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Furanic Molecules: Multiplexed Synchrotron Photoionization Investigations and Aerosol Studies

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Furanic Molecules: 
Multiplexed Synchrotron Photoionization Investigations 
and Aerosol Studies

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:

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12/7/2015
Furanic Molecules: Multiplexed Synchrotron Photoionization Investigations and Aerosol Studies

Thesis written by Audrey R. Smith

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

Master of Science
in Chemistry
at
The University of San Francisco

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Chapter 1

Introduction

1.1. Climate Change

Both climate change and air pollution have been identified as critical environmental issues on a global scale, and will continue to be identified as such for decades to come. Air pollution concentration levels have been exceeding the acceptable levels put forth by the World Health Organization (WHO), particularly in Asia and Europe in the past decade. President Obama has just initiated the Clean Power Plan in August 2015, which requires that carbon dioxide (CO$_2$) emissions are to be reduced by 32% by 2030 in the United States. The issues of climate change and air pollution are very much connected in that many of the sources affecting each of these issues also influence the other. An example of this is vehicle emissions, which consists of particulate matter, nitrogen oxides, carbon monoxide (CO), and CO$_2$. Taking a look at the particulate matter component, the direct impact on climate change (radiative forcing) is evident in the scattering or absorbing of incoming radiation by these particles, while at the same time proving to have an adverse effect on human health by contributing to air pollution.

There are various types of air pollutants that impact both the climate and human health, and are typically categorized as either a gaseous pollutant or an aerosol. Gaseous pollutants include a wide array of molecules, such as CO$_2$, CO, ozone (O$_3$), nitrogen oxides (NO$_x$), ammonia, methane, and non-methane volatile organic compounds
(NMVOCs) from both anthropogenic and biogenic sources.\textsuperscript{1,2} Road transportation, industrial sources, solvent use, and biomass burning make heavy contributions to generating these compounds.\textsuperscript{1} Many of these gaseous pollutants are toxic to humans, and have the ability to react with other compounds in the atmosphere to generate more toxic molecules.

Aerosols are defined as the suspension of fine solid or liquid particles in a gas.\textsuperscript{1} While not entirely accurate, particulate matter is often labeled with the term aerosol when regarding pollutants in the atmosphere, despite only referring to the specific particulate. Aerosols greatly contribute to both direct and indirect radiative forcing through either aerosol-radiation effects or aerosol-cloud effects, respectively.\textsuperscript{1} In addition to their impact on climate change, the particulate matter associated with aerosols has also been linked to cause adverse human health effects, including premature mortality, pulmonary disease, asthma, and other respiratory illnesses.\textsuperscript{11−13}

In recent decades, society has begun to make a shift from the use of petroleum towards more renewable resources. With gas prices constantly on the rise, consumers look for a cheaper alternative to power transportation.\textsuperscript{14} This alternative comes in the form of biofuels. Biofuels provide a long-term solution by providing both a renewable source of energy and by reducing harmful combustion emissions. This thesis focuses on select substituted furans that have been identified as potential biofuels. The chemical reactivity of these compounds is explored so that the chemical compositions of future fuels may be optimized.
1.2. Energy

The demand for reliable, renewable energy sources such as biofuels, wind, geothermal, and solar energy has been on the rise in recent decades. A major factor influencing this demand is the desire for energy security. An increase in energy security would reduce the threat of a supply crisis, and any economic or military impact associated with the lack of supply. In addition to this, the use of these renewable energies would greatly reduce the impact that the emissions from burning fossil fuels are currently posing.\textsuperscript{1-3} The renewable energy resource that is provided by biomass through the synthesis of biofuels is the focus of this thesis.

1.3. Fuels and Fuel Additives

Alternative fuels and fuel additives to current petroleum fuels are presently being researched in order to improve engine efficiency and reduce greenhouse gas (GHG) emissions. It is important to note that not all engines use the same type of fuel, or fuel additives, and therefore the compounds vary depending on the type of engine. There are two dominant engine types used for ground transportation, the gasoline engine, also known as the spark ignition engine, and the diesel, or compression ignition, engine. An explanation on how each of these engines operate is given in section 4 of this chapter.

For gasoline engines performance it is imperative that the fuel does not ignite before the external spark is initiated. If this premature explosion happens, engine knocking occurs, resulting in the incomplete combustion of the fuel/air mixture and perpetual
damage to the engine. Oxygenated fuel alternatives and fuel additives have the potential to improve the fuel mixture, providing it with better anti-knock properties. The inclusion of these additives can increase the ignition temperature, preventing the premature ignition that leads to the problems mentioned above. In addition to improving engine efficiency, these alternative fuel additives also have the potential to reduce consumption, and therefore decrease GHG emissions.  

Diesel engines are quite different in regards to what is needed for improving their efficiency. It is vital that spontaneous combustion (not spark initiated like gasoline) occurs just after the fuel is injected into the combustion chamber, when the piston is at the peak of its stroke. A slight delay after the injection is key in both engine performance and reduced emissions. Additives used with diesel engines are typically unstable compounds, which are believed to promote auto-oxidation, and therefore assist in the spontaneous combustion of the fuel that is required.

1.3.1. Chemical Composition

The most common example of a biofuel used in society today is ethanol, which is blended with gasoline. Ethanol is an oxygenated hydrocarbon, as are many potential biofuel compounds. The studies presented here focus on a few selected oxygenated hydrocarbons that have been identified as alternatives and additives to gasoline engines, namely alkylfurans, and the oxidation processes they undergo. The structures of the compounds studied are presented in Table 1.1.
Table 1.1 - Chemical structures of oxygenated hydrocarbons identified as potential fuels or fuel additives that are the focus the studies presented here.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylfuran</td>
<td><img src="image" alt="2-Methylfuran" /></td>
</tr>
<tr>
<td>2-Ethylfuran</td>
<td><img src="image" alt="2-Ethylfuran" /></td>
</tr>
<tr>
<td>Furfural</td>
<td><img src="image" alt="Furfural" /></td>
</tr>
<tr>
<td>2-Acetylfuran</td>
<td><img src="image" alt="2-Acetylfuran" /></td>
</tr>
</tbody>
</table>

1.3.2. Biofuels

Plant biomass is currently the only sustainable source of biofuels. It has been proven that biofuels generate less greenhouse gas emissions than fossil fuels upon combustion, and even have the potential to be GHG neutral based on the efficiency by which the biofuel is produced.\textsuperscript{17–19} It has been estimated by both the U.S. Department of Agriculture (USDA) and Oak Ridge National Laboratory that the U.S. could sustainably produce up to $1.3 \times 10^9$ metric tons per year of dry biomass, the energy equivalent to $3.8 \times 10^9$ boe (barrels of oil energy equivalent).\textsuperscript{20,21} Presently, the U.S. consumes approximately $7 \times 10^9$ barrels of oil per year, meaning that over 50% of the
nation’s oil needs can be taken care of through the use of biomass conversion into biofuels. The production of the dry biomass would require the use of the country’s agricultural and forest resources, with plenty of resources remaining to meet all needed food, feed, and export demands. A significant amount of the dry biomass would come from crop residues, which are materials like corn stover. Corn stover consists of the stalks, leaves, husks, and cobs that remain in the field after the corn has been harvested. The current production of corn stover amounts to 75 million dry tons per year of biomass that could be converted into biofuel. Figure 1.1 presents a flow chart portraying a biomass growth and manufacturing scheme.

![Flow Chart of Biomass Growth and Manufacturing Scheme](image)

**Figure 1.1 - Proposed sustainable production of transportation fuels from biomass.**

It would be ideal to produce biomass from high-yield crops that require few nutrients, little fertilizing, and minimal energy input. Furthermore, the biofuel developed from such an ideal source would preferably be able to fit into the existing
infrastructure, where current engines and pipelines could accommodate the new fuel source.\textsuperscript{14} It is through the development of novel biomass conversion technologies with higher thermal conversion efficiencies (where a greater percent of the energy stored in the biomass is actually transferred to the fuel) and through novel production routes that biofuels will become a more viable alternative energy option.\textsuperscript{24} Recently, these novel production routes have been identified and developed for alkylfurans such as 2-methylfuran (2MF) and 2,5-dimethylfuran (25DMF).\textsuperscript{25−27} Both of these compounds have been identified as potential biofuels.\textsuperscript{25−27} In addition, similar compounds such as 2-ethylfuran (2EF), 2-acetylfuran (2AF), and furfural, have the potential to act as key synthesis components for other biofuels, or as fuel additives to improve engine efficiency or reduce harmful emissions. These alkylfurans will be the focus of the studies included in this thesis.

1.4. Combustion and Advanced Engine Systems

In order for combustion to occur, there needs to be some type of fuel and an oxidizer (air) present in order to cause an exothermic reaction.\textsuperscript{28} The studies presented here focus on the conditions where fuel and oxidizers are pre-mixed prior to combustion. More specifically, the low temperature (less than 900 K) reactions that are characteristic of both ignition chemistry and interactions that occur in the upper part of our atmosphere (troposphere) are investigated for selected compounds. At these low temperatures, species containing peroxo radicals propagate, dominating the reaction
pathways labeled as chain propagating in the general mechanistic oxidation of a hydrocarbon in Scheme 1.1. While the propagation of these radical species are key in the breakdown of hydrocarbons used as fuels, they are also the cause of pollutants such as poly-aromatic hydrocarbons (PAHs).\textsuperscript{29}

The reaction mechanism presented in Scheme 1.1 was first proposed by Semenov.\textsuperscript{27,31} The peroxy radical species, denoted as R\(\dot{O}\)\(_2\) in Scheme 1.1, has been sought after by researchers for years after its proposal due to its importance in the hydrocarbon decomposition witnessed in these low temperature reactions.

\[
\begin{align*}
\text{RH} + \text{O}_2 & \rightarrow \text{R} + \text{HO}_2 \quad \text{(initiation)} \\
\text{R} + \text{O}_2 & \rightarrow \text{olefin} + \text{H\(\dot{O}\)}_2 \\
\text{R} + \text{O}_2 & \rightarrow \text{R\(\dot{O}\)}_2 \\
\text{R\(\dot{O}\)}_2 + \text{RH} + \text{ROOH} + \text{R} & \rightarrow \text{R\(\dot{O}\)}_2 \rightarrow \text{R'CHO} + \text{R''\(\dot{O}\)} \\
\text{H\(\dot{O}\)}_2 + \text{RH} & \rightarrow \text{H}_2\text{O}_2 + \text{R} \\
\text{ROOH} & \rightarrow \text{R\(\dot{O}\)} + \text{\(\dot{O}\)}_2 \quad \text{(degenerate branching)} \\
\text{R'CHO} + \text{O}_2 & \rightarrow \text{R'\(\dot{C}\)}_2 + \text{HO}_2 \\
\text{R\(\dot{O}\)}_2 & \rightarrow \text{destruction} \quad \text{(chain terminating)}
\end{align*}
\]

\textbf{Scheme 1.1} – General reaction mechanism proposed by Semenov\textsuperscript{30} for temperatures less than 900 K.
The reactions presented in Scheme 1.1 are under the spotlight once more due to the recent introduction of combustion engines that take advantage of compressed multi-site auto ignition in order to improve engine efficiency.\textsuperscript{32} The HCCI, or homogenous-charge compression ignition, engine is a combination of both the spark ignition gasoline engine and the compressed ignition diesel engine. The combustion reaction that occurs in spark ignition engines is initiated when the fuel/air mixture within the engine’s piston is ignited by an external spark. Conversely, the combustion that occurs in a compressed ignition engine occurs when the optimal temperature and pressure are reached through the adiabatic compression of the engine’s piston.\textsuperscript{33} A view of each engine’s piston setup is shown in Figure 1.2. HCCI engines feature positive characteristics of both gasoline and diesel engines, like low emissions of NO\textsubscript{x} and

\textbf{Figure 1.2} - Visualization of the differing ignition regions for three types of combustion engines.\textsuperscript{15}
particulate matter, and improved efficiency. The fuel/air mixture auto-ignites and burns volumetrically as a result of compression by the engine piston. Because of the nature of the HCCI engine, a variety of fuel types are being tested with prototypes, such as gasoline, diesel fuel, bio-derived fuels, alternative petroleum-based files, and others.\textsuperscript{33}
1.5. References


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Chapter 2

Experimental Apparatus

2.1. Introduction

These experiments were carried out at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory using a multiplexed synchrotron photoionization mass spectrometer (MSPIMS) at the Chemical Dynamics Beamline. The apparatus will be described in detail throughout this chapter with an overall schematic shown in Figure 2.1.¹

Figure 2.1 – The schematic of the oa-TOF-MS used in the experiments presented in this thesis.¹
The compounds that are to be studied are first purified using a bubbler and the freeze-pump-thaw technique to remove any dissolved gas impurities that might be present in the liquid. The vapors of the compound in question are allowed to equilibrate within a vacuumed steel gas cylinder, at a chosen pressure representative of the compound’s concentration in the cylinder. Helium is then flowed into the gas cylinder until the compound only contributes a partial pressure of approximately 1%. The total pressure should not be too low in order for the experiment to complete or else the initial concentration of the studied compound might be too low to analyze appropriately.

In the case where the studied compound does not have a high enough vapor pressure to satisfy the requirement for preparing a gas cylinder, usually designated as \( \leq 5 \text{Torr at } 25 \, ^\circ\text{C} \), a bubbler must be used instead. The preparation of the sample remains the same except one does not transfer any vapors to a gas cylinder. The bubbler is attached to the experimental apparatus so that its vapors can flow directly into the reactor by flowing helium through the bubbler. The flow rate of the gas is measured, and the concentration in molecules \( \text{cm}^{-3} \) can be determined using Equation 2.1, where \( P \) is the pressure maintained inside the chemical reactor, \( F_R \) is the flow rate of the reactant, \( F_T \) is the total flow rate of all components, and \( T \) is the temperature of the reactor.

\[
\text{Concentration} = (3.24 \times 10^{16})(P)(\frac{F_R}{F_T})(\frac{T}{298.15})^{-1} \tag{2.1}
\]

Equation 2.1 assumes that the reactant gas being flowed into the reactor is 100% pure. As this is usually not the case, the value obtained from Equation 2.1 should be
multiplied by the actual gas percent purity. If one is using a gas cylinder, the gas percent purity is calculated using Equation 2.2.1, where $P_{gas}$ is the partial pressure of the gas being studied, and $P_{tot}$ is the total pressure within the gas cylinder. If one is using a bubbler to introduce the sample into the reactor, a capacitive pressure gauge must be used to measure the total pressure inside of the bubbler ($P_{bub}$). The vapor pressure ($P_{vap}$) of the compound studied is then used to determine the percent purity of the gas flowed into the reactor using Equation 2.2.2.

$$\%P_{\text{Purity}_\text{gas}} = \frac{P_{\text{gas}}}{P_{\text{tot}}} \times 100$$  \hspace{1cm} (2.2.1)$$

$$\%P_{\text{Purity}_\text{gas}} = \frac{P_{\text{vap}}}{P_{\text{bub}}} \times 100$$ \hspace{1cm} (2.2.2)

2.2. Slow Flow Reactor

The compounds under investigation and the buffer gas (He) are flowed into a heatable, 62 cm long, slow flow quartz reactor, which has a 1.05 cm internal diameter.\textsuperscript{2,3} The flow rate of the reaction gases are measured by individual mass flow controllers. The reactor tube is insulated by an 18 µm thick Nichrome tape so as to improve temperature uniformity along the entire length of the tube, and reduce heat transfer from the tube itself to the vacuum chamber. For each system, both the temperature and pressure can be specifically set and maintained throughout the experiment. The temperature is measured by a thermocouple that uses a closed-loop feedback circuit to maintain the gas temperature anywhere in the range of 300-1050 K.\textsuperscript{1} For the studies presented here, the temperature and pressure were set and
maintained at room temperature (298-323 K) and 4 Torr, respectively. For experiments involving the oxidation of the compound in question, a suitable photolytic precursor (Cl$_2$) and molecular oxygen are also flowed into the reactor where the photolysis of the precursor is initiated by the excimer laser to produce a uniform radical profile. Photolysis refers to the breakdown of a chemical compound by photons. A fresh sample of reactant gas is present for each laser pulse throughout the experiment by utilizing the 4 Hz repetition rate of the laser in combination with maintaining a total gas flow rate of approximately 400 cm s$^{-1}$ into the reactor tube.

2.3. Excimer Laser

The unfocused excimer laser pulse (fluence 10-60 mJ cm$^{-2}$, pulse-width of 20 ns, and wavelength of 248 or 351 nm) operating at 4 Hz initiates the photolysis of Cl$_2$.\textsuperscript{2} The excimer laser produces radiation with the energy needed to break chemical bonds. The resulting Cl radicals initiate the oxidation reaction by abstracting a hydrogen atom from the reactant. The term laser stands for light amplification by stimulated emission of radiation, where the stimulated emission is the result of a molecule emitting a photon in order to release energy so that it may return from an excited state to a lower state.\textsuperscript{4}

The excimer laser (also referred to as an exciplex laser) has a lasing medium that consists of two atoms that when combined exist only in the excited state while in a buffer gas, where the two atoms will dissociate as soon as their excitation energy is released. It is important that the atoms present in the medium are in their excited states
in order to achieve efficient lasing action. The required excitation is induced by the pumping of the lasing medium. Pumping is usually achieved by one of two methods; fast transverse discharges, or by using high voltage, high current electron sources. The medium used in these experiments consists of a premixed gas containing 1% fluorine, xenon or krypton, and helium as a buffer gas. The exciplex KrF* and XeF* yield photons with wavelengths of 248 nm and 351 nm, respectively. When the exciplex molecule, denoted as AB*, releases energy and moves from the excited state to the ground state, lasing action occurs. This phenomenon is depicted in Figure 2.2.

![Figure 2.2](image)

**Figure 2.2** - The molecular potential energy curve of an exciplex molecule. Emission of energy occurs when the exciplex molecule, AB*, transitions to its lower dissociative state, AB.

Because the exciplex molecule will dissociate in the ground state, population inversion will occur as soon as there are atoms bound to form molecules in the excited
Population inversion occurs when a system exists in a state where more species are in an excited state than in lower energy states, shown in Figure 2.3.

![Figure 2.3 - A depiction of a system before and after population inversion occurs. Before population inversion, the majority of the species exist in a lower energy state, typically referred to as a thermal equilibrium state. After population inversion, the majority of the system exists at an excited energy state.](image)

### 2.4 Vacuum

The gaseous reaction mixture continuously flows through an ~650 µm hole in the sidewall of the reactor. The resulting molecular beam formed from the small sample of gas escaping into the vacuum surrounding the reactor flows towards a skimmer. This 1.5 mm skimmer selects a central portion of the beam to flow into a differentially pumped ionization chamber. There are three different vacuum pumps incorporated into the system, all of which are designed to be free of hydrocarbon contamination.

The first pump, which is also the largest of the three, is the turbomolecular pump, which is responsible for evacuating the reaction chamber at a rate of 3200 L s⁻¹. This pump is coupled with a Roots pump and a backing scroll pump in order to provide sufficient momentum transfer from the rotating blades of the rotor wheels to the gas molecules. Based on Equation 2.3 below, the pumping speed (S) of the
A turbomolecular pump depends on both the molecular mass of the gas pumped and parameters related to the blade itself where \( \nu \) represents blade speed, and \( \nu \) is the mean thermal velocity of the gas particle represented by Equation 2.4:

\[
S = \frac{\nu (\sin(2\alpha)) F}{4 \left( 1 - \frac{d_s h}{F} \right)^{\nu (\sin(2\alpha)) \nu}}
\]

\[\nu = \sqrt{\frac{2 k_B T}{m}} \tag{2.4}\]

In Equation 2.3, \( F \) represents the pumping aperture of the wheel, \( \alpha \) is the blade angle, \( d_s \) is the blade thickness, \( h \) is the blade distance, and \( k \) is the trapping probability (where \( k \leq 1 \)). When \( k = 1 \), the value determined for \( S \) will be the maximum attainable pumping speed for the turbomolecular pump. The trapping probability is a statistical factor that is directly related to the mass of the gas particles present, where molecules with smaller masses tend to have a higher trapping probability. A diagram of a turbo molecular pump is shown in Figure 2.3.

![Diagram of a turbomolecular pump](image.png)

**Figure 2.3** - The cross-section of a turbo molecular pump. The flow to the roughing pump refers to the connection with the other pumps, where the roughing pump is another term for a scroll pump.
The Roots pump, mentioned previously, is a dry rotary displacement pump. It consists of two synchronously counter-rotating impellors, which are synchronized by external gears and rotor bearings that are sealed from the internal vacuum. This synchronization is designed so that while the two impellors are rotating so close to one another and the vacuum housing, no physical contact actually occurs between the components. As the rotors progress through positions I and II, as shown in Figure 2.4, more intake gas is brought into the pump. As the rotors move to position III, a portion of the intake volume is blocked off from the intake entry. Proceeding to position IV, the same volume of intake gas that was blocked off from the intake entrance is opened to the exhaust exit. This cycle occurs twice per complete rotor turn, and operates at a

![Figure 2.4](image)

**Figure 2.4** - This figure shows four key stages of the operation of a Roots pump. The hashed area represents the gas intake flow, while the white areas represent vacuumed space.¹⁰
high speed due to the lack of physical contact with the interior walls.\textsuperscript{10} This individual vacuum system has a capacity of 75-30,000 m\textsuperscript{3} h\textsuperscript{-1} with an operation range of 10-10\textsuperscript{-3} mbar total pressure.

The previously mentioned scroll pump is the final dry pump in the series, and is also referred to as a roughing pump. This system consists of two identical scrolls, one stationary and one that moves in an orbital motion around the central point. As shown in Figure 2.5, the starting position has an access point that is opened to the inlet. As the moving scroll orbits, the intake gas is sealed off from its initial entry. Eventually, the trapped gas is completely sealed off from the inlet, and the scrolls orbit in such a way that the volume of the trapped gas is gradually reduced, compressing it within the scrolls. Once it reaches a minimum volume and a maximum pressure at the center of the two scrolls, it exits through the outlet located there.\textsuperscript{11} This pump has a pumping speed from 20-50 m\textsuperscript{3} h\textsuperscript{-1} with an operation range of 1000-10\textsuperscript{-2} mbar.

\textbf{Figure 2.5} – The four stages depicted above represent the operation of a scroll pump, where the blue shaded area portrays the intake gas.\textsuperscript{11}
2.5. Photoionization Source

Once the molecular beam enters the ionization chamber, it is orthogonally intersected by the quasi-continuous tunable vacuum ultraviolet (VUV) synchrotron radiation produced by the ALS. The ionizing energy supplied by this 3rd generation synchrotron is required to detect the reaction species studied. The ALS produces high brightness ($10^{21}$ photons cm$^{-2}$ s$^{-1}$), quasi-continuous, tunable (7.2-25.4 eV at the Chemical Dynamics Beamline), VUV radiation, with medium resolution ($E/\Delta E \sim 1000$). The synchrotron itself consists of an electron generator, linear accelerator, booster ring, storage ring, and all of the individual beamlines as shown in Figure 2.6.

**Figure 2.6** – A general schematic of the Advanced Light Source at Lawrence Berkeley National Laboratory displaying the key components. The hand points to the very beginning of each electron’s journey through the synchrotron.
The ALS begins with the electron generator producing electrons by thermionic emission from a heated barium aluminate cathode. The linear accelerator is then able to electromagnetically launch electrons, from an initial velocity of 0 m s\(^{-1}\) to a velocity near \(c\), the speed of light. The linear accelerator, or Linac, rapidly speeds up the electrons by passing them through oscillating electric fields along a linear path. The Linac then proceeds to inject the accelerated electrons into the booster ring, which boosts their velocity to 99.999994\% of \(c\) with the use of quadrupole magnets to keep the electron beam focused. The electron generator and Linac are both shown in Figure 2.7, and booster ring and storage ring are shown in Figure 2.8.

**Figure 2.7** – The silver box on the left contains the electron generator, also referred to as the electron gun. Connected to the electron generator are the Buncher and the linear accelerator, or Linac. This image was made available by the Lawrence Berkeley National Labs on their website.

Once the electrons have reached an optimum energy, they are injected into a storage ring, shown in Figure 2.8. With a total diameter of 63 m, the storage ring is the largest component in the ALS. Here, the electrons are accelerated to 1.9 GeV. Typically,
the electrons remain in the storage ring for approximately 6 hours, traveling about 4 billion miles during this time. In order to maintain this high speed, it is vital that the electrons do not collide with anything. Because operations at the ALS are continuous, the storage ring operates in a top-off mode, where electrons are continuously supplied to the storage ring, keeping the electron density constant, and therefore the photon density constant during experiments.

**Figure 2.8** – To the left is a portion of the booster ring. Shown to the right is a section of the storage ring. These images were made available by the Lawrence Berkeley National Labs on their website.\textsuperscript{14}

The storage ring, in addition to the booster ring and Linac, has nearly all of the gas pumped out of it, reducing its internal pressure to 0.000000000001% of atmospheric pressure.\textsuperscript{14} This makes it more likely for two electrons to collide than for one to collide with a gas molecule inside the storage ring.\textsuperscript{14} The storage ring itself is actually shaped like a dodecagon, or a 12-sided figure. Because it is not a perfect circle, three bending magnets are situated at each point of the dodecagon in order to change the trajectory of the electrons so that they do not collide with the walls of the storage ring. This layout
is called a Triple Bend Achromat. The triple bend comes from the use of three magnets to bend the electron’s trajectory, while the term achromat refers to how the triple bends treat all electrons, no matter how much they differ in energy, the same way. This results in all electrons being directed to the same route at every turn. At each turn however, the electrons lose up to 300 keV per revolution due to radiation loss. A pair of RF cavities operating at 500 MHz with a peak voltage of 1.5 Megavolts supply the electrons with the energy needed to make up for this loss, where one of the RF cavities is shown in Figure 2.9. From the storage ring, the synchrotron can direct light down each beamline. This will be explained in section 2.6.

![Figure 2.9 - One of the two RF cavities used to provide energy to the electrons in the storage ring at the ALS. This image was made available by the Lawrence Berkeley National Labs on their website.](image)

2.6. Beamline

The experiments presented here were performed at the Chemical Dynamics Beamline 9.0.2. The synchrotron directs light to each beamline, where at 9.0.2, the light
passes through a gas filter and monochromator in order to select the narrow band of photon energies required by the experiment from anywhere in the range of 7.2-25.4 eV.\textsuperscript{14}\textsuperscript{,}15

Along nine of the twelve straightaways in the storage ring are insertion devices, depicted in red in Figure 2.10. These insertion devices are long magnetic structures that accelerate electrons in a well-defined manner. As the electrons are accelerated, they give off large amounts of radiation at each of these locations. The ring is surrounded by large blocks containing concrete and lead so that the emitted radiation is contained. There are three different types of insertion devices equipped to the storage ring: undulators, wigglers, and elliptically polarizing undulators (EPUs). There are two varieties of wiggler at the ALS. The first is a 19 period planar wiggler with a 16.0 cm period length designed to produce photons up to 12.4 keV for protein crystallography.\textsuperscript{17}

\textbf{Figure 2.10} – A map displaying all of the beamlines at the ALS, referred to as ALS Beamclock. The beamline used for these experiment, 9.0.2 Chemical Dynamics, is in the upper right of this diagram.\textsuperscript{16}
The planar wiggler features a hybrid permanent magnet structure. With its tapered poles, the wiggler is able to achieve 2.0 T at a 1.4 cm magnetic gap.\textsuperscript{17} The second variety of wiggler is referred to as an elliptical wiggler. This insertion device is designed to produce circularly polarized photons in the energy range of 50 eV to 10 keV for use with magnetic circular dichroism spectroscopy.\textsuperscript{17} This wiggler has vertical and horizontal magnetic structures of 14 and 14.5 periods respectively, with each period being 20 cm in length. The vertical magnetic structure is a 2.0 T hybrid permanent magnet configuration, just like the planar wiggler, while the horizontal structure is an iron core electromagnetic design. Through the excitation of the horizontal poles with a trapezoidal current waveform, a maximum peak field of 0.1 T at an oscillating frequency up to 1 Hz can be achieved.\textsuperscript{17} An EPU is a magnetic device that provides tunable synchrotron radiation with the ability to provide photons from 20-1000 eV, enabling controlled beamline experiments in the soft x-ray spectrum.\textsuperscript{18} EPUs can be used in a variety of polarization modes, including circular, elliptical, horizontal, and vertical. Each mode can be chosen by selecting the appropriate phasing of the magnetic rows, shown in Figure 2.11.\textsuperscript{19}

\textbf{Figure 2.11} - Arrangement of the permanent magnetic blocks for the EPU at the ALS, where Q1 and Q3 (yellow) can be arranged to control the polarization.\textsuperscript{19}
The Chemical Dynamics Beamline in particular is attached to an undulator. The undulators at the ALS are typically quite large, 14 feet long and approximately 50,000 pounds. Inside the undulator are multiple magnets, lined up so that there are alternating magnetic poles as shown in Figure 2.12.

![Figure 2.12 - The arrangement of magnets with alternating poles inside of an undulator at the ALS.](image)

The distance between two opposite poles (an N and S in opposite rows (note the two rows of magnets shown in Figure 2.12)) is known as the undulator gap, which can be changed electronically when selecting a particular energy, typically in increments of 0.050 eV. The distance between two of the same pole (N and N, or S and S), in the same row, is a fixed value for each undulator, where the magnets can be arranged in 5 cm periods, 8 cm periods, or 10 cm periods. The Chemical Dynamics Beamline is connected to an undulator with a 10 cm period arrangement for a total of 43 periods. The spectral range that each undulator can cover is directly related to the period length. While the period is set in the undulator as 10 cm ($\lambda_u$), the electron, moving at a speed
near the speed of light \( (c) \), does not observe a period of 10 cm, but one much shorter \( (\lambda_e) \). This shortened period is defined by Equation 2.5, where Gamma \( (\gamma) \) is directed related to how relativistic a particle is, where at the ALS, \( \gamma \approx 4000 \).\(^{14}\)

\[
\lambda_e = \frac{\lambda_u}{\gamma} \quad (2.5)
\]

Using the values presented, \( \lambda_e \) is approximately \( 2.5 \times 10^{-3} \) cm. This value corresponds to light in the infrared region of the spectrum. Because the electrons are moving at speeds nearing \( c \), the light emitted by the electrons experiences a sort of “Doppler effect”. For light being emitted forward, the “Doppler” shift decreases the wavelength of the radiation by a factor of \( \gamma/2 \), or 2000 times. Now, the light that initially had a wavelength of \( 2.5 \times 10^{-3} \) cm has a wavelength of \( 1.25 \times 10^{-6} \) cm, which corresponds to the VUV region of the spectrum.\(^{14}\)

Once the radiation leaves the storage ring, heading down the beamline, it passes through the gas filter. The gas filter is a 4.5” pipe, that acts as a windowless absorption cell filled with 30 Torr of either Ar or Kr gas.\(^{12}\) Its purpose is to remove the unwanted high energy harmonics with energies above the ionization energies of Ar or Kr (15.759 eV and 13.99961 eV, respectively).\(^{12,16}\) The suppression of the photons at these higher energies can be determined using Beer’s Law, shown in Equation 2.6, where \( I \) is the transmitted photon intensity, \( I_0 \) is the incident photon intensity, \( \sigma \) is the photoabsorption cross-section, \( l \) is the path length, and \( N \) is the gas density.

\[
\frac{I}{I_0} = e^{-\sigma l N} \quad (2.6)
\]
As an example, if the cross-section is $10^{18} \text{ cm}^2$, the path length is 12 cm, and the gas density at 30 Torr is $10^{18} \text{ atoms cm}^{-3}$, then $I/I_0$ has a value of $10^{-5}$. This means that the higher harmonics are suppressed on a scale of five orders of magnitude.

After this point, the synchrotron radiation reaches the 3 m off-plane Eagle monochromator.\textsuperscript{12,19} This is an optical device that uses a concave spherical diffraction grating to filter a polychromatic spectrum of light to a specific wavelength.\textsuperscript{5} While the undulator has the ability to select the requested energy, the resulting electromagnetic radiation is still roughly polychromatic, portraying a Gaussian function that peaks at the requested energy. The monochromator then reduces this broad energy band to the single requested energy that is near the peak of the Gaussian curve produced by the undulator. When a diffraction grating is used, the angle, $\theta$, which satisfies Bragg’s Law (Equation 2.7) is determined by adjusting the grating through rotation until the correct wavelength, $\lambda$, is reflected back.

$$\lambda = 2d\sin(\theta)$$

(Equation 2.7)

Figure 2.13 shows an example of a diffraction grating, where an incident beam of light is scattered into multiple beams of monochromatic light.
2.7. Experimental Setup

The experimental apparatus used for the studies presented in this work consists of an orthogonal-acceleration time-of-flight mass spectrometer (oa-TOF-MS) that is coupled to the ALS. The mass spectrometer and its detector will be described in further detail in the following sections.

2.7.1. TOF-MS

Figure 2.1 provides a schematic of the oa-TOF-MS. Generally, a TOF-MS operates by scattering ions of varying mass-to-charge \((m/z)\) ratios, and then identifying them based on the time taken for their flight along a field free drift path of a known length. The ions focused into the ion beam enter the orthogonal accelerator at a velocity, \(v_{\text{beam}}\), where the ion kinetic energy in the beam is in the range of 10-100 eV.

Figure 2.13 - Diffraction gratings are used to separate polychromatic light into monochromatic light through the use of fine grooves cut into coated glass. The incident beam strikes the grating at an angle, \(\theta\), and the grating displaces monochromatic light at angles. \(\phi\).
A package of these ions of length $l_p$ is then pushed out orthogonally from its initial direction by a sharp pulse, and accelerated to a velocity of $v_{tof}$ into the TOF analyzer by a voltage set anywhere between 5-10 kV.\textsuperscript{20} The angle ($\theta$) between the ion beam and the path of the orthogonally accelerated ions is given by Equation 2.8.\textsuperscript{20} Using the energy ranges provided earlier in Equation 2.8 and 2.9, an angle close to 90° is easily obtained. For example, using the minimum value in each range would result in $\frac{5000}{10} = 500$ where $\tan^{-1}(500) = 89.89°$.

$$\theta = \tan^{-1}\left(\frac{v_{tof}}{v_{beam}}\right)$$

(2.8)

The respective velocities can be determined using Equation 2.9, where $e$ represents electron charge ($1.6021765 \times 10^{-19} C$), $z$ is the integer number of electron charges, $U$ is the applied voltage, $m_i$ is the ion mass, and $K_i$ is the ion kinetic energy.

$$v = \sqrt{\frac{2ezU}{m_i}} = \sqrt{\frac{2K_i}{m_i}}$$

(2.9)

While the ion package travels through the drift path of the TOF analyzer, and begins to disperse in time, the accelerator is refilled with a new ion beam from the ion source.\textsuperscript{20}

In our experiments, this process occurs after the effluent passes through the pinhole in the reactor tube, as mentioned previously. Once the effluent reaches the ionization region of the TOF analyzer, ions are extracted and focused into a continuous ion beam. The oa-TOF-MS continuously extracts ions at a repetition rate of 50 kHz, repeating once the heaviest ions have reached the detector.\textsuperscript{21} In this setup, the detector consists of micro-channel plates (MCP). In conjunction with MCP, time-to-flight
digital converters (TDC) are used to increase the resolution, and convert output from
the detector into accessible computer data for analysis.

2.7.2. Micro-Channel Plates (MCP)

Micro-channel plates are essentially linear channel electron multipliers (CEM),
also known as linear channeltrons, and are present in an electrooptical ion detector
(EOID). The MCP detector consists of an array of tubes, each of a micrometer
diameter, placed together to produce a channel electron multiplier array. The
manufacture of MCPs entails placing a rod of chemically etchable core glass inside a
tube of cladding glass that is typically composed of a lead glass composition. The core
is eventually etched out, leaving the cladding glass to make up the channels in the MCP
array. When the plate is completed, it is reduced in an oven in the presence of H$_2$ gas.
This process forms a semiconducting layer that involves the formation of lead from the
lead oxide in the glass on the inside of the channels. Nichrome (or alternative metallic
electrodes) are vacuum-deposited on both surfaces of the MCP. When a particle is
accelerated towards the MCP, it has a certain probability of striking the inside of a
channel. If it strikes the interior wall with enough energy, it will cause a secondary
emission of electrons. The MCPs are aligned in such a way that it does not lie parallel
with the ion beam, but slightly off this parallel axis. This ensures that ions strike the
channel wall, causing the emission of an electron in the process. The MCPs have a
voltage applied across both ends so they can generate an electric field. This electric
field is used to accelerate a secondary wave of electrons once the initially emitted electron comes into contact with the channel wall once again. A cloud of electrons will emerge from the rear of the MCP in such a way that it produces a specific pattern pertaining to the ion involved. This particular detector uses two MCPs that are stacked together with differing angles. This configuration is known as a Chevron configuration, allowing for the amplification of the resolution on the scale of $10^6$-$10^7$. A third configuration, consisting of three MCPs, is known as a z-stack, where the resolution can be amplified on the scale of $10^8$. An example of an MCP incorporated into a detector is shown in Figure 2.14.

Figure 2.14 – A schematic of an Electrooptical ion detector, which incorporates the use of a microchannel plate. Ions strike the microchannel plate, which produce a cascade of electrons that will strike the phosphorescent screen. The radiation from the screen passes into the array transducer via fiber optics, and the transducer converts the optical signal to an electric signal.
2.8. Data Acquisition

The time-resolved mass spectra were acquired from a compilation of TOF mass spectra taken at a set repetition rate over the course of a designated kinetic time frame. Complete mass-, time-, and energy-resolved data sets were obtained by recording time-resolved mass spectra as a function of the photon energy. When the laser fires to initiate a reaction, the corresponding reaction time is $t_0$. The photon energy is typically scanned in the range of 8.0-11 eV in steps of 0.025 eV and normalized for the photon current of the ALS using a calibrated VUV sensitive photodiode. This data, in conjunction with the mass-to-charge ratio ($m/z$), is collected by the time-to-digital converter (TDC) from the micro-channel plates output. In the studies presented here, the signal was background-corrected by subtracting the average prephotolysis signal.

2.8.1. Data Representation

Once the signal has been background-corrected, one can obtain a post-photolysis mass spectrum. Because of the multiplex capability of this apparatus, the ion signal is a function of multiple variables, i.e., $m/z$, reaction time ($t$), and photon energy ($h\nu$). This generates a three-dimensional data block, shown in Figure 2.15, which can be difficult to visualize and analyze. Therefore, a dimensionality reduction is performed by fixing one variable and plotting the other two to yield “two-dimensional slices,” the two most important of which are the time- and energy-dependent mass spectra. Then, for each individual $m/z$, a photoionization efficiency
Figure 2.15 – A representation of the 3-D data block obtained for analysis. The three different two-dimensional slices are shown, along with corresponding one-dimensional profiles.\textsuperscript{26}
(PIE) spectrum and a kinetic-time profile can be acquired; both considered a “one-dimensional slice”. The PIE spectrum is useful for obtaining important observables such as ionization energy while the kinetic-time profile provides visual information on the nature of the compound at the mass being analyzed. Utilizing these data, one has the resources to determine if a compound is a primary product, a depleting reactant, a result of fragmentation, or an unstable radical. Taking a look at Figure 2.15, some of the qualities that are characteristic of the mentioned species are presented. The spectra on the top left of the figure portrays the PIE spectra of two species, C\textsubscript{3}H\textsubscript{3} and C\textsubscript{6}H\textsubscript{6}. From this, one can already see that the concentration of C\textsubscript{6}H\textsubscript{6} is much higher than C\textsubscript{3}H\textsubscript{3} not only based on the quantitative scales provided, but also from the level of noise in each respective spectrum. In the spectrum shown on the top right of Figure 2.15, the same two species are presented in terms of their respective time traces, rather than by their PIE spectrum. The time trace provides information on the formation of the species, where C\textsubscript{6}H\textsubscript{6} forms relatively quickly and then maintains a fairly constant concentration which is characteristic of the formation of a product. The time trace of C\textsubscript{3}H\textsubscript{3} shows a rapid formation, and a quick depletion, characteristic of an unstable radical. Taking this knowledge back to the PIE spectra to the left, it makes sense that the PIE spectrum of the radical species would be noisier, and lower in concentration than a species that is a stable product. To further characterize products into primary or secondary products, the time trace of the product in question should be compared to the time trace of the starting material. If the rate of formation of the product matches the rate of depletion of the
reactant, then the compound portrays characteristics of a primary product. If, however, the product forms at a slower rate, it is more likely a result of secondary chemistry, and therefore a secondary product.

2.8.2. Analysis

Once the experimental photoionization spectra are collected, they can be compared to literature references, either experimental or calculated, in order to identify each species. This technique is also particularly useful when trying to identify multiple isomers at a single mass, as each isomer has specific Franck-Condon factors for the ionization transitions. To obtain a calculated, or simulated, PIE spectrum for a particular molecule, the composite model of theory, CBS-QB3, is used on the Gaussian09 molecular modeling program. For each specific compound, the neutral and cationic state must be submitted to the program for optimization. The results of the calculations provide values used in estimating the ionization energy, as well as produce a plot comparable to an experimentally obtained PIE spectrum. To determine the adiabatic ionization energy (AIE), for example, one needs the energy obtained from the neutral optimization calculation, as well as the value from the cation optimization. This is represented as Equation 2.10.

\[
AIE = E_{\text{cat}} - E_{\text{neut}}
\]  

(2.10)

Simulated spectra can then be obtained through a secondary calculation using the obtained check (*.chk) files for the neutral and cation in addition to the calculated AIE
value. This calculation does not use a basis set, but uses the neutral’s and cation’s Franck-Condon factors to generate a spectrum. The simulated results are photoelectron spectra, and need to be integrated so they can easily be compared to the experimentally observed photoionization spectra. Details regarding Franck-Condon factors, photoelectron spectra, and photoionization spectra will all be discussed further in Chapter 3.

Utilizing the Igor Pro software\textsuperscript{31} with the established protocol (series of ad hoc procedures), ALS Kinetic Tools v1.4a,\textsuperscript{32} the experimentally obtained photoionization spectra and corresponding kinetic time traces can be visualized for analysis. Each species observed on the post-photolysis mass spectrum is then identified as a primary product, chlorinated product, secondary product, or fragment based on the nature of the spectrum obtained. Each primary product then needs a corresponding suggested mechanism explaining its formation. Further details pertaining to each experiment’s analysis is provided in their respective chapters.
2.9. References


Chapter 3
Theoretical Concepts

3.1. Introduction

This thesis documents research that focuses on combustion chemistry, using both experimental and theoretical physical chemistry techniques. Specifically, experiments entail pseudo-combustion reactions where selected molecules are reacted with photolytic precursors (Cl radicals), and irradiated with photons from a synchrotron, portrayed by the experiment in Chapter 4. The experiment presented in Chapter 5, while still involved in the process of irradiation by photons from a synchrotron, does not incorporate any chemical reactions, but focuses on using theory to explain the experimentally observed nature of the compounds studied.

The focus on combustion chemistry comes from the recent demand for alternative energy sources, especially for biofuels. If a particular compound is found to have potential as a biofuel, it is important that a greater understanding is obtained involving its combustion reaction kinetics. In understanding how these smaller hydrocarbons, and any functional groups involved, react in a combustion setting, they can more easily be compared to the current performance of petrol-based fuels.¹

3.2. Photochemistry

Photochemistry is the study of the chemical reactions and physical behavior that can occur under the influence of visible or ultraviolet light. The Grotthus-Draper
Law² states that light must be absorbed by a compound in order to initiate a photochemical reaction. The experimental analysis presented in this text interprets the results obtained from the interaction of photons with chosen reactants. Table 3.1 lists the known photochemical reactions.

Table 3.2 – A list of the generalized photochemical reactions.³

<table>
<thead>
<tr>
<th>Process</th>
<th>General Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization</td>
<td>$A \cdot \rightarrow A^+ + e^-$</td>
</tr>
<tr>
<td>Electron Transfer</td>
<td>$A \cdot +B \rightarrow A^+ + B^-$</td>
</tr>
<tr>
<td>Dissociation</td>
<td>$A \cdot \rightarrow B + C$</td>
</tr>
<tr>
<td>Addition</td>
<td>$2A \cdot \rightarrow B$</td>
</tr>
<tr>
<td>Abstraction</td>
<td>$A \cdot +BC \rightarrow AB + C \cdot$</td>
</tr>
<tr>
<td>Isomerization</td>
<td>$A \cdot \rightarrow A'$</td>
</tr>
</tbody>
</table>

3.2.1. Photoionization

To understand how photoionization occurs, it is important to understand the environment of an atom or molecule in terms of its orbitals. Orbitals are used to describe the distribution of electrons within the confines of an atom or molecule, as well as the properties of the electrons. Electron spectroscopy is the study of the interaction of electromagnetic radiation with orbitals, and how electrons can transition between different orbitals through the absorption or emission of a photon.⁴

When approximating orbitals, it is determined that each orbital has a discrete energy, denoted by $E_n$, where $n$ is an orbital identifier. In order to move an electron from one orbital to another, it must absorb (or emit) an energy equal to the difference
in the corresponding orbital energies ($\Delta E$). This is portrayed by Equation 3.1, where $E_f$ and $E_i$ represent the energy of each orbital involved in the electronic transition.

$$\Delta E = E_f - E_i$$  \hspace{1cm} (3.1)

A photon is described as the smallest discrete value of electromagnetic radiation, or light. A photon’s energy, $E$, is defined by the following equation, where $\nu$ (frequency) is equal to $\frac{c}{\lambda}$. $\lambda$ is the wavelength, $c$ is the speed of light, and $h$ is Planck’s constant.

$$\Delta E = h\nu = \frac{hc}{\lambda}$$  \hspace{1cm} (3.2)

Ionization is the process in which an electron is removed entirely from an atom or molecule, shown in its general form in Table 3.1. This occurs when enough energy is supplied to an electron that it surpasses all of the bound orbitals, and thus escapes the binding forces of the atom or molecule. It is at this point that the electron has exceeded its ionization limit, with this energy being denoted as the first ionization energy of that specific orbital. Photoionization is therefore the result of an electron exceeding its ionization limit through the absorption of enough energy incident radiation to supply the required energy.

The absorption of the incident radiation by the electron, and any subsequent transition, occurs much faster than the corresponding reaction of the nucleus absorbing the incident radiation. Equation 3.3 represents the photoionization of the molecule, where both the molecule, $M$, and the cation, $M^+$, are considered to be in their electronic and vibrational ground state.
This, in turn, results in a difference in the internuclear distances within the molecule when compared to its cation. As a further result, if the electron is not ionized, the molecule will vibrate in an attempt to displace energy as the electron returns to the electronic ground state of the neutral molecule. The Franck-Condon principle, discussed further in section 3.3, explains the theory behind the transitions and spectral peaks that correspond to this vibration.

### 3.3. Franck-Condon Principle

The vibrational structure obtained from the electronic spectra of molecules can be further understood through nuclear motions that result from electronic transitions. The Franck-Condon principle states that because the nuclei are so much larger than the electrons, an electronic transition takes place much faster than the nuclei can respond. Because the nuclei do not react instantaneously, their reaction may be delayed, and occur at a later point in time. In classical terms, the nuclei are initially stationary, but once the electron density accumulates in a particular region, a newly generated force will act upon the nuclei, causing them to swing back and forth. The molecule, now vibrating, is outside of its initial equilibrium, thus displacing energy.

The Franck-Condon principle can also be explained using quantum mechanics. Instead of stating that the nuclei remain stationary during the electronic transition, quantum mechanics dictates that the nuclei retain their initial dynamic state.
dynamic state is expressed by the wavefunction, so as a result, the nuclear wavefunction does not change during an electronic transition. The nuclear state of the ion with a wavefunction that is closest to that of this initial wavefunction is the state to which the transition takes place. In Figure 3.1, the vertical transition, symbolized by a vertical arrow, represents the electronic transition that occurs without changing the nuclear geometry of the molecule.

Figure 3.1 – The diagram labeled (a) portrays the electronic transitions between similar nuclear equilibrium geometries, while (b) shows the electronic transitions between differing nuclear equilibrium geometries. The smaller spectra on the left are the absorption spectra associated with their respective electronic transitions.
In Figure 3.2, the transition is represented by a vertical arrow that begins at the ground state neutral configuration, and ends at the excited state, represented by a horizontal line. This vertical arrow represents a vertical transition to the excited state, or a transition that occurs without the nuclear geometry of the molecule changing in any way.\textsuperscript{6} The vertical transition occurs at the point where the two wavefunctions have the greatest overlap (this corresponds to the most intense peak in the first electronic band of a photoelectron spectrum).

\textbf{Figure 3.2} - Franck-Condon principle diagram.\textsuperscript{7}

The Franck-Condon principle is derived from the expression for the transition dipole moment, where the dipole moment operator, $\hat{\mu}$, is a sum of all nuclei and
electrons in the molecule, shown in Equation 3.4, where the vectors \( r_i \) and \( R_i \) are the distances from the center of charge of the molecule.\(^3\)

\[
\hat{\mu} = -e \sum_i r_i + e \sum_i Z_i R_i \tag{3.4}
\]

Utilizing the Born-Oppenheimer approximation, the transition dipole moment can be expressed by Equation 3.5. In this equation, \( n \) and \( m \) represent the initial and final states respectively.\(^6\)

\[
\mu_{nm} = \langle \Psi_n | \mu | \Psi_m \rangle \tag{3.5}
\]

The overlap is known as the Franck-Condon factor, and quantifies the match between the vibrational wavefunctions in both the upper and lower vibronic states. While this value is relatively easy to determine for diatomic molecules, the difficulty escalates quickly for polyatomic molecules, where symmetry rules and the Born-Oppenheimer approximation are needed to predict electronic transitions. Fortunately, these complex tools are incorporated into ab initio computational methods that can be utilized to predict these transitions.\(^7\) Ab initio methods make use of quantum mechanics and known physical constants to calculate the desired value, not needing any experimental parameters as other approximations would. These methods, in addition to the use of basis sets (mathematical representations of atomic orbitals within a molecule),\(^8\) are used for the electronic structure calculations explained further in section 3.5.
### 3.4. Photoionization Cross-Section

The cross-section of a molecule corresponds to the possible collision area (or area with the greatest probability for collision) of a particle with a molecule. In this case, the particle is a photon, the molecule depends on the compound being studied, and the cross-sections are referred to as photoionization cross-sections (PICS). The photoionization cross-section of a molecule can be defined as the effective area (cm\(^2\)) of a gaseous species that will interact with radiation (light) during ionization, and is measured in Megabarns (1 Mb = 1 × 10\(^{18}\) cm\(^2\)).

The absolute photoionization efficiency (APIE) spectrum is confirmed through the comparison of the experimental data with the APIE spectrum of a well-characterized species, such as ethene, propene, or 1-butene. These three calibration gases are all flowed into the cell, along with the compound being studied, with a known concentration for the purpose of comparison. The relationship of an individual species’ factors can be represented by Equation 3.6. It should be noted that both the relative ion signal and photoionization cross-section are energy dependent, and the values should be obtained for the same energy (\(E\)) throughout these calculations.

\[
S(E) = k\sigma(E)\delta C
\]  
(3.6)

The ion signal (\(S\)) of a compound is the product of the instrumentation constant \((k)\), the photoionization cross-section \((\sigma)\), the mass-dependent response \((\delta)\) (which for these experiments is approximately equal to \(m^{0.67}\), where \(m\) is the mass of the compound), and the concentration \((C)\) of the compound.
Utilizing these factors in combination with those of a known species (standard), the unknown cross-section of the target molecule (\(\sigma_T\)) can be determined as a ratio of its signal intensity (\(S_T\)) to the signal intensity of the standard (\(S_S\)), the concentration of the target and standard compounds (\(C_T\) and \(C_S\)), the mass discrimination factors of both (\(\delta_T\) and \(\delta_S\)), and the photoionization cross-section of the standard (\(\sigma_S\)). This is shown in Equation 3.7.

\[
\sigma_T(E) = \frac{S_T(E) \sigma_S(E) \delta_S C_S}{S_S(E) \delta_T C_T}
\]  

(3.7)

It is necessary to determine the PICS of molecules present in these experiments in order to determine product concentrations and branching fractions of specific isomers at each mass. Chapter 5 focuses on determining the PICS of three furanic compounds: 2-ethylfuran, 2-acetylfuran, and furfural.

3.5. Electronic Structure Calculations

The studies reported in this thesis all make use of computational methods, employing techniques that can obtain values used for PIE spectra approximations, bond lengths, angles, harmonic vibrational frequencies, and IR spectra. Each optimized electronic structure calculation is completed utilizing the CBS-QB3 composite method\(^{10-13}\) with the Gaussian09\(^ {14}\) program and viewed in GaussView 5.0.\(^ {15}\) Each ab initio computational method is made up of a level of theory and corresponding basis sets. These components are used to compute solutions to the Schrödinger equation through the use of various mathematical approximations. CBS-QB3\(^ {11-13}\) is known as
the complete basis set method, a composite method (ab initio and density functional) designed to overcome the greatest amount of error in electronic structure thermochemical calculations, i.e., basis set truncation. Bond distances and harmonic vibrational frequencies were optimized at the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP) level of theory and all electron 6-311+G* basis set.

The adiabatic ionization energy (AIE) of a specific molecule can be determined via the use of the zero-point vibrational corrected energy ($E_0$) obtained through optimization calculations. The $E_0$ must be obtained for both the ground state of the neutral and cationic molecule, where the AIE can be determined using Equation 3.8.

$$AIE = E_0(\text{cat}) - E_0(\text{neut})$$

(3.8)

The calculated AIE of a molecule is also used in generating Frank-Condon (FC) spectral simulations. These simulations are very useful when a PIE spectrum of a compound is not available in literature or cannot be obtained experimentally, as it generates a photoelectron spectrum by using Gaussian09. These spectra are generated through the calculation of FC factors for the transitions between the vibrational ground state of the neutral and the cation of a specific species at varying energies. The Gaussian09 output files include the determination of the wavefunctions with the greatest overlap between the neutral and cationic molecule, thus calculating the Franck-Condon factors. Once the resulting photoelectron spectra are integrated, the resulting simulated PIE spectra can be used to determine the identity of species at specific masses.
in these experiments. The AIE predicts the onset of the curve (an increase in signal from the baseline), and the FC factors predict the general shape of the spectrum.

3.6. Photoionization Efficiency Curves

The photoionization efficiency (PIE) spectra obtained from an experiment can further one’s understanding of gas phase oxidation reactions. It is a species’ individual Franck-Condon factors that create the distinct shape and onset of its specific PIE spectrum, shown in Figure 3.2. This is very useful when more than one isomer is observed at a given mass, as the PIE spectrum will show characteristics of each isomer present.

![Figure 3.2](image)

**Figure 3.2** - Experimental photoionization efficiency spectrum of $m/z = 110$ (red circles) with the experimental PIE spectrum of 2-acetylfuran superimposed (blue triangles).
When running experiments using the ALS, the photon energy generated by the synchrotron is used to scan a reaction in order to obtain a series of time-resolved mass spectra at each successive photoionization energy. It is through the analysis of each experimental PIE spectrum that one can begin to identify how the studied pseudo-combustion reaction proceeds. The experiments performed at the ALS, and reported in this thesis use this photochemical method based on PIE spectra for identification of combustion products. Figure 3.2 shows the comparison of an experimentally obtained PIE spectrum of 2-acetylfuran with the experimental spectrum at \( m/z = 110 \). This is considered to be a successful identification of the unknown compound that produced the PIE spectrum at \( m/z = 110 \) due to the matching onset (ionization energy) and the similarities in curvature (overall shape) throughout the spectrum. Figure 3.3 shows a similar comparison for a signal found at \( m/z = 42 \) but with multiple isomers contributing to the signal.

![Graph showing PIE spectra comparison](image)

**Figure 3.3** – Experimental photoionization efficiency spectrum obtained of \( m/z = 42 \) (red circles) is presented, along with the experimental absolute PIE spectra of cyclopropane and propene (blue and black line, respectively). The sum (dotted black line) of the cyclopropane and propene spectra is superimposed, showing that both species are contributing to the signal at \( m/z = 42 \).
3.7. References


Chapter 4

Synchrotron Photoionization Study of 2-Methylfuran and 2-Ethylfuran
Oxidation Initiated by Reaction with Cl(2P) Radicals

Abstract

The oxidation reactions of 2-methylfuran (2MF) and 2-ethylfuran (2EF) initiated by Cl radicals is studied at the low temperatures, 323 and 305 K respectively, and a pressure of 4 Torr. These experiments are carried out using synchrotron photoionization mass spectrometry (SPIMS) with an orthogonal time-of-flight spectrometer used for mass analysis at the Advanced Light Source of Lawrence Berkeley National Laboratory. CBS-QB3 calculated adiabatic ionization energies (AIE) agree well with the experimental results and published literature values. Furfural is found to be the dominant product of 2MF oxidation, with 2-acetylfuran and 2-vinylfuran being the dominant products of the 2EF oxidation reaction.

4.1. Introduction

The need for alternative fuel sources has become a growing global concern as petroleum sources begin to diminish.\(^1\,\text{,}\,2\) Furan and alkylfurans have been identified as potential alternative biofuels,\(^3\,\text{,}\,4\) both of which can be derived from biomass.\(^1\) These compounds have the potential to be used as primary fuel sources, and are already considered to be primary and secondary pollutants found in the atmosphere.\(^5\) Primary pollutants are generated predominantly by human activity, but also through natural
processes such as tropical forest fires and plant emissions.\textsuperscript{5,6} As secondary pollutants, they form as a result of atmospheric interactions involving other primary pollutants. Of the alkylfurans, 2,5-dimethylfuran (25DMF) has been a popular research topic due to its potential as a possible alternative fuel.\textsuperscript{1,7,8} 25DMF, with its newly established production processes,\textsuperscript{1} rivals the current market leading biofuel, ethanol;\textsuperscript{4,8} however, emission measurements of 25DMF showed that carbon monoxide (CO) and hydrocarbon (HC) emissions were lower than that of gasoline, but still higher than ethanol. In addition to this, nitrous oxide emissions were greater for 25DMF than both gasoline and ethanol.\textsuperscript{8}

The alkylfuran 2-methylfuran (2MF) has also been identified as a promising alternative biofuel.\textsuperscript{4,7,9} It has recently become a possible fuel source due to the establishment of novel production methods,\textsuperscript{8,10,11} while also a byproduct of the production of 25DMF.\textsuperscript{3} 2MF exhibits a drop in HC emissions by 61\% when compared to commercial fuel and ethanol with a research octane number of 95, in addition to efficiency improvements nearing 9.9\%.\textsuperscript{2,4,8} However, like 25DMF, greater nitrous oxide emissions were measured.\textsuperscript{2,8} Combustion intermediates of 2MF have been investigated using tunable synchrotron vacuum ultraviolet photoionization and molecular beam mass spectrometry by Wei et al.\textsuperscript{3} They provided photoionization mass spectra of MF/oxygen/argon flames, in addition to the photoionization efficiency curves (PIEs) and accompanying ionization energies (IEs) of the combustion intermediates. In their experiment with 2MF they also observed the production of 2-
ethylfuran (2EF), and provide speculation on potential species related to 2EF. They identified furfural as the oxidation product after hydrogen abstraction from 2MF, which was also observed in this study.

Villanueva et al.\textsuperscript{5} have provided insight on both 2MF and 2EF (structures shown in Scheme 4.1) utilizing FTIR absorption spectroscopy, solid phase microextraction gas chromatography by flame ionization, electron capture, and mass spectrometry (SPME GC-FID/ECD/MS). They provide mass spectra, FTIR spectra, and gas chromatograms on both the reactions of 2MF and 2EF with chlorine atoms. Potential products and suggested corresponding mechanisms are also presented. Of these products, it is identified that furfural is the result of hydrogen abstraction from 2MF, and that 2-acetylfuran and 2-vinylfuran are results of hydrogen abstraction from 2EF as found in this study.

![Structure of 2-methylfuran (2MF) and 2-ethylfuran (2EF) showing numbering of the carbons in the furan ring.](image)

**Scheme 4.1** – Structure of 2-methylfuran (2MF) and 2-ethylfuran (2EF) showing numbering of the carbons in the furan ring.

Davis et al.\textsuperscript{7} have calculated reaction rate constants as well as potential energy surfaces (PESs) corresponding to the oxidation behavior of 2MF at low temperatures through the initiation of OH radicals. The pathways covered include hydrogen abstraction by hydrogen atoms and OH radicals, as well as the addition of OH and O\textsubscript{2}
to 2MF. Somers et al.\(^8\) also presented kinetic modelling on 2MF oxidation. The modelling was based on the H-atom addition and abstraction by \(O_2\), \(·OH\), \(·CH_3\), or \(O\) radicals in previous calculations involving 25DMF and toluene published by Metcalfe et al.\(^{12}\) and Cabañas et al.\(^{13}\) have also studied the Cl-initiated oxidation of 2EF at 298 ± 2 K and 1 atm using a relative rate technique with GC-FID/MS to determine an absolute rate constant for Cl atoms reacting with 2EF to be \((4.6±0.3)\times10^{-11} \text{ cm}^3 \text{ molecul}e^{-1} \text{ s}^{-1}\).

This study will focus on the combustion reactions involving the alkylfuran 2MF and 2EF at 323 and 305 K, respectively, and 4 Torr, identifying probable reaction pathways and products. Utilizing a multiplexed mass spectrometer coupled with tunable synchrotron radiation, time- and energy-resolved profiles of both reactants and products are obtained. The resulting photoionization efficiency spectra (PIE) grant the ability to identify and differentiate isomeric species. Through this technique, this study aims to enhance previous studies on 2MF, and provide further insight on the lesser-studied 2EF, through the identification of possible intermediates and products of the primary chemistry in the Cl-initiated oxidation reactions of these species. The pathways of interest include the OH and HO\(_2\) elimination, which were found to occur through either a formally direct pathway, or through a QOOH intermediate. 2MF almost exclusively proceeds to the direct formation of furfural through hydrogen abstraction from the methyl group, which has been identified as one of the most prominent pathways.\(^8\)
4.2. Experimental

4.2.1 Apparatus

The study of the chlorine initiated oxidation reactions of 2MF and 2EF was carried out at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. The description of the experiment can be found in greater detail elsewhere,\textsuperscript{14–16} and will only be summarized here.

The utilized experimental apparatus is a multiplexed synchrotron photoionization mass spectrometer (mSPIMS). Initially, the gas mixture is flowed into a heated quartz reactor tube that has an inner diameter of 1.05 cm and is insulated in such a way so as to improve temperature uniformity along the length of the tube, and reduce heat transfer from the tube itself to the vacuum chamber. For each of the reactions with 2MF and 2EF, the temperature is maintained at 323 and 305 K, respectively, and a pressure of 4 Torr.

The gaseous mixture continuously flows into the reactor where a 351 nm excimer laser operating at 4 Hz initiates the photolysis of Cl\textsubscript{2}. With the total gas flow rate into the reactor tube maintained at \( \sim 400 \text{ cm s}^{-1} \), and the laser repetition rate at 4Hz, a fresh sample of gas is present for each laser pulse throughout the experiment. The resulting Cl· atoms initiate the reaction with O\textsubscript{2} by extracting a hydrogen atom from the reactants. Cl· atoms can bond directly to the reactants such as in the case of furanic compounds that possess a conjugated \( \pi \)-system, producing chlorinated products at larger masses. The concentration of chlorinated products can be minimized by using an
excess amount of the reactant mixture, and a relatively low concentration of Cl· atoms. The concentration of Cl₂ gas flowed into the reaction chamber was $3.5 \times 10^{13}$ molecules/cm³ in the 2MF experiment and $1.1 \times 10^{14}$ molecules/cm³ in the 2EF experiment. It is estimated that 1% of the Cl₂ is converted to Cl· atoms based on both the measured laser fluence of 10-60 mJ cm⁻² and photodissociation cross-section of $1.82 \times 10^{-19}$ cm² for Cl₂ at 351 nm. The 1.01% mixture of 2MF flowed into the reactor tube resulted in a concentration of $3.5 \times 10^{13}$ molecules/cm³, and the flow of the 1.01% mixture of 2EF resulted in a concentration of $3.48 \times 10^{13}$ molecules/cm³. After the reaction is initiated by the Cl· atoms present, the starting material reacts with O₂ that is present at a concentration of $1.9 \times 10^{14}$ molecules/cm³ in the 2MF experiment, and $2.2 \times 10^{14}$ molecules/cm³ in the 2EF experiment.

The reaction species then pass through a 1.5 mm skimmer into a differentially pumped ionization chamber where it is orthogonally intersected by the tunable-synchrotron radiation produced by the ALS. The resulting ions are then accelerated, and transferred, into the linear time-of-flight mass spectrometer for analysis. The mass resolution for these experiments is approximately 1,600, and the largest observable $m/z$ is 156 based on the current experimental set-up. Once the data are collected, a background subtraction using the averaged mass spectrum from pre-photolysis can be done to obtain a post-photolysis mass spectrum that shows a negative signal for depleting reactants, and a positive signal for products. Because of the multiplex capability of this apparatus, the ion signal is a function of multiple variables, i.e., $m/z$. 
reaction time \(t\), and photon energy \(h\nu\). This generates a three-dimensional data block, which is difficult to visualize and analyze. Therefore, a dimensionality reduction is performed by fixing one variable and plotting the other two yielding “two-dimensional slices,” the two most important of which are the time- and energy-dependent mass spectra. Then, for each individual \(m/z\) a photoionization spectrum and a kinetic profile can be acquired. Once the experimental photoionization spectra are collected, they can be compared to literature references, either experimental or calculated, in order to identify each species. This technique can be particularly useful when trying to identify multiple isomers at a single mass, as each isomer has specific Franck-Condon factors for the ionization transitions.

**4.2.2. Measurement Procedures**

Both 2MF and 2EF were purchased with a labeled purity of 99% from Sigma-Aldrich. Additionally, furfural was also purchased with a labeled purity of 99% (Sigma-Aldrich). Each sample was freeze-pump-thawed to remove any dissolved gases before they were prepared for use in the experiment. The concentrations of each reactant in their respective experiments are known, as described in the previous section. It is also possible to determine the concentration of each product relative to the reactant through the use of absolute photoionization cross-sections. Once calculated, these concentrations are used to help determine the branching fraction, or branching yield in
the case of a product that may result from several possible reaction pathways with respect to the reactant.

The absolute photoionization spectrum of the species in question can be obtained through the comparison of its experimental data with the absolute photoionization spectrum of a known species, such as ethene, propene, or 1-butene. The ion signal of a particular compound at a specified photon energy (\(S_E\)) is the product of the instrumentation constant (\(k\)), the photoionization cross-section at a specified photon energy (\(\sigma\)), the mass-dependent response (\(\delta\)) (which for these experiments is approximately equal to the mass (\(m\)) to the power of 0.67), and the concentration (\(C\)) of the compound in question, shown in Equation 4.1. The experimental procedure for the determination of the mass-dependent response (\(\delta\)) is described in detail by Savee et al.\(^{18}\)

\[
S_E = k\sigma_{E}\delta C
\]  

(4.1)

Utilizing these factors, the branching yield is calculated as the quotient of the concentration of the product (\(P\)) over the concentration of the reactant (\(R\)) as shown in Equation 4.2. Ideally, the ion signal used for both \(S_R\) and \(S_P\) should be compared where both of the respective photoionization spectra exhibit a plateau at the same photon energy.

\[
Branching\ Yield = \frac{C_P}{C_R} = \frac{S_P}{\sigma_{p}\delta_{p}} = \frac{S_P\sigma_R\delta_R}{S_R\sigma_{p}\delta_{p}} = \left(\frac{S_P\sigma_R}{S_R\sigma_{p}}\right)\left(\frac{m_R}{m_p}\right)^{0.67}
\]  

(4.2)
To determine the branching yields of the products resulting from the 2MF reaction, the absolute photoionization spectra of 2MF and furfural are collected along with a gas calibration mixture containing a known amount of ethene, propene, and 1-butene. These spectra are then compared to the absolute photoionization spectrum of 1-butene as recorded by Wang et al.²

The absolute photoionization cross-section of 2MF has been reported by Czekner et al.¹⁵ to be 27.29 Mb (1 Mb = 1 × 10⁻¹⁸ cm²) at a photon energy of 10.988 eV. The APICS of 2EF has been determined by Smith et al.¹⁶ to be 16.6 Mb at 11.0 eV. Both of these APICSs were obtained by using the same instrument that was used in this study, and accurately matched experimental data found in previous studies.¹⁹ Additionally, Smith et al.¹⁶ reported the cross-section of furfural as 10.9 Mb at 11 eV. Previous experiments using known gas mixtures have identified that the uncertainty measured for cross-sections obtained using this mass spectrometer are at most ± 20%.¹⁵

The branching yield of furfural in the 2MF study was determined to be 53%. The branching yields of 2-vinylfuran and 2-acetylfuran in the 2EF study were determined to be 1% and 2%, respectively. These values are shown in Tables 4.1 and 4.2 and discussed further.

4.3. Computational

All optimized electronic structure calculations are completed utilizing the CBS-QB3 composite method²⁰⁻²² with the Gaussian09 program²³ and viewed in GaussView
In the optimization of each structure, parameters such as bond lengths, bond angles, harmonic vibrational frequencies, force constants, and ionization energies are derived. The adiabatic ionization energy (AIE) of a particular molecule can be determined through use of the zero-point vibrational corrected energy ($E_0$) obtained through the optimization calculations. The $E_0$ must be obtained for both the ground state of the neutral and cationic molecule. Assuming that there is no dissociation barrier, $E_0$ is derived from the reaction portrayed by Equation 4.3, where the dissociative ionization fragment, or daughter ion, ($A^+$) and the neutral fragment ($B$) are the products, and the neutral parent ($AB$) is the reactant. Once the needed $E_0$ values are obtained, the AIE can be determined using Equation 4.4.

$$AB \xrightarrow{hv} A^+ + e^- + B$$

$$AIE = E_0(\text{cat}) - E_0(\text{neut})$$

The calculated AIE of a molecule is also used in generating Frank-Condon (FC) spectral simulations. Using the CBS-QB3 composite method in conjunction with Gaussian09 the FC spectral simulation can be generated for a specific compound. These simulations are very useful when a photoionization spectrum of a compound is not available in literature or cannot be obtained experimentally, as Gaussian09 generates a photoelectron spectrum to use instead. These spectra are generated through the calculation of FC factors for the transition between the vibrational ground state of the neutral and the cation of a specific species. The photoelectron spectra can then be
integrated, resulting in photoionization spectra that can be used to determine the identity of species at specific masses in this experiment.

The E₀ of the neutral molecule is also used when determining if a suggested mechanism is thermodynamically favorable by calculating the heat of reaction, ΔH_rxn. If the E₀ of a neutral product is higher than the sum of the E₀ of the initial H-abstraction radical + O₂, which is the reference threshold, that particular pathway is considered not to be thermodynamically feasible. The potential energy surface (PES) of both the 2-furylethyl + O₂ system and 2-furylmethyl + O₂ system proposed in this study were developed through relaxed PES scans at the B3LYP/6-31G(d) level. 2-furylethyl (2EF-A in Scheme 4.6) and 2-furylmethyl (2MF-A in Scheme 4.3) are the result of H-atom abstraction by a Cl- atom from 2MF and 2EF, respectively. Upon locating energy maxima, saddle points are identified and tested for the presence of a single imaginary vibrational frequency, which is characteristic of a transition state. Once the local energy minima before and after the identified transition state are finalized as the mechanistic steps desired for the reaction pathway, the relative enthalpy of the reaction can be determined. The structures at each of these local minima are then used to determine the E₀ of the corresponding neutral molecule using the CBS-QB3 model. The ΔH_rxn can then be determined through the use of Equation 4.5. The enthalpy changes are relative to the energy of the reactants (portrayed as 2-furylmethyl + O₂ or 2-furylmethyl + O₂ in Schemes 4.3 and 4.6, respectively), which are used as a reference point.

\[
\Delta H_{rxn} = \Sigma \Delta H_{\text{products}} - \Sigma \Delta H_{\text{reactants}} = \Sigma E_{0_{\text{products}}} - \Sigma E_{0_{\text{reactants}}}
\]  

(4.5)
4.4. Results and Analysis

4.4.1. 2-Methylfuran + Cl + O\textsubscript{2} Reaction

The oxidation of 2MF is first initiated by chlorine radicals in the presence of oxygen at 323 K. The reaction of 2MF and Cl can proceed through two channels, an addition pathway where a chlorine atom bonds to the furan ring, or through H-atom abstraction from the methyl group in 2MF. The aromatic hydrogens are not abstracted by Cl at this temperature due to the endothermicity (approximately +64 kJ mol\textsuperscript{-1} calculated with the CBS-QB3 model) identified in this study’s calculations and previously mentioned by Simmie et al.\textsuperscript{25} Products of the Cl addition pathway can be readily identified by the well-known isotopic abundance of the two chlorine isotopes \textsuperscript{35}Cl and \textsuperscript{37}Cl, unlike addition products in reactions where OH radicals are the source of initiation. However, there can be species that appear as a result of the decomposition of chlorinated compounds, such as 4-oxo-2-pentenal (m/z = 98) that do not contain any chlorine. 4-oxo-2-pentenal was identified in experiments by Wei et al.,\textsuperscript{3} and was proposed to be a result of the decomposition of 4-oxo-2-pentenoyl chloride (m/z = 132) by Villanueva et al.\textsuperscript{5} According to Simmie et al.,\textsuperscript{30} H-abstraction from the methyl group in 2MF is the most prominent extraction pathway. Villanueva et al.\textsuperscript{5} also identifies H-abstraction from alkyl groups as the dominant extraction channel, while also noting that chlorine addition is the dominant addition pathway at 296 ± 2 K. After two trials (298 K and 323 K), it has been determined that chlorine addition is the dominant reaction pathway in this study of 2MF, having resulted in the formation of the majority
of the species recorded at masses above m/z = 100. This result is in compliance with Tapia et al.\textsuperscript{26} study on 3-methylfuran with Cl atoms, where the majority of products form due to initial chlorination.

The dominant, non-chlorinated, product of the reaction of 2MF with chlorine and oxygen was identified as furfural (m/z = 96); however, based on its observed time trace (Figure 4.1), it did not form as a result of primary reaction chemistry. The difficulty in obtaining a transition state for this OH-elimination pathway, in conjunction with the slower rate of formation demonstrated by the time trace, provides evidence that an indirect mechanistic approach would be needed. A possible mechanism to consider is a peroxy self-reaction, a viable process for both the 2MF and 2EF systems, as shown in Scheme 4.2.

![Figure 4.1](image)

**Figure 4.1** – Time trace of the formation of m/z = 96 (blue triangles) from the 2MF system with the inverse time trace of the depletion of 2MF (red circles) superimposed.
As previously mentioned, H-abstraction occurs at the methyl group in 2MF. This results in three possible bonding sites for oxygen due to the radical rearrangement (allylic resonance) shown in Scheme 4.3 and, therefore, three potential 2-methylfuranylperoxy radicals, 2MF-B1, 2MF-B2, and 2MF-B3. Due to the three possible isomers of the peroxy radical, a variety of pathways are accessible as portrayed in the potential energy surfaces in Schemes 4.4, 4.5, and 4.6. Whereas the most stable

**Scheme 4.2** – Proposed peroxy-self reaction mechanism for the formation of furfural from 2MF, and for the formation of 2-acetylfuran from 2EF.

**Scheme 4.3** – Formation of the three possible peroxy radicals, 2MF-B1, 2MF-B2, and 2MF-B3 after hydrogen abstraction from 2MF.
peroxy radical grants a larger energy range for its OH and HO₂-elimination channels, the higher energy isomers still have the ability to produce unique pathways of their own.

There are two channels displayed in the PES in Scheme 4.4 portraying the decomposition of the 2-methylfuranylperoxy radical, 2MF-B1. The first channel has

![Diagram of possible reaction pathways from the peroxy radical 2MF-B1.](image)

**Scheme 4.4** - PES of possible reaction pathways from the peroxy radical 2MF-B1. The bracketed values represent the change in relative energy from each direction, with the first number corresponding to the barrier for the forward reaction, and the second for the reverse reaction. Transition states were identified using the B3LYP/6-31G(d) level of theory. All energies and optimized structures were calculated with the CBS-QB3 model.
the terminal oxygen abstracting a hydrogen intramolecularly from the C3 position on
the furan ring, forming the QOOH species, 2MF-Q1. The relative heat of reaction
pertaining to this step is calculated to be +139 kJ mol$^{-1}$ with a calculated barrier for the
forward reaction of 176 kJ mol$^{-1}$ (2MF-TS1). The O-O bond undergoes heterolytic
cleavage, resulting in the OH group leaving the molecule, and forming the four-
membered ring in the compound, 2MF-P1 (m/z = 96). The relative heat of reaction
associated with this forward step requires more energy (2MF-TS2, +145 kJ mol$^{-1}$,
totaling +284 kJ/mol) than was provided by the initial reactants (+187 kJ mol$^{-1}$), which
is portrayed by the dashed line in Scheme 4.4. Because of the large energy barrier, this
channel is highly improbable at this temperature; as a result, 2MF-P1 was not observed
as an isomer involved with the signal at m/z = 96 based on its simulated PIE curve.

The second channel corresponds to the formation of furfural (m/z = 96), the
dominant product observed in this study of 2MF. As mentioned previously, it is
suspected that 2MF-B1 undergoes the self-reaction portrayed in Scheme 4.2 with
another 2MF-B1 molecule, forming two furfural molecules and molecular oxygen as
products with no observed barrier. Intramolecular H-atom abstraction from the C4 and
C5 positions do not occur due to the steric hindrance involved in the peroxy group
reaching across the furan ring to abstract the hydrogen atoms.

The possible pathways for the peroxy radical, 2MF-B2 (Scheme 4.5), are just
as limited as those associated with 2MF-B1. H-atom abstraction from the ethylene
group requires too much energy, with its barrier peaking at 144 kJ mol$^{-1}$ (2MF-TS3),
again, above the energy threshold provided by the initial reactants. The only viable pathway from 2MF-B2 is the peroxy self-reaction to form 2-methylenefuran-3(2H)-one \((m/z = 96)\) and molecular oxygen, at a relative heat of reaction of \(-148 \text{ kJ mol}^{-1}\).

There were no signs of its formation during the experiment based on the comparison of the experimental PIE spectrum of \(m/z = 96\) in Figure 4.2 and the simulated PIE spectrum of methylenefuran-3(2H)-one.

The third isomer of the 2-methylfuranylperoxy radical, 2MF-B3 (Scheme 4.6), acts similarly to 2MF-B2, where it is predicted to undergo self-reaction to form the

**Scheme 4.5** - PES of possible reaction pathways from the peroxy radical 2MF-B2. The bracketed values represent the change in relative energy from each direction, with the first number corresponding to the barrier for the forward reaction, and the second for the reverse reaction. Transition states were identified using the B3LYP/6-31G(d) level of theory. All energies and optimized structures were calculated with the CBS-QB3 model.
products, protoanemonin ($m/z = 96$) and molecular oxygen. As with 2-methylenefuran-3(2H)-one, protoanemonin was not observed in this study.

Because there are three possible peroxo radicals, 2MF-B1, 2MF-B2, and 2MF-B3, there were three mechanistically feasible compounds at $m/z = 96$: furfural, 2-methylenefuran-3(2H)-one, and protoanemonin. Based on the experimental PIE
spectrum obtained for $m/z = 96$ (open red circles) in Figure 4.2, it has been determined that furfural (blue triangles) is the species present. The observed experimental onset is at $9.18 \pm 0.05$ eV and furfural’s IE is reported in literature as $9.22 \pm 0.01$ eV. Both Villanueva et al. and Wei et al. identified furfural as the species present at $m/z = 96$. The branching fraction of furfural was determined to be 53% as shown in Table 4.1. It is suspected that 2-methylenefuran-3(2H)-one and protoanemonin were not observed due to their association with the less stable peroxy radicals, 2MF-B2 (-129 kJ mol$^{-1}$) and 2MF-B3 (-154 kJ mol$^{-1}$).

Table 4.3 – List of dominant, non-chlorinated products and their experimental AIE’s, calculated AIE’s, and branching yields from the 2MF + Cl + O$_2$ reaction.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Name</th>
<th>Structure</th>
<th>CBS-QB3 AIE (eV)</th>
<th>Experimental AIE (eV)</th>
<th>Branching Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>furfural</td>
<td><img src="image" alt="Structure" /></td>
<td>9.26 ± 0.05$^a$</td>
<td>9.18 ± 0.05$^a$</td>
<td>53</td>
</tr>
</tbody>
</table>

$^a$ This work  
$^b$ NIST 27

4.4.2. 2-Ethylfuran + Cl + O$_2$ Reaction

As with 2MF, the oxidation of 2EF is first initiated by chlorine radicals in the presence of oxygen at 305 K. The preliminary reaction of 2EF and Cl can proceed through two channels, an addition pathway where a chlorine atom bonds to the furan ring, or through H-atom abstraction from the alkyl group in 2EF. The aromatic hydrogens are not abstracted by Cl at this temperature due to the endothermic energy
barriers (approximately +63 kJ mol\(^{-1}\) calculated at the CBS-QB3 level) as was the case with 2MF. Zhang et al.\(^6\) noted in their study of 2EF + \cdot OH that it was more energetically feasible for the OH radicals to abstract the hydrogens on the CH\(_2\) and CH\(_3\) groups when compared to the aromatic hydrogens on the furan ring. Villanueva et al.\(^5\) identifies chlorine addition to be the dominant reaction pathway for 2EF, as they did with 2MF when Cl radicals are involved.

The oxidation reaction products observed are at \(m/z = 94\) and \(m/z = 110\), identified as 2-vinylfuran and 2-acetylfuran, respectively, as shown in Table 2. Wei et al.\(^3\) and Wu et al.\(^28\) identified \(m/z = 94\) as 2-vinylfuran in their observations of the oxidation of 2EF, and Villanueva et al.\(^5\) identified both \(m/z = 94\) and \(m/z = 110\) as 2-vinylfuran and 2-acetylfuran, respectively. The time trace associated with \(m/z = 110\), when compared to the time trace of the depletion of 2EF, shows similarities to that of furfural and 2MF in the 2MF Cl-initiated reaction. This supports the possibility that the peroxy radicals in the 2EF study also undergo self-reaction to form the observed products.

H-atom abstraction can occur at either the methyl or ethyl carbon position in the alkyl group in 2EF. This results in four possible bonding sites for oxygen due to the allylic resonance of the methylene position radical with the aromatic furan ring, and therefore four 2-ethylfuranylperoxy radicals, 2EF-B1, 2EF-B2, 2EF-B3, and 2EF-B4, as shown in Scheme 4.7.
The 2-ethylfuranylperoxy radical, 2EF-B1, is the result of molecular oxygen bonding to the methyl site on the alkyl chain in 2EF, as portrayed in the PES in Scheme 4.8. The first two channels are a result of the peroxy group abstracting an intramolecular hydrogen from the β-carbon position in the alkyl chain, increasing the relative heat of reaction to +73 kJ mol\(^{-1}\) to form 2EF-Q1 with a barrier of +145 kJ mol\(^{-1}\) (2EF-TS1). From here, OH-elimination forms the product, 2-(oxiran-2-yl)furan (\(m/z = 110\)) with a lower relative enthalpy of -1 kJ mol\(^{-1}\), while HO\(_2\)-elimination forms 2-vinylfuran at a slightly increased heat of reaction of +74 kJ mol\(^{-1}\). The barriers for these two pathways are quite similar, represented by 2EF-TS2 and 2EF-TS3 at an additional +51 kJ mol\(^{-1}\) and +52 kJ mol\(^{-1}\), respectively. The third channel consists of the
formation of the QOOH species, 2EF-Q2, through abstraction of an H-atom from the C3 position on the furan ring; however, each subsequent transition state is too high in energy to occur at this temperature due to 2EF-Q2’s energy of +140 kJ mol$^{-1}$ being so
close to the energy threshold of +197 kJ mol$^{-1}$. The fourth reaction channel pertains to the peroxy self-reaction of 2EF-B1, forming 2-acetylfuran ($m/z = 110$) and molecular oxygen at a relative heat of reaction energy of -157 kJ mol$^{-1}$, and no observed barrier. Of these four possible pathways, only 2-vinylfuran and 2-acetylfuran were observed based on the experimental photoionization spectra shown in Figures 4.3 and 4.4.

**Figure 4.3** – Time trace of the formation of $m/z = 94$ (blue triangles) from the 2EF system with the inverse time trace of the depletion of 2EF (red circles) superimposed.

**Figure 4.4** – Experimental photoionization efficiency spectrum of $m/z = 94$ with the experimental PIE spectrum of 2-vinylfuran superimposed.

2EF-B2, whose PES is portrayed in Scheme 4.9, provides an alternative pathway to form 2-vinylfuran with a relative reaction enthalpy of +218 kJ mol$^{-1}$. This channel occurs through indirect HO$_2$-elimination through the QOOH intermediate, 2EF-Q3, which forms via H-atom abstraction from the ethyl position on the alkyl chain. OH-elimination of 2EF-Q3 produces 2EF-P2 at +181 kJ mol$^{-1}$. A second QOOH species, 2EF-Q4, can be formed via H-abstraction from the methyl-position, but requires much more energy (2EF-TS8, +341 kJ mol$^{-1}$), rendering all ensuing
mechanistic steps improbable at this temperature. As per the other furanylperoxy radicals, 2EF-B2 can undergo self-reaction, this time resulting in the formation of (E)-2-ethylidene-1,3-furan-3(2H)-one ($m/z = 110$) and molecular oxygen with a relative energy of -1 kJ mol⁻¹. This compound was not observed, most likely due to its association with
the less stable 2EF-B2 peroxy radical, where the observed products are associated with the more stable 2EF-B1 peroxy radical.

The 2-ethylfuranylperoxy radical, 2EF-B3, only has one energetically feasible pathway as shown in the PES in Scheme 4.10. It is once again a peroxy self-reaction, which is barrierless, forming (5E)-5-Ethylidene-2(5H)-furanone (m/z = 110) and

Scheme 4.10 - PES of possible reaction pathways from the peroxy radical 2MF-B3. The bracketed values represent the change in relative energy from each direction, with the first number corresponding to the barrier for the forward reaction, and the second for the reverse reaction. Transition states were identified using the B3LYP/6-31G(d) level of theory. All energies and optimized structures were calculated with the CBS-QB3 model.
molecular oxygen at the relative heat of +1 kJ mol\(^{-1}\). The compound was not observed in the experimental PIE of \(m/z = 110\).

Scheme 4.11 portrays the PES of the general oxidation of the 2-ethylfuranyloperoxy radical where the peroxy group is bonded at the ethyl carbon position, 2EF-B4. From this species, there are five channels through which the oxidation reaction can proceed. The first two channels include the QOOH intermediate, 2EF-Q7, which forms as a result of intramolecular H-atom abstraction from the β-position at the methyl carbon in the alkyl group. This intermediate is more stable (-9.9 kJ mol\(^{-1}\)) than the initial peroxy radical due to the resonance with the furan ring after

**Scheme 4.11** - PES of possible reaction pathways from the peroxy radical 2MF-B4. The bracketed values represent the change in relative energy from each direction, with the first number corresponding to the barrier for the forward reaction, and the second for the reverse reaction. Transition states were identified using the B3LYP/6-31G(d) level of theory. All energies and optimized structures were calculated with the CBS-QB3 model.
proceeding over a barrier of +105 kJ mol\(^{-1}\) (2EF-TS12). The QOOH species can then proceed via OH-elimination to form the product, 2-(oxiran-2-yl)furan \((m/z = 110)\), with a relative energy of −18 kJ mol\(^{-1}\), or through HO\(_2\)-elimination to form an additional pathway to 2-vinylfuran at +60 kJ mol\(^{-1}\). Both of these species are also predicted in 2EF-B1’s mechanism in Scheme 4.8.

The third and fourth channels of 2EF-B4 share the QOOH intermediate, 2EF-Q8. This species is much higher in energy than the 2EF-Q7 due to a lack of resonance, having a much larger relative enthalpy of +145 kJ mol\(^{-1}\) and a higher barrier of +150 kJ mol\(^{-1}\) (2EF-TS15). The fourth channel possesses an energy barrier that surpasses the energy threshold established by the initial reactants, peaking at a total of +352 kJ mol\(^{-1}\). This means that only the OH-elimination channel involving 2EF-Q8 has the potential to occur, forming 2EF-P5 \((m/z = 110)\) at -35 kJ mol\(^{-1}\). 2EF-P5 was not observed experimentally most likely due to its high energy barriers, maxing out at +214 kJ mol\(^{-1}\). 2-(furan-2-yl)acetaldehyde \((m/z = 110)\), at the more stable relative energy of -109 kJ mol\(^{-1}\), is the predicted product, along with molecular oxygen, of the peroxy self-reaction of 2EF-B4.

Of the products proposed by the potential energy surfaces, only eight of the eleven are energetically feasible to form at the temperature used in this study. Of these, 2-vinylfuran is the only proposed isomer of the species at \(m/z = 94\) based on the PESs presented. 2-vinylfuran’s calculated ionization energy (IE) was determined to be 8.12 ± 0.05 eV for the \(E\) and \(Z\) forms, agreeing with the calculated IE of 8.12 eV obtained
by Simmie et al. However, Giuliani et al. experimentally determined the AIE of 2-vinylfuran to be 8.057 eV, not quite matching the initial experimental onset at 8.15 eV shown in Figure 4.3. This experimental PIE spectrum of 2-vinylfuran was the only one available in literature, leaving us unable to explain the discontinuity between the data obtained in this study and the data obtained by Giuliani et al. The branching fraction of 2-vinylfuran was determined to be 1%, as shown in Table 4.2.

The remaining species predicted in the potential energy surfaces would all appear at $m/z = 110$. The compound 2-acetylfuran, identified as a product of 2EF-B1 undergoing peroxo self-reaction with Figure 4.5 showing the time trace, has a literature IE of 9.02 ± 0.02 eV as determined by Klapstein et al. This matches very well with the experimental onset of 9.00 ± 0.05 eV and the APIE of 2-acetylfuran presented in Figure 4.6. Villanueva et al. also identified $m/z = 110$ as 2-acetylfuran. The branching

**Figure 4.5** - Time trace of the formation of $m/z = 110$ (blue triangles) from the 2EF system with the inverse time trace of the depletion of 2EF (red circles) superimposed.

**Figure 4.6** - Experimental photoionization efficiency spectrum of $m/z = 110$ with the experimental PIE spectrum of 2-acetylfuran superimposed.
fraction of 2-acetylfuran was determined to be 2%, as shown in Table 4.2. The calculated IE’s for (E)-5-ethyldenefuran-2(5H)-one, 2-(furan-2-yl)acetaldehyde, 2-(oxiran-2-yl)furan, and 2EF-P5 are 8.88 ± 0.05 eV, 8.6 ± 0.05 eV, 8.55 ± 0.05 eV, and 7.75 ± 0.05 eV, respectively, all of which are too low to contribute to the experimental PIE spectrum. In order to form many of the predicted compounds, pathways need to proceed through high energy barriers, making them improbable at the low temperature used in this study. Additionally, some of the peroxy radicals from which these unobserved products are derived from are not nearly as stable as their counterparts as shown in Scheme 4.7.

Table 4.4 - List of dominant, non-chlorinated products and their experimental AIE’s, calculated AIE’s, and branching yields from the 2EF + Cl + O2 reaction.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Name</th>
<th>Structure</th>
<th>CBS-QB3 AIE (eV)</th>
<th>Experimental AIE (eV)</th>
<th>Branching Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>2-acetylfuran</td>
<td><img src="image" alt="Structure" /></td>
<td>9.02 ± 0.05a</td>
<td>9.00 ± 0.05a</td>
<td>2</td>
</tr>
<tr>
<td>94</td>
<td>2-vinylfuran</td>
<td><img src="image" alt="Structure" /></td>
<td>8.12 ± 0.05a</td>
<td>8.15 ± 0.05a</td>
<td>1</td>
</tr>
</tbody>
</table>

*a This work.

4.5. Conclusions

The chlorine-initiated oxidation of 2-methylfuran and 2-ethylfuran were studied at the Advanced Light Source of Lawrence Berkeley National Laboratory using a
multiplexed photoionization mass spectrometer at 323 and 305 K, respectively, at 4 Torr. These reactions are used to investigate the H-abstraction channels and the corresponding products, which are characterized through the identification of mass-to-charge ratios, ionization energies, photoionization spectra, and time profiles.

In the 2-methylfuran + Cl + O₂ reaction, H-atom abstraction by chlorine atoms forms 2-furylethyl, which can further react through oxidation or chlorine addition. The oxidation of 2-furylethyl is found to produce furfural through peroxy self-reaction, which is the most abundant oxygenated product observed, with a branching yield of 53%.

In the 2-ethylfuran + Cl + O₂ reaction, hydrogen abstraction by Cl· forms 2-furylethyl. Following its formation, 2-furylethyl can be further consumed by oxidation or chlorine addition. The oxidation product 2-vinylfuran, with a branching yield of 1%, is identified as a result of an HO₂-elimination pathway following oxidation. The oxygenated product 2-acetylfuran is found to be a product of a peroxy self-reaction with a branching yield of 2%. These low branching yields are due to the abundance of chlorinated species formed, which were observed in the experimental mass spectrum.
4.6. References


Chapter 5

Absolute Photoionization Cross-sections of Furanic Fuels: 2-Ethylfuran, 2-Acetylfuran and Furfural

Published in the Journal of Mass Spectrometry

Abstract
Absolute photoionization cross-sections of the molecules 2-ethylfuran, 2-acetylfuran and furfural, including partial ionization cross-sections for the dissociative ionized fragments, are measured for the first time. These measurements are important because they allow fuel quantification via photoionization mass spectrometry and the development of quantitative kinetic modeling for the complex combustion of potential fuels. The experiments are carried out using synchrotron photoionization mass spectrometry with an orthogonal time-of-flight spectrometer used for mass analysis at the Advanced Light Source of Lawrence Berkeley National Laboratory. The CBS-QB3 calculations of adiabatic ionization energies and appearance energies agree well with the experimental results. Several bond dissociation energies are also derived and presented.

5.1. Introduction
With the demand for alternative fuel sources steadily increasing, the search for and development of new biofuels is becoming more important than ever.\textsuperscript{1–3} Furan and
its derivatives have already been identified as alternative biofuels.\textsuperscript{4,5} With novel production methods able to derive these compounds from biomass,\textsuperscript{1,6–10} these potential biofuels have a large enough source to be used on an industrial scale. While combustion\textsuperscript{2,4,5,8,11,12} and decomposition studies\textsuperscript{13–15} of furanic biofuels have been performed, many furanic derivatives have not been studied extensively. There are several techniques used to determine the photoionization cross-sections of individual molecules. For example, using a double ion beam in a dual ionization chamber, Haddad and Samson\textsuperscript{16} measured the photoionization cross-section of water. Another method was used by West\textsuperscript{17} and Kjeldsen\textsuperscript{18} where a merged beam method measured the photoionization cross-sections of atomic ions. It was Cool et al.\textsuperscript{19,20} who developed the technique of using photoionization mass spectrometry (PIMS) to determine the cross-sections of numerous molecules by comparing them to a known standard such as ethene, propene or butene. The PIMS technique has already been used to identify the cross-sections of many biofuels,\textsuperscript{3,20–22} but many compounds have yet to be thoroughly studied. A common issue encountered with this technique is the difficulty in studying compounds with low vapor pressures (<5Torr at 25°C) as it makes it difficult to quantify their amount in the gas phase.

In this investigation, the synchrotron PIMS technique is used to determine the photoionization cross-sections (PICS) of three furans whose structures are shown in Figure 5.1, i.e., 2-ethylfuran (2EF), 2-acetylfuran (2AF) and furfural. To the best of our knowledge, no studies on the photoionization cross-sections of these three furanic
compounds have been previously reported. The importance of these measurements is the result of them directly providing quantities that allow fuel quantification via photoionization mass spectrometry and the development of quantitative kinetic modeling for the complex combustion of potential fuels.

2-Ethylfuran has been chosen for this study based on its role as a primary and secondary pollutant emitted into the atmosphere from both anthropogenic and biogenic sources.\textsuperscript{15,21,23–25} This alkylfuran also has potential to be a next-generation biofuel based on the promising characteristics of the alkylfurans 2-methylfuran and 2,5-dimethylfuran.\textsuperscript{5,13,26} Villanueva et al.\textsuperscript{15} has provided insight on the oxidation of 2EF using Fourier Transform Infrared (FTIR) absorption spectroscopy and solid-phase microextraction gas chromatography by flame ionization, electron capture and mass spectrometry. In the same study, it was identified that 2AF is a potential product of 2EF oxidation.\textsuperscript{15} Klapstein et al.\textsuperscript{27} presented the photoelectron spectra of several 2-carbonyl furans, including 2AF and furfural, using a high-voltage helium discharge lamp and a \textsuperscript{127°} cylindrical sector electrostatic deflection analyzer. The ionization energies obtained from this study match quite well those observed in this experiment. 2-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of the compounds used in this study; 2-ethylfuran (2EF), 2-acetylfuran (2AF), and furfural. The numbering of the furan ring for 2AF and furfural is the same as for 2EF.}
\end{figure}
Methylfuran (2MF) already has a reported photoionization cross-section;\textsuperscript{3,22} however, the PICS of its observed oxidation product, furfural,\textsuperscript{5,15} have not been reported as of this time. Furfural was chosen for this study based on its role as a high-impact platform molecule used in the production of alternative biofuels.\textsuperscript{9,10} This compound is the most common industrial chemical derived from lignocellulosic biomass, with over 200000 tons produced annually through the hydrolysis and dehydration of the xylan present in lignocellulose.\textsuperscript{9} This mass production is a result of furfural’s identification as a platform molecule, where its ability to be converted into biofuels such as 2-methylfuran and 2-methyltetrahydrofuran has been established and utilized at a commercial level.\textsuperscript{9,10}

5.2. Experimental

5.2.1 Apparatus

These experiments were carried out at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. While the experiment will only be summarized here, it can be found in greater detail elsewhere.\textsuperscript{22,28} The chemical systems under investigation and the buffer gas (He) are initially introduced into the reactor through the use of calibrated mass flow controllers. The gasses enter into a heatable 1.05 cm i.d. slow-flow quartz tube that is maintained at 4 Torr and 298 K for 2-ethylfuran and 2-acetylfuran, and at 2 Torr and 298 K for furfural. At 4 Torr and 298 K using 100 sccm total flow, it yields a total number density in the reactor of approximately $1.3 \times 10^{17}$
molecules cm$^{-3}$. The gaseous mixture then continuously flows through a ~650μm hole into a 1.5 mm skimmer, where the subsequent molecular beam is directed into a differentially pumped ionization chamber. This molecular beam is orthogonally intersected by the tunable-synchrotron beam produced by the ALS radiation, and the resulting ions are then accelerated, collimated and focused into the detector of an orthogonal time-of-flight mass spectrometer. All of the species are analyzed based on their mass-to-charge ratios and ion signal intensity at constant photon energy intervals ranging between 8 and 11 eV depending on the system. The mass resolution for these experiments is approximately 1600. After the signals are detected, they are normalized at each photon energy for the photon current of the ALS using a calibrated vacuum ultraviolet sensitive photodiode.

5.2.2. Measurement Procedures

2-Ethylfuran, 2AF and furfural were purchased with a stated purity of $\geq$99% (Sigma-Aldrich). The samples of 2EF and furfural were purified by the freeze–pump–thaw technique. 2EF was stored as a 1.35% mixture (28.0 Torr of 2EF in 2080 Torr total with He), and furfural as a 0.183% mixture (2.25 Torr of furfural in 1230 Torr total with He). 2-Acetylfuran, with a published melting point of 299 K and vapor pressure of 0.70 Torr at 298 K, was flowed into the system directly from a bubbler at a rate of 2.00 sccm resulting in a concentration of $2.22 \times 10^{12}$ molecules cm$^{-3}$ in the cell. The total pressure of 796 Torr inside the bubbler containing 2AF is measured using a
capacitive pressure gauge, which corresponds to a 0.0879% of 2AF in the gas phase. 2EF was flowed at a rate of 0.979 sccm, generating a concentration of $1.67 \times 10^{13}$ molecules cm$^{-3}$. Furfural was flowed at a rate of 5.48 sccm, producing a concentration of $1.26 \times 10^{12}$ molecules cm$^{-3}$.

The experimental adiabatic ionization energies (AIE) are determined by extrapolating the initial onsets of the photoionization energy curves using an exponential function in the form of $1-e^{bE}$ as described by Ruscic and Berkowitz,\textsuperscript{29} where $b$ and $E$ represent an adjustable constant and the energy in electron volts, respectively. The same method is used to determine the appearance energies (AE) of the dissociative ionization fragments using a pre-threshold exponential function in addition to a post-threshold exponential function. An associated uncertainty of ±0.05 eV is used to account for the presence of hot bands and photon energy calibration.

The absolute photoionization spectrum is obtained through the comparison of the experimental data with the absolute photoionization spectrum of a well-characterized species, such as ethene, propene or 1-butene. These three calibration gasses are all flowed into the cell with a known concentration for the purpose of comparison. The relationship of an individual species’ factors can be represented by Equation 5.1. It should be noted that both the relative ion signal and photoionization cross-section are energy dependent, and the values should be obtained for the same energy ($E$) throughout these calculations.

$$S(E) = k\sigma(E)\delta C$$

(5.1)
The ion signal \((S)\) of a compound is the product of the instrumentation constant \((k)\), the photoionization cross-section \((\sigma)\), the mass-dependent response \((\delta)\) (which for these experiments is approximately equal to \(m^{0.67}\), where \(m\) is the mass of the compound) and the concentration \((C)\) of the compound. The procedure for the experimental determination of the mass-dependent response \((\delta)\) is described in detail by Savee et al.\(^{30}\)

Utilizing these factors in combination with those of a known species (standard), the unknown cross-section of the target molecule \((\sigma_T)\) can be determined as a ratio of its signal intensity \((S_T)\) to the signal intensity of the standard \((S_S)\), the concentration of the target and standard compounds \((C_T\text{ and } C_S)\), the mass discrimination factors of both \((\delta_T\text{ and } \delta_S)\), and the photoionization cross-section of the standard \((\sigma_S)\).

\[
\sigma_T(E) = \frac{S_T(E) \sigma_S(E) \delta_S C_S}{S_S(E) \delta_T C_T}
\]  

Specifically, in this investigation, the absolute photoionization cross-section of propene measured by Person and Nicole\(^{31}\) of 12.4 Mb 11.0 eV with an assessed 10.0% error is used as a reference. Employing the uncertainties for our concentrations and the ion signal measurement of approximately 1.00% and for the mass discrimination factor of 15.0% with the 10.0% uncertainty for the photoionization cross-section of propene, the uncertainty measured for cross-sections obtained using this mass spectrometer is estimated to be ±18.1%.
5.3. Computational

All optimized electronic structure calculations are completed utilizing the CBS-QB3 composite method\textsuperscript{32–34} with the Gaussian09 program\textsuperscript{35} and visualized in GaussView 5.0.\textsuperscript{36} The adiabatic ionization energy of a particular molecule can be computed through use of the zero-point vibrational corrected energy \((E_0)\) obtained from the optimization calculations. The \(E_0\) must be obtained for both the ground state of the neutral and molecular cation, where the AIE can be determined using Equation 5.3.

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

(5.3)

The AE at 0 K of the observed dissociative fragment ions were determined from the \(E_0\) of the reactants subtracted from the \(E_0\) of the products, assuming absence of a dissociation barrier. In the reaction portrayed by Equation 5.4, the dissociative ionization fragment or daughter ion \((A^+)\) and the neutral fragment \((B)\) are the products, while the neutral parent \((AB)\) is the reactant:

\[
AB \xrightarrow{hv} A^+ e^- + B
\]  

(5.4)

The uncertainty that is associated with each computed value is estimated to be in the range of ±0.05 eV based on the computational accuracy of 4–5 kJ mol\(^{-1}\) provided by Montgomery et al.\textsuperscript{34}
5.4. Results

5.4.1 2-Ethylfuran

Figure 5.2 shows the photoionization spectrum of 2EF obtained from this experiment, with the corresponding photoionization cross-section values listed in Table 5.1. From these data, it was identified that the threshold for 2EF ionization at 8.43 ± 0.05 eV agrees very well with the literature value of 8.45 ± 0.05 eV,\(^{37}\) and the CBS-QB3 calculated AIE of 8.40 ± 0.05 eV. 2EF exhibits a shoulder at 10.0 ± 0.1 eV. The first spectral band is a result of the removal of an electron from the bonding π highest occupied molecular orbital (HOMO) localized on the C=C bonds shown in Figure 5.3 and also observed by Linda et al.\(^{37}\) This is also evident in the change of the C=C bond lengths between the neutral and molecular cation. Initially, the C\(_2\)=C\(_3\) bond length is 1.362 Å, which extends to 1.420 Å upon the first electron removal. The same pattern is observed with the C\(_4\)=C\(_5\) bond length of 1.355 Å increasing to 1.406 Å. This bond distance elongation is characteristic of the removal of an electron from a bonding orbital, which weakens (lowering the ‘bond order’) the chemical bonds of the atoms comprising the specific molecular orbital (MO). With the use of Koopmans’ theorem,\(^{38}\) it is estimated that a second spectral band (first cationic excited electronic state) should appear at 9.8 eV, which is in good agreement with the experimentally observed value of 10.0 ± 0.1 eV observed in the spectrum. This computed estimation is derived from the energy difference between the HOMO and HOMO\(^{-1}\) derived from the B3LYP/6-311G(2d,d,p) level of theory within the CBS-QB3 model (Figure 5.3). Strictly
speaking, Koopmans’ theorem has been used rigorously with Hartree–Fock orbital energies, where the negative value of the energy of a given orbital is taken as equal to the binding energy for ionization of an electron in that orbital. In this investigation, absolute values of orbital energies from the B3LYP computations are not used to derive ionization energies, but rather, we employ their difference to yield excitation energies, i.e., term energies for excited electronic states. This approach has been proved to provide reliable results.\textsuperscript{39–41} Based on the study of furan and some of its derivatives by Klapstein et al.,\textsuperscript{27} the second band appears as a result of the removal of an electron from the oxygen’s lone pair in the furan ring.
Table 5.1
The partial photoionization cross-sections (σ) of 2-ethylfuran (2EF), 2-acetylfuran (2AF), furfural, and the dissociative fragments reported in megabarns (Mb) at selected energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>2EF m/z = 95</th>
<th>2EF m/z = 81</th>
<th>2AF m/z = 95</th>
<th>Furfural m/z = 95</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>0.00</td>
<td>0.00</td>
<td>N/D</td>
<td>N/D</td>
</tr>
<tr>
<td>8.2</td>
<td>0.06</td>
<td>0.00</td>
<td>N/D</td>
<td>N/D</td>
</tr>
<tr>
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<td>N/D</td>
<td>N/D</td>
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<td>2.42</td>
<td>0.01</td>
<td>N/D</td>
<td>N/D</td>
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<tr>
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<td>N/D</td>
<td>N/D</td>
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<tr>
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<td>0.01</td>
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<td>N/D</td>
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<td>N/D</td>
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</tr>
<tr>
<td>10.9</td>
<td>17.37</td>
<td>0.26</td>
<td>32.19</td>
<td>9.98</td>
</tr>
<tr>
<td>11.0</td>
<td>16.59</td>
<td>0.33</td>
<td>33.69</td>
<td>10.86</td>
</tr>
</tbody>
</table>

N/D means no data was taken at that energy.
The overall shape of the photoionization cross-section of 2EF is very similar to that of 2MF. The literature ionization energies of 2EF and 2MF are $8.45 \pm 0.05$ and $8.38 \pm 0.03$ eV, respectively, which are very comparable with each other. These values are also very similar to our experimentally observed ionization energies for 2EF and 2MF of $8.43 \pm 0.05$ and $8.40 \pm 0.05$ eV, respectively. As mentioned previously, the experimental PICS of 2EF exhibit a second spectral band at $10.0 \pm 0.1$ eV. Similarly, the PICS of 2MF portray a second spectral band due to the first cationic excited electronic state at $9.9 \pm 0.1$ eV. These similarities are attributed to the same π system of the furan ring present in both 2EF and 2MF. The cross-section of 2EF at 11 eV is determined to be 16.6 Mb, while 2MF has a cross-section of 26.75 Mb at 11 eV measured by Xie et al., and 26.31 Mb measured by Czekner et al. at 11.188 eV. This difference between the measured 2EF and 2MF photoionization cross-sections can be
compared with that of toluene and ethylbenzene. These molecules are comparable in regard with their molecular structures to each other, i.e., furan ring for 2MF and 2EF and benzene for toluene and ethylbenzene, and with the presence of alkyl chains, i.e., methyl and ethyl. Ethylbenzene has a measured ionization energy of $8.77 \pm 0.01$ eV$^{42}$ and a reported cross-section at 11 eV of 29.65 Mb.$^{43}$ Toluene, whose structure consists of a benzene ring with an attached methyl group, has an ionization energy of $8.828 \pm 0.001$ eV$^{42}$ and a cross-section at 11 eV of 39.33 Mb.$^{43}$ The difference between the cross-sections of these two benzene derivatives at 11 eV is 9.68 Mb, which is very similar to the difference of 10.2 Mb between the cross-sections of the two alkylfurans at 11 eV, where the compound with the ethyl substituent has the smaller cross-section. Based on these similarities, these differences in values can be attributed to the change in length of the alkyl chain on the aromatic ring.

2-Ethylfuran presents a dissociative ionization fragment at m/z = 95 corresponding to the loss of a hydrogen atom from the CH$_2$ in the alkyl group. It is easier to remove an H atom from this location because the C$\text{sp}^3$–H bonds are much weaker than the C$\text{sp}^2$–H bonds located on the furan ring. The calculated AE at 0 K from the CH$_2$ moiety of 10.35 ± 0.05 eV are comparable with the experimentally observed value of 10.32 ± 0.05 eV. Removing a hydrogen atom from the CH$_2$ group is the most energetically favorable H-loss with a calculated bond dissociation energy (BDE) at 0 K of 344 ± 7.0 kJ mol$^{-1}$, which will be described in detail later, due to resonance stabilization with the furan ring. Removal of hydrogen from the CH$_3$ group has a
calculated BDE at 0 K of 423 ± 7.0 kJ mol⁻¹, 79 kJ mol⁻¹ higher in energy than the HC–H BDE. The dissociative fragment at m/z = 81 is most likely 2-furylmethyl, where 2EF experiences a CH₃ loss from the ethyl group. This fragment has a calculated appearance energy at 0 K (Equation 5.4) of 10.27 ± 0.05 eV, which is similar to the experimental AE of 10.14 ± 0.05 eV.

Using the experimentally observed AE corrected for 0 K of a given dissociative fragment, one can make use of the procedure outlined by Ruscic and Berkowitz⁴ to estimate the BDE at 0 K of the bond broken. If we take the m/z = 95 dissociative fragment of 2EF, we can obtain the BDE of the C–H bond at 0K ($D_0^o (R – H)$) on the CH₂ position in the alkyl group using Equation 5.5. $R – H$ represents the bond broken in 2EF, $AE(95^+, R – H)$ corresponds to the appearance energy (Equation 5.4) of the m/z = 95 fragment, and $AIE(95)$ is the adiabatic ionization energy of the fragment (Equation 5.3).

$$D_0^o (R – H) = AE(95^+, R – H) – AIE(95) \quad (5.5)$$

Using the CBS-QB3 calculated AIE at 0 K of 6.79 ± 0.05 eV for the m/z = 95 fragment and the previously stated experimental AE of 10.32 ± 0.05 eV, the ($D_0^o (R – H)$) is determined to be 341 ± 7.0 kJ mol⁻¹. The ($D_0^o (R – H)$) can also be determined by applying the heat content functions, $H_{298}^o – H_0^o$, for the species involved in the dissociation reaction, resulting in a value of 347 ± 7.0 kJ mol⁻¹. The BDE of the $R – H$ bond in 2EF can also be calculated using exclusively CBS-QB3 energies, resulting in a derived $D_{298}^o$ of 350 ± 5.0 kJ mol⁻¹. These values are in good agreement with the
literature value for the \( D_{298}^0(CH_2 = CH - CH_2 - CH_3) \) of 350.6 kJ mol\(^{-1}\).\(^{27}\) This molecule is chosen for comparison based on the \( CH - H \) bond in the allylic position, which would be similar to the situation of the \( CH - H \) bond in the \( CH_2 \) position of 2EF.

The corrected experimental value of \( D_0^0(R - CH_3) \) corresponding to the formation of the \( m/z = 81 \) dissociative fragment is determined to be 291 ± 7.0 kJ mol\(^{-1}\). The published value for the \( R - CH_3 \) BDE of 2EF at 298 K is reported as 313.8 ± 8.4 kJ mol\(^{-1}\),\(^{44}\) which is very similar to the CBS-QB3 calculated value of 311 ± 5.0 kJ mol\(^{-1}\), and more than 15 kJ mol\(^{-1}\) greater than the experimentally determined value of 298 ± 7.0 kJ mol\(^{-1}\). Each BDE can be found in Table 5.2.

**Table 5.2**

<table>
<thead>
<tr>
<th>Species</th>
<th>( D_0^0 ) (kJ mol(^{-1}))</th>
<th>( D_{298}^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CBS-QB3</td>
<td>Exp.</td>
</tr>
<tr>
<td>2EF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyl (CH - H)</td>
<td>344</td>
<td>341</td>
</tr>
<tr>
<td>ethyl (CH(_2) - H)</td>
<td>423</td>
<td>-</td>
</tr>
<tr>
<td>Furfural (R - H)</td>
<td>360</td>
<td>388</td>
</tr>
<tr>
<td>2EF (R - CH(_3))</td>
<td>304</td>
<td>291</td>
</tr>
<tr>
<td>2AF (R - CH(_3))</td>
<td>356</td>
<td>355</td>
</tr>
</tbody>
</table>

\(^a\) Luo\(^{44}\)
5.4.2. 2-Acetylfuran

Figure 5.4 shows the photoionization cross-section of 2AF obtained from this experiment. The threshold for 2AF ionization at $9.01 \pm 0.05$ eV agrees well with the literature value of $9.02 \pm 0.02$ eV obtained by Klapstein et al.\textsuperscript{27} from their 2AF experimental photoelectron spectrum, as well as the CBS-QB3 calculated AIE of $9.09 \pm 0.05$ eV. However, our experimental value does not agree well with the literature value of $9.27 \pm 0.05$ eV obtained by Linda et al.\textsuperscript{37} who used the electron-impact ionization (EI) technique. Arii et al.\textsuperscript{45} explain in their work the differences between

![Graph](image)

**Figure 5.4** – Molecular and dissociative fragments photoionization cross sections for 2-acetylfuran.
using the electron ionization technique and the photoionization with vacuum ultraviolet light technique when performing an evolved gas analysis. For the qualitative analysis of complex organic compounds, EI can increase the difficulty of the analysis due to the formation of fragment ions. The fragmentation, caused by the higher ionization potential of the EI technique, can prevent the classification of gaseous species, leading to the need for additional techniques such as gas chromatography/MS. A problem with using these secondary techniques to solve the issue is the loss of real-time monitoring and measuring of results as a function of temperature. This can make it difficult to confirm that the gaseous compounds are accurately traced directly. Photoionization is a technique that is considered to be both a selective and soft (fragment-free) technique, controlling fragmentation at the time of photoionization. It was concluded by Ariii et al.\textsuperscript{45} that the use of the more sensitive and precise PIMS greatly reduced fragmentation of the compounds being studied when compared with the conventional EI mass spectrometry. The issues identified by Arri et al.\textsuperscript{45} could have impacted the results obtained by Linda et al.,\textsuperscript{37} helping to explain the discontinuity in the results presented in this study and those by Klapstein et al.\textsuperscript{27}

The initial ionization is the result of the removal of an electron from the bonding $\pi$ molecular orbital\textsuperscript{27,37} localized on the C=C bonds just like the case of 2EF, shown in Figure 5.5. This is again evident in the change of the C=C bond lengths between the neutral and molecular cation where the C$_2$=C$_3$ bond length in the neutral is 1.372 Å and extends to 1.407 Å in the cation, and the C$_4$=C$_5$ bond length of 1.364 Å increases to
1.408 Å. With the use of Koopmans’ theorem, it is estimated that a second spectral band should appear at 11.08 eV, which is outside our experimental energy range. Similar to the case with 2EF, this band appears as a result of the removal of an electron from the oxygen’s lone pair in the furan ring based on the study by Klapstein et al. 

![Image](image1.png)

**Figure 5.5** - Orbital energy and electron distribution of 2-acetylfuran (2AF) obtained from the CBS-QB3 orbital calculations.

The overall shape of the photoionization cross-section of 2AF is quite different than that of 2EF. 2AF exhibits no defined shoulders, a characteristic that is also found in the PICS of furfural. These two cross-sections will be compared later on.

The dissociative fragment at $m/z = 95$ corresponds to the loss of a methyl group from the side chain where its calculated AE at 0 K is determined to be \(10.52 \pm 0.05\) eV, and its experimental appearance energy is observed at \(10.51 \pm 0.05\) eV. The corresponding experimental \(D_0^\circ (R - CH_3)\) is determined to be \(355 \pm 7.0\) kJ mol\(^{-1}\), and the experimental \(D_0^\circ (R - CH_3)\) value is derived to be \(361 \pm 7.0\) kJmol\(^{-1}\). This value
agrees quite well with the $D_{298}^0(H_3C \rightarrow CO - CH_3)$ value of 353.6 ± 1.7 kJ mol$^{-1}$.

Acetone is chosen for comparison based on its ketone functional group where the removal of an adjacent methyl group is possible. Both of these experimentally derived values agree very well with the CBS-QB3 BDEs as provided in Table 5.2.

### 5.4.3. Furfural

Figure 5.6 shows the photoionization cross-section of furfural obtained from this experiment. The threshold for furfural ionization at 9.22 ± 0.05 eV matches the literature value of 9.22 ± 0.02 eV and agrees well with the CBS-QB3 calculated AIE of 9.26 ± 0.05 eV. The initial ionization is again the result of the removal of an electron from the bonding π molecular orbital localized on the C=C bonds just as with the cases of 2EF and 2AF, evident in Figure 5.6. The C$_2$=C$_3$ bond length is 1.372 Å, which extends to 1.413 Å, and the C$_4$=C$_5$ bond length of 1.365 Å increases to 1.416 Å upon ionization. With the use of Koopmans’ theorem, it is estimated that a second spectral band should appear at 11.3 eV, which is out of our experimental energy range. Similar to the cases with 2EF and 2AF, this band appears as a result of the removal of an electron from the oxygen’s lone pair in the furan ring based on the study by Klapstein et al. The dissociative fragment at m/z=95 corresponds to the loss of a hydrogen atom from the aldehydic group with an experimental AE of 10.85 ± 0.05 eV, which is in good agreement with the calculated appearance energy at 10.73 ± 0.05 eV. The corresponding experimental $D_0^0(R - H)$ is determined to be 388 ± 7.0 kJ mol$^{-1}$. The
The $D_{298}^0(R - H)$ value is derived to be $394 \pm 7.0$ kJ mol$^{-1}$ compared with the CBS-QB3 derived value for $D_{298}^0(R - H)$ of $383 \pm 5.0$ kJ mol$^{-1}$ as shown in Table 5.2. This value is comparable with the $D_{298}^0(CH_3 - CO - H)$ value of $374.0 \pm 1.3$ kJ mol$^{-1}$. Acetaldehyde is chosen for comparison based on its aldehyde functional group where the hydrogen bond attached to the carbonyl site could be broken.

![Figure 5.6](image)

**Figure 5.6** – Molecular and dissociative fragments photoionization cross sections for furfural.

The total cross-sections of furfural and of 2AF are similar in shape. They also have comparable chemical structures, both consisting of a furoyl unit, i.e., a furan ring with an adjacent carbonyl group (as shown in Figure 5.1). Furfural represents a furoyl
unit with hydrogen attached at the carbonyl site, while 2AF represents a furoyl unit with an electron-donating CH$_3$ group bonded to the carbonyl site. This electron-donating group results in shifting spectral bands to lower ionization energies (IEs) when compared with the spectra of compounds such as furfural, which do not have an electron donating group. Klapstein et al.$^{27}$ observed a downshift of 0.15 eV from furfural for 2AF corresponding to the first observed band and a downshift of 0.20 eV for the second band.$^{27}$ Similarly, in this study, a downshift of 0.25 eV was observed from furfural to 2AF corresponding to the first spectral band, and a downshift of 0.26 eV was calculated for the unobserved second band. The HOMO and the HOMO-1 for 2AF (Figure 5.5) show the same differences that are evident in the HOMO and HOMO-1 of furfural (Figure 5.7). After the removal of an electron from the bonding $\pi$ molecular orbital localized on the C=C in both compounds, C=C bond lengths increase and result in the molecular orbitals shown in Figures 5.5 and 5.7. The difference in the orbital energies corresponding to the HOMO and HOMO-1 for 2AF is determined to be 2.17 eV, nearly identical to the 2.18 eV difference between the same two orbitals in furfural.

A comparison of the relationship between furfural and 2AF can be made to that of benzaldehyde and acetophenone, which have the same molecular structure as furfural and 2AF, respectively, but the furan ring is replaced with a benzene ring. Benzaldehyde is reported as having an IE of 9.50 ± 0.08 eV with a photoionization cross-section of 39.84 Mb$^{43}$ at 11 eV, and acetophenone presents a lower IE of 9.28
and larger PICS at 11 eV of 49.92 Mb. This results in the AIE of benzaldehyde being 0.22 eV greater than that of acetophenone, very similar to the difference in the IEs of furfural and 2AF, where furfural has an IE that is 0.25 eV greater than 2AF. The PICS at 11 eV of benzaldehyde is reported to be 10.08 Mb smaller than that of acetophenone, while we observed the PICS at 11 eV of furfural to be 22.8 Mb less than 2AF.

5.5. Conclusions

The adiabatic ionization energies, appearance energies and photoionization cross-sections of the parent and dissociative fragments for 2-ethylfuran, 2-acetylfuran and furfural are presented. The CBS-QB3 calculations agree with the experimental AIE and AE values observed in this study. Using Koopmans’ theorem with the calculated molecular orbital energies, the electronic transition to the first excited state of the 2EF

![Orbital energy and electron distribution of furfural obtained from the CBS-QB3 orbital calculations.](image-url)
cation is determined to be 9.8 eV. This is in good agreement with the experimentally observed shoulder at 9.9 ± 0.1 eV. For 2-acetylfuran and furfural, the transitions to the first excited state of the cation could not be observed because they are outside the photoionization energy range of this experiment. Within Koopmans’ theorem, these transitions have been calculated to have a term energy of approximately 2.2 eV. The measured photoionization cross-sections are compared with literature values of similar molecules showing that the addition of a CH₂ or CH₃ moiety lowers the PICS value. For each dissociative fragment observed, the bond dissociation energies at both 0 and 298 K are derived and compared with literature values.
5.6. References


[41] N. P. Bellafont, P. S. Bagus, F. Illas. Prediction of core level binding energies in


Chapter 6

An FT-IR Study of Aerosolized 2-Methylfuran and its Reaction with Ozone

6.1. Introduction

Aerosols are small particles (0.01-10 µm) suspended in the atmosphere that can be generated both by natural sources, such as volcanos and deserts, as well as by humans. Aerosols generated through the combustion of fuels is a growing concern due to how they scatter and absorb incoming radiation from the sun, known as radiative forcing, as well as their reactive nature that can result in environmental and health implications. It is exceptionally unlikely that the combined natural radiative forcing (solar irradiance, volcanic aerosol, and dust aerosol) has affected the increase in global warming as much as anthropogenic aerosol radiative forcing has in the last five decades. Secondary organic aerosols (SOAs) are a common product of reactions with fuel-based aerosols and atmospheric compounds. The reaction with ozone is of particular concern when aerosols can deplete the protective ozone layer in the stratosphere. Meanwhile, they are reacting at the same time with NOx gases to generate harmful ground-level smog consisting of ozone.

Radiative forcing, measured in W/m², is the primary measure of global warming, quantifying the energy that radiates from the sun when it approaches the Earth. As energy constantly flows from the sun to the Earth, a fraction of this is reflected back out into space, accounting for approximately 30% of the total energy transferred. The remaining energy is then absorbed by the atmosphere or absorbed at
the surface of the planet. If the net change in energy transfer is anything other than zero, then either global warming, or cooling, will occur.\(^2\)

Radiative forcing from aerosols can be categorized as direct or indirect effects. The direct result comes from the aerosols present in the atmosphere scattering or absorbing shortwave and longwave radiation, which affects Earth’s radiative balance.\(^6\) Anthropogenic based aerosols, such as fossil fuel organic carbon, fossil fuel black carbon, biomass burning, and mineral dust, all pose significant direct radiative forces.\(^6\) The indirect effect of aerosols in the atmosphere is their impact on the amount, lifetime, and radiative properties of clouds.\(^6\)

The understanding of the chemical reactions between organic particulate matter and common atmospheric oxidants such as \(\text{O}_3\), \(\text{NO}_3\), and \(\text{OH}\) has been of greater interest as the desire for alternative fuels has increased.\(^5\) While aerosols are not quite condensed-phase molecules, it has been determined that condensed-phase organic molecules typically react much faster than their gas-phase counterparts.\(^5\) With aerosols possessing properties of both phases, one could extrapolate that aerosolized compounds would react faster with these common atmospheric oxidants than those in the gas phase. If aerosolized biofuels are present in the atmosphere, and make their way up to the ozone present in the troposphere, it is possible that an even greater depletion of the ozone layer would occur. As the ozone layer diminishes, more energy can reach the Earth, which could greatly affect the global climate.
This study focuses on 2-methylfuran, an alkyl furan with biofuel capabilities, and its reaction as an aerosol with ozone. While this is not a complete study, it provided useful insight on the development of an apparatus that would allow one to investigate possible reactions of aerosols with atmospheric relevant species, such as ozone.

6.2. Experimental

The experimental apparatus (Figure 6.1) assembled for these experiments is made up of an aerosol generator (Figure 6.2), ozone generator (Figure 6.3), FT-IR gas

Figure 6.1 – The home-built experimental apparatus. Flow from a compressed air source (a) enters the aerosol generator (b). The aerosol continuous through the felon tube (c) into a small reaction flask (d) where it reacts with the ozone generated by the ozonator (e). The reaction mixture then flows into the gas cell (f) where the FT-IR will scan the contents for analysis. Excess aerosol is vacuumed from the gas cell, regulated by a pressure gauge (g). A trap (h) then catches any condensing aerosol before entering the vacuum pump (i).
cell, and an FT-IR spectrometer. All experiments were completed on-site at the University of San Francisco. 2MF was purchased from Sigma-Aldrich at 99% purity.

Gas-phase and aerosol spectra of 2MF are collected. Specifically, the FTIR gas spectra are acquired by flowing dry compressed air through the ozonator, which is turned off, at a pressure of approximately 8.1 psi into a 50 mL side-arm Erlenmeyer flask that contains approximately 10 mL of liquid 2MF. The ozonator used is a Polymetrics Laboratory Ozonator, model T-816\textsuperscript{10} pictured in Figure 6.3. The air flow forces the gaseous vapors near the surface of the liquid from the flask into the Pyrex FT-IR gas cell (a Storm 10 – Short Pathlength Gas Cell by Specac). The path length of the cell is measured to be 10 cm, with a clear aperture diameter of 38 mm and a volume of 132 cm\textsuperscript{3}. The cell was equipped with ZnSe windows each with a 47 mm diameter. The gas cell has an entry and exit port, both of which remain open to allow for a continuous flow of gaseous 2MF while avoiding pressure buildup within the cell. The exit port proceeds to a pressure gauge so the pressure in the gas cell can be continuously monitored throughout the experiment. The output pressure was recorded to be 0.4 kPa. While the gas flows through the FT-IR gas cell, a scan is taken at a resolution of 2 cm\textsuperscript{-1} to obtain the gas-phase spectrum of 2MF using a Vertex 70 FT-IR Spectrometer manufactured by Bruker.\textsuperscript{11} The source of the IR radiation comes from the mid infrared range, where fundamental molecular vibrations are excited, with an aperture setting of 6 mm. The detector used throughout these experiments was the room temperature deuterated, L-alanine doped triglycine sulfate detector (RT-DLaTGS). This type of
thermal detector is commonly used for high throughput (where >20% of the IR beam reaches the detector) and static experiments due to its full, specific detectivity in high-flux environments.\textsuperscript{12}

Aerosol spectra are obtained in a similar manner. The compressed air source flows dry air into an atomizer containing approximately 70 mL of 2MF at input pressures of 10, 15, and 25 psi. The atomizer used is a Model 9302 Atomizer sold by TSI, shown in Figure 6.2.\textsuperscript{13} In this specific aerosol generator, the compressed air expands through a 0.5 mm hole, producing a high-velocity jet. This jet then creates an area of low pressure near the aperture, where the solution in the sample reservoir is then pushed into the orifice. The liquid is then broken into small droplets (0.8 – 1.5 mm in diameter\textsuperscript{13}) that are carried by the compressed air through the outlet tube. This aerosol then continuously flows from the atomizer into the gas cell with a vacuum.

\textbf{Figure 6.2} – The Model 9302 Atomizer sold by TSI\textsuperscript{13} used to produce the aerosol studied.
pump connected to the end of the exit port line after the aforementioned pressure gauge. The output pressure for all experiments was recorded to be between 0.1-0.2 kPa.

IR spectra were then obtained after reacting ozone with aerosolized 2MF. First, the main water supply valve is opened on the ozonator, shown in Figure 6.3, and the cooling water is flowed through the apparatus. The compressed air source flows dry air into the ozonator, and is set at 6.5 psi after adjusting the pressure regulating valve to obtain a proper flow rate. The ozonator converts approximately 1% of the oxygen into ozone using a voltage setting of 70 V, where anything below 60 V does not produce ozone. This results in a flow rate of 6.8 L/min of a 1% O$_3$ gaseous mixture. At the same time, a compressed air source flows dry air into the atomizer at 15 psi, generating the aerosolized 2MF. Both the aerosol and ozone mixture meet in a small 50 mL Erlenmeyer reaction flask, then proceeding through to the FT-IR gas cell. The total output pressure was recorded at 0.6 kPa.
Figure 6.3 – The Polymetrics Laboratory Ozonator Model T-816 schematic obtained for the Ozonator Manual.\textsuperscript{10}
6.3. Computational

All optimized electronic structure calculations are completed utilizing the CBS-QB3\textsuperscript{14–16} composite method with the Gaussian09\textsuperscript{17} program and visualized in GaussView 5.0.\textsuperscript{18} The simulated FT-IR spectra used in this study were generated as a result of the optimization calculations for each respective molecule. In Figure 6.4, the blue-black spectrum shown in the diagram is an example of a simulated FT-IR spectrum. The overlap is very good, with only some peak shifting present. This could be due to the simulated FT-IR spectrum only representing a single conformation of 2MF, while the experimental spectrum should represent a combination of structural conformations.

6.4. Results

The results will be presented in three sections; the gas-phase 2MF IR results, the aerosolized 2MF IR results, and the IR results of mixing 2MF and ozone. Speculations are made about potential products with support of computational spectra and/or literature spectra.

6.4.1 Gas-Phase Results

The gas-phase IR spectrum of 2MF is shown in Figure 6.4. C-H bond wagging is evident in the range of 500-900 cm\textsuperscript{-1}. Bands corresponding to the C-O stretching can be observed from 900-1240 cm\textsuperscript{-1}, along with bands characteristic of C=C bonds in
aromatic rings evident in the 1500-1700 cm\(^{-1}\) range. The larger peak around 2900 cm\(^{-1}\) is a result of the C-H bond stretching in the methyl group, with the shorter peak around 3100 cm\(^{-1}\) characteristic of the stretching of the aromatic C-H bonds on the furan ring.

![Graph showing IR spectrum](image)

**Figure 6.4** – The experimental gas-phase IR spectrum of 2-methylfuran (red) compared to the CBS-QB3 simulated spectrum (black/blue).

### 6.4.2 Aerosol Results

The aerosol IR spectrum of 2MF is shown in Figure 6.5 (red) and is compared to the collected gas phase spectrum (blue). All of the bands in the aerosol spectrum are

![Graph showing IR spectrum](image)

**Figure 6.5** – The IR spectrum of aerosolized 2-methylfuran is shown in red, and for comparison, the experimentally obtained gas-phase 2MF spectrum is included.
much more prominent than they were in the gas-phase spectrum due to an increase in the concentration. While the baseline noise is now more prominent, there are no new peaks observed, as expected.

6.4.3 Aerosol + Ozone Results

The aerosolized 2MF produced a goldenrod color that coated the inside of the Teflon tubing between the atomizer and the reaction chamber. From the reaction chamber, the Teflon tubing took on a lighter goldenrod, slightly peach color. The color was so thorough, that it looked as if liquid were flowing through the tube to the gas cell. The gas cell was filled with a white vapor, concentrated enough that the laser from the FT-IR was visibly scattering off the particles present. Some of the vapor condensed in the gas cell, forming a sticky resin that was a dark-orange brown in color. The output tubing from the gas cell was coated in an eggshell hue.

The IR spectrum, Figure 6.6, of the reaction of aerosolized 2MF + O₃ portrays different peaks when compared to the 2MF gas and aerosol spectra. This is potential evidence that a reaction occurred when O₃ was introduced into the system. A broad band corresponding to the presence of an OH group has appeared between 3190-3580 cm⁻¹, corresponding to the presence of an alcohol. The peaks in the range of 2100-2200 cm⁻¹ are characteristic of a C≡C bond. Due to the lack of a strong sharp peak around 3300 cm⁻¹, it is believed that the C≡C bond is part of an internal alkyne, rather than a terminal alkyne. The peak located between 1650-1850 cm⁻¹, while present before the
reaction, has become much more prominent, nearly tripling in intensity, and corresponds to the presence of a C=O bond.

One study presented glyoxal, methyl glyoxal, formic acid, and acetic acid as products of the 2MF + O₃ reaction.¹⁹ The structures of these compounds can be found in Figure 6.7. This study was performed in chloroform at -60°C, and the products were identified after a reductive workup. Another study, performed by Arora,²⁰ focused on the reaction of furan with ozone, and it was observed that both the cis- and trans-isomers of glyoxal were produced. The mechanism proposed for the formation of glyoxal would be relevant to the reaction involving 2MF, as shown in Scheme 6.1. The presence of either glyoxal or methyl glyoxal would contribute to the C=O peak between

![Figure 6.7 - Structures of possible products of the 2MF + O₃ reaction; glyoxal, methylglyoxal, and formic acid.](image)

Figure 6.6 – IR spectrum of the results of the aerosolized 2MF + ozone reaction (blue) compared to the experimentally obtained aerosolized 2MF spectrum (red). The new peaks are labeled with their respective wavenumber values.
If formic acid or acetic acid are present, the narrow peak that should be around 3550 cm$^{-1}$ as a result of the OH group characteristic of a carboxylic acid would be covered up by the broad band that is currently there. The peak present between 3190-3580 cm$^{-1}$ is most likely from the presence of an alcohol.

Figure 6.8 shows the comparison of the 2MF + ozone IR spectrum to the literature gaseous methylglyoxal spectrum. Methylglyoxal contributes the observed OH band between 3190-3580 cm$^{-1}$, and portrays a C=O peak between 1650-1850 cm$^{-1}$. 

**Figure 6.8** - The FT-IR spectrum of the 2MF+ozone reaction (blue) compared to the literature spectrum of gaseous methylglyoxal (black).
It is possible that because the concentration of methylglyoxal produced is so low, that the bands present in the fingerprint region are covered up by those belonging to 2MF as shown in Figure 6.8. Glyoxal has a slightly broader OH band, and the C=O band does not align as well as that of methylglyoxal. If it is a product, it would be produced in relatively low concentrations. The OH band produced by formic acid is far too broad to contribute to the experimental spectrum, and is likely not to be a dominant product, if a product at all.

6.5. Conclusions

In this preliminary investigation, the resulting IR-spectrum of the reaction of aerosolized 2-methylfuran and ozone was obtained. A reaction was confirmed based on the evidence from the collected IR spectra of 2-methylfuran as an aerosol and the 2-methylfuran + ozone mixture, which exhibited additional peaks. Based on previous studies found in literature, it is possible that the compounds contributing to the C=O peak evident in the IR spectrum of 2-methylfuran + ozone are methylglyoxal and glyoxal. To further complete this study, it should be noted that additional analytical techniques, such as an HPLC with a UV/Vis or mass spectrometer, should be utilized in order to obtain more quantitative and qualitative data on this reaction. If the number of compounds is identified, the resin could potentially be collected and run through a column to separate the compounds for analysis via NMR.
6.6. References

[4] NASA Atmospheric Aerosols: What are They, and Why Are They So Important?


