Roaming Transition States and Highly Accurate Thermochemistry: A PEPICO Study of Two Small Combustion Systems

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ROAMING TRANSITION STATES AND HIGHLY ACCURATE THERMOCHEMISTRY: A PEPICO STUDY OF TWO SMALL COMBUSTION SYSTEM

by

Kyle J. Covert

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Pharmaceutical and Chemical Sciences

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2019
ROAMING TRANSITION STATES AND HIGHLY ACCURATE THERMOCHEMISTRY: A PEPICO STUDY OF TWO SMALL COMBUSTION SYSTEMS

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ROAMING TRANSITION STATES AND HIGHLY ACCURATE THERMOCHEMISTRY: A PEPICO STUDY OF TWO SMALL COMBUSTION SYSTEMS

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by

Kyle J. Covert
DEDICATION

This dissertation is dedicated to my beautiful wife, Ilona Covert, who has always supported me during my entire graduate career. We have gone through many phases of life during grad school; from moving in, to marriage, to giving birth to our wonderful daughter Anastasiya Lyubov Covert. Each step of the way, she was there to keep me going and I could not give her enough thanks and love for how amazing of a partner, mother, and woman she is.

In memory of Prof. Silvio Rodriguez. He was a great inspiration to many students, and I aspire to be as great of a man as him one day. He will be strongly missed but never forgotten.
ACKNOWLEDGMENTS

I would like to thank, first and foremost, Professor Bálint Sztáray, my research advisor, for his immense support during my years at University of the Pacific. I joined his research group within my first week of transferring to UOP as a junior and stayed with him all the way through grad school. He allowed me to foster my love for instrumentation without limits and challenged me to learn skills above and beyond graduate school. I am lucky to also know Bálint as a person outside of the university, from the many family gatherings and talks over how to properly enter downwind on a right-hand traffic pattern. I truly cherish all the memories I have gained in the Sztáray Lab and will continue to expand everyone’s knowledge on the world of PEPICO!

I could not have achieved any of this without the love and support of my amazing parents. They have never doubted me and always instilled the confidence in myself needed to get through life and college. Even when I would ramble on until 11 PM about trying to ignite a hydrogen discharge lamp, they would listen and nod with the most perplexed looks. I could not ask for better parents and will try my best to raise my daughter how they have raised me.

The best thing I have gained from graduate school is my beautiful wife, Ilona. She has helped me through graduate school more than any person and is always willing to supply better ideas than I could come up with on my own. Without seeing her hardwork and dedication through grad school and life, I’m not sure I would have made it this far or completed this dissertation.

I’m an only child but I have gained a sister from graduate school and that would be Chrissa Mozaffari-Easter. My lab mate and partner in crime for over three years, she is the only person to keep me half-sane during the most grueling times.
I would also like to thank the many other members of the Sztáray Lab: Sampada Borkar, Tyson Renali, Rosemarie Basi, Krisztina Voronova, Krisztian Torma and Peter Weidner. In addition, the beamline scientists at the Swiss Light Source: Andras Bodi and Patrick Hemberger.

And to my best friend, Matthew McClinton, So Say We All.
Abstract

by Kyle J. Covert

University of the Pacific
2019

Two small combustion systems, methyl hydroperoxide (CH$_3$OOH) and 2-propanol ((CH$_3$)$_2$CHOH), were studied using imaging photoelectron photoion coincidence spectroscopy (iPEPICO), which combines photoelectron spectroscopy and photoionization mass spectrometry to detect coincident photoelectron-photoion pairs.

In the photon energy range of 11.4–14.0 eV, energy selected CH$_3$OOH$^+$ ions dissociate into CH$_2$OOH$^+$, HCO$^+$, CH$_3^+$, and H$_3$O$^+$ ions. The lowest-energy dissociation channel is the formation of the cation of the smallest “QOOH” radical, CH$_2$OOH$^+$. A statistical rate model fitted to the experimental data yields a 0 K appearance energy of 11.647 ± 0.005 eV for the CH$_2$OOH$^+$ ion, and a 74.2 ± 2.6 kJ mol$^{-1}$ mixed experimental-theoretical 0 K heat of formation for the CH$_2$OOH radical. The proton affinity of the Criegee intermediate, CH$_2$OO, was also obtained from the heat of formation of CH$_2$OOH$^+$ (792.8 ± 0.9 kJ mol$^{-1}$) to be 847.7 ± 1.1 kJ mol$^{-1}$, reducing the uncertainty of the previously available computational value by a factor of 4.

RRKM modeling of the higher-energy fragmentation processes, supported by Born–Oppenheimer molecular dynamics simulations, found that the HCO$^+$ fragment ion is produced through a roaming transition state; H$_3$O$^+$ is formed in a consecutive process from the CH$_2$OOH$^+$ fragment ion; and direct C–O fission of the molecular ion leads to the methyl cation.
Experimentally, 2-propanol has been found to dissociate primarily into $\text{CH}_2\text{CHOH}^+$, $\text{CH}_3\text{CHOH}^+$, $\text{CH}_3\text{CHCH}_3^+$, and, as a minor product, into $(\text{CH}_3)_2\text{COH}^+$ ions within a photon energy range of 10.0–13.1 eV. There are interesting dissociation dynamics involving breaking the C–C bond: the lowest energy product (CH$_3$ loss) is quickly outcompeted by a kinetically favored CH$_4$ loss. At low internal energies of <0.3 eV, the loss of CH$_4$ dominates through a roaming pathway, when the leaving CH$_3$ abstracts a hydrogen atom from the other methyl group. At higher energy, the direct loss of CH$_3^*$ quickly takes over as its transition state is much less tight and, thus, it is kinetically favored. The statistical model fitted to the experimental data yielded the appearance energy corresponding to the thermochemical limit for the CH$_3$-loss dissociation and the 0 K heats of formation of the CH$_3\text{CHOH}^+$ ion was found to be in good agreement with ATcT values and with our previous study on ethanol.
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<tr>
<td>AE</td>
<td>appearance energy</td>
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<td>AIE</td>
<td>adiabatic ionization energy</td>
</tr>
<tr>
<td>ATcT</td>
<td>Active Thermochemical Tables</td>
</tr>
<tr>
<td>BDE</td>
<td>bond dissociation energy</td>
</tr>
<tr>
<td>BOMD</td>
<td>Born-Oppenheimer Molecular Dynamic</td>
</tr>
<tr>
<td>BSSR</td>
<td>Beyer-Swinehart-Stein-Rabinovitch</td>
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<tr>
<td>CCSD</td>
<td>coupled cluster theory</td>
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<tr>
<td>CRF-PEPICO</td>
<td>combustion reaction followed by PEPICO</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMS</td>
<td>dimethyl sulfate</td>
</tr>
<tr>
<td>E0</td>
<td>appearance energy</td>
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<tr>
<td>eV</td>
<td>electron volt</td>
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<tr>
<td>FDPI</td>
<td>first differential photoionization efficiency</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>IE</td>
<td>ionization energy</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>iPPEPICO</td>
<td>imaging PEPICO</td>
</tr>
<tr>
<td>IRC</td>
<td>intrinsic reaction coordinate</td>
</tr>
<tr>
<td>K</td>
<td>kelvin</td>
</tr>
<tr>
<td>KER</td>
<td>kinetic energy release</td>
</tr>
<tr>
<td>kJ</td>
<td>kilojoule</td>
</tr>
<tr>
<td>MCP</td>
<td>microchannel plate</td>
</tr>
<tr>
<td>MHP</td>
<td>methyl hydroperoxide</td>
</tr>
<tr>
<td>MPIMS</td>
<td>multiplexed photoionization mass spectrometer</td>
</tr>
<tr>
<td>MSMS</td>
<td>multiple-start-multiple-stop method</td>
</tr>
<tr>
<td>PEPICO</td>
<td>photoelectron photoion coincidence</td>
</tr>
<tr>
<td>PES</td>
<td>photoelectron spectroscopy</td>
</tr>
<tr>
<td>PIE</td>
<td>photoionization spectra</td>
</tr>
<tr>
<td>PIMS</td>
<td>photoion mass spectrometry</td>
</tr>
<tr>
<td>RAC</td>
<td>rigid activated complex</td>
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<tr>
<td>ROO</td>
<td>alkylperoxy radicals</td>
</tr>
<tr>
<td>RRHO</td>
<td>rigid rotor and harmonic oscillator</td>
</tr>
<tr>
<td>RRRK</td>
<td>Rice-Ramsperger-Kassel</td>
</tr>
<tr>
<td>RRRKM</td>
<td>Rice-Ramsperger-Kassel-Markus</td>
</tr>
<tr>
<td>SLS</td>
<td>Swiss Light Source</td>
</tr>
<tr>
<td>SSACM</td>
<td>simplified statistical adiabatic channel model</td>
</tr>
<tr>
<td>STQN</td>
<td>Synchronous Transit-Guided Quasi-Newton</td>
</tr>
<tr>
<td>TOF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>TPEPICO</td>
<td>threshold photoelectron photoion coincidence</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>TPES</td>
<td>threshold photoelectron spectrum</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>VMI</td>
<td>velocity map imaging</td>
</tr>
<tr>
<td>VRC-TST</td>
<td>variable-reaction-coordinate transition state theory</td>
</tr>
<tr>
<td>VTST</td>
<td>variable transition state theory</td>
</tr>
<tr>
<td>VUV</td>
<td>vacuum-ultraviolet</td>
</tr>
<tr>
<td>ZPE</td>
<td>zero-point energy</td>
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Chapter 1: Introduction

Understanding how a molecule dissociates is one of the key areas of research in chemistry. Knowing the products of a unimolecular reaction gives more information about a molecule’s safety, utility, and energetics.\textsuperscript{1-3} This is especially useful in the fields of atmospheric and combustion chemistry where reactions are occurring from molecules interacting with light or heat energy to generate radicals.\textsuperscript{4,5} This leads to low-temperature autoxidation processes which forms the backbone for most low energy reactions between radicals in the atmosphere.\textsuperscript{6} With the addition of further energy, molecules begin to ionize, and bonds begin to break leading to new products. Even if the parent molecule is well understood, the fragments formed could have completely different physical and chemical properties. Furthermore, understanding the dissociation process yields important thermochemical information which can be applied to models and other systems.\textsuperscript{7} While these reactions are occurring all around us, every day, studying them can be quite difficult as it requires more than just mixing two chemicals together. A fine control of the internal energy of a molecule and a way to detect products at very low concentrations is required. Experiments must be carried out with advanced instrumentation to better understand unimolecular dissociation mechanisms and products. Mass spectrometry provides the best way to analyze these reactions because it is universal; any molecule can be ionized, sensitive and selective; single molecules can be detected and distinguished, and multiplexed; large amounts of information can be gathered from a single experiment.
The first step to any mass spectrometry experiment is ionization. For unimolecular dissociations it is important to have enough energy to ionize a molecule but also enough control to scan across a small energy range (few eV) to monitor reaction products. Studying low energy dissociation processes is difficult with electron ionization or even collision-induced dissociation because the internal energy of the parent molecule is not well-defined. Vacuum-ultraviolet (VUV) photoionization is well suited for such studies, because the internal energy can be fine-tuned and very accurately known, to a few meV. When photoionization is coupled with photoelectron photoion coincidence (PEPICO) detection, unimolecular dissociation processes can be studied with very high energy accuracy and ion dissociation kinetics studies are also possible.
Chapter 2: Theory and Techniques

2.1 Photoelectron Photoion Coincidence Spectroscopy (PEPICO)

2.1.1 Background and applications. PEPICO combines photoion mass spectrometry (PIMS) and photoelectron spectroscopy (PES). The method is based on photoionization, i.e., the ejection of an electron due to the absorption of a photon:

\[ \text{AB} + h\nu \rightarrow \text{AB}^{+} + e^{-}, \]

where AB is a neutral molecule, \( h\nu \) is the incoming photon, \( \text{AB}^{+} \) is the resulting ion, and \( e^{-} \) is the leaving electron. Photoionization can ionize any molecular species and when coupled to a time-of-flight (TOF) mass analyzer, provides a multiplexed, sensitive, and selective technique with near zero-background detection. The photoionization spectrum (the integrated photoion current as a function of photon energy) can be used to separate up to 3 structural isomers, albeit requires favorable ionization energies of the isomers and good photoionization spectra (PIE) curve shape.\(^9\) PES is more selective than PIMS and provides sharp peaks corresponding to transitions to the final cationic state rather than relying on the changes of slope in PIMS. Although, PES is rarely used in itself to quantify mixtures because there is no mass selection. This is where PEPICO combines the best of both techniques, detecting both the photoelectrons and the corresponding molecular ions (photoions) in coincidence, yielding a photoelectron spectrum for each \( m/z \) value in the mass spectrum.\(^{10}\)

The first PEPICO experiments used a monochromatic light source to ionize neutral molecules and the energetic photoelectrons were kinetic energy analyzed and detected in coincidence with the photoions.\(^{11}\) Later advancements brought the use of a broadband VUV light source, typically a H\(_2\) discharge lamp, which used a monochromator to select the photon
energy. By varying the photon energy and detecting only zero kinetic energy (threshold) electrons in coincidence with the photoion, one can control the internal energy in the ion. This technique is known as threshold photoelectron photoion coincidence spectroscopy (TPEPICO) and offers better collection efficiencies and lower background than classical PEPICO.\textsuperscript{12} The energetics of the TPEPICO ionization process can be described as follows:

\begin{equation}
E_i = h\nu - IE_{ad} + E_{th} - KE_e - KE_i
\end{equation}

where $E_i$ is the internal energy of the ion, $h\nu$ is the photon energy, $IE_{ad}$ is the adiabatic ionization energy, $E_{th}$ is the original thermal energy of the neutral molecule, $KE_e$ is the kinetic energy of the electron, and $KE_i$ is the kinetic energy of the molecular ion. Because of conservation of momentum, the latter term is negligible and, due to the fact that only threshold electrons are detected, the kinetic energy of the electron is also zero, simplifying the equation to:

\begin{equation}
E_i = h\nu - IE_{ad} + E_{th}
\end{equation}

The internal energy of the ion is therefore well defined, considering the following information is known: the photon energy, which is selected incident radiation from a monochromator, the ionization energy is usually a well-established value, and the thermal energy of the neutral can be calculated as a Boltzmann’s thermal energy distribution. If there is not a well-established literature ionization energy, then a threshold photoelectron spectrum (TPES) or even a mass-selected photoelectron spectrum can be measured using TPEPICO, as well. A TPES gives sharp peaks for the electronic transitions in a molecule, and most often vibrational transitions can be resolved as well.

A modern TPEPICO experiment involves a TOF mass analyzer coupled to electron velocity map imaging (VMI) kinetic energy analysis and detection.\textsuperscript{13} This allows detection of
threshold photoelectrons and their corresponding photoion in coincidence. Single photons are absorbed by a neutral molecule and if the photon energy is above the dissociation limit, then the neutral molecule will ionize and may also undergo unimolecular dissociation:

\[ \text{AB} + h\nu \rightarrow \text{AB}^{++} + e^{-} \rightarrow \text{A}^{+} + \text{B}^{+} + e^{-} \]  

The parent and daughter ions are distinguished by their time of flight, and these spectra can also be used to measure unimolecular rate constants. From the fractional abundance of the photoions as a function of photon energy (the breakdown curve), together with the rate constants in case of slow dissociations, 0 K appearance energies \( E_0 \) can be derived for the \( \text{A}^{+} \) daughter ion. The 0 K heats of formation of the three species involved are directly related to the measured appearance energy by the following equation:

\[ E_0 = \Delta H_{0 \text{ K}}^f [\text{A}^{+} + \text{B}^{+} - \text{AB}] \]

If two of the heat of formations are known, then the third can be obtained with the \( E_0 \) from the experiment. With the PEPICO data analysis software developed in our group, the TPEPICO technique can also be used to obtain reliable appearance energies for parallel or consecutive dissociations, with statistical modeling of the reaction rates and ion energy distributions.\(^\text{14}\)

The use of synchrotron light sources and imaging optics has greatly enhanced sensitivity and selectivity of the PEPICO technique and our most recent experimental apparatuses at the Swiss Light Source can achieve sub-kJ mol\(^{-1}\) accuracy, corresponding to energy resolutions of a few meV.\(^\text{15}\) Current developments on a completely new prototype apparatus, combustion reactions followed by PEPICO (CRF-PEPICO) include a laser-photolysis flow tube reactor and a unique ion-deflection optics that offers a giant leap in the dynamic range, a difficult issue in all previous PEPICO experiments.\(^\text{16,17}\)
The experiments discussed in this dissertation were conducted on the imaging PEPICO (iPEPICO) apparatus on the VUV beamline at the Swiss Light Source (SLS), Paul Scherrer Institut, in Villigen, Switzerland. Development of the prototype CRF-PEPICO experiment was also undertaken at the SLS as a joint collaboration between the Sztáray research group and the Combustion Research Facility at Sandia National Laboratory, Lawrence Livermore National Lab, Livermore, CA.

2.1.2 Imaging PEPICO apparatus.

2.1.2.1 Overview. An image of the iPEPICO apparatus is shown in Figure 1. Synchrotron radiation is supplied to the beamline by bending magnet radiation and is dispersed by a grazing-incidence grating monochromator. Depending on the photon energy range and desired resolution, there are three gratings that can be used, with 300, 600, and 1200 mm\(^{-1}\) line density and our typically utilized 600 mm\(^{-1}\) grating offers approximately \(10^4\) resolving power. A series of mirrors focus the collimated beam into the exit slit inside an 80 cm long gas filter, which is located 26 m from the source radiation. A gas filter is required before the experimental chamber to absorb unwanted higher energy photons coming from the higher harmonics from the monochromator. A mixture of rare gases (Ne, Ar, Kr) are used to absorb photons above about 15 eV and the ratio of gases can be modified depending on the desired cut off energy. The entire gas filter contains eight differentially pumped chambers and can maintain the required \(10^{-10} - 10^{-9}\) mbar background pressure with 10 mbar of the rare gas mixture. For photons with \(< 10\) eV of energy, a MgF\(_2\) window is used to absorb virtually all the light above 11 eV.
After the gas chamber, at the ionization spot, the synchrotron light has a spot size of approximately $4 \times 2 \text{ mm}^2$ and the light intensity, photon flux, is roughly $10^{11} \text{ s}^{-1}$, but it depends on the photon energy. This intensity allows ionization rates that are orders of magnitude larger than in a typical lab based TPEPICO apparatus that uses a H$_2$ discharge lamp. Data acquisition using the multiple-start-multiple-stop method (MSMS) allows measurements at these high count rates where other coincidence acquisition methods suffer from signal paralysis.$^{18}$

The sample enters the experimental chamber through a 30 cm long Teflon tube effusing to the approximate location of the ionization spot. This chamber is pumped by a 1500 l s$^{-1}$ Leybold COOLVAC 1500 CL cryopump and a 500 l s$^{-1}$ Pfeiffer TMH 521 YP turbomolecular pump. The turbomolecular pumps are backed by an Adixen ACP 28 G series 2 Roots pump and the cryopumps are driven by a Leybold COOLPAK 6000D compressor unit and backed by an...
Adixen ACP 40 G series 2 Roots pump. The total high vacuum pumping capacity of 8250 l s$^{-1}$ backed with an oil-free foreline system provides a clean vacuum that minimizes the signal background.

The ejected electron from the ionized neutral parent and its corresponding photoion are extracted opposite of each other in a 40–120 V cm$^{-1}$ field by extraction plates within 11 mm of each other. For the time-of-flight, electrons act as the start signal and all ion detection events are recorded. All start signals are correlated to all stop signals in the MSMS data acquisition method. There is an equal and random chance for all false coincidences (unrelated electron and ion arriving within the coincidence time window) to occur, therefore all false coincidences are spread out across a flat baseline background; while true coincidences will appear as peaks above the baseline. Unfortunately, even this most sophisticated coincidence acquisition method leads to a significant baseline, limiting the dynamic range to approximately $10^3$. A breakthrough method to suppress false coincidences has been developed, which uses a temporal deflection of the ions and is discussed further in Section 2.2.2.

First, a description of the electron optics and detector is discussed. The electrons fly through a 265 mm flight tube and are focused by velocity map imaging onto a Roentdek DLD40 delay line detector with resistance matched Photonics microchannel plates (MCPs) mounted in a Chevron configuration. The collector consists of a grid of gold-plated copper electrodes which detect the x and y positions of an electron impact. The delay line allows for an extremely high throughput, when coupled to fast electronics, and single detection events can be distinguished with count rates higher than 100 kHz. A velocity mapped photoelectron image is shown in Figure 2. Electrons with zero transverse momentum are focused to a less than 1 mm diameter spot at the center of the detector. Typical best spot sizes achieved have full width at half
maximum (FWHM) of $0.9 \times 0.4$ mm$^2$, corresponding to 0.2 meV energy resolution, from a pure threshold electron signal of Ar. The kinetic-energy (“hot”) electron contamination of the threshold signal at the center of the image can be subtracted based on the average count rate in a surrounding ring area. With an 80 V cm$^{-1}$ extraction field, the total active range of the detector is 870 meV.

![Heat map of an iPEPICO image](image)

Figure 2: A heat map of an iPEPICO image. Threshold electrons are found at the center and hot electrons are found everywhere, including the area surrounding the center spot.

Photoions enter a long, 54 mm constant acceleration field at 80 V cm$^{-1}$ before being accelerated a second time to 1100 V within a space of 10 mm. The long first acceleration region allows metastable ions to dissociate while being under constant acceleration. This produces a tell-tale TOF peak that has a positive skew (tail) because the metastable ion decays exponentially. Modeling of the metastable TOF peaks to account for the kinetic shift can be undertaken for slow unimolecular dissociation. No metastable peaks were detected in this work, so a fully detailed description on the so-called kinetic shift can be found in ref. 18 and here I am only providing a quick description of this important concept in mass spectrometry. In general, an energized ion with internal energies above a dissociation limit will eventually fragment but whether or not the fragment ions will be detected as such depends on the time scale of the mass
analysis. If, for example, the dissociation rate at a certain internal energy is on the order of $10^3 \text{ s}^{-1}$ but mass analysis concludes within a microsecond, it will still be detected as the parent ion. Therefore, to actually record this dissociation, more internal energy has to be deposited into the ion and the difference between the energy where the fragment ion is practically detectable vs. where it could be if the experiment allowed infinitely long time for mass analysis is called the kinetic shift. Since one of the main goals of a modern PEPICO experiment is to measure accurate dissociation (or, appearance) energies, this kinetic shift needs to be accounted for, by measuring the dissociation rates and extrapolating the rate curve to the true appearance energy. As mentioned here, the experiments reported in this work showed no sign of “slow” dissociation, therefore, the kinetic shift did not need to be accounted for.

A ca. 550 mm long field-free section follows the two acceleration regions, at the end of which the photoions are detected. The second half of the field-free drift region consists of 15 plates, to each of which a different voltage can be applied. It is, thus, possible, to decelerate ions and introduce a second field-free drift region, which can be used to distinguish daughter ions formed in slow dissociation reactions in the first field-free region.\textsuperscript{19}

2.2 Combustion Reactions Followed by PEPICO

The following section is a cursory overview of the Combustion Reactions Followed by PEPICO (CRF-PEPICO) instrument. This project was undertaken as a complex collaboration between several research groups across the globe and, while our group were the lead in designing and building the instrument, quite a few other scientists contributed to individual parts of the project. My contribution was on the construction and testing of the prototype CRF-PEPICO instrument at the Swiss Light Source synchrotron in Switzerland. Specifically, I hand built the ion optics stack on site and installed it in the vacuum chamber. I assisted the beamline scientists
with putting together the rest of the components so we could begin testing the apparatus and, eventually, conduct our first experiments. For example, these testing stages involved energizing the ion/electron optics stacks for the first time and optimizing the voltages to maximize electron and ion collection efficiencies and the energy and spatial resolutions. Testing continued remotely once I returned home, with other grad students performing the first experiments with the flow tube reactor and laser in place. Even though I did not run any independent experiments using the CRF-PEPICO, providing an overview is important here, considering the knowledge I gained and large amount of my time that was invested into this project.

2.2.1 CRF-PEPICO instrument. Our latest edition of a PEPICO apparatus was the development of the prototype Combustion Reactions Followed by PEPICO (CRF-PEPICO) instrumental apparatus for the VUV beamline of the SLS. This instrument was conceived as a collaborative effort between our research group, the Chemical Dynamics group at the Swiss Light Source and the Combustion Research Facility of Sandia National Laboratories. This apparatus fulfills the requirements for universal, sensitive, selective, and multiplexed detection of gas-phase reaction intermediates, improving upon the well-established time-resolved multiplexed photoionization mass spectrometer (MPIMS) at the Chemical Dynamics Beamline of the Advanced Light Source. This latter technique only allows one to distinguish isomers that are “well-behaved”, that is, their PIE spectra are sufficiently different to allow separation. Ideally, two structural isomers are easily separated if there is a several tenths of eV difference between their first ionization energies and if the higher-IE isomer exhibits favorable Franck-Condon factors upon ionization to the ground state cation. As shown by our proof-of-concept experiments, employing PEPICO as a detection method can dramatically improve this. Instead of the PIE spectrum, in TPEPICO, as the photoelectrons are also detected in coincidence with
each photoion, one obtains a complete mass-selected TPES for each m/z value of the corresponding photoion. Since the TPES exhibits sharp peaks rather than just changes in the slope, its information content is much superior over a PIE spectrum. And, with PEPICO coincidence detection, each photoelectron is “labeled” with the m/z of the photoion it corresponds to, essentially combining the advantages of mass spectrometry and photoelectron spectroscopy.

Figure 3: Comparison of photoionization efficiency (PIE) curves and threshold photo-electron spectra (TPES). The slope of the PIE curve can be used to distinguish between individual isomers while the TPES contains sharp peaks unique to each isomer.

A prototype CRF-PEPICO instrument was designed and built to add TPEPICO detection to radical-initiated chemical reactor source. This new instrument contains a side-sampled flow
tube laser photolysis reactor inlet system, where photolytically generated radicals react with target molecules as shown in Figure 4.

Figure 4: Image of the side-sampled reactor flow tube on left. The reactor flow tube runs offset and parallel to the incoming VUV radiation with a pinhole orthogonal to the beamline to sample photolytically generated radicals. The schematic on the right represents the ion optics of the CRF-PEPICO.

A Nd-YAG pulsed laser, operating at 20 Hz, photolyzes the precursor molecules, which either react with other species introduced in a flow of argon gas or isomerize and/or decompose on their own. Reaction products are sampled through a small pinhole half-way down the flow tube and the linear flow velocity is set such that the reaction mixture is completely replenished before the next laser pulse. Tunable synchrotron radiation in the VUV range intersects the expanding plume of neutral gas mixture and the resulting photoelectrons and photoions are velocity-map imaged onto two delay-line fast imaging detectors. To improve sensitivity, a very short distance is kept between the pinhole and the synchrotron beam, while field homogeneity (responsible for mass resolution, ion VMI focusing, and photoelectron kinetic energy resolution)
is preserved in our design by the use of partially cut extraction plates with a small gap for the flow tube. The electron and ion optics are built from many individually voltage-controlled acceleration/focusing plates, fulfilling VMI focusing conditions and offering dynamically configurable extraction/focusing region lengths. This way, one can vary the photoelectron kinetic energy range on the imaging detection without having to alter the extraction field strength. As shown by a Simion simulation in Figure 5.

![Simion simulation of velocity mapped imaging at various accelerating/focusing voltages mimicking the actual construction of the CRF-PEPICO ion optics. The extraction field is kept constant while the effective photoelectron kinetic energy range can be dynamically modified. Note: the x and y scales are modified to fit onto this image.](image)

In one of the first experiments on this new setup, the mass-selected photoelectron spectrum of the elusive methylperoxy radical was measured and then analyzed using Frank-Condon spectral simulations. Since we also collected dissociative photoionization data for this species, the heat of formation of the methylperoxy radical was derived from the 0 K appearance
energy of CH$_3^+$ daughter ion, and is in good agreement with and improves upon the accuracy of
the literature value.$^{20}$ See Figure 6

![Figure 6: Positive ion thermochemical cycle of the methylperoxy system. The ionization energy of CH$_3$OO and the appearance energy of the CH$_3^+$ daughter ion, highlighted in blue, are experimentally measured.](image)

### 2.2.2 Improvements to dynamic range

Mass analysis of cations combined with kinetic energy analysis of electrons can produce mass-resolved photoelectron spectra *if and only if* the electrons and cations can be sorted into correlated pairs, each pair arising from the ionization of an individual neutral molecule. Such a correlated pair is called a true coincidence and requires detection of both charged particles. By contrast, an electron/cation pair in which the two particles did *not* arise from the same neutral molecule is termed a false coincidence.$^{18}$ False coincidences contribute to the background signal of a PEPICO experiment and limit dynamic range, obscuring weak signals of trace species, free radicals, and reaction intermediates. This is even true in the most sophisticated coincidence detection scheme (so-called multiple-start-
multiple-stop\textsuperscript{18}) where the false-coincidence background is flat but with a significant random noise. Therefore, although PEPICO has proven to be extremely versatile in studying energetics,\textsuperscript{21} unimolecular dissociation mechanisms\textsuperscript{22} and even quantum effects therein,\textsuperscript{23} its applications as a very selective detection technique for a wide range of gas-phase experiments may still be limited by this false coincidence barrier, which limits its dynamic range (the ratio between the most abundant and the least abundant but still detectable species) to about $10^3$. Recently, a few pyrolysis\textsuperscript{24,25} and even flame experiments\textsuperscript{26} have succeeded using PEPICO detection, but even in these applications, greater dynamic range would be a clear benefit.

When studying reactive intermediates in chemically reacting mixtures, a dynamic range of $10^5$ or greater is often required as it is normal for the excess reactant to be present in vastly higher concentration than other, usually more interesting species. In this case, almost all false coincidences arise from photoions of the dominant species. Therefore, the solution must lie in identifying false coincidences and removing them from the dataset so that both the TOF mass spectrum and the mass-selected photoelectron spectrum would have improved signal-to-noise ratio. A new method which is based on temporal ion deflection coupled with a position-sensitive ion detector has been implemented in the CRF-PEPICO instrument to increase the dynamic range. This method enables suppression of the false coincidence background, increasing the dynamic range of the PEPICO detection by more than two orders of magnitude.

To test the new coincidence measurement scheme, a skimmed beam of argon gas was expanded into the ionization chamber where single photon ionization was achieved using a monochromatic VUV synchrotron beam.\textsuperscript{17} Electrons and ions are extracted and accelerated in opposite directions using a double velocity map imaging setup, onto separate DLD40 Roentdek position-sensitive delay-line detectors. For photoelectrons, the energy resolution is better than 1
meV at threshold while the ion optics satisfies both space-focusing and velocity map imaging conditions. With this setup, the argon ions formed in the molecular beam are imaged onto a spot with FWHM between 0.8 and 0.9 mm. In the ion drift region, photoions enter an Einzel-lens-style deflector assembly in which antisymmetrically biased deflector plates provide finely-controlled deflection in both directions perpendicular to the flight path. Figure 7 shows a sketch of the experimental setup as relevant for this discussion.

![Figure 7: Sketch of the CRF-PEPICO false coincidence suppression experiment. Velocity mapped imaging occurs for both the electron and photoion, where electrons are extracted and focused to an imaging detector on the left and ions are extracted, deflected, and focused onto an imaging detector on the right.](image)

In our false coincidence suppression scheme, the ions are deflected dynamically using triangle waves and Figure 8 a) shows a resulting ion image of a tightly focused ion spot deflected to form periodic checkered patterns. As the ions experience a time-dependent electric deflection field at a well-defined fraction of their time of flight, this defines an $m/z$ and ionization-time dependent ion impact position for true coincidences. False coincidences, however, appear randomly outside this region and can be efficiently suppressed. As demonstrated in Figure 8 b), the false coincidence suppressed TOF spectrum shows an almost $10^3$ decrease in the background and a complete suppression of the periodic false-coincidence peaks resulting from the
synchrotron time structure. This last phenomenon occurs due to the bunched operational mode of the synchrotron light where the electrons are pulsed into the storage ring in discrete intervals. In these experiments, we have also shown that, when cold argon clusters are ionized, false coincidence suppression allows us to observe species up to Ar\textsubscript{9}\textsuperscript{+}, whereas Ar\textsubscript{4}\textsuperscript{+} is the largest observable cluster under traditional operation Figure 8 c).

Figure 8: a) Ion image from periodic triangle-wave deflections; b) Ar molecular beam coincidence spectra: red is the original, whereas the blue curve shows the result of false-coincidence suppression; c) False-coincidence suppressed spectrum of the larger argon oligomer ions.

2.3 PEPICO Data Analysis

In order to determine bond dissociation energies from the direct experimental results of the PEPICO measurements (breakdown curves and TOF distributions), a detailed modeling of the dissociation processes is carried out. In this section, we will shortly discuss why this is necessary, and then refer to the corresponding theories and their application to the particular case of PEPICO experiments.
2.3.1 Measuring unimolecular reactions. In PEPICO experiments, only unimolecular reactions take place, that is a single reactant can undergo either isomerization to one product or dissociation into two or more products. The well-known differential and integrated rate laws for unimolecular decay, \( A \rightarrow \text{products} \), describe the concentration of a reacting species \( A \), denoted as \([A]\), over time (\(t\)):

\[
\begin{align*}
(6a) & \quad -\frac{d[A]}{dt} = k[A] \\
(6b) & \quad [A] = [A]_0 e^{-kt}
\end{align*}
\]

where \(k\) is the unimolecular rate constant and \([A]_0\) is the initial concentration or number of species \(A\) at time, \(t = 0\). The rate constant \(k\) depends on the internal energy of \(A\) (\(k(E)\), microcanonical rate constant); or on the temperature, when the system can be described by a thermal energy distribution characterized by a given temperature (\(k(T)\), canonical rate constant). The connection between \(k(T)\) and \(k(E)\) can be written as:

\[
(7) \quad k(T) = \int_{E_0}^{\infty} P(E, T) \cdot k(E) \, dE
\]

where \(P(E, T)\) denotes the distribution of internal energies at temperature \(T\). The lower limit of the integration is set to \(E_0\), the activation energy, to emphasize that no reaction occurs unless the internal energy exceeds this threshold value (provided that tunneling is negligible). For dissociation reactions with no reverse barriers, \(E_0\) is equal to the bond dissociation energy (BDE); whereas for reactions with real barriers, \(E_0\) is equal to the barrier height.\\n
Most of our PEPICO experiments are carried out at room temperature, including the ones discussed in this dissertation. The room-temperature internal energy distribution of the neutral
molecule can extend across several hundred meV even though the PEPICO apparatus can measure with better than meV photon/photoelectron energy resolution. Therefore, we need to take the internal energy distribution and, for slow dissociations, the dissociation rates into account. For fast dissociations, the appearance energies can be observed in the experimental data where the parent ion decreases to zero abundance (for the first fragment ion) and near the onsets of parallel dissociations (for the rest of the ions formed in parallel). In some experiments, a shift of the experimental $E_0$ can be observed due to a variety of phenomena explained here: a “kinetic shift” is the result of a parent ion slowly dissociating within the acceleration region of the experiment. This results in a typical “metastable” TOF peak and excess energy is needed for the parent ion to dissociate, resulting in a higher apparent appearance energy.\textsuperscript{28,29} In addition, the nonzero thermal energy of the sample molecules shifts the observed appearance energy to lower values (thermal shift),\textsuperscript{30,31} which also has to be taken into account in order to obtain accurate energetics. If there are parallel dissociations, the threshold of the higher energy channel may suffer from a “competitive” shift from the lower energy channel, consequently leading to a higher $E_0$.\textsuperscript{32} Thus, careful statistical modeling of the dissociation process is essential, which can be performed by fitting the measured part of $k(E)$ to a unimolecular rate theory, and the extrapolation of the $k(E)$ curve over several orders of magnitude in order to correctly determine $E_0$.

2.3.2 Rice-Ramsperger-Kassel-Markus (RRKM) theory. Rice and Ramsperger (1927, 1928) and Kassel (1928) first developed the RRK theory for understanding the unimolecular reaction $A \rightarrow \text{products}$. This theory is based on a system of identical harmonic oscillators, one of which is truncated at an energy $E_0$, the activation energy for dissociation. If there is energy, $\varepsilon$ in excess of the activation energy, then it can be taken by the critical oscillator and the molecule
dissociates. This theory follows the assumption that the energy flows statistically among all of the oscillators and that there is an equal and random chance of finding the system in a particular arrangement of its internal energy. Due to its simplicity, RRK theory alone is incapable of accurately producing correct rate constants, therefore the theory would need to be refined.

Certain shortcomings associated with RRK theory were improved and corrected by Marcus and Rice (1951) and by Rosenstock, Wallenstein, Wahrhaftig, and Eyring (1952). The final theory, now known as RRKM/QET theory treats the vibrational (and rotational) degrees of freedom in detail. The RRKM rate equation yields the unimolecular dissociation rate constant for an ion at a given internal energy $E$ and with an activation energy of $E_0$:

$$
(8) \quad k(E) = \frac{\sigma N^\dagger(E-E_0)}{h \rho(E)}
$$

where $\sigma$ is the reaction degeneracy, $N^\dagger(E-E_0)$ is the transition state sum of states from 0 to $E-E_0$, $h$ is Planck’s constant, and $\rho(E)$ is the parent ion density of states at an energy $E$. Both $E$ and $E_0$ are referenced to the reactant ground-state energy in Eq. 8 The density and sum of states are usually calculated using harmonic vibrational frequencies with the Beyer-Swinehart direct count algorithm. A statistical approach to RRKM theory has been explained in detail elsewhere.

RRKM theory is only valid based on three major assumptions. First, the intramolecular vibrational energy redistribution (IVR) must be faster than the rate of reaction (either dissociation or isomerization). Therefore, the rate constant is only dependent on the energy and angular momentum of the ions, and the initial location of the energy in the phase space does not matter. Secondly, the reactants and products are divided by the transition state and once the trajectory passes through the transition state, it will not return. Small systems, such as the reaction between H and Cl$_2$ can indeed recross several times, but as the system size increases, the
chance of recrossing rapidly decreases.\textsuperscript{36,37} This is due to the phase space volume rapidly increasing away from the transition state in larger systems than in small molecules. Furthermore, at energies near the dissociation threshold, the phase space becomes very constricted and coupling between the reaction coordinate and modes perpendicular to it are very weak. Lastly, an assumption is made that the reaction coordinates are perpendicular to all other internal coordinates of the system and that they are, therefore, separable. At the saddle point, this is a good approximation and, at low energies, the vibrations can be treated as linearly independent normal modes.

\textbf{2.3.3 Experimental breakdown diagram.} The usual first step in PEPICO data analysis is plotting an experimental breakdown diagram. A breakdown diagram shows the fractional ion abundance of all the photoions involved in the dissociative photoionization process as a function of the photon energy. This is essentially a plot of the ratios of each fragment ion formed over the sum of all ions present at a given photon energy. Photoelectron-photoion coincidence data are collected during the experiment at fixed photon energies and stored as individual data files for each photon energy within the energy range of interest or availability. This raw coincidence data is analyzed to generate individual TOF spectra at each measured photon energy. This process starts by looking at the velocity map image on the electron detector. The center spot of the image, where threshold electrons are focused, is defined, along with a ring area around this center spot where only hot electrons are detected. The coincidence count corresponding to this ring area is subtracted from the center counts by a subtraction factor, first approximated as the ratio of the detector areas:

\begin{equation}
F \approx \frac{A_{\text{center}}}{A_{\text{ring}}}
\end{equation}
This factor is then adjusted manually to yield zero parent ion abundance beyond the appearance energy of the first fragment (for fast dissociations). Using this subtraction process, TOF spectra are generated corresponding to photoions in coincidence with true threshold electrons. TOF spectra near the ionization energy of the analyte (no dissociations yet) are used to identify the experimental time of flight for the parent ion. From here, all of the TOF spectra can be converted from time to m/z scale, yielding the mass spectra to identify the mass of fragment ions. Our experiments only generate singly charged ions and, therefore, the m/z value is the actual mass of the ion. Every mass spectrum is analyzed to ensure all of the fragment ions are identified and all of the TOF peaks are integrated to yield the total counts for each ion within its time window. If the TOF peaks overlap, then either a fitting procedure of the center-of-mass of the peaks can be used to separate them but, for most experiments, including the ones described in this dissertation, there is baseline separation of the TOF peaks.

The threshold coincidence counts of each photoion are then divided by the sum of all counts to generate the fractional ion abundances used to plot the breakdown diagram. To account for isotopic contamination of the TOF peaks, if two masses are within 1 amu of each other, then a subtraction is performed in the following manner, where \( C_X \) is the counts at the ions m/z, \( C_{X+1} \) is the counts at the ions m/z + 1 amu and \( N_{\text{carbon}} \) is the number of carbon atoms in the X species:

\[
C_{\text{corrected}} = C_{X+1} - (1.1\% \times N_{\text{carbon}} \times C_X)
\]

2.3.4 Statistical modeling of PEPICO data. In this section, the modeling of the experimental PEPICO data will be described. In order to obtain highly accurate thermochemical or kinetics data, careful modeling is required in terms of the energy distribution and dissociation
rates. Therefore, specialized software was developed by Sztaray, Bodi, and Baer\textsuperscript{14} to model experimental PEPICO data, in order to extract accurate appearance energies and dissociation rates. The software has been tested on hundreds of systems and can handle parallel or consecutive dissociations with linear or reflectron TOF setups, apply various rate theories such as RRKM, variable transition state theory (VTST), and simplified statistical adiabatic channel model (SSACM), model mechanisms such as isomerization or tunneling. Here, I am only presenting a short description of the modeling process from input to output and how we use this data to optimize a few parameters, ultimately leading to accurate appearance energies and well-defined reaction rates.

The first task is calculating the necessary density and number of states functions that are used to generate the internal energy distribution of the molecular ion. This depends on the ionization energy, temperature of the experiment, energy resolution functions, vibrational frequencies and rotational constants of the neutral precursor. The adiabatic ionization energy (AIE) of the parent neutral can usually be found in literature and if a TPES is measured, will be compared to our experimentally determined AIE. In the worst case, a series of high-level quantum chemical calculations (W1U, CCSD, CBS-APNO, etc.) can be performed to provide a theoretical estimate for the AIE, as was done for the project described later in Section 3.3.4. The experiments presented here were carried out at room temperature, so modelling is typically done at 298 K. In some cases, the temperature may need to be adjusted to account for adiabatic cooling of the neutral precursor due to rapid expansion of the sample from the needle valve to high vacuum. The energy resolution is set from the experimental parameters, which include the photon energy resolution and the FWHM of the electron kinetic energy analyzer.
Geometry optimization and frequency calculations are performed to obtain an optimized structure and the harmonic vibrational frequencies and rotational constants of the neutral precursor. A classical density of states function $\rho(E)$ is used for the molecular rotations and the direct count method\textsuperscript{27} is used to convolute this with the vibrational density of states. Rotational density of states are typically treated as symmetric tops but an internal hindered rotor can be taken into account as a Pitzer-rotor,\textsuperscript{40} which is convoluted with the $\rho(E)$ of the external rotations prior to folding in the vibrational modes.

The energy distribution of the neutral molecule $P(E)$ at temperature $T$ is calculated using the Boltzmann's formula as:

\begin{equation}
P(E) = \frac{\rho(E)e^{-E/k_BT}}{\int_0^\infty \rho(E)e^{-E/k_BT} dE}
\end{equation}

If the internal energy distribution of the neutral is assumed to be transposed onto the ion manifold upon threshold ionization, the molecular ion’s internal energy can simply be given as:

\begin{equation}
E_{\text{int}}^{M+} = E_{\text{int}}^M + h\nu - IE_{\text{ad}}
\end{equation}

where the terms are the internal energy of the molecular ion, the internal energy of the neutral, the photon energy and the adiabatic ionization energy, respectively. The energetics and kinetics of the dissociative threshold photoionization process is illustrated in Figure 9.
Figure 9: Illustration of the dissociative threshold photoionization process, taken from ref 14. The bottom potential energy well is the ground state of the parent neutral and the top is the ground state of the parent ion. The energy is scanned in PEPICO experiments, denoted as $h\nu$, and the thermal distribution of the parent ion is also taken into account, shown as a Boltzmann’s distribution orthogonal to the potential energy wells.

For consecutive dissociations, the internal energy distribution of the fragment ions has to be modeled. If we consider an ion, ABC$^+$, with an internal energy $E$, which dissociates with the loss of C with an AB$^+ – C$ bond energy of $E_0 – IE$:

$$\text{(15) } \text{ABC}^+(E) \to \text{AB}^+(E_i) + \text{C}(E_n)$$

The excess energy after the dissociation is $E – E_0$, which is partitioned between the ionic and neutral fragments as:

$$\text{(16) } E – E_0 = E_i + E_n + E_{\text{trans}}$$
where $E_i$ and $E_n$ are the internal energy of the ionic and neutral fragments, respectively and $E_{\text{trans}}$ is the translational energy released in the process. The product ions produced by consecutive dissociations come from a distribution of energies and each distribution is calculated for each $E$ in the energy distribution of the parent ion and then summed over the parent $P(E)$ distribution. The product energy distribution calculation yields the microcanonical energy distribution, $P(E_i, E-E_0)$, as:

$$
(17) \quad P(E_i, E-E_0) = \frac{\rho_{F+}(E_i) \int_{0}^{E-E_0-E_i} \rho_N(x) \rho_{\text{tr}}(E-E_0-E_i-x) dx}{\int_{0}^{E-E_0} \rho_{F+}(E-E_0-y) \rho_N(x) \rho_{\text{tr}}(E-E_0-y-x) dy}
$$

where $\rho_{F+}, \rho_N$ are the densities of states of the fragment ion and the neutral fragment, respectively and $\rho_{\text{tr}}$ is the translational density of states. The only inputs needed are the neutral’s and ion’s vibrational frequencies and the rotational degrees of freedom, which has no adjustable parameters. The rotational degrees of freedom are all that are needed for the rotational density of states and is chosen as follows: for a fragmentation process leading to nonlinear fragments, this is 3; for a linear fragment ion or neutral, it is 2, whereas for an atom-loss dissociation, it is 0. Similarly, the translational density of states is given as the degrees of freedom.

For slow or parallel dissociations, the dissociation rates have to be modeled. In evaluating $N^3(E-E_0)$, the conserved vibrational modes are separated from the translational modes, i.e. the modes which are converted from the vibrations into rotational and translational degrees of freedom along the reaction coordinate. There are five transitional modes for losing a nonlinear fragment, four transitional modes for a linear fragment and two transitional modes for an atom loss. The main difference between statistical rate theories is how they treat these transitional modes in calculating $N^3(E-E_0)$. For the systems in this dissertation, the rigid activated complex, RAC-RRKM, theory was utilized, which assumes fixed vibrational
frequencies in the transition state. One way to come up with initial estimates for the vibrational frequencies for loose transition states is to perform \textit{ab initio} calculations where the bond corresponding to the reaction coordinate is stretched to 4–5 Å.\textsuperscript{31} The translational modes are identified by the rapid change they undergo along the reaction coordinate. This provides a good starting point and then the transitional vibrational frequencies can be adjusted by a variable factor to fit the calculated peak shapes to the experimental TOF distributions (i.e., the experimental dissociation rates).

A breakdown curve is generated by the program as the fractional ion abundance of each ion as function of the photon energy. For a single, fast dissociation reaction, all ions that have excess energy above the reaction barrier will dissociate and form fragment ions, thus, the ratio of the parent ion (\textit{BD}) is given as:

\begin{equation}
BD(h\nu) = \int_{E_0}^{E_0-I_E} P_i(E, h\nu) \, dE
\end{equation}

where \( P_i \) is the normalized internal energy distribution of the parent ion as a function of the internal energy at a given photon energy. The width of the internal energy distribution of the ions is determined by the sample temperature and \( E_0 \) is independent of it. The fractional ion abundance is determined by the area of the (normalized) \( P(E) \) that is above the dissociation limit. This is shown in Figure 9. As the photon energy increases, more of the distribution shifts above the dissociation limit, therefore there is less parent ion abundance. Eventually, once the photon energy reaches \( E_0 \), the parent ion abundance will be zero (fully dissociated). In the case of a slow dissociating ion, one that has enough energy to dissociate but may not do so in the timescale of the experiment (kinetic shift, as briefly explained earlier), an additional term must
be added to the equation, which accounts for ions who have enough energy to dissociate but
dissociate too slowly to be detected as daughter ions:

\[
BD(h\nu) = \int_{0}^{E_{0}-IE} P_i(E,h\nu)dE + \int_{E_{0}-IE}^{+\infty} P_i(E,h\nu) \cdot \exp(-k(E) \cdot \tau_{max})dE
\]

where \(k(E)\) is the internal energy-dependent rate constant, and \(\tau_{max}\) is the maximum flight-time
within which an ion has to dissociate to be recorded as a fragment ion. The following integral is
a complement to this expression and is used to calculate the fragment ion abundance:

\[
BD_{\text{fragment}}(h\nu) = \int_{E_{0}-IE}^{+\infty} P_i(E, h\nu) \cdot (1 - \exp(-k(E) \cdot \tau_{max}))dE
\]

For parallel dissociations, the breakdown curve for a particular fragment ion can be calculated
as:

\[
BD_i(h\nu) = \int_{E_{0}-IE}^{+\infty} P_i(E, h\nu) \cdot \frac{k_i(E)}{\sum_j k_j(E)} \left( 1 - \exp\left(-\sum_j k_j(E) \tau_{max}\right) \right)dE
\]

where \(\frac{k_i(E)}{\sum_j k_j(E)}\) are the branching ratios at a particular ion internal energy.

The TOF distribution is also modeled because the fragment ion peaks contain the
unimolecular rate information. The fragment ion peak shape is computed as:

\[
Fr_i(h\nu) = \int_{E_{0}-IE}^{+\infty} P_i(E, h\nu) \cdot (\exp(-k(E) \cdot \tau(TOF_i)) - \exp(-k(E) \cdot \tau(TOF_{i+1})))dE
\]

where \(Fr_i(h\nu)\) is the normalized height of the fragment ion peak in channel \(i\), \(P_i(E, h\nu)\) is the
internal energy distribution of the parent ion and \(\tau(TOF_i)\) is the \(\tau\) value corresponding to the time
of flight of channel \(i\). The parent ion total abundance is calculated from eq. 21. The TOF
distribution that is calculated according to eq. 22 contains sharp peaks which are then convoluted
with a Gaussian function to account for real broadening in the experimental TOF data, i.e., thermal broadening or kinetic energy release (KER).

In modeling PEPICO data within the rac-RRKM framework, the 0 K appearance energy, $E_0$ describes the energetics and the transitional vibrational frequencies of the transition state are used to reproduce the $k(E)$ function. As mentioned earlier, the translational vibrational frequencies are uniformly scaled by a single factor to optimize fitting the modeled curve to the experimental breakdown curve data points. Therefore, there are only two parameters that are optimized for each dissociation, the $E_0$ and the scaling factor for the lower TS frequencies. A variety of other parameters can be optimized such as the TOF gaussian peak width and height, for temperature dependent experiments, the sampling temperature and the parameters for isomerization and tunneling parameters, to name a few.

The PEPICO modeling program uses the downhill simplex algorithm for optimizing these parameters. Typically, a least squares error function is used which is simply the sum of the square differences between the calculated and experimental data points. The error bars can be found by modifying parameters such as the $E_0$ and compare the modeled curve to the experimental points. As a rule of thumb, the $E_0$ is shifted between a range in which 90% of the experimental data points are accounted for in the modeled curves. This resulting range is used as the error bar for the appearance energy and is typically less than 10 meV for a good-quality set of experimental data; this corresponds to sub-kJ mol$^{-1}$ accuracy for heats of formation with accurate anchor values.
2.4 Quantum Chemical Calculations

Ab initio calculations play a vital role in helping to model and understand unimolecular dissociation reactions. The Gaussian 09 suite of programs was used to perform quantum chemical calculations. Neutral and ionic structures were optimized with harmonic frequencies using density functional theory (DFT) methods such as B3LYP or M062X as needed. Single point energy calculations, utilizing the G4 composite method, of the aforementioned structures are used to produce a potential energy diagram (PES). In cases involving very complex dissociation pathways, higher level calculations are performed using coupled cluster theory (CCSD(T)). Characterizing the PES is the first step in identifying possible dissociation products when compared with the experimentally observed appearance energies. A thermochemical limit is the minimum energy required for a product ion and its corresponding neutral fragment to form. The thermochemical limit of all possible product ions is used to rule out dissociation pathways that require more energy than observed in the experiment. A thermochemical limit will be the activation barrier for reactions that do not have any higher-lying saddle points before dissociation.

Relaxed potential energy scans of the bond breaking reaction coordinate are used to find transition state (TS) structures. A structure at the maximum of the potential energy surface scan is selected and optimized as a TS structure. Transition states can also be found by using the Synchronous Transit-Guided Quasi-Newton (STQN) method which searches for a saddle point along the potential energy surface between the reactant and product ions. There are two types of STQN calculations that can be performed in Gaussian-09, QST2 and QST3. For QST2 calculations, only the reactant and product ion structures are required, whereas for QST3 calculations, an initial guess of the TS structure is also required. In both cases, once a TS
structure is found, an intrinsic reaction coordinate (IRC) calculation is performed to confirm that the TS comes from and leads to the reactant and product ions, respectively. For systems with roaming transition states, Born-Oppenheimer Molecular Dynamic (BOMD) simulations were performed. BOMD simulations require input parameters that specify the velocity vector of each atom in a molecule which can be input individually or calculated based on quasi-classical fixed normal mode sampling. The input geometry is typically the TS and the calculation proceeds in time steps (≤1 fs) solving the electronic energy, gradient and Hessian at the end of each step to use as new inputs for the following step. Excess energy above the barrier can be specified to see how the dynamics change with more energy in the system. Finally, stopping criteria can be specified for any channels ending the calculations when criteria has been met. The major drawback of these calculations is their high computational cost. Each trajectory requires the PES to be calculated at every step and convergence of the energy. Typically, the simulations must be run for 200 or more steps equating to the same time to perform 200 geometry optimizations. In addition, at least hundreds of trajectories must be calculated to give a statistically significant result. Separate trajectories are input based on random number generation, which changes the distribution of energies very slightly along the various coordinates.

Specifics of the calculations (such as functionals and basis sets used) is described in detail for each project in the proceeding chapter
Chapter 3: Methyl Hydroperoxide

3.1 Introduction

Methyl hydroperoxide (MHP), CH$_3$OOH, the simplest organic hydroperoxide, plays an important role in combustion$^{6,51}$ and atmospheric chemistry.$^{52}$ MHP is formed when OH radicals react with CH$_3$O (methoxy radical): Jasper et al.$^{51}$ have shown that MHP is the major product in the 1–10$^5$ Torr pressure range, up to ca. 1500 K. MHP is also formed when CH$_3$OO reacts with molecules and radicals with easily abstractable hydrogen atoms, such as HO$_2$, H$_2$O$_2$, or CH$_3$O. MHP, like other organic hydroperoxides, is relatively unstable and easily decomposes thermally or photolytically, yielding radical or molecular fragments.$^{51,53}$ The other main loss route for MHP in an oxidative environment is through bimolecular reactions, primarily with OH,$^{54}$ forming mostly CH$_3$OO. However, when MHP reacts with Cl atoms, it forms mostly CH$_2$OOH,$^{55}$ the smallest hydroperoxyalkyl radical, generally termed as QOOH. These short-lived carbon-centered radicals can also be formed from the corresponding alkylperoxy radicals (ROO) via internal hydrogen abstraction for C$_n \geq 2$, and play a central role in autooxidation processes.$^{6,56,57}$ Longer-chain QOOH radicals are important in propagation and branching steps of radical chain reactions and are central in low-temperature autoignition combustion chemistry.$^6$ They are also unstable and decompose rapidly to form cyclic ethers + OH or alkenes + HO$_2$, or react quickly with O$_2$ and contribute to radical chain branching. The most unstable QOOH radicals are the ones where both the radical site and the OOH group are on the same carbon atom. These radicals, e.g., CH$_2$OOH, fall apart to a carbonyl and OH. So far, only one QOOH radical has been detected directly, the resonance stabilized 2-hydroperoxy-4,6-cycloheptadienyl,$^{57}$ with the kinetics of another one characterized directly.$^{56}$ There is no experimental thermodynamic data available for any QOOH in the literature.
To establish reliable thermochemistry for its fragments, the ionization energy (IE) and the heat of formation ($\Delta H^\circ$) of MHP are crucial as thermochemical anchor values and future studies involving more complex organic hydroperoxides will also benefit from such anchors. Matthews derived the 0 K MHP $\Delta H^\circ$ as $-113 \pm 4$ kJ mol$^{-1}$ in the gas phase from the O–O bond dissociation energy and the heats of formation of the formed fragments. Based on Khursan and Martem’yanov’s work, Komissarov reported a heat of formation of $-131.0$ kJ mol$^{-1}$ at 298 K, which converts to $-118.2$ kJ mol$^{-1}$ at 0 K, while the Active Thermochemical Tables (ATcT, version 1.122) value is $-114.90 \pm 0.74$ kJ mol$^{-1}$ at 0 K.

Using a positive ion thermochemical cycle is often one of the most accurate ways to derive experimental thermochemical data on elusive gas-phase species. These cycles generally include the ionization energy of the stable parent molecule, which in case of MHP was measured as 9.87 eV by Yi-Min et al. using He-I photoelectron spectroscopy. The IE can also be calculated using the ATcT heat of formation of the MHP$^+$ cation, 832.3 ± 2.5 kJ mol$^{-1}$, to be 9.82 ± 0.03 eV. There have been studies published on the dissociation of protonated alkyl hydroperoxides, but there is a lack of data on the fragmentation dynamics of relatively low-energy molecules formed in single-photon excitation or ionization, the type of experiments most useful for deriving accurate thermochemical information. In particular, TPEPICO is extremely well suited to determine very accurate dissociative photoionization energies and to explore the dissociation mechanisms of internal energy-selected gas phase ions. The goals of this work are to derive thermochemical data on the smallest QOOH species, CH$_3$OOH, and to understand the CH$_3$OOH$^+$ ion decomposition dynamics by iPEPICO experiments and ab initio quantum chemical calculations.
3.2 Experimental

3.2.1 Methyl hydroperoxide synthesis. MHP was synthesized by a nucleophilic addition reaction between dimethyl sulfate (DMS) and hydrogen peroxide (H₂O₂, 30%), in the presence of potassium hydroxide (KOH):  

\[(CH₃)₂SO₄ + 2 H₂O₂ + 2 KOH \rightarrow 2 CH₃OOH + 2 H₂O + K₂SO₄\]

All reagents were purchased from Sigma–Aldrich and used without further purification. DMS (77 g) and H₂O₂ (115 mL) were mixed in a 250 mL round bottom flask. The flask was submerged in an ice bath (0 °C) to keep the reaction temperature below 20 °C, while an aqueous KOH solution (40% w/v) was added dropwise. The byproduct, dimethyl peroxide, escaped as a gas. After the reaction came to completion, sulfuric acid (H₂SO₄, 98%) was added at 0 °C to acidify the reaction mixture to pH = 6. The formed K₂SO₄ precipitate was removed by filtration. Then, the solution was extracted with anhydrous diethyl ether and dried over MgSO₄. The product was fractionally distilled at 50 °C under vacuum (80 Torr). The purity of MHP (≈98%) was confirmed by the photoionization mass spectra in the iPEPICO experiment.

3.2.2 Imaging PEPICO experiments. The experiments were carried out on the iPEPICO endstation of the X04DB bending magnet VUV beamline at the Swiss Light Source within the Paul Scherrer Institut in Switzerland. A detailed description of the spectrometer is given elsewhere. The liquid MHP sample was placed in a glass vial at room temperature and the sample vapor was introduced into the iPEPICO ionization region from the headspace through a 30 cm long Teflon tube. The pressure in the ionization chamber was kept between 1.1–3.6 × 10⁻⁶ mbar during the experiments. The MHP sample was ionized within a 2 mm × 2 mm cross section by the incident VUV synchrotron radiation between 11.3 and 14.0 eV, after the higher
harmonics were removed in a gas filter containing a mixture of Ne, Ar, and Kr. The photon energy was calibrated using the Ar and Ne 11s’–14s’ autoionization lines in grating 1st and 2nd order. The photon energy resolution was measured to be better than 3 meV. After the photoelectrons and photoions are extracted with a constant 80 V cm⁻¹ electric field, the photoelectrons are velocity map imaged onto a Roentdek delay line detector, with an electron kinetic energy resolution better than 1 meV at threshold. The photoions were mass analyzed by a two-stage Wiley–McLaren TOF mass spectrometer with a 5.5 cm long extraction, a 1 cm long acceleration, and a 55 cm long drift region and detected by a Jordan TOF C-726 microchannel plate detector.

### 3.2.3 Theoretical methods

To characterize the CH₃OOH⁺ potential energy surface, we optimized stationary point geometries and calculated frequencies using the M06-2X/MG3S level of theory with ‘Grid = 150974’ and ‘verytight’ optimization parameters in Gaussian09, and calculated single-point energies at the RCCSD(T)-F12b/cc-pVQZ-F12 level using the Molpro 2012 suite of programs. We will refer to these energies as F12//M06-2X. The T1 diagnostics for some key species were above 0.025, but the agreement with the experiment in general suggests that the calculated energies are nevertheless accurate, perhaps due to the large basis set. In a few cases, calculations with the MG3S basis set (which is equivalent to 311G(2p) on H atoms and 6-311+G(2df) on C and O atoms), in combination with the M06-2X functional did not converge to a saddle point, although one was found with the other methods. In these cases, the geometry optimization and frequency calculations were done using one or more of these levels: M06-2X/6-311++G(d,p), B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) in Gaussian, or CASPT2/aug-cc-pVnZ (n = D or T), as implemented in Molpro 2012.
The breakdown curves were modeled using the RRKM framework for the ionic dissociation reactions. For tight or fairly tight transition states, we applied RRKM theory within the rigid rotor and harmonic oscillator (RRHO) framework, which was refined with inclusion of torsional anharmonicity and tunneling in 1-D through Eckart barriers. For these calculations, we used the MESS code to evaluate the state counts. Some of the transition states are barrierless and for these cases, we applied variable-reaction-coordinate transition state theory (VRC-TST) to count states, as implemented in the VaReCoF code.

In order to fit the experimental data, we assumed that the thermal internal energy distribution of CH$_3$OOH is shifted into the ion manifold faithfully in threshold photoionization, and varied model parameters, such as appearance energies and the lowest frequency vibrational modes, as outlined in Section 3 of Results and discussion. The latter was done by the Beyer-Swinehart-Stein-Rabinovitch (BSSR) anharmonic density count method where the symmetric top rotational density of states were calculated classically, and the anharmonic state count for the hindered rotors (H–C–O–O and C–O–O–H) was obtained by solving the vibrational Schrödinger equation on a free rotor basis set.

Moreover, BOMD simulations were performed (as implemented in Gaussian 09) to qualitatively investigate the importance of non-RRKM behavior of the dissociation channels beyond a roaming saddle point. The input velocities were calculated based on quasi-classical fixed normal mode sampling and the input geometry was selected as the saddle point of the isomerization TS. The calculation proceeded in 1 fs time steps, up to 1000 fs at the MP2/6-31+G(d) level. Excess energy above the barrier was specified as 0.1 and 1.0 eV to investigate the changes in dynamics with respect to energy in the system. An 8 Å threshold distance was
used between fragments and atoms of the various dissociation paths as termination criterion for
the calculations.

3.3 Results and Discussion

3.3.1 Experimental breakdown curves. Threshold photoionization TOF mass spectra
of energy-selected MHP+ cations were measured in the 11.3–14.0 eV photon energy range. The
area of each photoion’s TOF peak was integrated and the fractional parent and fragment ion
abundances were plotted as a function of photon energy in the breakdown diagram shown in
Figure 10. Below 11.4 eV, the only detected species is the MHP+ parent ion at m/z 48. Starting
at 11.40 eV, the abundance of the parent ion begins to decrease as the hydrogen-loss m/z 47
fragment ion appears, and the parent ion signal completely vanishes by 11.65 eV. From 12 eV,
the m/z 29 ion starts to appear and its ratio slowly increases throughout the rest of the
investigated photon energy range. Since there is only one carbon atom in the parent molecule
and double ionization is not possible in this energy range, m/z 29 can only correspond to an
HCO+ or COH+ ion. The next ion, m/z 19 (H$_3$O+) begins to appear at 12.55 eV as a trace species
and its abundance quickly rises starting at 13.0 eV until it starts to decline at 13.5 eV. The last
fragment ion observed is at m/z 15 (CH$_3$+). The methyl ion appears at 13.0 eV and its very slow
rise clearly indicates a parallel channel from the MHP+ molecular ion, similarly to the
appearance of the m/z 29 channel.$^{39}$
Contrastingly, the quicker rise of the $m/z$ 19 channel hints at a different mechanism for this dissociation process and suggests that it may be a secondary ion formation channel from CH$_3$OOH$.^+$ However, as the abundance of its proposed parent ion ($m/z$ 47) is also changing, a simple visual inspection of the full breakdown curve is inadequate to state with certainty the origin of the $m/z$ 19 signal. Therefore, the pairwise fractional abundances (i.e. $\frac{I_{19}}{I_{19}+I_{47}}$) of the $m/z$ 19 vs. 47, and 29 vs. 47 ions are shown in Figure 11, which illustrates that the two pairs exhibit markedly different behavior. The rise of the $m/z$ 29 ion does not show a clear break, rather a slow rise from the background, typical of a parallel channel, while the $m/z$ 19 ion appears much more suddenly at 13 eV, indicating consecutive dissociation of the $m/z$ 47 ion.
Figure 11: Pairwise fractional ion abundances for the m/z 29 vs. 47 and m/z 19 vs. 47 ions. The gradual rise exhibited by the first pair suggests parallel formation of these species, while the m/z 19 ion is likely formed in a consecutive dissociation step from the m/z 47 ion – apart from a small fraction that very gradually increases to a few percent in the 12–13 eV energy range.

3.3.2 Characterization of the CH$_3$OOH$^+$ PES. The CH$_3$OOH$^+$ radical cation can undergo a surprising number of possible dissociation and isomerization reactions as summarized in the schematic potential energy surface in Figure 12. Figure 13 shows the corresponding calculated ion structures and their energies, relative to the MHP$^+$ molecular ion.
The AIE of CH$_3$OOH to the lowest CH$_3$OOH$^+$ conformer is 9.84 eV at the F12//M06-2X level (the T1 diagnostic is 0.031 for the cation, suggesting a perhaps slightly larger than usual uncertainty in its energy), which is within the confidence interval of the ATcT recommended value of 9.82 ± 0.03 eV, in good agreement with the 9.87 eV by Yi-Min et al. The other conformer of CH$_3$OOH$^+$ is 0.30 eV higher in energy and differs in the dihedral angle of the O–OH hindered rotor. As also suggested by the experiments, we found that CH$_3$OOH$^+$ can undergo the following simple bond scission reactions:
\[ \text{CH}_3\text{OOH}^+ \rightarrow \text{CH}_2\text{OOH}^+ + \text{H} \quad \text{(1a)} \]

\[ \rightarrow ^3\text{CH}_3^+ + \text{OH} \quad \text{(1b)} \]

\[ \rightarrow \text{CH}_3^+ + \text{HO}_2 \quad \text{(1c)} \]

\[ \rightarrow ^3\text{CH}_3\text{OO}^+ / \ ^1\text{CH}_3\text{OO}^+ + \text{H} \quad \text{(1d)} \]

In the following section, we discuss the key properties of each channel, while more details and figures are provided in Appendix B. The experimentally observed threshold for \( \text{CO}_2\text{H}_3^+ \) \((m/z \ 47, \text{channel 1a})\) is \( 11.647 \pm 0.005 \) eV, in very good agreement with the F12//M06-2X calculations for the \( \text{CH}_2\text{OOH}^+ \) fragment ion, 11.64 eV. The zero-point energy, ZPE, exclusive energy profiles for channel 1a (Figure B 1) show that this reaction has a slightly submerged barrier, which is the dynamical bottleneck for dissociation at energies above the asymptote. The ZPE-corrected RCCSD(T)-F12b/cc-PVQZ-F12//CASPT2(3e,3o)/aug-cc-pVTZ energy of the barrier is 0.04 eV higher than the thermochemical limit but dissociation can proceed through tunneling already at the thermochemical threshold.
Wells (covalent and weakly bound)

\[
\begin{align*}
\text{CH}_3\text{OOH}^+ & \quad \text{CH}_3\text{OOH}^+ \quad [\text{CH}_2\text{O}...\text{H}_2\text{O}]^+ \quad [\text{CH}_2\text{OH}...\text{OH}]^+ \quad [\text{HCO}...\text{H}_2\text{O}]^+ \\
0.00 \text{ eV} & \quad 0.30 \text{ eV} \quad -1.90 \text{ eV} \quad -1.26 \text{ eV} \quad -2.63 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
[\text{HCO}...\text{H}_2\text{O}]^+ & \quad \text{c-C(H}_2\text{)OO(OH)}^+ \\
\text{conformer} & \quad 2.87 \text{ eV} \\
-2.77 \text{ eV}
\end{align*}
\]

Saddle points

\[
\begin{align*}
\text{CH}_3\text{OOH}^+ \leftrightarrow [\text{CH}_2\text{O}...\text{H}_2\text{O}]^+ \quad \text{roaming (1e)} \\
2.34 \text{ eV} & \quad 2.10 \text{ eV} \quad 2.23 \text{ eV} \quad -2.01 \text{ eV} \quad -0.66 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH}^+ \leftrightarrow \text{HCO}^+ + \text{H}_2 \quad \text{CH}_2\text{OH}^+ \leftrightarrow \text{COH}^+ + \text{H}_2 \\
(6a) & \quad (6b) \quad (6c) \quad (7a) \quad (7b) \quad \text{c-C(H}_2\text{)OO(OH)}^+
\end{align*}
\]

\[
\begin{align*}
2.66 \text{ eV} & \quad 3.60 \text{ eV} \quad 1.80 \text{ eV} \quad 4.19 \text{ eV} \quad 3.38 \text{ eV}
\end{align*}
\]
When breaking the O–OH bond (channel 1b) at DFT levels, the calculated energy becomes oscillatory, likely due to wave function instabilities and high multireference character. CASPT2(3e,3o) calculations show that the product is $^3$CH$_3$O$^+$ (Figure B 2). The potential energy scan in A$^*$ symmetry shows a flat region between 2.5 and 4.0 Å, which corresponds to the OH group interacting with the methyl end of the $^3$CH$_3$O$^+$ fragment through dipole-dipole and dipole-ion forces, forming a [OCH$_3$...OH]$^+$ complex. Scanning the bond along a straight line (*i.e.*, keeping angles and dihedral in the C–O–O–H motif fixed) shows no such feature. The plateau observed in the relaxed scan is more than 0.5 eV below the asymptote, suggesting that roaming reactions can play an important role in this system. Searching for such processes, we have found a saddle point where the OH radical abstracts an H atom leading to another loosely attached complex [CH$_2$O...H$_2$O]$^+$, which is 1.90 eV more stable than CH$_3$OOH$^+$ itself.
\[ \text{CH}_3\text{OOH}^+ \rightarrow [\text{CH}_3\text{O}...\text{OH}]^{\ddagger} \rightarrow [\text{CH}_2\text{O}...\text{H}_2\text{O}]^+ \quad (1e) \]

We were able to locate this saddle point at the MP2/6-311++G(d,p) level of theory. The accurate barrier height is 2.34 eV above CH$_3$OOH$^+$, which means that it is 0.38 eV below the \textsuperscript{3}CH$_3$O$^+$ asymptote, making this a feasible roaming pathway and we will show that it is indeed responsible for the observed HCO$^+$ signal.

For the CH$_3^+$ + HO$_2$ channel (1c), we scanned the energy along the C–O bond and found no reverse barrier at the M06-2X/MG3S level of theory (Figure B3). Note that \( m/z \) 15 appears around 12.7 eV in the experiments, and the calculated threshold for 1c is 12.73 eV, suggesting that this is the most likely route to this fragment.

CH$_3$OOH$^+$ can also isomerize in two more ways via tight transition states. One of the H-atoms from the methyl group can transfer to the outer oxygen atom via a 2.10 eV barrier:

\[ \text{CH}_3\text{OOH}^+ \rightarrow [\text{CH}_2\text{O}...\text{H}_2\text{O}]^+ \quad (1f) \]

Note that the product of this reaction is the same as that of 1e, but the corresponding saddle point geometry (see Figure 13) and thus the low frequencies are very different for these two isomerization channels.

The other isomerization channel starting from CH$_3$OOH$^+$ involves a methyl H atom transferring to the inner O atom via a 2.23 eV barrier, resulting in another weakly bound complex:

\[ \text{CH}_3\text{OOH}^+ \rightarrow [\text{CH}_2\text{OH}...\text{OH}]^+ \quad (1g) \]

The two weakly bound complexes, [CH$_2$O...H$_2$O]$^+$ and [CH$_2$OH...OH]$^+$, can undergo further reactions. The energetically most favorable pathway for [CH$_2$O...H$_2$O]$^+$ is to transfer another H
atom to the H\textsubscript{2}O part, forming another weakly bound complex, [HCO…H\textsubscript{3}O]\textsuperscript{+}, in an essentially barrierless reaction:

\[ \text{[CH}_2\text{O…H}_2\text{O]}^+ \rightarrow \text{[HCO…H}_3\text{O]}^+ \] (2a)

We were able to locate a saddle point 0.01 eV above the energy of the [CH\textsubscript{2}O…H\textsubscript{2}O]\textsuperscript{+} complex using M06-2X/MG3S, and we also confirmed its connectivity with IRC calculations, but this miniscule barrier disappears at the coupled cluster level. We also found another [HCO…H\textsubscript{3}O]\textsuperscript{+} conformer lying at a somewhat lower energy, –2.86 eV relative to CH\textsubscript{3}OOH\textsuperscript{+}, but it is not directly available from [CH\textsubscript{2}O…H\textsubscript{2}O]\textsuperscript{+}.

The weak [HCO…H\textsubscript{3}O]\textsuperscript{+} complex can dissociate in a barrierless reaction to form HCO and a hydronium ion, with a –1.96 eV asymptote, representing the most exothermic reaction channel.

\[ \text{[HCO…H}_3\text{O]}^+ \rightarrow \text{HCO} + \text{H}_3\text{O}^+ \] (3)

Aside from isomerization reactions, the formaldehyde–water ionic complex can also dissociate directly:

\[ \text{[CH}_2\text{O…H}_2\text{O]}^+ \rightarrow \text{CH}_2\text{O}^+ + \text{H}_2\text{O} \] (2b)

\[ \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}^+ \] (2c)

with the charge located on the formaldehyde being the much more favorable channel (–1.33 eV versus +0.36 eV relative to CH\textsubscript{3}OOH\textsuperscript{+}). Once the two fragments depart, the formaldehyde ion can lose an H atom in a process that has a slight reverse barrier at M06-2X/MG3S, but the barrier disappears at the coupled cluster level:
Because the threshold energy to make $[\text{CH}_2\text{O}...\text{H}_2\text{O}]^+$ is at least 2.10 eV, channels 2–4 are all open once the corresponding saddle point is surmounted. $[\text{CH}_2\text{OH}...\text{OH}]^+$ can either lose a neutral OH in a barrierless reaction, or, can isomerize into $[\text{CH}_2\text{O}...\text{H}_2\text{O}]^+$:

$$[\text{CH}_2\text{OH}...\text{OH}]^+ \rightarrow \text{CH}_2\text{OH}^+ + \text{OH} \quad (5a)$$

$$\rightarrow [\text{CH}_2\text{O}...\text{H}_2\text{O}]^+ \quad (5b)$$

The latter saddle point is a roaming-like internal H abstraction between the two parts of this weakly bound complex, but unlike in the previous case (1e), this saddle point is above the corresponding asymptote. The resulting $\text{CH}_2\text{OH}^+$ cation can further dissociate:

$$\text{CH}_2\text{OH}^+ \rightarrow \text{HCO}^+ + \text{H}_2 \quad (6a)$$

$$\rightarrow \text{COH}^+ + \text{H}_2 \quad (6b)$$

$$\rightarrow \text{CH}_2\text{O}^+ + \text{H} \quad (6c)$$

The H atom loss (6c) shows no reverse barrier, while the other two channels have a high reverse barrier and all three have an activation energy higher than the controlling barrier at 2.23 eV, making these channels less, if at all, important for our investigations.

In search for a path to $m/\epsilon$ 19, we have also investigated the fragmentation of the dissociation products of $\text{CH}_3\text{OOH}^+$. Running our KinBot code$^{56,80}$ on $\text{CH}_2\text{OOH}^+$ found two reactions with tight transition states:

$$\text{CH}_2\text{OOH}^+ \rightarrow [\text{CHO}^+...\text{H}_2\text{O}] \quad (7a)$$
\[ \rightarrow c\text{-}C(H_2)\text{OO}(H)^+ \quad (7b) \]

Channel 7a could in principle produce H_3O^+, i.e., \( m/z \) 19 if the H_2O molecule abstracts a proton from CHO^+ before the fragments separate completely, however, the barrier for this reaction is above 4 eV relative to CH_3OOH^+, which is much higher than the experimental appearance energy of this fragment. The barrier for the cyclic compound (7b) is also slightly too high (3.38 eV above relative to CH_3OOH^+, and 13.23 eV relative to CH_3OOH) and we were not able to locate a forward pathway from this cyclic structure to H_3O^+. However, it is very likely that similar electronic structure problems plague the channels of the decomposition of this fragment as are observed when CH_3OOH^+ loses the OH moiety, indicated by large T1 diagnostics. Interestingly, we found that a singlet scan along the O–O bond of CH_3OOH^+ results in two fragments by simple bond fission, while assuming a triplet electronic structure yields a roaming-like pathway, where the OH abstracts one of the H atoms of the CH_2O^+ moiety:

\[
\text{CH}_3\text{OOH}^+ \rightarrow \text{CHO}^+ + \text{H}_2\text{O} \quad (7c)
\]

We used the geometries along the triplet path and calculated CASPT2(4e,4o)/aug-cc-pVTZ and CCSD(T)-F12b/cc-pVQZ-F12 energies, and found that both methods yield a barrier, which is an encouraging agreement with the experimentally observed \( \approx 13 \) eV rise of H_3O^+. (Note that the O–O distance at the saddle point for 7a is \( \approx 1.5 \) Å, while it is \( \approx 2.2 \) Å for 7c according to the CCSD(T)-F12b potential.) For these potential curves, see Figure B 4. We were not able to optimize to a saddle point in this roaming region with any of the methods, because of convergence problems (similarly to the observations of ref. 81) and, therefore, the computational evidence that the second H abstraction indeed happens after the first one is only circumstantial.
The other primary fragments have no obvious dissociation pathways that yield exothermic products. We also considered other possible products, such as \( \text{CO}^+ + \text{H}_2 + \text{H}_2\text{O} \), which are also high in energy as shown in Figure 12.

In summary, the most likely ions to be observed based on the calculated PES are \( \text{CH}_3\text{OOH}^+ (9.84 \text{ eV, } m/z 48) \), \( \text{CH}_2\text{OOH}^+ (11.64 \text{ eV, } m/z 47) \), \( \text{H}_3\text{O}^+ (11.94 \text{ eV and } -13 \text{ eV, } m/z 19) \), \( \text{CH}_2\text{O}^+ (11.94 \text{ eV, } m/z 30) \), \( \text{HCO}^+ (11.94 \text{ eV, } m/z 29) \), \( \text{CH}_2\text{OH}^+ (12.08 \text{ eV, } m/z 31) \), \( ^3\text{CH}_3\text{O}^+ (12.57 \text{ eV, } m/z 31) \), and \( \text{CH}_3^+ (12.73 \text{ eV, } m/z 15) \), where the stated energies are the calculated dissociative photoionization thresholds relative to neutral \( \text{CH}_3\text{OOH} \).

3.3.3 RRKM modeling of the breakdown curves. Based on the PES (Figure 12), the fractional ion abundances were calculated as shown in Figure 10 within the RRKM framework for the 1a, 1b, 1c, 1e, 1f, and 1g reactions and including the 300 K thermal distribution of the neutral \( \text{CH}_3\text{OOH} \). In the case of a fast dissociation, ion abundances for the first daughter ion formation (in this case, 1a) simply reflect the room-temperature internal energy distribution of the neutral precursor, transposed to the ionic manifold by the ionizing photon. Ion abundances for parallel dissociation processes, which dominate the breakdown diagram above 12 eV, are determined by the fragmentation rate constant ratios, \( i.e. \), the relative transition state numbers of states as a function of internal energy.

To calculate the transition state number-of-state functions, we used VRC-TST for channels 1a, 1b, and 1c. Furthermore, we also took into account both the outer (long-range) and inner (saddle point) regimes in a two-transition-state model for 1a. More details can be found in Appendix A. A small number of parameters were varied in the RRKM fit to reproduce the experimental breakdown diagram: the lowest frequency of the roaming saddle point was changed.
from 50.4 to 12 cm\(^{-1}\) (corresponding to a loose OH rotor motion), the roaming barrier was decreased by 0.04 eV (4.2 kJ mol\(^{-1}\)), and the state count for the barrierless CH\(_3\) channel was decreased by a factor of 2.3. As the state count was obtained by sampling the PES, this decrease is only akin to increasing a low-frequency mode by a factor of 2.3 for a tight transition state, but was brought about directly by scaling the state count and not indirectly by scaling a transitional frequency. As for the 0 K appearance energy of this channel, we have used the calculated thermochemical limit (12.73 eV, see Figure 12). While the experimental breakdown curve hints at a possible earlier onset for methyl cation formation, the very low ion abundances do not allow for a more reliable experimental estimate. Furthermore, the RCCSD(T)-F12b/cc-PVQZ-F12//M06-2X/MG3S calculated \(E_0\) of 12.73 eV is in very good agreement with the ATcT (CH\(_3^+\) + HO\(_2\) – CH\(_3\)OOH) enthalpy difference of 12.741 ± 0.008 eV. Furthermore, the best fit to the slow decay of m/z 47 and the slow rise of m/z 29 above in the experimental breakdown curves was provided by decreasing the barrier for the tight transition state of channel 1f by 0.17 eV (16.7 kJ mol\(^{-1}\)). In the model, we assigned 30% of channel 1f to the formation of H\(_3\)O\(^+\), supported by our trajectory calculations, as discussed below (see also Table 1).

For the first (1a) dissociation channel, the optimized 0 K appearance energy that provides the best fit to the experimental data was 11.647 ± 0.005 eV, which is only 0.007 eV higher than the calculated value at the aforementioned coupled-cluster level. Furthermore, in order to properly fit the shape of the breakdown curve just before the \(E_0\), the \(k(E)\) values of this channel were tripled, compared to the calculated function. Note that if \(k(E)\) is very large, it corresponds to a prompt dissociation mechanism, while small \(k(E)\) values mean that some of the ions with energy larger than the dissociation threshold do not dissociate during the time it takes for them to reach the detector from the ionization region, blue shifting and broadening slightly the ideal
curve corresponding to infinitely fast dissociation. We included this experimental effect explicitly for channel $1a$ with 2.4 $\mu$s characteristic flight time.

Figure 14: Breakdown diagram of the first dissociation process. Open circles are the experimental fractional ion abundances, solid lines show the results of the RRKM modeling, while the shaded area represents the uncertainties in the 0 K appearance energy.

These RRKM simulations showed that the parent ion is very slightly metastable and taking this into account gives a calculated breakdown curve that is a better fit to the experimental data. However, this “kinetic shift” is miniscule and its only experimental manifestation is a small change in the curvature of the breakdown curve just before the disappearance energy of the $\text{CH}_3\text{OOH}^+$ parent ion signal. The best-fit model gives an $E_0$ of 11.647 ± 0.005 eV and Figure 14 shows the low-energy region of the breakdown curve, with the shaded area representing the confidence interval in the 0 K appearance energy.
The most exothermic product channel, \( \text{HCO} + \text{H}_2\text{O}^+ \), is only minor in the experiments, and the model predicts the ion abundances very well if we assume that \( \text{HCO}^+ \) is the main ion product after the roaming saddle point. To investigate the nature of the main channel after the roaming saddle point (lower red dot in Figure 12), we ran 100 BOMD trajectory calculations starting at 0.1 and 1 eV above the roaming saddle point. Within the 1000 fs window, only about a third of the trajectories converged, some terminated earlier due to errors, while no reaction happened for others and the ionic complex persisted. As seen in Table 1, approximately 85% of the productive trajectories ended up in \( \text{H}_2\text{O} \) and \( \text{CH}_2\text{O}^+ \) in both cases, or, less frequently, in \( \text{H}_2\text{O} + \text{H} + \text{HCO}^+ \). In ca. 15% of the cases, the product was \( \text{H}_3\text{O}^+ \) mostly with \( \text{HCO} \) or, in a few cases, \( \text{H} + \text{CO} \) as neutral fragments. In general, we observed that the fragments stayed together for a relatively long time even in the reactive cases and \( \text{H} \) atoms transferred back and forth many times before the fragments departed. Although the branching fractions in the BOMD calculations are not quantitative, they nevertheless show that the formation of \( \text{CH}_2\text{O}^+ \) is dominant over \( \text{H}_3\text{O}^+ \). This former ion, however, does not show up in the experimental data, which is explained well by the calculated lifetime of the \( \text{CH}_2\text{O}^+ \) ion after the water molecule leaves. Even if almost all of the excess energy is deposited into the \( \text{H}_2\text{O} \) neutral co-fragment, the \( \text{CH}_2\text{O}^+ \) ion dissociates in less than a microsecond (\( i.e. , \), \( k(E) > 10^6 \text{ s} \)). At higher energies, the lifetime of \( \text{CH}_2\text{O}^+ \) is orders of magnitudes smaller, which means that \( \text{CH}_2\text{O}^+ \) will readily and completely decompose under the experimental conditions into \( \text{HCO}^+ + \text{H} \). Our model also shows that the yields of \( \text{HCO}^+ \) via the tight transition states (1f and 1g) are minute. This means that the major source of the \( [\text{H}_2\text{CO}...\text{H}_2\text{O}]^+ \) complex is the roaming rearrangement channel. Further evidence for this proposed mechanism is the excellent agreement between the
The low yield of H$_3$O$^+$ in these trajectories can explain the slow rise of trace amounts of the 19 ion but it cannot be responsible for the sharper rise observed at 13 eV. Notably, at this photon energy, the calculated yield of CH$_2$OOH$^+$ starts to deviate from the experimental breakdown curve, the difference gradually reaching 15% at 14 eV. However, if a consecutive dissociation of this H-loss daughter ion is included in the model (7c), calculated from microcanonical product energy distribution functions, as described elsewhere in detail, the experimental and modeled $m/z$ 47 ion abundance shows almost perfect agreement. The calculated abundance of the H$_3$O$^+$ ion, shown with a solid tan line in Figure 10, also agrees reasonably well with the experimental data. Its deviation below 13.2 eV confirms that a minor fraction of this ion is formed in a parallel dissociation of the parent ion, in agreement with the low (but non-zero) H$_3$O$^+$ yield in the BOMD simulations.
Table 1: Number of reactive trajectories for the BOMD simulations categorized into various product channels.

<table>
<thead>
<tr>
<th>channel</th>
<th>0.1 eV excess energy</th>
<th>1.0 eV excess energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂CO⁺ + H₂O</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>H + HCO⁺ + H₂O</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>HCO + H₃O⁺</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>H + CO + H₃O⁺</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>HCO⁺ + H₂ + OH</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>total</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>HCO⁺ᵃ</td>
<td>28 (88%)</td>
<td>28 (85%)</td>
</tr>
<tr>
<td>H₃O⁺ᵇ</td>
<td>4 (12%)</td>
<td>5 (15%)</td>
</tr>
</tbody>
</table>

ᵃ All channels (eventually) forming HCO⁺
ᵇ All channels forming H₃O⁺

3.3.4 Thermochemistry. As expected, the most accurate fit of the experimental data was achieved for the primary channel of interest, CH₃OOH → CH₂OOH⁺ + H. The heat of formation for the QOOH⁺ ion can, therefore, be calculated from the fitted appearance energy of the QOOH⁺ ion and the heat of formation of MHP:

\[
\Delta H_{f,0,K} [\text{CH}_2\text{OOH}^+] = \Delta H_{f,0,K} [\text{CH}_3\text{OOH}] - \Delta H_{f,0,K} [\text{H}] + E_0
\]
As shown in Figure 14: Breakdown diagram of the first dissociation process. Open circles are the experimental fractional ion abundances, solid lines show the results of the RRKM modeling, while the shaded area represents the uncertainties in the 0 K appearance energy, the \( E_0 \) obtained by fitting the RRKM model to the experimental breakdown curve is 11.647 ± 0.005 eV (1123.8 ± 0.5 kJ mol\(^{-1}\)). Using 216.034 ± 0.000 kJ mol\(^{-1}\) for \( \Delta f H_{0\ K}^0 \) [H] and −114.90 ± 0.74 kJ mol\(^{-1}\) for \( \Delta f H_{0\ K}^0 \) [CH\(_3\)OOH] from the Active Thermochemical Tables gives a gas-phase 0 K heat of formation of 792.8 ± 0.9 kJ mol\(^{-1}\) for the CH\(_2\)OOH\(^+\) ion. In order to calculate a mixed experimental-theoretical value for the CH\(_2\)OOH radical’s heat of formation, we have obtained its ionization energy to be 718.59 kJ mol\(^{-1}\) at the F12//M06-2X level. Using this calculated value with a reasonable error estimate of ± 2.4 kJ mol\(^{-1}\) (25 meV), the 0 K heat of formation for the CH\(_2\)OOH radical was found to be 74.2 ± 2.6 kJ mol\(^{-1}\). For comparison, using the ATcT value of the MHP heat of formation, but the calculated ZPE-corrected energies of MHP, CH\(_2\)OOH, and H at the F12//M06-2X level, the 0 K heat of formation of CH\(_2\)OOH is 73.6 kJ mol\(^{-1}\).

The proton affinity of one of the Holy Grails of atmospheric chemistry, the CH\(_2\)OO Criegee intermediate,\(^{83,84}\) can also be directly obtained using our heat of formation of CH\(_2\)OOH\(^+\) combined with the ATcT recommended \( \Delta f H_{0\ K}^0 \) [CH\(_2\)OO] of 112.43 ± 0.61 kJ mol\(^{-1}\) and \( \Delta f H_{0\ K}^0 \) [H\(^+\)] of 1528.084 ± 0.000 kJ mol\(^{-1}\). The CH\(_2\)OO proton affinity of 847.7 ± 1.1 kJ mol\(^{-1}\) is in agreement with the 850.6 ± 4.2 kJ mol\(^{-1}\) (203.3 ± 1.0 kcal mol\(^{-1}\)) from CCSD(T)/CBS calculations by Nguyen et al.\(^{85}\) and reduces its uncertainty by a factor of 4.
Chapter 4: 2-Propanol

4.1 Introduction

2-Propanol, also commonly known as isopropyl alcohol, rubbing alcohol, or simply IPA, is one of the most common household and industrial chemicals; it has uses as a solvent, antiseptic, fuel additive and chemical intermediate. Because of its widespread use in industry and, in particular, as a fuel additive, the energetics of its dissociation products is of potential interest. Alcohols and other small oxygenated organic molecules are crucial components of many fuel blends and their fragments can substantially contribute to radical chain propagation in low-temperature autooxidation.

Furthermore, from a mass-spectrometry perspective, the two methyl groups on the molecular ion are good candidates to study alkyl vs. alkane elimination dissociation kinetics and energetics. The elimination of alkanes or alkyl radicals can be a complex and dynamic process during ionic dissociation reactions. Alkyl eliminations usually involve simple bond cleavage while alkane elimination typically involves a two-step process of alkyl radical roaming to form a neutral-ion complex, followed by hydrogen transfer to the alkyl radical to form a closed-shell alkane neutral. Most often, the alkyl elimination also occurs at the same bond cleavage site as alkane elimination and whether an ion loses a closed-shell alkane or open-shell alkyl radical depends both on the dissociation kinetics.
as well as the energetic stability of the product ions and one pathway may only be preferred in a narrow range of internal energy. 89,90 2-Propanol is a good candidate to study alkyl versus alkane eliminations, as it contains two, identical methyl groups and abstractable hydrogen atoms at three different sites: O–H, alpha and beta C–H, as shown later in Table 2.

In the literature, each of the three sites has been proposed for the methane-dissociation mechanism. 89,91,92 Trager et al. collected the first differential photoionization efficiency curves (FDPI) for 2-propanol and found that only alkane elimination is detected in the first 100 meV after the ionization threshold at around 10 eV. 89 However, alkyl elimination quickly takes over with as little as 100 meV higher ion internal energy. Therefore, to study these dissociation processes, high-resolution and accurate internal energy selection of the ion is a necessity.

Studying low energy dissociation processes is difficult with electron ionization or even collision-induced dissociation. VUV photoionization is well suited for such studies, because the internal energy can be fine-tuned and very accurately known, to a few meV. 8 When photoionization is coupled with PEPICO detection, unimolecular dissociation processes can be studied with very high energy accuracy and ion dissociation kinetics studies are also possible. 93 As, according to the literature, 2-propanol has two competing unimolecular dissociation channels within only a fraction of an eV after its ionization threshold, the iPEPICO apparatus at the VUV beamline of the Swiss Light Source synchrotron in Villigen, Switzerland is ideally suited to study this system.

4.2 Experimental

4.2.1 Imaging PEPICO experiments. Anhydrous 2-propanol (99.5%) was purchased from Sigma-Aldrich. The 2-propanol liquid sample was placed in a glass vial at room
temperature and the vapor in the headspace was led to the iPEPICO ionization region through a simple effusive inlet system. The pressure in the ionization chamber was kept between $3.2 - 3.4 \times 10^{-6}$ mbar during measurements and the sample was ionized within a $2 \times 2 \text{ mm}^2$ wide region by the incident VUV synchrotron radiation between approximately 10 and 13 eV. Higher harmonics of the bending magnet radiation were removed in a gas filter containing a mixture of Ne, Ar, and Kr. The photon energy was calibrated using the Ar 11s′−14s′ autoionization lines in both 1st and 2nd order and the photon energy resolution was measured to be better than 3 meV. After photoelectrons and photoions were extracted in a constant 80 V cm$^{-1}$ electric field, the electrons were velocity map imaged onto a Roentdek delay-line detector, with an electron kinetic energy resolution better than 1 meV at threshold. The photoions were mass analyzed by a two-stage Wiley–McLaren TOF mass spectrometer, as described previously.$^{13}$

4.2.2 Theoretical methods. The Gaussian 09 suite of programs were used to calculate, at the M06-2X/6-311++G(d,p) level of theory, the single point energies and harmonic vibrational frequencies at the optimized geometries of the neutral molecule, the parent ion, the various fragment ions and their corresponding neutral fragments involved in the unimolecular dissociation of 2-propanol.$^{41,43}$ The G4 composite method was then used to calculate accurate energetics of the aforementioned optimized structures.$^{44}$ Higher level W1U and CBS-APNO methods were also employed to calculate an averaged ionization energy for the 2-propanol neutral.$^{45,94}$ Transition states were located by relaxed potential energy scans along the bond length attributable to the reaction coordinates of interest. The saddle point structures thus identified were used as an initial guess in transition state optimizations. At low internal energies ($< 0.5$ eV), the CH$_3$ fragment was found to roam around the neutral–ion complex when gradually stretching the C–C bond. As a well-defined TS could not be found by this potential energy scan
alone, BOMD simulations were employed to simulate this, presumably roaming, channel.\textsuperscript{79} The BOMD simulations were used as a qualitative tool to help visualize the movement of the CH$_3$ fragment after the C–C bond was broken to simulate the roaming of the CH$_3$ fragment. In addition, the stopping criteria for the simulation was set to when a CH$_4$ fragment is 5 Å away from the ion. This allowed for the identification of which hydrogen atom was abstracted from the ion during the roaming transition.

The BOMD simulations outlined above helped identify that the most likely pathway for the internal H abstraction is from the other methyl group and a geometry was chosen from the simulations to be used as an initial guess for the TS leading to methane elimination. Harmonic vibrational frequency calculations confirmed a single negative frequency along a hydrogen translational mode. Ultimately, the potential energy surface, as shown in Figure 15 below, was constructed using optimized structures and single point energies for the parent ion, fragment ions plus neutrals using the G4 method.\textsuperscript{44}

\textbf{4.3 Results and Discussion}

\textbf{4.3.1 Experimental breakdown curves.} TOF mass spectra of energy-selected 2-propanol cations were measured in the 10–13.1 eV photon energy range. To generate the breakdown diagram, the area of each peak of interest was integrated in the hot electron-subtracted coincidence time-of-flight spectra and then divided by the total intensity of all peaks; plotted as a function of photon energy as shown in Figure 15.
Figure 15: Experimental breakdown diagram for 2-propanol between 10.0–13.1 eV. Open circles represent experimental data points and the solid line is the modelled fit.
Figure 16: Zoomed-in region of the breakdown diagram between 10.15–10.60 eV.

The abundance of the parent ions at m/z 60 starts out at more than 80% but never amounts to a full 100%. The reason for this can be found in the shallow potential energy well for the 2-propanol molecular ion, into which the whole internal energy distribution of the neutral cannot fully transpose. This effect was even more pronounced for bromofluoromethanes, where this phenomenon was, in fact, utilized to determine a reliable adiabatic ionization energy. Here, almost as soon as 2-propanol is ionized, it begins to fragment into ions m/z 45 and 44 and is completely dissociated by ≈10.3 eV. These fragment ions correspond to a loss of a methyl radical or methane molecule, respectively. As our calculations confirm (vide supra), the loss of a methane is the lowest activation energy dissociation pathway, and it is indeed the first major
channel to appear in the experimental data, peaking at 10.3 eV with more than 60% fractional abundance. Soon after the onset of $m/z$ 44, the $m/z$ 45 ion also appears, and it quickly dominates as the major dissociation channel already by 10.4 eV, which is consistent with the FDPI curve published by Traeger et al. This competition between the methane- and methyl-loss represents a classic case of kinetic control, where methane is a more stable product and its dissociation is the lowest-energy pathway, however, as the leaving methyl group must pick up a hydrogen along the way to form methane, its transition state is tighter than for the simple methyl radical loss. Therefore, while at low energies the $m/z$ 44 fragment ion dominates, its formation is quickly outcompeted by the energetically less favored but entropically (kinetically) favored simple methyl-loss dissociation.

The next dissociation channel we observed in the experimental data was an H loss, beginning at about 10.5 eV, but never amounting to more than 5% fractional abundance. According to our calculations, the alpha-carbon is the most energetically favorable site to lose a hydrogen atom from, producing the stable $(\text{CH}_3)_2\text{C}=\text{OH}^+$ cation, i.e., protonated acetone. Ab initio calculations indicate that if the hydrogen loss came from a methyl group, a triplet intermediate would form at a higher energy, which could in turn rearrange into the same $(\text{CH}_3)_2\text{C}=\text{OH}^+$ ion; albeit this process would be energetically unfavorable compared to the alpha-carbon C–H bond scission. Ultimately, H loss is a minor dissociative photoionization channel, and its 0 K appearance energy could not be established with comparable uncertainty to even the most basic computations. Therefore, it is only plotted in the full breakdown diagram in Appendix C. The highest energy dissociative photoionization channel in the studies energy range is the loss of an OH radical, which appears at around 11.4 eV with a very shallow slope in
the breakdown curve, indicating a competitive shift, due to the methane, methyl, and (minor) H-loss dissociations, and, consequently, that its precursor is the parent ion.

4.3.2 Characterization of the \((CH_3)_2CHOH^+\) PES. The dissociative photoionization pathways of 2-propanol were characterized by quantum chemical calculations on all the plausible low-energy fragmentation pathways. A potential energy diagram containing the lowest energy pathways, calculated at the G4 level of theory, is shown in Figure 17.

![Figure 17: Dissociative photoionization pathways for 2-propanol between 10.0–13.1 eV. The inset shows selected structures along the roaming coordinate, and the reported zero-point corrected energies were calculated at the G4 level of theory relative to the neutral (left scale) and cationic 2-propanol (right scale, values in parentheses).](image)

Table 2: Possible dissociation pathways of the 2-propanol cation leading to the observed fragment ions.
<table>
<thead>
<tr>
<th>Fragment Ion</th>
<th>Reaction Pathway</th>
<th>G4 Calculated Thermochemical Limit (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z 59</td>
<td>(CH$_3$)$_2$CHOH$^+$→(CH$_3$)$_2$COH$^+$ + H → CH$_3$CHOHCH$_3$ + H → (CH$_3$)$_2$CHO$^+$ + H</td>
<td>10.239 10.907 11.114</td>
</tr>
<tr>
<td>m/z 45</td>
<td>(CH$_3$)$_2$CHOH$^+$→ CH$_3$CHOH$^+$ + CH$_3$</td>
<td>10.431</td>
</tr>
<tr>
<td>m/z 44</td>
<td>(CH$_3$)$_2$CHOH$^+$→ CH$_2$=CHOH$^+$ + CH$_4$ → CH$_3$CH=O$^+$ + CH$_4$ → CH$_3$C=OH$^+$ + CH$_4$</td>
<td>9.947 10.490 10.807</td>
</tr>
<tr>
<td>m/z 43</td>
<td>(CH$_3$)$_2$CHOH$^+$→ (CH$_3$)$_2$CH$^+$ + OH</td>
<td>11.532</td>
</tr>
</tbody>
</table>

**m/z 45.** The simple methyl-loss pathway appears to have no reverse barrier and no saddle point was located when performing a relaxed potential energy scan along the C–C stretching coordinate. However, with respect to the OH group’s internal rotation, the two methyl groups are not equivalent and the one in gauche position with the hydroxyl is the preferred one to leave. Indeed, a relaxed potential energy scan along the C–C stretching coordinate of the methyl in anti-configuration exhibits a small saddle point at 180 meV ion internal energy, corresponding to the rotation of the OH into an *anti*-configuration with the methyl group on the CH$_3$CHOH$^+$ fragment ion. The calculated thermochemical limit of the methyl loss (9a) is 10.431 eV at the G4 level, which is in excellent agreement with the experimentally determined $E_0$ at 10.44±0.01 eV.

**m/z 44.** According to the experimental data, the lowest energy channel is the loss of a methane molecule. As briefly discussed in the modeling section (*vide supra*) an internal rearrangement of the parent ion adds another hydrogen atom to the CH$_3$ leaving group before it breaks away. There are three possible hydrogen-abstraction sites: it can come from the hydroxyl...
group, the alpha, or the other beta carbon. In the absence of slow dissociation (resulting in kinetic shift), the disappearance energy of the parent ion (at 10.33 eV in these experiments) is a reasonable first estimate for the dissociation energy of the first fragmentation pathway. Therefore, it is quite clear that the hydroxyl (10b) and alpha carbon (10c) hydrogen-abstraction pathways are both much too high in energy, at 10.807 eV and 10.490 eV, respectively. Therefore, the abstracted hydrogen must come from the other beta carbon (10a) and the thermochemical limit leading to \( \text{CH}_2=\text{CHOH}^+ + \text{CH}_4 \) is 9.947 eV at the G4 level. This energy, however, clearly does not correspond to the activation energy of the methane-loss channel and further calculations at various \( +\text{CH}_3\text{CHOH–CH}_3 \) distances helped elucidate the mechanism of the internal hydrogen abstraction. At around ~3.25 Å distance between the departing methyl and the alpha carbon, there was a slight dip in the potential energy scan, corresponding to a rearrangement into a quasi-planar structure with the \( \text{CH}_3 \) sitting roughly equidistant from the alpha and beta carbons. Further stretching of the C–C bond simply leads to a barrier-less dissociation but scanning along a decreasing C–C distance leads to structure with a bridging hydrogen atom on the other methyl carbon. The optimized structure features this hydrogen migrated over to the roaming methyl group, forming a loosely-bound complex at 9.96 eV (G4 level) between the eventual \( \text{CH}_2\text{CHOH}^+ \) fragment ion and a methane molecule. A transition state search at the M06-2X/aug-cc-pVTZ level of theory, between this structure and the original molecular ion, located a saddle point with one negative vibrational frequency corresponding primarily to a hydrogen-stretching motion. As this structure was not found with the B3LYP functional, the energy of this saddle point was approximated by a single-point G4 calculation at the M06-2X minimum. The calculated energy of 10.41 eV is in reasonable agreement with the experimentally determined \( E_0 \) of 10.33±0.01 eV. Furthermore, the harmonic vibrational
frequencies from the optimized TS structure at the M06-2X/aug-cc-pVTZ level were used in the RRKM model, with a less than 10% change in the transitional frequencies upon optimization.

**m/z 59.** Since the hydrogen-loss channel was only a minor pathway in the PEPICO experiments, amounting to less than 5% abundance, this channel was excluded from the statistical model shown in Figure 15 and Figure 16, it’s shown only in Appendix C. However, quantum-chemical calculations were performed nevertheless to elucidate the mechanism of this dissociation pathway. While it’s not possible experimentally to determine a reliable 0 K appearance energy for this channel, it is already observable at 10.5 eV, ruling out an O–H bond cleavage (8c) or H loss from a CH₃ group (8b) with G4 thermochemical limits of 11.114 eV and 10.907 eV, respectively. The alpha hydrogen loss (8a), however, has a calculated thermochemical limit of 10.239 eV, lower than the experimental onset of ~10.5 eV. A relaxed potential energy scan revealed a saddle point along the hydrogen-loss reaction coordinate, at 10.44 eV (G4 level), which is entirely in line with the experimental data.

**m/z 43.** The highest-energy major fragmentation channel corresponds to a loss of the hydroxyl group and calculations at various DFT levels found a simple barrierless C–O bond scission. The calculated thermochemical limit of 11.532 eV at the G4 level, however, is much higher than the E₀ of 11.01 eV determined from the experimental data using the statistical model. This discrepancy will be discussed further in the context of the statistical model.

**4.3.3 RRKM modeling of the breakdown curves.** The AIE of 2-propanol is evaluated to be 10.17 eV in the NIST Webbook and all of the proposed IE’s from NIST are above 10.0 eV ⁹⁷ Considering how close the first dissociation onsets are to these literature IE values, quantum chemical calculations at various levels of theory were performed to obtain theoretical
estimates for the IE. Three different methods were used: G4 composite, CBS-APNO, and W1U which gave 10.069, 9.899, and 10.078, with an average IE value of 10.015 eV. As we have previously reported, if the first dissociation onset \( (E_0) \) is close to the IE and the potential energy well of the cation cannot support the internal energy distribution of the sample, the parent ion’s fractional abundance may never reach 100%, because the high-energy tail of the internal energy distribution always reaches into the dissociative continuum. Indeed, the significant noise below 10.0 eV seems to be in line with the theoretical IE of 10.015 eV.

Modeling of the experimental ion abundances was carried out within the RRKM framework as described previously. Vibrational frequencies and rotational constants were used to calculate the thermal energy distribution of the neutral precursor molecules, as well as densities and numbers of states in the rate equation and to obtain the internal energy distribution of intermediate fragments based on statistical distribution of product internal energies. In the model, an ionization energy of 10.015 eV and a sample temperature of 298 K was used to calculate the parent molecules thermal energy distribution. To fit the statistical model to the experimental breakdown curves, the appearance energies, \( E_0 \), of the three dissociation channels, as well as the transitional vibrational frequencies of the transition state models were optimized. The optimized RRKM model is shown in Figure 15. The parent ion signal vanishes by 10.32 eV, thus the potential energy well of the parent ion is only \( \approx 0.33 \) eV deep. The parent ion abundance is never clearly 100% due to the fact that the width of the neutral thermal energy distribution is broader than a third of an eV. This makes it impossible to model the experimental data near the ionization energy, therefore the model was not extended below 10.15 eV. The assumption that the internal energy distribution is faithfully transposed into the ion manifold rests on the observation that sequence transitions have the same threshold photoionization cross section as
the origin transition. Even when this assumption holds, hot band like transitions accompanied by rovibrational relaxation may distort the internal energy distribution of the parent ion if only they yield bound parent ions and the relaxationless transition leads to the dissociative continuum at a different cross section. Because the conformational flexibility of bromofluoromethanes is limited, this has not affected the breakdown diagram, and it could be used to determine not only dissociative photoionization thresholds but also an accurate ionization energy. The orientation of the hydroxyl group in isopropanol changes upon ionization, coupled to a significant increase in a C–CH$_3$ bond length. This geometry change results in an unstructured photoelectron spectrum and is also responsible for the distortion of the internal energy distribution of the parent ion at low photon energies, which is why we only model the fractional ion abundances above 10.15 eV photon energy.

The CH$_4$ loss was modelled by an isomerization of the parent ion into an ion-molecule complex through an internal H-abstraction by the leaving methyl group. Indeed, at the lowest internal energies, < 0.4 eV, the leaving CH$_3$ group does not have enough energy to dissociate but forms a loosely-bound complex with the CH$_2$=CHOH$^+$ moiety. According to calculations, vide infra, this complex is formed when the CH$_3$ group roams around and forms a hydrogen bridge with the other beta carbon. The bridging hydrogen can then commit to the departing methyl group, yielding the m/z 44 CH$_2$=CHOH$^+$ fragment ion. At higher than 0.4 eV of internal energy, the CH$_3$ group can dissociate directly through a loose transition state. The tightness of the TS for the hydrogen transfer leading to the CH$_2$CHOH$^+$CH$_4$ complex is the deciding factor in the competition between the two pathways and at even slightly higher energies, the fractional abundance of the CH$_4$-loss channel drops to zero. The optimized $E_0$ for the CH$_4$ loss must
correspond to the isomerization barrier and we obtained a value of 10.33±0.01 eV, while the $E_0$ for the methyl loss is 10.44±0.01 eV.

The highest-energy channel in the dissociative photoionization of 2-propanol is the loss of a hydroxyl radical, with an onset of 11.01±0.01 eV. The tightness of its transition state model that correctly described the slope of the breakdown curve from 11.5 eV was found to be between the methyl-loss and the $\text{H}_3\text{C} \cdots \text{H} \cdots \text{CH}_2\text{CHOH}^+$ roaming transition states. However, as mentioned earlier, the appearance energy value, which was determined within the statistical model is in clear disagreement with calculations. The large difference between the model $E_0$ and the calculations suggest that the rise of the OH-loss daughter ion at around 11.6 eV cannot simply be attributed to competitive shift with a much lower real appearance energy but more complex dissociative photoionization mechanism may be at play. While the statistical model successfully described most of the PEPICO results we have analyzed over the past two decades, there have been notable cases when it was inadequate. The most similar such example was the hydroxyl loss channel from energy-selected methanol ions, where an excited state proved to be responsible to the abrupt appearance and then disappearance of the corresponding daughter ion. Therefore, we have started to explore a similar phenomenon for this system, as well, and found that, indeed there are repulsive ionic states that become available in this energy range, which promote the OH-loss dissociation of the molecular ion. That is, shortly after this dissociation pathway becomes energetically feasible, even though its statistical branching ratio for dissociating on the ionic ground state would be very small, it becomes competitive with the methyl-loss channel at energies close to its thermochemical limit. This explanation is also supported by literature PES data: the He-I photoelectron spectrum from ref. 98, shown in Figure 18 a) places the second band, corresponding to the first excited ionic state at 11.2–12 eV, where
the OH-loss dissociation indeed happens. Preliminary calculations at the TD-DFT B3LYP/6-311++G(d,p) level also support these arguments as the potential energy curve corresponding to the $A^+$ state is repulsive. The apparent breakdown of the statistical model means, however, that no accurate experimental appearance energy can be determined for this channel and, based on a visual inspection, the best estimate for the OH loss $E_0$ is $11.5\pm0.1$ eV.

Figure 18: a) He-I photoelectron spectrum of 2-propanol from ref. 98; b) Potential energy curves of the lowest six ionic states, calculated at the TD-DFT B3LYP/6-311++G(d,p) level

4.3.4 Thermochemistry. One of the two primary fragmentation channels, (CH$_3$)$_2$CHOH $\rightarrow$ CH$_3$CH=OH$^+$ + CH$_3$, proceeds via an attractive potential energy curve, and its threshold, which can be determined from the breakdown diagram accurately, corresponds to the dissociative photoionization energy. Therefore, the $E_0$ is a prime candidate to base accurate thermochemistry on. The heat of formation for the CH$_3$CH=OH$^+$ ion can be obtained from its appearance energy, $E_0$, and the well-established heat of formation of 2-propanol:
\[
\Delta H^0_0 \text{ K}[\text{CH}_3\text{CH}=\text{OH}^+] = \Delta H^0_0 \text{ K}[(\text{CH}_3)_2\text{CHOH}] - \Delta H^0_0 \text{ K}[\text{CH}_3] + E_0
\]

The \(E_0\) obtained by fitting the RRKM model to the experimental breakdown curve is 10.44 ± 0.01 eV (1007.30 ± 0.96 kJ mol\(^{-1}\)). Using 149.788 ± 0.080 kJ mol\(^{-1}\) for \(\Delta H^0_0 \text{ K}[\text{CH}_3]\) and −248.77 ± 0.36 kJ mol\(^{-1}\) for \(\Delta H^0_0 \text{ K}[(\text{CH}_3)_2\text{CHOH}]\) from the Active Thermochemical Tables gives a gas-phase 0 K heat of formation of 608.7 ± 1.0 kJ mol\(^{-1}\) for the \(\text{CH}_3\text{CHOH}^+\) ion. This value is within error bars with the heat of formation of 609.6 kJ mol\(^{-1}\) we reported from PEPICO studies on ethanol isotopologues. One the one hand, that 0K heat of formation value is, in fact coming from high level quantum-chemical calculations and was employed to quantify the reverse barrier and the effect of tunneling.\(^{99}\) On the other hand, our new \(\text{CH}_3\text{CHOH}^+\) heat of formation agrees very well with the latest ATcT value 609.14 ± 0.39 kJ mol\(^{-1}.\)\(^{60}\)
Chapter 5: Conclusions

5.1 Methyl Hydroperoxide

The dissociative photoionization of methyl hydroperoxide has been studied by imaging PEPICO experiments and extensive quantum-chemical and statistical rate calculations. A remarkable agreement has been achieved between the measured and modeled breakdown diagrams by adjusting just a few model parameters. Experimentally, MHP has been found to dissociate primarily into CH$_2$OOH$^+$ (the simplest QOOH$^+$ ion), HCO$^+$, H$_3$O$^+$, and CH$_3^+$ ion within a photon energy range of 11.4–14.0 eV. According to theory, CH$_2$OOH$^+$ and CH$_3^+$ are both formed by a simple bond scission, with only a small reverse barrier for the former channel. Since the CH$_2$OOH$^+$ daughter ion represents the ionized form of the corresponding QOOH radical, its thermochemistry is of considerable interest. As expected, this ion is the first dissociation product, with no overlap with other fragments and modeling this dissociation channel gave its appearance energy with sub-kJmol$^{-1}$ accuracy. Using the appearance energy of the QOOH$^+$ ion and the calculated ionization energy of the QOOH radical, a mixed experimental-theoretical heat of formation of 74.2 ± 2.6 kJ mol$^{-1}$ was obtained for the CH$_2$OOH radical. As a corollary, a proton affinity of 847.7 ± 1.1 kJ mol$^{-1}$ was also obtained for the smallest Criegee intermediate, CH$_3$OO.
The HCO+ fragment ion, which dominates the high-energy portion of the breakdown curve, was found to be produced by a non-statistical process, through a roaming transition state. Due to the dynamic nature of the roaming rearrangement process leading to the [CH2O…H2O]+ complex and its fragmentation, H3O+ formation represents only a minor channel from the MHP molecular ion. Direct dynamics simulations have shown that the roaming transition state almost always leads to the entropically more favored loss of water, effectively shutting out H3O+ formation. Then, in a consecutive process, the HCO+ ion forms through a fast dissociation of an H atom from the energized H2CO+ species. At higher energies, however, H3O+ appears with a steep rise in the breakdown curve and its formation is confirmed to proceed from the CH2OOH+ fragment ion, though a likely OH-roaming transition state. Together with the aforementioned direct C–O fission of the molecular ion leading to the methyl cation, the theoretical dissociation pathways show excellent agreement with the experimental data and a full RRKM modeling based on the proposed mechanism needed only small tuning to match the experimental ion abundances. From this model, the HCO+ and H3O+ appearance energies were determined to be 12.15 ± 0.05 eV and 13.1 ± 0.1 eV, respectively, while the calculated $E_0$(CH3+) of 12.73 eV did not need to be adjusted to fit the model.

5.2 2-Propanol

The dissociative photoionization processes of 2-propanol have been studied with imaging PEPICO experiments and quantum-chemical and statistical rate calculations. Experimentally, 2-propanol has been found to dissociate primarily into CH2CHOH+, CH3CHOH+, CH3CHCH3+, and, as a minor product, into (CH3)2COH+ ions within a photon energy range of 10.0 – 13.1 eV. The lowest-energy dissociation channel, yielding CHOCH2+ + CH4, is quickly outcompeted by the higher-energy, yet kinetically favored channel leading to CHOCH3+ + CH3, observed in the
experimental breakdown curves and successfully modeled using an isomerization model. Both reactions are initiated by the CH₃ group stretching away from the fragment ion but, at low internal energies of <0.3 eV, the loss of CH₄ dominates by way of a roaming pathway, when the leaving CH₃ abstracts a hydrogen atom from the other methyl group. At higher internal energy, the direct loss of CH₃⁺ dominates as the transition state leading to this fragmentation is much looser and, thus, kinetically favored. This roaming process of the methyl group abstracting a hydrogen atom is dependent on the momentum the CH₃ group carries as it stretches away from the fragment ion. Below the direct methyl-loss barrier, the CH₃ group cannot escape and orbits around the fragment ion and its dissociation is assisted by an internal hydrogen abstraction to separate from the fragment ion as a methane molecule. The minor hydrogen-loss dissociation channel was excluded from the statistical modeling but calculations found a small reverse barrier that lies slightly above the dissociation energy for the CH₃ loss. The highest-energy dissociation observed in these experiments, leading to CH₃CHCH₃⁺ + OH is formed by a simple C–O bond scission, but this dissociation is apparently enhanced in the first excited ionic state and its rapid rise in the experimental breakdown curve is beyond the validity of statistical rate theory. On the other hand, the statistical model fitted to the experimental data yielded accurate appearance energy corresponding to the thermochemical limit for the CH₃-loss dissociation and the 0 K heats of formation of the CH₃CHOH⁺ ion was found to be in good agreement with ATcT values and our previous study on ethanol.
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APPENDIX A

Cartesian coordinates (Å) and harmonic vibration frequencies (cm$^{-1}$) of the structure shown in Figure 13 of the main text. All structures are determined at the M06-2X/MG3S level of theory, unless otherwise stated.

**CH$_3$OOH$^+$**

C -0.002984 -0.008435 -0.053609
O 0.102482 -0.084886 1.399874
O 1.324637 0.091764 1.786308
H 1.295204 0.007491 2.769286
H 0.526084 0.886500 -0.375866
H 0.456133 0.919204 -0.442254
H -1.072899 0.026770 -0.227988
29.1951 483.6923 606.2834
828.5928 1113.9179 1148.7260
1330.6078 1422.6025 1452.1987
1462.8266 1509.9920 3062.8506
3168.7436 3226.8508 3568.4040

**CH$_3$OOH$^+$ conformer**

C -0.021220 0.016013 -0.031707
O 0.039240 0.097273 1.806436
O 1.206669 -0.008319 1.959336
H 1.895243 -0.132156 1.260506
H 0.572434 0.841997 -0.427463
H 0.359029 -0.966259 -0.317797
H -1.078306 0.127516 -0.250273
67.1032 473.2391 517.1296
850.3549 1108.6628 1165.1656
1328.0551 1429.9802 1461.9889

**[CH$_2$O...H$_2$O]$^+$**

C 0.000737 0.003475 -0.000618
O 0.002829 -0.023512 1.202945
O 2.083125 -0.015558 1.656387
H 2.155370 0.747814 2.250859
H 0.937889 0.024461 -0.571840
H -0.979643 0.006213 -0.503446
H 2.168886 -0.803448 2.216055
212.1816 241.6769 320.5458
373.9409 516.6394 611.5874
1094.1646 1182.9454 397.3732
1604.2922 1722.0921 2972.7328
3102.3353 3731.8144 3840.9237

**[CH$_2$OH...OH]$^+$**

C 0.007896 0.000001 0.014667
O 0.016059 -0.000006 1.244733
H 0.939252 -0.000009 -0.554296
H -0.961698 0.000018 -0.479889
H 0.958546 -0.000022 1.707461
O 2.322841 -0.000044 2.238538
H 2.482606 -0.000050 3.204583
139.4143 159.8340 346.8488
3052.4757 3155.8766 3216.2940 3525.1232
355.9676 507.5663 1209.2487
1231.3247 1264.9931 1502.6054
1518.1836 1753.7538
3099.2929 3236.4984 3691.2243

[HCO...H3O]+
C -0.000177 0.000131 -0.001229
O 0.003238 -0.009860 1.158789
O 2.536676 -0.002435 -1.026853
H 1.536470 -0.004365 -0.643573
H -0.889578 0.013498 -0.670528
H 3.020865 -0.827865 -0.850081
H 3.055980 0.771917 -0.747950

[CH3OOH]+ ↔ [CH2O...H2O]+ roaming
(at the MP2/6-311++G** level)
C 0.166539 -0.040084 0.042389
O -0.018574 -0.194287 1.401820
O 1.323230 0.122315 0.923230
H 1.481165 1.060584 1.184399
H 0.255783 -0.947812 -0.543807
H -0.195536 0.881832 -0.400960
780.3845 902.3883 944.0649
1044.8779 1212.2655 1262.5185
1288.0224 1308.7057 1534.9622
3143.3694 3280.0374 3572.7141

[CH3OOH]+ ↔ [CH2O...H2O]+ (1f)
C -0.002083 0.004819 0.000141
O -0.011037 0.028127 1.270052
O 2.675412 -0.105988 -0.662771
H 3.346751 -0.063133 -1.368749
H 1.173824 -0.040037 -0.309579
H -0.445275 -0.932505 -0.406327
H -0.392926 0.949673 -0.440342
-433.8385 50.4221 134.1464
301.9980 434.0817 860.6389
892.3774 1022.0716 1115.1075
1283.2407 1417.1595 1629.1459
2845.9268 2934.7198 3754.1001

[CH3OOH]+ ↔ [CH2O...H2O]+ (1e)
C -0.000177 0.000131 -0.001229
O 0.003238 -0.009860 1.158789
O 2.536676 -0.002435 -1.026853
H 1.536470 -0.004365 -0.643573
H -0.889578 0.013498 -0.670528
H 3.020865 -0.827865 -0.850081
H 3.055980 0.771917 -0.747950

55.7697 128.3581 293.6109
390.2926 539.6511 661.8329
1005.8922 1088.4077 1611.6462
1625.5956 2005.9279 2110.2849
2857.5848 3703.5817 3787.2640

870.3845 902.3883 944.0649
1044.8779 1212.2655 1262.5185
1288.0224 1308.7057 1534.9622
3143.3694 3280.0374 3572.7141

H 3-0.003154 0.034484 -0.000849
O 0.002289 -0.034955 1.182400
O 1.922205 -0.002717 2.710006
H 1.088690 -0.016013 2.034918
H 2.050314 -0.826223 3.207394
H 1.948812 0.766421 3.301349
H -0.901826 0.015216 -0.645015
49.0567 141.3610 331.7394
425.6481 526.2876 543.0460
1108.9298 1175.4495 1615.0201
1697.8174 1884.8437 2154.9824
2951.5658 3742.8973 3821.6440

CH3OOH+ ↔ [CH2O...H2O]+ (1f)
C -0.010407 -0.120885 0.210843
O -0.256706 0.206209 1.509691
O 1.126042 0.268541 1.872237
H 1.283645 -0.432695 2.546185
H 1.254116 0.129802 0.536437
\[ \text{H} 0.276292 -1.136594 0.012487 \]
\[ \text{H} -0.810414 0.340055 -0.469574 \]
\[ -1.136594 0.012487 \]
\[ 0.810414 0.340055 -0.469574 \]
\[ -1721.7931 458.9070 578.7971 \]
\[ 697.2571 935.8030 987.7497 \]
\[ 1058.4422 1138.2958 1213.6007 \]
\[ 1347.9788 1466.3955 1682.1145 \]
\[ 2980.0700 3236.5863 3589.3142 \]
\[ \text{CH}_3\text{OOH}^+ \leftrightarrow [\text{CH}_2\text{OH}...\text{OH}]^+ (1g) \]
\[ \text{C} -0.075543 -0.116585 0.022172 \]
\[ \text{O} 0.127248 0.239005 1.395014 \]
\[ \text{O} 1.323585 -0.017556 1.854253 \]
\[ \text{H} 1.365428 0.003142 2.769833 \]
\[ \text{H} 0.357584 1.069812 0.581160 \]
\[ \text{H} -0.116585 0.022172 \]
\[ 0.127248 0.239005 1.395014 \]
\[ 1.323585 -0.017556 1.854253 \]
\[ 1.365428 0.003142 2.769833 \]
\[ 0.357584 1.069812 0.581160 \]
\[ \text{H} 0.000000 0.000000 -0.264169 \]
\[ \text{H} 2.109437 0.000000 -2.187152 \]
\[ \text{H} -0.863387 0.000000 1.514584 \]
\[ -1782.4760 108.1775 142.9442 \]
\[ 425.1447 580.1565 786.0880 \]
\[ 1137.6673 1189.4779 1404.3288 \]
\[ 1419.8240 1478.7951 1792.5007 \]
\[ 2932.3005 3068.5002 3771.1157 \]
\[ \text{CH}_2\text{OH}^+ \leftrightarrow [\text{HCO}...\text{H}_2\text{O}]^+ \]
\[ \text{C} 0.165423 0.000004 0.138861 \]
\[ \text{O} -0.234284 -0.000520 1.268948 \]
\[ \text{H} 1.402932 -0.000575 -0.042195 \]
\[ \text{H} -0.327953 0.000933 -0.844008 \]
\[ 1.137384 -0.001088 0.951851 \]
\[ -2240.4670 299.1773 1063.4181 \]
\[ 1201.0050 1515.5645 1889.4368 \]
\[ 2209.0450 2290.4366 3089.1214 \]
\[ \text{CH}_2\text{OH}^+ \leftrightarrow \text{COH}^+ + \text{H}_2 \]
\[ \text{C} -0.000019 -0.000001 0.000021 \]
\[ \text{O} 0.000046 0.000004 1.232220 \]
\[ \text{H} 1.377411 0.000003 -0.268122 \]
\[ \text{H} 0.657566 -0.000003 -0.970297 \]
\[ 0.812551 0.000010 1.783455 \]
\[ -1795.5659 846.5086 921.5417 \]
\[
\begin{align*}
\text{CH}_3\text{OOH}^+ &\leftrightarrow \text{CH}_2\text{OOH}^+ + \text{H} \\
&\text{(at the M06-2X/6-311++G** level)}
\end{align*}
\]

\[
\begin{array}{cccc}
\text{C} & 0.000000 & 0.000000 & 0.000000 \\
\text{O} & 0.000000 & 0.000000 & 1.406852 \\
\text{O} & 1.251533 & 0.000000 & 1.735559 \\
\text{H} & 1.176686 & 0.000000 & 2.696669 \\
\text{H} & 0.492935 & 0.896090 & -0.385925 \\
\text{H} & 0.856796 & -1.557541 & -0.670796 \\
\text{H} & -1.052839 & 0.000000 & -0.281713 \\
\text{H} & -578.5919 & 219.4090 & 305.4380 \\
\text{H} & 454.1357 & 512.3021 & 820.2564 \\
\text{H} & 920.3706 & 1190.8196 & 1243.0296 \\
\text{H} & 1407.4290 & 1489.0438 & 1629.1707 \\
\text{H} & 3145.7283 & 3305.3691 & 3724.9259 \\
\end{array}
\]

\[
\begin{align*}
\text{CH}_2\text{OOH}^+ &\leftrightarrow \text{CHO}^+ + \text{H}_2\text{O} \\
&\text{(CCSD(T)-F12 max energy structure)} \\
&\text{along the triplet O-O bond breaking path)}
\end{align*}
\]

\[
\begin{array}{cccc}
\text{C} & -0.422891 & 0.000001 & -1.222652 \\
\text{O} & 0.566567 & -0.000001 & -0.539712 \\
\text{O} & -0.182901 & -0.000001 & 1.524812 \\
\text{H} & 0.662122 & 0.000015 & 2.032151 \\
\text{H} & -1.429944 & 0.000002 & -0.781991 \\
\text{H} & -0.282921 & 0.000001 & -2.317412 \\
\text{n.a.} & & & \\
\end{array}
\]

\[
\begin{align*}
\text{CH}_2\text{OH}^+ \\
&\text{C} 0.000179 & 0.000152 & -0.000025 \\
\text{O} & -0.000072 & -0.000410 & 1.239165 \\
\text{H} & 0.929350 & -0.000146 & -0.569933 \\
\text{H} & -0.978346 & 0.000954 & -0.476040 \\
\text{H} & 0.874797 & -0.001134 & 1.680872 \\
\text{H} & 1025.5485 & 1113.4142 & 1266.7308 \\
\text{H} & 1381.1429 & 1496.1364 & 1714.3991 \\
\text{H} & 3113.2403 & 3253.2288 & 3646.7628 \\
\end{array}
\]

\[
\begin{align*}
\text{CH}_3\text{O}^+ \\
&\text{C} -0.012538 & -0.021716 & -0.008866 \\
\text{H} & -0.014232 & -0.024651 & 1.116205 \\
\end{align*}
\]
\[ \text{H} 1.047624 -0.024651 -0.385486 \quad \text{O} -0.622049 -1.077420 -0.439855 \quad \text{H} -0.545160 0.894944 -0.385486 \]

\[ 842.0529 \quad 842.0600 \quad 1141.1774 \quad 1141.1781 \quad 1238.0495 \quad 1248.2855 \]

\[ 2725.4872 \quad 2751.8354 \quad 2751.8367 \]

\[ \text{CH}_2\text{OOH}^+ \]

\[ \text{C} 0.001315 \quad 0.000008 \quad 0.000870 \quad \text{O} 0.003973 -0.000004 \quad 1.236591 \quad \text{O} 1.289485 \quad 0.000008 \quad 1.781805 \quad \text{H} 1.094101 \quad -0.000005 \quad 2.738657 \quad \text{H} 0.943493 \quad 0.000027 \quad -0.546940 \quad \text{H} -0.989994 \quad 0.000000 \quad -0.446856 \]

\[ 306.3033 \quad 519.4868 \quad 717.7419 \quad 939.9378 \quad 1199.7799 \quad 1248.4000 \quad 1428.7326 \quad 1499.1051 \quad 1721.8556 \quad 3112.2957 \quad 3260.5715 \quad 3713.2040 \]

\[ \text{CH}_3\text{OO}^+ \]

\[ \text{C} 0.051653 -0.026935 -0.100503 \quad \text{O} 0.305510 -0.331108 \quad 1.325267 \quad \text{O} 1.050709 \quad 0.369783 \quad 1.911146 \quad \text{H} 0.639237 \quad 0.846784 \quad -0.363666 \quad \text{H} 0.331773 \quad -0.959374 \quad -0.599508 \quad \text{H} -1.034494 \quad 0.100850 \quad -0.130057 \]

\[ 192.1249 \quad 549.2839 \quad 729.3612 \quad 1041.5559 \quad 1195.4668 \quad 1381.2969 \quad 1402.9831 \quad 1446.3467 \quad 1707.0523 \quad 3035.0938 \quad 3124.8044 \quad 3227.5765 \]

\[ \text{CH}_3\text{OO}^+ \]

\[ \text{C} 0.004669 -0.001274 -0.168740 \quad \text{O} 0.168704 \quad 0.002627 \quad 1.430620 \]

\[ \text{O} 1.253305 \quad 0.004047 \quad 1.932084 \quad \text{H} 0.496982 \quad 0.921460 \quad -0.459357 \quad \text{H} 0.497333 \quad -0.925215 \quad -0.454889 \quad \text{H} -1.076606 \quad -0.001645 \quad -0.237039 \]

\[ 96.0182 \quad 328.2417 \quad 518.0732 \quad 1062.9573 \quad 1096.7323 \quad 1396.5173 \quad 1435.1990 \quad 1450.8976 \quad 1645.9003 \quad 3098.5379 \quad 3249.5466 \quad 3265.2685 \]
CH$_3$OOH$^+$ → CH$_2$OOH$^+$ + H (1a)

Figure B 1: Energy profiles along the C–H bond in CH$_3$OOH$^+$ at various levels of theory. All curves are fully relaxed and ZPE exclusive, unless noted in the legend. The asymptote is the zero of energy.

This reaction is near barrierless at the M06-2X/MG3S and M06-2X/6-311++G(d,p) levels (there is a slight barrier at ~3.3 Å), while it is barrierless at the B3LYP/6-311++G(d,p) one. With MP2/6-311++G(d,p) we found a barrier at ~2.0 Å, where the barrier is correlated with the planar-to-tetrahedral geometry change along the C–H coordinate. Using CASPT2(3e,3o)/aug-cc-pVDZ
we also found this saddle point at ~2.1 Å (the active space consists of the σ and σ* orbitals of the breaking bond and the HOMO). Such variations in the location of this very low barrier are not unexpected and the trends are similar to the findings of Harding et al.\textsuperscript{100} for neutral species. Using the CASPT2(3e,3o)/aug-cc-pVTZ geometries and ZPE correction we calculated F12 energies for this small barrier and obtained −0.04 eV, and remarkably, the CASPT2(3e,3o)/aug-ccpVTZ value is also −0.04 eV. These values in case of taking the MP2 geometries are −0.03 and 0.13 eV, respectively. We expect no variational effects to play a role in this region based on the ZPE corrected potential energy curve for MP2, because the ZPE corrected maximum coincides with the electronic one along the path, and it is also above the asymptote. The long-range part of the potential for channel 1a is largely invariant to basis set, active space, and geometry relaxation at the CASPT2 level. Therefore, we sampled the potential at the CASPT2(1e,1o)/aug-cc-pVDZ level between ~3.5 and 15 Å C–H separation of the rigid fragments using overall ~4000 sample points that converged the results to within 5%. At longer distances we only placed the pivot points on the center of mass of the fragments, while at closer separations we calculated fluxes with the pivot point being on the radical carbon atom. In the state counts we also accounted for the OH rotor, but not the C–O one. We found that rotation around the latter bond has a very high barrier and also leads to isomerization at energies higher than the experimental range.
\[ \text{CH}_3\text{OOH}^+ \rightarrow ^3\text{CH}_3\text{O}^+ + \text{OH} \] (1b)

Figure B 2: Energy profiles along the O–O bond in \( \text{CH}_3\text{OOH}^+ \) at various levels of theory. All curves are fully relaxed and ZPE exclusive. The asymptote is the zero of energy.

To account for the multireference character we calculated the energy along the breaking bond at the CASPT2(3e,3o)/aug-cc-pVTZ level of theory in Cs point group symmetry (A" state) shown in Figure B 2. The active space consisted of the radical orbital and the bonding and antibonding orbitals of the breaking bond, or, thinking in terms of the fragments, the radical orbital of the OH fragment and the two orbitals occupied by the unpaired electrons of the \( ^3\text{CH}_3\text{O}^+ \) located on its O atom. The product is \( ^3\text{CH}_3\text{O}^+ \) because the ZPE-exclusive asymptote at this level is 3.04 eV relative to \( \text{CH}_3\text{OOH}^+ \) and is correlated with the triplet \( ^3\text{CH}_3\text{O}^+ + \text{OH} \), for
which the ZPE exclusive F12//M06-2X energy is 3.10 eV. \( \text{CH}_3\text{O}^+ \) is a stable ion and isoelectronic with \( \text{O}_2 \); the singlet state at the \( \text{CH}_3\text{O}^+ \) geometry is much higher in energy and readily rearranges to \( \text{CH}_2\text{OH}^+ \). However, since \( \text{CH}_2\text{OH}^+ \) is 3.99 eV more stable than \( \text{CH}_3\text{O}^+ \), it is likely that the latter also eventually forms \( \text{CH}_2\text{OH}^+ \), but in the mass spectrum and breakdown curves the two species, if formed this way, are indistinguishable. Without orbital symmetries we found that it is difficult to converge the doublet state for channel 1b. At the same time the corresponding quartet state, a state that is much easier to converge, becomes degenerate above \( \sim 3 \) Å separation with the doublet one, and the geometry relaxation effects are also negligible in this region. Therefore, we sampled the interfragmental potential at the CASPT2(3e,3o)/aug-cc-pVDZ level of theory for the quartet state between 4 and 20 Å center-of-mass separation to variationally determine the bottleneck for this dissociation channel. We calculated \( \sim 6000 \) points. Due to the spin-orbit coupling of the OH radical we also lowered the asymptote by 70 cm\(^{-1} \) (\( \sim 0.009 \) eV) but ignored the rovibronic correction for the OH state count that only affects the lowest \( \sim 0.1 \) eV part of the kinetics.

\[
\text{CH}_3\text{OOH}^+ \rightarrow \text{CH}_3^+ + \text{HO}_2 \quad (1c)
\]

In addition to M06-2X/MG3S we also scanned this bond using MP2/6-311++G(d,p), and found no barrier either. We also found that above \( \sim 3.5 \) Å, where the potential is already very attractive (\( \sim 0.4 \) eV), the fragment geometries are essentially the same as at large separation, demonstrated by the rigid CASPT2(1e,1o)/aug-ccpVDZ scans.
Figure B 3: Energy profiles along the C–O bond in CH$_3$OOH$^+$ at various levels of theory. All curves are fully relaxed and ZPE exclusive, unless noted in the legend. The asymptote is the zero of energy.

For channel 1c we calculated the number of states using VRC-TST at the CASPT2(1e,1o)/aug-cc-pVDZ level without correcting for geometry relaxation effects. The CASPT2 energies are essentially the same as the MP2 ones in this case. We found that the results are fairly sensitive to the dividing surface optimization in this case, therefore, we sampled interfragmental distances between 2 and 20 Å and placed the pivot points on the center of masses of the two fragments, and at close distances also above and below the plane of the methyl group at 0.4, 0.8, and 1.0 Å. In total we generated 51 dividing surfaces and ~17000 samples.
Figure B 4: Energy profiles along the O–O bond in CH$_2$OOH$^+$ at various levels of theory. All curves are ZPE-exclusive, and the energies are shown relative to the neutral CH$_2$OOH. S: geometries along the singlet scan (the OH moiety simply goes away); T: geometries along the triplet scan (the OH moiety stays close to the CH$_2$O part and abstracts an H).
Figure C 1: Experimental breakdown diagram for 2-propanol between 9.95–13.20 eV. Open circles represent experimental data points and the solid line is the modelled fit.