>
<td>0.01</td>
</tr>
<tr>
<td>9.75</td>
<td>16.17</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>9.8</td>
<td>15.77</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>9.85</td>
<td>16.32</td>
<td>0.18</td>
<td>0.02</td>
</tr>
<tr>
<td>9.9</td>
<td>16.92</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>9.95</td>
<td>17.32</td>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>18.61</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>10.05</td>
<td>18.88</td>
<td>0.28</td>
<td>0.03</td>
</tr>
<tr>
<td>10.1</td>
<td>21.15</td>
<td>0.29</td>
<td>0.04</td>
</tr>
<tr>
<td>10.15</td>
<td>20.49</td>
<td>0.40</td>
<td>0.08</td>
</tr>
<tr>
<td>10.2</td>
<td>21.71</td>
<td>0.55</td>
<td>0.05</td>
</tr>
<tr>
<td>10.25</td>
<td>22.87</td>
<td>0.51</td>
<td>0.09</td>
</tr>
<tr>
<td>10.3</td>
<td>23.46</td>
<td>0.62</td>
<td>0.10</td>
</tr>
<tr>
<td>10.35</td>
<td>23.61</td>
<td>0.80</td>
<td>0.13</td>
</tr>
<tr>
<td>10.4</td>
<td>22.44</td>
<td>0.85</td>
<td>0.16</td>
</tr>
<tr>
<td>10.45</td>
<td>23.57</td>
<td>0.93</td>
<td>0.17</td>
</tr>
<tr>
<td>10.5</td>
<td>23.99</td>
<td>1.12</td>
<td>0.17</td>
</tr>
<tr>
<td>10.55</td>
<td>23.39</td>
<td>1.20</td>
<td>0.20</td>
</tr>
<tr>
<td>10.6</td>
<td>22.93</td>
<td>1.22</td>
<td>0.24</td>
</tr>
<tr>
<td>10.65</td>
<td>23.21</td>
<td>1.21</td>
<td>0.33</td>
</tr>
<tr>
<td>10.7</td>
<td>23.37</td>
<td>1.25</td>
<td>0.31</td>
</tr>
<tr>
<td>10.75</td>
<td>22.96</td>
<td>1.35</td>
<td>0.41</td>
</tr>
<tr>
<td>10.8</td>
<td>23.03</td>
<td>1.39</td>
<td>0.62</td>
</tr>
<tr>
<td>10.85</td>
<td>22.45</td>
<td>1.53</td>
<td>0.72</td>
</tr>
</tbody>
</table>
The threshold of ionization for cyclohexanone, obtained following Berkowitz procedure,[43] is 9.16 ± 0.05 eV, which agrees well with both our calculated CBS-QB3 AIE of 9.18 eV ± 0.05 eV and the literature value of 9.16 ± 0.01 eV.[58,59] Koopmans’ Theorem[53] predicts that a second spectral band (first cationic excited state) should appear around 11.1 eV, which is just outside this experimental range. The position of the second spectral band is computed using the energy difference between the HOMO and HOMO-1 energies (Figure 7). Figure 8 also presents two photoionization dissociative fragments (daughter ions), m/z = 70 and 80, the onset of which is displayed in Figure 9.

![Figure 9](image)

**Figure 9.** Appearance energies, calculated following Berkowitz[43] procedure, of CXO’s two dissociative ionization fragments

Other daughter ions seen in the spectrum are m/z = 46, 58, 68, 84, and 97, but their signals are about 67 times smaller than the parent and about 5 times smaller than the daughter ions m/z = 70 and 80. The m/z = 70 and 80 daughter ion’s intensity is approximately 13 times smaller than the parent. The onset of the appearance energy, obtained following the Berkowitz[43] procedure, for m/z = 70 is 10.4 ± 0.1 eV, whereas that of m/z = 80 is about 9.6 ± 0.1 eV.
To further this investigation, as completed with CPO, possible fragment identifications are carried out through appearance energy calculations of various structures (Table 6) but most resulted in energies that are too high (>11eV) to be considered.

**Table 6.** Possible photoionization dissociative fragments of CXO with their respective calculated appearance energies in eV.

<table>
<thead>
<tr>
<th>m/z 70</th>
<th>Neutral fragment (m/z 28)</th>
<th>Structure</th>
<th>Appearance Energy (eV±0.05)</th>
<th>m/z 80</th>
<th>Neutral fragment (m/18)</th>
<th>Structure</th>
<th>Appearance Energy (eV±0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td></td>
<td><img src="image" alt="CO" /></td>
<td>10.48</td>
<td>H₂O</td>
<td></td>
<td><img src="image" alt="H₂O" /></td>
<td>10.48</td>
</tr>
<tr>
<td></td>
<td>1-pentene</td>
<td><img src="image" alt="1-pentene" /></td>
<td>10.74</td>
<td></td>
<td>cyclohexa-1,4-diene</td>
<td><img src="image" alt="cyclohexa-1,4-diene" /></td>
<td>11.06</td>
</tr>
<tr>
<td></td>
<td>cyclopentane</td>
<td><img src="image" alt="cyclopentane" /></td>
<td>9.92</td>
<td></td>
<td>cyclohexa-1,3-diene</td>
<td><img src="image" alt="cyclohexa-1,3-diene" /></td>
<td>12.25</td>
</tr>
<tr>
<td></td>
<td>2-pentene</td>
<td><img src="image" alt="2-pentene" /></td>
<td>10.60</td>
<td></td>
<td>cyclohexyne</td>
<td><img src="image" alt="cyclohexyne" /></td>
<td>10.55</td>
</tr>
<tr>
<td></td>
<td>methylcyclobutane</td>
<td><img src="image" alt="methylcyclobutane" /></td>
<td>10.00</td>
<td></td>
<td>(E)-hex-2-en-4-yne</td>
<td><img src="image" alt="hex-2-en-4-yne" /></td>
<td>10.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(E)-hexa-1,2,4-triene</td>
<td><img src="image" alt="hexa-1,2,4-triene" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,2-dimethylcyclopropane</td>
<td><img src="image" alt="1,2-dimethylcyclopropane" /></td>
<td>10.45</td>
<td></td>
<td>3-methylenecyclopent-1-ene</td>
<td><img src="image" alt="3-methylenecyclopent-1-ene" /></td>
<td>9.31</td>
</tr>
<tr>
<td></td>
<td>ethylcyclopropane</td>
<td><img src="image" alt="ethylcyclopropane" /></td>
<td>10.93</td>
<td></td>
<td>1,3-dimethylenecyclobutane</td>
<td><img src="image" alt="1,3-dimethylenecyclobutane" /></td>
<td>11.16</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>buta-1,3-dien-2-ol</td>
<td><img src="image" alt="buta-1,3-dien-2-ol" /></td>
<td>10.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

110
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Log P</th>
<th>Compound</th>
<th>Structure</th>
<th>Log P</th>
</tr>
</thead>
<tbody>
<tr>
<td>buta-2,3-dien-2-ol</td>
<td><img src="image" alt="buta-2,3-dien-2-ol" /></td>
<td>11.40</td>
<td>1-ethylclobuta-1,3-diene</td>
<td><img src="image" alt="1-ethylclobuta-1,3-diene" /></td>
<td>11.08</td>
</tr>
<tr>
<td>but-3-yn-1-ol</td>
<td><img src="image" alt="but-3-yn-1-ol" /></td>
<td>13.00</td>
<td>1-methyl-2,3-dimethylene</td>
<td><img src="image" alt="1-methyl-2,3-dimethylene" /></td>
<td>11.75</td>
</tr>
<tr>
<td>but-2-yn-1-ol</td>
<td><img src="image" alt="but-2-yn-1-ol" /></td>
<td>12.73</td>
<td>1-ethynyl-2-methylcyclopropane</td>
<td><img src="image" alt="1-ethynyl-2-methylcyclopropane" /></td>
<td>11.36</td>
</tr>
<tr>
<td>but-3-en-2-one</td>
<td><img src="image" alt="but-3-en-2-one" /></td>
<td>11.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylcyclopropanone</td>
<td><img src="image" alt="2-methylcyclopropanone" /></td>
<td>11.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclobutanone</td>
<td><img src="image" alt="cyclobutanone" /></td>
<td>11.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclobut-2-enol</td>
<td><img src="image" alt="cyclobut-2-enol" /></td>
<td>10.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylene)cyclopropane</td>
<td><img src="image" alt="2-methylene)cyclopropane" /></td>
<td>12.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-methyl-2H-oxete</td>
<td><img src="image" alt="3-methyl-2H-oxete" /></td>
<td>11.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-but-2-enal</td>
<td><img src="image" alt="2-methylene)cyclopropane" /></td>
<td>11.77</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For \( m/z = 70 \), a loss of carbon monoxide (\( \text{CO}^n, m/z = 28 \)) or ethylene (\( \text{C}_2\text{H}_4^n, m/z = 28 \)) would take place, leaving \( \text{C}_5\text{H}_{10}^+ \) or \( \text{C}_4\text{H}_6\text{O}^+ \), respectively. For this mass, however, the most likely loss would be carbon monoxide since these calculated appearance energies are found to be closest to the experimental onset. Based on photolysis studies executed by Norrish et al.\(^{[14]}\), the most likely decomposition pathway of cyclohexanone yielded cyclopentane and carbon monoxide (92%), and a small amount (8%) of ethylene and propylene that resulted from the breakdown of cyclopentane. A later study\(^{[15]}\) provided a mechanism in which CO is eliminated, leaving a diradical, which would isomerize to 1-pentene. That same investigation\(^{[15]}\) showed that the primary, temperature independent, products were carbon monoxide, 1-pentene, and cyclopentane with minor products ethylene and propylene. As temperature increased the yields of carbon monoxide, 1-pentene, and cyclopentane also increased. A later investigation\(^{[16]}\), which sought to correct the findings of Norrish et al.,\(^{[14,15]}\) discovered that the remaining \( \text{C}_5\text{H}_{10} \) was a mixture of 1-pentene and cyclopentane. Possible structures for \( m/z = 70 \) in this experiment, highlighted in Table 6, would be 1- and/or 2-pentene and/or 1,2 dimethycyclopropane, with calculated appearance energies of \( 10.30 \pm 0.05 \text{ eV} \), \( 9.92 \pm 0.05 \text{ eV} \), and \( 10.00 \pm 0.05 \text{ eV} \), respectively.
A recent computational study performed by Zaras et al. [8] showed varying unimolecular decomposition pathways of cyclohexanone. This study found that CO elimination left 1-pentene and ethylene elimination left buta-1,3-dien-2-ol.

For m/z = 80 only a loss of water (H₂Oⁿ, m/z=18) would be possible leaving C₆H₈⁺, in agreement with a previous study. [60] Zaras et al. [8] also found that energetically, a loss of H₂O could be possible and left cyclohexyne. Possible structures for this fragment can be seen in Table 6. Those with calculated appearance energies that match the experimental onset are 3-methylenecyclopent-1-ene, with a calculated appearance energy of 9.34 ± 0.05 eV and 5-methylcyclopenta-1,3-diene with a calculated appearance energy of 9.46 ± 0.05 eV. Appearance energies are also found for structures that are like those calculated for m/z = 70. For example, hexa-1,2,4-triene’s structure is like pentene’s (m/z = 70) structure but results in an appearance energy of 10.43 ± 0.05 eV, which is too high to be considered in this investigation.

Both cyclohexanone and cyclopentanone have similar molecular structures with the exception that cyclohexanone has an extra -CH₂ group, which could cause a shift to a lower ionization energy. It is found in this investigation that the ionization energy of CPO is 0.11 eV higher than that of CXO. The same trend is seen with the difference of orbital energies between HOMO and HOMO-1, with CPO having a second spectral band 0.30 eV higher than that of CXO (figures 2 and 6). Comparison of the two molecule’s bond lengths show that the removal of an electron is from a σ bonding orbital localized on the α carbon bonded to the carbonyl group. In both molecules, the α carbon’s bond length to the carbonyl carbon increases from the neutral to cationic structure and the carbonyl group shortens, but the bond lengths of CXO stretch and compress to a larger extent than CPO. The overall photoionization cross section shape of both molecules is similar, but at 11 eV the cross section of CPO is 24.70 Mb while that of CXO is 22.72
Mb. The possible identifications for the dissociative ionization fragments for both are similar in structure, for at least $m/z = 70$ (CXO) and $m/z = 56$ (CPO). Both these fragments arise from a possible loss of carbon monoxide and appearance energies that are close to the experimental onset are 2-pentene and 2-butene, respectively.

4.7 Conclusions

Photoionization cross sections for both cyclopentanone and cyclohexanone are presented with their respective adiabatic ionization energy and description of their daughter ions. The CBS-QB3 calculated values for the adiabatic ionization energies agree well with the experimental values. Using Koopmans’ Theorem with the calculated molecular orbital energies, first cationic excited states are determined, but could not be observed since they are out of the current experimental energy range. Calculations for possible dissociative fragment structures have also been carried out for both molecules and are compared with literature findings to help identify both the neutral and cationic dissociative fragments.

4.8 Acknowledgements

The author thanks the American Chemical Society’s Petroleum Research Grant # 56067-UR6 and Dr. Taajtes and Osborn from Sandia National Laboratories for the use of the experimental apparatus located at the Advanced Light Source (ALS) of the Lawrence National Laboratory. The ALS is supported by the Director, Office of Science, and Office of Basic Energy Sciences of the U.S. Department of Energy under Contract # DE-AC02-05CH11231. The authors would also like to give thanks to the University of San Francisco’s Faculty Development Fund and Professors Karney and Castro for their use of the USF chemistry computer cluster.
4.9 References

17. F. E. Blacet and A. Miller. The photochemical decomposition of cyclohexanone, cyclopentanone, and cyclobutanone. Uni. CA. LA. 1957,


Chapter 5: Cl-initiated oxidation of propargylamine via synchrotron multiplexed photoionization mass spectrometry

5.1 Abstract

Propargylamine has been considered as a possible high-energy density fuel additive for rockets and jets. Its oxidation is initiated using chlorine radicals in the presence of oxygen at 298, 550, and 700 K, carried out at the Advanced Light Source at the Lawrence Berkeley National Laboratory. Products are distinguished based on their mass-to-charge ratio, ionization energy, and photoionization spectra. The CBS-QB3 composite model is used within the Gaussian09 program suite to optimize structures, determine the adiabatic ionization energies (AIE), scan potential energy surfaces to identify products and transition states.

5.2 Introduction

Increasing greenhouse emissions (GHG) expelled from urban and rural areas and transportation vehicles over the past decades make it imperative to develop alternative fuels to reduce both GHG and carbon dioxide (CO₂) emissions. The depletion of fossil fuels, likewise, creates unease towards future energy supplies and climate change.¹ To remedy this issue, biofuels are researched as both an alternative energy and fuel source.

Biofuels derived from sustainable biomass feedstock results in lower GHG emission than conventional fossil fuels and should not compete with food crop production.² Biofuels synthesized properly from (1) residual plants derived from agricultural waste, (2) crop residue, (3) harvested wood and forest debris, and (4) industrial waste supply an additional source of energy with lower GHG emissions.² We are interested in investigating biofuels acquired from biomass due to unknown possible influences of functional groups (alcohols, ethers, and esters) within the fuel that
may lead to soot, formation of pollutants, and particulate matter that are detrimental to the environment and an organism’s health.\textsuperscript{3-12} In addition, researchers need to consider the effect of heteroatoms such as nitrogen (N) and sulfur (S); both could lead to adverse combustion emissions.\textsuperscript{5, 13} Nitrogen is present in biomass structures\textsuperscript{14-17} and their pyrolysis results in an abundant amount of oxygenated products and small nitrogen-containing molecules (N\textsubscript{2}, HNCO, HCN, NO\textsubscript{2}, and C\textsubscript{2}N\textsubscript{2}); the oxidation of these structures, however, needs to be further explored.\textsuperscript{18-21}

Biofuel production from feedstock and biomass are both N dependent if a high energy yield is anticipated.\textsuperscript{22-23} The downfall of these processes is that N input leads to an excessive amount of reactive waste nitrogen, estimated to be \(\sim 65\) Tg N year\(^{-1}\) when combined with other sources (agricultural, livestock, and industrial).\textsuperscript{23-26} There is now a strong potential to use waste nitrogen in biofuel production (BPWN). BPWN compared to traditional biofuel production reduces GHG emissions because there is no need to treat waste reactive nitrogen, environmental N pollution, and reduces competition for agricultural crop land, maintaining fertile soil.\textsuperscript{24, 27} When BPWN is not used for biofuel production, it is used to renew soil fertility, which helps agricultural food.\textsuperscript{24} As an example, China produces \(\sim 18,291\) PJ year\(^{-1}\) of biofuel from feedstock and biomass, but when coupled with BPWN the potential biofuel production increases to \(21,595\) PJ year\(^{-1}\).\textsuperscript{24} This escalation in the production of biofuels shows that N containing biomass has great potential.

Scientists are also interested in high-energy density matter (HEDM) that shows promise for the creation of high-energy density (bio)fuels and (bio)fuel additives (HEDF/HEDFA).\textsuperscript{28-29} Energy density simply refers to the amount of energy stored in a compartment per unit volume of the storage facility, as in a fuel tank.\textsuperscript{29} If the energy density of a fuel is large, then more energy is stored and transported for the same amount of volume as conventional fuel. HEDM has high ratio
of energy output to density, which causes potential fuels to be extremely reactive. The energy density of potential HEDF made from HEDM is defined as the difference between the heat of formation ($\Delta H_f$) of starting materials and product per gram. Functional groups, such as acetylene, have been shown to increase the $\Delta H_f$ of starting materials without decreasing its energy density, while carbons and hydrogens improve energy density due to their successful combustion.\textsuperscript{28} Compounds with nitrogen, however, contribute less since the production of N\textsubscript{2} has a $\Delta H_{f,product}$ of 0 kcal mol\textsuperscript{-1}.

Other compounds (cubane, RP-1, quadracyclane), besides acetylene, under consideration for production of high-energy density fuels have their reaction enthalpies 1-3 times lower than acetylene. The closest compound to acetylene that has similar properties is cubane with a reaction enthalpy of 1,336 cal g\textsuperscript{-1} (C\textsubscript{8}H\textsubscript{8}), but its synthesis is complex and costly;\textsuperscript{28} therefore, it is of interest to explore other candidates for high-energy density fuels.

Other energetic fuels mirror acetylene’s structure, but use propyne (C\textsubscript{3}H\textsubscript{4}) as a precursor to nitrogen (derivatives of ammonia (NH\textsubscript{3})) containing propargylics.\textsuperscript{28} All nitrogen containing propargylic fuels produced reaction enthalpies comparable to cubane ($\Delta H_f > 1,000 \text{ cal g}^{-1}$) and acetylene.\textsuperscript{28} Elemental nitrogen (N\textsubscript{2}) has an exceptionally strong triple bond, which makes it arduous for industry to convert N\textsubscript{2} into anything useful. This idea may apply to nitrogen containing HEDM compounds. This study also notes that the incorporation of a heteroatom, N, into the structure improves energy density.\textsuperscript{28} Furthermore, the presence of a propargyl may also highly affect the reaction enthalpy and in turn the energy-density. One nitrogen containing compound in this investigation is propargylamine (PAM, C\textsubscript{3}H\textsubscript{5}N). When PAM undergoes combustion with oxygen its reaction enthalpy surpasses that of acetylene by 279 cal g\textsuperscript{-1} and is 1.7 times higher than cubane’s.\textsuperscript{28} PAM is easier to synthesize at a much lower cost than cubane and is much more stable.
than acetylene. PAM has shown promise as a HEDM fuel additive for hydrocarbon based fuels and it can be derived from biomass. Other properties of PAM make this HEDFA attractive. Chung et al. studied various jet fuels (JP-4, RJ-4, RJ-5, JP-9, JP-10) and noted that the flash point must be low in order to ease the flow and ignition of fuel and the specific gravity must be high in order to increase the heating values for these HEDFs.

Propargyl itself, however, is found to have resistance to pyrolysis at higher temperatures and slow reaction rates with oxygen, allowing large concentrations of propargyl radicals to exist. It has also been found that the absorption band of this radical at 330 nm is considerably weak making this species difficult to detect. Later studies performed by Slagle and Gutman explored the reaction of O2 and propargyl using a mass spectrometric method over the temperature range of 293-900 K. They discovered that at lower temperatures propargylperox radical form and at higher temperatures (380-430 K) there is an equilibrium between the peroxy radical and free O2 and propargyls, producing a ketene as a main product. At even higher temperatures (500-900 K), the main products become ketene and formyl radicals. All these reaction’s first step is the addition of O2 to the propargyl at a slow rate compared to related non-resonance stabilized hydrocarbon radicals.

Studies have also been performed on propargyl chloride and chlorine, by Atkinson and Hudgens, exposed to 351 nm laser light. This finding was confirmed by Atkinson and Hudgens in a later work, showing that at 351 nm laser light propargyl chloride remains inert while Cl2 dissociates into radicals. When the two are placed in the same reactor, chlorine radicals will react well with propargyl chloride adding to the center and terminal unsaturated carbon atoms.

This investigation will focus on the identification and characterization of products that result from Cl-initiated oxidation reactions of PAM in the presence of O2 at 298, 550, and 700 K.
5.3 Experimental Methodology

5.3.1 Apparatus

Experiments were performed using the third-generation synchrotron located in the Advanced Light Source (ALS) of the Ernest Orlando Lawrence Berkeley National Laboratory (LBNL) in Berkeley, CA. This multiplexed photoionization mass spectrometer (MPMIS) is both time- and energy-resolved, coupled with continuous and tunable synchrotron radiation provided by the ALS as the photoionization source. This is used to study reaction intermediates and products resulting from oxidation reactions; specifically, in this investigation the oxidation reaction of PAM + Cl + O₂ is studied. Only a brief overview of the experimental apparatus and setup is given here, but a more detailed description of the design and implementation can be found elsewhere.35-38 The reactant PAM (> 98.0%, Sigma Aldrich) is purified through the freeze-pump-thaw technique and is subsequently flowed into a gas cylinder until its concentration, in an excess of helium, composes about 1.5% (27.0 Torr PAM in 1776 Torr He). All gaseous reactants (PAM, Cl₂, and O₂) are introduced into a 62 cm long slow flow quartz reaction tube with an inner diameter of 1.05 cm and are regulated by calibrated mass flow controllers. Temperature of the reaction is adjusted from room temperature to higher temperatures by the 18 μm thick nichrome heating tape that wraps around the reaction tube. A Roots pump connected to the reaction cell maintains the pressure inside the reaction tube through a feed-back controlled throttle valve. Pressure inside the reaction tube is kept at 4 Torr at 298 K, 6 Torr at 550 K, and 7 Torr at 700 K. The Cl₂ precursor is photolyzed by a 4 Hz-pulsed, unfocused 351 nm (XeF) excimer laser. The number densities for the reactants are listed in table 1.
Table 1. Initial reactant concentration (molecules cm\(^{-3}\))\(^a\)

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>[PAM] (_0)</th>
<th>[O(_2)]</th>
<th>[Cl(_2)]</th>
<th>[Cl(^•)] (_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>2.52 X 10(^{13})</td>
<td>2.59 X 10(^{16})</td>
<td>2.07 X 10(^{14})</td>
<td>2.23 X 10(^{11})</td>
</tr>
<tr>
<td>550</td>
<td>6.97 X 10(^{13})</td>
<td>2.11 X 10(^{16})</td>
<td>2.25 X 10(^{14})</td>
<td>2.43 X 10(^{11})</td>
</tr>
<tr>
<td>700</td>
<td>7.00 X 10(^{13})</td>
<td>1.96 X 10(^{16})</td>
<td>1.82 X 10(^{14})</td>
<td>1.96 X 10(^{11})</td>
</tr>
</tbody>
</table>

\(^a\)Helium was added to reach a total pressure of 4 Torr, 6 Torr, and 7 Torr for 298, 550, and 700 K experiments, respectively.

When Cl\(_2\) is photolyzed, two Cl atoms result according to the following reaction:

\[
\text{Cl}_2 \xrightarrow{h\nu=351\,\text{nm}} \text{Cl}^*  \quad \text{(R1)}
\]

The quantum yield of the Cl\(_2\) photolysis is 1.00, as recommended by the IUPAC Subcommittee for Gas Kinetic Data Evaluation,\(^{39}\) whereas the absorption cross section at 351 nm is found as 1.82 X 10\(^{-19}\) cm\(^2\) determined by Maric et al.\(^{40}\) Based on the quantum yield value and the absorption cross section, the number density for Cl atoms after photodissociation is presented in table 1.

The reaction species flow through a 650 µm opening on the side of the reactor and are skimmed into the differentially vacuumed ionization region of the apparatus. The molecular beam is orthogonally intersected by continuous vacuum ultraviolet synchrotron radiation, which photoionizes the gaseous species according to their respective ionization energy. Ions are accelerated, collimated, and focused towards the detector of an orthogonal time-of-flight (TOF) mass spectrometer pulsed at 50 kHz, providing a mass resolution of roughly 1600 with the current setup.

During the reaction mass-to-charge ratio (m/z), ion intensity (I), and reaction time (ms) are recorded simultaneously as the photon energy (E) is varied from 9-11 eV at increments of 0.025
eV. At each photon energy step, the prephotolysis signal is background subtracted and normalized by the ALS photocurrent measured by a calibrated photodiode. Ion intensities are integrated over a photon energy range (9-11 eV for 298 and 550 K and 8.3-11 eV for 700 K) to create a kinetic plot for a specific m/z. When the photolysis (excimer) laser is fired, the reaction starts at t = 0 ms. Per contra, when the ion signal of a specific m/z is integrated over a definite time range (in this investigation 0-90 ms at 298 K, and 0-60 ms at 550 and 700 K), a photoionization spectrum results. The time range is selected to try to avoid the inclusion of signal coming from secondary chemistry. Reaction species are identified through comparison of the experimental photoionization spectra to its literature, measured, or calculated spectra counterpart. Photoionization spectra are unique to each species, including isomers, due to differences in vibrational modes and geometries, and, therefore, Franck-Condon (FC) factors, and are essential tools to distinguish and characterize reaction species. Furthermore, the adiabatic ionization energy (AIE) of photoionization spectra is determined by a linear extrapolation of its initial onset. The uncertainty associated with reported adiabatic ionization energies is estimated to be 0.05 eV as a result of the photon energy step size, the possible presence of hot bands, and energy resolution.

5.3.2 Computational Methods

Adiabatic ionization energies are essential to characterize unknown products and can be found using electronic structure calculations of their neutral and cationic states. The CBS-QB3 composite model, within the Gaussian 09 program, is used to optimize bond lengths, harmonic vibrational frequencies, force constants, and energetics of products. The adiabatic ionization energy of a product can then be found by using the difference between zero-point vibrational (ZPE) corrected total electronic energies ($E_0$) of the ground electronic states of the neutral and cationic molecules. All calculations are carried out using the CBS-QB3 composite
model because it provides accurate energy calculations at a low computational cost. This composite model also has a reported mean average deviation (MAD) of 4-5 kJ mol\(^{-1}\) (0.05 eV)\(^{42-43}\) for the energetics. ZPE corrected total electronic energies are also helpful in other areas: (1) in finding enthalpies of reaction \(\Delta_r H^0\) to establish that possible mechanisms are thermodynamically achievable (exothermic); (2) another application is in association with available literature enthalpies of formation \(\Delta_f H^0\) and \(\Delta_f H^0_{298}\) of the elements in the gas phase, which, in turn, are used to calculate the enthalpy of formation at 0 or 298 K of the reaction species, following the atomization reaction:

\[
C_xH_yO_z(g) \rightarrow zC(g) + yH(g) + zO(g), \text{where } \Delta_{at} H^0 = xE_0(C) + yE_0(H) + zE_0(O) - \\
E_0(C_xH_yO_z) = x\Delta_f H^0(C, g) + y\Delta_f H^0(O, g) - z\Delta_f H^0(O, g) - \Delta_f H^0(C_xH_yO_z, g)
\]

Furthermore, relaxed potential energy surface scans (PES) are completed at the B3LYP/6-31G(d) level of theory to discover possible transition states (saddle points) and minima. Both are then optimized using the CBS-QB3 composite model and confirmed through intrinsic reaction coordinate (IRC) calculations for the forward/reverse reaction mechanisms. Any new minima were re-optimized to validate their energy.

If there is no literature photoionization spectrum of a reaction species, a Franck-Condon (FC)\(^{45-48}\) and Franck-Condon-Herzberg-Teller (FCHT)\(^{47}\) are used within the Gaussian 09\(^{44}\) program, to simulate a photoelectron spectrum (PE) by approximating FC factors for the vibronic transition from the neutral to cationic state of the studied molecule. The FC overlap integrals are calculated using a set of recursive formulas established by Ruhoff,\(^{50}\) which are based on the Sharp-Rosenstock\(^{51}\) and Lermé\(^{52}\) methods. Once a calculated PE spectrum is completed, it is integrated and yields a simulated photoionization spectrum.
5.4 Results and Analysis

This investigation mimics the autoignition process carried out in a homogenous charge compression ignition engine (HCCI). Autoignition generates radicals that abstract a hydrogen from a fuel molecule. Figures 1-3 shows the mass spectra for the Cl initiated oxidation of PAM with background subtraction at all three temperatures. The three figures have the relative ion intensity of the reactant omitted. In this investigation, there are two reactants present dictated by the negative ion signal: PAM ($m/z = 55$) and chlorinated PAM (PAM-Cl, $m/z = 89$), the latter of which has an extremely large signal (1.2x at 298 K, 17x at 550 K, and 40x at 700 K) compared to PAM. This additional reactant is created by the reaction between Cl$_2$ and PAM before the laser hits Cl$_2$ to generate Cl radicals.

**Figure 1.** Background subtracted mass spectrum of reactants PAM $m/z = 55$ and Chlorinated PAM ($m/z = 89$) at 298 K over the photon energy range 9-11 eV. Inset shows the large negative signals of $m/z = 89$ and $m/z = 55$. 
Figure 2. Background subtracted mass spectrum of reactants PAM $m/z = 55$ and Chlorinated PAM ($m/z = 89$) at 550 K over the photon energy range 9-11 eV.

Figure 3. Background subtracted mass spectrum of reactants PAM $m/z = 55$ and Chlorinated PAM ($m/z = 89$) at 700 K over the photon energy range 8.3-11 eV.
In this study, chlorine radicals abstract a hydrogen from PAM to initiate the oxidation reaction. Also, the reaction of PAM-Cl must be considered to explain the species observed in the mass spectra (figures 1-3). Bond dissociation energies (BDE) determine the strength of a chemical bond and are calculated at the CBS-QB3 level to determine the enthalpy change to find an energetically feasible radical.

\[ BDE = E_{radical} + E_{hydrogen} - E_{molecule} \]  

(1)

The BDE$_{0K}$ of HCl is 103.42 ± 0.05 kcal mol$^{-1}$, which in combination with the other thermodynamic quantities reveals that hydrogen removals from PAM by the Cl radical are exothermic.$^{54}$

![Scheme 1](image)

**Scheme 1.** Adiabatic Bond Dissociation Energies (BDE) at 0 K of PAM calculated using the CBS-QB3 composite model.

BDEs of PAM are shown in scheme 1. When the sp$^3$ C-H bond is broken, it results in the smallest enthalpy (328 mol$^{-1}$), which shows that the C-H bond is easily broken compared to the N-H bond.
and the C(sp)-H bond. The sp carbon and its bound hydrogen contains sp hybridization with substantially increases the BDE due to its strong covalent bond. This BDE results in an enthalpy of 560 kJ mol\(^{-1}\).

Oxidation of PAM at the three temperatures is initiated by a hydrogen abstraction from either a C-H or N-H bond, which leads to the formation of an initial radical.\(^6\) The reaction of the initial radical (R) with \(\text{O}_2\) forms propargylperoxy species (RO\(_2\)), which either lose HO\(_2\) or OH through internal hydrogen abstraction.\(^55\) The reaction should be exothermic (\(-\Delta H\)) for both the hydrogen abstraction and reaction with \(\text{O}_2\) to yield 2 propargylperoxy radicals, as depicted in scheme 2.

Scheme 2. Reaction diagram of the initiation of oxidation of PAM. Numbers in parentheses represent enthalpy of reaction (kJ mol\(^{-1}\)) calculated at the CBS-QB3 level.

The third route does not yield the propargylperoxy radical because the hydrogen abstracted from the sp carbon by Cl is endothermic and unimportant compared to PAM_C and PAM_N. The most favorable reaction is found to be PAM_C with an enthalpy of -183.1 kJ mol\(^{-1}\) followed by PAM_N.

Chlorinated species, in this investigation, are formed through secondary reactions, such as addition to unsaturated carbon bonds, and are identified through their isotopic distribution of \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\)-containing species. This distribution produces identical photoionization spectra and time
profiles. The identification of chlorinated products, however, is not of importance to this study, but their presence in experimental data must be kept in mind. Considering previous findings,\textsuperscript{31, 34} it can be assumed that chlorine is a reactive species, and in this study may both add easily to the starting structure before the laser light hits and chlorine radicals may continue to add to more species. Scheme 3 presents the addition of Cl\textsubscript{2} to PAM (before light hits) to form PAM-Cl (m/z = 89).

Scheme 3. Reaction diagram of the Cl\textperiodcentered addition to starting structure PAM. Numbers in parentheses represent enthalpy of reaction (kJ mol\textsuperscript{-1}) calculated at the CBS-QB3 level.

Since all reaction enthalpy values are negative, this species (m/z = 89) is formed readily and it is considered as a starting reactant as well in the investigation. This is also proved by its depleting experimental time trace and photoionization spectrum. m/z = 91 is also present in the correct isotopic ratio, confirming m/z = 89 as an additional reactant.

Considering both m/z = 55 (PAM) and m/z = 89 as reactants (PAM-Cl), products result from both. m/z = 55 results in products at m/z = 53 and 69 at 298 K, m/z = 43 and m/z = 53 at 550 K, and m/z = 43 and 53 at 700 K. At all three temperatures, the PI spectrum of m/z = 53 matches
the simulated PI spectrum of C$_3$H$_3$N (Figure 4) well, but to our knowledge there is no literature spectrum for this species.

**Figure 4.** PI plot of $m/z = 53$ experimental PIE superimposed onto FC simulated PI spectrum at 298 K (a), 550 K (b), and 700 K (c) with structure of product in the inset.

The experimental onset of $m/z = 53$ at all three temperatures is 9.90 ± 0.05 eV, in good agreement with the FC simulated PI curve for 2-propyne-1-imine. The calculated AIE for this product is 9.92 eV. At 298 K, only one other product is seen at $m/z = 69$; many FC PI curves for various structures were simulated, but none fully matched the onset of the experimental PI curve. The closest onset result is displayed in Figure 5.
Figure 5. PI plot of $m/z = 69$ superimposed onto FC simulated PI spectrum at 298 K with structure in the inset.

The other possible molecule, depicted in Figure 6, has a calculated AIE of 9.36 eV, much closer to the experimental onset of 9.25 eV, than the structure in the inset of Figure. The simulated F.C. PI spectrum of this molecule, however, resulted in an onset of 9.7 eV and was therefore disregarded in this experiment.

Figure 6. Initially possible structure for $m/z = 69$ with AIE of 9.36 $\pm$ 0.05 eV.

As previously mentioned, O$_2$ has a slow reaction rate with propargylic compounds and it is believed that in this investigation the other starting reactant, PAM-Cl, reacts more readily than PAM.
At 298 K, this would result in speculated chlorinated products forming, seen in the correct isotopic ratios in both time traces and photoionization spectra. Some examples are observed at \( m/z = 123/125/127 \) (PAM-Cl + Cl), 119/121 (PAM-Cl + O\(_2\)), 104/106 (PAM-Cl + O), 141/143 (PAM-Cl + product \( m/z = 53 \)), 87/89 (product \( m/z = 53 + Cl \)) and 157/159 (PAM-Cl + product \( m/z = 69 \)). Many other species are seen in this experiment and can be attributed to further reactions of PAM-Cl with chlorine and oxygen.

At 550 K all masses seen at 298 K are also present, except \( m/z = 69 \). In addition, there is the presence of \( m/z = 52 \), which can be considered a dissociative ion of \( m/z = 89 \) because the time slope of \( m/z = 52 \) matches \( m/z = 89 \) perfectly and its ionization energy is about 0.55 eV higher than \( m/z = 89 \)’s. \( m/z = 43 \) is also detected at this temperature, but all optimizations and Franck-Condon simulations carried out on CHNO structural isomers resulted in adiabatic ionization energies (10.54 - 11.9 eV) that were too high to match the experimental onset of 9.5 eV. Other observed masses at this temperature may come from either further reactions of PAM/PAM-Cl plus chlorine and reactions of PAM-Cl with products arising from PAM. \( m/z = 69 \) (a product at 298 K) is not detected, but \( m/z = 103/105 \) is observed, suggesting \( m/z = 69 \) undergoes a reaction with chlorine. Masses 74/76 are too observed and prove to be chlorinated due their \(^{35}\text{Cl}/^{37}\text{Cl} \) isotopic ratio, and thus can be omitted from this investigation.

At 700 K detected masses include \( m/z = 43 \) and 53 as well as those from 298 K (minus \( m/z = 69 \)) and 550 K. As mentioned before, the signal of PAM and PAM-Cl at this temperature is extremely low, the latter being larger than the former. In addition, \( m/z = 79/81 \) is observed and are both depleting and chlorinated. \( m/z = 111/113/115 \) are also detected and may come from the reaction of \( m/z = 79 + Cl \), but there is also the presence of \( m/z = 79/81 \) which are both depleting and are chlorinated.
**Postulated mechanism**

$m/z = 53$ is the only confirmed product that arises from the species studied in this investigation, because higher masses and lower masses are chlorinated and possibly arise from the reaction of the other additional reactant $m/z = 89$. Figure 7 displays the proposed mechanism for $m/z = 53$.

**Figure 7.** Decomposition pathway for $m/z = 53$. Green line indicates energy level of PAM + O₂. All subsequent species are deemed thermodynamically favorable.

The PAM_C radical in figure 7 arises from the PAM reaction with oxygen to form a peroxy radical. The calculated enthalpy for this step is $-183$ kJ mol$^{-1}$. This species then undergoes an intramolecular hydrogen abstraction from nitrogen that results in an HO₂ loss, and product enthalpy around $-256$ kJ mol$^{-1}$. Multiple other scans were carried out to find other potential products, but resulting masses were either not seen in experimental data or proved to be chlorinated. Because of these discrepancies, branching fractions could not be measured for this experiment.
5.5 Conclusions

This experiment was carried out at the Lawrence Berkeley National Laboratory using synchrotron radiation to form chlorine radicals, which initiated the oxidation reaction of PAM at 298, 550, and 700 K. Only one product \((m/z = 53)\) was found, and proven, at all three temperatures that came directly from PAM. The other products, \(m/z = 69\) (298 K) and \(m/z = 43\) (550 and 700 K), could not be determined. All other products detected arose from the other starting reactant, PAM-Cl. This species is considered as a starting reactant due its presence before the laser hits to create chlorine radicals. PAM-Cl is extremely reactive compared to PAM with its experimental signal being much stronger than PAM’s and its presence in the mass spectrum as well. This may be why a variety of the masses in the experiment are chlorinated. Theoretical calculations are performed at the CBS-QB3 level to provide possible reaction mechanisms FC simulations. Only the formation of \(m/z = 53\) was proved.

5.6 Acknowledgements

This work was supported by the American Chemical Society, Petroleum Research Fund Grant 56067-UR6, as well the University of San Francisco (USF) Faculty Development Fund. Thanks is also extended to Dr. Karney and Dr. Castro for the use of their USF computer cluster. Finally, this work could not be completed without the experimental apparatus from the Sandia National Laboratories.
5.6 References


47. Santoro, F.; Lami, A.; Improta, R.; Barone, V., Effective method to compute vibrationally resolved optical spectra of large molecules at finite temperature in the gas phase and in solution. *Journal Chemical Physics* 2007, 126 (18), 184102.


Chapter 6: Computational Investigation of LiF Containing Hypersalts

6.1 Introduction

Salt formation depends on the use of charged moieties, i.e., cation and anion, such as alkali metals (electron donors) and halogens (electron acceptors). Their distinct properties are the foundation of novel materials.¹ For both, the valence (outer-shell) electrons follow the octet rule causing the outermost s and p orbitals to be full.² Group 1 alkali are characterized by low ionization energies (IE’s), Li (5.39 eV), Na (5.14 eV), K (4.34 eV), Rb (4.18 eV), and Cs (3.89 eV),³⁻⁴ whereas halogens possess large electron affinities (EA’s) with the topmost being Cl with an EA of 3.61 eV.⁵ Gutsev and Boldyrev⁴ investigated the possibility to create structures with lower IE’s and devised the formula M<sub>k+n</sub>L, where M represents the alkali metal atom, k the valence of the central atom M, with n being an integer greater than 1. Gustev and Boldyrev defined these species superalkalis because of their IE’s lower than the corresponding alkali elements.⁴ They adopted the same concept for the creation of species with large EA’s, and developed a formula to design superhalogens, following MX<sub>k+1</sub>, where M is the metal atom with valence k and X is a halogen atom.⁴,⁶⁻⁷ These species possess an EA surpassing those of halogens, specifically chlorine,⁵,⁸ are excellent oxidizing agents, and are weak coordinating anions.⁴,⁹ Both superalkalis and superhalogens have been studied due to their noteworthy potentials such as chemical bonding and nonlinear optical properties.²,¹⁰⁻¹⁷

Examples of superalkalis that have been studied are XLi₂ (X = F, Cl, Br, I)¹⁸ and OM₃ (M = Li, Na, K).¹⁹ Because of alkali metal’s strong electron donating character, they may violate the octet rule, forming hypervalent “superatom” clusters. The electropositive character of the alkali metals within superalkalis causes a delocalization of electrons leading to an increased electron
Various structures of superalkalis with similar or lower IEs than an alkali metal atom are building blocks for original nanostructured materials.\(^2\)

Comparable to alkali metals, the strong electronegativity of halogens in a compound may exceed the maximum valence of the metal atom, causing the extra electron to become delocalized over the halogen atoms, stabilizing the anion.\(^8\) These superhalogens possess a high EA making them appropriate as oxidizing agents, biocatalysts, and organic superconductors.\(^{21-23}\) Conversely, Reddy and Giri\(^{24}\) define a superhalogen as a compound with an electron affinity greater than Cl (\(>3.6\) eV). Past experiments performed by Lai-Sheng Wang \textit{et al}.\(^{10, 25-26}\) indicate the existence of superhalogens via anion photoelectron spectroscopy.

Using superalkalis as cations and superhalogens as anions the two combine to form \textit{supersalts}, analogous to ionic salts consisting of alkali cations and halogen anions.\(^9, 20\) This is possible because superalkalis possess great reducing properties allowing for the interaction with compounds containing high EAs to create charge-transfer salts. These species dissociate into ionic parts instead of neutral parts, as seen with alkali halides.\(^{27-29}\) Most developed supersalts, however, are formed using a metal cation core with superhalogen ligands. These include: CsAuF\(_6\) (Cs\([\text{AuF}_6]\))\(^{23}\) and KMnO\(_4\) (K\([\text{MnO}_4]\))\(^7\) in which the alkali metal is the cation core and the superhalogen is the anion. Supersalts have unique properties, such as enhanced non-linear optical responses and show potential for the use in energy storage and energy conversion materials, Li-ion batteries, and hybrid perovskite solar cells.\(^{30-32}\)

Investigations into species termed \textit{hyperhalogens} have gained interest due to their high EA, surpassing that of superhalogens.\(^8, 24, 33\) Hyperhalogens are formed using metal atom surrounded by superhalogens whose number exceeds the valence of the metal atom (M) by one, following the formula MY\(_{m+1}\), where M is the metal atom and Y is the superhalogen.\(^3, 34\) EA’s and vertical
detachment energies (VDE’s) of hyperhalogens are larger than the respective superhalogen building block. \(^9,33,35\) Implementing the same concept, hyperalkalis should be made up of a halogen surrounded by two superalkalis and should possess a lower AIE of the respective superalkali building block. To our knowledge, hyperalkalis have not been studied yet.

A new class of species, termed hypersalts, is constructed from a hyperhalogen anion counterbalanced by a metal cation, resembling the construction of a supersalt. \(^36-37\) These hypersalts have recently gained interest as several have been synthesized experimentally and have displayed some unusual properties. For example, at room temperature, the hypersalt KAl(BH\(_4\))\(_4\), synthesized by Knight \textit{et al.} \(^38\) is a stable solid, while, Al(BH\(_4\))\(_3\) is an ionic liquid and highly volatile and pyrophoric under the same ambient conditions. \(^9\) This category can be fundamental in the manufacturing of superoxidizing agents with enhanced magnetic properties to develop innovative new materials. \(^34,39-40\)

This work explores possible designs of novel hypersalts using the superalkali Li\(_2\)F and superhalogen LiF\(_2\) as building blocks for possible hyperalkalis and hyperhalogens. Although the definition for a hypersalt is vague, \(^37,41\) it is constructed by using a hyperhalogen anion and alkali metal, with little to no defining properties. In this study, possible combinations of hypersalts include: hyperhalogen plus alkali metal, hyperalkali plus halogen, hyperalkali plus hyperhalogen, hyperhalogen plus superalkali, and hyperalkali plus superhalogen. The last three of the series will be explored in the future.

\textbf{6.2 Theoretical Methods}

\textbf{6.2.1 Computational Methodology}

All \textit{ab initio} quantum chemical calculations are carried out using the Gaussian09 \(^42\) suite of programs and structures are visualized using \textit{GaussView} \(^5\). \(^43\) The CBS-QB3 composite method of Petersson and co-workers \(^44-45\) is originally used to perform all computations, but the geometry
optimization and vibrational frequency analysis steps are instead carried out using the Pople basis set 6-311+G(2d,d,p) (which is referred to as CBSB7+), rather than the 6-311G(2d,d,p) basis set, which does not include diffuse functions that are needed to evaluate molecular interactions between strongly electronegative (EN) and leftover atoms. These calculations do not necessarily provide optimized structures different from the “original” CBS-QB3 structures.

To keep the general CBS-QB3 composite\textsuperscript{35} computational structure, while adding diffuse functions in geometry optimizations, calls for the development of a multistep job that follows the same setup of the CBS-QB3 model and use of a density functional\textsuperscript{46} method for geometry optimizations and frequency steps. Like CBS-QB3, this method uses the popular density functional method of Becke’s hybrid 3-parameter exchange functional combined with the correlation functional of Lee, Yang, and Parr (B3LYP).\textsuperscript{46-47} This method is then combined with the CBSB7+ basis set for the geometry optimization and vibrational frequency analysis steps. All remaining parts of the job remain the same as those described for the CBS-QB3 model, and so this method will be referred to CBS-QB3+. This procedure parallels a previous study by Martin and co-workers\textsuperscript{48} who defined this change to the CBS-QB3 method. The mean average deviation (MAD) of this method is taken to be approximately the same as the CBS-QB3 method, 4-5 kJ mol\textsuperscript{-1}, at least for neutrals.\textsuperscript{49-50} For the purpose of clarity, the sequence of methods used in the calculations are outlined as follows:

1. B3LYP/CBSB7+: Geometry optimization
2. B3LYP/CBSB7+: Vibrational frequency analysis using geometry from step 1
3. CCSD(T)/6-31+G(d): Single-point energy using geometry and data taken from steps 1-2
4. MP4SDQ/CBSB4: Single-point energy using data from previous steps
5. MP2/CBSB3: Single-point energy and CBS extrapolation using data from previous steps
The zero-point corrected (ZPE) total electronic energy ($E^o$) is then calculated manually using data from steps 2 and 5, following the procedure outlined for CBS-QB3.44

Adiabatic ionization energies (AIE’s) are calculated using the energy difference between the ground state cation and neutral optimized structures.

$$\text{AIE}_{\text{super/hyperalkali}} = \Delta E = E^o_{\text{cat}} - E^o_{\text{neu}}$$

(1)

The AIE of the superalkali studied must be lower than the respective alkali metal, lithium (Li) with an IE of 5.4 ± 0.2 eV,51 whereas the AIE of hyperalkali must be lower than the respective superalkali.52 Adiabatic electron affinity (AEA), conversely, is defined as the energy difference between the ground state anion and the neutral geometries. This quantity is used to explore both superhalogens and hyperhalogens.8–9, 33

$$\text{AEA}_{\text{super/hyperhalogen}} = \Delta E = E^o_{\text{neu}} - E^o_{\text{an}}$$

(2)

AEA’s of superhalogens must be higher than chlorine atoms (> 3.6 eV),24,53 whereas others define superhalogens having AEAs higher than the respective halogen used. Hyperhalogens bear an AEA that is greater than its corresponding superhalogen building block.33

The frequency calculations, carried out at the same level of theory, B3LYP/CBSB7+, confirm that the ground state geometries having positive vibrational motions belong to a minima on the potential energy surface.8 Highest-unoccupied-molecular orbitals (HOMO) and lowest-unoccupied-molecular orbitals (LUMO) are generated to explore the stability of structures and it is found that those with larger HOMO-LUMO gaps are less reactive.2 Natural bond orbitals (NBO) are also explored in order to calculate the distribution of electron density within possible structures.53

In the case of hypersalts, the stability and bond energy (BE) of a salt is determined by the difference in energy between the two building moiety ions (hyperhalogen/alkali metal,
hyperhalogen/superalkali, hyperalkali/halogen, hyperalkali/superhalogen, and hyperhalogen/hyperalkali) and the salt structure. If the resulting energy is positive, this indicates that the salt cluster is stable with respect to its dissociation.

\[
BE = [E_{alkali}^+ + E_{hyperhalogen}^-] - E_{hypersalt}
\]  

(3)

\[
BE = [E_{alkali}^+ + E_{hyperhalogen}^-] - E_{hypersalt}
\]  

(4)

\[
BE = [E_{hyperalkali}^+ + E_{halogen}^-] - E_{hypersalt}
\]  

(5)

\[
BE = [E_{hyperalkali}^+ + E_{hyperhalogen}] - E_{hypersalt}
\]  

(6)

6.3 Results and Discussion

As mentioned previously, this investigation starts with the discussion of the building blocks that lead up to the construction of possible hypersalts, i.e., superalkali, superhalogen, hyperalkali, and hyperhalogens.

6.3.1 Superalkali

Experimental AIE for the superalkali is compared to the experimental ionization energy of lithium (Li), found as 5.40 ± 0.2 eV.\textsuperscript{31,51} Using the previously discussed computational procedure, the calculated AIE (Li) is 5.33 eV. In this study, two lithium atoms surround a fluorine atom forming dilithium fluoride, Li\textsubscript{2}F. The optimized neutral and cationic structures of this species are presented in Figure 1 with their corresponding bond lengths and angles. The neutral optimized geometry compares well to the Li-F bond lengths (1.70 Å), studied by Veličković \textit{et al.},\textsuperscript{18} but the Li-Li bond length differs by 0.84 Å. When compared to the neutral structure, the cationic structure adopts a linear geometry, with little deviation in the Li-F bond lengths (0.005 Å difference).
Figure 1. Optimized neutral and cation structures of superalkali Li$_2$F.

The experimental IE for Li$_2$F was measured using photoionization mass spectrometry by Yokoyama et al. as 3.78 ± 0.2 eV,$^{54}$ and Veličković et al.,$^{18}$ found the ionization energy experimentally for the same molecule as 3.80 ± 0.2 eV. Veličković et al.,$^{18}$ obtained this energy through a thermal ionization technique. The present calculated AIE of Li$_2$F is 3.89 eV, which is 1.44 eV lower than the Li atom and verifies that this species is indeed a superalkali. In a violation of the octet rule, this molecule contains 9 valence electrons, making this species hypervalent. The “extra” electron delocalizes over the lithium atoms to form a “cage,” surrounding the molecule with a negative charge. The HOMO of the neutral state shows how the “weakly” bound electron shared between the Li atoms is delocalized on the molecule. The HOMO and LUMO of both the neutral and cation are displayed in Figures 2 and 3, while differences in NBO charges are shown in Table 1.
HOMO-LUMO Gap
1.49 eV

Figure 2. HOMO (left) and LUMO (right) of the neutral superalkali Li$_2$F.

HOMO-LUMO Gap
9.58 eV

Figure 3. HOMO (left) and LUMO (right) of the cation superalkali (Li$_2$F).

Table 1. Differences in NBO charges between neutral and cation of the Li$_2$F superalkali.

<table>
<thead>
<tr>
<th></th>
<th>Li$_2$F</th>
<th>Li</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Neutral</strong></td>
<td>0.460</td>
<td></td>
<td>-0.920</td>
</tr>
<tr>
<td><strong>Cation</strong></td>
<td>0.975</td>
<td></td>
<td>-0.950</td>
</tr>
<tr>
<td><strong>Δ q</strong></td>
<td>0.515</td>
<td></td>
<td>-0.030</td>
</tr>
</tbody>
</table>
NBO’s show that the negative charge of the halogen atom, F, stays almost the same from the neutral to the cationic state, but there is an increase in positive charge of the Li atoms, showing from where the electron is removed.

The HOMO and LUMO gap can be used as an indicator for the stability of a structure.\textsuperscript{20,55} Other studies\textsuperscript{41,56-57} found that the larger the HOMO-LUMO gap, the more stable and less reactive the species is, which will later help determine the stability of various hypersalts. In this case, the HOMO-LUMO gap of the neutral superalkali is relatively small when compared to the HOMO-LUMO gap of the cation, which indicates an enhancement of stability for Li\(_2\)F in the ionic state.

6.3.2 Hyperalkali

To construct a hyperalkali, the same model used to make a hyperhalogen is followed, but a halogen replaces an alkali metal (F + 2 Li\(_2\)F). Two hyperalkali isomers with the formula Li\(_4\)F\(_3\) were found and optimized: a bent A and a cage B structure with AIE’s of 3.86 and 3.67 eV, respectively, illustrated in Figures 4 and 5. Bond lengths and angles of A are shown in Figure 4, but due to the complexity of B structure bond lengths and angles are shown in Table 2. Both AIE’s are lower than the superalkali building block, A by 0.03 eV and B by 0.22 eV, making the two species hyperalkalis. The neutral hyperalkali B is lower in energy than A by 23.1 kJ mol\(^{-1}\) (Table 3).
Figure 4. Optimized neutral (left) and cation (right) structures of hyperalkali A with corresponding bond lengths and angles displayed.

Figure 5. Optimized neutral (left) and cation (right) structures of hyperalkali B. The corresponding bond lengths and angles are presented in Table 2.

Table 2. Bond lengths and bond angles of neutral and cation of hyperalkali B.

<table>
<thead>
<tr>
<th>Hyperalkali</th>
<th>Bond</th>
<th>Neutral (Å)</th>
<th>Cation (Å)</th>
<th>Bond Angle Neutral (degrees)</th>
<th>Cation (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_{1/24}F_x</td>
<td>1.811</td>
<td>1.792</td>
<td>Li_x-Li_{1/24}-F_x</td>
<td>47.2</td>
<td>47.1</td>
</tr>
<tr>
<td>B. Li_{4}F_3</td>
<td>Li_{3}F_x</td>
<td>1.828</td>
<td>1.853</td>
<td>F_x-Li_{3}-Li_{3}</td>
<td>47.8</td>
</tr>
<tr>
<td></td>
<td>Li_{3}-Li_x</td>
<td>2.459</td>
<td>2.432</td>
<td>Li_x-F_x-Li_{3}</td>
<td>85.0</td>
</tr>
</tbody>
</table>
Table 3. Energy difference in kJ mol$^{-1}$ between hyperalkali Li$_4$F$_3$ isomers.

<table>
<thead>
<tr>
<th>Stability of Isomer</th>
<th>Neutral $\Delta E$</th>
<th>Cation $\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyperalkali A</td>
<td>23.1</td>
<td>41.2</td>
</tr>
<tr>
<td>Hyperalkali B</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Upon ionization, hyperalkali A becomes linear, whereas hyperalkali B maintains a cage-like structure. The first and terminal Li-F bonds in hyperalkali A decrease by 0.008 and 0.041 Å, respectively, whereas the medial Li-F distance increases by 0.019 Å (Figure 4). Hyperalkali B’s central Li$_3$-F$_x$ bond length stretches by 0.025 Å and the other Li-F bond lengths decrease by 0.019 and 0.027 Å. The bond angles in hyperalkali B do not change much upon ionization.

The HOMO, LUMO, and NBO values for hyperalkalis A and B are shown in Figures 6-9 and Table 4, respectively. Neutral hyperalkali A’s HOMO has the electron localized around the superalkalis Li$_2$F moieties, but the LUMO is localized around the whole species (Figure 6), seen as well in the cation’s LUMO (Figure 7). The same trend is observed in hyperalkali B (Figure 8 and 9). A is the more stable species based on the HOMO-LUMO gap, and B is the lowest energy isomer (Table 3). Both structures HOMO-LUMO gaps are higher than that of the superalkali building block, which makes the hyperalkali molecules to be more stable than the superalkali in the neutral state.
**HOMO-LUMO Gap**
5.64 eV

Figure 6. HOMO (left) and LUMO (right) of the neutral Li$_4$F$_3$ hyperalkali A.

**HOMO-LUMO Gap**
8.18 eV

Figure 7. HOMO (left) and LUMO (right) of the cation Li$_4$F$_3$ hyperalkali A (Li$_4$F$_3$).
Figure 8. HOMO (left) and LUMO (right) of the neutral Li$_4$F$_3$ hyperalkali B.

HOMO-LUMO Gap
2.05 eV

Figure 9. HOMO (left) and LUMO (right) of the cation Li$_4$F$_3$ hyperalkali B.

HOMO-LUMO Gap
9.08 eV
Table 4. Differences in NBO charges between neutral and cation of hyperalkali A and B.

<table>
<thead>
<tr>
<th></th>
<th>A. Li₄F₃</th>
<th>Li₂ &amp; Li₁</th>
<th>Li₅ &amp; Li₆</th>
<th>F₄ &amp; F₃</th>
<th>F₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>0.457</td>
<td>0.900</td>
<td>-0.908</td>
<td>-0.899</td>
<td></td>
</tr>
<tr>
<td>Cation</td>
<td>0.968</td>
<td>0.917</td>
<td>-0.930</td>
<td>-0.918</td>
<td></td>
</tr>
<tr>
<td>Δ q</td>
<td>0.511</td>
<td>0.017</td>
<td>-0.022</td>
<td>-0.019</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>A. Li₄F₃</th>
<th>Li₂ &amp; Li₁</th>
<th>Li₅ &amp; Li₆</th>
<th>F₄ &amp; F₃</th>
<th>F₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>0.583</td>
<td>0.842</td>
<td>-0.864</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cation</td>
<td>0.929</td>
<td>0.844</td>
<td>-0.877</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Δ q</td>
<td>0.346</td>
<td>0.002</td>
<td>-0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 4 the two terminal lithium atoms in hyperalkali A increase in charge by about 0.511, from the neutral to the cationic state, while other charges remain comparable. This shows the same trend as with the superalkali building block, in which the terminal lithiums increase in charge about 0.516, indicating that the terminal lithium atoms are going to be responsible for electron-transfer interactions.

Hyperalkali B shows a similar trend as A, except that the three outer lithium atoms gain a larger charge, 0.346, than the central lithium atom, 0.002, exhibiting a larger interaction with the outer fluorine and lithium atoms than the central lithium and fluorine atoms.

6.3.3 Superhalogen

The structure for the superhalogen is found by following the equation, MXₖ₊₁ (*vide supra*). The additional electron is delocalized over the halogen atoms, stabilizing the molecule. Behera et
al.\textsuperscript{36} defined a superhalogen differently than the conventional definition, stating that the EA of a superhalogen must be greater than that of its constituent halogen.

The same atoms as the superalkali are used, but there are two fluorine and one lithium atom, LiF\textsubscript{2}. The EA of the species must be greater than that of chlorine, 3.60 eV,\textsuperscript{20} and according to Behera et al.\textsuperscript{36} it must surpass that of fluorine, 3.41 eV.\textsuperscript{58} This study finds an AEA of 5.53 eV, which is about 1.93 eV higher than the EA of chlorine and 2.12 eV greater than that of fluorine, demonstrating that LiF\textsubscript{2} is indeed a superhalogen. The optimized configurations of the neutral and anionic state are displayed in Figure 10 with corresponding bond lengths and angles shown. The neutral and anionic structure resembles that of the superalkali, with neutral bond lengths around 1.71 Å and relaxation of the anion to a linear configuration.

![Figure 10](image1.png)

**Figure 10.** Optimized structures of neutral (left) and anion (right) of superhalogen LiF\textsubscript{2}.

As with the superalkalis, the HOMO and LUMO, and NBOs are calculated to show the energy band gap and electron delocalization (Figures 11-12 and Table 5).
**HOMO-LUMO Gap**

**8.76 eV**

**Figure 11.** HOMO (left) and LUMO (right) of the neutral LiF$_2$ superhalogen.

**HOMO-LUMO Gap**

**5.05 eV**

**Figure 12.** HOMO (left) and LUMO (right) of the anion LiF$_2$ superhalogen.

**Table 5.** Differences in NBO charges between neutral and anion

<table>
<thead>
<tr>
<th></th>
<th>LiF$_2$</th>
<th>F$_2$</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Neutral</strong></td>
<td>-0.457</td>
<td>0.914</td>
<td></td>
</tr>
<tr>
<td><strong>Anion</strong></td>
<td>-0.932</td>
<td>0.864</td>
<td></td>
</tr>
<tr>
<td><strong>Δ q</strong></td>
<td>-0.475</td>
<td>-0.05</td>
<td></td>
</tr>
</tbody>
</table>
The NBO charge on the metal atom, Li, both in the neutral and anion (Table 9) is positive and nearly the same (~ -0.05e difference), demonstrating that the electron is transferred from the metal atom to the ligands, F. The added electron is delocalized around the two F atoms, each gaining about 0.47e, increasing the negative electrostatic interaction between the Li and F atoms. Therefore, the bond lengths are slightly shorter in the anionic state.

**6.3.4 Hyperhalogen**

Possible structures of hyperhalogens were also explored. Hyperhalogens (vide supra) are formed using a metal atom surrounded by superhalogens with an EA higher than its corresponding superhalogen building block. Possible hyperhalogens have the molecular formula Li$_3$F$_4$ (Li plus 2 LiF$_2$) and the two lowest energy structures, A and B, are presented in Figures 13 and 14 with differences in bond lengths and angles in Table 6 and comparison of the stability of the neutral and anion in Table 7. Other configurations are explored, but they result in EAs that are lower than LiF$_2$’s AEA of 5.53 eV. The calculated AEA of hyperhalogen A is 7.61 eV and that of hyperhalogen B is 5.67 eV. Both possess larger AEAs exceeding the superhalogen by 2.08 and 0.14 eV, respectively. Although hyperhalogen A’s AEA is larger than hyperhalogen B’s by 1.94 eV, both are regarded as hyperhalogens because of their higher AEAs. Table 7 shows that hyperhalogen B is the lower energy neutral isomer by 223 kJ mol$^{-1}$. Both hyperhalogen isomers have comparable HOMO-LUMO gaps suggesting similar stability, with A being some what more stable than B.
Figure 13. Optimized neutral (left) and anion (right) structures of the Li₃F₄ hyperhalogen A.

Figure 14. Optimized neutral (left) and anion (right) structures of the Li₃F₄ hyperhalogen B with corresponding bond lengths and angles in Table 6.

Although the anion of hyperhalogen A maintains a similar structure to its corresponding neutral, hyperhalogen B’s anion increases bond lengths between atoms.
Table 6. Comparison of bond lengths and angles of neutral and anion of the Li$_3$F$_4$ hyperhalogen B.

<table>
<thead>
<tr>
<th>Hyperhalogen</th>
<th>Bond</th>
<th>Neutral (Å)</th>
<th>Anion (Å)</th>
<th>Average Bond Angle</th>
<th>Neutral (°)</th>
<th>Anion (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>F$_{1/2}$-Li$_5$</td>
<td>1.723</td>
<td>F$_1$-Li$_5$-F$_2$</td>
<td>128</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F$<em>{1/2}$-Li$</em>{6/7}$</td>
<td>1.715</td>
<td>Li$_5$-F$_2$-Li$_6$</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F$<em>{3}$-Li$</em>{6/7}$</td>
<td>1.897</td>
<td>F$_2$-Li$<em>6$-F$</em>{3/4}$</td>
<td>123</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F$_3$-Li$_5$</td>
<td>-</td>
<td>Li$<em>6$-F$</em>{3/4}$-Li$_7$</td>
<td>91.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F$<em>4$-Li$</em>{6/7}$</td>
<td>1.897</td>
<td>F$_{3/4}$-Li$_7$-F$_1$</td>
<td>123</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>Li$<em>{5/6/7}$-Li$</em>{5/6/7}$</td>
<td>-</td>
<td>averages of bonds in triangles</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$\Delta$L$_{Li_5}$-L$_{Li_6}$-L$_{Li_7}$ | - | 60.0 |
$\Delta$L$_{Li_e}$-F$_x$-L$_{Li_s}$ | - |
$<$F$_4$ | - | 79.9 |
$<$Li | - | 50.1 |
$\Delta$L$_{Li_s}$-F$_{1/2/3}$-L$_{Li_s}$ | - | - |
$<$F | - | 79.8 |
$<$Li | - | 50.1 |

Table 7. Energy difference of hyperhalogens A and B in kJ mol$^{-1}$.

<table>
<thead>
<tr>
<th>Stability of Isomer</th>
<th>Neutral $\Delta E$</th>
<th>Anion $\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyperhalogen A</td>
<td>223.6</td>
<td>36.2</td>
</tr>
<tr>
<td>Hyperhalogen B</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

HOMO and LUMO orbitals as well as NBO charges are calculated for both hyperhalogens and results are presented in Figures 15-18 and Table 8.
Figure 15. HOMO (left) and LUMO (right) of the Li$_3$F$_4$ neutral hyperhalogen A.

HOMO-LUMO Gap
9.08 eV

Figure 16. HOMO (left) and LUMO (right) of the Li$_3$F$_4$ anion hyperhalogen A.

HOMO-LUMO Gap
5.88 eV
**Figure 17.** HOMO (left) and LUMO (right) of the Li$_3$F$_4$ neutral hyperhalogen B.

**HOMO-LUMO Gap**
8.55 eV

**Figure 18.** HOMO (left) and LUMO (right) of anion hyperhalogen B (Li$_3$F$_4$).

**HOMO-LUMO Gap**
5.65 eV
Hyperhalogen A’s NBO illustrates that the neutral’s terminal F atoms have a low negative charge, but the anion causes them to increase by 0.47e, whereas the other atoms maintain similar values between the two geometries. Fluorine atoms contain a highly negative charge whereas Li atoms possess a highly positive charge. The HOMO and LUMO representations show that the addition of an electron causes the distribution to form a “cage” around the molecule. The position of the HOMOs in the neutral and the anion do differ, however, with the neutral HOMO on the central fluorines and anion HOMO on the terminal fluorines.

Hyperhalogen B’s NBO demonstrates that the fluorine atoms 3 and 4 (Table 8) gain approximately 0.45 e, increasing the negative charge and delocalizing the extra electron. The remaining atoms maintain almost the same values from neural to anion.

Hyperhalogen B has smaller energy gap for the neutral geometry than A’s, but a larger energy gap for the anionic geometry. This results in a more reactive neutral state for B, but a less
reactive anionic state. Considering the results for AEAs as well, hyperhalogen A is the most stable hyperhalogen, even though is higher in energy than B.

6.3.5 Hypersalt designed using hyperhalogen and metal cation

Hypersalts, described previously, are designed using a metal cation bound to a hyperhalogen anion. These species have not been explored to the extent of super-alkalis/halogens or hyperhalogens. There is an interest in these species to search any possible differences between supersalts and to determine experimentally if these compounds contain enhanced properties.

The hypersalts investigated use hyperhalogens A and B as building blocks, and add a Li atom as the metal cation to have the chemical formula Li₄F₄. The two neutral structures are illustrated in Figure 19 and Figure 20. Only the neutral structures are presented since the stability of the salt is being studied. Giri et al. presented binding energies and EAs in order to explain the stability of a supersalt, while a study performed by Behera et al. only presented binding energies to explore the stability of a hypersalt. These values are also presented in Table 9 for the currently investigated hypersalts A and B. The binding energy presented are calculated in two different ways, one for the dissociation of the salt into ions (BE ions) using equation (3) and for the dissociation into neutrals (BE neutrals) using equation (4). The AIE of the hypersalt A is not reported because its cation undergoes dissociative ionization. Their related HOMO, LUMO, and NBO charges are shown in Figures 21-24. The more stable isomer proves to be hypersalt B due to its larger HOMO-LUMO gap and lower overall energy (Table 9).
Figure 19. Optimized neutral structures of possible Li$_4$F$_4$ hypersalts A and B, with added alkali metal (Li) labeled 8.

Figure 20. Average bond lengths and angles in the faces of the Li$_4$F$_4$ hypersalt B; note that the Li$_x$-Li$_x$ bond alternates slope every face.
**Figure 21.** HOMO (left) and LUMO (right) of the neutral Li$_4$F$_4$ hypersalt A. Added lithium is on the left terminal side.

**Figure 22.** NBO of the neutral Li$_4$F$_4$ hypersalt A.

**Figure 23.** HOMO (left) and LUMO (right) of the neutral Li$_4$F$_4$ hypersalt B.
Hypersalt A’s HOMO has the neutral’s electron density around the terminal halogen and its LUMO spreads the electron density around the added lithium and the close by fluorine. Hypersalt B’s HOMO density is more evenly spread out than A’s in that orbitals are located on every halogen atom present in the structure and the LUMO creates a cage around the lithium atoms, leaving the halogens unveiled.

Table 9. Summary of properties of the Li₄F₄ hypersalts A and B.

<table>
<thead>
<tr>
<th>Hypersalt:</th>
<th>Binding Energy Ions (eV)</th>
<th>Binding Energy Ions (kJ mol⁻¹)</th>
<th>Binding Energy Neutrals (eV)</th>
<th>Binding Energy Neutrals (kJ mol⁻¹)</th>
<th>AEA (eV)</th>
<th>AIE (eV)</th>
<th>Relative Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Li₄F₄</td>
<td>5.45</td>
<td>526.2</td>
<td>7.73</td>
<td>745.8</td>
<td>1.58</td>
<td>-</td>
<td>252.9</td>
</tr>
<tr>
<td>B. Li₄F₄</td>
<td>7.69</td>
<td>742.8</td>
<td>8.03</td>
<td>775.0</td>
<td>-0.11</td>
<td>10.90</td>
<td>0</td>
</tr>
</tbody>
</table>

*Binding energies are calculated using equation 3 in eV and kJ mol⁻¹.
Because experimental descriptions of the properties of hypersalts are lacking within currently available literature, they will be compared both to what little is known as well as with the more established supersalts. The EA of supersalts computationally determined by Giri et al.\textsuperscript{56} are extremely low, ranging from 0.19 to 0.74 eV, with no published uncertainty. The binding energies of these same species range from 5.10 to 5.57 eV, which are smaller than the binding energy of LiF (8.02 eV), also calculated by Giri et al.\textsuperscript{56}. Behera et al.,\textsuperscript{41} also discovered structures with binding energies ranging from 4.00 to 4.24 eV (no reported uncertainties). The calculated AEA’s of the investigated hypersalts A and B are drastically lower than their respective hyperhalogen’s AEAs, hypersalt A with an AEA of 1.58 eV and hypersalt B with an AEA of -0.11 eV. Hypersalts A and B have binding energies (calculated using equation 3) of 7.73 and 8.03 eV, respectively, which are both positive and larger (or close to) than those found for previous supersalts and hypersalts.\textsuperscript{41, 56} These binding energies are also relatively close to or larger than that of LiF found by Veličković et al.,\textsuperscript{59} resulting in a more stable structure.

The even distribution of orbitals in hypersalt B, and lack of distribution in A, helps the argument that B would indeed be a great candidate for a hypersalt as well as the HOMO-LUMO band gap exceeding that of A by 5.97 eV.

**6.3.6 Hypersalts designed using hyperalkali and halogen**

To the best of our knowledge, hypersalts created from a hyperalkali and halogen have not been previously studied. Figure 25 displays the neutral structure of two possible hypersalts C and D, with D’s corresponding binding energy, AEA, and AIE in Table 10. The optimized neutral structure of C is the exact same as hypersalt B.
Hypersalt D (Figure 25) presents a perfect planar octagon structure with bond distances of 1.711 Å and alternating bond angles of 127° and 143°. Its HOMO, LUMO, and NBO are presented in Figures 26 and 27.

**HOMO-LUMO Gap**

8.54 eV

**Figure 26.** HOMO (left) and LUMO (right) of the neutral Li$_4$F$_4$ hypersalt D.
The HOMO of the neutral has electrons localized on the halogen atoms, but the LUMO has electrons localized around the lithium atoms. The HOMO-LUMO gap of D for the neutral is found as 8.54 eV, very close to the gap calculated for hypersalt B.

A previous study by Giri et al.\textsuperscript{56} used NBO of the neutral to show the ionic character of a salt. If the charges of the atoms (cations and halogens) are nearly the same then the salt shows strong ionic character. Similarly, to hypersalts A and B, the large total positive charge on hypersalt D on the metal atoms and the large total negative charge on the halogen atoms, 0.901 and -0.901, respectively, also demonstrates the strong ionic character of the hypersalt.

As completed with the previous hypersalts A and B, the AEA and binding energy D is explored and summarized in table 10. The stability of D is also compared to B (being the most stable isomer) and results in a difference of about +38 kJ mol\textsuperscript{-1} showing that the stability is close to that of B. In addition, Hypersalt D’s BE (equation 3) is 7.84 eV and its AEA is -0.15 ± 0.05 eV. Because hypersalt C is the same as B, its binding energy using ionic building blocks is also 7.69 eV, which makes D 0.15 eV higher in energy and therefore slightly more stable than B. Compared
to A’s BE of 5.45 eV, D is more stable by 2.39 eV, making D the most stable hypersalt in terms of ionic moieties. Using neutral building blocks, however, provides BEs for the three structures 7.73 eV for A, 8.03 eV for B/C’s, 7.52 eV for D. Hypersalt B/C is the most stable hypersalt when using neutral parts, but hypersalt D has the largest BE, when using ionic parts, making it the strongest ionic compound/hypersalt containing Li and F investigated nowadays.

**Table 10.** Binding energy, AEA, and AIE of hypersalt D.

<table>
<thead>
<tr>
<th></th>
<th>Binding Energy</th>
<th>Binding Energy</th>
<th>Binding Energy</th>
<th>AEA</th>
<th>AIE</th>
<th>Relative Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ions (eV)</td>
<td>Neutrals (eV)</td>
<td>Neutrals (kJ mol⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D. Li₄F₄</td>
<td>7.84</td>
<td>7.52</td>
<td>725.5</td>
<td>-0.15</td>
<td>10.9</td>
<td>38.3</td>
</tr>
</tbody>
</table>

*Binding energies are calculated using equation 5 in eV and kJ mol⁻¹*

### 6.4 Conclusions

This study explores the design of a superalkali, superhalogen, hyperalkali, and hyperhalogen, which in turn, are used to develop possible hypersalts. The investigation uses a multistep composite computational job that follows the same setup of the CBS-QB3 method, and uses B3LYP in combination with the CBSB7+ basis set for optimizations and calculations. AIE’s, AEA’s, HOMO-LUMO energy gaps, and NBO’s are calculated for each presented species. Results confirm that the constructed hyperalkalis Li₄F₃ result in even lower AIE’s (3.86 eV and 3.67 eV for hyperalkali A and B, respectively) than the starting superalkali. The study also confirms the structures for the designed hyperhalogens Li₃F₄ with higher AEA (7.61 eV and 5.67 eV for hyperhalogen A and B, respectively) than the superhalogen building block. Hyperhalogens A and B are used to create hypersalts, following the idea that hypersalts are built from an alkali metal bound to a hyperhalogen. This yields two possible salts A and B with the formula Li₄F₄. A and B have binding energies of 5.45 eV and 7.69 eV, respectively, and stable structures (using NBO)
indicating strong salts. Hypersalts C and D are designed from a hyperalkali plus a halogen atom with the formula Li₄F₄. Hypersalt C is identical to B, but D results in a binding energy of 7.84 eV. Between the three hypersalts, the ring structures of hypersalts B and D resulted in larger binding energies than linear hypersalt A. B and D's binding energy exceeding that of A by 2.24 eV and 2.12 eV, respectively. This may be due the ring structure causing a more even distribution among electrons. These conclusions bring into light a new way to make possibly more effective hypersalts using ring structures rather than linear. Considering a supersalt is constructed using a superhalogen and superalkali, future investigations will also explore the attainability of adding a hyperalkali to a hyperhalogen to create a hypersalt, as well as a hyperhalogen joined to a superalkali and hyperalkali joined to a superhalogen.

6.5 Acknowledgments
This work is funded by the University of San Francisco Faculty Development Fund. All calculations are performed on an in-house computer cluster. The authors would also like to thank the Director of Scientific Computing, of the Department of Computer Science, Mr. A. Fedosov, at the University of San Francisco for providing for the space and general upkeep of the computer cluster used to perform the calculations.
6.6 References


