The Study of Bimolecular Radical Reactions Using a Novel Time-Resolved Photoionization Time-of-Flight Mass Spectrometry and Laser Absorption Spectrometry Apparatus

by

Joshua E. Middaugh

B.S. in Chemical Engineering
The Pennsylvania State University (2006)

SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 2014

© Massachusetts Institute of Technology 2014. All rights reserved.

Author Signature: ____________________________

Department of Chemical Engineering
January 6, 2014

Certified by: ________________________________

William H. Green
Professor of Chemical Engineering
Thesis Supervisor

Accepted by: ________________________________

Patrick S. Doyle
Professor of Chemical Engineering
Chairman, Committee for Graduate Students
DISCLAIMER OF QUALITY

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort possible to provide you with the best copy available. If you are dissatisfied with this product and find it unusable, please contact Document Services as soon as possible.

Thank you.

Some pages in the original document contain text that runs off the edge of the page.
The Study of Bimolecular Radical Reactions Using a Novel Time-Resolved Photoionization Time-of-Flight Mass Spectrometry and Laser Absorption Spectrometry Apparatus

by

Joshua E. Middaugh

Submitted to the Department of Chemical Engineering on January 6, 2014 in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Abstract

This thesis discusses my work to design, build, troubleshoot, and utilize a novel experimental apparatus that is capable of quantitatively measuring the concentrations of reacting gas-phase species and their reactive intermediates with sufficient time-resolution and sensitivity to determine both the kinetics and the product distributions of these systems. The apparatus uses laser absorption spectrometry to probe a radical of interest and thus measure its transient concentration quasi-continuously to precisely determine the kinetics of the reaction. At the same time, the apparatus samples the reactive mixture at various reaction times after the start of reaction to determine the time-resolved product distribution of the chemical system. This combination of techniques was used to study the reactions of vinyl radicals with alkenes, which are important reactions in incipient soot formation in combustion systems. Revised chemical kinetic rate coefficients and, for the first time, temperature- and pressure-dependent product branching fractions were experimentally measured for these reactions. In addition, a new potential energy surface for the vinyl + ethene reaction was calculated using state-of-the-art F12 quantum chemistry calculations, and the master equation for this reactive system was solved using various methods to determine the temperature- and pressure-dependent rate coefficients and product branching fractions.

Thesis Supervisor: William H. Green
Title: Hoyt C. Hottel Professor of Chemical Engineering, Department Executive Officer
Acknowledgements

Though a Ph.D. is largely regarded as a solitary venture, I truly believe it would not be possible to finish one without the help, support, and advice from others. I would like to thank all of those individual who have helped me over the years.

First, I would like to thank my advisor, Professor William H. Green, for all of his insight, enthusiasm, and trust over the years. Bill was willing to give me a lot of responsibility and intellectual freedom in the laser lab, and I learned so much because of it. He was supportive and understanding through the long process of designing, building, and troubleshooting a new instrument. And, he gave me valuable opportunities to help design the new Combustion Dynamics Laboratory in building E17/E18.

I would like to thank Prof. Michael Strano and Prof. Robert Field for being on my thesis committee and for all of their advice and feedback throughout my Ph.D. Furthermore, I would like to thank Prof. Field for allowing me to sit with his research group for most of my time at MIT when the CDL was located in building 6. I learned a lot from him and his students, and I benefited greatly from the generous sharing of knowledge and resources with the Field group.

In addition, I would like to thank all of the colleagues I have had the pleasure with which to work over the years. When I first began my Ph.D., Huzeifa Ismail taught me all about the laser kinetics spectrometer that he built during his Ph.D., and he started me on my journey in the Combustion Dynamics Laboratory. At the same time, Franklin Goldsmith taught me about the fundamentals of combustion chemistry and about topics like pressure dependence. Later, he and I sat down together to design the time-resolved time-of-flight mass spectrometry and laser absorption spectrometry apparatus. I learned so much from these two individuals, and they played an invaluable role in getting me started on my Ph.D.

When I started building the apparatus, I had a lot of help from Young Seok Kim. Building the instrument was a long, tedious task, and it was Young’s patience and positive outlook that kept me going on some of those long days. Also, I had help from some diligent UROPs throughout my Ph.D. including Miles Honkawa and Katherine Eve. Miles and Katherine took on all kinds of projects in the lab to help bring the final apparatus to fruition.

Furthermore, I would like to thank Mickael Matrat, who was a visiting student from France for about 1 ½ years in the CDL. He began tackling many loose-ends when he arrived at MIT, and he helped
get the first ever signal with the TOF-MS using electron impact mode. I will never forget when we showed that signal to Bill, and Bill shouted “Woo-hoo” to the whole of a rather large patronage in the Muddy Charles. Mickael developed the MATLAB code we use to analyze and integrate the absorption and TOF-MS data, and he spent some really long days taking data with the instrument. Also, I would like to thank Zachary Buras, who came onto the project as a first-year graduate student and immediately started working side-by-side with Mickael and myself. Zach took over the LabVIEW project, and he too spent many long days toiling away to get the instrument running. And now, Zach has taken over the entire CDL in the new lab space, where I have no doubt he will continue to conduct interesting experiments.

I would also like to thank several very helpful post-docs and visiting professors. First, John Alecu came to MIT as a roving post-doc with the Combustion Energy Frontier Research Center (CEFRC), and helped setup the photolysis and photoionization lasers in the lab before focusing on some novel multi-structural torsion (MST) computational work in the group. Second, AJ Vasiliou joined us as a post-doc for about a year, bringing her expertise in photoionization time-of-flight mass spectrometry with her from Barney Ellison’s group at Boulder, CO to MIT. Finally, Prof. Andy Cooksy was a visiting professor from San Diego State University, and he wasn’t afraid to get his hands dirty in lab and to get the instrument going every day we were taking data. Also, AJ and Andy were both amazingly gracious helpers when it came to the laborious task of tearing down the instrument in the old lab and moving it to the new lab in building E17/E18.

Finally, I would like to thank my family. From an early age, my parents and grandparents always encouraged my innate curiosity, even when I almost burnt the house down (literally). Even though no one in our family had attended college before, they assured me I could do it. And without the curiosity they helped foster, I would never have gotten a B.S. in chemical engineering, or gone to graduate school, or even met my wife, whom I met while getting my B.S. at Penn State. In particular I would like to thank my wife, Kimberly, who above all has been my greatest source of support throughout my Ph.D. She supported my decision to attend graduate school, and she stood by me and reassured me of that decision through the rough patches. In addition, she gave me the greatest gift she ever could during the last year of my Ph.D., our son Michael. It is to my wife and my son that I dedicate my thesis.
Table of Contents

Acknowledgements .................................................................................................................. 4
Table of Contents .................................................................................................................. 6
List of Figures ......................................................................................................................... 8
List of Tables ......................................................................................................................... 13
Chapter 1: Introduction .......................................................................................................... 14
  Laser Absorption Spectrometry .......................................................................................... 20
  Time-Resolved Photoionization Time-of-Flight Mass Spectrometry ................................ 22
  Reaction Cell Design ......................................................................................................... 25
    Gas Flow and Pressure Control ....................................................................................... 26
    Temperature Control ....................................................................................................... 29
    Supersonic Free Jet Gas Sampling .................................................................................. 33
  Herriott Multi-pass Laser Absorption .............................................................................. 38
    Photolysis Laser .............................................................................................................. 38
    Overlap Path Length for Absorption .............................................................................. 43
    IR Laser for Absolute Concentration Determination ................................................... 44
    Herriott Cross Re-design ............................................................................................... 44
  Photoionization ................................................................................................................... 48
    Time-of-Flight Mass Spectrometer ................................................................................. 55
    Timing and Data Acquisition .......................................................................................... 57
  Characterization and Testing ............................................................................................. 60
    Laser Absorption Spectrometry ....................................................................................... 60

6
List of Figures

Figure 1: Primary energy use by fuel in quads from 1980 to 2040 (projected from 2012-2040). Figure is from the U.S. EIA Annual Energy Outlook 2013. ................................................................. 14

Figure 2: Energy use in 2012 broken down by source and by sector. Figure is from https://flowcharts.lnl.gov/. ................................................................................................... 16

Figure 3: Isometric view of the combined time-resolved photoionization time-of-flight mass spectrometry and laser absorption spectrometry apparatus. .................................................................................. 20

Figure 4: Laser kinetics spectrometer built by Dr. Huzeifa Ismail. The system included the reaction cell, photolysis laser, probe laser, I2 atom laser, optical layout, and differential amplification and detection scheme, all of which were used in the new instrument. Figure is from Dr. Ismail's thesis. ... 21

Figure 5: Custom reaction cell showing the cutaway region in the center of the tube to accommodate sampling from the PI TOF-MS. ...................................................................................................... 26

Figure 6: Mass flow controller rack piping and instrument diagram. All gases and vaporized precursors flow through calibrated MFCs and mix in a tee just before entering the reaction cell. Diagram is courtesy of Katherine Evey. .................................................................................................................. 27

Figure 7: Cross sectional view of the LAS/PITOF-MS chamber showing the reaction cell as well as the gas sampling region in the center ........................................................................................................ 29

Figure 8: Custom water-cooled 12" OD Conflat flange used at each end of the custom vacuum chamber. ................................................................. 30

Figure 9: Axial temperature profile inside the reaction cell. The measured temperatures are shown as points, and the average temperatures for the central 14" (•) and central 20" (---) are shown as lines. Vertical lines for the central 14" (•) and central 20" (---) are also shown for reference. ........................................................................................................ 32

Figure 10: Parity plot of average measured axial reaction cell temperature along the central 14" and the central 20" versus the nominal setpoint temperature. Vertical bars are ±3 standard deviations of the average measured temperature. ........................................................................................................ 33

Figure 11: Cross-sectional view of the gas sampling region showing how the photolyzed region was sampled via a 200 μm sampling cone and how the gas was skimmed using a 1.0 mm conical skimmer to form a molecular beam of gas that traveled to the photoionization region of the TOF-MS. ......................... 34

Figure 12: Schematic of typical free-jet gas expansion showing the nozzle, the zone of silence, and the Mach disk. Figure is from Miller. \( ^{26} \) .................................................................................................................. 35
Figure 13: Free jet properties along the centerline with (a) showing the location of the Mach disk as a function of reaction cell temperature and (b) showing the normalized temperature, pressure, and gas density as a function of distance from the nozzle. Figure is from Goldsmith. 

Figure 14: Probe laser setup with the Millennia diode pump laser, Tsunami Ti:Sapphire laser, and GWU doubler/tripler module. Figure is from Ismail.

Figure 15: Schematic of the set of four cylindrical lens used to correct the astigmatism of the Ti:Sapphire probe beam. One pair (H) correct the horizontal divergence and the other pair (V) correct the vertical divergence. A fifth lens is used to mode match the focusing of the probe beam to the Herriott multi-pass cavity. Figure is from Ismail.

Figure 16: Herriott multi-pass cell with two spherical Herriott mirrors spaced a distance L apart. The photolysis beam enter from the left passing through the hole in the center of each mirror, and the probe beam enters from the right though a slit. The probe beam bounces back and forth intersecting the photolysis beam in the overlap region multiple times before exiting via a slit in the left mirror.

Figure 17: View of Herriott mirror from behind using a monochrome camera for safely aligning the multipass setup.

Figure 18: Semi-custom Herriott mirror mount consisting of a 2" diameter rotation stage close-mounted to a flexure mirror mount on a 1-D translation stage.

Figure 19: Custom Herriott cross assembly with semi-custom Herriott mirror mount inside shown from a) the side furthest from the vacuum chamber, b) the side close the vacuum chamber, and c) in cross sectional view with relevant dimensions shown.

Figure 20: Huco teleshaft with telescoping shaft in the middle and two universal joints, one at each end. We actually used UJT-6 teleshafts from Accurate fasteners. Picture is from Huco website.

Figure 21: Side cross section of vacuum chamber showing the VUV generation setup with a) descriptions of each component and b) important dimensions in inches for focusing and alignment.

Figure 22: Measured (points) and calculated (line) distance of the 355 nm focal point from the flange face on the outlet side of the chamber with the VUV detector assembly removed. The outlet flange face was 15.5" from the MgF2 lens.

Figure 23: Cross-section of the photolyzed region, gas-sampling region, and photoionization region. The narrow gap through which the 355 nm and 118.2 nm beams must both pass is also shown.

Figure 24: Schematic of Kore TOF-MS design showing the relative positions of the ion optics, the reflectron, and the detector. The orientation shown is horizontal, whereas the TOF-MS was used in a vertical orientation in the apparatus. Figure is from the Kore manual.
Figure 25: Snapshot of the user interface for LabVIEW program used to control the experiment and acquire data. Note the tabs which correspond to separate panels to control each aspect of the apparatus. 58
Figure 26: Snapshot of the user interface for the MATLAB program used to analyze the time-resolved TOF-MS and LAS data. 59
Figure 27: Noise in the Ti:Sapphire laser intensity with a) showing the raw signal, b) showing the signal with differential amplification, and c) showing the noise spectra with (red) and without (blue) differential amplification. Figure is from Ismail. 17 61
Figure 28: Noise in PI TOF-MS signal measured with different numbers of averages showing the expected $n^{-2}$ dependence. 66
Figure 29: Mass discrimination factor versus mass-to-charge ratio (m/z) for 300 K (left) and 700 K (right). 68
Figure 30: Detection limit determined using the calibration gas mixture. The error bars are given by the ±1 standard deviation of the measured signal-to-noise ratio. 70
Figure 31: Normalized signal from the PI TOF-MS for the iodine atoms (m/z = 127) generated during the photolysis of vinyl iodide showing the increased spread in the apparent rise time when the pinhole is slightly misaligned. The dotted lines are moving averages of the signals. 71
Figure 32: Example of time-resolved PI TOF-MS spectra showing the growth of the butadiene (m/z = 54) and butenyl and methallyl radical (m/z = 55) products as well as the relatively slow changes in the I (m/z = 127) and the HI (m/z = 128) species. 78
Figure 33: Potential energy surface for the vinyl + ethene reaction showing the explicit treatment of the cis and trans pathways as well as the isomerization between cis- and trans-I-methallyl. 80
Figure 34: Simplified PES showing the collisionally-stabilized C$_4$H$_7$ isomers (m/z = 55) and the dissociative C$_4$H$_6$ (m/z = 54) and the H (m/z = 1) products. 81
Figure 35: Pseudo-first order plot of k' versus the concentration of ethene for the temperatures studied. 82
Figure 36: Replicated determinations of the time-dependent m/z = 55 and m/z = 54 signal from the PI TOF-MS showing the faster rise time of the m/z = 54 species. 83
Figure 37: Laser absorption data and model fit for cases with and without ethene present at 400 K and 25 Torr. 85
Figure 38: Temperature- and pressure-dependent vinyl radical cross section at 423.2 nm with the error bars showing the 95% confidence intervals based on the propagated uncertainties. 86
Figure 39: Arrhenius plot for the vinyl + ethene reaction rate showing the data at 25 Torr, the Arrhenius fit for the 25 Torr data, the 20 mbar and 100 mbar data from Ismail et al., and the rate coefficients obtained when using the pseudo-first order analysis for comparison.

Figure 40: Arrhenius plot for the vinyl + vinyl self-reaction rate showing the data at 25 Torr, the Arrhenius fit for the 25 Torr data, and the Arrhenius fit from Ismail et al. for comparison.

Figure 41: Arrhenius plot for the miscellaneous first order rate showing the data at several pressures.

Figure 42: Example of time-resolved peak areas for the products observed using PI TOF-MS at 600 K and 4×10^6 molecules/cm^3 ethene.

Figure 43: Species concentrations from model (left) and fraction of vinyl consumed by each reaction (right) for T = 400 K, P = 25 Torr, and [C_2H_4] = 1.6×10^17 molecules/cm^3 (27% ethene).

Figure 44: Time-resolved PI TOF-MS experimental signals and modeled signals showing the ability of the model to describe the system at a) 400 K and no ethene, b) 500 K and 4.0×10^16 molecules/cm^3 ethene, c) 600 K and 4.0×10^16 molecules/cm^3 ethene, and d) 700 K and 4.0×10^16 molecules/cm^3 ethene.

Figure 45: Product branching fractions versus temperature showing the effect the value of the upper-bound constraint on β_{54} has on α_{55} (left) and on β_{54} itself (right).

Figure 46: Product branching fractions α_{55} and β_{54} (left) and product branching ratios α_{55}/α_{54} (right) versus temperature with the values for β_{54} constrained to remain below a linear interpolation of β_{54} < 0.3 at 300 K to β_{54} < 0.1 at 700 K.

Figure 47: Product branching fractions α_{55} (left) and β_{54} (right) versus temperature showing the effect of the photoionization cross section for m/z = 55 (σ_{55}).

Figure 48: Theoretical kinetics versus temperature using the CSE method, MSC method, and RS method.

Figure 49: Theoretical kinetics versus temperature using the RS method with nominal ΔE_{down} values of 50 cm^−1, 100 cm^−1, 200 cm^−1, and 350 cm^−1.

Figure 50: Sensitivities of the rates to form each product to the energies of each transition state when using the RS method and ΔE_{down}(298 K) = 100 cm^−1.

Figure 51: Overall reaction rate for the vinyl + ethene reaction showing the agreement between the theoretically calculated rate and the experimentally measured rate. The error bars for the measured rate are given by the 95% confidence intervals from the Arrhenius fit to the experimental data.

Figure 52: Comparison of experimental (points) and theoretical (lines) product branching fraction α_{55} versus temperature (all at 25 Torr) showing good agreement to within the uncertainties in both results. Error bars
for the experiment are given by the uncertainty introduced to the fit for $\alpha_{55}$ by the photoionization cross section of m/z = 55...

Figure 53: Beer's law dependence of the signal from toluene, one of the species in the calibration mixture, with increasing propene concentration. The signal $S$ with propene compared to the signal $S_0$ without propene present was consistent with the VUV photons being lost to absorption from propene.............
List of Tables

Table 1: Comparison of time-resolved PIMS devices in the literature................................................... 24
Table 2: Measured average axial reaction cell temperature for the central 14" and central 20"............. 32
Table 3: Summary of available lasers and wavelengths in the Combustion Dynamics Laboratory .......... 39
Table 4: Typical settings for the BNC-575 delay generator ................................................................. 58
Table 5: Calibration gas mixture properties including photoionization cross sections and the mole- and mass-based fractions.................................................................................................... 65
Table 6: Detection limit of the species in the calibration mixture............................................................. 69
Table 7: Arrhenius parameters and 95% confidence intervals for the vinyl + ethene and vinyl self-reaction rates........................................................................................................................................... 88
Chapter 1: Introduction

Energy, or at least the extraction and the use of limited resources to produce it, is one of the great challenges facing humanity. As the Earth’s total population grows and as countries with large populations such as China and India continue to develop and industrialize, the competition for these limited resources will certainly increase. The difficulty of solving this problem is compounded by its immense scale. According to the Annual Energy Outlook 2013 produced by the U.S. Energy Information Administration, the United States alone uses approximately 95.1 Quads (1 quadrillion BTU = $10^{15}$ BTU $= 1.055 \times 10^{18}$ Joules) of energy every year.\(^1\) To put that in perspective, that is enough energy to power a single 100 watt light bulb for about 31.8 billion years. The vast majority of this energy, in fact 82% in the year 2011 as shown in Figure 1 below, is produced from non-renewable resources including petroleum, coal, and natural gas. According to the EIA’s projections in 2040, this number is not going to change drastically in the future with approximately 79% of the energy in the U.S. still coming from non-renewables. So, without a breakthrough in a scalable alternative energy technology, it is unlikely that the U.S., and furthermore the world, will drastically reduce its dependence on fossil fuels, and both will continue to use them to meet their energy needs well into the future.

![Figure 1: Primary energy use by fuel in quads from 1980 to 2040 (projected from 2012-2040). Figure is from the U.S. EIA Annual Energy Outlook 2013.\(^1\)](image-url)
When examining the energy use in the U.S. broken down by source and by sector, as shown in Figure 2 for 2012, two major observations become apparent. First, some energy sources are amenable to use in only certain sectors and, second, the use of these energy sources is not very efficient. As an example of the first observation, coal is not used to power transportation vehicles, but it is used as a relatively cheap fuel for stationary electricity generation. This specific example illustrates how the fact that certain fuels are best suited for certain energy conversion technologies leads to the disproportionate use of certain energy sources in certain energy sectors. Perhaps the most extreme example of this phenomenon is in the transportation sector where over 90% of the total energy used is derived from the combustion of petroleum fuels. The reason petroleum is the main fuel used in transportation is that petroleum-based fuels are liquids, and liquid fuels have relatively high energy densities and are easy to transport. As for the second observation that energy use in the U.S. is not efficient, Figure 2 shows that the U.S. converts only 39% of the total 95.1 Quads of energy it uses into usable work. That means 61% of the energy used in the U.S. is wasted in the form of transmission losses, thermodynamic limits for conversion processes, waste heat, etc. For the transportation sector in particular, the numbers are even worse than they are for the overall picture with about 79% of the energy used being wasted. And while the efficiency of the combustion engines that are widely used in the transportation sector is bound by fundamental thermodynamic-cycle efficiency limits (~40% for typical spark-ignition engines), real engines are nowhere near these limits with average vehicle efficiencies ~18%. So, there is a lot of room for improvement within the current infrastructure, and there is a large opportunity for improvement within the transportation sector specifically.
The widespread use of combusting fossil fuels for energy poses additional problems and challenges for the environment. Burning fossil fuels releases large amounts of carbon dioxide $CO_2$, which has been implicated in the anthropogenic rise in global $CO_2$ levels and consequently in the rise of global air and ocean temperatures. According to the IPCC 2013 report, $CO_2$ levels have increased from a pre-anthropogenic level of about 280 ppm to about 390 ppm in 2011. While at first glance this may seem like a relatively modest increase in the amount of $CO_2$ in the atmosphere, consider that most climate scientists put 450 ppm to 550 ppm as the tipping point beyond which dramatic climate change is very likely. And, according to the IPCC 2013 report, the concentration of $CO_2$ could reach the 450 ppm level as early as 2020, and will almost certainly reach that level by 2040. The consideration of this rising trend in $CO_2$ levels along with the lack of efficiency in current energy technologies led to a famous paper by Pacala and Socolow about the idea of stabilization wedges to curb $CO_2$ emissions and to keep atmospheric $CO_2$ levels below 500 ± 50 ppm through 2050 and potentially beyond. Their paper highlights how, with already feasible adjustments to the way energy is currently produced and used, the world could keep carbon emissions in check and provide additional time to develop more sustainable energy solutions.
However, combustion processes produce other pollutants in addition to generating large amounts of CO\textsubscript{2}. Other pollutants include NO\textsubscript{x}, SO\textsubscript{x}, and unburned hydrocarbons. These pollutants cause environmental hazards such as acid rain, smog, and particulates (soot) that result in physical damage to the environment and respiratory problems for humans, among other issues. Therefore, increasing efficiency to reduce the amount of carbon-based fuels consumed and thus their resultant pollutants is not enough. Additional advances must also be made to minimize, if not completely eliminate, the production of these pollutants. To encourage such advancements, some governments already have introduced stricter limits on emissions, and many are expected to follow suit in the near future. So how do we improve combustion processes to make them more efficient and less polluting? The answer is through understanding these processes better to allow intelligent and timely changes to current systems and to allow the discovery and development of completely new systems.

The way scientists and engineers usually understand things better is by conducting well-designed experiments and by building models to understand the underlying dynamics. Since combustion as an energy-conversion technology is very old and since scientists and engineers have been studying it for some time, one might expect that combustion systems are completely understood. However, it turns out that combustion processes are extremely complex and thus they are very difficult to model and to completely understand. Real combustion systems, such as internal combustion engines, combine concepts from across a number of fields including thermodynamics, fluid dynamics, mass and heat transfer, chemistry, and chemical kinetics. Thus, much work is still needed to develop a detailed understanding of combustion systems, and the methods to model the full complexity of real systems are still being developed.

In the Green group at MIT, we are mainly focused on enhancing the current state of the chemical understanding of combustion systems. For example, Green group researchers have generated reaction mechanisms for novel fuels such bio-butanol\textsuperscript{6-8} and the fungi-derived fuel, diisopropyl ketone (DIPK)\textsuperscript{9} using the Reaction Mechanism Generation (RMG) software package,\textsuperscript{10} which is developed internally by the group. In addition, thermochemistry parameters for small molecules, which are required to simulate the combustion of nearly any hydrocarbon fuel, were computed to enhance the accuracy of many future combustion simulations.\textsuperscript{11} Furthermore, the foundation of basic chemical understanding has been enhanced by other Green group members by introducing new reaction types, specifically the Korcek pathway, to the families of known reaction types.\textsuperscript{12} Experimentally, fundamental chemical kinetic rates were previously measured for key soot-forming reactions using a laser absorption spectrometry apparatus, and the product branching of these reactions were simulated using Rice–Ramsperger–Kassel–Marcus Master Equation
(RRKM/ME) simulations.\textsuperscript{13-15} And, there were many more contributions following this common vein of enhancing chemical knowledge that, while equally impressive, will not be mentioned here for the sake of brevity and space.

In this thesis, I discuss a new thrust in the Green group to provide the capabilities to measure the product distribution of chemical reactions that are important in combustion and in atmospheric chemistry. While this has historically been a difficult problem, the resurgent use of time-of-flight mass spectrometry and along with it the tabulation of reliable photoionization cross-section data for a large number of species has made such problems tractable. Thus, I will discuss the design, construction, and utilization of a new experimental apparatus to measure the kinetics and, for the first time directly, the product branching of the soot forming reactions of vinyl radicals with alkenes. In Chapter 2, I provide an overview of the new apparatus, and I discuss the important parameters to its design and function. In Chapter 3, I discuss how we used this new apparatus to measure the kinetics and product branching for the vinyl + ethene reaction. In Chapter 4, I briefly discuss the measurements we performed for the other vinyl + alkene reactions: vinyl + propene, vinyl + 1-butene, vinyl + 2-butene, and vinyl + iso-butene and the ongoing work to fully understand these chemical reactions.

In order to directly measure the chemical kinetics of specific reactions, it is necessary to probe the concentration of either one of the reactants or one of the products with a time-resolution sufficient to resolve the transient decay or rise of the probed reactant or product, respectively. To accomplish this task, both time-resolved time-of-flight mass spectrometry (TOF-MS) and laser absorption spectrometry (LAS) can be used, though LAS is better suited to the task. Also, in order to measure the product branching fractions of a chemical reaction, it is necessary to quantitatively determine the amount of each product species relative to the total concentration of limiting reactant or to all other products. While it is possible to measure product fractions using laser absorption spectrometry in some special cases where different absorption bands are available for each species, mass spectrometry is generally more suited to the task as it can in principle determine the difference in abundances of any species with different masses. Thus in order to measure the chemical kinetics of reactions with high resolution and to measure the product branching fractions of chemical reactions, we designed and built a novel apparatus that is the first to combine the LAS technique and the time-resolved TOF-MS technique in a single device. A snapshot of this new device is shown in Figure 3.
Laser Absorption Spectrometry

Laser absorption spectrometry is a technique wherein the concentration of a species is determined by measuring the fraction of light that is absorbed. The concentration is given by the Beer-Lambert law, which says the absorbance ($A$), defined as the natural logarithm of the ratio of the initial intensity of light ($I_0$) to the final intensity of light ($I$), is proportional to the concentration of the absorbing species ($C$), the path length for absorption ($l$), and the absorption cross section of the species ($\sigma$). By measuring the transient absorbance from a single species, one can then determine its relative transient concentration. If the cross section at the wavelength of light being used and the absorption path length are known, then one can determine the absolute concentration of the species.

$$A = \ln \left( \frac{I_0}{I} \right) = \sigma l C$$

The LAS technique has been used by a number of groups to determine the kinetics of various chemical reactions. In particular, the group in the Combustion Research Facility at Sandia National Laboratory has used a multi-pass absorption cell for studying gas-phase chemical kinetics. This multi-pass design was the inspiration for the apparatus built by Dr. Huzeifa Ismail during his graduate degree...
tenure in the Green group at MIT. The instrument built by Dr. Ismail is shown Figure 4 below. The laser systems (both the photolysis laser and the composite Ti:Sapphire laser system), the basic design for the multi-pass absorption configuration, the optical layout (including the beam shaping optics for the Ti:Sapphire laser and the telescoping optics for the photolysis beam), and the differential amplification and signal detection scheme used in Ismail's apparatus are also used in the new apparatus. Of course, some changes and improvements were made to these systems to accommodate the new instrument. The details of these systems, how they work, and how they were modified will be discussed later in this chapter.

Figure 4: Laser kinetics spectrometer built by Dr. Huzeifa Ismail. The system included the reaction cell, photolysis laser, probe laser, I atom laser, optical layout, and differential amplification and detection scheme, all of which were used in the new instrument. Figure is from Dr. Ismail's thesis.
Time-Resolved Photoionization Time-of-Flight Mass Spectrometry

Time-Resolved Photoionization Mass Spectrometry (PIMS) is a technique wherein a sample of a reactive mixture is ionized using light, usually in the vacuum ultraviolet (VUV) range, and then analyzed with enough time resolution to ascertain the reactive time-dependence of the relative abundance of the ions separated by their mass-to-charge (m/z) ratios. Provided the photoionization process is mostly single-photon (i.e. only one photon of ionizing radiation is absorbed per molecule), then the charge imparted to each ionized molecule is +1, and the only difference between the ions is their mass. Thus by applying a static electric field in the case of time-of-flight mass spectrometry or an oscillating radio-frequency field in the case of quadrupole mass spectrometry, the ions can be separated according to their masses with the abundance of each mass being proportional to the integrated signal for each mass-to-charge peak. The general time-resolved PIMS technique has been famously used by a number of groups to study the kinetics and the time-dependent species distribution of chemical reactions. Instruments include those from Fockenberg et al., Slagle and Gutman, Blitz et al., and Osborn et al. Recently, our instrument has joined the list of time-resolved PIMS devices, and a few devices from other groups including Prof. Ju’s group at Princeton, Prof. Mani Sarathy’s group at the King Abdullah University of Science and Technology (KAUST), and unknown others will too, as this method is quickly growing in popularity.

The real challenge of time-resolved PIMS, and thus the reason the number of research groups using it is limited to date, is to sample the reactive mixture without altering its composition in any way. For example, the reactive mixture cannot merely be sampled by a tube fed into a generic bench-top mass spectrometer since the mixture would continue to react while in transit to the mass spectrometer and/or the reactive intermediates would be quenched by the metal walls of the tubing, thus changing the composition of the sample before it reaches the mass analyzer. So, more advanced techniques are required to sample the gas and maintain its composition by quickly transporting it to the mass spectrometer for analysis before it can react further with itself or with other spurious entities. Typically, this involves using a custom-built apparatus to closely couple the reaction cell and the mass spectrometer together. Furthermore, all of the aforementioned designs including our design, utilize an effusive or a supersonic expansion to sample the reactive gas. Such an expansion of the gas sample accomplishes several desired objectives at once. First, it attenuates the gas and drops the pressure by several orders of magnitude to approach the high-vacuum (low-pressure) environment required to use a mass spectrometer. Typically, a second stage of pumping with a conical skimmer is used to further attenuate the gas and thus reduce the pressure even further, with
the exception being the design of Blitz et al.\textsuperscript{21} where the snout of the TOF-MS is coupled directly to the effusive expansion. Second, the gas expansion cools the reactive mixture and effectively “freezes” the composition of the gas sample for transit to the mass spectrometer. And finally, the collisions in the gas sample during the finite transit time to the PIMS are greatly reduced as a result of the attenuated gas density and as a result of the greatly accelerated motion in the direction away from the pinhole toward the PIMS. Therefore, the molecules in the gas sample quickly reach the ionization region of the mass spectrometer (typically in 10 to 100 microseconds) before they have had a chance to collide with each other or to collide with any surfaces and thus react any further.

The existing time-resolved PIMS designs do have some rather substantial differences however. For example, the designs use different methods for photoionization. Slagle and Gutman\textsuperscript{19,20} and Fockenberg et al.\textsuperscript{18} use the VUV emission from lamps to photoionize the gas sample. Blitz et al.\textsuperscript{21} also included the capability to use lamps in their design, but found better performance using the tripled 355 nm output of a Nd:YAG laser to make 118 nm light. Osbom et al.\textsuperscript{22} use tunable VUV radiation from the Advanced Light Source synchrotron at Lawrence Berkeley National Laboratory. The essentially continuous source of narrow-bandwidth tunable VUV light (7.2-25 eV with a 2.5% bandwidth) from the synchrotron is by far the best photoionization source in existence, as it allows species with different ionization energies to be analyzed and it even allows some isomers of the same m/z to be separated based on differences in their photoionization efficiency curves (i.e. isomers of the same m/z can be differentiated by observing the change in signal with respect to photoionization energy).\textsuperscript{23} The photoionization energy range available with lamps is quite limited, and it is plagued by large gaps in the available range, relatively low photon fluxes, and relatively large bandwidth photon energies. The higher-order harmonics of lasers, while offering relatively narrow bandwidths and the largest number of photons per shot (and thus the highest number of ions per mass spectrum), are very difficult to tune in the VUV range, requiring a very large and complex setup to accomplish a relatively narrow tuning range of even a few eV.\textsuperscript{24} Also, the pulsed nature of lasers combined with their limited repetition rates means the time-dependence of the mass spectra cannot be observed for each photolysis shot. Instead, it must be obtained by sequentially measuring a mass spectrum for each desired time during the course of reaction from separate photolysis shots. That is, time resolution is accomplished by delaying the photoionization pulse relative to the photolysis pulse to obtain mass spectra at different reaction times. The use of a nearly continuous photoionization source, such the synchrotron source, eliminates the laborious and time-consuming process of scanning laser time delays and allows the TOF-MS to be pulsed much more rapidly. In fact, data can be collected fast enough with a
continuous PI source to observe the time dependence of the mass spectra following each photolysis shot. However, we do not have access to a tunable VUV synchrotron source, and thus we opted to use the ninth harmonic of a Nd:YAG laser (i.e. the tripled-tripled output of a Nd:YAG laser which makes 118 nm (10.5 eV) light) as our photoionization source.

Another difference between the existing PIMS devices is in the type of mass spectrometer used. In particular, the oldest design by Slagle and Gutman uses a quadrupole mass spectrometer (Q-MS) instead of a time-of-flight mass spectrometer. This offers several advantages and several disadvantages. An advantage is that a single m/z peak can be monitored very rapidly (e.g. 1-2 kHz sample rate) when a continuous or quickly pulsed photoionization source, such as when a lamp like that used by Slagle and Gutman, is utilized. Rapid sampling allows the kinetics of a single m/z peak to be observed with every photolysis shot. However, a Q-MS cannot scan the mass range quickly enough to see more than one m/z peak at a time, as the mass-scanning time (e.g. ~100 ms) is far longer than the typical reaction timescales. The time dependence of each mass peak in Q-MS must be recorded individually, meaning that a Q-MS is not multiplexed like at TOF-MS wherein the entire mass spectrum is recorded at once. Thus, the tradeoff when using a Q-MS instead of a TOF-MS then becomes to have higher-resolution kinetic measurements in lieu of more precise relative mass abundances. Precise relative mass abundances are required to obtain more precise product distributions. All of the more recent PIMS instruments use TOF-MS to take advantage of its multiplexed nature and to exploit its ability to more precisely determine product distributions. A summary of the similarities and differences between the known time-resolved PIMS devices is shown in Table 1.

Table 1: Comparison of time-resolved PIMS devices in the literature.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Year</th>
<th>Reactor</th>
<th>Pinhole Size</th>
<th>Skimmer Size</th>
<th>T range</th>
<th>P range</th>
<th>Photolysis Source</th>
<th>Mass Spectrometer</th>
<th>Photolysis Rate</th>
<th>MS Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slagle and Gutman</td>
<td>1981</td>
<td>51 cm long, 1.05 cm ID, quartz</td>
<td>0.44 mm</td>
<td>?</td>
<td>300-811</td>
<td>1</td>
<td>193 nm or 248 nm excimer</td>
<td>atomic resonance lamp</td>
<td>Quadrupole</td>
<td>4 Hz</td>
</tr>
<tr>
<td>Fockenberg et al.</td>
<td>1999</td>
<td>43 cm long, 1 cm ID, quartz</td>
<td>1 mm</td>
<td>1 mm</td>
<td>300-873</td>
<td>10</td>
<td>193 nm excimer</td>
<td>hollow cathode lamp</td>
<td>TOF-MS</td>
<td>10-15 Hz</td>
</tr>
<tr>
<td>Blitz et al.</td>
<td>2007</td>
<td>70 cm long, 12.7 mm OD, quartz</td>
<td>1 mm</td>
<td>none</td>
<td>300-1000</td>
<td>0.5-2</td>
<td>248 nm excimer</td>
<td>tripled Nd:YAG or lamp</td>
<td>TOF-MS</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Osborn et al.</td>
<td>2008</td>
<td>62 cm long, 1.05 cm ID, quartz</td>
<td>400 μm or 650 μm</td>
<td>0.15 cm</td>
<td>300-1050</td>
<td>1-10</td>
<td>193 nm excimer</td>
<td>tunable synchrotron</td>
<td>TOF-MS</td>
<td>4 Hz</td>
</tr>
<tr>
<td>This work</td>
<td>2013</td>
<td>86 cm long, 6 cm ID, stainless steel</td>
<td>200 μm</td>
<td>1 mm</td>
<td>300-700</td>
<td>2-100</td>
<td>266 nm Nd:YAG</td>
<td>tripled Nd:YAG</td>
<td>TOF-MS</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>
While we mostly took inspiration for the design of the PI TOF-MS portion of the new apparatus from the designs by Osborn et al. and by Blitz et al., we employed several novel features in our design to address common issues with the previous designs. First, we used a longer reaction cell (~20% longer than the longest cell used by Blitz et al.) with a larger diameter (~6x larger than the average cell) to accommodate the simultaneous passage of the multi-pass laser beam with the photolysis beam. Second, the larger diameter reaction cell kept the reactive zone far from the walls to avoid secondary chemistry and heterogeneous effects. Third, we used a stainless steel cell instead of a quartz cell to allow a greater pressure range and to permit the ability to fabricate a tube with a small sampling cone protruding into the reaction zone. Since wall reactions are minimized by using a large diameter cell, it is also not as crucial to use quartz, which is generally used by the other groups because it is less reactive than stainless steel. And finally, we designed a custom vacuum chamber that is quite different from all of the other designs. It is this custom chamber that allows the PI TOF-MS to be closely coupled to the reaction cell and thus to the multi-pass laser absorption system.

**Reaction Cell Design**

The reactions are carried out inside a 2.5" OD (2.37" ID) stainless steel tube that is 33.75" inches long called the *reaction cell*. The reaction cell is shown in Figure 5, and a more detailed description of the dimensions of this part can be found in Appendix I. The radicals are generated in the reaction cell using the laser flash photolysis (LFP) technique, which was pioneered by Porter and Norrish in 1950. The LFP technique has been used extensively ever since then to study the kinetics of radical reactions. Essentially, the LFP technique employs a strong UV source such as a flash lamp or a laser to homolytically cleave a relatively weak bond in a precursor molecule, usually a carbon-halogen bond in a halogenated precursor. The result is the selective and nearly instantaneous (on the timescale of reaction) generation of a pool of radicals, the time-dependent decay of which can then be monitored using other techniques to determine the kinetics of reaction. The radical of interest can react with itself or with other species that are introduced into the reaction cell along with the radical precursor. Often, these reactions are carried out under pseudo-first order conditions wherein the species reacting with the radicals is put in large excess over the initial radical concentration. An excess of the species ensures most of the radicals react with this species, and it
simplifies the analysis of the transient concentration data greatly, as the kinetics obey a single exponential model.

![Custom reaction cell showing the cutaway region in the center of the tube to accommodate sampling from the PI TOF-MS.](image)

**Figure 5:** Custom reaction cell showing the cutaway region in the center of the tube to accommodate sampling from the PI TOF-MS.

**Gas Flow and Pressure Control**

To prepare the reactive gas mixture, a manifold of calibrated MKS mass flow controllers (MFCs), shown in Figure 6, is used to flow precisely controlled amounts of each component. This manifold, while similar to the manifold used by Ismail et al. for the laser kinetics spectrometer, was completely redesigned in a more compact format by Katherine Eve, a UROP in the Combustion Dynamics Laboratory. She reduced the number of fittings, connections, and plastic tubing, which greatly reduced the leak rate of the manifold. Furthermore, she simplified the vacuum connections to allow the gas lines and the MFCs to be evacuated before filling with fresh or different gases. Previously, gas lines could only be evacuated using the connection to the reaction cell, which meant the experiment needed to be interrupted to evacuate a line. The ability to evacuate the lines using a connection other than the reaction cell was necessary since some gases could contaminate the reaction cell when conducting mass spectrometry experiments. To ensure all
gas flows were accurate, Katherine also checked the calibration of all of the mass flow controllers and made adjustments as necessary. A summary of her work including the calibration curves for each MFC is given in Appendix II.

Figure 6: Mass flow controller rack piping and instrument diagram. All gases and vaporized precursors flow through calibrated MFCs and mix in a tee just before entering the reaction cell. Diagram is courtesy of Katherine Eve.

The reaction cell resides inside the custom vacuum chamber as shown in the cross-sectional view of the chamber in Figure 7. The gas mixture flows in through the tube on the left of the chamber, and out through the port on the right. Although not shown in the diagram, the exit port is connected to an automated butterfly valve to actively control the pressure in the reaction cell using a feedback controller. The pressure in the reaction cell is monitored using two capacitance manometers: one with a range of 1-100 Torr and the other with a range of 1-1,000 Torr. The feedback controller box automatically switches to the appropriate manometer for the pressure being measured. The setpoint for the automatic pressure control valve setup is
controlled and monitored via the LabVIEW program that runs the experiment, which is discussed in a later section. The outlet of the automated pressure control valve is connected to a Leybold WSU251/D65BS Roots blower pump package via a long 3" diameter stainless steel tube that runs from the laboratory to a separate pump room. This Roots blower has a pumping speed of about 300 m³/h. However the actual pumping speed is limited by the conductance of the 3" diameter tubing. It is difficult to estimate the exact conductance of the 3" diameter line, since the pressures (~100 millitorr) commonly observed in this line are in the crossover range between free-molecular flow and viscous flow. In practice, the Roots blower with the 3" diameter line was found to be more than sufficient to handle the 10,000 sccm maximum flow for a typical experiment and still keep the pressure at the inlet to the Roots blower in the 100s of millitorr range. While in principle it is possible to set the pressure in the reaction cell anywhere within the 1-1,000 Torr range, it is not recommended to go above atmospheric pressure (760 Torr) for safety reasons. If the pressure was set above 760 Torr, the dangerous gases inside the reaction cell could leak out since several components including the windows on either end of the chamber are not able to seal under positive pressure. If the TOF-MS and its associated pumps are turned on, the pressure should not be set above ~100 Torr in order to avoid exceeding the recommended pressure limits for the TOF-MS and its turbomolecular pumps. However, if only absorption experiments are being performed and the TOF-MS and its turbomolecular pumps are turned off, it is quite feasible to conduct experiments safely up to about 650 Torr, which still leaves some room to ensure the chamber is under negative pressure.
Temperature Control

The reaction cell was heated using four 1/8" diameter vacuum-safe stainless steel cable heaters from Durex Industries (www.durexindustries.com). The heated section of a 72" long (60" heated length, 12" cold length), 900 W, 120 V cable heater was wrapped tightly around the ~3" at each end of the reaction cell. The heated section of a 128" long (116" heated length, 12" cold length), 1000 W, 120 V cable heater was wrapped around the central region of the reaction cell with the spacing between the coils being tighter near the ends and more loose in the center near the gas sampling region. This spacing of coils was selected to provide as uniform a temperature profile along the axis of the reaction cell as possible. Since the conductance of heat along the stainless steel tube was the greatest source of heat loss from the reaction cell, custom water-cooled flanges, as shown in Figure 8, were used at both ends of the chamber where the reaction cell was connected. Without these water-cooled flanges, the conducted heat would have caused the vacuum chamber to get very hot. The cold sections of each cable heater passed from the reaction cell to the vacuum feed-through connections on the wall of the custom vacuum chamber. A 2.75" ID stainless steel shell was placed around the reaction cell and heaters to clamp the heater coils in place. After some
testing, it was found that the arm that connects to the middle of the reaction cell inside the chamber conducts heat away from that region creating a cold spot. So, a 49" long (19" heated length, 30" cold length), 475 W, 120 V heater was wrapped around the tubular protrusion in the center of the reaction cell to which the arm is connected. This effectively eliminated the cold spot in the middle of the reaction cell.

The temperature inside the reaction cell was measured using five 1/16" diameter stainless-steel-sheathed K-type grounded thermocouples from Omega Engineering. These thermocouples were of various lengths and were laid at the bottom of the reaction cell to measure the temperature at several points. Each point was selected to be within the region heated by each cable heater. Two thermocouples were placed in the long central region to give some flexibility in the control point. Only one of these two thermocouples was actively used to control the temperature. CN7500 series temperature controllers and solid state relays from Omega Engineering were used to provide feedback control of the temperature in the reaction cell at each point. The temperature control system was set up and the temperature controllers were interfaced to the LabVIEW program for the instrument by Mickael Matrat, a visiting graduate student from France.

Figure 8: Custom water-cooled 12" OD Conflat flange used at each end of the custom vacuum chamber.
In order to verify that the temperature profile inside the reaction cell was as uniform as possible, a 66" long \( \frac{1}{4}'' \) diameter stainless-steel-sheathed J-type grounded thermocouple was used to measure the axial temperature. Scaling factors for the setpoint temperature of each temperature controller were then developed to smooth the measured axial temperature profile. The resulting temperature profiles for nominal setpoint temperatures in the reaction cell from 300 to 700 K in 100 K increments are shown in Figure 9. The x-axis represents the full 33.75" flange face-to-flange face length of the reaction cell. Vertical lines show the central 14" (dots •) and central 20" (dashes ---) of the reaction cell, which represent the typical range of common overlap regions for the multi-pass probe laser. Horizontal dashed lines show the average temperature over the central 14" (dots ••) and central 20" (dashes ---). The average measured temperatures as well as the standard deviation of the temperature over both regions are summarized in Table 2 and in Figure 10. The standard deviation of the temperature increased with increasing average temperature, but stayed relatively constant as a percentage of the average temperature, as expected. The average measured temperatures in Table 2 should be used in place of the setpoint temperatures when specifying the temperature of an experiment and when using temperature to analyze the resulting experimental data, such as when conducting an Arrhenius analysis of kinetic data.
Figure 9: Axial temperature profile inside the reaction cell. The measured temperatures are shown as points, and the average temperatures for the central 14" (---) and central 20" (---) are shown as lines. Vertical lines for the central 14" (---) and central 20" (---) are also shown for reference.

Table 2: Measured average axial reaction cell temperature for the central 14" and central 20".

<table>
<thead>
<tr>
<th>Measured Temperature (K)</th>
<th>Temperature Setpoint (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>305</td>
</tr>
<tr>
<td>Middle 14&quot;</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>313</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>2</td>
</tr>
<tr>
<td>Middle 20&quot;</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>311</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 10: Parity plot of average measured axial reaction cell temperature along the central 14" and the central 20" versus the nominal setpoint temperature. Vertical bars are ±3 standard deviations of the average measured temperature.

**Supersonic Free Jet Gas Sampling**

The gas in the photolyzed region in the center of the reaction cell was sampled using a 200 micron orifice in the tip of a small sampling cone. A close-up of the gas sampling region inside the custom vacuum chamber is shown in a cross-sectional view in Figure 11. The tip of the sampling cone protruded slightly into the photolyzed region, and the gas was driven continuously through the pinhole by a large pressure gradient. Typical pressures inside the reaction cell ranged from 1-100 Torr, with 25 Torr found to be a good balance for most experiments. Typical pressures in the low-vacuum chamber outside the reaction cell were around $10^{-5}$-$10^{-4}$ Torr, and a very large 2,000 L/s Leybold turbomolecular pump was used to handle the relatively high gas load of a continuously sampled system while still achieving low enough pressures. The roughly 4-5 order of magnitude difference in pressure between the reaction cell and the low-vacuum chamber supersonically expanded the gas sampled from the pinhole. As mentioned above, such an
expansion of the gas sample accomplishes several objectives at once. First, it attenuates the gas and drops the pressure by several orders of magnitude to approach the high-vacuum (low-pressure) environment required to use a mass spectrometer. Second, the gas expansion cools the reactive mixture and effectively “freezes” the composition of the gas sample for transit to the photoionization region. And finally, the collisions in the gas sample during the finite transit time are greatly reduced as a result of the attenuated gas density and as a result of the greatly accelerated motion in the direction away from the pinhole toward the PIMS. Therefore, the molecules in the gas sample quickly reach the ionization region of the mass spectrometer (typically in 10 to 100 microseconds) before they have had a chance to collide with each other or to collide with any surfaces, and thus arrive without having reacted any further.

A schematic for a typical free jet gas expansion is shown Figure 12.26 After exiting the pinhole (or nozzle in free-jet parlance), the gas rapidly expands and attains speeds greater than the speed of sound, i.e. it becomes supersonic and has a Mach number greater than 1. This supersonic zone immediately outside the pinhole is called the zone of silence, and it is within this zone that the gas is both cooled and nearly
collision-free. To extract the gas from this zone, a 1.0 mm diameter Model 2 Beam Dynamics conical skimmer was placed about 1.0-2.0 mm away from the pinhole, depending on the position of the reaction cell. The skimmer eliminated the slower and less-cooled regions of gas away from the axis of the zone of silence, and it created a molecular beam to transport the gas sample continuously to the ionization region of the mass spectrometer. The skimmer also provided an additional reduction in pressure by reducing the gas load to the high-vacuum chamber were the gas sample is ionized. This reduction in pressure decreased the amount VUV photoionization light losses due to absorption by the scattered background gas, and it brought the high-vacuum pressure to a level suitable for the use of an electron impact ionization source, with which our TOF-MS is also equipped. Finally, the reduction of pressure due to the skimmer indirectly allowed the TOF-MS to be used with greater pressures in the reaction cell by decreasing the pressure at the TOF-MS snout and thus the pressure within the TOF-MS.

Figure 12: Schematic of typical free-jet gas expansion showing the nozzle, the zone of silence, and the Mach disk. Figure is from Miller.26
The location of the Mach disk, which corresponds to the location where the attenuated gas suddenly slows as it is influenced by the boundary conditions imposed by the slower higher density gas in the periphery, is given by the following empirical equation:

\[
\frac{x_M}{d} = \frac{2}{3} \left( \frac{P_{\text{reaction cell}}}{P_{\text{chamber}}} \right)^{1/2}
\]

where \(x_M\) is the distance of the Mach disk from the nozzle, \(d\) is the nozzle diameter, \(P_{\text{reaction cell}}\) is the reaction cell pressure, and \(P_{\text{chamber}}\) is the pressure in the low-vacuum chamber into which the gas expands. Thus, for a typical reaction cell pressure of 25 Torr, a conservative corresponding chamber pressure of \(10^{-4}\) Torr, and a nozzle (pinhole) diameter of 0.02 cm (200 μm), the Mach disk is 6.7 cm away from the pinhole. However, the pressure in the low-vacuum chamber is measured some distance away from the gas expansion. So, assuming about an order of magnitude higher pressure locally near the gas expansion due to conductance losses caused by obstructing surfaces between the expansion and the turbo pump, then the Mach disk is about 2.1 cm away from the pinhole. This distance agrees well with the estimate by Dr. C. Franklin Goldsmith in his thesis where he estimated the local pressure near the pinhole assuming conductance losses before we had experimentally measured the low-vacuum chamber pressure. Figure 13 shows Dr. Goldsmith’s predicted Mach disk location as a function of reaction cell temperature and the normalized temperature, pressure, and gas density as a function of distance from the nozzle. A detailed discussion of the equations required to compute these values can be found in his thesis.

Figure 13: Free jet properties along the centerline with (a) showing the location of the Mach disk as a function of reaction cell temperature and (b) showing the normalized temperature, pressure, and gas density as a function of distance from the nozzle. Figure is from Goldsmith.
The optimum distance of the skimmer from the pinhole can be calculated using the following two alternative empirical formulas\(^{26}\)

\[
x_{s}^{\text{max}} = x_{M} \left( \frac{1}{1 + \frac{\varepsilon \lambda_{M}}{x_{M}}} \right)
\]

\[
\frac{x_{s}^{\text{max}}}{d} = 0.125 \left[ \left( \frac{d}{\lambda_{0}} \left( \frac{P_{\text{reaction cell}}}{P_{\text{chamber}}} \right) \right) \right]^{1/3}
\]

where \(x_{s}^{\text{max}}\) is the distance of the skimmer tip from the nozzle that maximizes the molecular beam intensity, \(\lambda_{M}\) is the mean free path at the Mach disk, \(\varepsilon\) is an empirical factor approximately equal to \(3.7 \pm 2\), and \(\lambda_{0}\) is the mean free path in the reaction cell. In his thesis, Dr. Goldsmith calculated the optimum distances using both equations for the range of temperatures and pressures available in our reaction cell, and he found \(0.07 < x_{s}^{\text{max}} < 2.3\) mm. The values given by these equations are only guidelines, but it was reassuring that the range fell around the generally accepted rule of thumb to place the skimmer no more than 10 nozzle diameters away, or 2 mm for the 200 \(\mu\)m sampling pinhole, and no closer than a couple of nozzle diameters, or 0.4 mm. Since it was not possible to adjust the skimmer once it was in place inside the vacuum chamber and since the reaction cell could only be moved along this dimension by 1 mm or so, we chose to keep the pinhole-skimmer distance fixed at about 1.5 mm. While this distance was difficult to quantify exactly due to the tight space in which the skimmer resides inside the sampling cone, we adjusted the distance using flat O-rings of various thicknesses to get it as close as possible to 1.5 mm away. In the end, a \(\frac{1}{8}\)” thick, 1.199” OD, 0.921” ID O-ring (part # AS568-213S) was placed between the base of the skimmer and the recessed ledge in the face of the high-vacuum chamber, in which the skimmer is clamped. This O-ring also helped make a better seal between the low-vacuum and the high-vacuum chambers, further reducing the pressure in the high-vacuum chamber.
Herriott Multi-pass Laser Absorption

Photolysis Laser

As noted above, the geometry of the reaction cell was designed to sample the photolyzed region via a small pinhole without disturbing the ability to simultaneously probe the same region using the Herriott multi-pass laser absorption technique. The photolyzed region was defined by the region through which the photolysis beam passed, and the diameter of the photolysis beam was kept around 1.2 cm to 1.5 cm to ensure the tip of the sampling cone protruded into the photolyzed region. Typically, we used the fourth harmonic (266 nm) output of a Nd:YAG laser (1064 nm fundamental) fired at 10 Hz. When the Combustion Dynamics Laboratory was in building 6, we generated 266 nm light by externally frequency-doubling the second harmonic (532 nm) beam that was made via an internal frequency-doubling crystal inside a Big Sky CFR 200 laser. In the new lab location in building E18, we generated 266 nm by internally doubling the 1064 nm fundamental light twice using the harmonic generator crystal set inside a Spectra Physics Quanta-Ray LAB 170 laser. The harmonic generator box inside the Quanta Ray laser also contains a third-harmonic crystal and a Type I second-harmonic crystal to produce higher power 355 nm light. The 355 nm setup of the Quanta Ray laser was used as the photoionization source in the lab in the building 6, but in E18 it was replaced with a 20 Hz Quantel Brilliant laser, which also had the crystal modules to make 355 nm light. In addition to these Nd:YAG lasers, we also had a 308 nm XeCl Lambda Physik LPX240i excimer laser that was rebuilt after being damaged in the infamous Halloween Chemical Engineering building steam release. This laser also previously had issues with a leaky cavity that were fixed at the same time as the steam damage. A summary of the lasers available in the Combustion Dynamics laboratory is shown in Table 3.
Table 3: Summary of available lasers and wavelengths in the Combustion Dynamics Laboratory

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model</th>
<th>Rep. Rate (Hz)</th>
<th>Pulse width (ns, FWHM)</th>
<th>Available Wavelength (nm)</th>
<th>Energy (mJ/pulse)</th>
<th>Current Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Sky</td>
<td>CFR 200</td>
<td>10</td>
<td>&lt; 11</td>
<td>532</td>
<td>130</td>
<td>Field Group</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>266</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1064</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>Spectra Physics</td>
<td>LAB 170</td>
<td>10</td>
<td>&lt; 12</td>
<td>532</td>
<td>450</td>
<td>Photolysis Laser</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>355</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>266</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Quantel</td>
<td>Brilliant</td>
<td>20</td>
<td>5 ns</td>
<td>1064</td>
<td>350</td>
<td>Photoionization Laser</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>532</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>355</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Lambda Physik</td>
<td>LPX240i up to 400</td>
<td>15</td>
<td>308</td>
<td>200</td>
<td>Alternate Photolysis Laser</td>
<td></td>
</tr>
</tbody>
</table>

The probe laser was comprised of a Spectra Physics Tsunami Ti:Sapphire laser, a Spectra Physics Millennia Xs diode pump laser, and a Spectra Physics GWU doubler/tripler module, as shown in Figure 14. The Tsunami Ti:Sapphire laser was a mode-locked laser that produced 1.2 ps FWHM pulses of light at 80 MHz. The Millennia Xs pump laser was a 10 W 532 nm continuous wave (CW) diode-pumped laser. The output of the Ti:Sapphire laser was tunable from 690-1080 nm with the use of two optic sets, and the wavelength was measured using either an Ocean Optics HR 2000+ spectrometer (790-950 nm with 0.12 nm resolution) or an Ocean Optics USB 2000 spectrometer (~1 nm resolution). The Ti:Sapphire laser frequency could be either doubled to 345-540 nm or tripled to 230-360 nm using the GWU module. The power of the pump laser was feedback controlled, usually to around 7 W, to produce a final beam with stable power. Since the temporal resolution of the Ti:Sapphire laser was very high (1.2 ps), the frequency bandwidth was relatively large at 13 cm⁻¹. However, for the purposes of probing molecules in the UV-visible range where many absorption features are rather broad, this frequency bandwidth was sufficiently narrow to still probe a single transition in the molecule.
The beam from the Ti:Sapphire laser setup was rather astigmatic, meaning it diverged in more than one direction at different rates. An astigmatic beam is impossible to focus with a single spherical lens, and thus posed a problem when aligning and mode-matching the beam to the Herriott multi-pass cell. To compensate for this astigmatic divergence, Dr. Ismail designed a set of cylindrical lenses as shown in Figure 15. By aligning the axes of the first set of cylindrical lenses (labeled H) perpendicular to one of the axes of divergence that was more or less horizontal in the lab frame and by tuning the distance between the lenses, the divergence in the horizontal direction was removed. Similarly, by aligning the axes of the second set of cylindrical lenses (labeled V) perpendicular to one of the axes of divergence that was more or less vertical in the lab frame and by tuning the distance between these lenses, the divergence in the vertical direction was removed. Finally, the resultant (approximately) collimated beam was focused using a spherical lens on a long translation stage just before the multi-pass cell. A number of lenses from 500-2000 mm were available to compensate for any remaining divergence in the probe beam and to mode-match the focus of the probe beam with the cavity. By focusing the probe beam roughly in the center of the Herriott multi-pass cell, each successive pass of the probe beam also focused roughly in the center, leading to a stable cavity where the beam remained roughly the same diameter each time it was reflected from the Herriott mirrors. Since the Herriott mirrors were curved, even though the radius of curvature was a relatively slight 800 mm, the probe beam diameter would become unstable without mode-matching. Such an unstable probe beam would become very large in diameter in some regions causing it to clip undesired objects in the Herriott cell such as the edges of the mirror mounts and the exit slit of the most distant Herriott mirror. To improve this setup and to make the alignment more stable, I incorporated several combined multi-axis rotation, translation, and kinematic optical stages. Using these stages, the axis of each cylindrical
lens could be precisely rotated, the distance between them precisely set, the center of each lens placed on
the optical axis to avoid refraction and aberrations of the beam, and the plane of each lens slightly tipped
to remove deleterious back-reflections. The use of these stages also saved time by making the alignment
easier and more stable, requiring less frequent time-consuming adjustments.

Figure 15: Schematic of the set of four cylindrical lens used to correct the astigmatism of the Ti:Sapphire probe beam.
One pair (H) correct the horizontal divergence and the other pair (V) correct the vertical divergence. A fifth lens is
used to mode match the focusing of the probe beam to the Herriott multi-pass cavity. Figure is from Ismail.17

A schematic for the Herriott multi-pass setup is shown in Figure 16. The photolysis beam entered
from the left and passed through the middle of the hole in the center of each mirror. The probe beam entered
from opposite side of the cell on the right though a slit in the mirror. The probe beam bounced back and
forth intersecting the photolysis beam in the overlap region multiple times before exiting via a slit in the
left mirror. The Herriott mirrors were spherical mirrors with an 800 mm radius of curvature and a
380-550 nm 99% reflective coating on a clear BK7 substrate from Red Optronics. The number of passes
was calculated by summing the number of reflections on the Herriott mirrors and adding 1 for the exiting
beam. A Watec ½" monochrome high-sensitivity camera (WAT-902B) was used on each end of the
Herriott cell to safely view the backsides of each Herriott mirror and align the multi-pass setup. An example
image from one of these cameras is shown in Figure 17. The diameter of the ring of probe beams, which
is required to calculate the overlap pathlength of the probe beam as discussed in the next section, was
determined by analyzing a snapshot from the camera in ImageJ.28 ImageJ is a free image analysis software
developed by the National Institutes of Health. An image threshold was applied, and the image was scaled
by fitting a circle to the hole in the center of the Herriott mirror and specifying the diameter to be 1.93 cm.
Then a circle was fit to the centers of the probe beam dots, and its radius was reported by the software. This

41
method proved to be more accurate and much safer than the previously employed method of breaking vacuum and inserting a pair of digital calipers to measure the diameter of the ring of dots.

Figure 16: Herriott multi-pass cell with two spherical Herriott mirrors spaced a distance L apart. The photolysis beam enter from the left passing through the hole in the center of each mirror, and the probe beam enters from the right though a slit. The probe beam bounces back and forth intersecting the photolysis beam in the overlap region multiple times before exiting via a slit in the left mirror.

Figure 17: View of Herriott mirror from behind using a monochrome camera for safely aligning the multipass setup.
Overlap Path Length for Absorption

The characteristics of the Herriott multi-pass laser system have been extensively studied, and equations to describe the system have been published by others.\textsuperscript{16,29,30} The overlap path length of the probe laser beam within the photolyzed region was computed using the following equations, which were derived from the formulas given by Herriott et al.\textsuperscript{29} and Trutna et al.\textsuperscript{30} for the special case of a circular ring of probe beams. (The original formulas are given in a generalized form for an elliptical geometry.)

\begin{align*}
\ell_{\text{overlap}} &= N \sqrt{z_{\text{overlap}}^2 + r_{\text{overlap}}^2} \\
r_{\text{overlap}} &= 2 \sqrt{r^2 - r_c^2} \frac{L}{z_{\text{overlap}}} \\
z_{\text{overlap}} &= L \sqrt{\frac{r_{\text{YAG}}^2 - r_c^2}{r^2 - r_c^2}} \\
r_c &= r \sqrt{1 - \frac{L}{R}}
\end{align*}

In these equations, \( \ell_{\text{overlap}} \) is the overlap path length, \( N \) is the number of probe laser passes (total number of dots on both mirrors + 1), \( z_{\text{overlap}} \) is the axial distance over which the probe laser overlaps the photolysis laser, \( r_{\text{overlap}} \) is the radial distance over which the probe laser overlaps the photolysis laser, \( r \) is the radius of the ring formed by the probe beams on the Herriott mirrors, \( r_c \) is the radius of the ring formed by the probe beams inside the photolysis beam, \( L \) is the distance between the Herriott mirrors, \( r_{\text{YAG}} \) is the radius of the Nd:YAG photolysis beam, and \( R \) is the radius of curvature of the Herriott mirrors. Taking the partial derivatives of each of these equations with respect to each of the variables, and using those partial derivatives to propagate the uncertainty over each parameter through to the final overlap path length showed that the path length was most sensitive to \( r \) and \( r_{\text{YAG}} \). For a typical setup where \( r_{\text{YAG}} = 1.2 \text{ cm}, r = 1.50 \text{ cm}, N = 31, \) and \( L = 144.5 \text{ cm}, \) the path length was \( 1180 \pm 530 \text{ cm}. \) This level of uncertainty is far greater than the uncertainties typically quoted by others,\textsuperscript{13,16,30} which greatly underestimate the uncertainty in this parameter. We believe, as discussed later, that this uncertainty accounts for a number of discrepancies when absolute concentrations and thus absorption path lengths are required.
**IR Laser for Absolute Concentration Determination**

We also used a New Focus Vortex TLB-6025 CW diode laser centered at 1315.28 nm (see Figure 4 above) to probe the concentration of iodine (I) atoms made during the photolysis of iodinated precursor molecules such as vinyl iodide and allyl iodide. This laser beam was passed through the same slits in the Herriott mirrors as the probe beam, but only for a single pass. This put the beam on top of the probe beam inside the Herriott mirror slits and only 1-2 mm away from the probe beam outside the chamber. With the two beams so close together, spatial separation of the two beams was almost impossible. So, dichroic mirrors were used to counter-propagate the two beams. On the outlet side for the probe beam, the entering 1315.28 nm beam was passed through the back of broadband UV-visible dichroic mirror. This mirror allowed the infrared 1315.28 nm beam to pass while reflecting the outgoing probe beam to a Thorlabs DET110 Silicon detector. On the inlet side for the probe beam, the exiting 1315.28 nm beam was passed through the front of another broadband dichroic mirror. Similarly to the other dichroic mirror, this mirror reflected the probe beam (into the chamber) while passing the 1315.28 nm beam. The exiting 1315.28 nm beam was steered using gold and silver IR mirrors and focused onto a Thorlabs DET10C InGaAs detector.

**Herriott Cross Re-design**

In order to manipulate the alignment of the Herriott mirrors while under vacuum without disrupting the experiment (e.g. without the need to break vacuum and shut off pumping) each time an adjustment was being made, I designed a new set of Herriott crosses and Herriott mirror mounts. The semi-custom Herriott mirror mount, which was designed in conjunction with an applications engineer at Opto-Sigma, is shown in Figure 18. In essence, this semi-custom mount consisted of a rotational stage for a 2" diameter optic and a flexure mirror holder that were modified to allow the rotational stage to be directly attached to the adjustable mirror holder. The assembly was then attached to a 1-D translation stage. This combination of opto-mechanical components allowed the Herriott mirror to be tipped, tilted, rotated, and translated. The ability to adjust the tip and tilt degrees of freedom was required to precisely align the plane of the Herriott mirror with the plane of the opposing Herriott mirror. The ability to adjust the rotational degree of freedom was required to rotate the entrance/exit slit in each mirror to allow the unobstructed passage of the probe beam into/out of the Herriott cell. The ability to adjust the one-dimensional translational degree of freedom
was required to finely tune the distance between the two Herriott mirrors, which determined the fundamental number of passes for an aligned cell with a given radius of probe beam dots on the Herriott mirrors. When more than one circle of beams was used (i.e. more than one transit around the Herriott mirrors), then the translational degree of freedom could also be used to adjust the distance between the dots from the additional transits.

Figure 18: Semi-custom Herriott mirror mount consisting of a 2" diameter rotation stage close-mounted to a flexure mirror mount on a 1-D translation stage.

The semi-custom Herriott mirror mounts had special adjustment rods installed instead of the standard knobs for adjusting the degrees of freedom. These rods were ¼" in diameter and had flat spots machined into the side of each rod to allow it to be coupled to a teleshaft and secured in place using a set screw. The Herriott mirror mounts and teleshafts were placed inside a custom Herriott cross, as shown in Figure 19. The other end of each teleshaft was connected to a rotary vacuum feed through. A picture of a teleshaft, or telescoping shaft with two universal joints (one at each end), is shown in Figure 20. The rotary vacuum feed throughs allowed each degree of freedom for the semi-custom Herriott mirror mounts to be adjusted outside the vacuum chamber, thus eliminating the need to break vacuum each time an adjustment to the Herriott multi-pass system was required. In the old laser kinetics spectrometer apparatus designed by Dr. Ismail, adjustments to the Herriott mirrors were made by breaking vacuum and sometimes even
removing the Herriott crosses. This was a rather cumbersome way to align the Herriott multi-pass cell, since the entire system needed to be vented to atmosphere, the Herriott cross opened, the adjustment made blindly (the vacuum alignment was often lost at atmospheric pressures), and the system put back together and re-evacuated. Often, this sequence would need to be repeated numerous times in a trial-and-error fashion until an acceptable alignment under vacuum was obtained. Since it takes some time to even reach a vacuum suitable for mass spectrometry (e.g. it may take days to get low enough baseline pressures for the detector) and since it would be prohibitively time-consuming to turn off all of the equipment associated with the mass spectrometer (high-voltage, turbo pumps, backing pumps, etc.), the methodology of breaking vacuum to adjust the Herriott alignment, which requires adjustment at least every day, was not practical. Thus, the Herriott cross re-design was necessary to allow the Herriott mirror alignment to be adjusted when using the mass spectrometer.
Figure 19: Custom Herriott cross assembly with semi-custom Herriott mirror mount inside shown from a) the side furthest from the vacuum chamber, b) the side close the vacuum chamber, and c) in cross sectional view with relevant dimensions shown.

Figure 20: Huco teleshaft with telescoping shaft in the middle and two universal joints, one at each end. We actually used UJT-6 teleshafts from Accurate fasteners. Picture is from Huco website.31
At either end of the two Herriott cross assemblies used in the apparatus, a Brewster window was used to allow the passage of laser light into and out of the chamber with minimal back-reflections. The Brewster angle, defined here as the angle of incidence that best propagated p-polarized 266 nm light through the UV-fused silica windows (refractive index ~1.5 @ 266 nm according to Newport Corporation), was calculated to be 56° using the following formula

\[ \theta_B = \tan^{-1} \left( \frac{n_2}{n_1} \right) \]

where \( \theta_B \) is the Brewster’s angle, \( n_2 \) is the refractive index of the UV-fused silica window, and \( n_1 \) is the refractive index of the incident medium (air or vacuum for an entering or exiting beam, respectively). The angle of incidence is defined as the angle between the normal of the optical surface and the vector of the incident light, leading to the angle between the Brewster window surface and the optical axis of 56° + 90° = 146°, as shown in Figure 19. With both windows at this Brewster’s angle and the windows oriented as shown in Figure 19, only vertically polarized photolysis beams could be used and still obtain good transmission through the windows. If horizontally polarized light were to be used, then the polarization of the beam would either need to be rotated (as we did when using the Big Sky Nd:YAG laser for photolysis) or the Brewster windows would need to be rotated by 90°. However, even with good polarization alignment, the Brewster windows did not perfectly transmit the photolysis beam. Since the beam was rather strong (e.g. >30 mJ/pulse of UV light), even the weakly reflected beam was still rather dangerous and required a makeshift beam block above both Brewster windows to capture the reflected beams.

**Photoionization**

Typically, roughly 10 electron-volts (eV) of energy are required to ionize most stable molecules. Thus, high-energy radiation in the VUV range is required to be able to photoionize most molecules. To generate this type of radiation, the third harmonic (frequency-tripled) 355 nm output of Nd:YAG laser was frequency tripled in an Xenon/Argon gas mixture to produce the ninth harmonic 118.2 nm (10.487 eV) wavelength. To accomplish the conversion of 355 nm photons into 118.2 nm photons, the collimated 355 nm beam from either the Spectra Physics Quanta-Ray Lab 170-10 Nd:YAG laser or the Quantel Brilliant Nd:YAG laser was focused into the Xe:Ar gas mixture using a plano-convex UV-fused silica lens, as shown in Figure 21. The beam must be focused into the gas mixture because the nonlinear conversion
process by which the frequency-tripling occurs can only take place at sufficiently high power densities (W/cm²), as is the case for most nonlinear optical conversion processes. The nonlinear conversion process takes place when the electric field from the incident 355 nm radiation induces polarization of the Xe:Ar conversion medium according to

\[ P = \chi^{(1)} E_i + \chi^{(2)} E_i^2 + \chi^{(3)} E_i^3 \]

where \( P \) is the polarization density, \( \chi^{(n)} \) is the nth-order susceptibility of the conversion medium, and \( E_i \) is the electric field from the incident radiation. The resultant power generated by the tripling process is given by the following equation

\[ I(3\omega) \propto N^2 \left| \chi_a^{(3)}(\omega) \right|^2 I(\omega)^3 F(L, b, \Delta k) \]

where \( I(3\omega) \) is the power of the tripled light (118.2 nm), \( N \) is the number density of the conversion medium, \( \chi_a^{(3)} \) is the third-order susceptibility, \( \omega \) is the fundamental frequency, \( I(\omega) \) is the power of the incident light (355 nm), and \( F \) is a geometrical factor that depends on the length of the medium \( (L) \), the confocal parameter \( (b) \) and the wave vector mismatch \( (\Delta k) \). For a TEM₀₀ incident beam in the limit of tight focusing (the confocal parameter is much less than the length of the medium, \( b << L \)) and negative dispersion \( (\Delta k < 0) \), the geometrical factor is given by Equation 12.

\[ F(L, b, \Delta k) = (\pi b \Delta k)^2 e^{ibk} \]

\[ b = \frac{2\pi w_0^2 n}{\lambda_i} \]

\[ \Delta k = k(3\omega) - 3k(\omega) \]

where \( w_0 \) is the beam waist at the point of focus, \( n \) is the refractive index of the medium for 355 nm (1.0), \( \lambda_i \) is the wavelength of the incident radiation (355 nm), and \( k(3\omega) \) and \( k(\omega) \) are the length of the k-vectors for the tripled light and the incident light, respectively. Additional formulas, such as those to calculate the beam waist, if unknown, can be found in the article by Lockyer et al.
Figure 21: Side cross section of vacuum chamber showing the VUV generation setup with a) descriptions of each component and b) important dimensions in inches for focusing and alignment.
While the optimum conversion efficiency of 355 nm photons to 118.2 nm photons depends on a number of parameters, previous researchers have found that it is most important to phase match the negative dispersion of xenon by mixing in another gas with positive dispersion such as argon.\textsuperscript{32-34} The optimum composition of the Xe:Ar mixture to achieve phase matching of course itself depends on a number of parameters, but Lockyer et al. showed that at higher conversion medium pressures (e.g. >10 Torr), the optimum composition for 355 nm to 118.2 nm conversion should theoretically be around 1:10.9 Xe:Ar. In practice, many research groups have found a 1:10 Xe:Ar (or 9% Xe, balance Ar) mixture to work well, and some researchers have found pure Xe to give high enough conversion efficiencies to have enough 118.2 nm photons per laser pulse for their purposes. In the new apparatus, we found a 1:10 Xe:Ar mixture at around a total pressure of 80-100 Torr to give the highest 355 nm to 118.2 nm conversion, with the optimum total pressure depending on the focal length of the lens used to focus the 355 nm beam.

After the 118.2 nm light was generated, it was passed through a MgF\textsubscript{2} lens along with the residual 355 nm light. MgF\textsubscript{2} was used because it transmits about 60-80\% of the 118.2 nm light, while other common optical materials like UV-fused silica would absorb nearly all of the VUV light. MgF\textsubscript{2} also has the curious property of having substantially different refractive indices for the two wavelengths of light: \( n = 1.387 \) for 355 nm light and \( n = 1.679 \) for 118.2 nm light. This means that despite having similar k-vectors and divergence when striking the MgF\textsubscript{2} lens, the 355 nm light and the 118.2 nm light focused at different points. The distance from the MgF\textsubscript{2} lens at which each beam focused was calculated using ABCD matrices

\[
\begin{pmatrix}
0 \\
\theta_2
\end{pmatrix} = \begin{pmatrix}
1 & L \\
0 & 1
\end{pmatrix} \begin{pmatrix}
-\frac{1}{f_2(\lambda)} & 0 \\
1 & 1
\end{pmatrix} \begin{pmatrix}
1 & d \\
0 & 1
\end{pmatrix} \begin{pmatrix}
\frac{1}{f_1} & 0 \\
1 & 1
\end{pmatrix} \begin{pmatrix}
0 \\
\frac{r}{\theta_1}
\end{pmatrix}
\]

where \( r \) is the radius of the incident 355 nm beam, \( \theta_1 \) is the angle of the incident beam (zero for a collimated beam), \( f_1 \) is the focal length of the UV-fused silica lens used to focus the incident 355 nm beam, \( f_2(\lambda) \) is the focal length of the MgF\textsubscript{2} lens for the wavelength of interest (\( \lambda \)), \( d \) is the distance between the UV-fused silica lens and the MgF\textsubscript{2} lens, and \( L \) is the distance from the MgF\textsubscript{2} lens where the beam of wavelength \( \lambda \) is focused (\( r = 0 \)) with an angle \( \theta_2 \). The focal length of the MgF\textsubscript{2} lens for each wavelength \( \lambda \) was calculated using the Lensmaker’s equation for a plano-convex lens

\[
f_2(\lambda) = \frac{R}{n(\lambda) - 1}
\]
where \( R \) is the radius of curvature of the lens, and \( n(\lambda) \) is the refractive index of MgF\(_2\) at the wavelength \( \lambda \). Solving Equation 16, for \( L \) and \( \theta_2 \) yields the following equations, which were used to determine the distance from the MgF\(_2\) lens and the angle at which the 355 nm and 118 nm beams focused.

\[
L = \frac{(d - f_1)f_2(\lambda)}{d - f_1 - f_2(\lambda)}
\]

\[
\theta_2 = \frac{(d - f_1 - f_2(\lambda))r}{f_1f_2(\lambda)}
\]

Since the lenses were inside various components, there was no easy way to measure the distance between the lenses to compute where each beam focused. To determine this distance, the distance from the marked face of the LM1-A mount holding the UV-fused silica lens (P1) to the flange face of the custom flange holding the MgF\(_2\) lens (P2) that was closest to the chamber (shown to be 18.00” in panel (b) of Figure 21) was measured. Since the distance from the marked face of the LM1-A mount (P1) to the flat side of the UV-fused silica lens was known to be 0.46 ± 0.02” and since the distance from the flange face (P2) to the flat side of the MgF\(_2\) lens was known to be 0.224”, the distance between the lenses was computed by subtracting 0.68” from the measured distance between point P1 and P2. This gave the distance between the lenses (\( d \)) to within ± 0.08”.

\[
d(\text{in.}) = \text{dist}(P1 \text{ to } P2) \text{ in.} - 0.68 \text{ in.}
\]

The agreement between the calculated focal point and the measured focal point of the residual 355 nm outside the chamber was quite good, as shown in Figure 22. Since the 118.2 nm beam was invisible and did not propagate outside of vacuum, the distance of the 118.2 nm focal point from the MgF\(_2\) lens could not be measured. Instead, the comparison of the measured 355 nm beam focal point distance with the calculated distance was used to ensure the calculations were accurate, and the calculated focal point distance for the 118.2 nm beam was used to ensure the 118.2 nm beam was roughly focused at the point of ionization. For the lenses used in the final configuration (a CVI Melles Griot PLCX-25.4-103.0-UV lens for the UV-fused silica lens and a Thorlabs LA6007 lens for the MgF\(_2\) lens), the 118.2 nm beam was roughly focused in the photoionization region 9.1” away and the residual 355 nm beam was focused about 60” away (44” away from the outside flange face). This meant that the 355 nm beam was almost as large as the gap between the TOF-MS plates when passing through the photoionization region, as shown in Figure 23. With the distance between the plates of the mass spectrometer set by the manufacturer, Kore, the alignment of
the residual 355 nm light was quite difficult. Since the 355 nm to 118.2 nm conversion process was only about 3\% efficient at best, there was a large number of 355 nm photons left over that need to be steered out of the chamber to a beam dump. So, a bellows was used to center the MgF$_2$ lens and an XYZ translation stage was used to center the UV-fused silica lens along the optical axis to ensure both the 118.2 nm and the residual 355 nm beams passed cleanly through the gap between the plates of the mass spectrometer. If either beam clipped the plates, spurious signals that were suspected to be due to electron impact ionization from photoelectrons introduced into the high voltage field of the TOF-MS were observed. The Z-axis of the XYZ translation stage for the UV-fused silica lens was also used to fine tune the distance between the lenses.

![Distance of Focal Point from Bare Outlet Flange Face](image)

Figure 22: Measured (points) and calculated (line) distance of the 355 nm focal point from the flange face on the outlet side of the chamber with the VUV detector assembly removed. The outlet flange face was 15.5" from the MgF$_2$ lens.
The residual 118.2 nm light was partially reflected onto a NIST aluminum oxide-coated VUV photodiode using an uncoated UV-fused silica elliptical flat as the partial reflector. The remaining 118.2 nm light along with most of the residual 355 nm light passed through the elliptical flat to a beam dump outside the vacuum chamber. The NIST photodiode was used because it was supposed to be blind to 355 nm light and only give a signal for VUV photons. But, we observed baseline signals when the Xe:Ar cell was evacuated and only 355 nm photons were present. However, this did not pose much of a problem, as the VUV photodiode was ultimately used as a diagnostic tool to check the VUV energy/pulse from day to day. Only a portion of the 118.2 nm beam was reflected onto the VUV photodiode surface, instead of the entire beam, to avoid exceeding the damage threshold of the photodiode. The original intended use of the VUV photodiode was to measure the VUV energy for every laser pulse and to use that signal to normalize each corresponding TOF-MS spectrum for shot-to-shot fluctuations in VUV intensity. However, normal averaging of the TOF-MS spectra for around 500 shots without explicitly correcting the shot-to-shot VUV intensity fluctuations was found to be sufficient to get acceptable statistics.

The Kore TOF-MS used in the apparatus was also equipped with an electron impact ionization source. This e⁻-impact source essentially consisted of a filament in front of a slit with a plate behind it held
at a specific voltage. While the voltage of the plate could be changed, it required opening the power supply for the TOF-MS and changing some components. Therefore, the default setting of 70 V, which provided the de facto standard ionization energy for electron impact of 70 eV, was used. While time-resolved electron impact experiments could be performed, the data acquisition hardware was not optimized for such experiments. That is, data could only be collected at the repetition rate of the photolysis laser (10 Hz), even though electron-impact experiments could be conducted at much high repetition rates (e.g. 100 kHz) by pulsing the TOF-MS independently. This would allow the time evolution of the mass spectra to be observed in real time, much like what is done with any other continuous ionization source (as mentioned in an above section). Electron impact spectra are also difficult to interpret, as the relatively high ionization energy causes many of the parent ions for each molecule to fragment into smaller ions. Often, a single fragmentation peak arises from a number of parent peaks, making deconvolution of the mass spectra necessary and usually difficult. However, the electron impact source was a useful diagnostic tool for our system. For species that did not ionize when using 118.2 nm (10.487 eV) light, we could observe signals from them using electron impact ionization. Also, when troubleshooting issues such as a lack (or even complete absence) of signal when using photoionization, we could use the alternative electron impact ionization source to determine if the VUV ionization setup or if the TOF-MS voltage setup was the problem.

**Time-of-Flight Mass Spectrometer**

A schematic of the Kore TOF-MS used in the apparatus is shown in Figure 24. The positive ions produced by either photoionization or electron impact ionization were accelerated into the snout of the TOF-MS by the electric field applied between the extraction plate (held at ground) and the TOF-MS components (held at negative voltages). For the case of photoionization, the extraction plate voltage was held constant while, for the case of electron impact ionization (which is continuous), the extraction voltage was pulsed to give a time \( t = 0 \) for each time-of-flight mass spectrum. For photoionization, the time of the laser pulse is time \( t = 0 \) for each mass spectrum. After entering the snout (or entrance aperture) of the TOF-MS, the ions were spatially focused by an ion lens, which consisted of a Faraday cage with precisely-machined curved edges. Thereafter, the ion trajectories were steered using a set of X and Y deflector plates. After passing through the field-free region (FFR), the ions were reflected and focused both spatially and temporally using a reflectron. The reflectron consisted of a retard plate to slow the ions and a stack of
plates with a steep gradient of voltages to reflect the ions. Finally, after traveling back through the FFR region, the ions struck the discrete dynode electron multiplier detector. The signal from the detector was then amplified using an analog pre-amplifier when using photoionization (relatively large packets of ions for each m/z) or using a digital pre-amplifier when using electron impact ionization (single-ion counting for each m/z, i.e. the Poisson limit). The signal from the analog pre-amplifier was digitized and averaged over 500 photolysis shots using a 2.5 GHz (set to 1.0 GS/s) Tektronix DPO7254 oscilloscope. The signal from the digital pre-amplifier was histogrammed using a Kore time-to-digital converter. The amplifiers could be swapped relatively easily, but they could not be used together at the same time. Also, electron impact data could be taken using the analog pre-amplifier, and this is what was done when time-resolved electron impact ionization mass spectra were recorded. The TDC box for digital pre-amplification was not configured for time-resolved measurement. Instead, it would simply average together the mass spectra from every time point. To use the TDC for time-resolved measurements, it would need to be reprogrammed with the help of the TOF-MS manufacturer (Kore) or replaced with a more sophisticated TDC box.

Figure 24: Schematic of Kore TOF-MS design showing the relative positions of the ion optics, the reflectron, and the detector. The orientation shown is horizontal, whereas the TOF-MS was used in a vertical orientation in the apparatus. Figure is from the Kore manual.

The ions in the TOF-MS are separated according to m/z due to the application of the electric field. Because the ions are all exposed to the same electric field, the same kinetic energy is imparted to all of the ions (since they have the same charge), and thus the lighter ions have a greater velocity than the heavier ions causing the ions to arrive at the detector according to their masses. The correspondence between the m/z ratio and the time-of-flight in the mass spectrometer are given by the following equation

\[
\text{m/z} = \frac{2 \cdot \text{ETP}}{\text{ToR}}
\]
\[ m/z = \left( \frac{t - t_0}{C_b} \right)^2 \]

where \( t \) is the time of flight for the ion of mass-to-charge \( m/z \), \( t_0 \) is the delay time between time \( t = 0 \) (e.g. photoionization laser pulse) and the arrival of the fictitious \( m/z = 0 \) peak, and \( C_b \) is the calibration factor. Both \( t_0 \) and \( C_b \) and instrument dependent and are determined by fitting Equation 20 to a mass spectrum with known \( m/z \) peaks.

Converting a TOF-MS spectrum to concentrations of each species is a bit involved, and so it is discussed at length in a later section. Also, it worth mentioning that the head of the TOF-MS was modified slightly to place the ionization region 1 cm further away from the mounting flange of the TOF-MS. To accommodate the electron-impact vacuum feed through on the side of the TOF-MS mounting flange, a 1 cm thick spacer flange was placed between the TOF-MS mounting flange and the chamber. Drawings for the parts required to accomplish this modification of the TOF-MS are shown in Appendix I.

Timing and Data Acquisition

The timing of the experiment is controlled using a BNC 575 digital delay generator. Typical settings for the BNC 575 delay generator are shown in Table 4. The central clock of the delay generator is used to set a trigger at 20 Hz. The Quantel Brilliant laser for photoionization fires at 20 Hz while the rest of the experiment runs at 10 Hz, which is the maximum repetition rate of the Spectra Physics Quanta-Ray LAB 170-10 laser that is used for photolysis. The delay for the Q-switch triggers for each Nd:YAG laser is fixed relative to the respective flashlamp triggers. The delay of the flashlamp trigger for the photoionization laser is adjusted by the LabVIEW program to scan through different reaction times. The delay of the flashlamp trigger for the photolysis laser is fixed to force time \( t = 0 \) to coincide with when the delay of the flashlamp trigger for the photoionization laser is set to zero (i.e. the delay for the photolysis laser accounts for the net delay in firing the two lasers). The TOF-MS is triggered synchronously with the Q-switch (i.e. the actual laser pulse) from the photoionization laser. The other channels (F through G) are used to trigger the high-voltage pulser and steer large packets of ions from background gases away from the detector and thus avoid saturating the detector signal.
Table 4: Typical settings for the BNC-575 delay generator.

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Ch. A</th>
<th>Ch. B</th>
<th>Ch. C</th>
<th>Ch. D</th>
<th>Ch. E</th>
<th>Ch. F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>TO</td>
<td>Ch. A</td>
<td>TO</td>
<td>Ch. C</td>
<td>Ch. D</td>
<td>TOF-MS Trigger</td>
</tr>
<tr>
<td>Width (µs)</td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>20</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Delay (µs)</td>
<td>112.592</td>
<td>178</td>
<td>Adjustable (if 0 reaction time)</td>
<td>280</td>
<td>0</td>
<td>Adjustable</td>
</tr>
<tr>
<td>Output (V)</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>4</td>
<td>TTL Pulse</td>
<td>10</td>
</tr>
<tr>
<td>Duty Cycle</td>
<td>1 On, 1 Off (10 Hz)</td>
<td>1 On, 1 Off (10 Hz)</td>
<td>Continuous (20 Hz)</td>
<td>1 On, 1 Off (10 Hz)</td>
<td>1 On, 1 Off (10 Hz)</td>
<td>1 On, 1 Off (10 Hz)</td>
</tr>
</tbody>
</table>

The entire experiment including the temperature and pressure of the reaction cell, the gas flows, the IR laser settings, the TOF-MS calibration, and the data acquisition is controlled using a LabVIEW program. This program was written by Zachary Buras, Mickael Matrat, and myself, with some sub-VI's taken from the program written by Huzeifa Ismail for his laser kinetics spectrometer. A snapshot of the user interface for this program is shown in Figure 25.

![Figure 25: Snapshot of the user interface for LabVIEW program used to control the experiment and acquire data. Note the tabs which correspond to separate panels to control each aspect of the apparatus.](image-url)
The data taken using the instrument was analyzed using a MATLAB program written by Mickael Matrat. This program allowed mass spectra from multiple reaction times to be loaded simultaneously and the various m/s peaks assigned and integrated automatically. It also allowed simple pseudo-first order, second-order, and biexponential fits to be applied to the laser absorption data. A snapshot of the user interface for this program is shown in Figure 26. This program proved extremely useful for the on-the-fly evaluation of the data being taken, saving time by allowing problems to be identified and fixed before taking more data.

Figure 26: Snapshot of the user interface for the MATLAB program used to analyze the time-resolved TOF-MS and LAS data.
Finally, the transient absorption data and the time-resolved peak areas for every m/z peak of interest were analyzed using a MATLAB program that I wrote. This program could fit a more complex model to all of the data simultaneously at a given temperature and pressure (e.g. it could simultaneously fit several data traces for different excess-reactant concentrations) using a nonlinear least squares algorithm. Fitted parameters such as T- and P-dependent rate coefficients, product branching fractions, instrument factors, and the respective uncertainty in these parameters given as 95% confidence intervals were determined using this code.

Characterization and Testing

Laser Absorption Spectrometry

The laser absorption spectrometry (LAS) portion of the apparatus was previously characterized by Dr. Ismail in his thesis. He determined that the use of differential amplification greatly reduced the noise in the Ti:Sapphire probe laser signal, as the subtraction of the reference beam taken before the absorption cell removed most of the systematic fluctuations in the probe laser intensity. He found most of the intensity fluctuations in the probe beam were from the Spectra Physics Millennia Xs diode pump laser power supply. He determined that the pump laser was the major source of the noise by comparing the noise spectrum when using the Millennia pump laser to the noise spectrum when using a lower-noise Coherent Verdi pump laser that was borrowed from another research group. Thus, the noise in the absorption signals for the new apparatus could likely be improved further by replacing the Millennia pump laser with a state-of-the-art low-noise pump laser, such as the Finesse Pure CEP lase from Laser Quantum. Even when using the relatively noisy Millennia pump laser, differential amplification was able to remove most of the systematic noise, as shown in Figure 27. However, some noise peaks still exist at particular frequencies, generating noise in experiments with kinetic timescales similar to those frequencies (e.g. there is a noise peak at $3 \times 10^3$ Hz corresponding to noise that often shows up on the ~0.33 ms timescale). Some of these remaining noise peaks are not likely due to the pump laser, but due to other sources such as electronic noise (e.g. multiples of 60 Hz such as 120 Hz) and thermal lensing of the probe laser beam.
Thermal lensing is the movement of the laser beam due to the refraction of the beam from thermal gradients. Since the reaction cell is heated and since some of the components around the apparatus radiate heat, the laser beams pass through a number of transient thermal gradients. These transient thermal gradients, which move randomly with time much like the wavy lines above a paved surface on a hot day, refract the laser beam randomly, causing its position to wobble slightly. For the probe beam that is reflected
by the Herriott mirrors and passes through a steep thermal gradient within the reaction cell many times, the degree of random movement due to thermal lensing can be quite pronounced (e.g. ~1-2 mm of movement in the final beam at high reaction cell temperatures). The problem of thermal lensing is made worse by greater thermal gradients and by passing through gases with higher polarizabilities. The refractive index of a gas is a function of its polarizability, and gases with higher polarizabilities tend to exhibit greater changes in refractive index as the temperature is changed. Therefore, helium was typically used as a buffer gas for most experiments due to its relatively low polarizability. While other inert gases such as argon or nitrogen would have served equally well as a diluent gas, these gases possess greater polarizabilities than helium and thus result in higher levels of problem-causing thermal lensing.

Thermal lensing of the probe beam creates a number of practical issues, particularly regarding the alignment of the probe beam. If the probe beam is too close to an object, the edge of a mirror, or the entrance/exit slit of a Herriott mirror, then the movement of the beam due to thermal lensing can cause the measured intensity to fluctuate as the beam moves on and off of obstructions and/or the mirror surfaces. However, these problems can typically be ameliorated with careful alignment and the placement of the probe beam in the middle of the entrance/exit slits of the Herriott mirrors to allow for maximal movement. In some circumstances, such as at high reaction cell temperatures and high concentrations of the excess reactant (e.g. high alkene concentrations that cause the gas mixture in the reaction to have a higher polarizability), this type of thermal lensing cannot be removed. This more or less random thermal lensing is manifested, even in averaged absorption traces, as wiggles in the trace and/or as random baseline level shifts due to low-frequency fluctuations. In theory, these artifacts would disappear in the limit of an infinite number of averaged traces, but, in practice, averaging 500 traces was not always enough to average away these thermal lensing effects. In fact, some artifacts from thermal lensing in the averaged absorption signal actually sharpen with additional averaging. For example, each photolysis shot is partially absorbed by the gas mixture causing the photolyzed region to be nearly instantaneously heated while the surrounding gas temperature remains unchanged. Since the probe laser beams pass through both regions, the slight temperature change of the photolyzed region incurs a slight change in refractive index that causes the probe beam to move in a reproducible manner that is synchronized with the photolysis laser pulse. Thus, the resultant artifact in the absorption signal due to thermal lensing induced by the photolysis laser actually sharpens with averaging. The use of helium minimizes the intensity of this type of thermal lensing, but it is impossible to remove it completely.
Even with the residual noise from the pump laser for the Ti:Sapphire laser and with the noise from thermal lensing of this laser, it is still possible to detect transient absorption signals as small as 0.0001.\textsuperscript{17} For the 30 meter overlap path length used to determine this limit by Ismail et al., which can be achieved when using a relatively large number of passes of the probe beam (e.g. 55 passes), this detection limit corresponds to a concentration times cross section $C_i \sigma_i = 3.3 \times 10^{-8}$ cm$^{-1}$. For vinyl radical, which has an absorption cross section of $2.9 \times 10^{-19}$ cm$^2$, this corresponds to a minimum concentration of $\sim 10^{11}$ molecules/cm$^3$. For reference, most experiments with vinyl radicals were conducted using $\sim 10^{13}$ molecules/cm$^3$.

Under pseudo-first order conditions, the reaction kinetics follow a single-exponential decay ($e^{-k't}$), where $k' = 1/\tau$ is the pseudo-first order rate coefficient and $\tau$ is the timescale (or time constant). Although most of the noise in the absorption trace is due to the laser and thermal lensing sources discussed above, the uncertainty in the pseudo-first order rate is mostly due to the uncertainty in the concentration of the reactant in excess. Since $k' = k_i [\text{excess reactant}] + k_{rn}$, where $k_i$ is the rate coefficient for the reaction of interest, [excess reactant] is the concentration of the excess reactant (e.g. an alkene such as ethene), and $k_{rn}$ is the sum of all other reaction rates leading to the loss of radicals, the fitted value for $k'$ is sensitive to the concentration of excess reagent. According to the propagation of error analysis to determine the uncertainty in the composition of the gas mixture due to the error in the mass flow controllers, the error in the concentration of the excess reactant is typically 5-10%. Thus, typical uncertainties for pseudo-first order reaction rates are about 5-10%.

For second-order reactions, the decay of the concentration of radical with time, $[\text{rad}]_n$, follows $[\text{rad}]_t/[\text{rad}]_0 = 1/(1 + k_2[\text{rad}]_0t)$, where $k_2$ is the second order reaction rate coefficient and $[\text{rad}]_0$ is the initial concentration of radical species. Thus, for second-order reactions, the absolute concentration is required to determine $[\text{rad}]_0$ and $k_2$ independently. Without knowledge of the absolute concentration, only the composite rate $k'_2 = k_2[\text{rad}]_0$, which is of much use from a scientific standpoint, can be determined. The value of the absolute concentration depends on the absorption cross section ($\sigma$) and the absorption path length ($l$), according to Beer’s law (Equation 1). Although the level of uncertainty in both of these parameters can be rather large (e.g. >10%), the uncertainty in the absorption cross section often dominates the uncertainty in the absolute concentration, especially for molecules where the absorption cross section can often be uncertain by as much as a factor of 2 or more.
Since the Ti:Sapphire laser is actually pulsed at 80 MHz, or every 12.5 ns, the fastest reaction timescale that can be measured is limited to $10^5$ this value in order to have at least 10 points to fit during the decay. For a pseudo-first order system, this timescale corresponds to a maximum reaction rate of $k' = 8 \times 10^6 \text{ s}^{-1}$. For a typical reaction cell pressure of 25 Torr and the lowest temperature of 300 K, the maximum concentration of excess reactant is given when absolutely no diluent is used and equals $P/RT = 8.0 \times 10^{17} \text{ molecules/cm}^3$. If only 1% of this maximum concentration is used to determine the reaction rate, which is within the currently available dynamic range of the mass flow controllers, the concentration of excess reactant would be $8.0 \times 10^{15} \text{ molecules/cm}^3$. The corresponding fastest reaction rate coefficient $k_f$ that could be measured under these conditions is $1.0 \times 10^{-9} \text{ cm}^3/\text{molecule-s}$. The slowest possible reaction rate that could be measured is limited by the flow timescale, as the reaction must proceed sufficiently to measure a change in the concentration of the probed radical before the reactants are swept out of the reaction cell. For the vinyl + ethene experiment discussed in the next chapter, the reaction cell contents were typically cleared every 0.6 seconds. For a reaction on this timescale, the corresponding minimum pseudo-first order reaction rate coefficient is $k' = 1.67 \text{ s}^{-1}$. Of course, for a reaction this slow, other processes, such as diffusion out of the photolyzed region and wall losses would contribute to the decay of radicals. Also, for the practical reason of taking data as quickly as possible, the photolysis laser is often fired at its maximum repetition rate of 10 Hz, or every 0.1 s. This laser repetition rate imposes a practical limit that the radical must be mostly gone by the time of the next laser shot (i.e. 3 time constants elapsed to consume 95% of the radicals, or $3 \tau = 0.1 \text{ s}$). For this constraint, the corresponding minimum reaction rate is $k' = 30 \text{ s}^{-1}$. Using the maximum concentration of excess reactant at 300 K and 25 Torr of $8.0 \times 10^{17} \text{ molecules/cm}^3$ to speed up the reaction as much as possible, this minimum pseudo-first order rate corresponds to a minimum reaction rate coefficient $k_f$ of $\sim 4 \times 10^{-17} \text{ cm}^3/\text{molecule-s}$. Thus, the absolute greatest range of bimolecular reaction rate coefficients that can be measured using the LAS method is as follows.

$$4 \times 10^{-17} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} < k_f < 1 \times 10^{-9} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
Photoionization Time-of-Flight Mass Spectrometry

The PI TOF-MS portion of the apparatus was characterized using a custom calibration gas mixture and using the vinyl iodide precursor. The calibration gas mixture, which contained 9 species with known concentrations in helium, was typically used to calibrate the TOF-MS and to determine the time-to-mass conversion parameters (Equation 20). The species in the calibration mixture were chosen to be almost uniformly spread over the m/z range typically used in experiments (i.e. up to 100 amu) and to have known photoionization cross sections at 10.487 eV (118.2 nm). The properties of the calibration mixture are given in Table 5, with the photoionization cross sections reported by 2003 Cool et al., 2005 Cool et al., 2010 Zhou et al., and 2012 Yang et al.

Table 5: Calibration gas mixture properties including photoionization cross sections and the mole- and mass-based fractions.

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Mass (amu)</th>
<th>118.2 nm (10.487 eV) Cross Section</th>
<th>Molar Fraction</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mb (10^-18 cm²)</td>
<td>σ_i/σ_p</td>
<td>Reference</td>
</tr>
<tr>
<td>Monomethylamine</td>
<td>CH3NH2</td>
<td>31.1</td>
<td>10.7</td>
<td>1.0</td>
<td>2012 Yang et al. (CRF)</td>
</tr>
<tr>
<td>Propene</td>
<td>C3H6</td>
<td>42.1</td>
<td>10.7</td>
<td>1.0</td>
<td>2003 Cool et al. (CRF)</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>C4H6</td>
<td>54.1</td>
<td>16.3</td>
<td>1.5</td>
<td>2012 Yang et al. (CRF)</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>C3H8O</td>
<td>60.1</td>
<td>3.3</td>
<td>0.3</td>
<td>2005 Cool et al. (CRF)</td>
</tr>
<tr>
<td>Furan</td>
<td>C4H4O</td>
<td>68.1</td>
<td>14.4</td>
<td>1.3</td>
<td>2012 Yang et al. (CRF)</td>
</tr>
<tr>
<td>Benzene</td>
<td>C6H6</td>
<td>78.1</td>
<td>31.8</td>
<td>3.0</td>
<td>2005 Cool et al. (CRF)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C6H12</td>
<td>84.2</td>
<td>21.3</td>
<td>2.0</td>
<td>2005 Cool et al. (CRF)</td>
</tr>
<tr>
<td>Toluene</td>
<td>C7H8</td>
<td>92.1</td>
<td>31.2</td>
<td>2.9</td>
<td>2010 Zhou et al.</td>
</tr>
<tr>
<td>Heptane</td>
<td>C7H16</td>
<td>100.2</td>
<td>9.9</td>
<td>0.9</td>
<td>2010 Zhou et al.</td>
</tr>
<tr>
<td>Helium He</td>
<td>He</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
<td>999091</td>
</tr>
</tbody>
</table>

The signal in the PI TOF-MS for any given species i \((S_i)\) is given by the following equation

\[ S_i = \sigma_i F R_i C_i \]

where \(\sigma_i\) is the photoionization cross section for species \(i\) at 10.487 eV, \(F\) is an instrument-dependent factor, \(R_i\) is the mass-dependent response factor for species \(i\), and \(C_i\) is the concentration of species \(i\) in the reaction cell. The instrument factor \((F)\) depends on the gas-sampling characteristics such as the size, geometry, number density, and speed of the molecular beam. It also depends on the distance the gas travels before being photoionized as well as on the VUV photoionization power and the TOF-MS detector efficiency.
In practice, this factor can be treated as a calibration factor for the instrument that varies from day-to-day as the gas-sampling alignment is changed, the VUV power varies with the age of Xe:Ar mixture, and the detector gain drifts.

The random baseline noise in a given mass spectrum is mostly due to shot noise, or the random electronic noise due to the natural fluctuations in electric charge that occurs in electrical devices. The high-voltage amplification of the discrete dynode electron multiplier detector and the additional amplification of the resultant signal using the analog pre-amplifier dramatically increase the level of this noise, as evidenced by the sharp jump in noise observed when energizing these devices. However, this amplified shot noise was observed to apparently increase by up to a factor of two when increasing the reaction cell pressure by a factor of 4. This indicated that some of the baseline noise was likely due to random ion hits. Random ions are increased at higher pressures where the higher gas densities lead to a greater rate of random ions being generated by the high-voltage electric field present inside the TOF-MS. When averaging typical PI TOF-MS signals \( n \) times, the noise decreased with a \( 1/\sqrt{n} \) dependence, as expected for random noise (Figure 28). Based on this analysis, 500 averages was taken as point of diminishing returns in further reducing the level of baseline noise at the expense of longer experiment durations. Thus mass spectra were typically averaged 500 times in most experiments.

![Figure 28: Noise in PI TOF-MS signal measured with different numbers of averages showing the expected \( n^{1/2} \) dependence.](image)
The noise associated with the signal for a given species $i$ is generally $>10\times$ larger than the baseline noise. For a typical signal produced from the detection of a packet of ions hitting the detector at nearly the same time, the noise is mostly due to the pulse-to-pulse fluctuation in the intensity of the VUV power. Since the VUV is generated via two nonlinear frequency-tripling process to produce the ninth harmonic of a Nd:YAG laser, the relatively modest pulse-to-pulse fluctuations in the fundamental wavelength intensity of $\pm2\%$ causes up to $\sim20\%$ fluctuation in the pulse-to-pulse intensity of the final VUV beam. The result is $\sim20\%$ noise in the signal for a given species. For a signal produced in the limit of single-ion counting (i.e. the Poisson limit), the noise in the analog signal is determined by the error associated with the discrete nature of counting hits from single ions and is a function of the Poisson distribution (i.e. the standard deviation ($\sigma$) of the mean value ($\lambda$) is proportional to the square root of the mean, $\sigma \sim \sqrt{\lambda}$). The noise in a typical signal (i.e. not in the Poisson limit) averaged 500 times was typically about 10-20% of the signal.

The relative signals in the TOF-MS do not depend on the instrument factor ($F$) and are given by the following equation

$$\frac{S_i}{S_P} \propto \left[ \frac{\sigma_i (10.487 \text{ eV})}{\sigma_P (10.487 \text{ eV})} \right] \left[ \frac{R_i}{R_P} \right] \left[ \frac{P_i}{P_P} \right]$$

where $S_i$ is the signal (integrated m/z peak area) from species $i$, $S_P$ is the signal from the reference species $P$ (usually taken to be propene, when present), $\sigma_i$ and $\sigma_P$ are the respective species $i$ and reference species $P$ photoionization cross sections at 10.487 eV, $R_i$ and $R_P$ are the respective species $i$ and reference species $P$ mass-dependent response factors, $P_i$ and $P_P$ are the respective species $i$ and reference species $P$ partial pressures in the reaction cell, Propene is often taken as the reference species for historical reasons since propene was one of the first species with an appreciable photoionization cross section below 10.5 eV to have its photoionization efficiency (PIE) curve carefully measured (i.e. its photoionization cross section as a function of photon energy was measured).\textsuperscript{35,38} Since the photoionization of propene was well characterized, the PIE curves for many other species, including those in Table 5, were measured using propene as a standard (i.e. they were determined relative to propene). Hence, propene seems to have become the de facto standard reference species in the literature.
By solving Equation 23 for \( \frac{R_i}{R_p} \) and using the information in Table 5, the mass discrimination factor \( \frac{R_i}{R_p} \) for the PI TOF-MS was determined using the calibration mixture as a standard. The mass discrimination factor is an instrument-dependent factor that accounts for any systematic differences in signal due to differences in the gas sampling and the detection efficiencies for each species. Technically, every species has its own mass discrimination factor, but typically this parameter is mostly a function of mass-to-charge ratio (m/z) and is not strongly dependent on the exact identity and features of the species being detected. The mass discrimination factor for the PI TOF-MS using propene as the reference species is shown in Figure 29. The mass discrimination factor was fit to the following equation

\[
\frac{R_i}{R_p} = A[m/z]^b
\]

which is the functional form typically used to fit mass discrimination factor data. However, over the 100 amu range characterized by the calibration gas mixture, the mass discrimination factor exhibited no strong trend for our system, unlike the strong trend seen in other systems. The mass discrimination factor was also determined at the maximum reaction cell temperature (700 K), and again no strong trend was observed (Figure 29). Therefore, to first-order approximation, the mass discrimination factor for our PI TOF-MS systems was determined to be temperature independent and roughly equal to 1.0. Essentially, this meant that the response factors \( R_i \) for our system were not mass dependent.

![Figure 29: Mass discrimination factor versus mass-to-charge ratio (m/z) for 300 K (left) and 700 K (right).](image-url)
The detection limit for the PI TOF-MS was estimated by measuring signals from the species in the calibration mixture using various levels of dilution and comparing them to the noise in the baseline of the mass spectra after averaging the mass spectra 500 times. To account for the fact that each species had a different photoionization cross section and thus gave a different signal for the same concentration, the signal-to-noise ratio \((S/N)\) was plotted versus the concentration times the cross section \((C_\sigma_i)\) instead of being plotted versus the concentration (Figure 30). Plotting versus \(C_\sigma_i\) effectively collapsed all of the data onto a single line, which was fit using the least-squares method to a line constrained to have a zero intercept. Defining the minimum discernable signal to correspond to \(S/N = 2\), the detection limit for the PI TOF-MS was estimated to be \(C_\sigma_i = 1.7 \times 10^6 \text{ cm}^{-1}\). In terms of propene, this detection limit corresponds to 160 ppbv (parts per billion by volume) in the reaction cell. The estimated detection limit for all of the species in the calibration mixture is shown in Table 6. Of course, species with larger photoionization cross sections had lower detection limits, and vice versa.

Table 6: Detection limit of the species in the calibration mixture.

<table>
<thead>
<tr>
<th>Species</th>
<th>Detection Limit ((S/N = 2))</th>
<th>(\text{molecules/cm}^3)</th>
<th>ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomethylamine</td>
<td></td>
<td>1.62E-07</td>
<td>162</td>
</tr>
<tr>
<td>Propene</td>
<td></td>
<td>1.61E-07</td>
<td>161</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td></td>
<td>1.06E-07</td>
<td>106</td>
</tr>
<tr>
<td>1-Propanol</td>
<td></td>
<td>5.31E-07</td>
<td>531</td>
</tr>
<tr>
<td>Furan</td>
<td></td>
<td>1.20E-07</td>
<td>120</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>5.42E-08</td>
<td>54</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td>8.11E-08</td>
<td>81</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>5.52E-08</td>
<td>55</td>
</tr>
<tr>
<td>Heptane</td>
<td></td>
<td>1.74E-07</td>
<td>174</td>
</tr>
</tbody>
</table>
Figure 30: Detection limit determined using the calibration gas mixture. The error bars are given by the ±1 standard deviation of the measured signal-to-noise ratio.

The range of kinetic timescales that can be measured using the time-resolved PI TOF-MS technique are limited compared to the timescales that can be measured using the LAS technique. Although the BNC 575 delay generator has sub-nanosecond time resolution and thus can control the relative timing of the photolysis and the photoionization lasers to well within the ~10 ns laser pulse durations, the time resolution of the time-resolved PI TOF-MS data is limited to much larger timescales by other factors. In particular, the fastest possible measurement timescales are limited by the inherent spread of velocities in the molecular beam that samples the gas, and this spread in velocities varies as the alignment of the pinhole in the reaction cell with the axis of the TOF-MS varies from day to day. The spread of velocities cause the gas sample that is ionized at any particular time point to contain gas from a distribution of reaction times. The result is a time-dependent response that is a convolution of the kinetics of the reaction with the gas-sampling behavior of the instrument. The convolution of the molecular velocity distribution in a gas expansion with the kinetic measurements being performed by time-resolved TOF-MS has been characterized by Taatjes\textsuperscript{39} and by Moore and Carr\textsuperscript{40}. The convolution function is given by the following relation\textsuperscript{41}.
\[ S_i(t) \propto \int_0^t \frac{A}{(t-s)^4} e^{-k's} ds \]

where \( S_i(t) \) is the time-dependent signal from species \( i \) at time \( t \), the first term inside the integral is the distribution function that accounts for the spread of velocities in the gas expansion, the second term inside the integral is the pseudo-first order reaction rate, and \( s \) is a place-holder for integrating up to time \( t \). The time-resolved signal for iodine atoms (I) at \( m/z = 127 \) amu, which are generated in \( \sim 10 \) ns by laser flash photolysis of vinyl iodide, is shown in Figure 31 for the case with reaction cell pinhole optimally aligned with the axis of the TOF-MS and for the case with it slightly misaligned. On the timescales shown in Figure 31, the rise of I atoms should be nearly instantaneous. However, the measured rise time is stretched due the gas-sampling effects. Note that for the slightly mis-aligned case, the spread in the apparent rise time is greater since the spread of velocities in the gas expansion is greater when gas is sampled further from the central axis of the expansion.

Figure 31: Normalized signal from the PI TOF-MS for the iodine atoms \((m/z = 127)\) generated during the photolysis of vinyl iodide showing the increased spread in the apparent rise time when the pinhole is slightly misaligned. The dotted lines are moving averages of the signals.
For a well-aligned gas-sampling setup, the shortest timescale observable is set by the shortest time scale given by the spread of velocities, which corresponds to about 100 μs for our apparatus. No time-resolved PI TOF-MS measurements can be made that are faster than this timescale. For a pseudo-first order reaction, this timescale corresponds to an absolute maximum reaction rate of \( k' = 10,000 \text{ s}^{-1} \). However, to be able to resolve the kinetics of a reaction that fast, the convolution of the gas-sampling velocity distribution with the time-dependence of the reaction would need to be explicitly calculated according to Equation 25. For practical reasons, reaction rates determined using the time-resolved PI TOF-MS method can be limited to be slow enough to essentially ignore the time-dependent contribution from gas sampling. To satisfy this limit, the timescale of reaction would need to be at least 10× longer than the sampling timescale, or 1,000 μs. For a pseudo-first order reaction, this timescale corresponds to a reaction rate of \( k' = 1,000 \text{ s}^{-1} \). Using 1% of the maximum concentration of excess reactant at \( T = 300 \text{ K} \) and \( P = 25 \text{ Torr} \), which equals \( 8.0 \times 10^{15} \text{ molecules/cm}^3 \), the maximum bimolecular rate coefficient \( k_i \) that could be measured without complications from gas-sampling effects is \( 1.0 \times 10^{-13} \text{ cm}^3/\text{molecule-s} \). The maximum rate that can be measured using PI TOF-MS method for this apparatus is about four orders of magnitude slower than the maximum rate than can be measured using the LAS method. The time resolution of the PI TOF-MS method is ~1,000 lower than the time resolution of the LAS method. As for the LAS method, the slowest pseudo-first order reaction rate that can be measured is limited by the reaction cell flow timescale or the photolysis laser repetition rate, whichever timescale is shorter. For a 10 Hz laser repetition rate, or one shot every 0.1 s, the slowest rate is \( k' = 30 \text{ s}^{-1} \), which corresponds to a minimum reaction rate coefficient \( k_i \) of \( -4 \times 10^{-17} \text{ cm}^3/\text{molecule-s} \). Thus, the range of bimolecular reaction rate coefficients that can be measured using the PI TOF-MS method is as follows.

\[
4 \times 10^{-17} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} < k_i < 1 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}
\]

There are also a number of practical considerations in obtaining useful and accurate time-resolved PI TOF-MS data. Some are listed here. First, care must be taken to align the pinhole with the axis of the TOF-MS to minimize the gas-sampling effects on the apparent time-dependence of the signals. If pseudo-first order reaction rates greater than \( k' = 1,000 \text{ s}^{-1} \) are to be determined, either the gas-sampling lag-time must be measured every day to account for the day-to-day variations in the alignment of the reaction cell pinhole, and the convolution must be used to analyze the time-dependence of the data. Otherwise, the LAS method must be used to determine the kinetics and the PI TOF-MS data must only be used to determine the product distributions. Second, the gain of the detector must be set to an appropriate level to see as much
signal as possible without over-driving the electronics to cause ringing and baseline artifacts. At the gains required to see signals from the radical species, saturation of the detector by the excess reactant and any other species in large concentrations cannot be avoided by adjusting the gain. Instead, the ion packets for these species can be pulsed away using the DEI PVX-4140 high-voltage pulse generator. Third, the range of the scope must be set to adequately resolve the signals of interest: not too zoomed in so as to truncate peaks as they vary in intensity and not too zoomed out so as to cause digitization errors. The bits used to digitize the signal are scaled according the screen of the oscilloscope, and so a peak that is too small to see on the screen is also likely too small to digitize. Finally, photoionization cross sections are required to interpret the signals and compute the relative abundance of each species. These cross sections, which are often ~ 20% uncertain at best, can sometimes be as uncertain as 50-60%. These uncertainties tend to dwarf the other uncertainties in the measurements and thus usually determine the uncertainties in the final production branching fractions that are computed from PI TOF-MS data.

Conclusions

In this chapter, I have discussed my efforts to design, build, troubleshoot, and characterize a novel instrument capable of simultaneously measuring the kinetics and the product branching of gas-phase radical reactions using laser absorption spectrometry (LAS) and photoionization time-of-flight mass spectrometry PI TOF-MS. The time resolution of the LAS method is about 1,000× greater than it is for the PI TOF-MS method, making the LAS method superior for determining the kinetics of the reaction being studied. The PI TOF-MS method is more general in that it can probe the relative abundances of any species with different mass-to-charge ratios, making PI TOF-MS method superior for determining the product branching of the reaction being studied. Combined in a single device, these two methods provide a more complete understanding of the kinetics and products of gas-phase bimolecular radical reactions without the concern of systematic differences that plague the comparison of data taken in separate apparatuses. This device has been constructed with the underlying philosophy to make it as general and as easy-to-use as possible, while also attempting to streamline repetitive processes using process controls and computer automation. This device can be used well into the future to study reactions that are important in combustion and in atmospheric processes.
Chapter 3: The Vinyl + Ethene Reaction

Introduction

The vinyl radical C$_2$H$_3$ is an important intermediate in combustion and pyrolysis processes for both saturated and unsaturated hydrocarbons. Even methane, which contains a single carbon, combusts via a two-carbon pathway involving vinyl radicals. When oxygen is present, the vinyl radical can react quickly with oxygen to form oxygenated products including vinylperoxy radical C$_2$H$_5$O$_2$, vinyloxy radical C$_2$H$_3$O + atomic oxygen O, formaldehyde CH$_2$O + formyl radical CHO, and other well-known oxygenated species that can further react to form the ultimate combustion end-products of carbon monoxide CO and carbon dioxide CO$_2$. In the absence of oxygen, the vinyl radical can unimolecularly decompose to form acetylene C$_2$H$_2$ and H radicals. In addition, the vinyl radical can react with itself to form butadiene C$_4$H$_6$, ethene C$_2$H$_4$ + acetylene C$_2$H$_2$, and methyl CH$_3$ + propargyl radical C$_3$H$_3$. Finally, the vinyl radical can add to other unsaturated hydrocarbons to form larger unsaturated species, which can in turn react to form even larger unsaturated species including polycyclic aromatic hydrocarbons (PAH) and eventually soot. While the oxidative, unimolecular, and recombination reaction pathways for the vinyl radical have been studied extensively, the addition of the vinyl radical to other unsaturated species has only been studied to a limited extent. It is important to understand the kinetics and product branching of the vinyl + alkene reactions since these addition reactions compete with the aforementioned oxidative, unimolecular, and self-reaction pathways in real combustion systems, especially those systems in which oxygen-deficient regions exist, leading to incipient soot formation in these regions.

The overall kinetics of vinyl reacting with ethene, propene, and various butene isomers were previously measured using laser absorption spectrometry (LAS). However, only limited product investigations exist for vinyl + ethene indicating that the major products are a combination of butenyl and methylallyl radical isomers C$_4$H$_7$ and butadiene C$_4$H$_6$. No products have been directly observed for the other vinyl + alkene reactions. Also, the pressure dependence of the products has never been directly observed for any of the vinyl + alkene reactions, despite the prediction of highly pressure-dependent product distributions according to Rice-Ramsperger-Kassel-Marcus (RRKM) master equation (ME) simulations. We give refined temperature- and pressure-dependent kinetic parameters and, for the first time, directly-
measured product branching ratios for the simplest reaction of the vinyl radical with an alkene: the vinyl +
ethene C₂H₄ reaction.

\[
C₂H₃ + C₂H₄ \rightarrow \text{products}
\]

**Experimental Methods**

The vinyl + ethene reaction was the first reaction to be studied using the new combined
photoionization time-of-flight mass spectrometry and laser absorption spectrometry (PI TOF-MS/LAS)
apparatus in the Combustion Dynamics Laboratory (CDL) at MIT. The details of this apparatus, which
were described above, are also planned to be published in the *Review of Scientific Instruments.*\(^7\)
The details of the vinyl + ethene experiment are also planned to be published in the *Journal of Physical Chemistry A.*

Vinyl radicals C₂H₃ were generated via laser flash photolysis of vinyl iodide using the 266 nm
fourth-harmonic output of a Nd:YAG laser that has a <10 ns pulse width. This process to produce vinyl
radicals from vinyl iodide occurs via a predissociation-type mechanism, for which the lifetime of the excited
state is expected to have a shorter timescale than the duration of the photolysis pulse. Also, the quantum
yield to produce vinyl + I when using 266 nm light to photolyze vinyl iodide is >97%.\(^7\) Thus, for the
intents and purposes of studying the kinetics of vinyl radical reactions, the photolysis of vinyl iodide almost
exclusively generates vinyl + I radicals nearly instantaneously.

\[
C₂H₃I + hν (266 \text{ nm}) \rightarrow C₂H₃ + I
\]

The vinyl iodide precursor was obtained from Oakwood Products, Inc. and was ≥95% pure. It was
further purified by freeze-pump-thaw cycling it several times using liquid nitrogen. The ethene (≥99.5%
pure) and helium (UHP grade 5.0, 99.999% pure) were obtained from Airgas, Inc. and used without any
further purification. These gases were mixed in a tee and flowed through the 2.37” ID, ~34” long reaction
cell with the flow rates controlled using calibrated MKS mass flow controllers. The total flow of gas was
maintained to ensure the reactive mixture was flashed six times on average before exiting the cell with the
photolysis laser flashing at 10 Hz. The concentration of vinyl iodide was maintained at 9.6×10¹⁴
molecules/cm³ and the concentration of ethene was varied from 0–1.6×10¹⁷ molecules/cm³ in most
experiments. The balance of the gas mixture was helium, and the flow of this gas was varied to adjust the
total gas flow and maintain the same number of photolysis flashes per refresh (~6.1 on average) even as the
temperature and the pressure of the reaction cell, which both affect the actual flow rates of gas and thus the
flashes per refresh, were varied. Six flashes per refresh was chosen as a trade-off between minimizing the
amount of accumulated products (and thus the secondary chemistry of reactions with those products) and
keeping the required flows of gases reasonable (e.g. total gas flows ≤10,000 sccm). The temperature of the
reaction cell was varied in 100 K increments from 300–700 K and the pressure was held at 25 Torr. At
600 K, experiments were also conducted at 50 Torr, and at 300 K, some LAS experiments were conducted
at 10 Torr and 100 Torr.

The overall kinetics for the vinyl + ethene reaction were determined using the LAS method. While
the time resolution of the PI TOF-MS method is sufficient to resolve the time-dependent evolution of the
vinyl + ethene reactive system, the time resolution of the LAS method is ~1,000 times higher since the time
resolution of PI TOF-MS method is limited by the gas-sampling lag time. Also, the laser pulse-to-pulse
uncertainty and thus the error in the LAS method determination are lower than for the PI TOF-MS method
since the LAS method uses a quasi-CW laser beam to probe the concentration of vinyl radicals effectively
continuously after each photolysis laser shot, leading to higher fidelity rate measurements. The laser used
for the LAS method was a tunable mode-locked Spectra Physics Tsunami® Ti:Sapphire laser (80 MHz
pulsed laser with 1.2 ps FWHM wide pulses), which was pumped by a 532 nm Millennia® diode laser. The
output of this probe laser was doubled using a BBO crystal to produce 423.2 nm light, which was used to
detect the time-dependent concentrations of vinyl radicals in the vinyl + ethene reaction system without
interferences due to absorption by other species. To increase the path length for absorption, which is
required to make the relatively-weakly absorbing vinyl radicals detectable, a multi-pass Herriott cell was
used to pass the probe beam through the photolyzed region 29–33 times. The resultant time-dependent
absorption traces were averaged over 500 photolysis shots and converted to normalized concentrations of
vinyl radicals ([C\textsubscript{2}H\textsubscript{3}]\textsubscript{t}/[C\textsubscript{2}H\textsubscript{3}]\textsubscript{o}) using the Beer-Lambert law. A simple kinetic model including
contributions to the loss of vinyl radicals from the vinyl + vinyl reaction and miscellaneous pseudo-first
order vinyl reactions in addition to the vinyl + ethene title reaction was used to fit this data, as described in
the Results and Discussion section below.

The relative time-dependent product concentrations were determined using the PI TOF-MS
method. Simultaneous with the LAS experiments, a small amount of the reactive gas mixture was
continuously sampled via a small pinhole at the tip of a cone that protruded slightly into the cross section
of the photolysis beam at the center of the reaction cell. The sampled gas was supersonically expanded, and the center of the resultant free jet was passed through a Beam Dynamics skimmer to form a collimated molecular beam. The gas in the molecular beam, being substantially cooled and nearly collisionless, was effectively “frozen” in composition while in transit to the ionization region of the PI TOF-MS, where it was photoionized using 118.2 nm (10.487 eV) light. The 118.2 nm light was generated by focusing the third harmonic (355 nm) output of a pulsed Nd:YAG laser (<12 ns FWHM wide pulses at 10 Hz) in a 1:10 Xe:Ar gas cell at a total pressure of 90–100 Torr. The relative abundance of ions at different mass-to-charge ratios (m/z) were analyzed using a Kore Time-of-Flight mass spectrometer and detected using the Kore-supplied discrete dynode electron multiplier detector and analog pre-amplifier. The correspondence between time-of-flight and m/z was determined by calibration with a mixture of known stable species. The time-of-flight mass spectra were digitized and averaged over 500 photolysis shots using a 2.5 GHz (set to 1.0 GS/s) Tektronix DPO7254 oscilloscope. The peaks at each m/z were automatically identified and integrated in the time-of-flight domain using a peak-search algorithm and the trapezoidal numerical integration method in a user-written MATLAB program.

To obtain time-resolved mass spectra, the timing of the photoionization pulse was varied relative to the photolysis pulse using a BNC 575 Pulse Generator as the central clock for the experiment. Mass spectra were averaged over 500 photolysis shots and recorded for about twenty different reaction times, with reaction time defined as the time between the photolysis laser shot and the photoionization laser shot. Time-resolved mass spectra were obtained for each set of experimental conditions (i.e. each combination of temperature, pressure, [ethene], etc.). The signals for species that were present in orders of magnitude higher concentrations, such as the ethene (m/z = 28), vinyl (m/z = 27) from VUV fragmentation of vinyl iodide, and vinyl iodide (m/z = 154) itself, were too large in amplitude to be properly detected and quantified at the relatively high detector gains required to observe signals from the species of interest, such as butadiene C4H6 (m/z = 54), butenyl and methylallyl radicals C4H7 (m/z = 55), iodine atoms I (m/z = 127), HI (m/z = 128), and molecular iodine I2 (m/z = 254). So, ions with m/z values near 27–28 and 154 were pulsed away from the detector by temporarily changing the voltage on the X-deflect steering plate in the Kore TOF-MS using a DEI PVX-4140 high-voltage pulse generator. By pulsing these large packets of ions away from the detector, the large-amplitude ringing and pre-amplifier saturation that would otherwise occur were mediated, allowing the signals from the other species to be properly detected and quantified. An example of a time-resolved PI TOF-MS mass spectrum with the deleterious m/z peaks pulsed away and the desired time-dependent m/z peaks remaining is shown in Figure 32.
Figure 32: Example of time-resolved PI TOF-MS spectra showing the growth of the butadiene (m/z = 54) and butenyl and methallyl radical (m/z = 55) products as well as the relatively slow changes in the I (m/z = 127) and the HI (m/z = 128) species.

Theoretical Methods

The temperature- and pressure-dependent kinetics and product branching of the vinyl + ethene reaction were calculated by solving the master equation (ME) for this reactive system using three solution methods including the reservoir state (RS) method, the modified strong collision (MSC) method, and the chemically significant eigenvalue (CSE) method. The geometries and frequencies for the potential energy surface (PES) used in these calculations were optimized using the B3LYP functional with the 6-311+G(2df,2p) basis set, also known as the MG3S basis set, in the Gaussian 03 software package. The electronic energies for the stationary points were refined using the UCCSD(T)-F12a method with the VTZ-F12 basis set in MolPro software package. Hindered rotors were treated by performing one-dimensional scans of the relevant dihedral angles at the B3LYP/6-311+G(2df,2p) level of theory. A Fourier series was then fit to these 1-D hindered rotor scans, and the frequency matrix was re-diagonalized to produce new vibrational frequencies and account for the separate treatment of the hinder rotors. An Eckart
model was used to estimate tunneling effects. A single-exponential down model was used to compute the energy transfer, with the value of $\Delta E_{\text{down}}$ varied from (50-350 cm$^{-1}$) ($T$/298 K)$^{0.8}$ to observe the effect of $\Delta E_{\text{down}}$ on the predicted product branching. A Lennard-Jones collision model was used to estimate the collision frequency with $\sigma = 5.81$ Å and $\varepsilon = 288$ K for all C$_4$H$_6$ and C$_4$H$_7$ species, $\sigma = 4.59$ Å and $\varepsilon = 201$ K for vinyl and ethene, and $\sigma = 2.55$ Å and $\varepsilon = 6.95$ K for helium.$^{92}$

The potential energy surface (PES) shown in Figure 33 used to model the vinyl + ethene reaction system was similar to the PES used by Shestov et al.$^{74}$ and the PES used by Ismail et al.$^{13}$ However, these previously published PESs assumed that some or all of the cis-trans isomers could be treated using hindered rotors. To check this assumption, other versions of this PES with some or all of the cis-trans isomers treated with hindered rotors were also used to calculate the product branching and were found to produce substantially different results, indicating the use of hindered rotors to account for the separate cis and trans pathways was not a good assumption. So, when possible, the full PES shown in Figure 33 was used. While both Miller$^{93}$ (from which Shestov et al.$^{74}$ obtained their PES) and Ismail et al.$^{13}$ were able to find saddle point geometries for TS$_{\text{exit-2}}$ using the G3 compound method,$^{94}$ no saddle point was found when using the B3LYP functional with the MG3S basis set. The lack of a clear saddle point was likely due to the fact that the TS$_{\text{exit-2}}$ transition state was relatively "loose", with this transition state representing the beta scission of 1-methylallyl to form 1,3-butadiene + H. The angles at which the H atom could leave 1-methyallyl in this transition state were relatively broad, as scans of the C-H bond length for a variety of orientations showed a plateau in energy. To address this issue, Ismail et al.$^{13}$ also calculated the properties of this transition state using the CASPT2(5e,5o)/aug-cc-pVDZ method to account for any multireference character exhibited by such a loose transition state. They found that the Hartree-Fock (HF) geometry and frequencies, which the G3 compound method uses, were similar to those obtained using the multireference treatment, and they thus concluded the HF method sufficient to describe this transition state. So, for the calculations in this study, the UHF functional was used with the 6-311+G(2df,2p) basis set to obtain the geometry and frequencies for TS$_{\text{exit-2}}$ (both the cis and the trans isomers).
Results and Discussion

Based on the PES shown in Figure 33 and the previous observations by Shestov et al.\textsuperscript{74} and Ismail et al.\textsuperscript{13}, it was expected that the overall kinetics of the vinyl + ethene reaction were not pressure dependent since the overall rate is determined by the height of the entrance barriers, TS\textsubscript{entrance} (cis and trans). However, the distribution of products was expected to exhibit pressure dependence, as the initial adduct species formed after passing through the entrance barriers could skip over some of the later barriers at lower pressures and higher temperatures to form chemically activated products. For the purposes of studying the product distribution using the PI TOF-MS, the products could be divided into two groups according to mass, as shown in Figure 34. All of the collisionally stabilized products formed at a total rate for all isomers of $k$, are m/z = 55, and the dissociative final products formed at a rate of $k_d$ are m/z = 54 (1,3-butadiene) and m/z = 1 (H). While time-dependent signals for the m/z = 55 and m/z = 54 were measured, the m/z = 1
signal was not reliable, as H atoms are notoriously difficult to quantitatively measure in a TOF-MS tuned for higher masses.

![Diagram of chemical reactions and mass spectrometry analysis]

Figure 34: Simplified PES showing the collisionally-stabilized \( C_4H_7 \) isomers (m/z = 55) and the dissociative \( C_4H_6 \) (m/z = 54) and the H (m/z = 1) products.

**Overall Kinetics from LAS**

Although the ethene concentration was typically in excess of that of the vinyl radicals during these experiments, it was found that a simple pseudo-first order analysis was not sufficient to describe the data. Under pseudo-first order conditions, it is assumed that the concentration of ethene is approximately constant during the course of reaction, and thus the decay in the concentration of vinyl radicals is described by a single exponential decay \( (e^{-k’t}) \) where \( k’ = k_1[C_2H_4] + k_{int} \). \( k_1 \) is the rate coefficient for the reaction, \( [C_2H_4] \) is the concentration of ethene, and \( k_{int} \) is the sum of all other reaction rates leading the loss of vinyl radicals. However, a single exponential fit was not able to fit the absorption traces well at early reaction times, especially at low temperatures and low ethene concentrations. Also, the resultant pseudo-first order plot, as shown in Figure 35, had a relatively large intercept \( (k_{int}) \) compared to the total pseudo-first order rate \( k’ \) at high ethene concentrations. For example at 300 K, this large intercept indicated that more than half of
the loss of vinyl radicals was due to another process than the reaction with ethene. The vinyl + ethene reaction consumed more than half of the vinyl radicals only at higher temperatures (e.g. >500 K) and high ethene concentrations. Furthermore, it was observed that the m/z = 55 and the m/z = 54 products exhibited different rise times in the PI TOF-MS, especially at low temperatures and low ethene concentrations. All products from the same reaction should have the same kinetics and thus the same rise time. This observation further corroborated that another reaction was competing with the vinyl + ethene reaction to consume vinyl radicals, and this observation indicated that this other reaction was also producing m/z = 54 products at a faster rate (see Figure 36).

![Graph](image)

Figure 35: Pseudo-first order plot of k' versus the concentration of ethene for the temperatures studied.
Figure 36: Replicated determinations of the time-dependent m/z = 55 and m/z = 54 signal from the PI TOF-MS showing the faster rise time of the m/z = 54 species.

In order to fit the vinyl radical decays measured using the LAS technique, two reactions were considered in addition to the vinyl + ethene reaction.

\[ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{products} \]  

\[ \text{C}_2\text{H}_3 \rightarrow \text{products} \]  

These reactions accounted for the loss of vinyl radicals due to self-reaction at a rate \( k_2 \) and due to other first-order loss processes occurring at a total rate \( k_3 \) (e.g. the unimolecular decay of vinyl, the diffusion of vinyl out of the photolyzed region, the pseudo-first order reactions of vinyl with the vinyl iodide precursor and/or with residual oxygen in the system). The differential equation for the loss of vinyl due to these three reactions (Equation 31) has an analytical solution (Equation 32).

\[ \frac{d[\text{C}_2\text{H}_3]}{dt} = -k_1[\text{C}_2\text{H}_4][\text{C}_2\text{H}_3]_t - 2k_2[\text{C}_2\text{H}_3]_t^2 - k_3[\text{C}_2\text{H}_3]_t \]
This three-reaction model was used to globally fit the absorption data for each temperature and pressure. That is, a single set of rate constants \((k_i, k_2, k_3)\) for each temperature and pressure was obtained by simultaneously fitting all of data with different concentrations of ethene at the same temperature and pressure. The three-reaction model was able to capture the full behavior of the absorption decays at low temperatures and low ethene concentrations where the pseudo-first order analysis began to fail. The reason the pseudo-first order analysis began to fail at low temperatures and low ethene concentrations is because it is under those conditions where the rate of the vinyl radical self-reaction, which exhibits a negative temperature dependence, is fastest and where the vinyl + ethene reaction is slowest, thus maximizing the competition from the vinyl self-reaction. The self-reaction, by virtue of the fact that it is second order, does not fit a single exponential function. But, the three-reaction model combines the behavior of a first-order decay with a second-order decay, allowing it to fit the data, even at both extremes where the reaction is nearly all first-order or where it is nearly all second-order. The model is shown fitting the absorption data with ethene (mostly first-order) and without ethene (mostly second-order) at 400 K and 25 Torr in Figure 37.

Note that absorption data and the model did not extrapolate exactly to a value of 1.0 at time \(t = 0\) in Figure 37. The reason was that the data were normalized using an arbitrary data point immediately after time \(t = 0\) since the data were relatively noisy (e.g. a single point could not possibly be selected to represent the value at time \(t = 0\) exactly). Although not shown in Figure 37, the absorption decays did not always return exactly to baseline at long times either, with the value oscillating slightly due to thermal lensing of the probe laser beam. So, scaling \((a)\) and shift \((b)\) parameters for each absorption decay were introduced to the model to account for these artifacts in the data, as shown in Equation 33. At time \(t = 0\), Equation 33 reduces to Equation 34, showing that the sum of the scaling and shift parameters gives the value of the fitted model at time \(t = 0\), which was about 1.1 for the traces shown in Figure 37.
The initial vinyl radical concentration, which was required to fit the data using Equation 33, was determined using Beer’s law (Equation 1) with the absorption path length given by Equation 5 and the known absorption cross section for vinyl radicals at 423.2 nm. However, the absorption cross section for vinyl radicals at 423.2 nm at 300 K that was previously determined by Ismail et al.,\textsuperscript{17,69} was potentially too low since it was determined assuming that the path length of the laser used to probe I atoms was equal to one pass of the multi-pass laser used to probe vinyl radicals. A more rigorous examination of the path length for the I atom laser showed this assumption may have been invalid. Also, the temperature and pressure dependence of the vinyl radical absorption cross section had not been previously determined. So, the temperature- and pressure-dependent absorption cross section at 423.2 nm was determined for the vinyl radical by simultaneously measuring the absorption from both the vinyl radicals and the I atoms. When photolyzing an iodinated precursor such as vinyl iodide, one I atom is generated for each vinyl radical, and thus it can be assumed that the initial concentration of I atoms is equal to the initial concentration of vinyl radicals. By probing the absorption from the I atoms using the tunable narrow bandwidth diode laser centered at 1315.28 nm, the absolute concentration of I atoms\textsuperscript{95} was determined by estimating the
temperature and pressure broadening\textsuperscript{96,97} of the known line strength for the 3 \(\leftrightarrow\) 4 hyperfine transition of the \(1^2P_{3/2} \rightarrow 1^2P_{1/2}\) structure.\textsuperscript{98} The vinyl radical absorption cross section was then calculated using the following equation

\[
\sigma_{C_2H_3}(423.2 \text{ nm}) = \frac{A_{\text{probe,0}}}{l_{\text{probe}}[I]_0}
\]

where \(\sigma_{C_2H_3}(423.2 \text{ nm})\) is the absorption cross section of vinyl at 423.2 nm, \(A_{\text{probe,0}}\) is the absorption signal for vinyl at time \(t = 0\), \(l_{\text{probe}}\) is the path length of the multi-pass laser used to probe vinyl, and \([I]_0\) is initial concentration of \(I\) atoms determined from probing the 3 \(\leftrightarrow\) 4 hyperfine transition of the \(1^2P_{3/2} \rightarrow 1^2P_{1/2}\) structure. A more detailed explanation of how the vinyl radical cross section was determined can be found in Appendix IV. The new temperature- and pressure-dependent vinyl cross section is shown in Figure 38, with the error bars representing the 95% confidence interval from the propagated uncertainty in the equations used to determine the values.

![Figure 38: Temperature- and pressure-dependent vinyl radical cross section at 423.2 nm with the error bars showing the 95% confidence intervals based on the propagated uncertainties.](image)

The Arrhenius plot for the rate of the vinyl + ethene reaction is shown in Figure 39. The Arrhenius fit in Equation 36 was for the data at 25 Torr and the uncertainties in Table 7 are given by the 95%
confidence intervals for the fit. The Arrhenius fit is shown in Figure 39 along with the Arrhenius fits at 20 mbar and 133 mbar from Ismail et al.\textsuperscript{13} for comparison. Also, the rate coefficients obtained when using the pseudo-first order analysis as well as rate measurements conducted at other pressures (10, 50, and 100 Torr) are shown. The new rate agreed reasonably well with the previously published rates by Shestov et al.\textsuperscript{24} and Ismail et al.\textsuperscript{13} given the level of uncertainty typical in rate measurements.

\begin{equation}
    k_1 = (4 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}) e^{\frac{1830K}{T}}
\end{equation}

Figure 39: Arrhenius plot for the vinyl + ethene reaction rate showing the data at 25 Torr, the Arrhenius fit for the 25 Torr data, the 20 mbar and 100 mbar data from Ismail et al.,\textsuperscript{13} and the rate coefficients obtained when using the pseudo-first order analysis for comparison.

Although the experimental conditions were not optimized to determine the vinyl self-reaction rate \( k_2 \) with much certainty, the fit using the three-reaction model was able to obtain a value for this rate coefficient in good agreement with the previously published rate by Ismail et al.,\textsuperscript{69} as shown in Figure 40. However, the uncertainty in this parameter was rather high since the experimental conditions were not optimized to determine this rate. Therefore, the 95% confidence intervals for the Arrhenius parameters for the vinyl self-reaction rate in Table 7 are relatively large (i.e. a factor of 100).
Figure 40: Arrhenius plot for the vinyl + vinyl self-reaction rate showing the data at 25 Torr, the Arrhenius fit for the 25 Torr data, and the Arrhenius fit from Ismail et al. 69 for comparison.

Table 7: Arrhenius parameters and 95% confidence intervals for the vinyl + ethene and vinyl self-reaction rates

<table>
<thead>
<tr>
<th>Rate</th>
<th>Parameter</th>
<th>Fitted Value</th>
<th>-95% CI</th>
<th>+95% CI</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_1</td>
<td>A</td>
<td>4.1E-13</td>
<td>2.0E-13</td>
<td>8.7E-13 cm^3/molecule-s</td>
</tr>
<tr>
<td></td>
<td>E_a/R</td>
<td>1831</td>
<td>1531</td>
<td>2189</td>
<td>K</td>
</tr>
<tr>
<td>k_2</td>
<td>A</td>
<td>7.2E-12</td>
<td>2.4E-14</td>
<td>2.1E-09</td>
<td>cm^3/molecule-s</td>
</tr>
<tr>
<td></td>
<td>E_a/R</td>
<td>-647</td>
<td>-18</td>
<td>-23782</td>
<td>K</td>
</tr>
</tbody>
</table>

Finally, the rate for the miscellaneous first order losses of vinyl radicals (k_3) versus 1000/T is shown in Figure 41. This parameter exhibited no clear trend and was likely fitting random noise in the data in addition to the miscellaneous first-order loss processes for the vinyl radical.
Product Branching from PI TOF-MS

The products observed in the PI TOF-MS data were butadiene C₄H₆ (m/z = 54), butenyl and methylallyl radicals C₄H₇ (m/z = 55), iodine atoms I (m/z = 127), HI (m/z = 128), and molecular iodine I₂ (m/z = 254). Only the m/z = 54 and the m/z = 55 products could be directly attributed, at least in part, to the vinyl + ethene reaction. The I atom signal (m/z = 127) rose promptly following photolysis consistent with the production of I atoms from the photolyzed precursor, and it decayed at a much slower rate than the vinyl radical decay measured by laser absorption. The HI signal (m/z = 128) rose at roughly the same timescale as the 1,3-butadiene (m/z = 54) signal, and was likely the result of the H atoms that are produced along with the 1,3-butadiene quickly reacting with I atoms and with the vinyl iodide precursor to produce HI. The signal from I₂ (m/z = 254) was relatively small, and grew at timescales consistent with the recombination of I atoms. The time-resolved peak areas for these signals, except for the relatively small m/z = 254 signal, are shown in Figure 42.
Figure 42: Example of time-resolved peak areas for the products observed using PI TOF-MS at 600 K and $4 \times 10^6$ molecules/cm³ ethene.

The following reactions were used to model the PI TOF-MS data, and, in particular, to model the formation and loss of the $m/z = 54$ and $m/z = 55$ species.

$$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 \xrightarrow{\alpha_{54}} \text{C}_4\text{H}_6 (m/z = 54) + \text{H} (m/z = 1)$$

$$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 \xrightarrow{\alpha_{55}} \text{C}_4\text{H}_7 (m/z = 55)$$

$$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \xrightarrow{\beta_{54}} \text{C}_4\text{H}_6 (m/z = 54)$$

$$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \xrightarrow{\beta_{other}} \text{C}_2\text{H}_2 (m/z = 26) + \text{C}_2\text{H}_4 (m/z = 28) + \text{C}_3\text{H}_3 (m/z = 39) + \text{CH}_3 (m/z = 15)$$

$$\text{C}_2\text{H}_3 \xrightarrow{k_3} \text{products}$$

$$\text{C}_4\text{H}_7 + \text{C}_2\text{H}_4 \xrightarrow{k_4} \text{products}$$

$$\alpha_{54} + \alpha_{55} = 1$$

$$\beta_{54} + \beta_{other} = 1$$
where $k_1, k_2, k_3$ were the reaction rates determined from the laser absorption data, $\alpha_{54}$ and $\alpha_{55}$ were the product branching fractions for the vinyl + ethene reaction to make products of $m/z = 54$ and $m/z = 55$, respectively, $\beta_{54}$ and $\beta_{oher}$ were the product branching fractions for the vinyl + vinyl self-reaction to make products of $m/z = 54$ and other products of various $m/z$ ratios, respectively, and $k_4$ was the rate by which the $C_4H_7$ (m/z = 55) products reacted with the excess ethene. In addition to these rates, a flow-loss rate ($k_{flow}$) was used to represent the relatively slow loss of products due to flow in the reaction on long timescales. The products shown in Equation 40 were not observed in the PI TOF-MS data for several reasons. First, the acetylene $C_2H_2$ (m/z = 26) product did not ionize at the photoionization energy used (10.487 eV). Second, the ethene $C_2H_4$ (m/z = 28) product interfered with the reactant in large excess, and it was not observable anyway due to the masses in that range being pulsed away to protect the detector. Finally, small signals were observed for methyl $CH_3$ (m/z = 15) and propargyl radical $C_3H_3$ (m/z = 39), but these signals were too small to reliably resolve their time-dependence and thus their relative growth during the course of reaction.

This relatively simple reaction mechanism was used to model the PI TOF-MS data and to fit for the product branching ratios $\alpha_{54}$ and $\beta_{54}$. The relationship between the modeled concentrations of each species and the signals in the PI TOF-MS are given by the following equations

\begin{align}
S_{54} &= \sigma_{54}FR_{54}[m/z = 54] \\
S_{55} &= \sigma_{55}FR_{55}[m/z = 55]
\end{align}

where $S_{54}$ and $S_{55}$ are the respective $m/z = 54$ and the $m/z = 55$ signals (given as integrated peak areas), $\sigma_{54}$ and $\sigma_{55}$ are the respective $m/z = 54$ and the $m/z = 55$ photoionization cross sections at 10.487 eV, $R_{54}$ and $R_{55}$ are the respective $m/z = 54$ and the $m/z = 55$ mass-dependent response factors ($R_{54} \approx R_{55}$), and $F$ is an instrument-dependent factor. The instrument factor ($F$) was fit using the PI TOF-MS data along with the product branching fractions ($\alpha_{54}$ and $\beta_{54}$), and the rate coefficients $k_4$ and $k_{flow}$. In addition to numerically solving the set of differential equations corresponding to the reaction mechanism shown in Equations 37-44 to compute the time-dependent species concentrations, the fraction of vinyl radicals consumed by each reaction was calculated as follows
\[
\frac{dC_i}{dt} = \sum_j R_{i,j}
\]

\[
X_i = \frac{C_i}{[C_2H_3]_0}
\]

where \( C_i \) is the concentration of species \( i \), \( X_i \) is the fraction of vinyl consumed to produce species \( i \), and \( R_{i,j} \) is the rate of production of species \( i \) by reaction \( j \). Examples of the species concentrations and the fraction of vinyl converted to each product are shown in Figure 43 for \( T = 400 \) K, \( P = 25 \) Torr, and \([C_2H_4] = 1.6 \times 10^{17}\) molecules/cm\(^3\) (27% ethene). Under these conditions, only about 56% of the initial vinyl radicals reacted with ethene, with most of the remaining initial vinyl radicals reacting via the competing vinyl self-reaction. The reason the vinyl self-reaction rate was high at low temperatures was that the vinyl radical concentration was relatively high to give sufficiently high signals in the PI TOF-MS, with vinyl concentrations about 4\( \times \) higher than those used by Ismail et al.\(^{13} \) Using 4\( \times \) higher vinyl radical concentrations meant that the vinyl self-reaction, which is second order in vinyl radical concentration, was made a net 4\( \times \) faster than the vinyl + ethene reaction, which is first order in vinyl radical concentration. This higher vinyl radical concentration used in our experiments is one of the reasons the second-order vinyl self-reaction was more of a problem for us than it was for Ismail et al.\(^{13} \)

Figure 43: Species concentrations from model (left) and fraction of vinyl consumed by each reaction (right) for \( T = 400 \) K, \( P = 25 \) Torr, and \([C_2H_4] = 1.6 \times 10^{17}\) molecules/cm\(^3\) (27% ethene)
The photoionization cross section for 1,3-butadiene ($\sigma_{55}$) was previously measured by others, and the most recent value of $\sigma_{55} = 16.3$ Mb from Yang et al. was used. The photoionization cross section for $m/z = 55$, which was not previously known, is technically the mole-fraction-weighted average of the cross sections of three species: 3-buten-1-yl, 1-methallyl, and 1-buten-1-yl. According to the theoretical predictions discussed later however, the $m/z = 55$ species is mostly comprised of 3-buten-1-yl throughout the experimental temperature range of 300-700 K. To estimate this cross section, a separate experiment was performed where a small amount of a calibration mixture with several species of known concentration and photoionization cross section was flowed along with the other gases for the experiment, and the signal from $m/z = 55$ relative to the signals for the calibration mixture species was used to determine the cross section according to

$$
\sigma_{55} = \frac{\sum_{n=1}^{N_{55}} X_n \sigma_n}{\sum_{n=1}^{N_{55}} X_n} = \sigma_i \frac{S_{55,\text{max}}}{S_i} \frac{C_i}{y_{55} [C_2H_3]_0}
$$

where $X_n$ is the fraction of species $m/z = 55$ isomer $n$ as defined by Equation 48, $\sigma_n$ is the photoionization cross section of isomer $n$, $N_{55}$ is the number of $m/z = 55$ isomers, $\sigma_i$ is the photoionization cross section of species $i$ in the calibration gas mixture, $S_{55,\text{max}}$ is the maximum signal from $m/z = 55$, $S_i$ is the signal from species $i$, $C_i$ is the concentration of species $i$, and $y_{55} = \sum_{n=1}^{N_{55}} X_n$ is the fraction of the initial concentration of vinyl radicals $[C_2H_3]_0$ converted to $m/z = 55$ radicals. The value of $y_{55}$ was calculated from the modeled concentrations, which depends on the value for $\sigma_{55}$. Therefore, the modeled concentrations and the value for $\sigma_{55}$ given by Equation 49 were solved iteratively until the values for $y_{55}$ and $\sigma_{55}$ were self-consistent. Using this method, the value of $\sigma_{55}$ at 10.487 eV was estimated to be $27 \pm 15$ Mb. The relatively large uncertainty was due to the already large uncertainty ($\pm 20\%$) of the known cross sections for the species in the calibration mixture, the uncertainty in the experimental PI TOF-MS signals, and the uncertainty in the initial concentration of vinyl radicals $[C_2H_3]_0$ of almost a factor of 2. Since the uncertainty in the initial concentration of vinyl radicals was the largest source of the uncertainty in the cross section for $m/z = 55$, this uncertainty was roughly given by $\Delta \sigma_{55}/\sigma_{55} \approx \Delta [C_2H_3]_0/[C_2H_3]_0$. A more in-depth explanation of how $\sigma_{55}$ was estimated and how Equation 49 was derived can be found in Appendix V.

Examples of the how the model fit the experimental data are shown in Figure 44 for $T = 400-700$ K, $P = 25$ Torr, and $[C_2H_4] = 0-4.0 \times 10^{16}$ molecules/cm$^3$. At 400 K and 0% ethene, only the vinyl self-reaction (and some miscellaneous first-order losses) consumed vinyl radicals to produce 1,3-butadiene ($m/z = 54$) and the other vinyl self-reaction products that we were unable to detect. Without ethene, there was no
source for the $m/z = 55$ products, and thus the points for this $m/z = 55$ are given by the noise in the baseline. At higher temperatures, the vinyl self-reaction comprised a smaller fraction of the initial vinyl radical lost. So, for the moderate concentration of $4.0 \times 10^{16}$ molecules/cm$^3$ ethene, only a small fraction of the C$_4$H$_6$ ($m/z = 54$) product was produced by the vinyl self-reaction, with most of this product arising from the vinyl + ethene title reaction, especially as the temperature increased. The only manifestation of the contribution of the vinyl self-reaction in the PI TOF-MS data at higher temperatures was the slightly faster rise time of the $m/z = 54$ peak (due to the reaction rate $\beta_{sik_2}$) relative to the rise time of the $m/z = 55$ peak. However, with the normal noise associated with the PI TOF-MS data, it was not possible to accurately resolve this difference in timescale at higher temperatures, and thus it was not possible to precisely determine the product branching fraction to make $m/z = 54$ from the vinyl self-reaction ($\beta_{s2}$) at higher temperatures when fitting the data.
Because of the relatively large number of parameters, the fact that all the species could not be measured, and the relatively large uncertainties in some of the parameters, not all of the model parameters were tightly constrained. Thus there were ranges of the fit parameters ($\alpha_{54}, \beta_{54}, F, k_4$, and $k_{\text{flu}}$) that would give reasonable fits to all the available information. To quantify the uncertainties in the fitted parameters, particularly for the product branching fractions ($\alpha_{55}, \beta_{55}$), the effect of varying a number of uncertain parameters was tested. First, to quantify the effect of the imprecisely-fitted values for $\beta_{54}$ on the resulting fitted values for desired product branching fraction $\alpha_{55}$, the model was re-fit to the data using several different constraints on the fitted values for $\beta_{54}$. As shown in Figure 45, the choice of the upper-bound constraint on the fitted value for $\beta_{54}$ had little effect on the resulting fitted value for $\alpha_{55}$. The $\beta_{54}$ fraction is
expected to decrease with increasing temperature as more of the chemically activated products for the vinyl self-reaction are formed and thus less of the initial adduct C_4H_6 (m/z = 54) product is formed. Without any constraint imposed on $\beta_{54}$ (i.e. $\beta_{54} < 1.0$), its fitted value increased (unphysically) with increasing temperature as the model incorrectly attributed some of the m/z = 54 products from the vinyl + ethene reaction to the vinyl self-reaction. If the constraint on $\beta_{54}$ was made too tight (i.e. $\beta_{54} < 0.1$), its value was held too low at low temperatures causing the model to incorrectly attribute some of the m/z = 54 products formed from the vinyl self-reaction to the vinyl + ethene reaction (i.e. causing $\alpha_{55}$ to decrease at low temperatures, which is also unphysical).

![Graphs showing product branching fractions versus temperature](image)

Figure 45: Product branching fractions versus temperature showing the effect the value of the upper-bound constraint on $\beta_{54}$ has on $\alpha_{55}$ (left) and on $\beta_{54}$ itself (right).

Without any constraint imposed on $\beta_{54}$, its value was determined to be around 0.23 at 400 K. This was consistent with the value for $\beta_{54} = 0.2 \pm 0.1$ that was previously determined by Ismail et al. at 300 K using PI TOF-MS. However, at temperatures above 400 K, the competition from the vinyl self-reaction decreased, and the value of $\beta_{54}$ could not be reliably determined from our PI TOF-MS data. Given that the value for $\beta_{54}$ was expected to decrease with increasing temperature, the values for $\beta_{54}$ were constrained to remain below a linear interpolation of $\beta_{54} < 0.3$ (maximum value from Ismail et al. with the error bound included) at 300 K and $\beta_{54} < 0.1$ at 700 K. This temperature-dependent constraint on $\beta_{54}$ ameliorated the problem of too tight or too loose a constraint as previously discussed for the results shown in Figure 45. The fitted values for $\beta_{54}$, which basically followed the upper bound of the constraint for temperatures above...
400 K, are shown in Figure 46. Note that even if this assumption is inaccurate, the fact that the resulting fitted values \( \alpha_{55} \) were relatively insensitive to the value of \( \beta_{54} \) would have diminished its effect, especially at high temperatures. That is, the same values for \( \alpha_{55} \) were effectively obtained regardless of the choice of \( \beta_{54} \), especially at high temperatures.

![Figure 46: Product branching fractions \( \alpha_{55} \) and \( \beta_{54} \) (left) and product branching ratios \( \alpha_{55}/\alpha_{54} \) (right) versus temperature with the values for \( \beta_{54} \) constrained to remain below a linear interpolation of \( \beta_{54} < 0.3 \) at 300 K to \( \beta_{54} < 0.1 \) at 700 K.](image)

The fitted values for \( \alpha_{55} \) from 400-700 K at 25 Torr and at 600 K and 50 Torr are shown in Figure 46. The product branching ratio, which was calculated by simply taking the ratio \( \alpha_{55}/\alpha_{54} = k_{55}/k_{54} \), is also shown in as alternative way of viewing the product distribution. Consistent with m/z = 55 being comprised of the collisionally-stabilized species (mostly 3-buten-1-yl), the branching fraction to make m/z = 55 (\( \alpha_{55} \)) decreased with increasing temperature and increased with increasing pressure. That is, as more energy was present in the initial adduct species \([\text{C}_4\text{H}_7]^+\) at higher temperatures and lower pressures (less energy-removing collisions), the initial adduct skipped over the relatively low barriers between wells more frequently to form more chemically activated products, 1,3-butadiene (m/z = 54) and H (m/z = 1) and less collisionally-stabilized products \( \text{C}_4\text{H}_7 \) (m/z = 55). The fitted values for \( \alpha_{55} \) were however highly dependent on the relative value of the photoionization cross sections (\( \sigma_{54} \) and \( \sigma_{55} \)) for these two products. As mentioned above, the value for \( \sigma_{54} \) is known to with \( \pm 20\% \), and the value we estimate for \( \sigma_{55} \) is known
to within about ± 55%. Since the uncertainty in the value of $\sigma_{55}$ was much larger, this parameter was varied within its entire uncertainty range from 10-45 Mb to demonstrate the effect on the resulting fitted values for the desired product branching fraction $\alpha_{55}$, as shown in Figure 47. The uncertainty in this parameter was by far the largest source of the uncertainty in the fitted values for $\alpha_{55}$, and thus this uncertainty was used to estimate the uncertainty in the fitted values for the product branching fraction $\alpha_{55}$.

![Figure 47: Product branching fractions $\alpha_{55}$ (left) and $\beta_{54}$ (right) versus temperature showing the effect of the photoionization cross section for m/z = 55 ($\sigma_{55}$).](image)

**Theoretical Results**

Of the three methods used to solve the master equation (ME) for vinyl + ethene reaction system, the reservoir state (RS) method, the modified strong collision (MSC) method, and the chemically significant eigenvalue (CSE) method, the CSE method was expected to be the most accurate. However, the CSE method is also the least robust, as the method often fails when the eigenvalues for the chemical timescales approach the energy relaxation timescales or when the eigenvalues become too disparate and the problem becomes numerically ill-conditioned. So, the more robust approximate MSC and RS methods are often used to solve the pressure-dependent ME system over the full range of conditions, including the conditions where the CSE method fails. To determine which of these approximate methods was best suited for the
vinyl + ethene reaction system from 300-1,000 K and 10^{-3}-10 bar, all three methods were used and the results compared to the available CSE results.

When solving the ME for the full potential energy surface shown in Figure 33, the CSE method converged only over the narrow temperature range of 400-600 K at a pressure of 25 Torr. The failure at higher and lower temperatures was mostly due to the rapid equilibrium of the cis- and trans-1-methylallyl species, which made the problem numerically ill-conditioned. Simplifying the PES to include a single 1-methylallyl species with the two isomers treated instead using hindered rotors improved the convergence of the CSE method to include temperatures from 300-800 K at 25 Torr. Also, eliminating the relatively slow minor channel to form 1-buten-1-yl further improved the numerical conditioning and the range over which the CSE method converged to 300-1,000 K at 25 Torr. The predicted kinetics using the CSE method with the 1-methylallyl cis and trans isomers combined and with the 1-buten-1-yl product removed are shown in Figure 48. The kink in the 3-buten-1-yl rate, and thus the total rate, above 1000/T = 3.33 are where the CSE method began to fail at a pressure of 25 Torr.

The results from the MSC method and the RS method at 25 Torr are also shown side-by-side for comparison in Figure 48. The results from MSC method were both qualitatively and quantitatively different from the CSE and RS results, while the CSE and RS results were very similar. The discrepancy of the MSC results was likely due to the fact that the temperatures (300-1,000 K) and pressures (10^{-3}-10 bar) were rather low, where the approximations used in the MSC method begin to break down and the agreement between the MSC method and CSE method is known to deteriorate. So, the RS method was used for the remainder of the calculations, as it agreed with the CSE method and was robust.
Since the selection of a specific value for $\Delta E_{\text{down}}$ is difficult and since the selection of values for this parameter varies in the literature, the value of $\Delta E_{\text{down}}$ was varied from (50-350 cm$^{-1}$) ($T/298$ K)$^{0.8}$ to observe its effect on the predicted kinetics and product branching fractions. As shown in Figure 49, increasing the value of $\Delta E_{\text{down}}$ from 50 cm$^{-1}$ to 350 cm$^{-1}$ lead to an overall increase in the rates to form 3-buten-1-yl and 1-buten-1-yl and an overall decrease in the rate to form H + 1,3-butadiene. The rate to form the cis- and trans-1-methylallyl isomers increased at high temperatures and decreased at low temperatures with increasing $\Delta E_{\text{down}}$, with the net effect appearing as a shift in the curves to higher temperatures. For all values of $\Delta E_{\text{down}}$, the total rate for the overall vinyl + ethene reaction stayed more or less constant, as expected.
The sensitivities of the rates to form each product to the calculated energies for each barrier are shown in Figure 50. The rates for all products were most sensitive to height of the lower-energy entrance barrier [TS\textsubscript{entrance (cis)}], since this barrier determined the overall kinetics for the vinyl + ethene reaction and thus the rates of formation for all products. The rate to form 1,3-butadiene + H was relatively sensitive to the height of the barrier (TS\textsubscript{exit-1}) between the 1,3-butadiene + H and the initial adduct well (3-butene-1-yl) since this barrier directly affected the rate at which stabilized adduct could react to form 1,3-butadiene + H.
The rates to form the cis- and trans-1-methylallyl isomers were both sensitive to the height of the barriers \[ \text{[TS}_\text{iso-1 (cis)} \text{ and TS}_\text{iso-1 (trans)} \] since these barriers determined the rate at which the stabilized adduct (3-buten-1-yl) could react to form these isomers.

![Diagram](image)

Figure 50: Sensitivities of the rates to form each product to the energies of each transition state when using the RS method and \( \Delta E_{\text{down}}(298 \text{ K}) = 100 \text{ cm}^{-1} \).

The theoretical overall reaction rate for the vinyl + ethene reaction agreed quite well with the experimentally measured overall reaction rate to with the uncertainty in the measured rate, as shown in Figure 51. The error bars for the experimentally measured rates rate are given by the 95% confidence intervals from the Arrhenius fit to the data. The theoretical rate is also shown calculated using several values for \( \Delta E_{\text{down}}, \) which had very little effect on the overall rate as discussed above. The difference in the slope of theoretical data compared to the slope of the experimental data, was likely due to slight differences in the actual (experimental) activation energy of the reaction and the calculated energies for the entrance barriers. The F12a methods used to calculate the single point energies for these entrance barriers are good to within about 1 kcal/mol, or range of “chemical accuracy.”

102
Figure 51: Overall reaction rate for the vinyl + ethene reaction showing the agreement between the theoretically calculated rate and the experimentally measured rate. The error bars for the measured rate are given by the 95% confidence intervals from the Arrhenius fit to the experimental data.

The theoretical rate to form all m/z = 55 isomers \((k_{55})\) was calculated by summing the theoretical rates for 3-buten-1-yl, cis- and trans-1-methylallyl, and 1-buten-1-yl. The theoretical rate to form m/z = 54 \((k_{54})\) was simply given by the theoretical rate for H + 1,3-butadiene. The theoretical branching fraction for m/z = 55 \((\alpha_{55})\) was calculated by dividing the total m/z = 55 rate by total overall rate for reaction. The branching fraction for m/z = 54 \((\alpha_{54})\) could have been calculated in a similar fashion, but it is also given by \(\alpha_{54} = 1 - \alpha_{55}\) by definition. The theoretical m/z = 55 product branching fractions \((\alpha_{55})\) using the RS method with the value of \(\Delta E_{\text{down}}\) varied from (50-350 cm\(^{-1}\)) \((T/298\ K)^{0.8}\) are shown in Figure 52. For comparison, the experimental values for \(\alpha_{55}\) are also shown with error bars indicating the uncertainty due to the photoionization cross section of m/z = 55 \((\sigma_{55})\). The experimental and theoretical values agreed quite well to within the uncertainties in both results.
Figure 52: Comparison of experimental (points) and theoretical (lines) product branching fraction $\alpha_{55}$ versus temperature (all at 25 Torr) showing good agreement to within the uncertainties in both results. Error bars for the experiment are given by the uncertainty introduced to the fit for $\alpha_{55}$ by the photoionization cross section of m/z = 55.

**Conclusions**

The rates for the vinyl + ethene reaction $k_1 = (4 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}) \exp(-1830K/T)$ and the vinyl + vinyl self-reaction $k_2 = (7 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}) \exp(650K/T)$ were determined using laser absorption spectrometry and found to be in good agreement with previous measurements. Time-resolved photoionization time-of-flight mass spectrometry was used to determine the relative abundance of the products from these reactions, and the temperature- and pressure-dependent product branching fractions for the vinyl + ethene reaction were determined. The uncertainty of the product branching fractions was estimated by determining the effect of the uncertainty in the photoionization cross section for m/z = 55 at 10.487 eV on the fitted branching ratios. The theoretical temperature- and pressure-dependent kinetics and product branching fractions were calculated by solving the master equation (ME) for this reactive system using three solution methods including the reservoir state (RS) method, the modified strong collision (MSC) method, and the chemically significant eigenvalue (CSE) method. The RS method was found to resemble the high-accuracy CSE results for the temperatures (300-1,000 K) and pressures (10^3-10 bar) simulated. The RS method was used to examine the effect of the single-exponential energy transfer parameter $\Delta E_{\text{down}}$ on the predicted kinetics and branching fractions. The theoretical kinetics and product branching fractions agreed well with the experimental kinetics and product branching fractions to within the uncertainties inherent in both the theoretical and experimental methods.
Chapter 4: Ongoing and Future Work

The other vinyl + alkene reactions (i.e. vinyl + propene, vinyl + 1-butene, vinyl + 2-butene, and vinyl + iso-butene) were also studied using the new apparatus. However, a number of difficulties were encountered during these experiments, and thus they are included here as ongoing and future work. Since the overall rates for these reactions were previously measured using laser absorption spectrometry by members of the Green group, the new main insights we tried to obtain were the product branching fractions for these reactions using the PI TOF-MS portion of the apparatus, much like we did for the vinyl + ethene reaction. However, the observed signals decreased markedly when going from ethene to propene and the butene isomers. The likely reason for this observed drop in signal was that the photoionization cross section at 118.2 nm, which would follow the same trend as the absorption cross section at 118.2 nm, increased substantially in that order: ethene (0.17 Mb), propene (10.7 Mb), and 1-butene (9.91 Mb). cis-2-butene (11 Mb), trans-2-butene (11.96 Mb), and isobutene (10.15). To test this hypothesis, the PI TOF-MS signals from the species in the calibration mixture described in Table 5 were measured with increasing propene concentrations and the dependence was determined to be consistent with Beer's law (Equation 1), as shown in Figure 53. Therefore, the more propene (or butene) placed in the system, the more the VUV photons were absorbed by the alkene and thus the less VUV photons were available to ionize the other molecules which were present in relatively low concentrations. This led to much lower signals for the low concentration species that we wanted to measure under pseudo-first order conditions (e.g. measuring the small radical concentrations with large propene/butene concentrations). This factor made the quantitative determination of the product distributions for these other vinyl + alkene systems much more difficult. However, with some careful tuning of the PI TOF-MS, we were able to get some good data for vinyl + propene at 700 K where some of the chemically activated product channels become active and some limited data at 500 K where very little chemically activated products are made. Also, we were able to use the probe laser to measure the product branching of one of the products, allyl radical, at these temperatures. This work is still ongoing as Zachary Buras, the graduate student taking over the Combustion Dynamics Laboratory project, is taking more data on this system. If possible, he will also try to improve the signal-to-noise enough to examine the vinyl + butene systems further too. However, the signals for these systems were observed to be even lower than for the propene system.
In addition to the vinyl + alkenes work, Zachary Buras has a number of other interesting experiments planned for his own thesis. In fact, we have already used the laser absorption portion of the apparatus to determine the reaction kinetics of the elusive Criegee intermediate with several alkenes (ethene, propene, 1-butene, 2-butene, and iso-butene). Zach plans to continue working in this vein to also observe the distribution of products formed by these reactions using the PI TOF-MS portion of the apparatus, which he has already begun. And there are even more potential experiments that Zach has proposed in his thesis proposal in addition to aforementioned experiments.
References


Appendix I: Manufacturing Drawings

This text was sent to the manufacturer along with the drawings to give guidance on the fabrication of the custom and semi-custom vacuum parts. It is included here in case any part needs to be replaced or modified in the future.

In addition to the drawings for the individual components, a few extra drawings have been provided: “compact chamber all components”, which shows an assembly of all the components provided by K.J. Lesker, and compact chamber complete”, which shows additional components used in the apparatus but not provided by K. J. Lesker. These two drawings are included to show how everything (such as turbo pumps, mass spectrometer, etc) fit together since some of the critical dimensions in our design were derived from the dimensions of parts that are only shown in these drawings.

**Reaction Cell**

The pressure inside this tube is typically between 10 and 100 Torr during normal operation. The chemical reactions take place inside this volume. A tiny orifice on the tube allows a small volume of gas to effuse from this tube into the low-vacuum chamber.

The reactor cell is heated during normal operation. The outside of the tube is wrapped in Durex heating elements. Isothermal conditions are maintained for the central 25 inches of the cell; with temperatures in excess of 700 K. The ultimate maximum temperature is determined by the active water cooling of the outside flanges and the maximum heating rate of the cable heaters.

There are two drawings associated with the reactor cell: “reaction cell tube”, and “reaction cell plate”.

**Reaction Cell Tube**

The reaction cell is a stainless steel tube 2.5 inches in diameter and 33.75 inches from flange-face to flange-face. The tube has 4.5 inch CF flanges on both ends, both through-bolted. One of the flanges is fixed; the other end is rotatable. Two additional custom modifications were made to this tube: the reaction cell plate, and the reaction cell block.

**Reaction Cell Plate**

First, an 8 inch section in the middle of the tube is replaced with a flat plate. Prior to machining, the plate is a sheet of stainless steel, 8.000” x 2.332” x 0.250” inches. After machining, it is a sheet of
stainless steel, 8.000" x 2.332" x 0.065", with a cone protruding from one side of the plate (referred to as the inside face). The total thickness of the plate – from the tip of the cone to the outside face – will remain 0.250". The flat portion of the plate is 0.065". Thus, the cone protrudes 0.185" from the inside face of the plate.

The plate is welded directly onto the cutaway of the reactor cell tube. The cutaway is 0.799” deep. The angle connecting the plate to the top of the tube is shown to be 30°. Anywhere between 30° and 60° would be adequate. The exact dimensions of the angle are not critical.

The interior angle of the cone is 120° (i.e. 30° from the outside face of the place to the inside of the cone). It could be greater than 120°, but it should not be less than 120°. The exterior angle of the cone should be several degrees greater than 120°, so as to provide stability. An exterior angle of 130° (e.g. 25° from the inside face of the plate to the outside of the cone) is shown.

The tip of the cone is a flat circle. It is shown with a diameter of 0.070 inches, but it is best to minimize the diameter of this circle as much as possible. In the center of this circle is a small orifice, 200 microns (0.008 inches) in diameter. It is through this orifice that gas is sampled.

There is a large pressure gradient across this cone. Under normal operation, the pressure gradient is 100 Torr on the inside face and 10⁻⁴ Torr on the outside face. However, for safety, the cone should to be able to withstand a pressure difference of 1 atmosphere across the cone.

It is critical that the tip of the cone be 0.266" ± 0.010" from the centerline of the tube. This is the most important constraint.

To summarize, the design constraints for the cone are:

1) The distance from the center of the 2.5" OD tube to the tip of the cone should be 0.266” ± 0.010”.
   This is the most critical constraint.
2) The cone should protrude 0.185” from the inside face of the plate (0.250” from the outside face).
3) The interior angle of the cone should be no less than 120°. It could be greater.
4) The tip of the cone should have a small orifice, 200 microns in diameter. The tolerance on this orifice is very tight: ± 0.001”.
5) The cone should be able to withstand a pressure differential of 1 atm on one side and 10⁻⁴ Torr on the other side.
6) The flat area on the tip of the cone should be as small as possible. A diameter of 0.070” is shown, but it is best for this diameter to be as small as possible, while still maintaining the pressure-differential stability requirement.
Reaction Cell Block

The second modification to the reaction cell is a small block of steel to be welded to the bottom of the cell, on the opposite side of the cell from the plate. The block is 2.000" long, 0.500" wide, and 0.293" deep. There are two holes, blind tapped for 6-32 thread. A separate rod (the “reactor handle assembly”) is mounted onto this plate, and this rod is connected to an XYZ translation stage, external to the low-vacuum chamber. This rod is used to align the 200 micron orifice with the high-vacuum chamber (the handle is described in detail later).

Low-vacuum Chamber

This section is detailed in two drawings “low-vacuum chamber” and “low-vacuum chamber plus high-vacuum chamber”.

This large volume chamber consists of a section of stainless steel tubing, 10 inches in diameter and 39.5 inches from flange-face to flange-face. There are several ports coming off of the tube. The dimensions and purposes of these ports are described below. The pressure in this chamber is maintained between $10^{-3}$ and $10^{-4}$ Torr. The gas beam effuses from the 200 micron orifice in the high-pressure reactor cell. Because the pressure differential between the reactor cell and the low-vacuum chamber is so large (i.e. nearly six orders of magnitude), the gas beam forms a super-sonic free jet expansion.

A large turbomolecular pump is required to maintain a pressure of $10^{-4}$ Torr. This turbo pump connects to the single ISO 250 flange in the center of the 10” tube. For reference orientation, we will refer to the ISO 250 flange as the “bottom” of the reactor. The reactor cell is oriented within the low-vacuum chamber so that the reactor cell plate with the 200 micron orifice is facing the top (i.e. away from the turbo pump). Because this flange is for a vacuum pump, its dimensions and tolerances are not critical.

On one side of the 10” tube are two ISO 200 flanges. These two ports serve primarily as access ports (to allow access to critical areas). They may also serve as ports for extra turbo pumps, should there be a need for higher gas throughput in the future. The dimensions and tolerances of these two ports are not critical.

On the same side of the 10” tube as the two ISO 200 fittings is a single 2-3/4” CF flange. This flange is centered on the 10” tube. This flange is connected to an XYZ translation stage (to be purchased separately from MDC vacuum). Please note the following critical requirement: as indicated on the drawing, it is critical that the holes for this 2-3/4” CF flange be aligned so that two of the holes are parallel to the tube axis (and thus there are no bolt holes on the same axis as the ISO 250 flange). This is extremely important.
On the opposite side of the 10” tube is a single ISO 160 flange. This flange is centered on the 10” tube. This port is used for access, so its dimensions are not critical. Inside this tube is also a small 1/2” thick metal block with three #6-32 tapped hole spaced 1.00” apart. Note that this block is welded inside the 6” tube such that its innermost face is on the edge of the tube for the ISO-250 flange.

On the top of the chamber (i.e. on the side opposite of the ISO 250) are two small ports. One port has a KF 40 flange. This port is used to rough down the chamber with a rotary vane pump before the large turbo pump kicks in. The other small port has a 2-3/4” CF flange. This port is used to connect an ion gauge. Thus, the exact dimensions of these two ports are not critical.

The high-vacuum chamber is attached to the top to 10” tube. The high-vacuum chamber is shown in the drawing “complete chamber”. In the drawing “low-vacuum chamber”, the high-vacuum chamber is omitted. In its place is an 8” hole bored into the top of the 10” tube. The 8” hole is centered on the top of the tube, directly opposite of the ISO 250 flange. The high-vacuum chamber is inserted (and welded) into this hole.

At each end of the 10” tube are two “wings”. These wings are mounting tabs, to help secure low-vacuum chamber to the frame. The dimensions of these tabs are 1.500” x 1.25” x 0.375”. A 0.520” hole is bored through the tab (a ½ inch threaded rod will run through each hole).

The end flanges on the 10” tubes are rotatable 12” CF flanges. These 12” flanges connect to the custom flanges, “12” CF flange end caps”, which are described in a later section.

**High-vacuum Chamber**

This section is detailed in two drawings: “high-vacuum chamber” and “low-vacuum chamber plus high-vacuum chamber”.

This small volume chamber consists of a section of stainless steel tubing, 8” in diameter and 3.690” from end-face to end-face, with six ports. The pressure in this chamber is maintained around 10^-6 Torr. To summarize, the gas effuses from the 200 micron orifice in the high-pressure reactor cell and forms a supersonic free jet expansion. A nickel skimmer protrudes from the high-vacuum chamber into the low-vacuum chamber. This skimmer collimates the gas jet into a beam and direct it towards the mass spectrometer. (The nickel skimmer is purchased separately from Beam Dynamics Inc.).

Each face of the tube requires custom machining, with several critical dimensions; these dimensions are described first. There are six ports coming off of the tube. The dimensions and purposes of the ports are described later.
One face of the 8 inch tube is capped with a 0.625" thick stainless steel plate. In the center of this plate is machined a 4.5" CF flange. The holes for the flange are blind tapped. The time-of-flight mass spectrometer is mounted on this flange, so it is critical that this flange be perfectly centered on the face of the tube.

On the opposite face is a stainless steel plate 0.375" thick. The outside face of this plate sits inside the low-vacuum chamber. The nickel skimmer is attached to this face. The nickel skimmer sits on a lip or a shelf. This shelf is created by machining two concentric circles. In the center of this plate is a hole, 0.940" in diameter, that penetrates all the way through the plate. In addition to this hole, a circle 1.200" in diameter is machined into the face. The depth of this 1.200" circle is 0.187" into the face. This 1.200" circle creates a circular lip, >0.100" wide. The nickel skimmer rests on this lip. The skimmer is held in place by the “skimmer mounting plate”, the dimensions of which are described in a later section.

In addition to the two concentric circles, there are four holes drilled into the outside face of this plate. These holes are centered 1.000" from the center of the plate. They are blind tapped for 6-32 threads. The position of these blind-tapped holes should align with the through holes in the “skimmer mounting plate”. The skimmer mounting plate is held in place with four 6-32 bolts. These four holes are 90° apart. Please note: it is critical that the holes are not aligned with the two 2-1/8" CF flanges. They should be staggered 45° from the axis of the two 2-1/8" CF flanges.

The following dimensions are extremely critical: The shelf created by 1.200" circle must be parallel to the 4.5" CF flange on the opposite side to within 0.001". If these two faces are not parallel, then the molecular beam formed by the skimmer will not align properly with the sampling orifice on the mass spectrometer. Additionally, the distance between the outside edges of the two end plates should be 3.690" ± 0.05".

The first pair of ports is two 2-1/8" CF flanges. These two ports are on opposite sides of the tube (e.g. 180° apart). These flanges are connected to 1.0" OD tubes. These tubes are centered 2.559" from the end plate with the 4.5" CF flange. One of these flanges houses a MgF2 lens, through which a vacuum ultra-violet (VUV) laser beam passes. The flange on the opposite side houses a VUV mean power detector.

The second pair of ports is two 2-3/4" CF flanges. These two ports are on opposite sides from one another (e.g. 180° apart). The flanges are connected to 1.75" OD tubes. These two tubes centered 1.595" from the end plate with the 4.5" CF flange. The axis of the tubes are 30° from the axis of the two 2-1/8" CF flanges. One of these flanges is connected to an ion gauge. The opposite side is blanked off.
The fifth port is a KF 40. It is centered 1.595" from the end plate with the 4.5" CF flange. The axis of the tube is 30° from the axis of the two 2-1/8" CF flanges. This port is blanked off in normal operation.

The sixth port is opposite the KF 40 port. This port is a conical expansion from a 3” to a 4” tube, with a 6” CF flange. This 6” CF flange is connected to a turbo pump. Please note that this pump is attached at an angle of 30°.

As shown the drawing “low_vac_chamber_w_high_vac_chamber”, the high-vacuum chamber is welded into the low-vacuum chamber. The depth that the high-vacuum chamber sits inside the low-vacuum chamber is a critical dimension. The distance from the outside edge of the plate with the 4.5” CF flange to the centerline of the 10” tube 6.500” ± 0.010” inches.

**12” CF custom end caps**

These two end plates cap the 10” OD tube in the low-vacuum chamber. They also allow the reactor tube to be connected to outside the low-vacuum chamber. There are a few peculiarities with this end cap.

First, on each side of the flange a 4.5” CF flange is machined directly into the face. The holes for these flanges is blind tapped. Because these 4.5” flanges are directly opposite one another, their respective holes must be staggered, or out of phase.

Second, please note that these 4.5” CF flanges are not perfectly centered on the 12” CF flange. Instead, they are centered on one axis (shown as the vertical axis in the drawing), but they are 1.730” off center on the perpendicular axis (shown as the horizontal axis in the drawing).

Lastly the 12” CF flange has a water trace cut into the outside face of the flange. This water trace is used to actively cool this flange. As mentioned in the Reaction Cell section, the reaction cell is heated. Specifically, we intend to maintain isothermal conditions in the central 25 inches of the reactor cell, and these temperatures may exceed 800 K (and ideally as high as 1000 K). However, the CF flange gaskets cannot sustain temperature cycles above 450 degrees C. Thus, by actively cooling the 12” flange, the 4.5” CF flanges are somewhat cooler than the central region of the reaction cell; so they do not exceed 450 degrees C limit.

**Skimmer Mounting Plate**

This small plate holds the nickel skimmer in place. It is a disk of stainless steel, 3.000” in diameter. It is machined to look like a top hat, with the central column 0.250” thick and the outside brim 0.060” thick. A hole is drilled through the disk, 1.000” in diameter. The central column (i.e. the hat portion) is 1.197” wide. There are four through holes, 0.188” in diameter, centered 1.000” from the center of the disk.
Please note that this mounting plate must “mate” with the high-vacuum chamber. The central column must slide into the 1.200” cut-away region of the high-vacuum plate, and the four holes must align properly with the 6-32 tapped holes. It is important that the fit be very snug, with no slop.

**Reaction Cell Handle Assembly**

On the bottom side at the center of the reaction cell is the reaction cell block. A handle (handle_w_rot_flange) is bolted on one end to this block and on the other end to a MDC XYZ translation stage. This handle is comprised of a 3/8” solid stainless rod welded to the center of a 2 3/4” OD CF rotatable blank flange on one end and welded to the center of a 1/2” x 3/8” x 2” block on the other end. The block has two holes spaced 1.00” apart drilled through it for two #6-32 screws, which is used to attach the handle to the reaction cell block. The centers of these holes should be located 13.205” from closest face of the 2-3/4” OD CF flange. While it is critical that the #6 holes mate with the reaction cell block, the other dimensions are not critical, including the distance of the holes from the flange face. A little slop can be tolerated by the XYZ-translation stage to which the 2-3/4” flange attaches.

**Xe Cell**

To generate vacuum ultraviolet (VUV) light for photoionization of the sampled gas in the high-vacuum chamber, Xenon (Xe) gas is used to triple the frequency of the 355 nm output of a Nd:YAG laser. This Xe gas is stored for long periods of time (at least months) at about 100-200 Torr in the 1.00” tube and standard 2-1/8” OD CF 4-way cross attached to the 2-1/8” OD CF flange on the front of the high-vacuum chamber (this connection between components can be seen in “chamber-chamber-all_components”). The 1.00” tube (drawing “Xe_cell”), while relatively simple, is somewhat custom in that it needs to have a 2-1/8” OD CF fixed through-hole CF flange on one side and a 2-3/4” OD CF fixed though-hole flange (with a 0.935” bore) on the other side. The flange face to flange face distance is 9.879”. Standard manufacturing tolerances suffice for this component.

**2-1/4” OD CF Custom Flange For 1.0” Optic**

After the VUV is generated in the Xe gas, it needs to be focused into the high-vacuum chamber. This is accomplished using a plano-concave MgF₂ lens (purchased separately). This lens is mounted inside a double-sided 2-1/4” OD CF flange (drawing “2_125in_OD_CF_custom_optic_flange”). To make this component, a 0.875” hole should be drilled through the center of 2-1/4” OD CF double-sided blank. Then, a second hole 1.020” in diameter and 0.246” deep should be placed on one side. The flat side of the MgF₂ lens is cemented to the recessed lip created inside this flange.
Mount for VUV Reflector

The leftover VUV light is too intense to shine directly on the power meter. So, a small percentage of it is reflected to the detector using a 1/4” thick Quartz flat (purchased separately). This flat is held in place by cementing it to a mount, labeled “2_125in_OD_CF_VUV_reflector_mount”. This mount consists of a 2-1/8” OD CF fixed through-hole blank with a 3/4” OD tube welded to the vacuum side. The 3/4” tube is cut away at a 45° angle such that the distance of the angled face is 1.69” at its center from the closest flange face. This distance and the angle are the critical dimensions for this component.

ISO-63 to 4.5” OD CF Adapter with Bellows

This part, labeled “2_5in_OD_tube_w_bellows_ISO_63_and_4_5in_OD_CF”, is used to convert flange types while providing an inlet for the reactive gases and a means to take up slack via a bellows. The tube should be a 2.5” OD nominal tube with a hydraulically-formed bellows between a ISO-63 flange and a 4.5” OD fixed through-hole CF flange. The 3/8” OD tube should be welded 1.25” from the face of the ISO-63 flange, and the tube should protrude radially 3.0” from the center of the 2.5” tube. The mean flange face to flange face distance should be 4.72”. The hydraulically-formed bellows should be made as long as possible between the 3/8” tube and the 4.5” OD CF flange.

Short 4-way Cross

Another part, labeled “short_4-way_cross”, is used to convert flanges types on the other end of the chamber while providing connections for thermocouple feed throughs and a Roots blower. The cross consists of a 2.5” tube with a ISO-63 flange on one side and 4.5” OD fixed through-hole CF flange on the other side crossed by a 1.5” OD tube with KF 40 flanges on both ends. The distance between the ISO-63 flange face and the 4.5” OD CF flange face is 4.72”, and this distance is important. The distance between the faces of the two KF40 flanges is 5.12”, and this distance is not critical. In fact, the distance between the KF 40 flanges can be made shorter, if more convenient for machining, so long as there is no conflict in attaching flange hardware.

4.5” OD CF Flex-metal Bellows

Since the reaction cell is heated, it has substantial thermal expansion, and thus bellows are required on both ends of the reaction cell to keep the sampling cone centered in the chamber. These bellows are standard parts MEW3502501C2, but with the holes in the rotatable 4.5” OD flange through-drilled. These holes need to be through-drilled so that bolts can be threaded into the tapped holes of the 4.5” OD CF flange faces machined into the 12” OD CF end caps.
ISO-200 Flange with Feedthroughs

One of the ISO-200 blank flanges on the back of the chamber needs to have two high-voltage or some equivalent feedthroughs. These feedthroughs are used to provide power to the Durex heating element on the reaction cell.

2-3/4” OD CF Flange with Feedthroughs

A 2-3/4” OD CF flange with feedthrough for four wires is required to power and retrieve signal from the VUV photodiode used to monitor the VUV pulse power.

Semi-Custom Herriott Mirror

Drawings are given for the semi-custom Herriott mirror mounts from Opto-Sigma

Herriott Crosses

Drawings are given for the custom Herriott crosses and VUV photodiode mount, which were all manufactured by MDC Vacuum.

TOF-MS Modified Parts

Drawings are given for the parts that were fabricated to elongate the head of the TOF-MS. These parts were made by the MIT Central Machine Shop.
BILL OF MATERIALS

<table>
<thead>
<tr>
<th>NO.</th>
<th>PART NUMBER</th>
<th>DRAWING NUMBER</th>
<th>DESCRIPTION</th>
<th>QTY</th>
<th>U/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>RR/SA00158</td>
<td></td>
<td>ROUND BAR, SS304L, 2.5&quot; DIA DIAMETER</td>
<td>0.25</td>
<td>IN</td>
</tr>
</tbody>
</table>

NOTES:

1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.

ACKNOWLEDGEMENT REQUEST

The attached drawings are related to your current order and are provided for your review. No work will begin until we have received your approval. Please contact your sales representative as soon as possible. Please note that changes to the drawing package (that are determined to be out of scope) may result in chargeable expenses, a delay of the project schedule, and ultimately a delayed delivery. Your acknowledgement authorizes KJL to manufacture the components as described in the drawing package.
BILL OF MATERIALS

STUBLING S103041 "OD, 0.65" WALL ASTMA 270 POLIAHED OD & D

ACKNOWLEDGEMENT REQUEST

The drawings are related to your current order and are provided for information purposes only. Please contact us for more information.

NOTES:
1. ALL DIMENSIONS ARE INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCE INFORMATION.
2. ALL WELDS TO BE INTERNAL, FULL PUSHER.
3. ALL WELDS TO BE CHECKED WITH A TUBING WELD TESTER TO DETERMINE WELD QUALITY.
4. REMOVED ALL WELD MOUNTING FEATURES, OR EXIST WELD MOUNTING FEATURES. ORIGINAL APPEARANCE.
5. DIMENSIONS FOR ALL PARTS LISTED IN THE BILL OF MATERIALS ARE NORMAL.
6. ORIENT ALL FLANGES AS SHOWN.

ADDITIONAL INFORMATION:
- SPECIFICATIONS: AS N/A
- MATERIAL: AS N/A
- MANUFACTURER: AS N/A

ACCOMMODATION:
- DISTRIBUTION: AS N/A
- LOCATION: AS N/A
- ORDER NUMBER: AS N/A
- QUANTITY: AS N/A
- SHIP TO: AS N/A

SIGNATURES:
- ENGINEER: AS N/A
- INSPECTOR: AS N/A
- APPROVER: AS N/A
- DATE: AS N/A

COMMENTS:
- AS N/A
## BILL OF MATERIALS

<table>
<thead>
<tr>
<th>NO.</th>
<th>PART NUMBER</th>
<th>DRAWING NUMBER</th>
<th>DESCRIPTION</th>
<th>QTY</th>
<th>U/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>DFF212XOO0</td>
<td>P0000530</td>
<td>DBL FACED 2.125&quot;OD, UHV, SS, BLANK</td>
<td>1</td>
<td>EA</td>
</tr>
</tbody>
</table>

### CLEANING PROCEDURE

CLEANING PROCEDURE: MSW-DCP-101, LEVEL 11

### ACKNOWLEDGEMENT REQUEST

The attached drawings are related to your current order and are provided for your review. No work will begin until we have received your approval. Please contact your sales representative as soon as possible. Please note that changes to the drawing package (that are determined to be out of scope) may result in chargeable expenses, a delay in the project schedule, and ultimately a delayed delivery. Your acknowledgement authorizes KJLC to manufacture the components as described in the drawing package.

### NOTES

1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.
**NOTES:**

1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.
2. REMOVE ALL WELD DISCOLORATION BY SCOTCHBRITE OR SST WIRE BRUSH MAINTAINING ORIGINAL APPEARANCE.
3. DIMENSIONS FOR ALL PARTS LISTED IN THE BILL OF MATERIALS ARE NOMINAL.
4. ORIENT FLANGE AS SHOWN.

---

**TUBE CUT TABLE**

<table>
<thead>
<tr>
<th>TUBE PIN</th>
<th>LENGTH</th>
<th>QTY</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST-007511</td>
<td>2.36</td>
<td>1</td>
</tr>
</tbody>
</table>

---

**BILL OF MATERIALS**

<table>
<thead>
<tr>
<th>NO.</th>
<th>PART NUMBER</th>
<th>DRAWING NUMBER</th>
<th>DESCRIPTION</th>
<th>QTY</th>
<th>U/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>P07213X00DN</td>
<td>P000054</td>
<td>FLANGE, UHV, SS, BLANK FIXED, 2.125&quot; OD</td>
<td>1</td>
<td>EA</td>
</tr>
<tr>
<td>02</td>
<td>SST-007511</td>
<td></td>
<td>TUBING, 304L SS, IDGID, 3/4 OD, .049 WALL, PER INCH BRIGHT ANNEA</td>
<td>2.51</td>
<td>IS</td>
</tr>
</tbody>
</table>

---

**SECTION A-A**

**ACKNOWLEDGEMENT REQUEST**

The attached drawings are related to your current order and are provided for your review. No work will begin until we have received your approval. Please contact your sales representative as soon as possible. Please note that changes to the drawing package (that are determined to be out of scope) may result in chargeable expenses, a delay in the project schedule, and ultimately a delayed delivery. Your acknowledgement authorizes KLC to manufacture the components as described in the drawing package.

---

**CLEANING/PROCEDURE**

MSW-DCP-101, LEVEL II

63 Ra / AS SUPPLIED

SCALE

DATE: 12/21/2009

NOTE: THIS DRAWING, CONTENTS, IS THE CONFIDENTIAL AND PROPRIETARY INFORMATION OF KURT J. LESKER COMPANY AND CAN NOT BE DISCLOSED OR USED EXCEPT WITH THE EXPRESS WRITTEN PERMISSION OF KURT J. LESKER COMPANY.
NOTES FOR ITEM 01:

1. SURFACE FINISH: 63 Ra / AS SUPPLIED
2. CLEANING PROCEDURE #: NOT REQUIRED FOR WELDING
3. Q.C. BY USING 1:1 DRAWING: NO
4. QUANTITY REQUIRED: 1
5. DRAWING BASED ON: N/A
6. APPROXIMATE WEIGHT: 0.415 lbm
7. FILE NAME: A0033187.01 - REV A
NOTES:
1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.
2. ALL WELDS TO BE INTERNAL FULL FUSION.
3. VACUUM WELDS UNLESS OTHERWISE NOTED.
4. VACUUM WELDS TO BE LEAK CHECKED WITH A HELIUM MASS SPECTROMETER WITH A SENSITIVITY TO 2 X 10^-6 STD CC/SEC FOR HELIUM.
5. REMOVE ALL WELD DISCOLORATION BY SCOTCH-BRITE OR SST WIRE BRUSH MAINTAINING ORIGINAL APPEARANCE.
6. DIMENSIONS FOR ALL PARTS LISTED IN THE BILL OF MATERIALS ARE NOMINAL.
7. ORIENT FLANGE AS SHOWN.
8. REFERENCE DIMENSIONS ARE SHOWN FOR CUSTOMER REFERENCE ONLY.

Acknowledgement Request
The attached drawings are related to your current order and are provided for your review. No work will begin until we have received your approval. Please contact your sales representative as soon as possible. Please note that changes to the drawing package (that are determined to be out of scope) may result in chargeable expenses, a delay in the project schedule, and ultimately a delayed delivery. Your acknowledgment authorizes KJLC to manufacture the components as described in the drawing package.

Cleaning Procedure: MSW-DCP-101, LEVEL II
- AS SUPPLIED

Section A-A

Bill of Materials

<table>
<thead>
<tr>
<th>NO</th>
<th>PART NUMBER</th>
<th>DRAWING NUMBER</th>
<th>DESCRIPTION</th>
<th>QTY</th>
<th>U/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>MH-SPL??</td>
<td>A0033225</td>
<td>CUSTOM HYDRAULICALLY FORMED BELLOW, 4.5&quot; CF TO ISO-83K</td>
<td>1</td>
<td>EA</td>
</tr>
<tr>
<td>02</td>
<td>SST-0037CI</td>
<td></td>
<td>TUBING, 316L, SST, RIGID, 3/8&quot; WALL, ELECTROPLATED PER INCH</td>
<td>1.89</td>
<td>IN</td>
</tr>
</tbody>
</table>

Material Specification:
- AS NOTED

Drawing No.: A0033188

Acknowledged for Customer Approval:
- 1/3/2010

Printed: 3.073 lbm

Sheet: 1 of 1
NOTES:
1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.
2. ALL WELDS TO BE INTERNAL FULL FUSION VACUUM WELDS UNLESS OTHERWISE NOTED.
3. VACUUM WELDS TO BE LEAK CHECKED WITH A HELIUM MASS SPECTROMETER WITH A SENSITIVITY TO 2 X 10^-9 STD CC/SEC FOR HELIUM.
4. REMOVE ALL WELD DISCOLORATION BY SCOTCHBRITE OR SST WIRE BRUSH MAINTAINING ORIGINAL APPEARANCE.
5. DIMENSIONS FOR ALL PARTS LISTED IN THE BILL OF MATERIALS ARE NOMINAL.
6. REFERENCE DIMENSIONS ARE FOR CUSTOMER REFERENCE ONLY.
7. BAG AND TAG ITEMS 04 - 06. SHIP SEPARATE.

ACKNOWLEDGEMENT REQUEST

The attached drawings are related to your current order and are provided for your review. No work will begin until we have received your approval. Please contact your sales representative as soon as possible. Please note that changes to the drawing package (that are determined to be out of scope) may result in chargeable expenses, a delay in the project schedule, and ultimately a delayed delivery. Your acknowledgement authorizes KJL to manufacture the components as described in the drawing package.
NOTES FOR ITEM 01:
1. SURFACE FINISH: 63 Ra / AS SUPPLIED
2. CLEANING PROCEDURE #: AS REQUIRED FOR WELDING
3. Q.C. BY USING 1:1 DRAWING: NO
4. QUANTITY REQUIRED: 1
5. DRAWING BASED ON: N/A
6. APPROXIMATE WEIGHT: 1.995 lbm
7. FILE NAME: A0033194-01 - REV A
8. SEPARATE INNER AND OUTER RINGS PRIOR TO MACHINING.
NOTES FOR ITEM 02:

1. SURFACE FINISH: 63 Ra / AS SUPPLIED
2. CLEANING PROCEDURE #: AS REQUIRED FOR WELDING
3. Q.C. BY USING 1:1 DRAWING: NO
4. QUANTITY REQUIRED: 1
5. DRAWING BASED ON: N/A
6. APPROXIMATE WEIGHT: 1.921 lbm
7. FILE NAME: A0033194-02 - REV A
NOTES:
1. ALL DIMENSIONS ARE IN INCHES, REFER TO TABLE 1 FOR STANDARD TOLERANCING INFORMATION.
2. ALL WELDS TO BE INTERNAL FULL FUSION VACUUM WELDS UNLESS OTHERWISE NOTED.
3. VACUUM WELDS TO BE LEAK CHECKED WITH A HELIUM MASS SPECTROMETER WITH A SENSITIVITY TO 2 × 10⁻⁹ STD CC/SEC FOR HELIUM.
4. REMOVE ALL WELD DISCOLORATION BY SCOTCHBRUTE OR S/S WIRE BRUSH MAINTAINING ORIGINAL APPEARANCE.
5. DIMENSIONS FOR ALL PARTS LISTED IN THE BILL OF MATERIALS ARE NOMINAL.
DETAIL FOR ITEM 01
1/2

NOTES FOR ITEM 01:
1. SURFACE FINISH: 63 Ra / AS SUPPLIED
2. CLEANING PROCEDURE #: AS REQUIRED FOR WELDING
3. Q.C. BY USING 1:1 DRAWING: NO
4. QUANTITY REQUIRED: 1
5. DRAWING BASED ON: N/A
6. APPROXIMATE WEIGHT: 9.021 lbm
7. FILE NAME: A0033195-01 - REV A
NOTES: UNLESS OTHERWISE SPECIFIED
1. ALL DIMENSIONS IN mm.
2. VACUUM GREASE USED: FOMBLIN YVAC2

REVISION HISTORY

ZONE | REV | DESCRIPTION | DATE | APPROVED
--- | --- | --- | --- | ---
A | ORIGINAL RELEASE | 6/15/2010 | --- | ---

MIRROR MOUNT WITH ROTATION

TOLERANCES

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>CS</th>
<th>DATE</th>
<th>FINISH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mm</td>
<td>10/10/2010</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

OPTOSIGMA® CORPORATION
2001 Deere Ave., Santa Ana, CA 92705
949-851-5881

PART NUMBER
100614RT09

PAGE 1 of 1
UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN METRIC
ALL EDGES ARE TO BE BEVELED
DO NOT SCALE DRAWING

- Custom spec -
  - Driving screw D cutting (3.5mm x 6mm)
  - Grease: VIM2

![Diagram of mechanical component with dimensions and notes]

Size of adjustment wrench B-3

OptoSigma Corporation
949-851-5681

Drawing Number: NTE-108-00
ISO-160K 5-way cross with three additional ISO-63K ports located 7.0" from center of cross and one ISO-63K located 4.25" from center.
ISO-160K half-nipple with Brewster window plate mounted at Brewster’s angle (56 deg)
0.27” space not exact, but to be kept as short as reasonably possible
ISO-160 centering ring groove and various mounting holes

8x M4 tapped holes
(not to break through opposite side)
ISO-160K blank with a 1" through bored hole for a rotary feedthrough.

SECTION A-A
SECTION A-A

4 x Ø 0.130 THRU ALL
M4x0.7 - 6H THRU ALL

2 x Ø 0.177 THRU ALL
[ ] Ø 0.315 ↓ 0.157

UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN INCHES
TOLERANCES:
FRACTIONAL: ± 2
ROUND: ± 0.005
THRU: ± 0.030

THREE PLACE DECIMAL ± MFG APPROX.
ANGULAR: MACH± 0.005
FINISH: DRAUGHT
CHECKED:
NAME DATE
JIM 7/22/00

THE INFORMATION CONTAINED IN THIS DRAWING IS THE SOLE PROPERTY OF M. ANY REPRODUCTION IN PART OR AS A WHOLE WITHOUT PERMISSION OF M. IS PROHIBITED.

SCALE: 1:1
WEIGHT:

B mounting_plate
REV 1

SHEET 1 OF 1
ISO-160K flange with 4" hole bored through the center, an O-ring groove 0.100" deep to accommodate a 4-3/8" ID, 1/8" fractional width round O-ring, and four tapped 1/4"-20 holes.

1/4"-20 tapped holes, 0.25" deep (not to interfere with ISO centering ring groove on opposite side)
4 x Ø 0.250 THRU ALL

SECTION A-A
4.5" OD CF blank with four #6-32 tapped holes placed on a 1.0" radius for attaching VUV photodiode mount.
3 x 1/4"-20 tapped holes

4 x through-drilled holes for #6 screws

SECTION A-A

4.625

1.370

0.500

1.750

2.000

0.750

0.250

D C 3 D C 63
R13.3 ±0.0075
R15.3

4 x \( \phi 1.6 \) THRU ALL
M2x0.4 - 6H THRU ALL

Equally-space on 35.5 mm PCD

CSK 4Dia @90Deg
**KORE TECHNOLOGY LTD**

**MATERIAL** | **SS**
---|---

**TOLERANCE UNLESS STATED**

$\pm 0.25$ mm LINEAR

$\Phi 0.25$ HOLES

$0.25$ ON ALL DIAMETERS RELATIVE TO OTHERS.

**TITLE** | **Pillar**
---|---

**DRG No.** | **E 6721 C**
---|---

**SCALE** | **2:1**
---|---

**INIT** | **DATE** | **SCALE**
---|---|---

**DRN** | **CAC** | **09/08**
---|---|---

**CKD** | **ALL DIMS IN mm**
---|---

**APP** | **INTERNAL REF**
---|---
Appendix II: Summary of Mass Flow Controller Calibration and MFC Rack Design

Courtesy of Katherine Eve
March 2011

Summary of Mass Flow Controller Rack

The mass flow controller rack was condensed from the previously existing rack. The aluminum plate was designed in SolidWorks and machined at the chemistry department machine shop. Swagelok fittings and valves were used for assembly. The system was leak checked with nitrogen to the point of holding about 3/4 of the gas overnight. The mass flow controllers were then calibrated.

Calibration of the Mass Flow Controllers

Mass flow controllers were calibrated using the DC-Lite flow reader after being added to the rack. Measurements were performed to ensure that no changes had occurred to the calibration of the MFCs during the assembly process. The following calibration curves show a comparison of the MFC reading to the DC-Lite reading. The DC-Lite reading represents the average of 10 individual readings. The DC-Lite consistently read less than 10 percent above the mass flow controller value set in Labview. Because the DC-Lite reading was within 10 percent, MFCs were not recalibrated.
Calibration Curve MFC 1

\[ y = 1.0926x + 0.1798 \]

\[ R^2 = 0.9999 \]

Calibration Curve MFC 2

\[ y = 1.0937x - 0.122 \]

\[ R^2 = 0.9999 \]
Calibration Curve MFC 3

\[ y = 1.0726x + 0.2543 \]
\[ R^2 = 1 \]

Calibration Curve MFC 4

\[ y = 1.0876x - 4.3782 \]
\[ R^2 = 0.9999 \]
Calibration Curve MFC 5

\[ y = 1.0648x - 23.923 \]

\[ R^2 = 1 \]

Calibration Curve MFC 6

\[ y = 1.0802x + 1.231 \]

\[ R^2 = 0.9999 \]
Calibration Curve MFC 7

\[ y = 1.0529x + 0.17 \]
\[ R^2 = 1 \]

Calibration Curve MFC 8

\[ y = 1.113x - 21.574 \]
\[ R^2 = 1 \]
Appendix III: Standard Operation Procedures

Courtesy of Prof. Andy Cooksy

Start-up Procedure for CDL

1. Safety:
   - Take off your watch.
   - Put on laser goggles.
   - Turn on hallway “Laser On” light.

2. If the LabView Master Program is not already running:
   - First open National Instruments Measurement and Automation Explorer (NIMAX). This may take a while to initialize.
   - Click to open Interfaces, and then open all of its subfolders so that all of the COM ports are displayed. Click COM4 and F5 to make sure communications look okay.
   - Then open MASTER program (presumably most recent version).
   - Click “run” icon (right arrow). Temperatures and pressures should update.
   - Be aware that you will have to update all the entries in the experimental conditions window that opens at the beginning of each experiment. So don’t turn off the program unless you have to.

3. Check that the temperature is set to the value you want, and check pressures (all in torr) on LabView Reactor display:
   - Mass spec should be $<5 \times 10^{-7}$ when operating (lower when no load)
   - Hi-vac: $3 \times 10^{-4}$ (no load)
   - Lo-vac: $2 \times 10^{-7}$ (no load)
   - Reactor: $\sim 0$ (no load)
4. Clean cell windows and evacuate crosses:
   - Put on gloves.
   - Crosses should be vented, but check by lifting top flange on each.
   - For each window, remove the four retaining screws from the flange, remove the window.
   - Blow across each window with squeeze-bulb. Then wipe with acetone on lens paper.
   - Replace windows, tighten flanges only slightly past finger-tight.
   - Switch 3-way valve near lefthand cross to vacuum and open quarter-turn valves to pump out lines leading to crosses.
   - Once that pressure is below 200 mT, open valves on crosses to evacuate crosses. This takes several minutes. You may need to push down on or re-center top flanges on crosses to get them to seal at first.
   - Once pressure in pump line drops below about 500 mT, close the two roughing valves on each cross. Then slowly open each gate valve while monitoring the roots line pressure to make sure it doesn’t exceed 2 torr.

5. Turn on SP Millenium Xs by pushing “Laser Power” button on controller. Readout should display “Stabilizing”.

6. Start He flow.
   - Verify that there’s enough pressure in the tanks for the day’s run.
   - Set pressure to 25 torr in LabView ("System conditions" -> “Set Pressure or Valve Angle”).
   - Set He flow rate to 100 sccm in LabView (“Gas Flow control”) and activate MFC by clicking on green button.

7. Start Quanta-Ray photodissociation (PD) laser:
   - Check that nitrogen dewars are hooked up to provide purge.
   - Check that a beam block or power meter is in place before reaction cell—it should stay in place while laser warms up.
   - Check that “Lamp Energy Osc” dial in turned all the way down (counterclockwise).
   - Switch on “Enable”
   - Wait until “Lamp Energy” light stops flashing (a few seconds).
   - Turn “Lamp Energy Osc” dial all the way on (fully clockwise).
   - Push “Lamp On” switch (light goes off).
   - Give laser about 20 minutes to warm up before adjusting. The power does gradually rise.
8. Turn on Quantel photoionization (PI) laser:
   - Turn key to “On” position. Wait 15 minutes.
   - Open QLVision software on spectrometer computer. If the computer is communicating with the laser, the number of shots will appear (otherwise you get all zeros).
   - Select “Flash Simmer”.
   - Open the aperture (the switch on the top center of the laser, admits the YAG fundamental into the harmonic generation optics).
   - Check that beam block is in place between silica lens and Xe cell—it should stay in place while laser warms up.
   - [Check Q switch delay to 210 µsec at BNC box (channel E).]
   - Push “Flash Start” to start laser. Wait 8 seconds for the interlocks to clear, and then push “Q-switch Start”.
   - Let warm up for 15-20 minutes, but then start optimizing the power using the two knobs on top of the front casing. The laser appears to need at least two rounds of adjustment—one early on when the optics are cool to get the power up at all, and a second after the optics are warm to maintain the power. It does not warm up on its own.
   - Once the power is steady, unblock the beam so the mass spec detector can go through its induction period.

9. Start mass spec:
   - Switch on “Power”, “Operate”, and “Override” on Kore HV supply.
   - Turn on DEI PVX-4140 pulse generator by pushing “Enable” button. The “Output Enabled” light should go on.
   - Increase gain on Kore supply slowly to 8.5.
   - Turn on HV switch on Fluke 415B VUV photodiode power supply.
   - Carry out next steps while this warms up (about 45 min).

10. Back to the Millenium Xs controller:
    - Hold “Power” button down (until “Laser Emission” stops blinking) to start.
    - Select “Setup” and set shutter=open and check that mode=current (so that power doesn’t ramp up too fast).
    - Return to “Main” and increase current set point to 90%, wait for about 1 minute while power gradually rises.
- When power reaches about 3 W, increase current gradually to get power of 5.5 W. This is sufficient to check the alignment.
  Return to “Setup” and set mode=power.

- Return to “Main.” To run, you will increase power, probably to about 7.0 W.
- Push “Status” on SP Model 3955 above the laser to see the pulses on the scope.

11. Check Ar:Xe cell pressure. If greater than about 95 torr, it’s time to refill it. The mix should be 8.1 torr Xe and fill to 90.0 torr with Ar.

12. Check the Ti:Sapph laser Herriott alignment

- Put cameras in place at each of the two big Brewster windows. Images are viewable on ULEAD software (on analysis and Ti:sapph computers). Select “Capture->Video Capture”
- Study the Herriot alignment. The spots should be well-defined (although glare can make this hard to see at high power, which is why it makes sense to start at lower power). They should be roughly evenly spaced (this gives greater clearance around the slits), and the ring of spots should be circular and as close to the center as possible without sacrificing power. If you need to adjust the alignment to correct , do it now
- Back in ULEAD, hit “Capture image”, move to Edit tab, you must click on the image you captured (in general this is not the one displayed) to open it and hit “Print Screen” on keyboard. Open Microsoft Paint, paste image into window with CtI-V. Crop around Herriot cell image and save as bitmap file in the desktop/Herriott_copy_and_paste folder.
- Close Paint, open ImageJ. Open bmp file in ImageJ
- First use the circle/oval tool to draw a circle along the inner diameter of the cell tube in the image. This should be fairly clear away from specular reflections of the output beam. Select “Edit-Selection-Fit Circle”. Then “Analyze-Measure” gives the “major axis” and “minor axis” (should be the same).
- From “Analyze-Set scale”, enter diameter of the circle in pixels and then set the diameter of the circle to be 1.93 cm. Select “Process-Find edges “, draw and fit a circle through the middles of the Herriot spots, and use “Analyze-Measure” to read the diameter of the Herriott cell.
- Use the pen tool to write the diameter on the image, and save the image as a jpeg in the appropriate experiment folder in C:/network/cdlPC/e/.
- Check that the beam is centered on the photodiodes by scanning with the mirrors. Should get at least 1.8 V on channel B, 1.7 V on channel A.
13. Check the Ti:Sapph laser output
   - Turn on Ti:Sapphire chopper (switch on laser table) and slide chopper into beam path. Check chopped signal on LeCroy 6100A scope.
   - Use differential amplifier to select individual signals vs difference signal (A = output side, B=input side)
   - Should get about 1.8V on output without excessive fluctuation (which indicates the beam is clipping one of the slits). Std dev should be less than 10 mV (be sure to hit “clear sweeps” first on scope).
   - Optimize the mode-locking on the Ti:sapph by first making sure that it is locked to the right wavelength. Using the OOIBase spectrometer program (only on the computer by the Millenium), zoom in to display the signal between roughly 835 and 850 nm and set cursor in middle of peak to verify that the laser is locked close to 846.4 nm. Double-check that the correct spectrometer model is selected under “config check”. (A doubler subsequently takes this to 423.2 nm.)
   - Adjust the GTI knob to optimize power, but back off by ~0.1 V of signal to ensure setting is stable.
   - Only if necessary, adjust the four mirror knobs on roof of laser housing to optimize power. Adjust these only one at a time, as it is easy to completely lose the alignment by changing these.

14. Check the photolysis laser alignment and power.
   - Open StarLab software on analysis computer and select the checkbox for Juno Pyroelectric power meter, “Together”.
   - Select “energy” from Juno control menu, and make sure it is set to 248 nm.
   - Adjust the two HG optics alignment screws under the laser cover to optimize power to 90-100 mJ (directly out of laser) or 26-30 mJ (after 30% reflector).
   - Roughly every week, check beam diameter by imaging on paper in plastic bag (to prevent debris from coating optics).
   - With the photolysis beam still blocked, set up the paper target in the mount on the photolysis output side of the chamber.
   - Use the last iris on the photolysis input side to attenuate the photolysis beam to a pinpoint.
   - Unblock the beam and check that it hits the center of the target. If it is off slightly, center the spot by adjusting the horizontal and vertical position of the second (downstream) lens. (If the target has been misaligned, or if the spot is way off center, then you may need to do a more careful realignment of the photolysis beam, not described here.)
- Block the beam to remove the target, and measure the power after the reaction cell (use readout on LabView program). Should be at least 16.5 mJ for about 27 mJ on the input side.

15. On mass spec, the helium peak should now be small. (Over the first 45 min or so that signal decays.) Check the PI laser power and instrument pressures.

16. Start the I-atom diode laser:
   - Start Vortex I-atom laser by selecting “local” and then pushing “power” on Vortex front panel.
   - Wait about 15 minutes for it to stabilize.

17. Check alignment of lasers on photodiodes.
   - Have choppers running for both Ti:sapphire and I-atom lasers.
   - With scope on channel 1, diff amp mode A (Ti:sapphire: reference signal before cell) adjust last mirror before photodiode to verify that beam not at photodiode edge.
   - With scope on channel 1, diff amp mode B (Ti:sapphire: after cell) adjust the XYZ position of the photodiode. Do not adjust the output side mirror.
   - Monitoring scope channel 2, diff amp mode A (I-atom laser: after cell) adjust photodiode back & forth and XY position.
   - Check with IR sensor card that I-atom beam is aligned below Ti:sapphire beam on both sides of cell.


20. Mass spec calibration gas run is 94.8 sccm He + 5.2 sccm calibration mixture at 25 T, gain of 9.5.
   - Charge the calibration gas regulator and then close the tank again. That should be enough to run.
   - Set “MS only” in Data Acquisition.
   - Set the MS to 2V/div
   - Click on the Populate Delay Times button and select “OK” to clear current times.
   - Set delay times to 0, 1, 2, 3.
Shutdown Procedure for CDL

1. Block photolysis laser.

2. Stop gases:
   - Close vinyl iodide sample valve.
   - Close valve from precursor MFCs to reaction cell; open valve to pump out that line.
   - Set reaction cell pressure (System Conditions tab in LabView) to 0 so butterfly valve is full open.
   - Close hydrocarbon valve by MFC; close valve at hydrocarbon tank. Leave flows on in LabView to evacuate MFC lines.
   - Let helium flow for another 15-20 minutes while shutting down lasers.
   - Close He valve by MFCs.
   - Turn off helium (and any other gas) tank valve but leave regulator valves open.
   - From LabView “Gas Flow Control”, set all MFC flows to zero and turn off green buttons.

3. Turn off Quanta-Ray photodissociation laser:
   - Push “Inhibit” switch.
   - Dial down laser power to zero.
   - Leave laser on for 15-20 minutes for cooling.
   - Push “Stop” switch.

4. Turn off Quantel photoionization laser:
   - Select “Q-Switch Stop” and “Flash Stop” in QL software.
   - Wait 15-20 minutes for water to cool laser.
   - Turn key to OFF.
   - Check that beam block is in path of laser.

5. Turn off SP Millenium Xs laser:
   - turn off 3955 pulser
   - Switch back to “Current” mode and decrease setting to zero.
   - Hold power button down to switch off.
   - Set shutter to “OFF”
   - Put the beam block down over the aperture.
   - Turn off any choppers still running.

6. Turn off I-atom laser:
   - Hit “power”
   - If it doesn’t turn off, it may think it’s under remote control so hit “local” first, then “power”.

172
7. Turn off mass spec:
   - Turn off UV photodiode HV switch (but leave power supply on)
   - Turn gain slowly down to zero.
   - Turn off DEI PVX-4140 pulse generator by pushing "Enable" button. The "Output Enabled" light should go off.
   - At KORE panel, set Protect, Standby, and turn off Power.

8. Vent crosses:
   - Close both gate valves.
   - Open valves on top of crosses.
   - Set 3-way valve to nitrogen.
   - Open shut-off valve over Ti:sapph output side cross.
   - Open valves on cross top flanges to let nitrogen into crosses.
   - When the crosses are vented, close shut-off and metering valves.
Appendix IV: Determination of Temperature-dependent Vinyl Absorption Cross Section

Courtesy of Zachary Buras

The starting point for calculating initial photolytically produced \( I \) atom concentrations, \([I]_0\), is Beer’s Law:

\[
A = -\ln \left( \frac{I}{I_0} \right) = \sigma_A I_l [I]_0
\]

\[
[I]_0 = \frac{-\ln \left( \frac{I}{I_0} \right)}{\sigma_A I_l}
\]

where the variables are defined below:

\( A \) = Absorbance (=) unitless

\( I \) = Intensity of transmitted light with \( I \) atom present (=) mV

\( I_0 \) = Reference intensity of transmitted light without \( I \) atom present (=) mV

\( \sigma_A \) = Wavelength dependent \( I \) atom cross section (=) \( \text{cm}^2 / \text{molecule} \)

\( I_l \) = \( I \) atom laser pathlength (=) cm

It is convenient to rewrite \( I \) in terms of \( I_0 \) and the change in light intensity, \( \Delta I \), as shown below:

\[
I = I_0 - |\Delta I|
\]

\[
[I]_0 = \frac{-\ln \left( \frac{I_0 - |\Delta I|}{I_0} \right)}{\sigma_A I_l} = \frac{-\ln \left( 1 - \frac{|\Delta I|}{I_0} \right)}{\sigma_A I_l}
\]

\( I \) atom produced by photolysis initially exists in either the \(^2\text{P}_{3/2}\) ground state, or the \(^2\text{P}_{1/2}\) excited state [1].

The branching between these two states, termed the quantum yield (\( \Phi_i^* \)), depends on the nature of the photolytic precursor. The excited \( I \) atom, \( I^* \), is capable of undergoing stimulated emission at the wavelength of the \( I \) atom laser (~1315 nm), leading to a gain in laser intensity for certain precursors and conditions. For vinyl iodide, \( \Phi_i^* = 0.25 \pm 0.6 \) [2]. Eventually the \( I^* \) is quenched back to its ground state by collision with other molecules. The rate at which the quenching occurs is dependent on the reactor conditions and
the quenching gas(es) present. Finally, on a typically longer time scale, the ground state I atoms decay away, either via secondary reaction or diffusion out of the beam path. The combined effect of these physical phenomena is to produce I atom traces such as the one shown below. Also shown are exponential fits to the quenching decay of I* and the long-time decay of I. These fits are back-extrapolated to reaction time zero to yield $S_i$ and $S_f$, which represent the initial number of I atoms formed in the ground state and the total number of I atoms formed, respectively. Therefore:

$$\Delta I = S_f$$

![Graph showing quenching decay and long-time decay of I atoms.](image)

Figure 1: Representative I atom trace data and fits to quenching decay of I* and long time decay of I.

Hess, et. al. [1] derived a simple relationship between $S_i$, $S_f$, and $\Phi_I^*$ shown below:

$$\Phi_I^* = \frac{1}{3} \left( \frac{S_i}{S_f} + 1 \right)$$

This equation can be rearranged to solve for $S_f$:

$$S_f = \frac{S_i}{3\Phi_I^* - 1}$$

This equation can be substituted for $\Delta I$ in the equation for $[I]_0$ above:

$$[I]_0 = \frac{-\ln \left( 1 - \frac{S_i}{3\Phi_I^* - 1} \right)}{\sigma_h I_I}$$
Values for both $\sigma_h$ and $l$ are needed to complete the calculation. $l_I$ is calculated by using measurements of the position of the I atom laser beam entering and exiting the reactor relative to the photolysis laser. The equation used for $l$ is shown below along with variable definitions.

\[ l_I = \sqrt{r_{ol}^2 + z_{ol}^2} \]

\[ r_{ol} = \left( \frac{z_{ot}}{z_{tot}} \right) \sqrt{(x_{out} - x_{in})^2 + (y_{out} - y_{in})^2} \]

\[ z_{ol} = 2 \frac{z_{tot}^2 (r_{yag} (x_{in}^2 - 2x_{in}x_{out} + x_{out}^2 + (y_{in} - y_{out})^2) - (x_{out}y_{in} - x_{in}y_{out})^2)}{x_{in}^2 - 2x_{in}x_{out} + x_{out}^2 + (y_{in} - y_{out})^2} \]

\[ z_{tot} = z \text{ distance between inlet and outlet measuring points } \text{[=] cm} \]

\[ x_{in} = x \text{ distance between inlet I atom beam and center of photolysis beam } \text{[=] cm} \]

\[ y_{in} = y \text{ distance between inlet I atom beam and center of photolysis beam } \text{[=] cm} \]

\[ x_{out} = x \text{ distance between outlet I atom beam and center of photolysis beam } \text{[=] cm} \]

\[ y_{out} = y \text{ distance between outlet I atom beam and center of photolysis beam } \text{[=] cm} \]

To calculate $\sigma_h$ the hyperfine transition of the I atom that is being probed must first be identified by the piezo voltage setting of the I atom laser. The integrated cross section, $G$ (defined below), of the appropriate transition can then be found in Table 2 of Ha, et. al. [3].

\[ G = \int_{\text{line}} \sigma_\nu \tilde{\nu}^{-1} d\tilde{\nu} \text{[=]} \text{cm}^2 \text{ molecule} \]

Where

\[ \tilde{\nu} = \text{ wavenumber[=]cm}^{-1} \]

$G$ is a constant that should be independent of experimental conditions. Typically the $3 \leftrightarrow 4$ hyperfine transition within the $^2P_{3/2} \rightarrow ^2P_{1/2}$ transition is probed because it has the largest cross section.

Because the linewidth of the I atom laser is $\sim$3 orders of magnitude smaller than the typical FWHM of a hyperfine transition ($<0.5$ MHz compared to $\sim$300 MHz for typical experimental conditions), the wavelength (or wavenumber) dependent cross section, $\sigma_h$ (or $\sigma_\nu$), is the value of interest, not the integrated
value, \( G \). Figure 2 shows the resolution at which we are able to measure a hyperfine transition of the I atom (in this case it is the 3\( \leftrightarrow \)4 transition). As shown, there is sufficient resolution to be able to locate the peak maximum quite accurately.

![Graph showing absorbance vs. I atom laser piezo voltage](image)

Figure 2: Measured 3\( \leftrightarrow \)4 hyperfine transition of I atom

Whiting, et. al. [4] derived a simple set of equations to relate \( G \) to the maximum line strength of the transition, \( I_{\lambda,max} \), by approximating the Voigt line shape profile of the transition:

\[
I_{\lambda,max} = \frac{G}{w_{v}a_{v}}
\]

\[
w_{v} = \frac{w_{c}}{2} + \sqrt{\frac{(w_{c})^2}{2} + w_{d}^2}
\]

\[
a_{v} = 1.065 + 0.447 \left( \frac{w_{c}}{w_{v}} \right) + 0.058 \left( \frac{w_{c}}{w_{v}} \right)^2
\]

where

- \( I_{\lambda,max} \) = maximum line strength of transition [\( \text{cm} \text{ molecule}^{-1} \)]
- \( w_{v} \) = approximate FWHM of Voigt profile, in wavelength [\( \text{cm} \)]
- \( a_{v} \) = correction factor [\( \text{unitless} \)]
- \( w_{c} \) = approximate FWHM due to collisional broadening, in wavelength [\( \text{cm} \)]
- \( w_{d} \) = approximate FWHM due to Doppler broadening, in wavelength [\( \text{cm} \)]
The relation between wavelength-dependent line strength, \( I_\lambda \), and cross section, \( \sigma_\lambda \), can be derived by comparing the definition of \( G \) from Ha, et. al. \([3]\) above with that of Whiting, et. al. \([4]\):

\[
G = \int_{\text{line}} I_\lambda d\lambda \quad [4]
\]

\[
G = \int_{\text{line}} \sigma_\lambda \frac{1}{\nu} d\nu = \int_{\text{line}} \sigma_\lambda \left( \frac{1}{\lambda} \right)^{-1} d \left( \frac{1}{\lambda} \right) = \int_{\text{line}} \sigma_\lambda \left( \frac{1}{\lambda} \right)^{-1} \left( \frac{1}{\lambda} \right)^2 d\lambda = \int_{\text{line}} \frac{\sigma_\lambda}{\lambda} d\lambda \quad [3]
\]

By comparison of the two definitions of \( G \) above:

\[
I_\lambda = \frac{\sigma_\lambda}{\lambda}
\]

or

\[
\sigma_\lambda = I_\lambda \lambda
\]

During an experiment, the piezo voltage of the \( I \) atom laser is set such that the signal is maximized. Therefore, it is assumed that the \( I \) atom traces are obtained at the maximum of the peak transition and the appropriate cross section is \( \sigma_{\lambda,\text{max}} \), which can then be calculated using Whiting’s approximation:

\[
\sigma_{\lambda,\text{max}} = I_{\lambda,\text{max}} \lambda_0 = \frac{G}{w_\nu a_\nu} \lambda_0
\]

Where

\[
\lambda_0 = \text{centerline wavelength of hyperfine transition} \quad [=] \text{cm}
\]

To complete the calculation, \( w_c \) and \( w_d \) are needed. The value of \( w_c \) depends on the temperature, pressure and composition of the gas mixture. Empirical correlations in the form shown below exist to describe all of these effects in terms of the frequency width of the peak, \( \nu_c \) \([5]\):

\[
\nu_c = \sum_{i}^{\text{species}} 2\gamma_i P_i \left( \frac{T_0}{T} \right)^{n_i}
\]

Where

\[
\nu_c = \text{approximate FWHM due to collisional broadening, in frequency} \quad [=] \text{MHz}
\]

\[
2\gamma_i = \text{broadening coefficient for species } i \quad [=] \text{MHz/Torr}
\]

\[
P_i = \text{partial pressure of species } i \quad [=] \text{Torr}
\]
$T_0 =$ reference temperature $[= ]$ K

$n_i =$ empirical fit to describe temperature dependence $2\gamma_i$ $[= ]$ unitless

Values of $2\gamma_i$ and $n_i$ are reported for He, O$_2$ and N$_2$ in [5]. For hydrocarbons the $2\gamma_i$ value for N$_2$ and the $n_i$ value for O$_2$ are used. $v_c$ must then be converted to $w_c$, which is in wavelength units.

The effect of Doppler broadening on the wavenumber width of the transition peak, $\bar{\nu}_d$, is described by the following equation [6]:

$$\bar{\nu}_d = \frac{2\bar{\nu}_0}{c} \sqrt{\frac{2RTln2}{M}} [= ] \text{cm}^{-1}$$

where

$\bar{\nu}_0 =$ centerline wavenumber of hyperfine transition $[= ]$ cm$^{-1}$

$R =$ gas constant $[= ]$ m$^3$Pa/mol K

$M =$ molecular weight of molecule being probed $[= ]$ kg/mol

$\bar{\nu}_d$ must then be converted to $w_d$.

With $w_p$ and $\alpha_p$ calculated, and $G$ and $\lambda_0$ known from the literature, $\sigma_{\lambda,max}$ can be computed at the relevant reactor conditions. $[I]_0$ is then computed using the Beer's Law formula above.
Procedure for computing vinyl cross sections

Vinyl radical cross sections, $\sigma_{\text{C}_2\text{H}_3}$, were measured at all of the experimental temperatures and pressures employed in this study. The cross sections were computed from the initial jump in the probe laser absorbance following the photolysis of vinyl iodide using the rearranged form of the Beer-Lambert law shown below.

$$\sigma_{\text{C}_2\text{H}_3} = \frac{A_{\text{probe,0}}}{l_{\text{probe}} [\text{C}_2\text{H}_3]_0}$$

$A_{\text{probe,0}}$ = Initial probe laser absorbance following photolysis [\text{\_}\text{\_}] \text{unitless}

$l_{\text{probe}}$ = Probe laser pathlength [\text{\_}\text{\_}] \text{cm}

$[\text{C}_2\text{H}_3]_0$ = Initial vinyl radical concentration [\text{molecules \_\_\_}] \text{cm}^3

Furthermore, it was assumed that $[\text{C}_2\text{H}_3]_0 = [I]_0$ and therefore the above equation can be rewritten.

$$\sigma_{\text{C}_2\text{H}_3} = \frac{A_{\text{probe,0}}}{l_{\text{probe}} [I]_0}$$

$[I]_0$ is computed using the simultaneously acquired I atom laser data, as described in “Procedure for computing initial photolytically produced I atom concentrations”.

$A_{\text{probe,0}}$ is computed using the following equation.

$$A_{\text{probe,0}} = -\ln \left( 1 - \frac{\Delta I}{I_0} \right)$$

$\Delta I$ = Initial drop in probe laser intensity following photolysis [\text{\_}\text{\_\_}] \text{V}

$I_0$ = Reference probe laser intensity [\text{\_}\text{\_\_}] \text{V}

$\Delta I$ is obtained by fitting an exponential function to the early time portion of the probe laser traces and back-extrapolating to time zero, as shown in Figure 1.

180
The pathlength of the probe laser beam that intersects with the photolysis beam, $l_{probe}$, can be computed using the equations below.

$$l_{probe} = N_{Herriott} \sqrt{z_{probe,ol}^2 + r_{probe,ol}^2}$$

$$r_{probe,ol} = 2 \frac{\sqrt{r^2 - r_c^2}}{L} z_{probe,ol}$$

$$z_{probe,ol} = L \frac{r_{yag}^2 - r_c^2}{\sqrt{r^2 - r_c^2}}$$

$$r_c = r \sqrt{1 - \frac{L}{R}}$$

$N_{Herriott} =$ Number of passes of the probe laser in the Herriott alignment [=] unitless

$r =$ Radius of Herriott circle at end mirrors [=] cm

$r_c =$ Radius of Herriott circle at center point between the end mirrors [=] cm

$L =$ Distance between Herriott end mirrors [=] cm

$r_{yag} =$ Radius of YAG photolysis laser beam [=] cm

$R =$ Radius of curvature of Herriott mirrors [=] cm

The equations above can be derived from the formulas developed by Herriott, et. al. [7] and Trutna, et. al. [8] for the special case of a circular Herriott multi-pass alignment such as ours.
The vinyl radical has been reported to absorb strongly around 423 nm [9]. This was confirmed using our apparatus by measuring the coarse spectrum shown in Figure 2.

Figure 4: Coarse vinyl spectrum at 300 K and 25 Torr. Dashed black line is 423.2 nm, the wavelength chosen for all absorbance experiments.

As indicated by the dashed black line, all of the absorbance experiments reported here were conducted at 423.2 nm, close to the maximum of the absorbance feature.

$\sigma_{C_2H_3}$ was measured at 423.2 nm at each experimental temperature and pressure condition over a range of at least five different $[C_2H_3]_0$ values. $[C_2H_3]_0$ was varied by adjusting the precursor concentration as well as the photolysis laser power. Only at 298 K and 10 Torr was just one nominal $[C_2H_3]_0$ value used. Figure 3 shows the results of these measurements.
Figure 5: Measured vinyl cross sections, $\sigma_{C_2H_3}$, at 423.2 nm and a.) 298, b.) 390, c.) 494, d.) 599, and e.) 700 K. Error bars represent 95% Confidence Intervals based on propagated uncertainty. Dashed lines are averaged values.

The measurements above were averaged at each condition to obtain a representative $\sigma_{C_2H_3}$ value for each given temperature and pressure. Figure 4 and Table 1 summarize these values with their associated 95% confidence intervals based on propagated error and compares to the value reported by Ismail, et. al. [10] at 300 K and 20 Torr.
Figure 6: Measured temperature and pressure dependence of vinyl radical cross section at 423.2 nm. Error bars represent 95% Confidence Intervals based on propagated uncertainty.

Table 1: Measured $\sigma_{C_2H_3}$ values. Units are Megabarns and error bars represent 95% Confidence Intervals based on propagated uncertainty.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>297.96</th>
<th>390.495</th>
<th>493.535</th>
<th>599.14</th>
<th>700.205</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (Torr)</td>
<td>10</td>
<td>0.23 ± 0.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.29 ± 0.12</td>
<td>0.25 ± 0.11</td>
<td>0.21 ± 0.09</td>
<td>0.15 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>0.17 ± 0.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.52 ± 0.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The noticeable difference between our value at 300 K and Ismail’s value is explainable by the two different ways in which $l_I$, the I atom laser pathlength, was measured. In our case, $l_I$ was obtained by measuring the relative position of the I atom and photolysis laser beams at the inlet and outlet to the reactor and using the equations given in “Procedure for computing initial photolytically produced I atom concentrations”. In Ismail’s case, the assumption was made the $l_I = l_{probe}/N_{Herriott}$, which is geometrically possible but not guaranteed unless the experimentalist takes great care that it is true. If we were to make the same assumption in our analysis we would obtain $\sigma_{C_2H_3}$ = 0.22 ± 0.11 MB, which is much closer to Ismail’s value of 0.18 ± 0.02 MB. It is also worth noting that because of the size and complexity of our apparatus it is not convenient to simply pull it out of the way in order to visually verify path length as Ismail was able to do, hence our error bars are much larger.

The temperature and pressure dependent cross sections reported above were used to compute the $[C_2H_3]_0$ values used in the analysis of the vinyl + ethene data.
References


Appendix V: Estimation of m/z = 55 Photoionization Cross Section

Courtesy of Zachary Buras

In order to obtain quantitative branching fractions for the reaction of vinyl radical with ethylene using TOF-MS, it is necessary to know absolute photoionization cross sections of the respective products at the relevant photoionization energy, $\sigma_{i,PI}(E)$. In our case $E = 10.49$ eV and the photoionization cross section of 1,3-butadiene (54 amu) has been reported at this energy.[1] The other major product channel forms a radical, however, at $\frac{m}{z} = 55$ amu, the main isomer of which is expected to be 3-buten-1-yl. No value of $\sigma_{55,PI}(10.49 \text{ eV})$ has previously been reported in the literature, so it was necessary to measure our own value following the procedure described below.

$\sigma_{i,PI}(E)$ is related to the observed signal of that species, $S_i$, by the following equation.

$$S_i = R\left(\frac{m}{z}\right) \sigma_{i,PI}(E) C_i$$

$R\left(\frac{m}{z}\right)$ is the mass discrimination factor, which is instrument dependent, and $C_i$ is the concentration of species $i$. In this formulation, $R\left(\frac{m}{z}\right)$ includes all day-to-day variations in signal so its value will also vary day-to-day. Barring any drastic changes to the instrument itself, however, its relative dependence on the mass-to-charge ratio, $\frac{m}{z}$, should be constant.

The above equation can be rearranged to solve for $\sigma_{i,PI}$.

$$\sigma_{i,PI}(E) = \frac{S_i}{R\left(\frac{m}{z}\right) C_i}$$

To measure $\sigma_{55,PI}(10.49 \text{ eV})$ experimentally we produced the species with $\frac{m}{z} = 55$ amu via the reaction of vinyl and ethene at 400 Kelvin and 25 Torr and recorded its reaction-time dependent TOF-MS signal, $S_{55}(t)$. A known amount of calibration gas mixture consisting of equal amounts methyamine, propene, 1,3-butadiene, propanol, furan, benzene, cyclohexane, toluene and heptane was simultaneously present in the reactor at concentrations commensurate with the 55 amu species to act as an internal standard. Of the nine potential internal standards listed above, only three were satisfactory for this purpose:
benzene, cyclohexane and toluene. The others were either thermally unstable (methylamine and propanol), had signals that overlapped with other species (1,3-butadiene and propene), had signals that varied with temperature (furan) or signal that was too close to the noise (heptane). Control experiments were conducted to ensure that: 1.) the three internal standards chosen above were the sole contributors to the signal at their respective \( \frac{m}{z} \) values and 2.) that \( S_{55}(t) \) did not change noticeably with and without the calibration mixture present.

One can use the equation above to describe \( \sigma_{\text{calmix}, P_1} \), the photoionization cross section of one of the three calibration mixture species used as an internal standard, and \( \sigma_{55, P_1} \). If the ratio of these two equations is taken and the result rearranged for \( \sigma_{55, P_1} \) one arrives at the following equation.

\[
\sigma_{55, P_1} = \sigma_{\text{calmix}, P_1} \frac{R \left( \frac{m}{z} \text{ for cal mix} \right) S_{55}(t) C_{\text{calmix}}}{R \left( \frac{m}{z} = 55 \text{ amu} \right) S_{\text{calmix}} C_{55}(t)}
\]

The advantage of calculating \( \sigma_{55, P_1} \) in this manner is that all of the constants contained in \( R \left( \frac{m}{z} \right) \) related to the conditions that day (temperature, pressure, molecular beam alignment, photoionization laser power, etc.) cancel each other out and all that is left from the ratio of \( R \left( \frac{m}{z} \right) \) values is the relative mass dependence. Furthermore, as shown in Figure 1 for 300 and 700 K, the \( \frac{m}{z} \) dependence of \( R \left( \frac{m}{z} \right) \) is negligible compared to the noise in the data. Therefore, we assume this ratio is equal to one and the equation above simplifies to the following:

\[
\sigma_{55, P_1} = \sigma_{\text{calmix}, P_1} \frac{S_{55}(t) C_{\text{calmix}}}{S_{\text{calmix}} C_{55}(t)}
\]
Figure 1: $\frac{m}{z}$ dependence of $R(\frac{m}{z})$ at 300 and 700 K. Y axis labels are omitted because the absolute value of $R(\frac{m}{z})$ varies from day to day and it is the qualitative behavior with respect to $\frac{m}{z}$ that is of interest.

Values of $\sigma_{\text{calmix,PI}}$ are reported in the literature for benzene[2], cyclohexane[2], and toluene[3]. The authors quote 20% uncertainty in these values at most, which we use in the propagation of error for our own calculation.

$S_{\text{calmix}}$ and $C_{\text{calmix}}$ should both be constant for the duration of the experiment. The measured $S_{\text{calmix}}$ over the course of the experiment for the three internal standards is shown in Figure 2 along with the average value and 95% confidence intervals that were used in the calculations. $C_{\text{calmix}}$ and its associated uncertainty was calculated based on the mole fraction of calibration gas present, the temperature and pressure of the reactor and their respective uncertainties.
Figure 2: $S_{catmix}$ measurements over course of experiment along with average values and 95% confidence intervals.

$S_{SS}(t)$ was fit to the following simple kinetic model in order to capture the basic behavior of the data.

\[
\frac{dC_{C_2H_3}}{dt} = -k_1C_{C_2H_3} - k_2C_{C_2H_3}^2
\]

\[
\frac{dS_{SS}}{dt} = F(k_1C_{C_2H_3} - k_3S_{SS})
\]

\[C_{C_2H_3}(t = 0) = C_{C_2H_3,0}\]

\[S_{SS}(t = 0) = 0\]

$C_{C_2H_3}(t)$ is the concentration of vinyl. $k_1, k_2, k_3$ are all fit parameters in the model that are meant to represent the rate constants for vinyl and ethene reaction, vinyl self-reaction and secondary reaction of the 55 amu species, respectively. $F$ and $C_{C_2H_3,0}$ are also fit parameters that represent a unit conversion factor and the initial concentration of vinyl, respectively. The measured $S_{SS}(t)$ and the fit obtained using this model are shown in Figure 3.
As shown, the formation of the 55 amu species occurs at least an order of magnitude faster than its consumption. Therefore, we assume that the maximum value of the fit, \( S_{55}^{\text{fit, max}} \), corresponds to what the steady-state value would be with no secondary reactions. The uncertainty of \( S_{55}^{\text{fit, max}} \) is assigned by simple visual inspection of the fit. The concentration of the 55 amu species at steady-state, \( C_{55,ss} \), is related to the initial vinyl concentration, \( C_{C_2H_3,0} \), through a simple algebraic expression.

\[
C_{55,ss} = \gamma_{55} C_{C_2H_3,0}
\]

\( \gamma_{55} \) is the fraction of the initially produced vinyl radical that becomes the 55 amu species at steady state. \( C_{C_2H_3,0} \) is known within \( \sim 60\% \) (95% confidence interval) of its absolute value.

Using \( S_{55}^{\text{fit, max}} \) and making the assumption above regarding steady-state, the equation for \( \sigma_{55,PI} \) simplifies to the following.

\[
\sigma_{55,PI} = \sigma_{\text{calmix,PI}} \frac{S_{55}^{\text{fit, max}}}{C_{\text{calmix}}} \frac{C_{\text{calmix}}}{\gamma_{55} C_{C_2H_3,0}}
\]

All of the values in the equation above are known either from this experiment or from literature except for \( \gamma_{55} \), which depends on our analysis of the larger body of vinyl + ethene absorbance and TOF-MS data.

190
course the results from our analysis of this larger body of data depends on the value of $\sigma_{55,PI}$, therefore $\sigma_{55,PI}$ has to be determined iteratively in the larger analysis.

As an initial guess, we can simply assume $\gamma = 1.0$, which is reasonable for the conditions of this experiment (400 K and 25 Torr). For this case, the calculated $\sigma_{55,PI}$ using the three different internal standards with propagated 95% confidence intervals is given in Table 1.

Table 1: $\sigma_{55,PI}$ calculated using three different internal standards, assuming $\gamma = 1.0$ (i.e., 100% of initially formed vinyl goes to the 55 amu species).

<table>
<thead>
<tr>
<th>Internal Standard</th>
<th>Benzene</th>
<th>Cyclohexane</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{55,PI}$ (MB)</td>
<td>14.6 ± 9.1</td>
<td>14.9 ± 9.1</td>
<td>14.6 ± 9.1</td>
</tr>
</tbody>
</table>

As shown, the values agree very well with one another. The large uncertainty is primarily due to the large uncertainty in the value of $C_{CH_2}$. Taking an average of these values we report our final value (assuming $\gamma = 1.0$) as the following.

$$\sigma_{55,PI} = 14.7 \pm 9.1 \text{ MB}$$

Substituting this value into the real equation for $\sigma_{55,PI}$ gives the following final equation.

$$\sigma_{55,PI} = \frac{14.7}{\gamma} \text{ [MB]}$$

This equation essentially acts as a constraint in our fit to the larger body of data.

References:

