THE ROLE OF LATTICE EXCITATION IN Si ETCHING

by

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ABSTRACT

The chemistries of fluorine, $F_2$, and xenon difluoride, $XeF_2$, with clean Si are basically the same, while their chemistries diverge dramatically past 1 ML F coverage. With a clean Si surface, $F_2$ and $XeF_2$ react utilizing an atom abstraction mechanism, where a surface dangling bond abstracts a F atom from the incident molecule, scattering the F atom or $XeF$ fragment into the gas phase. Past 1 ML coverage, further exposure to $F_2$ results in no increase in F coverage, indicating that reaction of $F_2$ with the fluorinated Si surface does not occur. In contrast, further exposure to $XeF_2$ results in additional reaction, increasing the coverage sufficiently beyond 1 ML F to produce the volatile etch product, SiF$_4$. The experiments described in this thesis explain the observed difference in reactivity of $F_2$ and $XeF_2$ with a fluorinated Si surface as vibrational excitation of the Si lattice, induced by the initial collisions of $XeF_2$ with the surface that enable a barrierless reaction of the fluorine carried on the Xe with the Si-Si bonds of the surface or lattice.

The possibility of enhancement of the reactivity of $F_2$ by vibrational excitation of the fluorinated Si lattice is studied using the van der Waals dimer Kr($F_2$). Kr($F_2$) is produced by co-expansion of $F_2$ and Kr in a molecular beam. It has the mass of bound KrF$_2$ with the chemical properties of $F_2$. Any increase in Si reactivity using Kr($F_2$) compared to that of $F_2$ can be attributed to the mass of the molecule, since the dimer is basically a heavy $F_2$ molecule.

After exposure of the fluorinated Si to Kr($F_2$) molecules, the final F coverage is measured. With an estimate of Kr($F_2$) exposure already calculated, the reaction probability is then found. The Kr($F_2$) species is shown to have a reaction probability ($P_{ads} = 0.04$) that is several orders of magnitude greater than that measured for $F_2$ ($P_{ads} \sim 10^{-4}$) and around 20 times less than that for $XeF_2$ ($P_{ads} = 0.9$).

A simple classical model is presented to explain the reactivity difference of $F_2$ and $XeF_2$ with Si. Using simulation, the amount of energy transferred by a given mass to the Si surface, along with number of collisions and Si lattice excitation time, is determined. From the simulation, $XeF_2$ suffers 2-3 more collisions with Si than does $F_2$. Since more collisions are occurring using $XeF_2$, the Si lattice is deformed for a longer period of time. Therefore, the Si-Si lattice bonds are stretched and compressed for a longer period of time, an advantageous situation for further reaction with the fluorine bound to the Xe.

Excitation of the surface lattice may play a role in the reactivities of $XeF_2$ and $F_2$ with Si. This mechanism has not been fully investigated previously, and may account for the large difference in reactivity that is observed for these species. This study shows for the first time that...
the energy transferred to a surface as a result of a molecule's initial collision with it plays a critical role in the reaction probability in a molecule-surface interaction. Furthermore, this mechanism should apply to other semiconductor etchants, and must be considered in future kinetic models of such etchant systems.

Thesis Supervisor: Sylvia T. Ceyer
Title: J.C. Sheehan Professor of Chemistry and Head, Department of Chemistry
With love to my parents, grandparents and Lindsay
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Almost ten years ago when I first moved here, I never thought I would have been so lucky to meet the people I have met and experience the things I have, well, experienced. Though it is impossible to thank everyone I have come across over the years, I can at least give it my best shot.

First, I’d like to thank my advisor, Sylvia Ceyer. She is simply put the hardest working professor I have come across here, even if her working hours are still foreign to me to this day. I have learned to become a better, more thorough scientist from being in this group and I know, now more than ever, that the devil is indeed in the details.

When I joined the Ceyer Lab, Dave Lahr helped me get used to MIT. Without him around the first couple of months, I am unsure whether I would have made it here.

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My grandparents deserve all the thanks in the world. They supported me 100% over the years, which is all a grandson could ask. To Grandma and Papa, thanks so much for everything. I will never forget all the good times we had together in Jamestown. And to Papa, I still miss you every day and always will. To Grandma Kathy, thank you for all the times at Cape Vincent and for supporting me. Lastly, I can’t say enough about Pop. I always like to think that we are one in the same and the one thing I always look forward to every summer is going to the Travers. Hopefully that continues for many years to come.

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Table of Contents

ABSTRACT ................................................................................................................................... 2
Acknowledgements ....................................................................................................................... 5
List of Figures ................................................................................................................................ 9
List of Tables ............................................................................................................................... 11

Chapter I: Introduction .............................................................................................................. 13
  Chapter I References .............................................................................................................. 16

Chapter II: Experimental ........................................................................................................... 18
  II.1. Brief Description of Experimental Apparatus ............................................................... 18
  II.2. Mass Spectroscopy: Experimental Setup ..................................................................... 19
  II.3. Heating the Si Crystal .................................................................................................... 20
    II.3.1. Linear Ramping of the Crystal Temperature: Experimental Conditions .......... 22
  II.4: Time-of Flight (TOF) Mass Spectroscopy .................................................................... 25
    II.4.1: Setting up the Time of Flight .................................................................................. 25
    II.4.2: Finding the Neutral Flight Length During Time-of-Flight Experiments ............ 28
      II.4.2.1: Calculating the Ionizer Flight Time ................................................................ 29
      II.4.2.2: Calculating the Quadrupole Flight Time ......................................................... 32
      II.4.2.3: Finding the Most Probable Total Time of Flight ............................................ 34
      II.4.2.4: Solving for the Neutral Flight Length and Electronic Delay Time ............... 35
      II.4.2.5: Time of Flight Analysis of Doubly Ionized Ar, Kr and Xe ............................ 41
  II.5: Modifications to the Source Nozzle for Increased Cooling ......................................... 43
  II.6: Remaking of the Ionizer Cryostat Flange .................................................................... 50
  II.7: New Detector Beam Valve Insert .................................................................................. 58
  Chapter II References: .......................................................................................................... 61

Chapter III: Initial Studies into the Fluorine Atom Reaction Probability For Kr(F₂) ........... 62
  III.1: XeF₂ Etches Si(100) More Readily than F₂. Why? .................................................... 62
  III.2: Making Fluorine Heavy .............................................................................................. 70
    III.2.1. Temperature of the Source Nozzle ..................................................................... 70
    III.2.2. Optimization of the Production of van der Waals Dimers Kr(F₂) ..................... 71
  III.3: Determination of the Quadrupole Transmission Function ......................................... 76
    III.3.1: Effusive Molecular Beams ................................................................................... 77
    III.3.2: Determination of Transmission Ratios for Masses 19, 38, 84 and 129 ............. 78
  III.4: Time of Flight and Absolute F Atom Flux Analyses of Kr(F₂) ................................... 85
    III.4.1: Time of Flight Mass Spectroscopy of a 75% F₂/Kr Molecular Beam ............... 85
    III.4.2: Determination of Absolute F Atom Flux for Kr(F₂) in a 75% F₂/Kr Beam ....... 87
  III.5: Probability of Adsorption of Kr(F₂) and F₂: Thermal Desorption Results ............. 93
    III.5.1: Reaction Probability of Kr(F₂) Using Lee’s Method ......................................... 96
    III.5.2: Reaction Probability of Kr(F₂) Using Lee’s Method Including Transmission Ratios ..... 104
    III.5.3: Reaction Probability of Kr(F₂) Using the Absolute Flux of Kr(F₂) ................. 106
  Chapter III References: .......................................................................................................... 109
Chapter IV: Understanding the Energy Transfer to the Si Surface

IV.1: Introduction

IV.2: Energy Transfer to a Si(100) Surface: Model

IV.2.1: Choosing the Mass of Si Taking Part in Collisions with F₂ and XeF₂

IV.2.2: Trajectories of F₂, or Xe(F₂) and Si-Si Dimers

IV.2.2.1: Movement of the Incoming Gas Molecules, F₂, or XeF₂

IV.2.2.2: The Si Surface and its Movement

IV.2.2.2.1: “Strength” of the Spring System

IV.2.2.2.2: Energy Dissipation Into the Lattice: The Bath

IV.2.2.3: Choosing a Proper Timestep for Calculations

IV.2.2.4: Detecting a Collision and Terminating the Program

IV.3: Velocity and Position of XeF₂ or F₂ and the Si Surface at First Collision

IV.4: Other Considerations in the Simulation

IV.5: Results of the Simulation for an Estimated Surface Mass of 47, a Si-F Fragment

IV.5.1: Simulation of F₂ and XeF₂ Colliding with SiF at a Spring Constant of 225 N/m

IV.6: Simulation of F₂ and XeF₂ Interactions with SiF at Other Spring Constants

IV.7: Simulation of F₂ and XeF₂ Interactions with Non-SiF Fluorinated Si Fragments

IV.8: Conclusions from Model and Future Considerations

Chapter IV References

Appendix

Appendix A: Renovated Electric and Water Distribution in Big Machine Lab

Appendix B: IGORPro Code for Fitting Time-of-Flight Spectra

Appendix C: Data and Figure Sources

Chapter II

Chapter III

Chapter IV

Appendix A

Appendix D: Curriculum Vitae
List of Figures

Chapter II:

Figure 1: Floating programmable power supply ................................................................. 24
Figure 2: Schematic of the pseudo-random cross correlation chopper wheel ...................... 27
Figure 3: Assembly drawing of quadrupole housing .......................................................... 33
Figure 4: Plot of neutral plus electronic delay time versus the square root of mass for He, Ne, Ar, Kr and Xe ......................................................... 36
Figure 5: Plot of neutral plus electronic delay time versus the square root of mass for Ne, Ar, Kr and Xe ............................................................. 37
Figure 6: Plot of neutral plus electronic delay time versus the square root of mass for He, Ne, Ar and Kr ................................................................. 39
Figure 7: Schematic of stainless steel piece of the nozzle holder ....................................... 47
Figure 8: Schematic of PEEK pieces for nozzle holder ....................................................... 48
Figure 9: Nozzle holder assembly ..................................................................................... 49
Figure 10: The original welding diagram of the ionizer cryostat flange and tube setup .... 51
Figure 11: Frame of reference for the ionizer cryostat flange ........................................... 53
Figure 12: Final machined ionizer flange and tube setup .................................................. 54
Figure 13: Drawing of new detector beam valve plate and extension .............................. 60

Chapter III:

Figure 1: Top and side views of the reconstruction of the Si(100) surface ......................... 64
Figure 2. Thermal desorption spectra after exposing Si(100) to Pure F₂ beam .................. 68
Figure 3: Comparison of dimer production with nozzle pressure ....................................... 73
Figure 4: Comparison of Kr(F₂) dimer production using a 75% F₂/Kr beam at two temperatures ................................................................. 75
Figure 5: Time-of-flight spectrum of an effusive Ar molecular beam .................................. 78
Figure 6: Time-of-Flight distribution of an effusive Ne beam P_stag = 0.5 Torr, T_Nozzle = 27°C ................................................................. 81
Figure 7: Time-of-Flight distribution of an effusive Ar beam P_stag = 0.5 Torr, T_Nozzle = 27°C ................................................................. 82
Figure 8: Time-of-Flight distribution of an effusive Kr beam P_stag = 0.5 Torr, T_Nozzle = 27°C ................................................................. 83
Figure 9: Time-of-Flight distribution of an effusive Xe beam P_stag = 0.5 Torr, T_Nozzle = 27°C ................................................................. 84
Figure 10: Top: Time of flight data for an incident 75% F₂/Kr molecular beam using a cold nozzle collected at m/e = 122. Bottom: Time of flight data for an incident 75% F₂/Kr molecular beam using a room temperature nozzle collected at m/e = 122 ................................................................. 86
Figure 11: Time-of-Flight distribution of an incident 75% F₂/Kr Beam, P_stag = 300 Torr, T_Nozzle = -69°C ................................................................. 91
Figure 12: Time-of-Flight distribution of an incident 75% F₂/Kr Beam, P_stag = 300 Torr, T_Nozzle = -69°C ................................................................. 92
Figure 13. Thermal desorption spectra after exposing Si(100) to a Pure F₂ beam ............ 94
Figure 14. Thermal desorption spectra after exposing Si(100) to a 75% F₂/Kr beam .... 95
Figure 15. Total fluorine coverage (counts) versus dose time ........................................... 98
Figure 16. F₂ signal (m/e= 38) measured while beam shutter is turned on and off .......... 99
Figure 17: F Coverage vs. F Atom Exposure of Si to 75% F₂/Kr and Pure F₂ ............... 102
Figure 18: F Coverage vs. F Atom Exposure (up to 3 ML) of Si to 75% F₂/Kr and Pure F₂ .... 103
Figure 19: F Coverage vs. F atom exposure of Si to 75% F₂/Kr and pure F₂ ............... 104
Figure 20: F Coverage vs. F atom exposure (up to 3 ML) of Si to 75% F₂/Kr and pure F₂ ..... 105
Figure 21: F Coverage vs. F Atom Exposure of Si to 75% F₂/Kr and Pure F₂ ................... 106
Figure 22: F Coverage vs. F atom exposure (up to 12 ML) of Si to 75% F₂/Kr and pure F₂ .... 107

Chapter IV:

Figure 1: Potential energy diagram of XeF₂ reaction with a Si-Si dimer or lattice bond ........ 111
Figure 2: Si spring setup for model ...................................................................................... 116
Figure 3: Position of the Si-Si dimer (Mass 56) at equilibrium versus time ......................... 118
Figure 4: Equilibrium velocity of Si-Si dimer versus time .................................................. 119
Figure 5: Si velocity versus position when the surface is at thermal equilibrium .................. 119
Figure 6: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time .......... 125
Figure 7: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time .......... 126
Figure 8: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time .......... 127
Figure 9: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time .......... 128
Figure 10: Comparing the energies of SiF and F₂ (top) and XeF₂ (bottom) versus time ........ 129
Figure 11: Comparing the energies of SiF and F₂ (top) and XeF₂ (bottom) versus time ........ 130
Figure 12: Comparing the energies of SiF and F₂ (top) and XeF₂ (bottom) versus time ........ 131
Figure 13: Comparing the energies of SiF and F₂ (top) and XeF₂ (bottom) versus time ........ 132
Figure 14: Schematic of the vibrational mode at a 7.72 meV (10.7 N/m) frequency .............. 139
Figure 15: Schematic of the vibrational mode at a 69.25 meV (865 N/m) frequency .............. 141
Figure 16: Schematic of the vibrational mode with a frequency of 150 N/m ......................... 142
Figure 17: Schematic of the swing mode of a reconstructed Si(100) 2x1 surface ............... 143
Figure 18: Schematic of the rocking mode of a reconstructed Si(100) 2x1 surface ............... 143
Figure 19: Graph of the excitation time of SiF vs. SiF spring constant ............................. 145
Figure 20: Molecular geometries of the four other Si fragments used in calculations ............. 146
Figure 21: Graph of the excitation time of SiF₂ vs. SiF spring constant ............................. 152
Figure 22: Graph of the excitation time of Si₂F₂ vs. SiF spring constant ............................. 153
Figure 23: Graph of the excitation time of Si₄F₂ vs. SiF spring constant ............................ 153
Figure 24: Graph of the excitation time of Si₆F₂ vs. SiF spring constant ............................ 154

Appendix A:

Figure 1: Electric box distribution for Big Machine inside the pump room ......................... 162
Figure 2: Electrical box distribution for Big Machine diffusion pumps and adjacent outlets .... 164
Figure 3: Electrical box distribution above the Big Machine and in electronics repair area ... 166
Figure 4: Rough schematic of renovated water delivery manifold for Big Machine ............... 169
List of Tables

Chapter II:

Table 1: The Voltage and Flight Time Through Each Ionizer Section ................................................. 32
Table 2: Most Probable Flight Times for Noble Gas Beams at 301.5K .............................................. 35
Table 3: Average Energy for He, Ne, Ar, Kr and Xe Beams, all in kcal/mol, $T_{\text{nozzle}} = 301.5$ K.. 39
Table 4: Average Energy of Neutral Ar, Kr and Xe Following Double Ionization, $T_{\text{noz}} = 301.5$ K ............................................................................................................................................ 42

Chapter III:

Table 1: Relative Amount of Kr(F₂) Produced with Nozzle Pressure, 75% F₂/Kr Beam ............ 74
Table 2: Relative Amount of Kr(F₂) Produced with Nozzle Temperature, 75% F₂/Kr Beam...... 74
Table 3: Absolute Cross Sections for Electron Impact Ionization of Noble Gases 62 .................... 80
Table 4: Transmission Ratios in the Quadrupole Mass Spectrometer ........................................... 80
Table 5: Quantities Used for Kr(F₂) Flux Determination in a 75% F₂/Kr beam ......................... 89
Table 6: Measured Counts for F₂ Signal Using On/Off Shutter Method ..................................... 97
Table 7: Best Fit Parameters to the Integrated TD Signals vs. Time Plots, Signal = a + bx ....... 97
Table 8: Mole Fraction of Kr(F₂) in a 75% F₂/Kr Beam, $T_{\text{nozzle}} = 203$K, $P_{\text{stag}} = 300$ Torr ....... 101

Chapter IV:

Table 1: Excitation times for the Collision of F₂ and XeF₂ with SiF, Si spring constant = 225 N/m ........................................................................................................................................... 133
Table 2: Number of surface Collisions of F₂ and XeF₂ with SiF for any Si spring constant .... 133
Table 3: Maximum energy transfer of F₂ and XeF₂ with SiF for any Si spring constant, in kcal/mol ............................................................................................................................... 134
Table 4: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 10. N/m ............................................................. 140
Table 5: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 850 N/m ............................................................................................................................... 141
Table 6: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 150 N/m ............................................................................................................................... 142
Table 7: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 50. N/m ............................................................................................................................... 143
Table 8: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 400 N/m ............................................................................................................................... 144
Table 9: Excitation times for the collision of F₂ and XeF₂ with a SiF₂ (Mass 75) fragment, various Si spring constants (in femtoseconds) ................................................................. 147
Table 10: Number of Surface Collisions of F₂ and XeF₂ with a SiF₂ (Mass 75) Fragment for Any Si Spring Constant ........................................................................................................ 147
Table 11: Maximum Energy Transfer of F₂ and XeF₂ with a SiF₂ (Mass 75) Fragment for Any Si Spring Constant, in kcal/mol ........................................................................................................ 147
Table 12: Excitation Times For The Collision of F₂ and XeF₂ with a Si₂F₂ (Mass 94) Fragment, Various Si Spring Constants (in femtoseconds) .......................................................... 148
Table 13: Number of Surface Collisions of $F_2$ and $XeF_2$ with a $Si_2F_2$ (Mass 94) Fragment for Any Si Spring Constant ......................................................................................................................... 148
Table 14: Maximum Energy Transfer of $F_2$ and $XeF_2$ with a $Si_2F_2$ (Mass 94) Fragment for Any Si Spring Constant, in kcal/mol ..................................................................................................................... 149
Table 15: Excitation Times For The Collision of $F_2$ and $XeF_2$ with a $Si_4F_2$ (Mass 150) Fragment, Various Si Spring Constants (in femtoseconds) ........................................................................ 149
Table 16: Number of Surface Collisions of $F_2$ and $XeF_2$ with a $Si_4F_2$ (Mass 150) Fragment for Any Si Spring Constant ......................................................................................................................... 150
Table 17: Maximum Energy Transfer of $F_2$ and $XeF_2$ with a $Si_4F_2$ (Mass 150) Fragment for Any Si Spring Constant, in kcal/mol ..................................................................................................................... 150
Table 18: Excitation Times For The Collision of $F_2$ and $XeF_2$ with a $Si_6F_2$ (Mass 206) Fragment, Various Si Spring Constants (in femtoseconds) ........................................................................ 151
Table 19: Number of Surface Collisions of $F_2$ and $XeF_2$ with a $Si_6F_2$ (Mass 206) Fragment for Any Si Spring Constant ......................................................................................................................... 151
Table 20: Maximum Energy Transfer of $F_2$ and $XeF_2$ with a $Si_6F_2$ (Mass 206) Fragment for Any Si Spring Constant, in kcal/mol ..................................................................................................................... 151
Chapter I: Introduction

Semiconductors are presently at the heart of modern day electronics. From computer chips to the light emitting diodes in flat screen televisions/monitors to nanometer-sized electronic gates, semiconductors are found in our everyday lives. Much of the processing of semiconductors is performed through etching, where surface layers of the semiconductor are reacted off to provide the desired structures to produce the electrical and mechanical components of the device. These days, the race is on to etch semiconductors to channels down to 20-30 nm using high-k dielectrics because the smaller the technology, the more power that is available in the smaller package. However, for all that is known on WHAT compounds can etch semiconductors, little is understood about the actual chemical, atom-by-atom, mechanism of the isotropic dry, plasmaless etching process.

Isotropic, dry etchants are desirable because they do not react with complimentary metal oxide semiconductor (CMOS) materials. One example of this type of etchant is xenon difluoride, XeF$_2$, which etches Si rapidly and isotropically without the use of damaging plasma. XeF$_2$ is especially advantageous because it is selective towards Si atoms. It does not react with masks of oxide, nitride, etc. CMOS materials are used in Si microchips where the electronics are integrated with three-dimensional mechanical components called microelectromechanical systems, or MEMS. MEMS are used in many applications, such as actuators, inkjet print heads, accelerometers, optical switching, pressure sensing and even biomedical analysis$^{1-8}$.

This thesis tackles the etching of Si by answering a question that has confused scientists for the last thirty years: Why can the stable linear molecule XeF$_2$ rapidly etch Si in the absence of a plasma, while molecular fluorine cannot? This question becomes more intriguing when one realizes that the reaction of F$_2$ with Si is 20 kcal/mol more exothermic than the same reaction
with XeF$_2$. Based on simple energetics, F$_2$ should be the better etchant! However, studies by our group and others show that the reaction (and thus etching) probability of XeF$_2$ with Si is $10^3$-$10^4$ higher than that of F$_2$ with a fluorinated Si(100) surface.$^9$-$^{13}$

The molecular beam scattering apparatus, described in greater detail in Chapter II and in a past publication,$^{14}$ has been used to discover many mechanisms behind the interactions of fluorine and its associated compounds with Si, namely atom abstraction$^{15}$-$^{17}$, gas-phase dissociation$^{18}$-$^{20}$ and lattice vibrational excitation$^{21}$. The last of these discoveries is the focus of this study. As opposed to interactions where translational energy is needed to surmount the activation barrier, the etching of Si needs lattice vibrational excitation to turn the corner of the potential energy surface because there is a late transition barrier to reaction. Due to the need for lattice excitation, heavier species that encounter multiple collisions with the surface may be better at etching Si. If sufficient deformation occurs for a long enough time from multiple surface collisions, the Si-Si lattice bonds are sufficiently vibrationally excited that reaction with an incoming molecule is made more favorable. So, in the comparison noted above, maybe it is the mass of the XeF$_2$, which is five times greater than that of F$_2$, and 6 times more massive than a single Si surface atom that makes it so reactive. This hypothesis is studied in detail in Chapter IV.

To correlate this mass effect, a different "type" of fluorine-rare gas compound is used. As a trick, fluorine is made heavier by attaching it via a van der Waals interaction to an inert gas atom to form van der Waals dimers Xe(F$_2$) and Kr(F$_2$). These molecules have a theorized T-shape like He(I$_2$), Ne(Cl$_2$) and Kr(Cl$_2$)$^{22}$-$^{26}$ and act like molecular fluorine, just heavier. If the idea that lattice vibrational excitation is the origin of the reactivity difference between XeF$_2$ and F$_2$ with Si is correct, then the reactive probability of the dimers with Si should scale with
increasing mass. Namely, Xe(F₂) should have a similar etching probability with fluorinated Si as XeF₂. Initial studies of Xe(F₂) van der Waals dimers and their reactivity with a fluorinated Si surface have been performed by Hefty²⁷. His experiments showed a reaction probability for Xe(F₂) of 0.9, which is very close to the reported reaction probability of XeF₂ with the same surface, 0.6. This finding lends credence to the idea that the mass of XeF₂ plays a role in increasing reactivity with the Si surface.

This thesis studies the reactivity of Kr(F₂) van der Waals dimers with Si. Kr(F₂) has a mass (122 amu) that is greater than F₂ (38 amu) and less than XeF₂ (167 amu.) If the mass effect holds, Kr(F₂)’s reactivity with the Si surface should lie somewhere between those of F₂ and XeF₂. Chapter III will show that this reactivity trend indeed occurs. This lattice vibrational excitation pathway could explain why many other heavy fluorinated compounds, like BrF₃ and ClF₃ readily etch Si²⁸⁻⁻³⁴, while less heavy compounds, like CF₄, SF₆ and NF₃, do not³⁵⁻⁻³⁷.

The van der Waals dimer Kr(F₂) must be produced using our molecular beam apparatus. The challenges of producing the dimers are discussed in Chapter III. In the same chapter, the mass spectroscopic identification of the dimers and the measurement of their flux are shown. It is necessary to know the dimer flux in order to calculate its reaction probability with the Si surface.

Chapter III also delves into the absolute dimer reactivity with the Si surface. Calculated is the reaction probability of the dimers with a Si surface, especially after one monolayer of fluorine coverage on the Si(100) surface. Our group has shown that between zero and one monolayer of fluorine coverage, F₂ and XeF₂ react exactly the same³⁸. After this initial fluorination, the reactivity difference occurs. Using thermal desorption spectroscopy (TDS), the fluorination of the Si surface is tracked. Knowing the absolute F atom flux from the dimers in
Chapter III, along with the absolute F atom coverage of the Si surface, the probability of adsorption can be found and correlated to the amount of Si etching.

As stated above, the gas-surface energy transfer theory is described in detail in Chapter IV. Using simulation, the amount of energy transferred by a given mass to the Si surface is determined. Comparison of the incoming and scattered energies is made and the energy transfer is calculated. The simulation reveals the number of collisions each species will suffer with the Si surface, and this number of collisions is correlated with the reaction dynamics.

The proposed mechanism of surface vibrational excitation is hoped to provide a roadmap for choosing better, more efficient, plasmaless etchants. This mechanism can also be carried over to other reactions involving covalent solids. The picture provided shows for the first time that the energy transferred to a surface as a result of an incident molecule's initial collision plays a critical role in its reactivity with a surface.

Chapter I References

8) D. Berman, J. Krim, Progress in Surface Science. 88, 171-211 (2013)
Chapter II: Experimental

11.1. Brief Description of Experimental Apparatus

The molecular beam-surface scattering apparatus used in this study has been described in detail. Pertinent details to the experiments in this thesis are described here. The apparatus is comprised of two triply differentially pumped molecular beam source chambers precisely coupled to an ultrahigh vacuum (UHV) main chamber (base pressure = 5 x 10^{-11} Torr.) The molecular beams are precisely arranged to intersect at a Si single crystal positioned at the center of the UHV main chamber. The beams are skimmed and collimated through the first two differentially pumped regions before reaching the crystal.

The main chamber houses a single Si(100) 2x1 crystal that is mounted between two Ta clamps attached to a manipulator. The crystal can be translated linearly in two dimensions and rotated around the normal to the scattering plane. The crystal can be cooled using liquid nitrogen to 110 K and resistively heated to 1100 K. It is p-doped with small resistivities (8-12Ω) at room temperature and is cleaned using the Shiraki wet etching procedure before installation inside the vacuum chamber. To clean the crystal in vacuum, the machine is equipped with an ion gun for sputtering using 1.5 keV Ar⁺ ions. The crystal is annealed to around 1100 K for one minute after sputtering to finish the cleaning process. The crystal is considered clean when less than one percent C or O is found on the surface as determined through Auger Electron Spectroscopy (AES.) The Auger spectrometer in the apparatus is equipped with a cylindrical mirror electrostatic energy analyzer for the analysis. The main chamber is also equipped with a quadrupole mass spectrometer used for residual gas analysis (RGA) to check the cleanliness and vacuum integrity of the UHV chamber.
The scattered and desorbed products are detected before suffering any collisions with the walls of the chamber by a rotatable, triply differentially pumped, line-of-sight mass spectrometer set up coplanar with the Si crystal and the beam. Detected species are produced using electron bombardment ionization. A channeltron is used as the ion-counting device. The mass spectrometer is attached to an ionizer cryostat that is cooled using liquid nitrogen for background reduction. The rotation of the detector ranges from $25^\circ$-$180.3^\circ$ with respect to the primary molecular beam. The mass spectrometer is also equipped with a pseudo-random chopper wheel for cross correlation time-of-flight (TOF) analysis. The chopper wheel consists of 255 slots and it spins at either 280 or 392 Hz using a synchronous hysteresis motor. Using a cross correlation TOF technique, the velocity (and energy) distributions of both the incident beams and the scattered products can be found at any allowed detector angle.

**II.2. Mass Spectroscopy: Experimental Setup**

Mass spectroscopy is the technique of choice for these experiments. Using a rotatable, triply differentially pumped, line of sight quadrupole mass spectrometer, reaction and scattered products, along with the composition of incoming molecular beams, are detected. Once a species is ionized using electron bombardment, it travels through the quadrupole and reaches the channeltron that produces an electron cascade that is picked up by electronics outside the machine. This small 30 to 40 mV pulse is isolated and amplified before being converted to a 5 V TTL pulse. This TTL pulse is detected by the lab computer in a setup described previously. To produce a less noisy signal pulse to the computer, changes were made to the electronics that convert the original pulse to TTL. Similar to the old setup, the 40 mV long, 15 ns wide NIM pulse from the channeltron reaches a preamplifier (Phillips Model 6931) that amplifies the NIM pulse to around 3 V with a similar pulse width. The changes come in the
conversion of this pulse to TTL. Following the initial pulse amplification, the old setup used a 300 MHz discriminator that would convert the NIM pulse to a TTL pulse followed by a homemade pulse lengthener that both amplified the pulse and widened it for unambiguous determination. This setup was found to be too noisy for the current experimental purposes, especially during time of flight experiments. The origin of the noise stems from the circuit picking up some signal from the RF power circuit powering the quadrupole mass spectrometer. This noise was especially prevalent at high masses, where the RF voltage and current is especially high. Replacing the discriminator and pulse lengthener is an Amptek A101 charge sensitive preamplifier-discriminator\textsuperscript{42}. The A101 is placed on a PC-11 test board, also provided by Amptek. The purpose of the PC-11 is multifold: it tests the A101 chip, provides component location for the A101 and its construction reduces external signal pickup, especially from RF sources. There are two input lines on this test board. The “test” line accepts the incoming pulse and produces the desired output pulse. The “in” line accepts the pulse, but has a variable capacitor connected to it to provide extra discrimination of the pulse to further weed out spurious signal. Using the test line of this circuit produces a TTL pulse 5V in amplitude. A capacitor connected between pins 3 and 4 of the A101 controls the pulse width of the output signal. A 2.8 pF capacitor is used for this purpose, producing a pulse width of around 250 nm. The “test” line is used in all the experiments described here because of reduced noise pickup and its pulse stability. The output pulse is sent directly to the lab computer.

II.3. Heating the Si Crystal

Since Si is a semiconductor, resistively heating the crystal from 200 K to 1000 K is challenging. When the temperature of a semiconductor increases, its resistance varies. From 200 K to around 400 K, the resistance increases to the kiloohm range. Above 400 K, the
resistance drops greatly, acting as if it were a metal. This property differs from heating a metal surface, where a linear voltage controlled ramp can be used for heating because the resistance across the crystal remains almost constant. If a voltage only control is used for silicon, the current supplied to the crystal will be far too high, causing the crystal to crack or the heating apparatus to fall apart. To alleviate this problem, a programmable floating power supply is used. The main concept of this supply is to fully control three modes of operation: 1) A low voltage control at low temperatures (from 130 K to around 250 K); 2) A high voltage control at intermediate temperatures (from 250 K to 470 K) and 3) A current control mode at temperatures greater than 470 K. A new supply was made in 2008 to do just these things using more modern electronics. The design is very similar to the control box designed by Gladstone. The changes made to the original design were small yet necessary. All the transistors (three NTE385 for voltage control and eight 2N3055 for current control) used can withstand higher power usage, which helps prevent transistor breakdown. An added operational amplifier (OP3) was added before the input to the isolation amplifier (ISOAMP) as a voltage follower to diagnose any problems. The interlock, which will turn off any electronic control when the thermocouple breaks or is disconnected, is controlled by a better logic chip.

The final major change deals with the current coming across the crystal. In the old setup, a voltage is developed across two “sense” resistors that is measured and scaled by one op-amp and is fed to the non-inverting outputs of the two op-amps that control the use of transistors in the circuit. In the new design, there are four op-amps used for the same purpose. The first op-amp (OP9) is installed before the current reaches the crystal and is used to keep track of the voltage/current supplied to the crystal. The second op-amp (OP10) has the same purpose of the one op-amp in the old design. Both of these signals combine and are fed through two op-amps in
series (OP11 and OP12) that then provide the output voltage to the transistor controlling op-amps (OP7 for voltage control and OP8 for current control.) The purpose of new op-amps is to provide another interlock for crystal heating. There is a BNC output on the box that provides a voltage that directly relates to the current being supplied to the crystal. To determine how much current is being used, multiply the voltage output by two (i.e. a reading of one volt equated to two amps supplied to the crystal.) As in the prior design, this output is also sent to the computer. If the computer determines the output to be too high, it will shut off all current going to the crystal. This output is programmed into the computer before the experiment begins.

II.3.1. Linear Ramping of the Crystal Temperature: Experimental Conditions

The crystal temperature range used in this study is from 250 K to 1000 K. The crystal is held at 250 K through liquid nitrogen cooling. The rate of temperature increase of the surface is 5 K/s and the computer, interfaced with a home-made PID controller, controls this ramp. As with the old design, an ideal temperature curve for linearity is programmed into the computer based on the thermocouple voltage at each temperature. The thermocouple voltage is directly sent to the PID, which then sends a control signal to the programmable power supply. The linear ramping is controlled by three factors: 1) The amount of liquid nitrogen used in cooling the crystal; 2) The setpoint of switching from voltage control to current control and 3) The PID controller itself. During the experiment, liquid nitrogen is still flowing to the crystal. If its flow rate is too low or too high, the PID may not be able to keep the ramp linear. The temperature setpoint of the voltage to current control switch is crucial. If chosen incorrectly, the resistance change in the crystal may be too drastic for the PID to handle. This setpoint is controlled by a rotatable switch on the heating control box and is monitored using a voltmeter. Lastly, the PID controls must be tuned to keep linearity at all times. Adjusting the screws on the box associated
with the proportional, integration and derivative settings does this. Briefly, to tune the PID for a linear ramp, the proportional term is first adjusted so the current does not overload when the temperature is ramped from 250 to 1000 K. Overloading means having the power supply provide too much current to the crystal. In general, the maximum current allowed to reach the crystal should be set at 8 A. The maximum current allowed is set on the lab computer. Following the proportional change, the derivative and integral terms are changed until the ramp is linear. This procedure is used in concert with the procedure outlined by Beckerle\textsuperscript{44}, with extra attention paid to the change of resistivity that occurs with the temperature change of Si. Once linearity is assured, the mass spectrometer is set to monitor both masses 66 and 85 during the heating and the thermal desorption spectra are obtained. A circuit schematic for the floating programmable power supply designed by J. G. Lee is found in Figure 1.
Figure 1: Floating programmable power supply

The top circuit is from the first control board the controls the interlock and the signal to the second board. The circuit for the second board is on the bottom and includes the transistors and circuits used to heat the crystal.
II.4: Time-of Flight (TOF) Mass Spectroscopy

Time-of-flight spectroscopy is useful to determine the energy of both the molecular beam used in an experiment and also the energy of any reaction or scattering products from the surface. It is also useful as a basis for finding the flux of van der Waals dimers in the molecular beam, as will be explained in Chapter III. Here, the procedure for setting up the time-of-flight apparatus and its operation is described.

II.4.1: Setting up the Time of Flight

The core of the TOF setup is the pseudo-random chopper wheel. The wheel consists of 255 slots, 128 “open” and 127 “closed” in a pseudo-random pattern. This pattern leads to an optimized matrix that is used to deconvolute the signal from the machine to produce the proper distribution. The deconvolution procedure is described in another thesis.

In the past, the chopper wheels were machined with the slots cut into the edge of the wheel at a final diameter of 7”. The problem with this setup is twofold: 1) It is very difficult to cut the slots of the wheel to within 0.0005” as is desired and 2) With no edge on the wheel as a barrier for the slots, the edge of the wheel is easily bent. A bent chopper wheel, even at one small spot, is ruined since the pattern of the wheel is slightly altered, as well as the balancing of the setup. To alleviate these problems, a ¼” rim was added to the diameter of the wheel, making it 7.5” in diameter. Before adding this rim, calculations were made to ensure the wheel with added material could withstand the forces caused by spinning at up to 400 Hz. The design for this new wheel is seen in Figure 2.

Prior to 2007, the wheels were made by cutting the slots into either a beryllium-copper or stainless steel wheel. A more accurate method is photoetching the wheel. Photoetching using a given pattern ensures greater reproducibility in each wheel, while it is also cheaper than
machining. The company used for photoetching was PCM Products in Titusville, FL. Typically, ten to twenty wheels should be produced at each time. Once the wheels are received, two or three of them are checked for correct slot size using a comparator at the MIT Central Machine Shop. If each slot is not set to within 0.002”, the TOF experiment could be compromised.

After confirming that the wheels are properly etched, it is essential to make sure they are properly balanced with the rest of the time of flight setup. The setup is described in Holt’s thesis.

The following section will explain how the neutral flight length is found for the experiments described in Chapter III, using the new chopper wheels.
Figure 2: Schematic of the pseudo-random cross correlation chopper wheel
II.4.2: Finding the Neutral Flight Length During Time-of-Flight Experiments

After the big machine explosion in November 2003, a new quadrupole mass spectrometer was installed in the machine, along with a new quadrupole housing. Also, the electron ionizer was remade with a new mount. Since the equipment is now different, the neutral flight length of the gas molecules in a time-of-flight experiment is remeasured, along with the delay times associated with the new ionizer and quadrupole. To properly find the correct number of dimers in the molecular beam, a correct neutral time-of-flight analysis is crucial. In the time-of-flight analysis, the relative flux is calculated in a procedure using IgorPro, reproduced in Appendix B. If the time-of-flight parameters are not correct, the flux will be calculated incorrectly and thus the counting of dimers will be incorrect. The neutral flight length determination is similar to the same performed by McGonigal\textsuperscript{47} with the original equipment. However, there are some crucial differences that are described below.

As a brief introduction, to calculate the neutral flight length, the total time of flight of the scattered or directly incoming species is considered. The total time of flight is the sum of the time it takes for a molecule to travel from the time of flight chopper wheel to the electron multiplier of the quadrupole plus an electronic delay time caused by the fact that the trigger signal slot and the slot on the chopper wheel through which the beam passes are not collocated. This sum is composed of four components: 1) The time for the neutral molecule to travel from chopper wheel to the ionizer entrance \((t_n)\); 2) The time it takes the ionized molecule to reach the quadrupole \((t_i)\); 3) The time it takes the molecule to go through the quadrupole \((t_q)\) and 4) The electronic delay time, \(t_{\text{delay}}\). In equation form, the total time of flight is:

\[
t_{\text{total TOF}} = t_n + t_i + t_q + t_{\text{delay}}
\]

\[2.1\]
The ionizer and quadrupole flight times are calculated using simple electrostatic equations as described by McGonigal with a couple of changes, explained below. Then, the neutral flight length and delay time are found using a linear fit of the total time of flight, taking the calculated ionizer and quadrupole flight times into account. The points on the linear fit are the five noble gas atoms used to determine the flight path: He, Ne, Ar, Kr and Xe. These atoms are chosen because they are monatomic, unreactive gases where there is a simple expression for the average energy at a given temperature, shown in the next section. The overall procedure for finding the neutral flight path is explained in more detail in the following sections.

II.4.2.1: Calculating the Ionizer Flight Time

The ionizer flight time is calculated according to the electrostatic equations used by McGonigal\textsuperscript{47}, with one change that is described below. Assuming that the ions are uniformly accelerated in the ionizer, the equation for the length of the ionizer is solved as:

\[ l_i = \frac{1}{2}at_i^2 + v_0t_i \]  

(2.2)

Where \( l_i \) is the length of the flight path through the ionizer, \( a \) is the ion acceleration and \( v_0 \) is the velocity of the neutral particles. Substituting the electrostatic equation for the acceleration and the classical equation for the velocity yields:

\[ l_i = \frac{qE_i}{2m_i}t_i^2 + \left( \frac{2E_N}{m_N} \right)^{\frac{1}{2}}t_i \]  

(2.3)

where \( q \) is the charge of the ion produced, \( E_i \) is the ion energy, \( m_i \) is the mass of the ion, \( m_N \) is the mass of the neutral atom and \( E_N \) is the energy of the neutral atom. Since the mass of an electron is much smaller than the overall mass of the atom, we can assume that \( m_i = m_N \). Solving for the ionizer time, \( t_i \), yields:
Since the point of this analysis is to find the neutral flight length, it is better to substitute the energy of the molecular beam for \( E_N \) to Equation 2.4, since the translational and rotational degrees of freedom are cooled during expansion. Briefly, the expression for average energy comes from the supersonic nature of the molecular beam. A supersonic expansion is adiabatic, where the enthalpy of the gas is converted into a very uniform flow velocity. Through this enthalpy conversion comes a maximum energy for the beam consisting of a monatomic gas,

\[
C_p \left( T_0 - T \right) = C_p T_0 = \bar{E}
\]

\[
C_p = \frac{5}{2} k_B \quad \text{and} \quad \bar{E} = \frac{5}{2} k_B T_0
\]  

(2.5)

where \( C_p \) is the constant pressure molar heat capacity, \( T_0 \) is the nozzle temperature, \( T \) is the molecular beam temperature and \( k_B \) is Boltzmann’s constant. For an ideal supersonic expansion, \( T \) will be much less than \( T_0 \) and thus the final energy result is as seen in Equation 2.6. Substituting this result into Equation 2.4 yields:

\[
E_N = \frac{5}{2} k_B T_{noz}
\]

Substituting into Equation 2.4,

\[
t_i = \frac{1}{l_{m_i} m_i^{\frac{1}{2}}} \left[ \frac{\left( 5k_B T_{noz} + 2 q E_i \right)^{\frac{1}{2}} - \left( 5k_B T_{noz} \right)^{\frac{1}{2}}}{q E_i} \right]
\]  

(2.6)

where \( k_B \) is Boltzmann’s constant and \( T_{noz} \) is the temperature of the nickel nozzle face, which governs the energy of the beam. In the calibration experiments, the temperature at expansion is around 300 K.

In McGonigal’s calculation, the ion flight time through the ionizer lenses was determined solely by the ion energy. In this new method, the acceleration and deceleration of the ion are
taken into account as it travels through the lens stack, meaning that the flight time varies between lenses. A diagram of the ionizer and lens stack is found in McGonigal's thesis. To optimize the ion trajectory through the ionizer, along with conserving the mass resolution, the three lenses in the ionizer stack, labeled as L1/L2/L3, are set at different voltages. So, to properly calculate the ionizer flight time, the energy of the ion in between each lens is calculated, and thus the time of flight in between each lens is calculated. The ionizer flight length/time is split into six distinct sections, each with their own distinct values. The description of the sections is as follows:

Section 1: From the center of the ionizer to the end of the ionizer cage, 1.50 cm
Section 2: From the end of the cage to half the distance between the extractor and L1, 0.68 cm
Section 3: From half the distance between the extractor and L1 to half the distance between L1 and L2, 0.74 cm
Section 4: From half the distance between L1 and L2 to half the distance between L2 and L3, 0.79 cm
Section 5: From half the distance between L2 and L3 to half the distance between L3 and the quadrupole entrance, 0.58 cm
Section 6: Half the distance between L3 and the quadrupole entrance, 0.16 cm.

The locations of each section were chosen to be in between each of the lenses as an attempt to calculate the flight times as an overall average of the voltage seen in each of the ionizer sections. Also, the voltage at each section is found as the sum of the initial ion energy, -24.6 eV, plus the energy at each lens, -250 eV for the extractor, 0 eV at L1, -203.7 eV at L2 and +3.7 eV at L3. The value at section 6 is equal to the initial ion energy because the ion is treated as being free from the lens stack just before it enters the quadrupole. Table 1 provides the
voltages and calculated flight times in each ionizer section, in terms of the square root of mass, because the mass will vary with the species entering the ionizer.

Table 1: The Voltage and Flight Time Through Each Ionizer Section

<table>
<thead>
<tr>
<th>Ionizer Section</th>
<th>Voltage (eV)</th>
<th>Flight Time ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.6</td>
<td>$1.015 \cdot 10^{13} \left( m_i^{0.5} \right)$</td>
</tr>
<tr>
<td>2</td>
<td>274.6</td>
<td>$1.43 \cdot 10^{12} \left( m_i^{0.5} \right)$</td>
</tr>
<tr>
<td>3</td>
<td>24.6</td>
<td>$5.01 \cdot 10^{12} \left( m_i^{0.5} \right)$</td>
</tr>
<tr>
<td>4</td>
<td>228.3</td>
<td>$1.81 \cdot 10^{12} \left( m_i^{0.5} \right)$</td>
</tr>
<tr>
<td>5</td>
<td>20.9</td>
<td>$4.23 \cdot 10^{12} \left( m_i^{0.5} \right)$</td>
</tr>
<tr>
<td>6</td>
<td>24.6</td>
<td>$1.08 \cdot 10^{12} \left( m_i^{0.5} \right)$</td>
</tr>
</tbody>
</table>

This analysis provides an overall ionizer flight time of $(2.371 \cdot 10^{13} \mu s/ kg^{0.5}) m^{0.5}$ for singly ionized species.

**II.4.2.2: Calculating the Quadrupole Flight Time**

To calculate the flight time of the ionized species through the quadrupole, first the length of the quadrupole is found. This length is defined as the distance between the quadrupole entrance (the end of the ionizer length analysis) and the front of the electron multiplier (channeltron.) It is found through a careful analysis of the drawings for the quadrupole housing, the quadrupole itself and the channeltron flange. J. G. Lee prepared the drawings for each individual piece, which are found in electronic form. A summary drawing of the quadrupole housing, indicating the dimensions used to find the quadrupole flight length, is found in Figure 3. The analysis of the quadrupole length is found in the big machine drawing cabinet and the length
is found to be 23.95 cm. With the length found, the quadrupole flight time is calculated, from McGonigal’s thesis, as:

\[
    t_q = \frac{m}{q} \sqrt{\frac{m}{2E_N + 2qE_i}} = \frac{m}{q} \sqrt{\frac{m}{5k_B T_{noz} + 2qE_i}}
\]  

At a nozzle temperature of 300 K, the quadrupole flight time is \((8.525 \cdot 10^{13} \text{μs/kg}^{0.5}) m^{0.5}\).

Figure 3: Assembly drawing of quadrupole housing

All of the dimensions relevant to finding the quadrupole flight length shown are in inches. They add up to the quadrupole flight length of 9.43” = 23.95 cm.
II.4.2.3: Finding the Most Probable Total Time of Flight

Before finding the neutral flight length, the most probable total time-of-flight for each noble gas species must be found. To obtain this value, the raw, uncorrected time of flight spectra for He, Ne, Ar, Kr and Xe are fit to the following functional form of number of counts at each point versus the time of flight, taken from Holt’s thesis:\(^4^1^):

\[
\text{Counts} = f(t) = B + A \frac{L^3}{t^4} \exp \left[ - \left( \frac{mL^3}{2k_B k_B T} \right) \left( \frac{1}{t} - \frac{1}{t_f} \right)^2 \right]
\]  

(2.8)

where \( B \) is the baseline of the spectrum, \( A \) is a normalization coefficient to fit the spectrum, \( L \) is the length, estimated in this case for the fit, \( t \) is the time, \( t_f \) is a time variable, produced in the fitting algorithm, that shows the flow velocity in the molecular beam, \( T \) is the temperature of the molecular beam, indicating the width of the spectrum, and \( m \) is the mass of the detected species. Each raw, deconvoluted time of flight mass spectrum is fit to this form using IgorPro that provides the smallest chi squared value after many fit iterations. For the calibration experiments, the chopper wheel was spinning at 392 Hz, providing a dwell time (resolution) of 10 microseconds. Therefore, the time axis for this fitting is set so each data point is 10 microseconds apart. The time axis is made manually on IgorPro to ensure correct x-axis fitting.

Then, the most probable flight time value is found by plugging the values of each variable from the initial fit into the most probable value equation which is just the maximum calculated from the first derivative of Equation 2.8, \( \frac{d(f(t))}{dt} \):

\[
t_{np} = \frac{mL^2}{8k_B k_B T t_f} \left[ -1 + \sqrt{1 + \frac{16k_B k_B T t_f^2}{mL^2}} \right]
\]  

(2.9)
The most probable total flight time was found for each of ten runs for He\(^+\), Ne\(^+\), Ar\(^+\), Kr\(^+\) and Xe\(^+\) and then averaged to give the total flight time for each of those species, and is shown in Table 2.

Table 2: Most Probable Flight Times for Noble Gas Beams at 301.5K

<table>
<thead>
<tr>
<th>Species</th>
<th>Most Probable TOF (microseconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(^+)</td>
<td>176.8</td>
</tr>
<tr>
<td>Ne(^+)</td>
<td>391.6</td>
</tr>
<tr>
<td>Ar(^+)</td>
<td>548.4</td>
</tr>
<tr>
<td>Kr(^+)</td>
<td>793.4</td>
</tr>
<tr>
<td>Xe(^+)</td>
<td>999.8</td>
</tr>
</tbody>
</table>

II.4.2.4: Solving for the Neutral Flight Length and Electronic Delay Time

The neutral flight length and electronic delay time are found using a similar procedure as McGonigal\(^{47}\). The flight time for neutral molecules is expressed as:

\[
t_N = l_N \sqrt{\frac{m_N}{E_N}}
\]  

(2.10)

where \(l_N\) is the neutral flight length. Combining the ionizer, quadrupole, neutral and electronic delay times provides the following total flight time equation:

\[
t_{\text{total}} = m^{0.5} \left[ l_i \left( \frac{5k_B T_{\text{noz}} + 2qE_i}{qE_i} \right)^{\frac{1}{2}} - \left( \frac{5k_B T_{\text{noz}}}{5k_B T_{\text{noz}} + 2qE_i} \right)^{\frac{1}{2}} \right] + l_q \sqrt{\frac{m}{5k_B T_{\text{noz}} + 2qE_i}} + l_N \sqrt{\frac{1}{5k_B T_{\text{noz}}}} + t_d
\]

(2.11)

Here, a plot of total flight time versus the square root of mass will provide a slope that is the sum inside the brackets and a y-intercept that is the electronic delay time. McGonigal plotted the total flight time versus the square root of the mass and then subtracted the ionizer and quadrupole contributions to the slope before finding the neutral flight length. Here, the
quadrupole and ionizer flight times were subtracted before the time versus (mass)^0.5 plot was made to simplify the analysis of the slope to extract the neutral flight length.

Once the quadrupole and ionizer flight times are properly subtracted using the values calculated above, the plot of “Neutral Flight Time Plus Delay Time” versus the square root of mass is made using contributions for He, Ne, Ar and Kr and Xe. Figure 4 shows the linear fit. As is shown on the graph, this analysis yields a neutral flight length of 29.3 cm and an electronic delay time of -1.0355 microseconds.

Figure 4: Plot of neutral plus electronic delay time versus the square root of mass for He, Ne, Ar, Kr and Xe.

The data points are the average of the most probable flight times for each species with ionizer and quadrupole flight times subtracted. The data are fit to a line with a slope that yielded the neutral flight length and a y-intercept that yielded the electronic delay time.
From this plot, it is noted that the point for Xe diverges the most from the linear fit. This divergence may arise from the larger width of its time of flight spectrum, and thus higher beam temperature ($T_{\text{beam}} = 5-10$ K for the Xe beams.) This higher beam temperature makes the molecular beam for pure Xe slightly less supersonic, leading to an artificially longer flight time, and thus a larger neutral flight length than actually is present. Also, the electronic delay time is found to be negative for this analysis. It is expected that the electronics would add time to the total time-of-flight, not subtract time from it. However, the beam temperature for He is also higher than expected for a supersonic beam, again 5-10 K. Figure 5 shows the same plot as in Figure 4 with He removed from the plot to see if Xe is less divergent from the linear fit.

Figure 5: Plot of neutral plus electronic delay time versus the square root of mass for Ne, Ar, Kr and Xe.

The data points are the average of the most probable flight times for each species with ionizer and quadrupole flight times subtracted. The data are fit to a line with a slope that yielded the neutral flight length and a y-intercept that yielded the electronic delay time.
The analysis with He excluded from the plot yields a neutral flight length of 29.55 cm and an electronic delay time of -6.3336 \( \mu s \). The delay time is now more negative, along with a longer neutral flight length. The point for Xe is still divergent from the linear fit. Perhaps, again, the total time of flight for Xe is just too long because the beam is not fully supersonic. Also, the point for Kr is much lower than the linear fit in this plot than it was in the Figure 4 plot. The greater neutral flight length and more negative delay time could also be an artifact of the overly long flight time for Xe causing a steeper slope for the line, which gives a worse fit for the other data points.

Figure 6 is the same plot as in Figures 4 and 5, but this time provides a linear fit for the most probable flight times of He, Ne, Ar and Kr. The analysis with Xe excluded from the plot yields a neutral flight length of 28.82 cm and an electronic delay time of +5.2889 \( \mu s \).

Excluding Xe from the analysis excludes the least supersonic molecular beam, which takes out a point where the most probable flight time is too large. Now, the data points for He, Ne, Ar and Kr are less divergent from the linear fit in Figure 6 than Xe was in Figures 4 and 5. Also, the electronic delay time is now a positive value, something that did not happen in the last two plots. Even though He also has a large beam temperature, it is well fit in this plot. Removal of He from the analysis in Figure 5 did not lead to an improvement in linear fit, while removal of Xe from the analysis in Figure 6 did. Table 3 shows the average energy found for He, Ne, Ar, Kr and Xe supersonic beams using the neutral flight length and delay time found using the all the He/Ne/Ar/Kr and He/Ne/Ar/Kr/Xe ans Ne/Ar/Kr/Xe analyses. Each energy is the average from three time-of-flight experiments for each species. The expected energy of each beam at the experimental temperature of 301.5 K is 1.498 kcal/mol, as found using Equation 2.5.
Figure 6: Plot of neutral plus electronic delay time versus the square root of mass for He, Ne, Ar and Kr.

The data points are the average of the most probable flight times for each species with ionizer and quadrupole flight times subtracted. The data are fit to a line with a slope that yielded the neutral flight length and a y-intercept that yielded the electronic delay time.

Table 3: Average Energy for He, Ne, Ar, Kr and Xe Beams, all in kcal/mol, $T_{\text{nozzle}} = 301.5$ K

<table>
<thead>
<tr>
<th>Species</th>
<th>Energy $l_a = 28.82$ cm, 5.09 $\mu$s delay</th>
<th>Energy $l_a = 29.3$ cm, -1.04 $\mu$s delay</th>
<th>Energy $l_a = 29.55$ cm, -6.336 $\mu$s delay</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.500</td>
<td>1.433</td>
<td>1.37</td>
</tr>
<tr>
<td>Ne</td>
<td>1.483</td>
<td>1.475</td>
<td>1.459</td>
</tr>
<tr>
<td>Ar</td>
<td>1.502</td>
<td>1.509</td>
<td>1.505</td>
</tr>
<tr>
<td>Kr</td>
<td>1.497</td>
<td>1.515</td>
<td>1.520</td>
</tr>
<tr>
<td>Xe</td>
<td>1.443</td>
<td>1.466</td>
<td>1.484</td>
</tr>
</tbody>
</table>
As seen in Table 3, the average energy found for He, Ne, Ar and Kr are within 1.5% of the theoretically calculated energy using 28.82 cm as the neutral flight length. However, Xe has a lower energy than expected for a truly supersonic beam, further evidence that the Xe beams are not fully supersonic upon expansion.

Using 29.3 cm as the neutral flight length changes the results for average energy. However, two issues arise with these values. First, the energies of Ar and Kr are greater than 1.498 kcal/mol, which is physically impossible. Second, the He beam energy is now 5% lower than expected. The Xe beam has an energy closer to 1.498 kcal/mol, but the unphysical results for Ar and Kr, along with the very low energy of He, makes this result not work as well.

The same trend applies for column 3 of the analysis with a neutral flight length of 29.55 cm. First, the He and Ne energies are too low, 1.37 kcal/mol and 1.459 kcal/mol, respectively, indicating the flight length is too long. Also, the Ar and Kr energies are still greater than the theoretical energy, which is unphysical. The results from the linear fit in Figure 6 (28.82 cm flight length with a 5.09 μs delay time) are now used time-of-flight analyses.

A caveat is necessary to properly use the values calculated above in the time of flight fitting algorithm. To fit a time of flight spectrum in IgorPro, the quadrupole, ionizer and electronic delay times are subtracted from the total time of flight. To properly subtract the ionizer and quadrupole flight time contributions, a quick conversion must be made that is shown in Equation 2.12. Basically, the ionizer and quadrupole flight time calculation performed above used units of kg for the mass. The time-of-flight fitting algorithm treats mass as g/mol. Equation 2.12 converts the $\frac{\mu s}{kg^{0.5}}$ unit to $\frac{\mu s \cdot mol^{0.5}}{g^{0.5}}$, yielding the final value for the subtraction of the ionizer and quadrupole flight times in the time of flight fitting procedure:
\[
t_i + t_q = \left(2.371 \cdot 10^{13} + 8.525 \cdot 10^{13}\right) m^{0.5} = \left(1.0896 \cdot 10^{14} \text{ kg}^{0.5} \right) \sqrt{m} \text{ for } q = 1
\]

Convert: \[1.0896 \cdot 10^{14} \text{ kg}^{0.5} \cdot \frac{\mu \text{s}}{10^7 \text{ g}} \cdot \frac{10^7 \text{ g}}{6.022 \cdot 10^{23}} = 4.4401 \mu \text{s} \cdot \text{mol}^{0.5}
\]

\[\therefore t_i + t_q = 4.4401 \sqrt{m} \mu \text{s}
\]

With this value in hand, the total subtracted time from the total time of flight spectrum is set in IgorPro as:

\[4.4401 \sqrt{m} + 5.2889 \mu \text{s}
\]

This time of flight analysis is good for the current setup inside the Big Machine. If the chopper wheel is changed because it becomes bent or broken, or if the chopper motor shaft is replaced, recalibration must be performed according to the procedure above. That is, the ionizer flight time is recalibrated according to the lens voltages chosen for the experiment, and the delay time is found again based on the total flight time of monatomic noble gases.

### II.4.2.5: Time of Flight Analysis of Doubly Ionized Ar, Kr and Xe

To show that the neutral flight length and delay time are accurate for the time-of-flight analysis further, doubly ionized TOF spectra for Ar, Kr and Xe were taken. He and Ne were not studied because the second electron impact ionization cross sections for them (\(\text{He}^+ \rightarrow e^- + \text{He}^{2+}\) or \(\text{Ne}^+ \rightarrow e^- + \text{Ne}^{2+}\)) are small enough that detection of the doubly ionized species is difficult, precluding sufficient counting for taking a spectrum. To properly study the double ionized times of flight, the ionizer and quadrupole flight times must be adjusted, since the charge of the final ion is now +2. Without going into the detailed calculation, the flight time equation through the ionizer and quadrupoles for doubly ionized species is shown below as it is written in the IgorPro program.
42

\[ t_i + t_q + t_{\text{delay}} \ (\text{for } q = +2) = \left( 3.152 \cdot \sqrt{m} + 5.2889 \right) \mu s \]  
\hspace{1cm} (2.14)

For the doubly ionized species, the neutral flight length (28.82 cm) and electronic delay time (5.2889 \mu s) found in the last section are used to fit the TOF spectra. The electronic delay time is treated to be the same for both the singly and doubly ionized species. Just like the single ion experiments, the chopper wheel is spinning at 392 Hz throughout the double ion experiments. The average neutral energy is found for the doubly ionized spectra and should be almost identical to the energies for the singly ionized beams, since the mass is still the same (the m/e ratio changes, but the overall mass of the species is approximately the same since only two electrons have been lost). Also, the ionizer and quadrupole flight times are adjusted for double ions. Table 4 shows the average energy results.

Table 4: Average Energy of Neutral Ar, Kr and Xe Following Double Ionization, T_{\text{noe}} = 301.5 K

<table>
<thead>
<tr>
<th>Species</th>
<th>Average Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar\textsuperscript{2+}</td>
<td>1.485</td>
</tr>
<tr>
<td>Kr\textsuperscript{2+}</td>
<td>1.476</td>
</tr>
<tr>
<td>Xe\textsuperscript{2+}</td>
<td>1.466</td>
</tr>
</tbody>
</table>

Here, it is seen that the average energies for each beam are slightly less than the expected value for a nozzle temperature of 301.5K, 1.498 kcal/mol, but are still within 1-2%. By merely adjusting the ionizer and quadrupole flight times and nothing else, the spectra are almost identical to the singly ionized spectra (see Table 3, Column 1), further showing that the neutral flight length and delay time found in the last section are accurate.
II.5: Modifications to the Source Nozzle for Increased Cooling

Cooling the nickel nozzle is accomplished using a helium cryostat. The nozzle is connected to the cryohead using a tinned copper braid. The braid is clamped to the cryohead by an aluminum plate attached using four 8-32 screws. Monitoring of cryostat performance and nozzle temperature is accomplished through the use of two thermocouples. One thermocouple is pressed to the aluminum plate by one of the washers used in the 8-32 screw attachment to the cryohead to determine the approximate temperature of the cold head and thus the coldest end of the Cu braid. The other thermocouple is spot welded to the front face of the nozzle to measure the nozzle, and thus molecular beam, temperature at the onset of expansion. Optimally, the nozzle temperature would reach -75 to -100°C and be consistent throughout the experiments, usually 8-12 hours. The nozzle used in the current experiments is the same design (and same nozzle) as that used by R. C. Hefty\textsuperscript{27}.

The setup described above was used for both the old and new nozzle cooling setup, which will be described below. However, there are crucial differences that spurred the need for a new design, mainly with the nozzle holder. The former setup utilized the old nozzle holder that is optimized for heating the nozzle to temperatures of 1100 K. The holder was made of a solid Cu block surrounding the nozzle. The main problem with using a copper nozzle holder is that Cu is an excellent thermal conductor. Even though the cold head temperature is plenty cold (around -210°C as read at the Al plate), the nozzle temperature would not go below -55°C, even with the use of Cu braids screwed tightly to the bottom of the cold head. At this temperature, it has been shown that dimer production is not optimized, especially for Xe(F\textsubscript{2}) dimers\textsuperscript{27}. Clearly, a nozzle holder made of a material with lower thermal conductivity, while being suitable for high vacuum and fluorine applications, is ideal.
The new nozzle holder assembly, as designed by J. G. Lee, utilizes polyetheretherketone (PEEK,) a polymer that has the desired properties just mentioned. Notably, the thermal conductivity at room temperature is $3.15 \text{ BTU} \cdot \text{in} / \text{ft}^2 \cdot \text{hr} \cdot \text{°C}$, compared to $4.81 \cdot 10^3 \text{ BTU} \cdot \text{in} / \text{ft}^2 \cdot \text{hr} \cdot \text{°C}$ for pure copper. Basically, a thermal insulator replaces a conductor, which is essential for the cooling that is needed. PEEK also has excellent resistance to gaseous halogens up to temperatures of $150^\circ \text{C}$. Though the concentration of fluorine gas used in this study is small, the material needs to be highly fluorine resistant because it is holding the nozzle in place, while encountering the highest fluorine concentration in the experiment. If it degrades in the presence of fluorine, the nozzle will become misaligned in front of the molecular beam skimmer, preventing the beam from reaching the crystal and detector apparatus. A $\frac{1}{2}''$ hole $5/16''$ deep is tapped on this piece to hold the nozzle in place. There is also a $\frac{1}{4}''$ slot cut into the holder for the nozzle to rest. A second piece, also made of PEEK, is a support for the nozzle tube. It is attached to the PEEK piece described above with two 4-40 screws. This piece provides extra stability for the nozzle.

Along with the PEEK portion of the nozzle holder, a stainless steel piece connects the nozzle holder directly connected to the chamber wall. It is shown in Fig. 7. It is attached to the source chamber using four 8-32 screws and two $3/16''$ dowel pins. The PEEK piece is attached to the stainless steel piece using four 10-32 screws and two $3/16''$ dowel pins. This piece replaced a similar piece made out of copper. Stainless steel, though having a higher thermal conductivity than PEEK (but lower than copper), is fine for this application because the nozzle, which is the cooled element of the assembly, does not rest in this piece, it rests in the PEEK. The schematics for the nozzle holder are found in Figures 7-9.
Once these pieces are attached to the nozzle and source chamber, the tinned copper braid mentioned above must be attached. Ideally, this braid must be as short as possible from the cold head to the nozzle with a little bit of extra length in case added modifications are needed in the future. The current setup uses three braids stacked on top of each other and are bound tightly together using thin copper wire. The braids are tightly squeezed between the aluminum plate and the bottom of the cold head using four screws. The braids are then attached to the nozzle using thin copper wire. Any added length of the braids are bundled up and tied with copper wire. Care must be taken not to have the braids touch the bottom of the source chamber, thus leading to a heat sink that would prevent ideal cooling of the nozzle. Care must also be taken not to knock the nozzle out of alignment. Even though the setup described here is solid, it is not perfect. If too much force is used to connect the copper braid, the nozzle could move. Should the nozzle be displaced, alignment must be re-done using a procedure described previously.

After the nozzle cooling setup is fully assembled, other necessary procedures are used to ensure consistent cooling of the nozzle to the desired temperature. First, the helium inside the cryostat has to be ultrapure using 99.999% pure He. Performing a purification cycle ensures this. Briefly, a He transfer system is filled with ultrapure helium gas and is attached to the cryopump. Then, the cryopump is pressurized to around 280 psi He and is bled to around 30 psi. This cycle is repeated 5-10 times. With each run, the purity of He in the cryopump should increase. Once He purification is done, the lines are disconnected and the pump is ready to work. Second, the nozzle face needs to be clear of any oil or other contamination. To remove contaminations, the nozzle is heated to 70°C overnight using two wires attached to the nozzle face that provide the necessary heating current. The heating wires are connected to a variac that is plugged into a PID controller. This controller also displays the temperature of the nozzle. With the variac powered
at around 15 V, the nozzle can easily heat to 70°C and the temperature remains constant within one-tenth of a degree. Once this variac is turned off, it takes around one hour for the nozzle to cool to room temperature. If the nozzle is especially dirty, it can be heated to 200°C for around 5-10 minutes without affecting the PEEK holder.

Once helium purity and nozzle cleanliness is ensured, the nozzle can be cooled. Using all the steps above, the nozzle is easily cooled to around -75°C with a cold head temperature of -210°C. If these numbers are not reached, wait for one day, bake out the nozzle front and perform the cooling procedure again. The wait is necessary to allow the whole cooling setup to properly thaw, thus removing any excess pump oil from the cooling area. The bake out further helps the removal of the pump oil from the nozzle face.

The temperature of the nozzle can reach around 180 K if the cryogenic cooler has not been used for a few days and the whole nozzle setup is cleaned with acetone and/or toluene and thus free of oil contamination. However, the source chamber has a base pressure of around 10^{-6} Torr and, unlike the main chamber and second stage of the molecular beam chamber, there is no water or liquid nitrogen cooled baffle on the source pump that prevents diffusion pump oil from entering the chamber. Consequently, there is a slight coating of oil on the nozzle cooling apparatus that hinders it from being cooled to the lowest possible temperature all the time. However, consistent cooling to 200 K is obtainable daily, which is still an improvement over past results.
Figure 7: Schematic of stainless steel piece of the nozzle holder

NOTE: THE DOWEL PIN HOLES ON FRONT AND REAR PLATES MUST BE ALIGNED WITHIN 0.001"
Figure 8: Schematic of PEEK pieces for nozzle holder
**Figure 9: Nozzle holder assembly**

The Ni nozzle is shown in green, the black is the PEEK Nozzle Holder and the Stainless Steel Piece is shown in yellow. The curved piece is the molecular beam skimmer.
II.6: Remaking of the Ionizer Cryostat Flange

In March 2011, a vacuum leak was found on the lid of the scattering machine at the flange where the ionizer cryostat is installed inside the detector box. This leak was caused by corrosion over the years due to ice buildup as the ionizer cryostat is cooled to liquid nitrogen temperatures. Also, there was evidence of indents on the lid due to installation of bolts that were slightly too large, which could have “lifted” the weld enough to cause the stress necessary for a leak.

The challenge of such a leak is that the flange is welded to a tube that is welded to the bottom of the lid inside the machine. For helium leak checking purposes, both of these welds are equivalent. That is, it is impossible to truly differentiate between the “upper” weld where the tube is welded to the flange and the “lower” weld where the tube is welded to the machine lid. The scanned drawing of what is meant by “upper” and “lower” weld is shown in Figure 10. The best idea of where the leak is located is found by timing how long it takes for the helium to be detected by the leak checker. If the leak is at the upper weld, the helium would arrive more quickly than it would if the leak were at the bottom weld since the leak is closer to the helium flow.

When the original leak was found, evidence showed it was at a concentrated spot on the upper weld. Scott Spence at the MIT Central Machine Shop rewelded this spot. This re-weld fixed the leak but two more leaks opened to the left and to the right of the repaired weld. The heat used to re-weld the original leak opened up these leaks. There was enough corrosion inside the flange and tube area that the weld overall was quite weak. Eventually, the whole top weld was rewelded but the lower weld started to leak. The repair of the lower weld quickly failed due to the corrosion “falling out” of the tube with every attempt,
Figure 10: The original welding diagram of the ionizer cryostat flange and tube setup.
As scanned by S.T. Ceyer. The upper and lower welds are indicated on the drawing.

leading to an impossible welding situation. The tube and flange had to be completely removed and a new one installed.

The most crucial part of making and installing a new flange and tube is ensuring that the position of the flange is absolutely correct. Any error makes it impossible to install the ionizer cryostat at the correct position, thus preventing proper detection of molecules coming from the direct molecular beam or the crystal. As an aside, there are two machined slits on the ionizer cryostat that allow detectable particles from experiments to pass through to the quadrupole mass
spectrometer. The entrance slit is where the particles enter the cryostat and the exit slit is where the ionized particles enter the quadrupole. If these slits are not aligned, it would be impossible to count the particles correctly at the correct angle/orientation. There is a limit to the horizontal and vertical positions where new slits could be machined. Initial calculations were made to find out how much room for error was present in the new installation. Based on the design of the entrance and exit slits from the last time the cryostat was properly aligned, the maximum horizontal (x-axis) error was 0.026" translationally, or a 0.075 degree maximum rotation error. The maximum vertical (y-axis) error was 0.143" translationally, or 3.03 degrees rotationally. Figure 11 shows the frame of reference used for these calculations. All these calculations take into account the length of the ionizer cryostat, found in Tate’s thesis\(^4\), where the cryostat axis is the z-axis, which is not shown in Figure 11. This axis is perpendicular to the x-y plane and is necessary to ensure the correct reference point is used to solve for the values indicated.

The best way to ensure correct positioning would be to remove the lid of the scattering machine and perform all the machining and welding using the bottom of the bearing surface on the lid as a reference point. However, to save time and money, the top of the bearing surface was used as a reference to find the correct flange position on the z-axis with respect to this surface. For the correct translational x and y-axis positions, the dowel pin reference on the original flange was used, which is located at the very bottom of the flange in Figure 11. A hole was drilled \(\frac{1}{4}\)" into the lid through the dowel pin hole to indicate the correct position. Another challenge is making sure the flange is rotationally at the correct position. To ensure this, tabs were tack welded on the lid at three positions around the diameter of the flange. Through these tabs, a locking nut and screw were used to replicate the correct flange position. Here, the locking screw was made to just barely touch the original flange. The correct position was found when a
0.0015" feeler gauge could no longer slide in between each screw and the flange. Once these tabs were correct, the original flange was cut out of the machine and the whole area was cleaned to ensure no more rust or other sediment was trapped in the area.

![Figure 11: Frame of reference for the ionizer cryostat flange.](image)

The bottom ridge is always at the bottom in all measurements because the ridge is closest to the edge of the lid.

Once the original flange was removed, the MIT Central Machine Shop made measurements to replicate the diameter of the flange, along with the thickness, so it would fit properly once installed. The flange and the tube were first rough machined with the tube length made intentionally long so a cap could be welded to the bottom of it. The purpose of the cap is to close the bottom of the flange and tube so it could be properly leak checked before final machining. After the flange/tube weld was shown not to leak, the cap was cut off and the tube
machined to the proper length. Also, the through holes for the bolts were drilled into the flange and the dowel pin hole precisely placed. The final machined flange is shown in Figure 12.

Figure 12: Final machined ionizer flange and tube setup
As a preliminary check, once the flange and tube were final machined, the setup was tack welded to the top of the lid to ensure the x/y-axis alignment was correct using the tabs set up on the lid. Following the tack welding, the ionizer cryostat was installed and the x/y-axis positions of the entrance and exit slits were checked and then compared to the same positions measured before the original flange was removed from the machine. Note that the z-axis position could not be checked because the tack welds cannot hold vacuum. Since the z-axis position is calibrated when the cryostat is pumped down to vacuum and cooled to liquid nitrogen temperatures, it is impossible to correctly check that during this test. If the x/y-axis position is not correct, the tack welds can easily be removed. Then, the flange is set up to the correct position by incrementally moving the locking screws at the positions where the flange movement would fix the problem. Once the flange was as close as possible to the correct position, the flange and tube were fully vacuum welded to the machine at the top and bottom of the cryostat flange entrance.

Once welding was complete, there was distortion in the new flange due to the heat from the welding. The flange went slightly concave, where the locking key diameter changed from 6.120” to 6.115”, making the ionizer cryostat unable to fit inside the machine. On the ionizer cryostat, there is a key that is 6.119” in diameter that enables precise entry into the machine. The MIT Central Machine Shop performed the measurement of the key. To make the hole the correct diameter, a replicate flange was made of Stainless Steel A2, an extra hard stainless tooling steel that could withstand grinding against it. With a set hole diameter of 6.120”, the flange was bolted on top of the newly installed flange and the new flange was ground until it reached the correct diameter. The correct diameter was confirmed using micrometers at many places on the flange.
Also, the flange topology was changed enough such that the aluminum gasket used when the cryostat is installed would not seal properly. Namely, along the top surface closest to the gasket, there was waviness up to 0.005", which would lead to improper sealing and/or impossibility of correctly replicating the tightness of the seal whenever the cryostat needed to be removed for repairs then reinstalled. This problem was solved using a process called lapping. In lapping, a piece of heavy steel was machined such that it would fit against the flange and could be moved back and forth. Grease made with fine alumina is placed on this piece where it meets with the flange. When the lapping piece is moved back and forth, the stainless steel flange sands down. After many iterations, the flange was determined flat enough to proceed.

With complete installation of the flange, the ionizer entrance and exit slits were aligned using the procedure explained in M. R. Tate’s Ph.D. Thesis\textsuperscript{49}, with two slight changes. First, the detector box was pumped down using the sorption pump cart designed for the new machine. With constant liquid nitrogen addition to the sorption pumps, the pressure inside the detector box would remain constant at 10 mTorr for at least 20 hours. This process is easier than the old procedure of installing all the turbomolecular pumps and evacuating the detector box with them. Second, to measure the movement necessary for the entrance slit alignment, the old entrance slit was used. Since the entrance slit is rectangular, the horizontal and vertical off centeredness is measured and the new entrance slit is machined using the measurements of the off centeredness of the old slit. The final results, compared to the old entrance slit as made by J. G. Lee, moved 0.002" vertically up or down and 0.011" to the left. To properly set up the ionizer exit slit, a set of crosshairs was made in the middle of the rough machined ionizer flange and the off centeredness was measured. Currently, the exit slit is positioned 0.009" to the left and 0.046"
above the center of the ionizer flange, looking from the direction of the incoming beam. That is, from the source side of the machine.

One final change that came from the new flange is the straight through angle on the lid. This angle is defined as the angle where the molecular beam would directly enter the detector box. Before the new flange installation, this angle was 270.15°, as read on the lid. Currently, a straight through angle is approximately 270.05°. It is difficult to place the detector at this angle because the vernier on the lid is precisely measured every 0.0825 degrees. So, the correct angle is found by rotating the lid to a place where the angle indicator is approximately in between the scribe marks at 270.000° and 270.0825°.
II.7: New Detector Beam Valve Insert

Many time-of-flight spectra are measured of the incident beam. These measurements are crucial to finding the energy of a beam, as well as calibrating the ionizer and delay flight times of the total time of flight, among other applications. The biggest challenge in measuring such a spectrum resides in the data handling. The multi-channel scaler and the data acquisition computer can only store a certain amount of counts from the experiment until a data overload occurs. To alleviate this problem, a beam valve insert was designed and machined that includes a small entry hole for the beam. This hole, 0.012” in diameter, is machined much smaller than the diameter of the entrance slit into the detector for the purpose of allowing fewer molecules into the ionizer. To make this hole, a hole 0.093” in diameter was bored 0.06” deep, which acts as a counterbore. Then, the 0.012” hole was drilled through the piece, directly in the middle of the counterbore. This counterbore was made to make sure only the molecules we want to detect enter the ionizer cryostat. If the hole drilled was 0.012” throughout, there is a greater chance of molecules colliding with the side-walls of the beam valve before entering the ionizer region. Such molecules lead to increased background and cloud up the results of the experiment. With this insert, the time of flight and general mass spectroscopy of a straight through molecular beam is taken without any counting problems. This new plate replaces the old beam valve plate that had a small piece of metal attached to the bottom of it to effectively block some of the beam. The drawing is included in Figure 13. This insert is attached to the beam valve using two 8-32 screws. The screws are inserted through the two 0.15” drilled holes on the insert, encountering two 8-32 tapped holes on the beam valve itself.

To properly use this smaller entrance hole, first shoot a molecular beam of Ar into the chamber. Then, with the mass spectrometer set to detect $^{40}$Ar, track the counts on the MASSET4
program until a maximum is obtained as the position of the detector beam valve is varied. At this maximum, it is assumed that the beam is correctly aligned with the center of the small beam hole. Note that this procedure may take multiple iterations of raising and lowering the beam valve. Counts are displayed once per second on the computer. There is a slight delay of one to two seconds in finding a change in counts when changing the height of the beam valve. Taking this delay into account can prevent the user from constantly moving the beam valve up and down too quickly, which makes it tougher to find the correct position.
Figure 13: Drawing of new detector beam valve plate and extension
Chapter II References:


42) Amptek A101 preamplifier, Amptek Inc., Bedford, MA

43) D. J. Gladstone, Ph.D. Thesis, Massachusetts Institute of Technology, 1988


46) Calculations were based on a method from Timoshenko’s “Strength of Materials”


49) M. R. Tate, Ph.D. Thesis, Massachusetts Institute of Technology, 1999
Chapter III: Initial Studies into the Fluorine Atom Reaction Probability For Kr(F₂)

III.1: XeF₂ Etches Si(100) More Readily than F₂. Why?

Past results from our group have shown that a low energy molecular beam of F₂ (<3.8 kcal/mol) does not react with a fluorinated Si surface, while low energy XeF₂ does¹⁵,⁵⁰. To explain the reactivity difference between XeF₂ and F₂ with a fluorinated surface, it is instructive to review the complete mechanism of Si fluorination, since this difference is coverage dependent.

The Si surface that was used to find this difference is Si(100)2x1, a reconstructed Si(100) surface where the surface atoms relax to form asymmetric dimers (Si-Si σ-bonds) to reduce the overall free energy of the surface for stability. The main consequence of this reconstruction is that each surface Si atom now has only one dangling bond, instead of two dangling bonds per Si atom for a non-reconstructed surface. Figure 1 shows schematically the reconstruction of the Si(100) surface.

For any fluorine coverage less than one monolayer, F₂ and XeF₂ react with the surface via an atom abstraction mechanism¹⁶. In atom abstraction, a single F atom is abstracted by the Si dangling bond, while its complementary radical, be it F or XeF, is scattered into the gas phase. This mechanism has been found to occur in the interactions of F₂ and XeF₂ with Si(100) up to 1 ML (monolayer) of coverage. Once the coverage reaches 1 ML, the reactivities of F₂ and XeF₂ diverge. Past results from our group have shown the probability of reaction of F₂ with a fluorinated Si(100) 2x1 surface is on the order of 10⁻⁴, while the same probability using XeF₂ is 0.9, essentially unity. Using helium atom scattering, our group found that one mechanism for further fluorination has XeF₂ reacting with the Si-Si dimer bonds. The other mechanism has XeF₂ reacting with the Si-Si lattice bonds. Both mechanisms are in play as shown in studies of
high energy F\textsubscript{2} (4 - 13 kcal/mol) interacting with a fluorinated Si surface\textsuperscript{16} and are also likely in play for XeF\textsubscript{2}. That is, there seems to be no preference for high energy F\textsubscript{2} or XeF\textsubscript{2} to react with either the Si-Si dimer bonds or the lattice bonds. Perhaps the reaction would be preferential to the Si-Si dimer bonds to start, since the surface dimer bonds are weaker than the Si-Si lattice bonds, based on simulation\textsuperscript{51}. Mechanistically, the Si-Si lattice and dimer bonds are excited when interacting with XeF\textsubscript{2} enough to help promote reaction with more F atoms, a mechanism that does not occur when F\textsubscript{2} is used. Following the initial reaction with the fluorinated Si surface, the underlying layers of Si(100), which react readily with fluorine, are now open for further reaction. This process is called plasmaless or isotropic dry etching and is carried out with both the incident molecule and the surface at room temperature. Its advantage over plasma etching rests in the absence of ions, where the ions from the plasma may implant into the Si and function as traps for charge carriers.
Figure 1: Top and side views of the reconstruction of the Si(100) surface.
On the left is unreconstructed Si(100) with two dangling bonds, shown in green, for each surface Si atom. On the right is the reconstructed surface with alternating rows of Si-Si dimers and one dangling bond per surface Si atom.

The results and proposed mechanism are contrary to what is expected thermodynamically. The reaction of F\textsubscript{2} with a fluorinated surface is around 20 kcal/mol more exothermic than the same reaction using XeF\textsubscript{2} and hence, it might be expected that the F\textsubscript{2} reaction occur with a higher probability than that of XeF\textsubscript{2}. However, past research from our and other groups shows that this is not the case\textsuperscript{9,13,38}: the reaction rate of XeF\textsubscript{2} with a Si surface to make the volatile SiF\textsubscript{4} etch product is 10\textsuperscript{3}-10\textsuperscript{4} times higher than it is for F\textsubscript{2}.

To track the fluorine coverage on the Si surface, Thermal Desorption Spectroscopy (TDS) is the technique of choice. Briefly, the surface is exposed to a known quantity of F\textsubscript{2}. Then, the surface is heated to 1000 K at a rate of 5 K/s, as described in Chapter II. The amount of SiF\textsubscript{2} and SiF\textsubscript{4} that desorbs during heating is proportional to the coverage. These species are
detected by mass spectroscopy. The features arising from these species, m/e = 66 for SiF$_2^+$ and m/e = 85 for SiF$_3^+$ (originating from the dissociative ionization of the volatile etch product SiF$_4$), are detected. Example thermal desorption spectra of a Si(100) surface fluorinated using pure F$_2$ to 1 ML F is shown in Figure 2.

At 1 ML (monolayer) of fluorine coverage, the primary desorbed product is SiF$_2^+$ and is accompanied by a small amount of SiF$_3^+$. In fact, results from Holt$^{41}$ have shown that the SiF$_4$ thermal desorption yield is always very small, never exceeding 9% of the SiF$_2$ yield, no matter the coverage at or below 1 ML. The distinctive desorption temperatures of each species correlate to their binding energies. In the SiF$_4$ spectrum, desorption is detected at 540 K, and increased desorption is found at 655 K. In the SiF$_2$ spectrum, the main desorption feature is found at 800K. There is a small shoulder on the raw SiF$_2$ spectrum, at the same desorption temperature as the higher temperature desorption feature in the SiF$_4$ desorption spectrum. To be more specific, this shoulder arises from the cracking of SiF$_4$ in the ionizer to SiF$_2$. In Fig. 2, and in all the thermal desorption analyses, this shoulder is subtracted from the SiF$_2$ spectrum to provide a SiF$_2$ spectrum that has zero contributions from SiF$_4$.

Finding the total F atom coverage is not trivial. Merely summing the SiF$_2^+$ and SiF$_3^+$ integrated signals provides inaccurate results due to three factors: 1) The absolute electron impact ionization cross sections for the production of SiF$_2^+$ and SiF$_3^+$ are different; 2) The velocities of both SiF$_2^+$ and SiF$_3^+$ are different at each of their desorption temperatures and 3) The amount of SiF$_2^+$ and SiF$_3^+$ entering the detector box is different due to their different angular distributions. Therefore, these values must be taken into account to find the amount of SiF$_4$ produced in the experiment. A detailed description of how these values were obtained, along
with how the calibration is performed, can be found in a paper by D. P. Pullman, et. al\textsuperscript{50}. The equation for finding the relative thermal desorption yield of SiF\textsubscript{4} is shown in Equation 3.1\textsuperscript{48},

\[
N_{\text{SiF}_4} = 2 \left( \frac{v_{\text{SiF}_2}}{v_{\text{SiF}_4}} \right) \left( \frac{\sigma_{\text{SiF}_2 \rightarrow \text{SiF}_4}}{\sigma_{\text{SiF}_4 \rightarrow \text{SiF}_2}} \right) \left( \frac{\eta_{\text{SiF}_2}}{\eta_{\text{SiF}_4}} \right) \left( \int_0^{2\pi} \int_0^{\pi/2} D_{\text{SiF}_4} (\theta, \varphi) \sin \theta d\theta d\varphi \right) \int_{T_0}^T \frac{T}{T_0} S_{\text{SiF}_4} (T; \Theta) dT \tag{3.1}
\]

where \(N_{\text{SiF}_4}\) is the relative thermal desorption yield of SiF\textsubscript{4}, \(v\) is the velocity of either SiF\textsubscript{2} or SiF\textsubscript{4}, determined by time-of-flight spectroscopy of each species desorbing from the Si surface at 1000 K, \(\sigma\) is the ionization cross section for the detected species, \(\eta\) is the transmission of the detected species and the value of the single integral is the result of integrating the TD spectrum for SiF\textsubscript{4} before calibration. \(D_{\text{SiF}_4} (\theta, \varphi) \sin \theta d\theta d\varphi\) is the angular distribution of the desorbing SiF\textsubscript{4} and \(D_{\text{SiF}_2} (\theta, \varphi) \sin \theta d\theta d\varphi\) is the angular distribution of the desorbing SiF\textsubscript{2} integrated over the desorption angle \(\theta\) and the azimuthal angle \(\varphi\). The transmissions of SiF\textsubscript{2}\textsuperscript{+} and SiF\textsubscript{3}\textsuperscript{+} through the quadrupole are treated as equal, given their closeness in mass. The velocity of SiF\textsubscript{4} is 862 m/s, that of SiF\textsubscript{2} is 597 m/s, \(\sigma_{\text{SiF}_2 \rightarrow \text{SiF}_4}\) is 12 Å\textsuperscript{2} and \(\sigma_{\text{SiF}_4 \rightarrow \text{SiF}_2}\) is 1.34 Å\textsuperscript{2}. The 2 is present because there are double the amount of F atoms in SiF\textsubscript{4} compared to SiF\textsubscript{2}. The value of the ratio of angular distributions in the parentheses in Equation 3.1 is 0.373. When the calculation is performed, the numerical result before the integral in Equation 3.1 is 0.12. That is,

\[
2 \left( \frac{v_{\text{SiF}_2}}{v_{\text{SiF}_4}} \right) \left( \frac{\sigma_{\text{SiF}_2 \rightarrow \text{SiF}_4}}{\sigma_{\text{SiF}_4 \rightarrow \text{SiF}_2}} \right) \left( \frac{\eta_{\text{SiF}_2}}{\eta_{\text{SiF}_4}} \right) \left( \int_0^{2\pi} \int_0^{\pi/2} D_{\text{SiF}_4} (\theta, \varphi) \sin \theta d\theta d\varphi \right) = 0.121 \tag{3.2}
\]

Therefore, the integrated value of SiF\textsubscript{3}\textsuperscript{+} in all TD spectra taken here, \(\int_{T_0}^T \frac{T}{T_0} S_{\text{SiF}_4} (T; \Theta) dT\), is multiplied by a factor of 0.12 to properly count the F atoms reacted in this analysis. Note here
that this value provides the relative amount of SiF$_4$ in the experiment, as compared to SiF$_2$. It
does not provide the absolute surface coverage in the experiment, just a value that is proportional
(relative to) the fluorine coverage on the surface. To find the absolute F coverage, first a set of
TD spectra from long F$_2$ exposures are integrated and represent 0.94 ML F coverage on the Si
surface$^{53}$. Using the integrated signal at 0.94 ML as a reference, the fit to the integrated TDS
signal is plotted as coverage versus exposure time. Now, the integrated signal measured for any
exposure of a fluorinated reactant with Si can be converted to an absolute coverage.

The TD spectra show that at fluorine coverages greater than 1 ML, the amount of SiF$_2^+$
remains constant, while the etch product, SiF$_4$, steadily increases$^{8,9}$. Tracking the increase in the
signal of SiF$_4$ (by integrating the SiF$_4$ signal over temperature) provides a measure of the F
coverage beyond 1 ML and in turn is used to calculate the reaction probability of the incident
molecule with a fluorinated surface.

Using TDS as a measure of F coverage, the question of why XeF$_2$ can etch Si and F$_2$ can
now be tested. The hypothesis considered in this chapter is lattice vibrational excitation of the Si
surface upon impact of the incident molecule. The mass difference between XeF$_2$ (169 amu) and
F$_2$ (38 amu) is large. With its heavier mass, XeF$_2$ produces a larger degree of lattice vibrational
motion upon its collision with the Si surface due to its multiple collisions with the surface.
Increased vibrational excitation of the Si-Si bonds increases the average length of the Si-Si bonds
local to the collision site. With an increased bond length comes the enhanced ability of an F
atom to insert itself between the two Si atoms and eventually break the Si-Si bond and react,
creating a Si dangling bond and a new Si-F bond. This situation is analogous to a reaction with a
late vibration barrier, where the Si-Si bond must be vibrationally excited to turn the corner of the
potential energy surface.
Figure 2. Thermal desorption spectra after exposing Si(100) to Pure F\textsubscript{2} beam.

The silicon surface is held at 250 K and exposed for 240 sec to a Pure F\textsubscript{2} beam incident perpendicular to the crystal. The crystal is heated from 250 K to 1000 K at a rate of 5 K/sec while two signals [m/e=66 (SiF\textsubscript{2}, lower graph) and m/e=85 (SiF\textsubscript{3}, upper graph)] are simultaneously measured with a dwell time of 0.1 sec.

One way to prove that mass is indeed a critical variable in the etching reaction is to make the actual F\textsubscript{2} molecule “heavier” as in a van der Waals molecule, Xe(F\textsubscript{2}) . This molecule contains a rare gas atom attached to the molecular F\textsubscript{2} through a weak van der Waals interaction, around a few kcal/mol. This van der Waals molecule does not perturb the electronic structure/properties of either F\textsubscript{2} or Xe, making this molecule an unperturbed F\textsubscript{2} molecule, just much heavier\textsuperscript{24}. Xe(F\textsubscript{2}) likely has a T-shaped structure based on analyses of similar van der Waals molecules\textsuperscript{22-26}. If lattice vibrational excitation governs the etching reaction, then the
reaction probability of Xe(F₂) with a fluorinated surface should be similar to that of XeF₂. The reactivity of Xe(F₂) with a fluorinated Si surface was studied by R. C. Hefty⁷⁷. It was shown that the probability of Xe(F₂) with the surface is approximately 0.9, a very similar value to that found for XeF₂, indicating that the large mass of XeF₂ indeed impacts the reaction. However, these results are not fully confirmed yet, because the signal at m/e = 167 may come from either molecularly bound XeF₂ or the Xe(F₂) dimer, although mass spectrometric examination of the incident beam showed no presence of XeF₂. The XeF₂ may arise because the walls of the Ni nozzle used for expansion can catalyze its formation. Further studies will be performed with the new nozzle cooling system explained in Chapter II, since a colder nozzle should inhibit the formation of XeF₂ and ensure that the only species at m/e = 167 is Xe(F₂).

To take the vibrational excitation hypothesis further, Kr(F₂) van der Waals dimers were made and their reactivity with the Si surface studied. The structure of these dimers is the same as that for Xe(F₂). Since Ni does not catalyze the formation of KrF₂ like it does for XeF₂ upon expansion⁵⁵, it is unambiguously known that the KrF₂ in the molecular beam is the van der Waals dimer. If the mass effect holds, the reaction probability of Kr(F₂) with its mass of 122 amu with the fluorinated surface should be lower than that of XeF₂ (167 amu) and higher than that of F₂ (38 amu).

This chapter first highlights the production of Kr(F₂) van der Waals dimers and the mass spectroscopy of the mixtures used to produce the dimers. Then, time-of-flight analysis of the dimers is performed, which leads to the determination of the dimer flux in the beam in terms of F atom monolayers. Finally, the probability of reaction of these dimers with the fluorinated Si surface is found.
III.2: Making Fluorine Heavy

One of the main challenges is the actual production of the Kr(F₂) and Xe(F₂) dimers. Van der Waals dimers do not come supplied in a bottle due to the very small energy of the dimer bond, around 0.5 kcal/mol. Their syntheses must come from the expansion of a supersonic molecular beam that contains a mixture of F₂ and the rare gas. The proper ratio of F₂ to the rare gas atom is essential so a maximum number of van der Waals dimers are produced. To find this ratio, the stagnation pressure of the gas mixture pre-expansion, along with the temperature and the diameter of the source nozzle must also be optimized. The correct conditions are met when the concentration of dimers inside the beam are at their maximum, while other species, like higher order dimers (Kr₂(F₂), Xe₂(F₂), Kr₂, Xe₂, etc) are not present or are present at a very low concentration. Past studies, such as those on Ar clusters⁵⁶⁻⁵⁷, and dimers of N₂ and NO⁵⁸, have provided good starting conditions for the production of the desired dimers. The detection system must also be optimized to detect the correct concentration of dimers in the molecular beam⁵⁹. All these conditions are explained in detail in the following section.

III.2.1. Temperature of the Source Nozzle

The temperature of the source nozzle is crucial for the production of van der Waals dimers. Studies have shown that the concentration of dimers increases when the temperature of the nozzle is well below room temperature⁵⁷,⁵⁸. However, the temperature cannot become too low because the production of higher clusters (trimers, quadramers, etc) increases, precluding the production of the desired species. For example, when the nozzle on the experimental apparatus is cooled to liquid nitrogen temperatures, a pure Ar molecular beam contains clusters of at least ten Ar atoms⁴⁹. Clusters this large would distort the experimental results we desire, because
there is no way to distinguish reaction coming from the van der Waals complex we desire and that from higher order clusters.

In the case of Xe(F₂), the temperature of the nickel nozzle must be very cold (at least below 223 K) because at elevated temperatures, the Ni can catalyze formation of molecularly bonded XeF₂ from the mixture used. Indeed, the first ever synthesis of XeF₂ used Ni heated to 400°C as a catalyst⁶⁰. XeF₂ production must be avoided at all costs because it will react with a fluorinated surface and the reactivity of the Xe(F₂) dimer could not be determined. Therefore, a method must be used to make the nozzle very cold, but not so cold to produce huge clusters.

Studies by R. C. Hefty showed a dramatic increase in Xe(F₂) dimer production as the temperature of the source nozzle decreased to 223K²⁷. However, there was a concern that a small, undetectable amount of XeF₂ was produced in the nozzle at this temperature. This temperature was the lowest one obtained in that study. So, measures were taken to enable the cooling of the nozzle to even lower temperatures. The modifications to the nozzle mount to increase the cooling were described in Chapter II.

**III.2.2. Optimization of the Production of van der Waals Dimers Kr(F₂)**

As stated earlier, four variables must be optimized to produce the desired dimers in the molecular beams at the greatest concentrations: 1) The ratio of F₂ to rare gas in the mixture; 2) The pressure of the gas mixture behind the nozzle, also known as the stagnation pressure or P_{stag}; 3) The diameter of the nickel nozzle and 4) The temperature of the nozzle.

For Kr(F₂), the ideal mixture was found to be 75% F₂/25% Kr. Many mixtures were tested and this one was found to be the best using the same procedure as that for beam temperature.
The stagnation pressure at the nozzle is controlled using a variable leak valve connected to the nozzle entrance in the gas manifold. The pressure is monitored using a baratron capacitance manometer that provides pressure readings up to 5,000 Torr. For Kr(F₂), five different nozzle pressures were compared at a nozzle temperature of -75°C: 67 Torr, 200 Torr, 300 Torr, 500 Torr and 600 Torr. The results are shown in Figure 6. From the graphs, it is clear that the number of Kr(F₂) dimers increases with increasing pressure up to 500 Torr. At 600 Torr, Kr(F₂) production actually decreases, possibly due to the high concentration of gas in the nozzle forming higher order/mass dimers, since Kr₂ dimer production is much increased when the nozzle pressure is 600 Torr. The dominant dimer in all the beams is Kr₂. However, even though the most dimers, by far, are produced with a nozzle pressure of 500 Torr, the 300 Torr beam was chosen for the coverage experiments. This beam was chosen to conserve the amount of F₂/Kr mixture in the gas tank, along with wanting to use an amount of Kr(F₂) dimer that would provide smaller increments of exposure.
Figure 3: Comparison of dimer production with nozzle pressure.

All experiments were performed using the 75%F₂/Kr molecular beam at -70°C.
The nickel nozzle was described in Chapter II. The nozzle is the same as the one used by Hefty.

The most critical parameter, the nozzle temperature, was determined by simply finding the lowest temperature that is obtained consistently. Figure 7 shows the mass spectra from KrF through Kr(F₂) for a 75% F₂/Kr beam at both 203 and 300 K. The nozzle pressure was 300 Torr for both experiments. Clearly, the number of dimers produced is greater for the colder beam. The cold beam temperature was determined according to the procedure outlined in Chapter II.

Combining these four parameters provides an optimal setup for the production of van der Waals dimer Kr(F₂). With these parameters in hand, the mass spectra of these and the F atom flux of these molecular beams can be found. Table 1 shows the counts of Kr(F₂) produced at m/e = 122 at each pressure from Figure 3. Table 2 shows the same thing, but at the two different temperatures from Figure 4. All the mass spectrometer settings for the lenses were the same for the results in Tables 1 and 2.

Table 1: Relative Amount of Kr(F₂) Produced with Nozzle Pressure, 75% F₂/Kr Beam

<table>
<thead>
<tr>
<th>Nozzle Pressure (Torr)</th>
<th>Number of Kr(F₂), m/e = 122 (counts/sec)</th>
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<tbody>
<tr>
<td>67</td>
<td>180</td>
</tr>
<tr>
<td>200</td>
<td>1460</td>
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<td>300</td>
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<tr>
<td>500</td>
<td>3500</td>
</tr>
<tr>
<td>600</td>
<td>3060</td>
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Table 2: Relative Amount of Kr(F₂) Produced with Nozzle Temperature, 75% F₂/Kr Beam

<table>
<thead>
<tr>
<th>Nozzle Temperature, °C</th>
<th>Number of Kr(F₂), m/e = 122 (counts/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>2470</td>
</tr>
<tr>
<td>27</td>
<td>630</td>
</tr>
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</table>
Figure 4: Comparison of Kr(F₂) dimer production using a 75% F₂/Kr beam at two temperatures.

On top is a spectrum taken at a nozzle temperature of -70°C and the bottom is a spectrum taken at a nozzle temperature of 27°C.
III.3: Determination of the Quadrupole Transmission Function

Once the neutral ionizer flight length is calculated, the transmission function of the quadrupole must be determined. The transmission of an ion through the quadrupole differs with mass to charge ratio. It also differs with the use of different quadrupoles (the quadrupoles are new as of 2006,) and the overall resolution setting of the quadrupole. Therefore, the ratio of transmissivities of different ions under the same experimental conditions is essential to correctly account for the relative flux of molecules with different mass.

For the Si etching experiments performed, molecular beams consisting of either F2/Kr or F2/Xe are used. Thinking about the different ionized species that are found in the quadrupole during these experiments, four come to mind: F+, F2+, Kr+ and Xe+. The transmissivities of these ions must be found. To do this, effusive molecular beams of noble gases Ne, Ar, Kr and Xe are used. Luckily, Ne and Ar have molecular masses comparable to F and F2. Assuming that the transmission does not change with a very small change in mass to charge ratios (20 for Ne vs. 19 for F and 40 for Ar vs. 38 for F2,) the noble gases are used to calculate the transmission ratios. Ideally, mixtures of noble gases would be used to calculate the relative transmissions, but Mach number focusing precludes the analysis because the amount of the heavier species of the mixture detected would be artificially large. More details on Mach number focusing are found in D. Gosalvez-Blanco's thesis. The calculation of the transmission function is done in the same manner as found in the thesis of R. C. Hefty. Briefly, the time-of-flight spectra for rare gas effusive molecular beams are taken and analyzed. From this analysis comes the relative flux of the incident molecular beams from the IGORpro time-of-flight fitting algorithm. Then, calculations, described below, are used to find the transmission ratios for different rare gas species, which are then extended to the different species in the 75% F2/Kr molecular beam.
III.3.1: Effusive Molecular Beams

To produce an effusive molecular beam, the pressure behind the nozzle must be very small, less than 1 Torr. Pressures greater than 2 Torr cause molecular beam cooling upon expansion through the nickel nozzle, making the molecular beam partially supersonic. As a reference, the pressure behind the nozzle for a truly supersonic molecular beam is greater than 300 Torr. Once the effusive beam time-of-flight is taken, it is initially fit to a model distribution on IgorPro,

\[
\text{Counts} = f(t) = B + A \frac{L^3}{t^4} \exp \left[ -\frac{mL^2}{2k_BT} \left( \frac{1}{t} \right)^2 \right]
\]  

(3.3)

where B is the baseline of the spectrum, A is a normalization factor to match the y-axis maximum, L is the neutral flight length (28.82 cm), T is the nozzle temperature (approximately 300K), \(k_B\) is Boltzmann's constant, t is the time and m is the mass of the incoming atom. This functional form is the same as in Equation 2.8 but in the case of effusive beams, there is no \(t_f\), because there is zero cooling in an effusive beam and hence, no flow velocity.

To show that a molecular beam is effusive, the TOF data are fit using Equation 3.3. Before the fit is performed, the ion and quadrupole flight times, along with the electronic delay time, are subtracted from the total effusive time of flight spectrum. An example fit for Ar using this procedure is shown in Figure 5. It is seen that the calculated spectrum using Equation 3.3 matches the experimental Ar spectrum closely. With proof that the molecular beams are indeed effusive, the transmission analysis can now be made.
Figure 5: Time-of-flight spectrum of an effusive Ar molecular beam.
The solid line is the calculated fit to the data (markers.) The data are fit according to an effusive
Maxwell-Boltzmann distribution. The temperature of the beam is 301.6 K and its pressure is
0.15 Torr. The neutral flight length is 28.82 cm.

### III.3.2: Determination of Transmission Ratios for Masses 19, 38, 84 and 129

The transmission ratios are determined according to a procedure initially designed by D.
Gosalvez-Blanco\(^5\) and then revised by R. C. Hefty\(^27\). Briefly, the transmission ratio is
determined according to the following equation:

\[
\frac{T_y}{T_x} = \left( \frac{\text{flux}_{\text{mass}(y)}}{\text{flux}_{\text{mass}(x)}} \right) \left( \frac{\sigma_{y \rightarrow x}}{\sigma_{y \rightarrow y'}} \right) \left( \frac{I_y}{I_x} \right)
\]

(3.4)

where \( \text{flux}_{\text{mass}(x)} \) is the relative flux of the measured incident molecular beam “x” determined by
the IGORpro time-of-flight fitting algorithm. More specifically, this relative flux is the integral
of the velocity-weighted TOF distribution according to Equation 3.5.
\[ \text{flux}_x^{\text{mass}(x)} = \int_0^\infty t^{-1} f(t) \, dt \quad (3.5) \]

Effusive beam time-of-flight analyses are shown in Figures 6-9 for Ne, Ar, Kr and Xe to show the relative, integrated flux results for each beam. The other variables in Equation 3.3 are \( \sigma \), the ionization cross section of the neutral gas atom at a given electron impact energy (the experiments outlined here used an electron energy of 75eV), and \( I_x \), the absolute flux of species “x” into the detector. Since the beams are effusive, it is possible to use the ideal gas law to find the ratio of the absolute fluxes for two different species, \( \frac{I_y}{I_x} \). This ratio is

\[ \left( \frac{I_y}{I_x} \right) = \sqrt{\frac{M_y}{M_x}} \quad (3.6) \]

where \( M_y \) and \( M_x \) are the molecular masses of species y and x, respectively. A detailed proof of this conversion is found in Hefty’s thesis. Substituting the ratio in Equation 3.6 into Equation 3.4 yields an overall transmission ratio Equation of:

\[ \frac{T_y}{T_x} = \left( \frac{\text{flux}_y^{\text{mass}(y)}}{\text{flux}_x^{\text{mass}(x)}} \right) \left( \frac{\sigma_y}{\sigma_x} \right) \sqrt{\frac{M_y}{M_x}} \quad (3.7) \]

The relative fluxes in the expression \( \frac{\text{flux}_y^{\text{mass}(y)}}{\text{flux}_x^{\text{mass}(x)}} \) for each noble gas species are found as the average fluxes of three separate time of flight experiments run consecutively for each noble gas. The relative flux found in the fitting for any rare gas atom is then multiplied by its natural abundance ratio to find the true relative flux, since each atom has more than one isotope. For example, the isotopic abundance of \(^{20}\text{Ne} \) is 90.5\% \(^6\text{Li} \). The relative flux for \(^{20}\text{Ne} \) is multiplied by \((100/90.5)\) to provide the relative flux for all possible Ne atoms, assuming the transmission does
not change with a change in isotope. The absolute ionization cross section values used for the
noble gases in this analysis are shown in Table 3.

Finally, Table 4 shows the transmission ratios necessary for complete study of the F₂/Kr
molecular beam. The ratios were measured for ¹²⁹Xe compared to Ne, Ar and Kr to be
analogous to the transmission ratios of Kr(F₂) compared to F, F₂ and Kr.

Table 3: Absolute Cross Sections for Electron Impact Ionization of Noble Gases

<table>
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<th>Ionization</th>
<th>E_e (eV)</th>
<th>σ_{x→+x'} (Å²)</th>
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<tr>
<td>Ne → Ne⁺</td>
<td>75</td>
<td>0.505</td>
</tr>
<tr>
<td>Ar → Ar⁺</td>
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<td>2.51</td>
</tr>
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<td>Kr → Kr⁺</td>
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<tr>
<td>Xe → Xe⁺</td>
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<td>4.655</td>
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Table 4: Transmission Ratios in the Quadrupole Mass Spectrometer

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<th>Species</th>
<th>Transmission Ratio</th>
</tr>
</thead>
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<td>( \frac{T_{129}}{T_{20}} = \frac{T_{Xe}}{T_{Ne}} \approx \frac{T_{Kr(F₂)}}{T_{F₂}} )</td>
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<td>( \frac{T_{129}}{T_{84}} = \frac{T_{Xe}}{T_{Kr}} \approx \frac{T_{Kr(F₂)}}{T_{Kr}} )</td>
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**Ne+ May21130**

**pure Neon**

**Mass Spectrometer Settings**
- m/e: 20, resolution/ΔM: 7.4, Emission: 0.5 mA
- Signal Averaging
  - chopper frequency: 392 Hz, sets: 1, triggers/sweeps: 5000x40

**Incident beam**
- Detection angle: 270
- Flight path: 0.288 m, Ionizer length: 0.0445 m

---

**Figure 6: Time-of-Flight distribution of an effusive Ne beam** $P_{stag} = 0.5$ Torr, $T_{Nozzle} = 27^\circ C$

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 20. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 1.24±0.01 kcal/mol, an average velocity of 676.6±2.1 m/s and a relative flux of 13540±93 counts.

---

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**Ar+ May2113b**

**Mass Spectrometer Settings**
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**Signal Averaging**
chopper frequency:392 Hz, sets:1, triggers/sweeps:5000x40

**Incident beam**
Detection angle:270
Flight path:0.288 m, Ionizer length:0.0445 m

---

**Figure 7: Time-of-Flight distribution of an effusive Ar beam P_{stag} = 0.5 Torr, T_{Nozzle} = 27°C**

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 40. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 1.22±0.01 kcal/mol, an average velocity of 475.1±1.3 m/s and a relative flux of 21870±135 counts.
Kr+ May2113m

pure Krypton

Mass Spectrometer Settings
m/e:84, resolution/ΔM:7.4,-1, Emission:0.5 mA

Signal Averaging
chopper frequency:392 Hz, sets:1, triggers/sweeps:5000x40

Incident beam
Detection angle:270
Flight path:0.288 m, ionizer length:0.0445 m

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<td>flux 1</td>
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<td>average velocity 1 (m/s)</td>
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<tr>
<td>reduced chisq</td>
<td>2.07</td>
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Figure 8: Time-of-Flight distribution of an effusive Kr beam $P_{stag} = 0.5$ Torr, $T_{Nozzle} = 27^\circ C$

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 84. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of $1.19 \pm 0.01$ kcal/mol, an average velocity of $325.5 \pm 1.8$ m/s and a relative flux of $11490 \pm 131$ counts.
pure Xenon

Mass Spectrometer Settings

m/e: 129, resolution/ΔM: 7.4, Emission: 0.5 mA

Signal Averaging

chopper frequency: 392 Hz, sets: 1, triggers/sweeps: 5000x40

Incident beam

Detection angle: 270°

Flights path: 0.288 m, Ionizer length: 0.0445 m

**Figure 9: Time-of-Flight distribution of an effusive Xe beam**

\( P_{stag} = 0.5 \text{ Torr}, T_{nozzle} = 27^\circ \text{C} \)

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 129. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 1.22±0.02 kcal/mol, an average velocity of 266.7±2.6 m/s and a relative flux of 4556±98 counts.
III.4: Time of Flight and Absolute F Atom Flux Analyses of Kr(F₂)

With the neutral flight length and transmissions known, the amount of Kr(F₂) van der Waals dimers in a 75% F₂/Kr molecular beam can now be determined using the same procedure as D. Gosalvez-Blanco⁵³ and R. C. Hefty²⁷. To do this, first the incident F₂/Kr beam is characterized by straight through time of flight mass spectroscopy. Then, the absolute fluorine flux from the Kr(F₂) dimers in the 75% F₂/Kr beam is found.

III.4.1: Time of Flight Mass Spectroscopy of a 75% F₂/Kr Molecular Beam

To find the flux of Kr(F₂) dimers produced in the supersonic expansion of a 75% F₂/Kr molecular beam, the time of flight distribution at mass 122 (⁸⁴KrF₂) is taken. The quadrupole mass spectrometer is positioned in the straight through position, so the molecular beam enters directly into the detector chamber, through the beam valve pin hole described in Chapter II. Figure 10 shows the time of flight distribution of Kr(F₂) upon expansion of a 75% F₂/Kr mixture at 300 Torr from a cold (-70°C) nickel nozzle. Figure 10 also shows the TOF distribution of Kr(F₂) upon expansion from a room temperature nozzle. The relative flux values are found for each expansion and show further that the use of a cold nozzle increases the production of the dimer. A comparison of the integrated time of flight spectra from the cold and room temperature nozzles shows that cooling the nozzle more than doubles the Kr(F₂) dimer production. The time of flight data, along with the mass spectra found earlier in this chapter, prove that using a cold nozzle is essential for producing enough van der Waals dimers to enable sufficient counting during the Si etching experiments.
Figure 10: Top: Time of flight data for an incident 75% F₂/Kr molecular beam using a cold nozzle collected at m/e = 122. Bottom: Time of flight data for an incident 75% F₂/Kr molecular beam using a room temperature nozzle collected at m/e = 122.

The data on the top spectrum are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 2.7±0.4 kcal/mol, an average velocity of 431.5±32.6 m/s and a flux of 1360±313.

The data on the bottom spectrum are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 4.5±0.7 kcal/mol, an average velocity of 556.7±41.6 m/s and a flux of 587±135.
III.4.2: Determination of Absolute F Atom Flux for Kr(F2) in a 75% F2/Kr Beam

The determination of the absolute flux of Kr(F2) in terms of monolayers of F atoms is carried out as described in R. C. Hefty’s thesis, pages 269-274, with some changes. All the detailed equations for finding the flux are found there. Briefly, the absolute flux of F2 determined by Hefty is used in the present determination of the absolute flux of F2 in the F2/Kr beam, because there was insufficient time to repeat the calibration. Hefty’s procedure went as follows. He determined the absolute flux of an Ar beam. Because the masses of F2 and Ar are similar, there is negligible Mach number focusing in the molecular beam, so the absolute F2 flux can be found by multiplying the Ar absolute flux by the percentage of F2 in the molecular beam, as shown in Equation 3.8,

\[ I_{\text{F2}}^{\text{in}} = I_{\text{in}}^{\text{Ar}} \cdot X_{\text{F2}/\text{Ar}} \]  

where \( I_{\text{in}}^{\text{Ar}} \) is the absolute flux of a Ar beam, \( I_{\text{in}}^{\text{F2}} \) is the absolute flux of F2 in the F2/Ar mixture and \( X_{\text{F2}/\text{Ar}} \) is the ratio of F2 to Ar in the mixture.

The absolute F2 flux in the 75% F2/Kr mixture at 300 Torr was determined by using the absolute flux of F2 determined by Hefty in a 5% F2/Ar mixture at a nozzle pressure of 150 Torr. His absolute flux is extrapolated to match the composition of the 75% F2/Kr mixture at 300 Torr for the production of Kr(F2). With 15 times the F2 in the mixture at double the pressure, Hefty’s absolute F2 flux for a F2/Ar beam is multiplied by 30 to estimate the absolute F2 flux for the current conditions. Therefore, the fluorine flux in a 75% F2/Ar beam with \( P_{\text{stag}} = 300 \) Torr is \( (0.614 \, \text{ML F/s})(30) = 18.42 \, \text{ML F/s} \). In the future, a 75% F2/Ar molecular beam will be studied to find the absolute F2 flux of that beam without using estimations from Hefty’s thesis.
With an approximate absolute flux of F₂ in the 75% F₂/Kr beam determined, it is possible to estimate the flux of Kr(F₂) present in the molecular beam as follows:

\[
I_{\text{in}}^{\text{Kr(F₂)}} = I_{\text{in}}^{F₂/F₂/Kr} \left( \frac{\text{flux}_{\text{Kr(F₂)}}}{\text{flux}_{F₂}} \right) \left( \frac{\sigma_{\text{Kr(F₂)}}}{\sigma_{F₂}} \right) \left( \frac{T_{\text{Kr(F₂)}}}{T_{F₂}} \right)
\]

\[
I_{\text{in}}^{\text{Kr(F₂)}} = I_{\text{in}}^{F₂/F₂/Kr} \left( \frac{\text{flux}_{\text{Kr(F₂)}}}{\text{flux}_{F₂}} \right) \left( \frac{\sigma_{\text{Kr(F₂)}} + \sigma_{F₂}}{\sigma_{F₂}} \right) \left( \frac{T_{\text{Kr(F₂)}}}{T_{F₂}} \right)
\]

where \( I_{\text{in}}^{\text{Kr(F₂)}} \) is the approximate absolute flux of F₂ in the 75% F₂/Kr beam, \( \left( \frac{\text{flux}_{\text{Kr(F₂)}}}{\text{flux}_{F₂}} \right) \) is the ratio of the relative flux (integrated counts) of Kr(F₂) to that of m/e = 38 for the incident 75% F₂/Kr beam, \( \sigma \) is the absolute ionization cross section for either Kr(F₂), estimated as the sum of the cross sections of Kr and F₂, and F₂ and \( \left( \frac{T_{\text{Kr(F₂)}}}{T_{F₂}} \right) \) is the ratio of transmission functions of Kr(F₂) and F₂, estimated as \( \left( \frac{T_{\text{Kr(F₂)}}}{T_{F₂}} \right) \) calculated earlier. Table 5 contains the values used in the equation and the approximate absolute F₂ flux of Kr(F₂). The relative flux of Kr(F₂) is found by taking the measured relative flux from the time-of-flight spectrum at m/e = 122 and multiplying it by (100/57) to account for all possible Kr isotopes (\(^{84}\text{Kr}\) has an isotopic abundance of 0.57.)

One note to make is how the relative flux of F₂ was found in the F₂/Kr mixture. To be able to count the Kr(F₂) dimers properly in the time-of-flight experiment, a high emission current was used. As a result, the F₂ signal became saturated, hindering proper counting of F₂ molecules in the beam. However, since F₂ can “crack” in the ionizer upon electron impact \((F₂ \rightarrow F^+ + F\) or \(F₂ \rightarrow F^+\)), the F atom species at m/e = 19 is detected and a cracking ratio is used to count up the amount of F₂ in the molecular beam. The cracking ratio used is the same as that
used by Hefty\textsuperscript{27}, F\textsuperscript{+}:F\textsuperscript{2+} = 0.263:1. The overall relative flux of F\textsubscript{2} in the molecular beam can be estimated using the relative flux of F detected as:

\[
\text{Rel. Flux}(F \textsuperscript{+}) = \frac{\text{Rel. Flux}(F \textsuperscript{+})}{0.263} + \text{Rel. Flux}(F \textsuperscript{+})
\]

Estimated Expt. Counts of F\textsuperscript{+} \textsubscript{2}

Also, for the Kr(F\textsubscript{2}) dimer, the length of counting time was longer than it was for F atoms, to obtain a better signal-to-noise ratio. The length of the Kr(F\textsubscript{2}) experiment was 20.83 times longer than that of the F atom experiment. Therefore, the flux of F atoms is multiplied by 20.83 to properly account for the counting time for a more accurate percentage of Kr(F\textsubscript{2}) in the beam. Figures 15 and 16 show the analyzed TOF data from IGORPro for Kr(F\textsubscript{2}) and the F atoms. The values for the fluxes found in this manner are also in Table 9. All the values for the F\textsubscript{2}/Kr beam relative fluxes are from the average fluxes of two experiments for m/e = 122 and 19.

Table 5: Quantities Used for Kr(F\textsubscript{2}) Flux Determination in a 75% F\textsubscript{2}/Kr beam

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<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Measured Value</th>
</tr>
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<tbody>
<tr>
<td>Flux of 5% F\textsubscript{2}/Ar, P\textsubscript{stag} = 150 Torr</td>
<td>(T_{\text{in}}^{F_2,F_{2}/Ar})</td>
<td>0.614 ML F/s</td>
</tr>
<tr>
<td>Flux of 75% F\textsubscript{2}/Kr, P\textsubscript{stag} = 300 Torr, T\textsubscript{Nozzle} = -65°C</td>
<td>(T_{\text{in}}^{F_2,F_{2}/Kr})</td>
<td>18.42 ML F/s</td>
</tr>
<tr>
<td>Measured flux at m/e = 122 for 75% F\textsubscript{2}/Kr beam</td>
<td>(\text{flux}_{\text{Kr}(F_2)})</td>
<td>1296 counts</td>
</tr>
<tr>
<td>Flux of Kr(F\textsubscript{2}) with all Kr isotopes taken into account</td>
<td>(\text{flux}_{\text{Kr}(F_2)})</td>
<td>2274 counts</td>
</tr>
<tr>
<td>Measured flux at m/e = 19 for 75% F\textsubscript{2}/Kr beam</td>
<td>(\text{flux}_F)</td>
<td>47520 counts</td>
</tr>
<tr>
<td>Time-adjusted flux of F atoms at m/e = 19</td>
<td>(\text{flux}_F)</td>
<td>(9.9 \times 10^5) counts</td>
</tr>
<tr>
<td>Calculated flux of F\textsubscript{2} atoms from cracking ratio</td>
<td>(\text{flux}_{F_2})</td>
<td>(4.75 \times 10^6) counts</td>
</tr>
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<td>Absolute ionization cross section for Kr(F\textsubscript{2})</td>
<td>(\sigma_{F_2 \rightarrow Kr^+} + \sigma_{F_2 \rightarrow F_2^+})</td>
<td>(4.289 \times 10^{-16}) cm(^2)</td>
</tr>
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<td>Absolute ionization cross section for Kr</td>
<td>(\sigma_{Kr \rightarrow Kr^+})</td>
<td>(3.45 \times 10^{-16}) cm(^2)</td>
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<td>Absolute ionization cross section for F\textsubscript{2}</td>
<td>(\sigma_{F_2 \rightarrow F_2^+})</td>
<td>(83.58 \times 10^{-18}) cm(^2)</td>
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<td>--------------------------------------------------------</td>
<td>---------------------------------</td>
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</tr>
<tr>
<td>Approximate flux of Kr(F$_2$)</td>
<td>$I_{\text{in}}^{\text{KrF}_2}$</td>
<td>0.038 ML F/s</td>
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</table>

From the above table, the Kr(F$_2$) flux provides approximately 0.21% the F atom flux as compared to the estimated flux of the 75% F$_2$/Kr beam. It is again noted that this value is an approximation of the true flux of Kr(F$_2$). First, contributions from the dissociation ionization of Kr(F$_2$) to KrF$^+$ and Kr$^+$ were neglected. Second, the absolute F$_2$ flux for these experiments is an estimate based on Hefty’s results from 10 years ago. A 75% F$_2$/Ar beam must be analyzed at the same experimental conditions as the 75% F$_2$/Kr beam. Once the F$_2$ flux of a 75% F$_2$/Ar is determined, the F$_2$ and Kr(F$_2$) fluxes in the 75% F$_2$/Kr beam can be determined accurately.
Oct2010a Kr(F2)

75% F2/Kr

Mass Spectrometer Settings

m/e: 122, resolution/ΔM: 7.4/-1

Signal Averaging

Chopper frequency: 280 Hz, sets: 1, triggers/sweeps: 5000 x 25

Incident beam

Detection angle: 270

Flight path: 0.288 m, Ionizer length: 0.0445 m

Parameter | Value | Uncert | Hold?
--- | --- | --- | ---
Baseline | 6.065 | 30.83 | 0
Normalization 1 | 2.64e-07 | 2.203e-09 | 0
Mass 1 (amu) | 122 | 0 | 0
Flow velocity 1 (m/s) | 426.7 | 0.2688 | 0
Temperature 1 (K) | 10.04 | 0.1966 | 0

Properties | Value | Uncert
--- | --- | ---
Total counts (from data) | 2.275e+05 | 476.9
Flux 1 | 1360 | 313
Average velocity 1 (m/s) | 431.5 | 32.6
Average energy 1 (kcal/mol) | 2.727 | 0.4106
Reduced chisq | 1.232

Figure 11: Time-of-Flight distribution of an incident 75% F2/Kr Beam, P_{stag} = 300 Torr, T_{Nozzle} = -69°C

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 122. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 2.7±0.4 kcal/mol, an average velocity of 431.5±32.6 m/s and a relative flux of 1360±313 counts.
Oct2010c F Atoms

75% F2/Kr
Mass Spectrometer Settings
m/e: 19, resolution/ΔM: 7.4/-1
Signal Averaging
chopper frequency: 280 Hz, sets: 1, triggers/sweeps: 1000x6
Incident beam
Detection angle: 270
Flight path: 0.288 m, ionizer length: 0.0445 m

Figure 12: Time-of-Flight distribution of an incident 75% F2/Kr Beam, P_stag = 300 Torr, T_Nozzle = -69°C

Time-of-flight data (hollow circles) and Maxwell-Boltzmann fit (solid line) for the incident beam collected at m/e = 19. "Mass 1" is set for 38 because the ionized F atoms come from the neutral F2 parent. The data are best fit by a single Maxwell-Boltzmann feature resulting in an average energy of 0.91±0.13 kcal/mol, an average velocity of 444.8±32.9 m/s and a relative flux of 48750±11090 counts.
III.5: Probability of Adsorption of Kr(F₂) and F₂: Thermal Desorption Results

The probability of fluorine adsorption from Kr(F₂) and F₂ on a fluorinated surface is found in this section. The F atom coverage is found using thermal desorption spectroscopy, as explained earlier in the chapter. Combining the TDS results with the fluorine flux in the molecular beams provide the reaction probabilities. The probabilities for Kr(F₂) and F₂ reaction are found using three different approaches to the absolute flux of F₂ in the respective beams: 1) Using a method designed by J. G. Lee, explained below; 2) Using Lee's flux values, but adjusting for the transmission ratios found in Section III.3.2 and 3) Using both the transmission and the absolute flux values found earlier in this chapter.

For the reactivity comparison experiments for Kr(F₂) and F₂ presented here, the clean Si surface is exposed to either a 300 Torr 75% F₂/Kr beam at a nozzle temperature of -60°C or a 225 Torr F₂ beam held at room temperature. Exposure times range from 0.1 up to 360 seconds to find the amount of fluorine that reacted at different fluorine exposures. The stagnation pressure of the F₂ beam is different from the mixed beam to approximate an equal amount of fluorine atoms exposure in each experiment. Once the surface is exposed for a given amount of time, the thermal desorption experiment is performed. The surface is held at 250 K during all beam exposures.

Figures 13 and 14 show the thermal desorption spectra of a Si(100) surface fluorinated using the pure F₂ and 75% F₂/Kr molecular beams, respectively, at a nozzle temperature of -64°C. The length of exposure in these experiments was the same. As expected, the shape of the thermal desorption peaks remains the same for SiF₃⁺ and SiF₂⁺ in each experiment. Also, the SiF₂⁺ peak height and area for exposure to the 75% F₂/Kr beam is similar in counts to the pure F₂ beam. The one difference is that the counts of SiF₃⁺ increase by around 35-40% when the 75%
F₂/Kr beam is used, indicating that more etching product is formed and thus more fluorine atoms have reacted with the Si surface. Since it is known that the van der Waals complex Kr(F₂) is in the mixed beam, its presence must be increasing the amount of fluorine reaction with the fluorinated Si(100) surface.

![Thermal desorption spectra after exposing Si(100) to a Pure F₂ beam.](image)

**Figure 13.** Thermal desorption spectra after exposing Si(100) to a Pure F₂ beam.

The silicon surface is held at 250 K and exposed for 240 sec to a F₂ beam incident perpendicular to the crystal. The crystal is heated from 250 K to 1000 K at a rate of 5 K/sec while two signals [m/e=66 (SiF₂, lower graph) and m/e=85 (SiF₃, upper graph)] are simultaneously measured with a dwell time of 0.1 sec.
Figure 14. Thermal desorption spectra after exposing Si(100) to a 75% F$_2$/Kr beam.

The silicon surface is held at 250 K and exposed for 240 sec to a 75% F$_2$/Kr beam incident perpendicular to the crystal. The crystal is heated from 250 K to 1000 K at a rate of 5 K/sec while two signals [m/e=66 (SiF$_2$, lower graph) and m/e=85 (SiF$_3$, upper graph)] are simultaneously measured with a dwell time of 0.1 sec.
III.5.1: Reaction Probability of Kr(F₂) Using Lee’s Method

Figure 15 shows the total integrated thermal desorption signal versus time of exposure for both the cold nozzle Kr(F₂) and room temperature pure F₂ molecular beams. The procedure for making the fits to the curves in Figure 15 is explained here using a procedure designed by J. G. Lee⁶³. First, a relative flux analysis was made for each molecular beam since the amount of fluorine exposure in the cooled F₂/Kr beam is slightly different from the pure F₂ due to the different velocities of each beam. The relative F₂ flux in each beam is measured to correct for this difference. Without using time-of-flight analysis, the molecular beam is shot into the main chamber with the quadrupole mass spectrometer positioned at an angle 140° away from the beam. The molecular beam shutter is turned on and off every 100 seconds to ensure correct background counting, since very little F₂ will enter the main chamber while the shutter is blocking the beam. Assuming that the molecular beam is directionally randomized by several collisions with the chamber walls after entrance into the main chamber, the F₂ signal detected by the detector chamber mass spectrometer is proportional to the incoming relative F₂ flux for either the F₂/Kr beam or the pure F₂ beam. Counted in this experiment is the number of F₂ molecules entering the detector chamber when the beam is introduced to the main chamber. When the shutter is open, the beam enters the main chamber and the F₂ signal increases. When the shutter is closed, the beam will not enter the main chamber and any F₂ counts found establish the background of the experiment. The measured F₂ counts for each molecular beam using this method are shown in Table 6. The F₂ signal measured is the result of subtracting the average F₂ counts when the shutter is open from the average counts when the shutter is off. An example experiment for this on/off beam shutter method is found in Figure 16. After exposure
recalibration, the total integrated thermal desorption signal is plotted as total counts vs. exposure time to evaluate the fluorine coverage on the silicon surface, as shown in Fig. 15.

Table 6: Measured Counts for F₂ Signal Using On/Off Shutter Method

<table>
<thead>
<tr>
<th>Beam Conditions</th>
<th>Measured Counts (Counts/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75% F₂/Kr (Tₙozzle = -70 °C, Pₚstag = 300 Torr)</td>
<td>855.6 ± 2.7</td>
</tr>
<tr>
<td>Pure F₂ (Tₙozzle = 26 °C, Pₚstag = 225 Torr)</td>
<td>1533.9 ± 3.0</td>
</tr>
</tbody>
</table>

From the data shown in Table 6, the ratio of measured F₂ counts for the pure F₂ beam to that of the 75% F₂/Kr beam is (1533.9/855.6) = 1.792. The difference in ratio is taken into account in the analysis in Figure 20. Here, the exposure time of pure F₂ in the TDS experiments is multiplied by 1.792 to provide a proper comparison to the F₂ exposure from the F₂/Kr beam. For example, a 240 second pure F₂ exposure is plotted as a 430 second exposure since a 430 second exposure of F₂/Kr provides the same amount of F₂ as a 240 second exposure of pure F₂.

The plots in Fig. 15 are fit according to a power function, \( a + bx^c \) and the best fit values of the variables a, b and c are shown in Table 7 for both F₂/Kr and F₂ exposures.

Table 7: Best Fit Parameters to the Integrated TD Signals vs. Time Plots, Signal = \( a + bx^c \)

<table>
<thead>
<tr>
<th>Beam Conditions</th>
<th>A</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Nozzle (Tₙozzle = -70 °C)</td>
<td>8224</td>
<td>6232.7</td>
<td>0.07845</td>
</tr>
<tr>
<td>Pure F₂, Warm Nozzle (Tₙozzle = 26 °C)</td>
<td>8353.8</td>
<td>4496.5</td>
<td>0.10007</td>
</tr>
</tbody>
</table>
Figure 15. Total fluorine coverage (counts) versus dose time.

Summation of integrated thermal desorption signal at m/e = 66 (SiF$_2^+$) and 85 (SiF$_3^+$) from exposure to 75% F$_2$/Kr beam with P$_{stag}$ = 300 Torr and T$_{nozzle}$ = -60 °C (open circles) and pure F$_2$ beam with P$_{stag}$ = 225 Torr and T$_{nozzle}$ = 26 °C (open squares). The signal for SiF$_3^+$ was calibrated according to a procedure described by Pullman, et. al.
Figure 16. $F_2$ signal ($m/e=38$) measured while beam shutter is turned on and off.

A room temperature pure $F_2$ molecular beam with a 225 Torr stagnation pressure is shot inside the main chamber. The detector chamber mass spectrometer is positioned 140° away from the molecular beam direction. Higher $F_2$ counts arise when the molecular beam shutter is open. Lower counts, the background, come when the shutter is closed.
Knowing that the absolute F coverage on the surface is 0.94 ML for long exposure times of pure F\(_2\), as described earlier in the chapter, the coverage versus exposure time fit from Figure 15 can be used to convert an arbitrary exposure time into the absolute fluorine coverage.

Figure 17 shows a plot of F coverage versus F atom exposure for both the 75% F\(_2\)/Kr and pure F\(_2\) beams. The exposure for Kr(F\(_2\)) in this analysis is the approximate F\(_2\) exposure for a pure F\(_2\) beam multiplied by 6.5x10\(^4\), the fraction of Kr(F\(_2\)) in the molecular beam as found by Lee. This Kr(F\(_2\)) fraction comes from a number density analysis of the mass spectrum of a 75% F\(_2\)/Kr beam. Briefly, a mass spectrum of a 300 Torr 75% F\(_2\)/Kr molecular beam, swept from F atoms (m/e = 19) through Kr\(_2\) dimers (m/e = 168 amu), with a nozzle temperature of 203 K was taken. The peak heights for F\(_2\), Kr, Kr(F\(_2\)) and Kr\(_2\) were recorded and the signal, in counts per second, was converted to number density according to Equation 3.11,

\[
\frac{S_M}{\sigma_{M\rightarrow M^*} T_M d_e} = \frac{I_M}{v_M} = N_{\text{density}}
\]

where \(S_M\) is the signal from the mass spectrometer in counts per second, \(I_M\) is the absolute flux of the beam, \(\sigma_{M\rightarrow M^*}\) is the absolute ionization cross section for species M, \(T_M\) is the transmission coefficient of the species, \(d_e\) is the ionization length and \(v_M\) is the velocity of the beam. In this analysis, the transmission coefficient was assumed to be one for all species included. The transmission for each species is included in the second analysis of these results. Once the number density of all the species in the molecular beam is found, the mole fraction of Kr(F\(_2\)) is calculated as the quotient of the number density of Kr(F\(_2\)) molecules divided by the number density sum of all the species in the beam. Table 8 shows the estimated mole fraction of Kr(F\(_2\)) in the molecular beam using this method.
Table 8: Mole Fraction of Kr(F₂) in a 75% F₂/Kr Beam, T_{nozzle} = 203 K, P_{stag} = 300 Torr

<table>
<thead>
<tr>
<th>Species</th>
<th>Number Density</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>3.296±0.003x10^{21}</td>
<td>0.623±0.0006</td>
</tr>
<tr>
<td>Kr</td>
<td>1.987±0.002x10^{21}</td>
<td>0.376±0.004</td>
</tr>
<tr>
<td>Kr(F₂)</td>
<td>3.425±0.021x10^{18}</td>
<td>6.5±0.04x10^{-4}</td>
</tr>
<tr>
<td>Kr²</td>
<td>4.588±0.030x10^{18}</td>
<td>8.7±0.06x10^{-4}</td>
</tr>
</tbody>
</table>

The slope of each line for the Kr(F₂) and pure F₂ plots provide the reaction probability of each species with a fluorinated Si surface. Figure 18 is the same plot as that for Figure 17, but with the x-axis limited to 3 ML F atom exposure to better show the slope of the Kr(F₂) linear fit.

The results here are interesting. Kr(F₂) has a reaction probability with a fluorinated Si surface of 0.04, which is around 10^{2} times higher than the reaction probability of pure F₂ with the same surface, 1x10^{-4}. This observation suggests that the mass of the Kr atom enables F₂ to react with the Si-Si dimer bonds following fluorination. Also, the mass effect can be taken further when the reaction probability of Kr(F₂) is compared to that of Xe(F₂). Kr(F₂)’s reaction probability is around 20-25 times smaller than that of Xe(F₂), found by Hefty to be 0.9^{27}. For the mass effect hypothesis to work, P_{react}(F₂) < P_{react}(Kr(F₂)) < P_{react}(Xe(F₂)). This trend is seen in the initial studies into the reaction probabilities of van der Waals dimers Kr(F₂) and Xe(F₂) with a Si surface.
Figure 17: F Coverage vs. F Atom Exposure of Si to 75% F₂/Kr and Pure F₂

Integrated thermal desorption data from exposure of clean Si(100) to a 75% F₂/Kr beam with $P_{stag} = 300$ Torr and $T_{nozzle} = -60^\circ$C (circles) with best fit line, as well as a pure F₂ beam with $P_{stag} = 225$ Torr and $T_{nozzle} = 26^\circ$C (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. The probability of F atom adsorption on a fluorinated surface (past 1 ML exposure) is indicated in the legend for each molecular beam. This analysis was performed by J. G. Lee.
Figure 18: F Coverage vs. F Atom Exposure (up to 3 ML) of Si to 75% F₂/Kr and Pure F₂

Integrated thermal desorption data from exposure of clean Si(100) to a 75% F₂/Kr beam with $P_{stag} = 300$ Torr and $T_{nozzle} = -60^\circ$C (circles) with best fit line, as well as a pure F₂ beam with $P_{stag} = 225$ Torr and $T_{nozzle} = 26^\circ$C (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. This graph is an expanded plot of Figure 17 to better show the slope of the fit for F₂/Kr exposure. This analysis was performed by J. G. Lee.
III.5.2: Reaction Probability of Kr(F₂) Using Lee’s Method Including Transmission Ratios

Lee’s method of finding the reaction probability did not take into account the transmission ratio of Kr(F₂) and F₂. With that value calculated in section III.3.2, the F atom exposure for the Kr(F₂) beam found by Lee is adjusted (multiplied by 0.840, the transmission ratio Kr(F₂):F₂) and the reaction probability recalculated. The new reaction probabilities are found in Figures 19 and 20, which are analogous to Figures 17 and 18.

Figure 19: F Coverage vs. F atom exposure of Si to 75% F₂/Kr and pure F₂
Integrated thermal desorption data from exposure of clean Si(100) to a 75% F₂/Kr beam with $P_{\text{stag}} = 300$ Torr and $T_{\text{nozzle}} = -60^\circ C$ (circles) with best fit line, as well as a pure F₂ beam with $P_{\text{stag}} = 225$ Torr and $T_{\text{nozzle}} = 26^\circ C$ (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. The probability of F atom adsorption on a fluorinated surface (past 1 ML exposure) is indicated in the caption for each molecular beam.
Figure 20: F Coverage vs. F atom exposure (up to 3 ML) of Si to 75% F₂/Kr and pure F₂

Integrated thermal desorption data from exposure of clean Si(100) to a 75% F₂/Kr beam with $P_{stag} = 300$ Torr and $T_{nozzle} = -60^\circ$C (circles) with best fit line, as well as a pure F₂ beam with $P_{stag} = 225$ Torr and $T_{nozzle} = 26^\circ$C (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. This graph is an expanded plot of Figure 19 to better show the slope of the fit for F₂/Kr exposure.

Adjusting the Kr(F₂) exposure for the transmission ratio increases the reaction probability slightly, from 0.4 to 0.45. However, the results are still in concert with the heavy mass hypothesis, since the reaction probability of Kr(F₂) is still 20 times lower than Xe(F₂) and $10^2$ times higher than that of F₂.
III.5.3: Reaction Probability of Kr(F₂) Using the Absolute Flux of Kr(F₂)

The final approach used to find the reaction probability of Kr(F₂) and F₂ with a fluorinated Si surface takes out Lee’s approach for finding the F₂ flux and uses the absolute fluorine flux found in Section 3.4.2. The transmission ratios were already taken into account in the absolute flux calculation. Doing this changes the values for F₂ exposure to the surface. The integrated thermal desorption signals, and thus F atom coverage on the surface, remain the same. Figures 21 and 22 show the reaction probability results using this analysis.

![Figure 21: F Coverage vs. F Atom Exposure of Si to 75% F₂/Kr and Pure F₂](image)

Integrated thermal desorption data from exposure of clean Si(100) to a 75% F₂/Kr beam with \( P_{stag} = 300 \) Torr and \( T_{nozzle} = -60^\circ C \) (circles) with best fit line, as well as a pure F₂ beam with \( P_{stag} = 225 \) Torr and \( T_{nozzle} = 26^\circ C \) (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. The probability of F atom adsorption on a fluorinated surface (past 1 ML exposure) is indicated in the caption for each molecular beam.
1.2- F Coverage vs. F\textsubscript{2} Exposure

Coverage Values are from J.G. Lee's Analysis

Exposures are from transmissions and fluxes calculated by M.R. Blair

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**Figure 22: F Coverage vs. F atom exposure (up to 12 ML) of Si to 75% F\textsubscript{2}/Kr and pure F\textsubscript{2}**

Integrated thermal desorption data from exposure of clean Si(100) to a 75% F\textsubscript{2}/Kr beam with \( P_{\text{stag}} = 300 \) Torr and \( T_{\text{nozzle}} = -60^\circ\text{C} \) (circles) with best fit line, as well as a pure F\textsubscript{2} beam with \( P_{\text{stag}} = 225 \) Torr and \( T_{\text{nozzle}} = 26^\circ\text{C} \) (squares) with best fit line. Error bars are propagated from the statistical uncertainty in the count rate. This graph is an expanded plot of Figure 21 to better show the slope of the fit for F\textsubscript{2}/Kr exposure.

Adjusting the Kr(F\textsubscript{2}) and F\textsubscript{2} exposure for the absolute flux estimated earlier in this chapter decreases the reaction probability for Kr(F\textsubscript{2}) by a factor of 4, from 0.04 to 0.01. This probability is treated here as the minimum reaction probability that Kr(F\textsubscript{2}) has with the fluorinated Si surface because the value of the absolute fluorine flux found for Kr(F\textsubscript{2}) is the maximum possible value based on Hefty's analysis. Once the absolute fluorine flux is found experimentally for a 75% F\textsubscript{2}/Kr beam as explained earlier, the results found above will be recalculated. However, the results are still in concert with the heavy mass hypothesis, even with the reaction probability of Kr(F\textsubscript{2}) now being almost \( 10^2 \) times lower than Xe(F\textsubscript{2}).
The results were measured by exposing a clean Si surface to either the F₂/Kr or pure F₂ beam. To extract a more precise reaction probability of Kr(F₂) with fluorinated Si, the Si surface will be pre-fluorinated with 1 ML F coverage. Then, the surface will be exposed to a 75% F₂/Kr beam and the resulting surface coverage will be found using TDS. This method will more accurately find the reaction probability of Kr(F₂) with a Si surface past 1 ML of coverage. This same experiment has been performed for Xe(F₂) to find its reaction probability by Hefty²⁷ and its reaction probability with a fluorinated Si surface is approximately 0.9.

However, the initial results found in this chapter certainly point towards there being a mass effect that would explain why the reaction of XeF₂ with a fluorinated Si surface occurs, while the same reaction using F₂ does not, due to lattice vibrational excitation. The focus here on is vibrational motion because examination of previous studies of halogens with semiconductors reveals that translational energy has a minimal effect on the reaction¹⁶. The following chapter will study this mass effect further using a simple simulation of the collision dynamics of XeF₂ versus those of F₂ with a Si surface.
Chapter III References:

61) All isotopic data was taken from the NIST database.
63) J. G. Lee, Private Communication
Chapter IV: Understanding the Energy Transfer to the Si Surface

IV.1: Introduction

To explain the reactivity difference of XeF$_2$ and F$_2$ with a fluorinated Si(100) surface, an energy transfer hypothesis has been used. In Chapter III, the reactivities of van der Waals dimers Kr(F$_2$) and Xe(F$_2$) with the fluorinated surface were probed and compared to that of molecular fluorine. This chapter will discuss the underlying principles that were learned from the results of Chapter III, along with those by Hefty$^{27}$.

Theoretical studies have shown that when the molecular mass of the incoming species is large relative to that of the surface atom, multiple collisions with the surface occur$^{64,65}$. Visually, the more massive molecule collides with the surface but does not change trajectory, meaning that it still is traveling towards the surface. Its direction is not changed at the first collision. Thus, it hits the surface again. Each collision adds to the energy transferred to the surface, along with adding to the length of time that the Si lattice is deformed. The collisions continue until the surface recoils with enough energy to scatter the incoming molecule away. With its much higher mass, XeF$_2$ should endure more collisions with the fluorinated Si surface than F$_2$. In the case of both chemically stable XeF$_2$ and Xe(F$_2$) van der Waals dimers, these collisions displace the Si lattice for enough time that the F atoms can easily react with the Si-Si dimer or lattice bonds. This mechanism is similar to a gas phase reaction between a gas atom and a diatomic molecule with a late transition barrier. Here, the vibrational excitation of the Si-Si bonds (the diatomic) provided by the XeF$_2$ (the atom) is necessary for the trajectory to turn the corner of the potential energy surface. A F atom from XeF$_2$ now has a higher probability of reaction with the vibrationally excited Si-Si bond. In this picture, F$_2$ is not massive enough to provide the vibrational excitation (and excitation timescale) necessary to promote reaction with the
fluorinated Si-Si bonds. It merely scatters unreacted in the gas phase. A picture of the potential energy diagram for this mechanism is shown in Figure 1.

![Potential energy diagram of XeF$_2$ reaction with a Si-Si dimer or lattice bond.](image)

**Figure 1: Potential energy diagram of XeF$_2$ reaction with a Si-Si dimer or lattice bond.**

This chapter will present a simple classical model comparing the collision dynamics of F$_2$ and XeF$_2$ with the fluorinated Si(100)2x1 surface. In this model, the length of time these molecules interact with the surface is tracked, along with the number of collisions each species endures with the surface. Also, the amount of energy transferred to the surface and/or the incoming atom at each collision event is calculated. Combining these three values will shed light
upon the reactivity of not just fluorinated molecules with the Si surface, but also other reactions where there is evidence of energy transfer governing a gas-surface reaction.

IV.2: Energy Transfer to a Si(100) Surface: Model

As stated above, a simple classical model is used to track the energy transfer to the Si(100) surface. It works as follows. The incoming gas molecule is treated as a hard sphere colliding elastically with the Si surface, as if it were a hard cube. That is, the energy calculated is the exact elastic energy that is transferred at each collision. The value of energy transfer, for example, when XeF₂ suffers its first collision with Si is

\[
E_{\text{Transferred}}(\text{Si}) = \frac{4m_{\text{Si}}m_{\text{XeF}_2}}{(m_{\text{Si}} + m_{\text{XeF}_2})^2} \cdot E_{\text{XeF}_2}
\]

(4.1)

where \(m_{\text{Si}}\) is the mass of Si, \(m_{\text{XeF}_2}\) is the mass of XeF₂ and \(E_{\text{XeF}_2}\) is the incoming energy of XeF₂.

Each collision is assumed to be instantaneous and the position of the Si-Si dimer and gas molecule does not change at the very moment of collision. The equations for the velocities of each species following the collision are shown below. Note: in Equations 4.2 and 4.3, \(m_g\) is the mass of the gas species and \(m_{\text{Si}}\) is the mass chosen for Si. Section IV.2.1 explains in more detail how the Si mass is chosen.

For the incoming gas species:

\[
v_{g_i} = \frac{\left(1 - \frac{m_g}{m_{\text{Si}}}\right) \cdot v_{g_i} + 2 \cdot \left(\frac{m_g}{m_{\text{Si}}}\right) \cdot v_{\text{Si}}}{\left(\frac{m_g}{m_{\text{Si}}} + 1\right)}
\]

(4.2)
where \( v_{g_i} \) is the velocity of the gas before a collision, \( v_{g_f} \) is the gas velocity following a collision and \( v_{si_i} \) is the velocity of silicon before a collision. The velocity of the Si species, or any surface species, following collision is:

\[
2 \cdot v_{g_i} + \frac{m_g}{m_{si}} - 1 \cdot v_{si_i} \left( \frac{m_g}{m_{si}} + 1 \right)
\]

where, similar to the final gas velocity calculated above, \( v_{si_i} \) is the velocity of Si immediately following a collision.

To take multiple collisions into account, it is instructive to show the parameters used for the Si surface, especially the portion of the surface that takes part in the collision(s), to accurately model the dynamics of each collision with the surface.

**IV.2.1: Choosing the Mass of Si Taking Part in Collisions with F\(_2\) and XeF\(_2\)**

Choosing the mass of the Si atom in the calculation is not trivial. Over the years, some theory papers have shown that the effective surface mass involved in a collision may range from one surface atom to up to 20 atoms based on gas collisions with graphite\(^{67,68}\) or metal surfaces\(^{69}\). Therefore, multiple Si masses are tested to determine the effect of mass on the lattice excitation dynamics. The masses chosen, where the structures of each mass are described when the calculations for each mass are presented, are 47 (SiF), 75 (SiF\(_2\)), 94 (Si\(_2\)F\(_2\)), 150 (Si\(_4\)F\(_2\)) and 206 (Si\(_6\)F\(_2\)). Any value greater than 94 (F-Si-Si-F) would imply that energy transfer is highly affected by Si atoms in the second layer. Any value less than 47 would imply that a single Si atom (28 amu) participates in the reaction. Remembering that the number of collisions is
governed by the mass of the surface species being smaller than the mass of the incoming gas molecule, smaller masses are good places to start calculations.

**IV.2.2: Trajectories of F₂, or Xe(F₂) and Si-Si Dimers**

Simulating the trajectories of both the incoming gas atom/molecule and the Si-Si dimers is essential to define the initial collision conditions, along with calculating what happens after each collision. The incoming gas species and the surface are treated as separate entities at all times except for the exact moment of collision. Following collision, calculations of the velocities and/or trajectories for each species continue until it is determined that no more collisions will occur. Also calculated is the energy transfer that occurs at each collision, and the energies of both the incoming molecule and the Si species in between collisions. How those trajectories and energies are determined is also shown below.

**IV.2.2.1: Movement of the Incoming Gas Molecules, F₂, or XeF₂**

To make this classical model as simple as possible, only one dimension is used in all calculations: a single mass that is adjustable (Si, SiF, etc) attached to a spring attached to a wall. Doing this simplifies all variables to be treated as scalars without worrying about the multi-component position of velocity vectors. The incoming gas molecules are treated as point masses moving freely in the designated direction, perpendicular to the surface wall. The velocity/energy of the molecule remains constant until a collision occurs, when a new velocity (and thus new energy) is calculated. The new velocity remains constant until another collision occurs. With each timestep, a new position is calculated for the gas molecule, calculated simply as:

\[ x_t = x_0 + v_{gas} t \]  
(4.4)
where $x_0$ is the location of the last collision, $t$ is the amount of time since the last collision and $v_{gas}$ is the velocity following the collision. How the timestep was found is described in Section IV.2.2.3.

**IV.2.2.2: The Si Surface and its Movement**

The surface is modeled as a simple point mass-on-spring system treating the mass of the Si species participating in all interactions, as the “mass” on a spring with a set spring constant attached to an infinite wall that acts as a bath. The Si mass is variable in the calculations and can be chosen based on the number of bare or fluorinated Si atoms the user wants to investigate. In this model, either F$_2$ or XeF$_2$ hits the Si species directly and the excitation of the spring is monitored. The bath is described in Section IV.2.2.2.2 and it takes into account the viscous damping of the spring system.

**IV.2.2.2.1: “Strength” of the Spring System**

Before simulating the interaction of Si with F$_2$ or XeF$_2$, the “spring constant” for the Si spring is calculated. The Si species of interest is connected to the bath through the spring. All other Si atoms in this picture comprise a bath for energy dissipation, as is shown in Figure 2. Every spring constant used in a simulation run (only one spring constant is used per calculation) is found using either theory or experimental papers that provide a vibrational mode or phonon mode of the surface that may be of interest to use in the simulation. Each spring constant used will be described as the calculation results from those spring constants are discussed later in the chapter.
Figure 2: Si spring setup for model

The bold Si atom is where the collisions take place in one dimension, with only up and down movement. The bath, indicated by the gray square, is set perpendicular to the spring.

IV.2.2.2.2: Energy Dissipation Into the Lattice: The Bath

The overall spring is connected to a bath where the energy of Si is lost due to spring damping and is ‘released’ as heat. The damping in the simulation determines how fast the surface will return to equilibrium following all collisions. To begin the simulation, the Si species is at its equilibrium energy, calculated for a spring moving in one dimension:

\[ E(Si) = k_B T \]  \hspace{1cm} (4.5)

where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of the Si surface, which is set at 250 K, the temperature of the surface during experiments. The Si species on the spring also has a corresponding angular frequency,

\[ \omega = \sqrt{\frac{k}{m_{Si}}} \]  \hspace{1cm} (4.6)

where \( k \) is the spring constant and \( m_{Si} \) is the chosen mass of the Si species. Once the values in equations 4.5 and 4.6 are chosen, they never change while the program is running.

The Si position at a dimer mass of 56 amu versus time at equilibrium, defined as thermal equilibrium with zero damping and no collision dynamics, is shown in Figure 3. The dotted line
shows the equilibrium position, defined as halfway between the two turning points of the spring. A “positive” position is chosen as the position of the dimer when it is closer to the bulk surface wall. The negative position is when the dimer is past the equilibrium position towards the vacuum. The calculated maximum distance the point Si mass moves from the equilibrium position is 5.5 pm at a spring constant of 225 N/m. To find if this displacement is reasonable, it is compared to the maximum displacement of a Si surface atom at its surface Debye temperature, 458 K. The maximum displacement, \( x_{\text{Si}} \), is calculated according to

\[
\langle x_{\text{Si}}^2 \rangle = \frac{3\hbar^2 T_{\text{surf}}}{m_{\text{Si}} k_B \Theta_D^2}
\]  

(4.7)

where \( \hbar \) is Planck’s constant divided by \( 2\pi \), \( T_{\text{surf}} \) is the temperature of the Si surface, 250K, \( m_{\text{Si}} \) is the silicon mass, treated here as the mass of a Si surface dimer, 56 amu, \( k_B \) is Boltzmann’s constant and \( \Theta_D \) is the surface Debye temperature of Si. The maximum displacement calculated using this method for a Si-Si dimer is 5.6 pm, which is very close to the displacement used in the simulation. Even though the displacement in the calculations is slightly smaller than the maximum displacement, it is still well within an order of magnitude, which is reasonable for the calculations presented here.
Figure 3: Position of the Si-Si dimer (Mass 56) at equilibrium versus time.
Each position is calculated every 0.1 fs with 0 being the defined equilibrium position.

Figure 4 shows the velocity of the Si dimer (considered as a single Si particle of mass 56) at equilibrium and how it changes with time. The solid line indicates zero velocity, which is where the dimer is at its maximum position either towards the bulk or the vacuum. Values of the velocity vector greater than zero indicate Si movement towards the surface, while velocities less than zero indicate Si movement away from the bulk wall.

Finally, Figure 5 shows the relationship between the Si dimer position and velocity to explain more clearly the movement of the dimer towards and away from the surface. In the diagram, the scenarios are as follows, moving clockwise on the graph starting at the upper left: 1) Position closer to the vacuum, moving towards the surface. 2) Position closer to the surface moving towards the surface; 3) Position closer to the bulk wall, moving away from the surface and 4) Position closer to the vacuum, moving away from the surface.
Figure 4: Equilibrium velocity of Si-Si dimer versus time.
Each velocity is calculated for Si mass 56 every 0.1 fs with zero velocity occurring when the dimer is at its maximum position towards and away from the surface.

Figure 5: Si velocity versus position when the surface is at thermal equilibrium.
The graph is split into quadrants each showing the position and velocity conditions chosen with each calculation.
Since the bath is treated as a heat sink for the effective Si mass following a collision, a damping constant is found to estimate how much energy is lost to the bath and how fast that energy is lost. This constant, \( C \), is a user-defined input. It was chosen such that, after the final collision, it would take around 0.5 ps for Si to return to its equilibrium energy. That time value was chosen so it would take multiple vibrational periods for Si to return to equilibrium. The period of a Si vibration using a spring constant of 225 N/m and a reduced mass of 47, the mass of a SiF unit, is \( 1.2 \times 10^{-13} \) s. Therefore, it will take approximately 2-7 vibrations for the Si to return to equilibrium in the simulation. The range is present because Si will return to equilibrium in a different number of vibrations, depending on the spring constant chosen. The value for the damping constant to replicate the desired vibrational dynamics is \( C = 0.05 \frac{N\cdot s}{m} \), making the spring system an underdamped oscillator since the Si mass is oscillating about its equilibrium position, which is defined in Section IV.3.

Once the Si damping constant, equilibrium energy and spring constant are all chosen/calculated, the position and velocity of the effective Si mass following a collision are computed through numerical integration of the following differential equation:

\[
0 = \ddot{X} + 2 \omega_0^2 + 2 \left( \frac{C}{2M} \dot{X}^2 + \frac{1}{2} KX^2 - E \right)
\]

Use of Equation 4.8 has the Si oscillation return to a non-perturbed equilibrium state within 2-7 vibrational periods following all collisions.
IV.2.2.3: Choosing a Proper Timestep for Calculations

The collision checking timestep, defined as the amount of time in between each position, velocity and energy calculation, was chosen as a compromise value, short enough to give precise collision detection but long enough that simulations could be run in a reasonably short amount of time. A collision checking timestep of 0.1 fs was found to work well for this purpose. In the python program, the numerical integration routine used to find the position and velocity of the effective Si mass uses a timestep of one-tenth the collision-checking timestep (0.01 fs). This smaller timestep is needed to allow more accurate numerical integration, while making sure that a collision has indeed occurred when indicated.

IV.2.2.4: Detecting a Collision and Terminating the Program

At each timestep, the positions, velocities and energies of the gas molecule and Si surface species are recorded to a text file where the program outputs are stored. If the program finds that the gas molecule has “passed” the effective Si mass, or vice versa, based on the direction each species is moving, a collision is recorded and the positions, velocities, and energies are updated accordingly.

The simulation is set to continue running until the gas molecule is at a position ten times the maximum silicon amplitude away from the surface. This distance was selected arbitrarily to ensure that the simulation would continue until no further collisions were possible.

IV.3: Velocity and Position of XeF₂ or F₂ and the Si Surface at First Collision

Before the energy transfer to the Si surface can be calculated, the velocity of both the incoming gas molecule and the effective Si mass is input into the program. Since the molecule has a set velocity, it therefore will have a set initial kinetic energy. The velocities are set to be
the velocities of the molecules described in the experiments in Chapter III. To calculate the velocities, the proper mixture is first used for Xe(F\textsubscript{2}), 5% F\textsubscript{2}/95% Xe, as was determined by Hefty\textsuperscript{27}. The time of flight spectrum of the Xe(F\textsubscript{2}) dimer at a nozzle temperature of 223 K for m/e = 167 yielded an average energy of 1.46 kcal/mol. The theoretical average energy of a supersonic beam of F\textsubscript{2}, using Hefty’s nozzle conditions, is not much different from the experimental Xe(F\textsubscript{2}) energy, 1.55 kcal/mol. So, to provide a true comparison of energy transfer dynamics with the Si surface, the F\textsubscript{2} energy is set to be exactly the same as Xe(F\textsubscript{2}) in the calculations. Converting to velocity for 1.46 kcal/mol beams, v(F\textsubscript{2}) = 564.1 m/s and v(XeF\textsubscript{2}) = 269.1 m/s.

For each combination of spring constant, effective Si mass, gas mass and gas velocity, four calculations are made based on the position/velocity vector of the Si species at the first collision. These positions are called Positions 1-4. For the input in the Python program, the equilibrium spring position is labeled as “0”, position closest to the surface is “+1” and position farthest from the surface is “-1.” A positive velocity vector is input as +1 and a negative vector is -1. The definition of Positions 1-4 is shown below:

Position 1: SiF is fully compressed at its turning point near the surface with a velocity of 0 m/s at the first collision.
Position 2: SiF is moving towards the surface and is at its equilibrium spring position. SiF is moving at its maximum unperturbed velocity.
Position 3: SiF is moving away from the surface and is at its equilibrium spring position. SiF is moving at its maximum unperturbed velocity.
Position 4: SiF is fully extended at its turning point away from the surface with a velocity of 0 m/s at the first collision.
IV.4: Other Considerations in the Simulation

There are two other scenarios to note in the simulations, which will occur depending on the conditions used during the simulations. First, when the chosen Si mass is less than 40 amu, there are some positions where no collision occurs with XeF$_2$, or any other slow moving molecule. This zero collision scenario occurs only when dimer is moving towards the surface faster than XeF$_2$ is moving when the first collision is set to occur.

The second scenario is actually the opposite of scenario one: there are calculations where a very large number ($10+$) of collisions occur between XeF$_2$ and the surface. This over counting is an effect of the timestep used in the analysis. At some of the positions where the number of collisions is greater than ten, the velocity of the dimer and the incoming gas species is quite similar. The way a collision is detected explains why this occurs, as quoted below from a writeup by D. W. Rowlands:

“It takes the initial and final positions of the fluorine and silicon and determines if a collision has occurred by checking to see if either the fluorine has passed the silicon or the fluorine and the silicon are in the same location. If a collision has taken place, the function outputs “1”, otherwise it outputs “0”.”

So, in the cases of a very large number of collisions, the XeF$_2$ is moving at the same or very similar velocity as the surface and is basically nestled in with the dimer in such a way that many collisions are detected.

IV.5: Results of the Simulation for an Estimated Surface Mass of 47, a Si-F Fragment

An instructive simulation is one where the Si surface is fully fluorinated. Since it is known that the reactivities of XeF$_2$ and F$_2$ with Si(100) are essentially the same up to one monolayer of surface coverage, an energy transfer analysis of the fluorinated surface is necessary
to properly show the reactivity difference. SiF is a good species to investigate because on interaction with a fully fluorinted surface, an incoming molecule may first encounter a fluorine atom that is connected to a single Si atom. Also, SiF has a similar mass to molecular fluorine (47 amu vs. 38 amu) and a much smaller mass than XeF₂ (47 amu vs. 167 amu), providing a good mass comparison to start simulating the interactions with a fluorinated silicon surface.

**IV.5.1: Simulation of F₂ and XeF₂ Colliding with SiF at a Spring Constant of 225 N/m**

For the first spring constant used in the simulations, a value of 225 N/m was chosen based on a study by Wei and Chou\(^7\)\(^1\). Using a pseudopotential method, they calculated the phonon spectrum for Si(100). Their calculated planar force constants for the longitudinal and transverse modes are 252.7 and 208.5 N/m, respectively. A force constant of 225 N/m was chosen based on these values, since it is approximately the average force constant of the two modes.

Compared here are the energy transfer interactions between F₂ and XeF₂ with a Si-F fragment. Figures 6-9 show the positions of both SiF and the F₂ (top) and XeF₂ (bottom) molecules during interaction. Figures 10-13 show the energies of F₂ (top plot), XeF₂ (bottom plot) and SiF (both plots) throughout the interactions. Each of the Figures 7-10 and 11-14 have SiF at one of the four initial SiF positions described earlier. Note that the first collisions occur at \(t = 100\) ps on all the plots. This time was chosen so the unperturbed pre-collision dynamics for SiF and F₂/XeF₂ can be shown. Positions 1-4 are the positions of Si at \(t = 100\) ps.
Figure 6: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time.
The position of SiF at the initial collision is at its turning point near the surface with zero velocity. The initial velocity/energy of F₂ is 564.1 m/s while that for XeF₂ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 7: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time.

The position of SiF at the initial collision is at the equilibrium position and SiF is moving towards the surface. The initial velocity/energy of F₂ is 564.1 m/s while that for XeF₂ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 8: Comparing the position of SiF and F$_2$ (top) and XeF$_2$ (bottom) versus time.

The position of SiF at the initial collision is at the equilibrium position and SiF is moving away from the surface. The initial velocity/energy of F$_2$ is 564.1 m/s while that for XeF$_2$ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 9: Comparing the position of SiF and F₂ (top) and XeF₂ (bottom) versus time.

The position of SiF at the initial collision is the farthest it can be from the bulk wall with zero velocity. The initial velocity/energy of F₂ is 564.1 m/s while that for XeF₂ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 10: Comparing the energies of SiF and $F_2$ (top) and XeF$_2$ (bottom) versus time.

The position of SiF at the initial collision is closest to the wall with zero velocity. The initial velocity/energy of $F_2$ is 564.1 m/s while that for XeF$_2$ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 11: Comparing the energies of SiF and $F_2$ (top) and XeF$_2$ (bottom) versus time.

The position of SiF at the initial collision is at the equilibrium position and SiF is moving towards the surface. The initial velocity/energy of $F_2$ is 564.1 m/s while that for XeF$_2$ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 12: Comparing the energies of SiF and F$_2$ (top) and XeF$_2$ (bottom) versus time.

The position of SiF at the initial collision is at the equilibrium position and SiF is moving away from the surface. The initial velocity/energy of F$_2$ is 564.1 m/s while that for XeF$_2$ is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
Figure 13: Comparing the energies of SiF and F\textsubscript{2} (top) and XeF\textsubscript{2} (bottom) versus time.

The position of SiF at the initial collision is farthest from the wall with zero velocity. The initial velocity/energy of F\textsubscript{2} is 564.1 m/s while that for XeF\textsubscript{2} is 269.1 m/s and the energy of both species is 1.46 kcal/mol.
To analyze these results, the calculated excitation time of SiF was found during the interaction, along with the number of collisions each incoming molecule has with the SiF fragment. The excitation time is defined as the amount of time the Si-F fragment is compressed past its non-perturbed equilibrium point. That is, Si-F is compressed further than it would be if it were just a non-colliding, freely moving spring with a given spring constant. Table 1 shows the excitation time results for F$_2$ and XeF$_2$ interacting with the SiF at simulated positions 1-4. Table 2 shows the number of collisions F$_2$ and XeF$_2$ have with the surface at the four different positions. In the simple calculations presented, the spring constant does not affect the number of collisions Si has with F$_2$ and XeF$_2$. The mass of Si is the only variable that affects the number of collisions. Table 3 shows the calculated maximum energy that F$_2$ and XeF$_2$ transfers to the surface during the interactions. The maximum energy is defined as the difference between the highest Si energy found during a calculation and the equilibrium Si energy before any collision occurs. Note that the maximum Si energy can occur following any collision during F$_2$ or XeF$_2$ interactions.

Table 1: Excitation times for the Collision of F$_2$ and XeF$_2$ with SiF, Si spring constant = 225 N/m

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>37 fs</td>
<td>47 fs</td>
<td>30 fs</td>
<td>32 fs</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>76 fs</td>
<td>84 fs</td>
<td>36 fs</td>
<td>62 fs</td>
</tr>
</tbody>
</table>

Table 2: Number of surface Collisions of F$_2$ and XeF$_2$ with SiF for any Si spring constant

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th># of Collisions (SiF Position 1)</th>
<th># of Collisions (SiF Position 2)</th>
<th># of Collisions (SiF Position 3)</th>
<th># of Collisions (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>5</td>
<td>6</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 3: Maximum energy transfer of \( F_2 \) and \( XeF_2 \) with SiF for any Si spring constant, in kcal/mol

*Note: In the parentheses is the percent energy lost by \( F_2 \) and \( XeF_2 \) in each interaction.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Max Energy Transfer (SiF Position 1)</th>
<th>Max Energy Transfer (SiF Position 2)</th>
<th>Max Energy Transfer (SiF Position 3)</th>
<th>Max Energy Transfer (SiF Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_2 )</td>
<td>1.43 (97.9%)</td>
<td>1.11 (76.0%)</td>
<td>.76 (52.1%)</td>
<td>1.42 (97.2%)</td>
</tr>
<tr>
<td>( XeF_2 )</td>
<td>1.3 (89.0%)</td>
<td>1.26 (86.3%)</td>
<td>1.43 (97.9%)</td>
<td>0.99 (67.8%)</td>
</tr>
</tbody>
</table>

The results shown in Tables 1 and 2 are quite revealing. There is a correlation between the number of collisions either \( F_2 \) or \( XeF_2 \) suffer with the surface and the excitation time for the SiF fragment during the interaction. The proposed collision dynamics at each of the four positions is described here.

In position one, fluorine suffers two collisions with the SiF fragment. The first collision compresses the SiF fragment farther into the bulk wall, while the second collision has SiF rebounding and colliding with \( F_2 \), essentially knocking \( F_2 \) away far enough that no more collisions can occur. The energy transfer from \( F_2 \) to Si is very efficient in this position during the first collision with 98.5 percent of its energy transferred. Si now has enough energy that it will rebound quickly and hit \( F_2 \) again, explaining why \( F_2 \) with a smaller mass has two collisions with SiF. This second collision has Si transferring some of the energy it gained form the first collision to \( F_2 \), scattering it away in the process. In the same position, \( XeF_2 \) suffers five collisions with SiF. Here, the mass of \( XeF_2 \) plays a large role. When the first collision with SiF occurs, the \( XeF_2 \) still has enough momentum to keep moving forward towards the surface. Also, the energy transfer from \( XeF_2 \) to SiF is not as efficient as it is for \( F_2 \). In fact, SiF is most energetic following the second collision with \( XeF_2 \). The efficiency of energy transfer between \( XeF_2 \) and SiF explains why two more collisions are suffered before \( XeF_2 \) changes direction back
towards the vacuum, since XeF$_2$ does not lose most of its energy at the first collision. When XeF$_2$'s direction is finally changed, it still takes 2 collisions for Si to scatter it fully away, because the light SiF fragment is colliding with a slow moving, higher mass species, which is an inefficient path for energy transfer. With the increased number of collisions, and the slow movement of the XeF$_2$, the XeF$_2$ spends around double the time compressing the SiF bond past its unperturbed maximum compression, compared to F$_2$. In fact, this trend is seen in all the four interactions calculated for both F$_2$ and XeF$_2$.

The energy transfer of each species to SiF in position one seems counterintuitive for the mechanism proposed here. In position one, F$_2$ is much more efficient at energy transfer than that of XeF$_2$. The efficiency of energy transfer comes from the hard cube model being used here. The maximum energy transfer should occur when the masses match and/or are very close to each other, as they are with SiF and F$_2$. To go along with the hard cube model, the most energy transfer (97 percent) from F$_2$ occurs when SiF is stationary at the first collision. One would think that if F$_2$ is that much better at transferring its energy to SiF, then the SiF should be more vibrationally excited and thus reaction should occur more readily. However, two main points can be made to show this will not happen: 1) The energy of the incoming F$_2$ molecule is 1.46 kcal/mol, which is not greatly different than the energy of one vibrational mode in the SiF (E = k$_B$T = 0.497 kcal/mol at T$_{SiF}$ = 250 K.) Even if the energy transfer is 100 percent, the amount of energy excitation of the Si species is still very small. To expand this argument using SiF position one results, the difference in the amount of energy transferred to the surface for F$_2$ and XeF$_2$ is 0.13 kcal/mol, which is one quarter the energy of a vibrational degree of freedom at 250K; 2) Since damping is included in this system, one can see, especially in the top plot of Figure 11, that the SiF energy decreases rapidly once it hits maximum energy in the interaction
with F_2. In fact, the calculation in Figure 11 for F_2 shows a loss of 0.4 kcal/mol SiF energy to the bath within 15 fs, which is, on average, one to two orders of magnitude smaller than the time length of one vibration at a 225 N/m spring constant. The energy loss is so fast that the larger energy provided by F_2 quickly loses its importance compared to the residency time of XeF_2 collisions. The larger energy transfer from F_2 might deform the Si lattice more at the instant of collision, but the multiple collisions from XeF_2 keep the lattice deformed for a greater amount of time. Therefore, the multiple collisions suffered by XeF_2 with SiF are necessary to keep the lattice deformed longer, increasing the probability of fluorine reaction.

In position two, the most difficult result to envision is how XeF_2 suffers more than five collisions with the surface. One reason for a high collision count is that XeF_2 is compressing the lattice enough to cause many more collisions. However, a result of 6 collisions is probably due to the breaking down of the hard cube model used in the simulation. This model is based on all the collisions being impulsive. Perhaps, when XeF_2 has a similar velocity, 269.1 m/s, than SiF, 297 m/s, in position two, the two species are so intertwined with each other that most of the collisions are not impulsive. Section IV.4 explained the reason for high collision count computationally. A reasonable guess is that four to five collisions occur in the interaction of XeF_2 with the surface initially at position 2, based on the analysis of collision number in the other three positions. During the interactions, the amount of energy transfer is similar for both F_2 and XeF_2 when SiF is in position two. Once again, the main difference is in number of collisions and the excitation time for SiF. XeF_2 again suffers more collisions with the surface, increasing the SiF excitation time.

For position three, SiF is moving away from the bulk wall, and thus towards the incoming F_2 and XeF_2 molecules at the initial collision. The change in direction of SiF is the
reason why SiF collides with F₂ only once in this scenario. Basically, the SiF scatters F₂ away instantly. The collision impact is enough to cause compression of the SiF bond, but for a much shorter amount of time. Similarly for XeF₂, there are less collisions with SiF compared to the first two scenarios because the SiF moving towards XeF₂ to start. However, since there are more collisions with XeF₂, SiF is still compressed for two times longer during its interaction with XeF₂ compared to fluorine. Also, when SiF is initially at position 3, XeF₂ transfers more energy to SiF than F₂. The energy transfer change here comes from the difference in mass between XeF₂ and F₂ because F₂ is light enough to be scattered away, while XeF₂ is not.

When SiF is in position four, it is stationary but as far away from the surface wall as possible for the spring constant chosen. When F₂ collides with SiF in this position, it transfers most of its energy, but still suffers only one collision with the surface. The proposed dynamics are as follows: F₂ hits SiF and it trajectory is reversed towards the vacuum. SiF is compressed, but in the time it takes for SiF to return for another collision, F₂ is too far away. No further collisions will occur. However, after XeF₂ hits SiF for the first time, it is still moving towards the surface, since a stationary SiF species will not reverse the trajectory of a much heavier molecule. XeF₂ is calculated to suffer three collisions with SiF here with less energy transfer than for F₂. However, XeF₂ provides double the excitation time for SiF again due to multiple collisions.

Overall, some interesting collision dynamics are seen using very simple calculations in the interaction of F₂ and XeF₂ with a SiF species. First, the position and velocity of the SiF species as the first collision occurs are important because those help dictate the number of collisions and the interaction time. Also, the total energy transferred by F₂ and XeF₂ after the final collision or interaction is not as important as one would think for two reasons: 1) The
surface has enough heat loss with the damping term that the excess energy is lost quicker than one vibrational period and 2) The energy transferred is small compared to the dissociation energy of a Si-Si bond. The difference in reactivity of $\text{F}_2$ and $\text{XeF}_2$ with a fluorinated Si surface may actually be because multiple collisions cause a longer excitation time of $\text{SiF}$. With the longer excitation time comes a longer amount of time during which the fluorine carried on the Xe atoms can achieve a favorable orientation to react with the stretched and compressed Si, fluorinating the surface past 1 ML.

The following sections perform the same types of calculations as explained above, only with different spring constants and different Si masses.

**IV.6: Simulation of $\text{F}_2$ and $\text{XeF}_2$ Interactions with $\text{SiF}$ at Other Spring Constants**

The use of a SiF spring constant of 225 N/m is a good start for comparing the reactivity of $\text{F}_2$ and $\text{XeF}_2$ with a SiF fragment on a fluorinated Si(100) surface. However, this value was found using average spring constants of phonon modes of the Si surface. Five other spring constants were used, each based on the vibrational frequencies of different phonon modes of Si and the Si surface. Even though different spring constants have been included, the basic model used in the calculations has not changed. The model still has an adjustable Si mass on a spring attached to an infinite mass wall. However, some different spring force constants are chosen based on past experimental/theoretical results that provided vibrational frequencies for individual modes.

The first frequency is based on a phonon mode found in EELS experiments ran by Tagaki\textsuperscript{72}, et. al. In this paper, the mode is called $A^\prime_2$ and it shows the movement of the Si-Si asymmetric dimer system vibrating exactly perpendicular to the surface. It is shown in Figure 14 for convenience. Its frequency is 7.72 meV, which equates to a spring constant of 10.74 N/m.
For simplicity of the simulation inputs, a spring constant of 10 N/m was used for this mode. The calculation of the frequency conversion to spring constant is shown below. In the calculation, \( N_A \) is Avogadro’s number and \( k \) is the spring constant. The reduced mass in this classical spring equation is treated as the SiF mass since it is vibrating against an infinite mass wall. Using SiF as the mass is a gross approximation for finding the spring constant here. The basis for this choice is estimating the spring constant of SiF attached to the wall based on the vibrational frequencies of all the modes presented in this section.

\[
\nu_{\text{mode}} = 7.72 \text{meV} = 62.27 \text{cm}^{-1} = \frac{1}{2\pi} \left( \sqrt{\frac{k}{\mu}} \right)
\]

\[
62.27 \text{cm}^{-1} = \frac{1}{2\pi} \left( \sqrt{\frac{k}{0.047 \text{kg} \cdot \text{mol}^{-1} / N_A}} \right)
\]

\[
k = 10.73 \text{N} \cdot \text{m}^{-1}
\]

**Figure 14: Schematic of the vibrational mode at a 7.72 meV (10.7 N/m) frequency.** Adapted from an EELS study by Tagaki, et. al.

Based on the simplicity of the calculations, the maximum energy transferred to the surface and the number of collisions with the surface does not change with a change in spring constant of SiF. This effect is due to the velocity of the spring remaining the same since SiF is still the mass being studied in the calculations shown here. What does change is the residence time with the surface. All the calculations of interaction of SiF (10 N/m) with both F$_2$ and XeF$_2$
were performed at the same four positions as explained earlier. The excitation time of SiF with a spring constant of 10 N/m is shown in Table 4:

Table 4: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 10. N/m

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>176 fs</td>
<td>223 fs</td>
<td>142 fs</td>
<td>151 fs</td>
</tr>
<tr>
<td>XeF₂</td>
<td>360 fs</td>
<td>398 fs</td>
<td>171 fs</td>
<td>293 fs</td>
</tr>
</tbody>
</table>

The excitation time results make physical sense. With a lower spring constant, the amount of time SiF is excited upon collision with both F₂ and XeF₂ is much greater, coming closer to a picosecond. The longer excitation time is because the maximum displacement of Si is much longer but the Si spring still has the same energy. So, it takes Si longer to rebound and hit F₂ and XeF₂ again, increasing the interaction time which, in turn, will increase the excitation time. Still, XeF₂ resides at the surface for a much longer time period than F₂. Again, the maximum energy transfer and the number of collisions remained the same. The same correlations to the 225 N/m results can be made with the results at a spring constant of 10 N/m.

Another interesting phonon mode to investigate from the same EELS study is one at a frequency of 69.25 meV, which yields a spring constant of 865 N/m. This mode has the Si-Si dimers moving parallel to the surface, while the each Si atom bonded to a dimer atom vibrates perpendicular to the surface bath. For this study, the value used for this spring constant is 850 N/m. The schematic of the vibration of the surface at this frequency is found in Figure 15. Also, since an 850 N/m spring is much stiffer than any other used in the calculations, it is a good reference for the extreme case of a high spring constant. Table 5 shows the calculated excitation time of SiF at this spring constant.
Figure 15: Schematic of the vibrational mode at a 69.25 meV (865 N/m) frequency.
Adapted from an EELS study by Tagaki, et. al.

Table 5: Excitation Times For Collisions of F\textsubscript{2} and XeF\textsubscript{2} with SiF, Si Spring Constant = 850 N/m

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{2}</td>
<td>19 fs</td>
<td>24 fs</td>
<td>15 fs</td>
<td>16 fs</td>
</tr>
<tr>
<td>XeF\textsubscript{2}</td>
<td>39 fs</td>
<td>43 fs</td>
<td>19 fs</td>
<td>32 fs</td>
</tr>
</tbody>
</table>

Zerbi, et. al. studied the dispersion curve for diamond-like Si crystals\textsuperscript{23}. This group treated the lattice dynamics and the vibrational spectra of Si using a valence force potential. One of the Si modes prevalent has one of the Si-Si bonds as shown in Fig. 16 vibrating while the other bonds remain still. The spring constant for this mode is calculated to be 146.9 N/m. For this study, a spring constant of 150 N/m was chosen for the calculations. Table 6 shows the excitation time of SiF after interaction with F\textsubscript{2} and XeF\textsubscript{2} using this spring constant for the calculations at each of the four positions.
Figure 16: Schematic of the vibrational mode with a frequency of 150 N/m.
Adapted from a study by Zerbi, et. al.

Table 6: Excitation Times For Collisions of F_2 and XeF_2 with SiF, Si Spring Constant = 150 N/m

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F_2</td>
<td>45 fs</td>
<td>58 fs</td>
<td>37 fs</td>
<td>39 fs</td>
</tr>
<tr>
<td>XeF_2</td>
<td>93 fs</td>
<td>103 fs</td>
<td>44 fs</td>
<td>76 fs</td>
</tr>
</tbody>
</table>

Tiersten, et. al. calculated the vibrational properties of the reconstructed Si(100) 2x1 surface using a Keating model. This group found two main vibrational modes for the reconstructed Si surface. One is a “swing” mode, which is shown in Figure 17. This mode has a calculated frequency of 11.47 THz, which, using the same type of calculation shown for the 10 N/m calculation, has an overall spring constant of 405 N/m. For the purposes of this study, a value of 400 N/m was used in the calculations. The other mode is a “rocking” mode, shown in Figure 18. This mode has a calculated frequency of 3.61 THz, which gives an overall spring constant of 40.1 N/m. For the purposes of this study, a value of 50 N/m was used in the calculations, to provide a bit more of a difference in spring constants compared to the 10 N/m
mode explained earlier. The results of the calculations for excitation time of SiF after interaction with F₂ and XeF₂ for both of these modes are shown in Tables 7 and 8.

![Schematic of the swing mode of a reconstructed Si(100) 2x1 surface.](image1)

**Figure 17:** Schematic of the swing mode of a reconstructed Si(100) 2x1 surface. As explained by Tiersten, et. al. This mode has a spring constant of 405 N/m.

![Schematic of the rocking mode of a reconstructed Si(100) 2x1 surface.](image2)

**Figure 18:** Schematic of the rocking mode of a reconstructed Si(100) 2x1 surface. As explained by Tiersten, et. al. This mode has a spring constant of 40 N/m.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF at Position 3)</th>
<th>Time (SiF at Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>78 fs</td>
<td>100 fs</td>
<td>64 fs</td>
<td>68 fs</td>
</tr>
<tr>
<td>XeF₂</td>
<td>161 fs</td>
<td>178 fs</td>
<td>76 fs</td>
<td>132 fs</td>
</tr>
</tbody>
</table>

Table 7: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 50. N/m
Table 8: Excitation Times For Collisions of F₂ and XeF₂ with SiF, Si Spring Constant = 400 N/m

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>28 fs</td>
<td>35 fs</td>
<td>23 fs</td>
<td>24 fs</td>
</tr>
<tr>
<td>XeF₂</td>
<td>57 fs</td>
<td>63 fs</td>
<td>27 fs</td>
<td>47 fs</td>
</tr>
</tbody>
</table>

Figure 19 is a plot of SiF excitation time versus the spring constant for each mode described above. Also, the maximum fraction of energy transferred to SiF by F₂ and XeF₂ is shown in the inset of the graph. SiF is excited for a much longer time with its interaction with XeF₂ than that of F₂, no matter the spring constant. The inclusion of multiple collisions in the simulation helps explain this observation for all spring constants. Also, as shown in the inset, when the Si surface was treated as a SiF fragment interacting with fluorine and xenon difluoride, the maximum energy transfer changes with each initial SiF position. At different positions, F₂ can transfer more energy to SiF than XeF₂ or vice versa. However, XeF₂ always provides a longer SiF excitation time, due to multiple collisions, making multiple collisions due to the mass of the incoming species a crucial element in the etching ability of XeF₂ as compared to that of F₂. The next section will provide similar analysis of the interaction of F₂ and XeF₂ with a Si(100) surface using fluorinated Si fragments with much different masses.
Upon collision with F$_2$ and XeF$_2$ in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from F$_2$ or XeF$_2$ versus initial SiF position.

**IV.7: Simulation of F$_2$ and XeF$_2$ Interactions with Non-SiF Fluorinated Si Fragments**

The simulations were continued with four different fluorinated Si fragments, to see if there is a better Si mass to help explain the differing reactivities of F$_2$ and XeF$_2$ with a flourinated Si(100) surface. The four masses are: SiF$_2$ (Si mass 75), Si$_2$F$_2$ (Si mass 94), Si$_4$F$_2$ (Si mass 150) and Si$_6$F$_2$ (Si mass 206.) Figure 20 shows the proposed geometries of each of these fragments.
Figure 20: Molecular geometries of the four other Si fragments used in calculations.
Top left is that of SiF$_2$, top right is Si$_2$F$_2$, bottom left is Si$_4$F$_2$ and bottom right is Si$_6$F$_2$.

Outside of SiF$_2$, each fragment consists of the Si-Si dimer bond still intact, with subsurface Si atoms used in Si$_4$F$_2$ and Si$_6$F$_2$. One would expect that the number of collisions should essentially go to one when both F$_2$ and XeF$_2$ interact with the heavier species.

Table 9 shows the excitation times of SiF$_2$ during interactions with F$_2$ and XeF$_2$ at the five spring constants explained by the phonon modes/simulations described above. This analysis is extended to each of the 4 initial collision positions for each spring constant. Table 10 shows the calculated number of collisions F$_2$ and XeF$_2$ suffers with the SiF$_2$ fragment at each of the four collision positions. Table 11 shows the calculated maximum energy transferred to SiF$_2$ by F$_2$ and XeF$_2$ at each of the four collision positions.
Table 9: Excitation times for the collision of $F_2$ and XeF$_2$ with a SiF$_2$ (Mass 75) fragment, various Si spring constants (in femtoseconds)

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$, 225 N/m</td>
<td>46</td>
<td>55</td>
<td>29</td>
<td>40</td>
</tr>
<tr>
<td>XeF$_2$, 225 N/m</td>
<td>76</td>
<td>87</td>
<td>44</td>
<td>66</td>
</tr>
<tr>
<td>$F_2$, 10. N/m</td>
<td>218</td>
<td>261</td>
<td>138</td>
<td>190</td>
</tr>
<tr>
<td>XeF$_2$, 10. N/m</td>
<td>360</td>
<td>413</td>
<td>209</td>
<td>313</td>
</tr>
<tr>
<td>$F_2$, 50. N/m</td>
<td>98</td>
<td>117</td>
<td>62</td>
<td>85</td>
</tr>
<tr>
<td>XeF$_2$, 50. N/m</td>
<td>161</td>
<td>185</td>
<td>93</td>
<td>140</td>
</tr>
<tr>
<td>$F_2$, 150. N/m</td>
<td>56</td>
<td>67</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>XeF$_2$, 150. N/m</td>
<td>93</td>
<td>107</td>
<td>54</td>
<td>81</td>
</tr>
<tr>
<td>$F_2$, 400. N/m</td>
<td>35</td>
<td>41</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>XeF$_2$, 400. N/m</td>
<td>57</td>
<td>65</td>
<td>33</td>
<td>50</td>
</tr>
<tr>
<td>$F_2$, 850. N/m</td>
<td>24</td>
<td>28</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>XeF$_2$, 850. N/m</td>
<td>39</td>
<td>45</td>
<td>23</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 10: Number of Surface Collisions of $F_2$ and XeF$_2$ with a SiF$_2$ (Mass 75) Fragment for Any Si Spring Constant

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th># of Collisions (SiF Position 1)</th>
<th># of Collisions (SiF Position 2)</th>
<th># of Collisions (SiF Position 3)</th>
<th># of Collisions (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>3</td>
<td>14</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 11: Maximum Energy Transfer of $F_2$ and XeF$_2$ with a SiF$_2$ (Mass 75) Fragment for Any Si Spring Constant, in kcal/mol

*Note: In the parentheses is the percent energy lost by $F_2$ and XeF$_2$ in each interaction.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Max Energy Transfer (SiF Position 1)</th>
<th>Max Energy Transfer (SiF Position 2)</th>
<th>Max Energy Transfer (SiF Position 3)</th>
<th>Max Energy Transfer (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$</td>
<td>1.29 (88.3%)</td>
<td>1.37 (93.8%)</td>
<td>0.32 (21.9%)</td>
<td>1.29 (88.4%)</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>1.31 (89.7%)</td>
<td>1.12 (76.7%)</td>
<td>1.40 (95.9%)</td>
<td>1.23 (84.2%)</td>
</tr>
</tbody>
</table>
Table 12 shows the excitation times of Si$_2$F$_2$ during interactions with F$_2$ and XeF$_2$ at the five spring constants explained by the phonon modes/simulations described above. This analysis is extended to each of the 4 initial collision positions for each spring constant. Table 13 shows the calculated number of collisions F$_2$ and XeF$_2$ suffers with the Si$_2$F$_2$ fragment at each of the four collision positions. Table 14 shows the calculated maximum energy transferred to Si$_2$F$_2$ by F$_2$ and XeF$_2$ at each of the four collision positions.

Table 12: Excitation Times For The Collision of F$_2$ and XeF$_2$ with a Si$_2$F$_2$ (Mass 94) Fragment, Various Si Spring Constants (in femtoseconds)

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$, 10. N/m</td>
<td>242</td>
<td>232</td>
<td>109</td>
<td>209</td>
</tr>
<tr>
<td>XeF$_2$, 10. N/m</td>
<td>360</td>
<td>427</td>
<td>228</td>
<td>213</td>
</tr>
<tr>
<td>F$_2$, 50. N/m</td>
<td>108</td>
<td>104</td>
<td>49</td>
<td>93</td>
</tr>
<tr>
<td>XeF$_2$, 50. N/m</td>
<td>161</td>
<td>191</td>
<td>102</td>
<td>95</td>
</tr>
<tr>
<td>F$_2$, 150. N/m</td>
<td>62</td>
<td>60</td>
<td>28</td>
<td>54</td>
</tr>
<tr>
<td>XeF$_2$, 150. N/m</td>
<td>93</td>
<td>110</td>
<td>59</td>
<td>55</td>
</tr>
<tr>
<td>F$_2$, 225 N/m</td>
<td>51</td>
<td>49</td>
<td>23</td>
<td>44</td>
</tr>
<tr>
<td>XeF$_2$, 225 N/m</td>
<td>76</td>
<td>90</td>
<td>48</td>
<td>45</td>
</tr>
<tr>
<td>F$_2$, 400. N/m</td>
<td>38</td>
<td>37</td>
<td>17</td>
<td>33</td>
</tr>
<tr>
<td>XeF$_2$, 400. N/m</td>
<td>57</td>
<td>68</td>
<td>36</td>
<td>34</td>
</tr>
<tr>
<td>F$_2$, 850. N/m</td>
<td>26</td>
<td>25</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>XeF$_2$, 850. N/m</td>
<td>39</td>
<td>46</td>
<td>25</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 13: Number of Surface Collisions of F$_2$ and XeF$_2$ with a Si$_2$F$_2$ (Mass 94) Fragment for Any Si Spring Constant

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th># of Collisions (SiF Position 1)</th>
<th># of Collisions (SiF Position 2)</th>
<th># of Collisions (SiF Position 3)</th>
<th># of Collisions (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>3</td>
<td>8</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 14: Maximum Energy Transfer of \( \text{F}_2 \) and \( \text{XeF}_2 \) with a \( \text{Si}_2\text{F}_2 \) (Mass 94) Fragment for Any Si Spring Constant, in kcal/mol

*Note: In the parentheses is the percent energy lost by \( \text{F}_2 \) and \( \text{XeF}_2 \) in each interaction.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Max Energy Transfer (SiF Position 1)</th>
<th>Max Energy Transfer (SiF Position 2)</th>
<th>Max Energy Transfer (SiF Position 3)</th>
<th>Max Energy Transfer (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2 )</td>
<td>1.19 (81.5%)</td>
<td>1.42 (97.3%)</td>
<td>.13 (8.9%)</td>
<td>1.18 (80.8%)</td>
</tr>
<tr>
<td>( \text{XeF}_2 )</td>
<td>1.33 (91.1%)</td>
<td>1.29 (88.4%)</td>
<td>1.33 (91.1%)</td>
<td>1.33 (91.1%)</td>
</tr>
</tbody>
</table>

Table 15 shows the excitation times of \( \text{Si}_4\text{F}_2 \) during interactions with \( \text{F}_2 \) and \( \text{XeF}_2 \) at the five spring constants explained by the phonon modes/simulations described above. This analysis is extended to each of the 4 initial collision positions for each spring constant. Table 16 shows the calculated number of collisions \( \text{F}_2 \) and \( \text{XeF}_2 \) suffers with the \( \text{Si}_4\text{F}_2 \) fragment at each of the four collision positions. Table 17 shows the calculated maximum energy transferred to \( \text{Si}_4\text{F}_2 \) by \( \text{F}_2 \) and \( \text{XeF}_2 \) at each of the four collision positions.

Table 15: Excitation Times For The Collision of \( \text{F}_2 \) and \( \text{XeF}_2 \) with a \( \text{Si}_4\text{F}_2 \) (Mass 150) Fragment, Various Si Spring Constants (in femtoseconds)

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2 ), 10. N/m</td>
<td>289</td>
<td>294</td>
<td>0</td>
<td>247</td>
</tr>
<tr>
<td>( \text{XeF}_2 ), 10. N/m</td>
<td>408</td>
<td>446</td>
<td>323</td>
<td>275</td>
</tr>
<tr>
<td>( \text{F}_2 ), 50. N/m</td>
<td>129</td>
<td>132</td>
<td>0</td>
<td>110</td>
</tr>
<tr>
<td>( \text{XeF}_2 ), 50. N/m</td>
<td>182</td>
<td>199</td>
<td>144</td>
<td>123</td>
</tr>
<tr>
<td>( \text{F}_2 ), 150. N/m</td>
<td>75</td>
<td>76</td>
<td>0</td>
<td>64</td>
</tr>
<tr>
<td>( \text{XeF}_2 ), 150. N/m</td>
<td>105</td>
<td>115</td>
<td>83</td>
<td>71</td>
</tr>
<tr>
<td>( \text{F}_2 ), 225 N/m</td>
<td>61</td>
<td>62</td>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>( \text{XeF}_2 ), 225 N/m</td>
<td>86</td>
<td>94</td>
<td>68</td>
<td>58</td>
</tr>
<tr>
<td>( \text{F}_2 ), 400. N/m</td>
<td>46</td>
<td>47</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>( \text{XeF}_2 ), 400. N/m</td>
<td>65</td>
<td>71</td>
<td>51</td>
<td>44</td>
</tr>
</tbody>
</table>
Table 16: Number of Surface Collisions of F\(_2\) and XeF\(_2\) with a Si\(_4\)F\(_2\) (Mass 150) Fragment for Any Si Spring Constant

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th># of Collisions (SiF Position 1)</th>
<th># of Collisions (SiF Position 2)</th>
<th># of Collisions (SiF Position 3)</th>
<th># of Collisions (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XeF(_2)</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 17: Maximum Energy Transfer of F\(_2\) and XeF\(_2\) with a Si\(_4\)F\(_2\) (Mass 150) Fragment for Any Si Spring Constant, in kcal/mol

*Note: In the parentheses is the percent energy lost by F\(_2\) and XeF\(_2\) in each interaction.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Max Energy Transfer (SiF Position 1)</th>
<th>Max Energy Transfer (SiF Position 2)</th>
<th>Max Energy Transfer (SiF Position 3)</th>
<th>Max Energy Transfer (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(_2)</td>
<td>0.93 (63.7%)</td>
<td>1.42 (97.2%)</td>
<td>0 (0%)</td>
<td>0.93 (63.7%)</td>
</tr>
<tr>
<td>XeF(_2)</td>
<td>1.44 (98.6%)</td>
<td>1.00 (68.5%)</td>
<td>1.13 (77.4%)</td>
<td>1.44 (98.6%)</td>
</tr>
</tbody>
</table>

Table 18 shows the excitation times of Si\(_6\)F\(_2\) during interactions with F\(_2\) and XeF\(_2\) at the five spring constants explained by the phonon modes/simulations described above. This analysis is extended to each of the 4 initial collision positions for each spring constant. Table 19 shows the calculated number of collisions F\(_2\) and XeF\(_2\) suffers with the Si\(_6\)F\(_2\) fragment at each of the four collision positions. Table 20 shows the calculated maximum energy transferred to Si\(_6\)F\(_2\) by F\(_2\) and XeF\(_2\) at each of the four collision positions.
Table 18: Excitation Times For The Collision of F₂ and XeF₂ with a Si₀F₂ (Mass 206) Fragment, Various Si Spring Constants (in femtoseconds)

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Time (SiF at Position 1)</th>
<th>Time (SiF at Position 2)</th>
<th>Time (SiF At Position 3)</th>
<th>Time (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂, 10. N/m</td>
<td>323</td>
<td>342</td>
<td>0</td>
<td>275</td>
</tr>
<tr>
<td>XeF₂, 10. N/m</td>
<td>370</td>
<td>460</td>
<td>299</td>
<td>318</td>
</tr>
<tr>
<td>F₂, 50. N/m</td>
<td>144</td>
<td>153</td>
<td>0</td>
<td>123</td>
</tr>
<tr>
<td>XeF₂, 50. N/m</td>
<td>165</td>
<td>206</td>
<td>134</td>
<td>142</td>
</tr>
<tr>
<td>F₂, 150. N/m</td>
<td>83</td>
<td>88</td>
<td>0</td>
<td>71</td>
</tr>
<tr>
<td>XeF₂, 150. N/m</td>
<td>96</td>
<td>119</td>
<td>77</td>
<td>82</td>
</tr>
<tr>
<td>F₂, 225 N/m</td>
<td>68</td>
<td>72</td>
<td>0</td>
<td>58</td>
</tr>
<tr>
<td>XeF₂, 225 N/m</td>
<td>78</td>
<td>97</td>
<td>63</td>
<td>67</td>
</tr>
<tr>
<td>F₂, 400. N/m</td>
<td>51</td>
<td>54</td>
<td>0</td>
<td>44</td>
</tr>
<tr>
<td>XeF₂, 400. N/m</td>
<td>59</td>
<td>73</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>F₂, 850. N/m</td>
<td>35</td>
<td>37</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>XeF₂, 850. N/m</td>
<td>40</td>
<td>50</td>
<td>32</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 19: Number of Surface Collisions of F₂ and XeF₂ with a Si₀F₂ (Mass 206) Fragment for Any Si Spring Constant

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th># of Collisions (SiF Position 1)</th>
<th># of Collisions (SiF Position 2)</th>
<th># of Collisions (SiF Position 3)</th>
<th># of Collisions (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XeF₂</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 20: Maximum Energy Transfer of F₂ and XeF₂ with a Si₀F₂ (Mass 206) Fragment for Any Si Spring Constant, in kcal/mol

*Note: In the parentheses is the percent energy lost by F₂ and XeF₂ in each interaction.

<table>
<thead>
<tr>
<th>Incoming Species</th>
<th>Max Energy Transfer (SiF Position 1)</th>
<th>Max Energy Transfer (SiF Position 2)</th>
<th>Max Energy Transfer (SiF Position 3)</th>
<th>Max Energy Transfer (SiF At Position 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>0.76 (52.1%)</td>
<td>1.34 (91.8%)</td>
<td>0 (0%)</td>
<td>0.76 (52.1%)</td>
</tr>
<tr>
<td>XeF₂</td>
<td>1.43 (97.9%)</td>
<td>1.11 (76%)</td>
<td>0.76 (52.1%)</td>
<td>1.43 (97.9%)</td>
</tr>
</tbody>
</table>
Figure 21 shows the plot of SiF$_2$ excitation time versus SiF$_2$ spring constant for interactions with F$_2$ and XeF$_2$ at each of the four collision positions. The inset of this graph shows the maximum energy transferred by F$_2$ and XeF$_2$ by to SiF$_2$ at each collision position. The same analysis is performed in Figure 22 for Si$_3$F$_2$, Figure 23 for Si$_4$F$_2$ and Figure 24, for the Si$_6$F$_2$ fragment.

**Figure 21: Graph of the excitation time of SiF$_2$ vs. SiF spring constant.**

Upon collision with F$_2$ and XeF$_2$ in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from F$_2$ or XeF$_2$ versus initial SiF$_2$ position.
Upon collision with $F_2$ and XeF$_2$ in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from $F_2$ or XeF$_2$ versus initial Si$_2$F$_2$ position.

**Figure 22:** Graph of the excitation time of Si$_2$F$_2$ vs. SiF spring constant.

Upon collision with $F_2$ and XeF$_2$ in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from $F_2$ or XeF$_2$ versus initial Si$_2$F$_2$ position.

**Figure 23:** Graph of the excitation time of Si$_4$F$_2$ vs. SiF spring constant.

Upon collision with $F_2$ and XeF$_2$ in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from $F_2$ or XeF$_2$ versus initial Si$_4$F$_2$ position.
Upon collision with F\textsubscript{2} and XeF\textsubscript{2} in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from F\textsubscript{2} or XeF\textsubscript{2} versus initial Si\textsubscript{6}F\textsubscript{2} position.

For each Si effective mass, XeF\textsubscript{2} excites the surface for a longer period of time than F\textsubscript{2}. However, with higher Si mass, the excitation time caused by F\textsubscript{2} is much closer to that of XeF\textsubscript{2}. For Si\textsubscript{6}F\textsubscript{2}, the number of collisions suffered by F\textsubscript{2} and XeF\textsubscript{2} is similar. F\textsubscript{2} suffers one collision in all scenarios, while XeF\textsubscript{2} suffers only 1-3 collisions, where the three collision scenario is when Si\textsubscript{6}F\textsubscript{2} is travelling towards the surface at the initial collision, indicating that even when the Si mass is high, XeF\textsubscript{2} still can have multiple collisions with the surface with the right conditions.

The observation of a smaller number of collisions with higher Si mass is consistent with the expectations of the model. That is, the Si mass is now greater than both incoming gas masses. Since multiple collisions occur primarily when the gas species has a higher mass than the solid, there should only be one to two collisions at most when the Si mass is so great. With a similar number of collisions comes the similar excitation times at higher Si mass. One other observation

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**Figure 24: Graph of the excitation time of Si\textsubscript{6}F\textsubscript{2} vs. SiF spring constant.**

Upon collision with F\textsubscript{2} and XeF\textsubscript{2} in all four positions, as described earlier. The inset is the maximum fraction of energy transfer from F\textsubscript{2} or XeF\textsubscript{2} versus initial Si\textsubscript{6}F\textsubscript{2} position.
from these calculations is that the fraction of energy transferred to the Si surface by \( F_2 \) greatly decreases with increasing Si mass. In fact, when \( \text{Si}_4\text{F}_2 \) and \( \text{Si}_6\text{F}_2 \) are moving towards \( F_2 \) at the initial collision, the Si species actually transfers some of its energy to \( F_2 \). There is no lattice deformation using \( \text{Si}_4\text{F}_2 \) and \( \text{Si}_6\text{F}_2 \) in this case because these species are so much heavier than \( F_2 \) and have enough energy that the simple model demands that the energy gets transferred to \( F_2 \), not the Si species. This mass effect also applies to why, in other scenarios, the energy transfer from \( F_2 \) to heavy Si is much less efficient. Since \( \text{Si}_4\text{F}_2 \) and \( \text{Si}_6\text{F}_2 \) are 4 and 6 times heavier, respectively, than \( F_2 \), they will scatter \( F_2 \) away before any chance of further energy transfer can occur.

The most interesting Si mass in this analysis is mass 94, the fully fluorinated Si-Si dimer. On average, \( \text{XeF}_2 \) suffers 3-4 collisions with the surface, while \( F_2 \) suffers 1-2, depending on the position of \( \text{Si}_2\text{F}_2 \) at the initial collision. The excitation time calculations further this point, with \( \text{XeF}_2 \) deforming the lattice for an average of 1.5 times longer than does \( F_2 \). Also, on average, \( \text{XeF}_2 \) transfers a greater fraction of its energy (0.90 average) to the surface at this mass than \( F_2 \) (0.67 average.) \( \text{XeF}_2 \) has such a greater energy transfer efficiency because its mass is now getting closer to that of Si, while \( F_2 \) is 2.5 times lighter than \( \text{Si}_2\text{F}_2 \), which is a non-ideal scenario for energy transfer. The combination of all three of these factors (number of collisions, excitation/lattice deformation time and average energy transfer) makes it feasible that the increased mass of \( \text{XeF}_2 \) compared to \( F_2 \) and the Si surface fragment helps facilitate the overall dry etching of the Si surface. Namely, \( \text{XeF}_2 \) excites/deforms the Si lattice for a long enough period of time to make reaction with the fluorine carried on the Xe possible, just like the late vibrational barrier model explained earlier would predict.
IV.8: Conclusions from Model and Future Considerations

Using simple classical mechanics, it is possible to simulate the interactions of F\(_2\) and XeF\(_2\) with a Si surface as an attempt to explain why XeF\(_2\) readily etches Si(100) while F\(_2\) does not. A multiple collision model was used here to explain this reactivity difference. Treating Si as a simple mass on a damped spring provides the vibrational dynamics to estimate the Si excitation time during any interaction with F\(_2\) and XeF\(_2\). On average, XeF\(_2\) suffers more collisions with a Si surface than does F\(_2\), no matter the mass of Si used in the model, up to the largest mass studied, because XeF\(_2\) is much more massive than F\(_2\). The increased number of collisions leads to an increased excitation time for the Si surface. The longer excitation time helps justify the proposed late vibrational barrier reaction pathway. The Si-Si bonds are stretched and compressed for a longer period of time upon collision with XeF\(_2\), increasing the amount of time available for reaction, and thus the overall reaction probability.

As an initial study of the collision dynamics with a Si surface, this model shows the necessity of multiple collisions to activate a reaction with a late vibrational barrier. Further studies that would treat the fluorinated Si surface as a slab that would provide more accurate Si lattice deformation dynamics, along with having the Si surface vibrating with a proper frequency in all possible dimensions would be helpful. Also, this study was performed having the incoming gas molecule interact at the surface normal with no angular scattering in the interactions. Inclusion of angular scattering and the interactions from that would provide a more complete picture of the dynamics occurring at each collision.
Chapter IV References:

64) C. Steinbruchel, Surf. Sci. 66, 131-144 (1977)
Appendix

Appendix A: Renovated Electric and Water Distribution in Big Machine Lab

From 2004-2006, the 40-year-old laboratory space was completely renovated. As a part of that renovation, the distribution of electrical power was completely redone. For the Big Machine, located in Building 2, there are three main areas of the electrical distribution: 1) Inside the pump room for the air compressor, mechanical pumps and Roots blowers; 2) Along the wall separating the scattering machine and the pump room for machine electronics (interlocks, pressure indicators, instruments, etc.) and the diffusion pumps and 3) Above the scattering machine and the electronics repair area.

Two main concerns need addressing while installing the new electric system: enough outlets for the current equipment, all with the correct voltages and currents, which vary part-by-part and some flexibility (i.e. added outlets of differing voltages/currents) for equipment that may be added in the future. Both of these concerns are mitigated using a Starline bus system from the Universal Electric Corporation. Its function and properties are described in another thesis\(^1\). Note that there are separate buses for each of the three areas described above, and all these buses are supplied by a general circuit breaker box located in the pump room.

Figure 1 shows the setup of the electrical distribution in the pump room. First, each piece of equipment has an electrical distribution box containing a 30 A circuit breaker that is connected to the bus. These are indicated by letter A-H in Figure 1. This distribution box is then connected to a motor starter by a short piece of cable. The motor starters are indicated in letters I-W in Figure 1. The electrical equipment is attached, using high quality plugs, to locking receptacles that are connected to the motor starters. The equipment is either single phase or
three-phase delta. These labels for each pump are indicated on the following pages for each receptacle.

The motor starters used are Square D brand and consist of external start and stop buttons and contain small bimetallic thermal elements. When the current exceeds a certain threshold value, the thermal elements deform, interrupting the flow of current to the device. The temperature change in the thermal elements is slow to compensate for the extra current provided to the starter when operation commences. There is one element for each phase used in the equipment (i.e. three elements for three-phase, one element for single phase, etc.) The thermal elements used for each piece of equipment are also indicated on the list of receptacles. The bimetallic elements are chosen based on approximate maximum current ratings at room temperature. Basically, these elements are not rated for a specific current. Rather, the maximum current before the circuit is interrupted varies with temperature. For the scattering machine, five types of bimetals were used (with approximate maximum currents in parentheses): B17.5 (11A), B25 (15A), B32 (19A), B36 (22A) and B40 (25A.)

Inside the laboratory, there are power distribution boxes for each of the diffusion pumps, along the wall separating the Big Machine and the pump room. First, the diffusion pumps are connected using 30A circuit breakers, labeled in Figure 2 as 1-10, each of which is used for a single diffusion pump. The breakers are equipped with the proper number of phases and current for the different types of diffusion pumps used. A secondary distribution box is connected to each primary distribution box and contains a MotorLogic motor starter (Square D, P/N:9065-SS110-D). Like the bimetallic motor starters, the MotorLogic units are able to detect excessive current and interrupt the circuit as necessary. However, unlike the bimetallic elements in the pump room, the current threshold can be set on these starters by adjusting a potentiometer.
Current thresholds are 21 A, 15 A, 10 A and 13 A, for the source chambers, first differential pumping stages, second differential pumping stage and main chamber, respectively. These values were determined by measuring the current that flows when the pump is running and adding 20% to those values. Instead of push button operation like the motor starters in the pump room, relays are used to switch the power to the diffusion pumps on and off. The relays are connected to an external interlock box that monitors pump and vacuum parameters such as foreline pressure, water flow rate and pump temperature, and hence controls the status of the pumps. The relays have 120VAC coils and are configured to be normally open so that if the relay is disconnected from the interlock box or if a power outage occurs, the pumps will be shut down. Also, these relays can detect a loss of one of the phases in a three-phase circuit. If this is detected, the diffusion pump is also shut down.

Lastly, for the main chamber only, a toroidal current transformer and a current sensing relay are used to monitor the current flowing through the main chamber diffusion pump. The relay and transformer are mounted in a small aluminum box, located on the floor in between the diffusion pump and the electronics rack that contains the machine interlocks. The box also has a twist lock plug and receptacle of the same type used for the diffusion pump. This style of connection allows the current sensing circuit to be easily inserted in series with the diffusion pump. The current sensing relay is configured like the other sensors, providing a pair of closed contacts under normal conditions and open contacts in the event of a failure. This arrangement allows the current sensing relay to be placed in series with the thermal sensor on the main chamber diffusion pump so that the interlock system will respond in the event of either sensor detecting a fault. The purpose of this added interlock is to allow the interlocks to respond appropriately in the event of a diffusion pump heater failure or the partial interruption of
electricity to the laboratory. Also, an additional interlock is connected to the interlock box for the main chamber diffusion pump system for current sensing, which does not allow the pump to be powered up until the current supply to the pump is detected. This extra interlock was added due to the interlock box having an error of not shutting down the main chamber diffusion pump and gate valve when a current shortage occurred for the receptacle of that pump. The interlock box in the electronics rack was inspired by an original design by Fischer.\textsuperscript{71}

Along with the diffusion pump power receptacles, there are many circuit breakers throughout the Big Machine lab area for powering lab electronics and as extra miscellaneous outlets for future use. All these breakers are powered using Starline buses and are labeled in greater detail in the descriptions following Figures 2 and 3. Briefly, for the remaining Figure 2 breakers, the breakers to the left of the diffusion pump boxes power the interlocking systems, pressure gauges for forelines and individual chambers and bakeout power supplies on an electronics rack nearest the source chambers of the Big Machine. Additional plugs are available for baking out the gas manifold and in case one of the breakers fails in operation. To the right of the diffusion pump breakers are the circuit breakers that supply power for machine electronics on the rack closer to the Room 2-115 door and for some turbo pumps on the machine lid.

The breakers on Figure 3 are above the Big Machine, both in the machine and the electronic repair areas and are used for powering the lab computers, the crystal heater and other future uses. These are shown, labeled both in picture and list forms, in Figure 3 and its following page.
Figure 1: Electric box distribution for Big Machine inside the pump room

Each input on boxes A-H connect to one of the starters on letters I-W. The next page describes the uses and relevant values for each box.
Labels for Electric Distribution of the Big Machine in Pump Room:

Note: All mechanical pumps listed are produced by Alcatel Vacuum Corp.
All Single Phase Plugs are rated for 30A/120V
All 3-Phase Plugs are rated for 30A/240V

Letters A-D are for the Upper Starbus Supplying 60A, 300V:

A: 3-Phase, 30A/240V Breaker  
B: 3-Phase, 30A/240V Breaker  
C: 3-Phase, 30A/240V Breaker  
D: 3-Phase, 30A/240V Breaker

Letters E-H are for the Lower Starbus Supplying 100A, 600 V:

E: 3 Single Phase, 30A/120V Breakers  
F: 3 Single Phase, 30A/120V Breakers  
G: 3 Single Phase, 30A/120V Breakers  
H: 2 Single Phase, 30A/120V Breakers

Letters I-W are the Motor Starters for the Air Compressor and EACH Mechanical Pump. They are connected to one of the 30A breakers A-H described above:

I: Air Compressor, Phase X, B25 Bimetal  
J: First Seals Mechanical Pump, Phase Y, B25 Bimetal  
K: Blank Plug, Phase Z, B17.5 Bimetal  
L: Blank Plug, Phase X, B40 Bimetal  
M: First Stage A 2033CP Mechanical Pump, Phase Y, B40 Bimetal  
N: First Stage B 2033 Mechanical Pump, Phase Z, B36 Bimetal  
O: Second Stage 2033 Mechanical Pump, Phase X, B32 Bimetal  
P: Main Chamber 2033 Mechanical Pump, Phase Y, B32 Bimetal  
Q: Detector Box Roughing Mechanical Pump, Phase X, B17.5 Bimetal  
R: Gas Manifold Mechanical Pump, Phase Y, B17.5 Bimetal  
S: Blank Plug, Phase Z, B17.5 Bimetal  
T: Roots Blower A, 3-Phase, B17.5 Bimetal  
U: Source B 2063CP Mechanical Pump, 3-Phase, B17.5 Bimetal  
V: Roots Blower B, 3-Phase, B17.5 Bimetal (Currently not in use)  
W: Source A 2063CP Mechanical Pump, 3-Phase, B17.5 Bimetal
Figure 2: Electrical box distribution for Big Machine diffusion pumps and adjacent outlets

Circuit Breakers labeled A-J and K-Q and R-V control the electronic equipment on the lab racks. Breakers labeled 1-10 control the diffusion pumps. Also connected to the motor logic relays are the interlock box on the electronics rack that supply power to these relays and the final power cord that goes to the diffusion pumps. The next page describes the uses and relevant values for each box.
Labels for Electric Distribution of Diffusion Pumps and Starbuses Along Same Wall

Boxes 1-10 are the Breakers for the Diffusion Pumps; Both Starbuses supply 60A/300V. Each box, 1-10, is connected to a 120V motor logic relay that, if disconnected by either the interlock box on the electronics rack or a power outage, prevents power from reaching the diffusion pumps.

1: **Source A** diffusion pump, 3-Phase, 30A/240V Breaker
2: **Second Stage** diffusion pump, Phase Y, 30A/120V Breaker
3: **Source B** diffusion pump, 3-Phase, 30A/240V Breaker
4: Blank Box, Phase Z, 30A/120V Breaker
5: **First Stage B** diffusion pump, Phases X and Z, 30A/120V Breaker
6: **Main Chamber** diffusion pump, 3-Phase, 30A/240V Breaker
7: Blank Box, Phase X, 30A/120V Breaker
8: **First Stage A** diffusion pump, Phases Y and Z, 30A/120V Breaker
9: Blank Box, 3-Phase, 30A/240V Breaker
10: Blank Box, 3-Phase, 30A/240V Breaker

Boxes A-J are along the wall to the left of the diffusion pump boxes with a 60A/300V Starbus. Each box also contains a circuit breaker at the given currents:

A: Two 30A/125V Outlets, Phases X and Z
B: One 30A/125V Outlet, Phase X
C: Two 20A/120V Outlets, Phase Z
D: Two 30A/125V Outlets, Phases X and Z
E: One 30A/240V Outlet, 3-Phase
F: Two 20A/120V Outlets, Phase X
G: One 30A/240V Outlet, 3-Phase
H: One 30A/125V Outlet, Phase Y
I: Two 20A/120V Outlets, Phase Y
J: One 30A/240V Outlet, 3-Phase

Boxes K-Q are along the wall to the right of the diffusion pump boxes with a 60A/300V Starbus. Each box also contains a circuit breaker at the given currents:

K: One 30A/240V Outlet, 3-Phase
L: One 30A/240V Outlet, 3-Phase
M: Two 30A/125V Outlets, Phases Y and Z
N: Two 30A/125V Outlets, Phases X and Y
O: One 30A/208V outlet, phases X and Y
P: Two 20A/120V Outlets, Phase Z
Q: Two 20A/120V Outlets, Phase Z

Boxes R-V are along the wall above the diffusion pump boxes with a 60A/300V Starbus. Each box also contains a circuit breaker at the given currents:

R: One 30A/240V Outlet, 3-Phase
S: One 30A/240V Outlet, 3-Phase
T: Two 20A/120V Outlets, Phase Z
U: Two 20A/120V Outlets, Phase Y
V: One 30A/125V Outlet, Phase X
Figure 3: Electrical box distribution above the Big Machine and in electronics repair area

The next page describes the uses, locations and relevant values for each box.
Labels for Electric Distribution of All Electrical Boxes Above the Big Machine

Note: All Starbuses used are 60A/300V, and the box labels all read from left to right.

Boxes A-E are above the Big Machine nearest the Room 2-115 Door. Each box also contains a circuit breaker at the given currents:

- A: Two 30A/125V Outlets, Phases X and Y
- B: One 30A/125V Outlet, Phase Z
- C: One 60A/250V Outlet, 3-Phase
- D: Two 20A/120V Outlets, Phase X
- E: Ethernet Hookup for Big Machine Computer

Boxes F-I are above the Big Machine in between boxes A-E and the Main Chamber. Each box also contains a circuit breaker at the given currents:

- F: Two 20A/120V Outlets, Phase Z
- G: One 30A/240V Outlet, 3-Phase
- H: One 20A/120V Outlet, Phase X
- I: Two 20A/120V Outlets, Phase Y

Boxes J-N are directly above the crystal manipulator of the Big Machine. Each box also contains a circuit breaker at the given currents:

- J: One 20A/120V Outlet, Phase X
- K: Two 20A/120V Outlets, Phase Y
- L: Two 20A/120V Outlets, Phase Z
- M: Two 30A/125V Outlets, Phases Y and Z
- N: One 30A/240V Outlet, 3-Phase

Boxes O-S are above the Electronics Table, nearer the side lab door. Each box also contains a circuit breaker at the given currents:

- O: One 20A/120V Outlet, Phase Z
- P: Two 20A/120V Outlets, Phase Y
- Q: Two 20A/120V Outlets, Phase X
- R: Two 30A/125V Outlets, Phases Y and Z
- S: One 30A/240V Outlet, 3-Phase

Boxes T-X are above the Electronics Table, nearer the large set of windows. Each box also contains a circuit breaker at the given currents:

- T: One 30A/240V Outlet, 3-Phase
- U: One 60A/250V Outlet, 3-Phase
- V: Two 30A/125V Outlets, Phases X and Z
- W: Two 20A/120V Outlets, Phase X
- X: Two 20A/120V Outlets, Phase X
Renovated Water Cooling Distribution for Building Two Lab

The experimental apparatus used in this study requires cooling water for the diffusion pumps, helium cryostat, turbomolecular pumps and the motor for spinning the time of flight chopper wheel. Water is supplied to the machine using a water manifold. A schematic diagram of the water manifold is presented as Figure 4. The water source used for the Big Machine, as it is with the Little Machine, is potable water, not processed water. This change is due to three reasons: 1) The processed water in Building 2 contains too much rust for the water to flow consistently for a long enough period of time; 2) The water is too warm, especially in the summer months and 3) The water pressure from this processed line is not high enough to supply all the water lines at once, especially for the source stages of the machine.

A backflow adapter is also used to prevent potentially contaminated laboratory water from entering the potable water system in the event of a loss of water pressure. A temperature gauge is present to verify that the cooling water meets specifications, is below 80 °F. The water pressure is typically between 50 and 60 psi and the water temperature is about 60 °F.

Though potable water is used, there is still a relatively significant amount of rust and other suspended particles. To make sure the water is as solid-free as possible, commercially available water filters are used. The setup where the incoming water goes through the water filters has valves E, D, A and B open and valves C and F closed in Fig. 4 (valves G and H correspond to the Little Machine water supply; valve G is closed and H is open, where H is Building 6 processed water.) The water flows from the Building 6 potable water supply through three water filters and then to the machine. The first water filter has a pore size of 100 microns, the second 50 microns and the third five microns. Water filter condition is estimated by measuring the pressure drop across the filter band using the pressure gauges before and after the
filters, indicated by the P labels. A pressure drop of more than 5 psi indicates that the filters must be changed. In order to change the filters, valve C is opened slowly and then valves A and B are shut, causing cooling water to flow through the bypass pipe so that the flow of water to the machine continues uninterrupted. Then the filter housings are opened and the filters are replaced. The filter housing is reassembled and valve A is opened. Residual air in the filters is then removed by pressing the red button on top of the filter housing until the air is completely displaced and water slowly leaks out. Valve B is then opened slowly and valve C is closed.

Figure 4: Rough schematic of renovated water delivery manifold for Big Machine
There are times where the Building 6 water supply is shut off, with or without warning. For this scenario, the water manifold is designed to allow multiple sources of water to be used. In addition to the primary potable water supply from Building 6, there is an inlet located at valve F. This valve is connected to the Building 2 processed water supply and can be used when the potable water in Building 6 is shut down. To use, open valve F slowly to allow the water to enter and then close valve D. This process prevents total loss of water pressure across the manifold.

After passing through the filter bank, cooling water, flowing from the filters at around 5 gallons per minute, is distributed to the diffusion pumps using standard copper tubing. Tubing with 3/8" diameter is used to connect to the source and main chamber diffusion pumps and 1/4" diameter tubing is used to connect to the first and second differential pumping stage diffusion pumps. The same tubing sizes are used for the drain lines, to which water flow meters are attached. The drain lines are connected to a drain manifold, which is ultimately discharged into an open drain located in the pump room.
Appendix B: IGORPro Code for Fitting Time-of-Flight Spectra

Below is the code used in IGORPro 6.3 for fitting the time-of-flight spectra. Bolded is the way the relative flux from the integrated velocity-weighted TOF distribution is calculated. The flux calculations are the same that Hefty used. The only major change is to the delay time.

*Lines beginning with “//” are comments.

1. #pragma rtGlobals=1 // Use modern global access method.
2. //******************************************************************************
3. // This procedure fits a multicomponent Maxwell-Boltzmann plus flow velocity distribution to standard TOF data.
4. //******************************************************************************
5. // f(v)=A + B1 v^2 exp(-m1(v-vf1)^2/2kT1) + B2 v^2 exp(-m2(v-vf2)^2/2kT2) + ...
6. // The following variables are fitting parameters: the baseline A, the normalization constant Bi, the flow velocity vf, and the temperature Ti of the ith component.
7. // It creates new waves specific to the data containing the fitting parameters and physically significant properties of the distribution as well as its individual components like the flux density, average velocity, and average energy. In addition it creates a layout with a graph of the TOF data and fit, tables containing the fitting parameters and properties of the distribution, as well as a P(E) distribution. Fitting parameters can be individually held constant during the fitting procedure; the preexponential velocity power, neutral mass, and flight path length are not fitting parameters. However, the uncert of the flight path length is incorporated into the uncert analysis.
8. // The TOF data must be loaded and correctly scaled in microseconds to account for the multichannel scaler bin size and the combined ion flight time plus electronic delay. The Macro Load_data will load data from a list of file names (see Macro and accompanying Function for details).
9. // In relation to the BASIC program TOFFITV, the delay is half a bin size less because the value of each point is integrated over the previous bin size and is representative of the midpoint between the limits of this integration.
10. //
11. // Modified 4/6/01
12. // Added single-file loading capability - in this macro the delay time is calculated from the user-entered mass and the formula determined by MRT. Also converted from eV to kcal/mol energy units using the conversion factor 23.06 (kcal/mol)/eV. Also changed the P(E) plot to include the raw data, transformed to energy coordinates.
13. //
14. // Modified 8/11/01
//Changed TOF function to correctly account for the wrap-around for all dwell times
//Modified 10/6/01
//Included a modified fitting procedure that is able to any correctly spaced wave to the fit.
//This is presently used to include a component to the fit arising from XeF* dissociation
//derived from the fast-F atom TOF distribution. Also included a function to create a XeF
//dissociation wave when given the relevant F-atom parameters and XeF speed.
//Modified 11/27/01
//Changed the error propagation and the MB equations to reflect the derivation in Yang, thesis.
//Modified 12/15/01
//Condensed the flux, vavg, Eavg and error of the same into one large TOF_stats function
//Modified 2/19/02
//Removed the XeF* dissociation fitting as it has been replaced by the forward convolution calculation
//Modified 3/7/02
//Changed the error analysis to include the covariance matrix off-diagonal elements
//- JRH
//Modified 7/15/02
//Made compatible with Igor 4.
//Modified 7/29/02
//Changed default output for 'Append Comments' macro.
//Modified 8/1/02
//Added TOF_fit_Hz() to label output plots as Count rate instead of N(t). This addition is nothing
//more than a brute force way to display "Count Rate (Hz)" on the TOF layout, instead of "N(t)".
//Any changes made to the TOF_fit() function will also have to be made to the TOF_fit_Hz()
//function.
//Modified 2/21/03
//Corrected weighting wave to be compatible with Igor 4, wsubi is now in denominator, not numerator
//like Igor 3, so weighting wave needs to be sigmasubi, not 1/sigmasubi.
*******
//The above correction is incorrect due to the /I flag in Igor 4. This note is included for future
//reference. since the /I flag is not included in the FuncFit statement for the fit, the default value of
///I=0 is used, which calls for the weighting wave to be 1/sigmasubi, as was originally programmed
//for the Igor 3 fit procedure. The values for chisquare need only be corrected as described by the procedure
//in RCH Thesis, Appendix A for normalized or subtracted data. It is the correct value for fits to raw data.
********
//RCH
************
Menu "Macros"
173

81. "Load TOF data/0", Load_data()
82. "Initialize TOF fitting /1", Initialize()
83. "Add components /2", Add_components()
84. "Guess /3", TOF_guess()
85. ":-
86. "Fit Raw Data/4", TOF_fit()
87. "Fit Count Rate", TOF_fit_Hz()
88. ":-"
89. "Normalize /5", Normalize()
90. "Append comments /6", Append_comments()
91. ":-"
92. "Load single TOF file /9", Load_single_file()
93. End
94.
95. Macro Load_single_file(dwell,mass,wavename)
96. //
97. //Macro added in order to avoid the slightly more cumbersome list loading procedure.
98. //
99. //J.R. Holt 4/6/01
100. //
101. //This function loads TOF data from a single file. First you are prompted to browse for
102. //the TOF file you wish to analyze. Then you are prompted to enter the dwell time (in
103. //microseconds) and the atomic mass in amu. The delay time is then calculated using a
104. //equation that was determined empirically by MRT. Basically, the delay time was determined
105. //by measuring the TOF of several known mixtures, and then adjusting the delay time until the
106. //velocity distribution was reproduced. The delay should scale roughly with the square root of the
107. //mass since it is simply a conversion of potential energy (electrostatic) into kinetic. The precise
108. //equation is delay_time = -14.06 - 4.9924*(sqrt(mass)).
109. //Then the appropriate wave scaling is performed.
110. //
111. String wavename
112. Variable dwell=10
113. Variable mass=129
114. Prompt dwell,"Dwell time (default 10 for 392 Hz or 14 for 280Hz)"
115. Prompt mass,"Enter the mass setting"
116. Prompt wavename,"Enter the wavename"
117. LoadWave /G/O/N
118. Variable delay=-5.2889-4.4401*(sqrt(mass))
119. if (wave0[0]==1)
120. if (wave0[1]==2)
121. SetScale/P x,delay, dwell, "", wave1 // one column
(matlab output)or two (raw TOF output)
122. duplicate /o wave1 $wavename; KillWaves wave0 wave1
123. else
124. SetScale/P x,delay, dwell, "", wave0
125. duplicate /o wave0 $wavename; KillWaves wave0
126. endif
127. else
128. SetScale/P x,delay, dwell, "", wave0
duplicate /o wave0 $wavename; KillWaves wave0
endif
End Macro
Macro Load_data(TOF_data_list)
  String TOF_data_list
  Prompt TOF_data_list,"TOF data list",popup, WaveList("*_list","","")
  String TOF_data_num=TOF_data_list[0,strsearch(TOF_data_list,"_list",0)-1]+"_num"
  Load_TOF_Data($TOF_data_list, $TOF_data_num)
End Macro
Macro TOF_Guess(TOF_data_guess)
  String TOF_data_guess
  Prompt TOF_data_guess,"TOF data",popup, WaveList("","","")
  Guess($TOF_data_guess)
End Macro
Macro TOF_Fit(TOF_data)
  String TOF_data
  Prompt TOF_data,"TOF data",popup, WaveList("","","")
  Fit($TOF_data)
End Macro
Macro TOF_Fit_Hz(TOF_data)
  String TOF_data
  Prompt TOF_data,"TOF data",popup, WaveList("","","")
  Fit_Hz($TOF_data)
End Macro
//*****************************************************************************/
Function Load_TOF_Data(TOF_Data_List_text, TOF_Data_List_num)
  //This function loads TOF data from a three dimensional text wave with the suffix "_list" where the
  //columns correspond to the path name (set using the Igor function NewPath), the data file name,
  //and the name of the wave to be created, respectively. A corresponding two dimensional wave
  //with
  //the suffix "_num" consists of the ion flight/electronic delay time and the dwell time, both in
  //microseconds,
  //is necessary to perform the appropriate wave scaling.
  Wave/T TOF_Data_List_text
  Wave TOF_Data_List_num
  Variable i=0
do
  String pathname=TOF_Data_List_text[i][0]
  String filename=TOF_Data_List_text[i][1]
  String wavename=TOF_Data_List_text[i][2]
  LoadWave /G/O/N/L={0,0,0,1,1}/P=$pathname filename
  Variable delay=TOF_Data_List_num[i][0]
  Variable dwell=TOF_Data_List_num[i][1]
  SetScale/P x,delay, dwell,"", wave0
175. duplicate /o wave0 $wavename; KillWaves wave0
176. i+=1
177. while (i<DimSize(TOF_Data_List_text,0))
178. End
179.
180. Macro Initialize(maximum_components, path_length,path_length_uncert)
181. //This macro creates a default fitting parameter wave (parameter) along with a descriptive text
182. //wave (parameter_text) and a constraint wave (constraint). A parameter is constrained if its
183. //respective constraint value is nonzero (typically =1). These three waves are displayed in a table
184. //table parameter). This macro also creates a fit properties wave (fit_stats) along with a
185. //descriptive text wave (fit_stats_text) that yields the flux density (flux weighted counts), average
186. //velocity, and average energy for the overall TOF as well as the individual contributions. In addition,
187. //two uncert waves are created that correspond to the uncert in the average value given
188. //the goodness of fit (fit_stats_uncert), and the standard deviation of the distribution, i.e., the
189. //width of the distribution (fit_stats_sigma). Note that the overall average velocity and average
190. //energy lose much of their physical significance for a multicomponent fit, especially if the neutral mass is
191. //different for the various components. These three waves are displayed in a table (table_fit_stats).
192. //
193. //SET MAXIMUM NUMBER OF COMPONENTS TO DESCRIBE DISTRIBUTION
194. Prompt maximum_components, "Maximum number of components"
195. //**************************************************************
196. Variable maximum_components=NumVarOrDefault("max_components",3)
197. Variable path_length=0.2882
198. Variable path_length_uncert=0.0455
199. //**************************************************************
200. //SET NEUTRAL PATH LENGTH
201. Prompt path_length, "Neutral flight path length (m)"
202. //**************************************************************
203. Variable/G max_components=maximum_components
204. Variable/G components=max_components
205. Variable/G L=path_length
206. Variable/G 1_sigma=path_length_uncert/2
207. Silent 1
208. Make /n=(1+4*max_components)/o parameter parameter_uncert constraint
209. Make /n=(1+4*max_components)/T/o parameter_text constraint_text
210. parameter_text[0]={"baseline"}
211. parameter[0]=0
212. constraint[0]=0
213. Make /n=(1+3*max_components+1)/o fit_stats_text fit_stats_uncert fit_stats_sigma
214. Make /n=(1+3*max_components+1)/T/o fit_stats_text
215. fit_stats_text[0]={"total counts (from data)"
216. fit_stats_sigma[0,3]=NaN
217. fit_stats_text[numpnts(fit_stats_text)-1]={"reduced chisq"}
fit_stats=NaN
fit_stats_uncert=NaN
fit_stats_sigma=NaN

Variable i=0
do
  parameter_text[1+4*i]="normalization "+num2str(i+1)
  parameter[1+4*i]=1e-7
  constraint[1+4*i]=0
  parameter_text[2+4*i]="mass "+num2str(i+1)+" (amu)"
  parameter[2+4*i]=40
  constraint[2+4*i]=NaN
  parameter_text[3+4*i]="flow velocity "+num2str(i+1)+" (m/s)"
  parameter[3+4*i]=0
  constraint[3+4*i]=0
  parameter_text[4+4*i]="temperature "+num2str(i+1)+" (K)"
  parameter[4+4*i]=250
  constraint[4+4*i]=0
  fit_stats_text[1+3*i]="flux "+num2str(i+1)
  fit_stats_text[2+3*i]="average velocity "+num2str(i+1)+" (m/s)"
  fit_stats_text[3+3*i]="average energy "+num2str(i+1)+" (kcal/mol)"
i+=1
while (i<max_components)
DoWindow /K table_parameter
DoWindow /K table_fit_stats
table_parameter()
table_fit_stats()
Variable/G initialized=1 //flag for initialization
End Macro

//****************************************************************************
** ** * *** *************** ****** *** *****
Macro Add_Components(number_to_add)
//This macro adds number_to_add components to the distribution by appropriately increasing the size
//of the fitting parameter waves as well as the fitting statistics waves.
Variable number_to_add=1
Prompt number_to_add, "Number of additional components"
Silent 1
Variable /G components
InsertPoints numpnts(parameter), 4*number_to_add, parameter_text, parameter, parameter_uncert, constraint
InsertPoints numpnts(fit_stats), 4*number_to_add, fit_stats_text, fit_stats, fit_stats_uncert, fit_stats_sigma
Variable i=components
do
  parameter_text[1+4*i]="normalization "+num2str(i+1)
  parameter[1+4*i]=1e-7
  constraint[1+4*i]=0
  parameter_text[2+4*i]="mass "+num2str(i+1)+" (amu)"
  parameter[2+4*i]=40
constraint[2+4*i]=NaN
parameter_text[3+4*i]="flow velocity "+num2str(i+1)+" (m/s)"
parameter[3+4*i]=0
constraint[3+4*i]=0
parameter_text[4+4*i]="temperature "+num2str(i+1)+" (K)"
parameter[4+4*i]=250
constraint[4+4*i]=0
fit_stats_text[4+4*i]="counts "+num2str(i+1)
fit_stats_sigma[4+4*i]=NaN
fit_stats_text[5+4*i]="flux counts "+num2str(i+1)
fit_stats_sigma[5+4*i]=NaN
fit_stats_text[6+4*i]="average velocity "+num2str(i+1)+" (m/s)"
fit_stats_text[7+4*i]="average energy "+num2str(i+1)+" (kcal/mol)"
i+=1
while (i<components+number_to_add)
components=components+number_to_add
max_components=components
fit_stats_text[numpnts(fit_stats)-1]="reduced chisq"
fit_stats_sigma[numpnts(fit_stats)-1]=NaN
DoWindow /K table_parameter
DoWindow /K table_fit_stats
table_parameter()
table_fit_stats()
End Macro

Function Guess(TOF_data)
//This function displays the initial guess of the overall distribution as well as the individual components
//of the TOF distribution superimposed on the TOF data.
Wave TOF_data

//
Duplicate /o TOF_data time_scale
time_scale=x
Variable/G time_step=time_scale[1]-time_scale[0]
Variable t=0
do
if (time_scale[t]==0)
SetScale/P x time_scale[0]+1e-3,time_step,"",TOF_data
endif
t+=1
while (time_scale[t]<=0)
//
Variable/G initialized
if (initialized!=1)
Execute("Initialize()")
print "Adjust fitting parameters, if necessary, and try again."
else
Wave parameter=parameter
Wave-parameter_uncert = parameter_uncert
Wave-constraint = constraint
Wave-fit_stats = fit_stats
Wave-constraint = constraint

// Determine true number of fitting components (components whose normalization constant is nonzero)
// and shift fitting parameters if necessary to compact fitting parameters.
Variable i=0
Variable/G max_components
Variable/G components=0
Variable previous=1
Variable j=1
Variable k=1
Variable lastnonzero=1
do
  if (parameter[1+4*i]!=0) // normalization constant nonzero; shift up component, if necessary
    components+=1 // count components
    if (previous==0) // if previous component was zero, shift up component
      j=1
do
  parameter[j+4*(i-lastnonzero)]=parameter[j+4*i]
  parameter_uncert[j+4*(i-lastnonzero)]=parameter_uncert[j+4*i]
  if (j!=2) // mass is never an adjustable parameter
    constraint[j+4*(i-lastnonzero)]=constraint[j+4*i]
    constraint[j+4*i]=0
  endif
  j+=1
while (j<=4)
else // normalization constant zero; set associated parameters to zero
  k=1
do
  parameter[k+4*i]=0
  parameter_uncert[k+4*i]=0
  if (k!=2) // mass is never an adjustable parameter
    constraint[k+4*i]=0
  endif
  k+=1
while (k<4)
  if (previous==0)
    lastnonzero+=1 // remember how many components to shift up
  endif
  previous=0
endif
i+=1
while (i<max_components)
DeletePoints 4*components+1, 4*(max_components-components), parameter_text, parameter
DeletePoints 4*components+1, 4*(max_components-components), parameter_uncert, constraint
DeletePoints 4*(components+1), 4*(max_components-components), fit_stats_text, fit_stats
DeletePoints 4*(components+1), 4*(max_components-components), fit_stats_uncert, fit_stats_sigma
max_components=components
Variable /G L
String TOF_data_fit=NameOfWave(TOF_data)+"_fit"
Duplicate /o TOF_data Initial_Guess
Initial_Guess=TOF(parameter,x)
Duplicate /o Initial_guess $TOF_data_fit
DoWindow /K Graph0
Display TOF_data $TOF_data_fit
i=1
do
String TOF_data_fit_fci=NameOfWave(TOF_data)+"_fc"+num2str(i)
Duplicate /o TOF_data Initial_guess_fci
Initial_guess_fci=TOF_i(parameter, x, i)
Duplicate /o Initial_guess_fci $TOF_data_fit_fci
AppendToGraph $TOF_data_fit_fci
i+=1
while (i<=components)
Execute("TOF_styleo")
KillWaves Initial_Guess Initial_guess_fci
endif
End
//*****************************************************************************/
** ******* * ********* **** *** ***** *** *****/
THE FITTING ALGORITHM
//*****************************************************************************/
Function Fit(TOF_data)
Wave TOF_data
//
//Kill old graphs and layout.
//
DoWindow /K Graph1
DoWindow /K Layout0
//
Guess(TOF_data)
Variable/G components
Variable/G reduced_chisq
//
Wave parameter=parameter
Wave parameter_uncert=parameter_uncert
Wave constraint=constraint
Wave constraint_text=constraint_text
Wave fit_stats=fit_stats; fit_stats=NaN
Wave fit_stats_uncert=fit_stats_uncert; fit_stats_uncert=NaN
Wave fit_stats_sigma=fit_stats_sigma
String TOF_data_fit=NameOfWave(TOF_data)+"_fit"
String TOF_data_fit_energy=TOF_data_fit+_E"
String TOF_data_energy=NameOfWave(TOF_data)+"_E"
String TOF_data_fit_params=NameOfWave(TOF_data)+"_params"
String TOF_data_fit_params_uncert=TOF_data_fit_params+_u"
String TOF_data_fit_stats=NameOfWave(TOF_data)+"_stats"
String TOF_data_fit_stats_uncert=TOF_data_fit_stats+_u"
String TOF_data_fit_sigma=TOF_data_fit_stats+_s"
String holdstring=""

//Calculate standard deviation of each TOF data point for cross-correlation TOF data (See Appendix B of D. Gosalvez-Blanco, Ph.D. thesis, 1997) and create weighting wave for fitting algorithm.

Variable TOF_data_sigma=TOF_uncert(TOF_data)
Duplicate /o TOF_data weight
weight=1/TOF_data_sigma

//DO THE FIT

FuncFit/H=WaveToHoldString(constraint)/M=2 TOF parameter TOF_data /D=$TOF_data_fit
/W=weight
//See the help file for funcfit regarding the parameters; /M=2 creates a covariance matrix in the wave M_Covar, which is later used for the error analysis. The covariance matrix is also later saved to be wavename_covar

//killwaves weight
Duplicate /o W_sigma parameter_uncert
Duplicate /o TOF_stats(TOF_data)
Duplicate /o parameter $TOF_data_fit_params
Duplicate /o parameter_uncert $TOF_data_fit_params_uncert
Duplicate /o M_Covar $TOF_data_fit_params_covar
variable k=0
Do
If (abs(parameter[3+k*4])<1e-5)
    parameter[3+k*4]=0
endif
k+=1
While (k<components)
//

//Calculate the reduced chi squared

variable deg_freedom=255
variable i=0
do
if (constraint[i] == 0)
    deg_freedom = 1
endif

i = i + 1
while (i < numpnts(constraint))
    reduced_chisq = reduced_chisq / deg_freedom
    fit_stats[numpnts(constraint) - 1] = reduced_chisq
    //
    // Separate individual components.
    //
    Variable temp_constraint = 0
    i = 0
    do
        Duplicate /o TOF_data TOF_data_fit_fci
        if (constraint[1 + 4*i] == 0)
            if (constraint[1 + 4*i] == 1)
                temp_constraint = constraint[1 + 4*i]
                constraint[1 + 4*i] = 1
                TOF_data_fit_fci = TOF_i(parameter, x, i + 1)
            else
                TOF_data_fit_fci = temp_constraint
            endif
        else
            TOF_data_fit_fci = TOF_i(parameter, x, i + 1)
        endif
    enddo
    TOF_data_fit_fci = TOF_i(parameter, x, i + 1)
    String TOF_data_fit_fci_name = NameOfWave(TOF_data) + "_fc" + num2str(i + 1)
    Duplicate /o TOF_data_fit_fci $TOF_data_fit_fci_name
    String TOF_data_energy_fci = NameOfWave(TOF_data) + "_fc" + num2str(i + 1) + "_E"
    // Transform f(t) to P(E) for each component.
    //
    PofE($TOF_data_fit_fci_name, parameter[2 + 4*i])
    if (i == 0)
        Display $TOF_data_fit_energy_fci vs $TOF_data_energy_fci
    else
        AppendToGraph $TOF_data_fit_energy_fci vs $TOF_data_energy_fci
    endif
    i = i + 1
while (i < components)
    PofE(TOF_data, parameter[2])
    AppendToGraph $TOF_data_fit_energy vs $TOF_data_energy
    //
    // Change layout to include reduced chi squared instead of total uncert
    //
    fit_stats[numpnts(fit_stats) - 1] = reduced_chisq
    fit_stats_uncert[numpnts(fit_stats) - 1] = NaN
    fit_stats_sigma[numpnts(fit_stats) - 1] = NaN
    //
// Create layout.
Execute("PofE_styleo")
Duplicate /o fit_stats $TOF_data_fit_stats
Duplicate /o fit_stats_uncert $TOF_data_fit_uncert
Duplicate /o fit_stats_sigma $TOF_data_fit_sigma
Preferences 1
Execute("Layout/W=(5.25,41.75,370,500) Graph0, Graph1, table_parameter, table_fit_stats")
Preferences 0
Textbox/N=text0/F=0/A=LB/X=5.78/Y=92.95 "$\text{\texttimes} 24" + NameOfWave(TOF_data)
Execute("layout_styleo")
End

Function Fit Hz(TOF_data)
Wave TOF_data
//
// Kill old graphs and layout.
//
DoWindow /K Graph1
DoWindow /K Layout0
//
Guess(TOF_data)
Execute("TOF_style_Hz()")
Variable/G components
Variable/G reduced_chisq
Wave parameter=parameter
Wave parameter_uncert=parameter_uncert
Wave constraint=constraint
Wave constraint_text=constraint_text
Wave fit_stats=fit_stats; fit_stats=NaN
Wave fit_stats_uncert=fit_stats_uncert; fit_stats_uncert=NaN
Wave fit_stats_sigma=fit_stats_sigma
String TOF_data_fit=NameOfWave(TOF_data)+"_fit"
String TOF_data_fit_energy=TOF_data_fit+"_E"
String TOF_data_energy=NameOfWave(TOF_data)+"_E"
String TOF_data_fit_params=NameOfWave(TOF_data)+"_params"
String TOF_data_fit_params_uncert=TOF_data_fit_params+"_u"
String TOF_data_fit_params_covar=TOF_data_fit_params+"_C"
String TOF_data_fit_stats=NameOfWave(TOF_data)+"_stats"
String TOF_data_fitUncert=TOF_data_fit_stats+"_u"
String TOF_data_fit_sigma=TOF_data_fit_stats+"_s"
String holdstring=
//
// Calculate standard deviation of each TOF data point for cross-correlation TOF data (See Appendix B/of D. Gosalvez-Blanco, Ph.D. thesis, 1997) and create weighting wave for fitting algorithm.
//
Variable TOF_data_sigma=TOF_uncert(TOF_data)
Duplicate /o TOF_data weight
weight=1/TOF_data_sigma
183

558. //
559. //DO THE FIT
560. //
561. FuncFit/H=WaveToHoldString(constraint)/M=2 TOF parameter TOF_data /D=$TOF_data_fit
   /W=weight
562. //See the help file for funcfit regarding the parameters; /M=2 creates a covariance matrix in the
   wave M_Covar, which
563. //is later used for the error analysis. The covariance matrix is also later saved to be
   wavename_covar
564. //killwaves weight
565. Duplicate /o W_sigma parameter_uncert
566. TOF_stats( TOF_data)
567. Duplicate /o parameter $TOF_data_fit_params
568. Duplicate /o parameter_uncert $TOF_data_fit_params_uncert
569. Duplicate /o M_Covar $TOF_data_fit_params_covar
570. variable k=0
571. Do
572. If (abs(parameter[3+k*4])<le-5)
573. parameter[3+k*4]=0
574. endif
575. k+=1
576. While (k<components)
577. //
578. //Calculate the reduced chi squared
579. //
580. reduced_chisq=V_chisq
581. variable deg_freedom=255
582. variable i=0
583. do
584. if (constraint[i]==0)
585. deg_freedom-=1
586. endif
587. i+=1
588. while (i<numpnts(constraint))
589. reduced_chisq/=deg_freedom
590. fit_stats[numpnts(constraint)-1]=reduced_chisq
591. //
592. //Separate individual components.
593. //
594. Variable temp_constraint=0
595. i=0
596. do
597. Duplicate /o TOF_data TOF_data_fit_fci
598. if (constraint[1+4*i]!=0)
599. if (constraint[1+4*i]!=1)
600. temp_constraint=constraint[1+4*i]
601. constraint[1+4*i]=1
602. TOF_data_fit_fci=TOF_i(parameter, x,i+1)
603. constraint[1+4*i]=temp_constraint
604. else
605. TOF_data_fit_fci=TOF_i(parameter, x,i+1)
endif
else
  TOF_data_fit_fci=TOF_i(parameter, x,i+1)
endif
String TOF_data_fit_fci_name=NameOfWave(TOF_data)+"_fc"+num2str(i+1)
Duplicate /o TOF_data_fit_fci $TOF_data_fit_fci name
String TOF_data_fit_energy_fci=NameOfWave(TOF_data)+"_fc"+num2str(i+1)+"_fit_E"
String TOF_data_energy_fci=NameOfWave(TOF_data)+"_fc"+num2str(i+1)+"_E"

// Transform f(t) to P(E) for each component.
//
PofE($TOF_data_fit_fci_name, parameter[2+4*i])
if (i==0)
  Display $TOF_data_fit_energy_fci vs $TOF_data_energy_fci
else
  AppendToGraph $TOF_data_fit_energy_fci vs $TOF_data_energy_fci
endif
i+=1
while (i<components)
PofE(TOF_data,parameter[2])
AppendToGraph $TOF_data_fit_energy vs $TOF_data_energy
//
fit_stats[numpnts(fit_stats)-1]=reduced_chisq
fit_stats_uncert[numpnts(fit_stats)-1]=NaN
fit_stats_sigma[numpnts(fit_stats)-1]=NaN
//
// Create layout.
Execute("PofE_style()")
Duplicate /o fit_stats $TOF_data_fit_stats
Duplicate /o fit_stats_uncert $TOF_data_fit_uncert
Duplicate /o fit_stats_sigma $TOF_data_fit_sigma
Preferences 1
Execute("Layout/W=(5.25,41.75,370,500) Graph0, Graph1, table_parameter, table_fit_stats")
Preferences 0
Textbox/N=text0/F=0/A=LB/X=5.78/Y=92.95 "\F"Times\Z24"+NameOfWave(TOF_data)
Execute("layout_style()")
End

//*****************************************************************************
//The following functions describe the overall TOF distribution and the individual components.
//*****************************************************************************
Function TOF(parameter, x)
  Wave parameter; Variable x
  Wave constraint=constraint
  Wave time_scale=time_scale
Variable/G components, L

Variable v, v2, x2, time_of_flight, m, A, T, vf

Variable k=1.38e-23

v=L/(x*1e-6)

x2=x+time_scale[254]+(time_scale[254]-time_scale[253])

v2=L/(x2*1e-6)

Variable i=1

time_of_flight=parameter[0]
do
if (parameter[4+4*(i-1)]!=0)
  A=parameter[1+4*(i-1)]
  m=parameter[2+4*(i-1)]*1.66e-27
  vf=parameter[3+4*(i-1)]
  T=parameter[4+4*(i-1)]

// The following eqns reflect what is in Yang, thesis except using flow velocity instead of flow time:
time_of_flight+=(A*v^4/L)*exp(-(m/(2*k*T))*(v-vf)^2)
time_of_flight+=(A*v2^4/L)*exp(-(m/(2*k*T))*(v2-vf)^2)

// The following TOF equations reflect the equations in Yang, thesis, pg. 42-43

time_of_flight+=parameter[1+4*(i-1)]*L^3*(x*1e-6)^-4*exp(-1.66e-27*parameter[2+4*(i-1)]*L^2*((1e6/x)-(1/parameter[3+4*(i-1)]))^2/(2*1.38e-23*parameter[4+4*(i-1)]))
time_of_flight+=parameter[1+4*(i-1)]*L^3*(x2*1e-6)^-4*exp(-1.66e-27*parameter[2+4*(i-1)]*L^2*((1e6/x2)-(1/parameter[3+4*(i-1)]))^2/(2*1.38e-23*parameter[4+4*(i-1)]))

// The following TOF equation have been modified to accurately reflect the equations in MRT, thesis, pg. 125-6

time_of_flight+=parameter[1+4*(i-1)]*(velocity^2*exp(-(1.66e-27*parameter[2+4*(i-1)]*(velocity-parameter[3+4*(i-1)]))^2/(2*1.38e-23*parameter[4+4*(i-1)])))(x*1e-6)^-2
time_of_flight+=parameter[1+4*(i-1)]*(velocity2^2*exp(-(1.66e-27*parameter[2+4*(i-1)])*(velocity2-parameter[3+4*(i-1)])^2/(2*1.38e-23*parameter[4+4*(i-1)])))(x2*1e-6)^-2

else
  print "Temperature is zero for component "+num2str(i)+"."
endif

i+=1
while (i<=components)
i=1
return time_of_flight
End

Function TOF_i(parameter, x,i)
Wave parameter; Variable x, i
Wave constraint=constraint
Variable /G L
Variable v, time_of_flight_i, m, A, T, vf
Variable ratio_flag=0
Variable k=1.38e-23
v=L/(x*1e-6)
time_of_flight_i=parameter[0]
if (parameter[4+4*(i-1)]!=0)

A=parameter[1+4*(i-1)]
m=parameter[2+4*(i-1)]*1.66e-27
vf=parameter[3+4*(i-1)]
T=parameter[4+4*(i-1)]

The following eqns reflect what is in Yang, thesis except using flow velocity
instead of flow time:
time_of_flight_i+=(A*v^4/L)*exp(-(m/(2*k*T))*(v-vf)^2)

The following TOF equation reflects the equations in Yang, thesis, pg. 42-43
time_of_flight_i+=parameter[1+4*(i-1)]*L^3*(x*1e-6)^-4*exp(-1.66e-27*parameter[2+4*(i-1)]*L^2*((x*1e-6)-(1/parameter[3+4*(i-1)]))^2/(2*1.38e-23*parameter[4+4*(i-1)]))

Modified to accurately reflect MRT, thesis, pg. 125-6
time_of_flight_i+=parameter[1+4*(i-1)]*(velocity-parameter[3+4*(i-1)])^2/(2*1.38e-23*parameter[4+4*(i-1)]))

Original equation
time_of_flight_i+=parameter[1+4*(i-1)]*(velocity^2*exp(-(1.66e-27*parameter[2+4*(i-1)])*(velocity-parameter[3+4*(i-1)])^2/(2*1.38e-23*parameter[4+4*(i-1)])))(x*1e-6)^-2

time_of_flight_i=0
print "Temperature is zero."
endif
return time_of_flight_i
End

Function/WaveToHoldString(w)
This function creates a string HoldString to hold the fitting parameters whose respective constraint
values are nonzero.
Wave w
String HoldString=""
Variable i=0
do
if (w[i]!=0)
    Holdstring="0"
else
    Holdstring="1"
endif
i+=1
while (i<numpnts(w))
return HoldString
End

//******************************************************************************************
//PROPERTIES OF DISTRIBUTION
//******************************************************************************

//Macro Normalize(TOF_data, sets, triggers, frequency, display_string)
//String TOF_data
//Variable sets=NumVarOrDefault("gsets",1)
//Variable triggers=NumVarOrDefault("gtriggers",5000)
//Variable frequency=NumVarOrDefault("gfrequency",280)
//String display_string
//Prompt TOF_data,"TOF data",popup, WaveList("*", ";", "")
//Prompt sets, "Number of sets of data"
//Prompt triggers, "Number of triggers per set"
//Prompt frequency, "Chopper frequency (Hz)"
//Prompt display_string, "Display?", popup ("Yes;No")
//Variable display_flag=strsearch(display_string, "y", 0)
//if (display_flag==0)
// Normalize_TOF($TOF_data, sets, triggers, frequency,0)
//else
// Normalize_TOF($TOF_data, sets, triggers, frequency,1)
//endif
//End Macro

Function Normalize_TOF(TOF_data, sets, triggers, frequency, display_flag)
Wave TOF_data
Variable sets, triggers, frequency, display_flag
Variable scale=sets*triggers/frequency
String TOF_data_norm=NameOfWave(TOF_data)+"_norm"
String TOF_data_fit=NameOfWave(TOF_data)+"_fit"
String TOF_data_fit_params=NameOfWave(TOF_data)+"_params"
String TOF_data_fit_params_uncert=TOF_data_fit_params+_uncert"
String TOF_data_fit_stats=NameOfWave(TOF_data)+"_stats"
String TOF_data_fit_uncert=TOF_data_fit_stats+_uncert"
Duplicate /0 TOF_data $TOF_data_norm
Wave temp_TOF_data_norm=$TOF_data_norm
Wave temp_TOF_data_fit=$TOF_data_fit
Wave temp_params=$TOF_data_fit_params
Wave temp_params_uncert=$TOF_data_fit_params_uncert
Wave temp_stats=$TOF_data_fit_stats
Wave temp_stats_uncert=$TOF_data_fit_uncert
Wave parameter=parameter
Wave parameter_uncert=parameter_uncert
Wave fit_stats=fit_stats
Wave fit_stats_uncert=fit_stats_uncert
temp_TOF_data_norm/=scale
temp_TOF_data_fit/=scale
temp_params[0]/=scale
temp_params_uncert[0]/=scale
temp_stats[0]/=scale
temp_stats[1]/=scale
temp_stats_uncert[0]/=scale
temp_stats_uncert[1]/=scale
temp_stats_uncert[numpnts(temp_stats_uncert)-1]/=scale
Variable i=0
do
    String TOFdatafit_fci_name=NameOfWave(TOF_data)+"_fc"+num2str(i+1)
    String TOFdatafitenergy_fci=NameOfWave(TOF_data)+"_fc"+num2str(i+1)+"_fit_energy"
    Wave temp_TOF_datafit_fci=$TOFdatafit_fci_name
    Wave temp_TOF_datafitenergy_fci=$TOFdatafitenergy_fci
    temp_TOF_datafit_fci/=scale
    temp_TOF_datafitenergy_fci/=scale
temp_params[1+4*(i)]/=scale
temp_params_uncert[1+4*(i)]/=scale
temp_stats[4+4*(i)]/=scale
temp_stats_uncert[4+4*(i)]/=scale
temp_stats[5+4*(i)]/=scale
temp_stats_uncert[5+4*(i)]/=scale
temp_stats[0]+=temp_stats[4+4*(i)]
temp_stats[1]+=temp_stats[5+4*(i)]
i+=1
while (4*i+4<numpnts(temp_stats)-1)
if (display_flag==1)
    parameter[0]/=scale
    parameter_uncert[0]/=scale
    fit_stats[0]/=scale
    fit_stats_uncert[0]/=scale
    fit_stats[1]/=scale
    fit_stats_uncert[1]/=scale
    i=0
do
    parameter[1+4*i]/=scale
    parameter_uncert[1+4*i]/=scale
    fit_stats[4+4*i]/=scale
    fit_stats_uncert[4+4*i]/=scale
    fit_stats[5+4*(i)]/=scale
    fit_stats_uncert[5+4*(i)]/=scale
    i+=1
while (4*i+4<numpnts(temp_stats)-1)
endif
End

Function TOF_stats(TOF_data)
Wave TOF_data
Variable /G L, L_sigma, components
Wave parameter=parameter
The factor of $10^{-6}$ is there to account for $dt$. To determine $dt$, but that is off from the true $dt$ because the scaling is in microseconds, not seconds.

$$v(x\cdot 10^{-6}) = \frac{L}{10^{-6}}$$

$$v[x2\text{pnt}(v,0)] = \frac{L}{10^{-6}}$$

$$D_1 = 0$$

$$D_v = 0$$

$$D_E = 0$$

Variable $k = 1.38 \times 10^{-23}$

Variable $i = 0$

Do

A = parameter[1+4*i]

m = parameter[2+4*i] $\times 1.66 \times 10^{-27}$

vf = parameter[3+4*i]

T = parameter[4+4*i]

f = TOF_i(parameter, x, (i+1)) - parameter[0]

// $f = \left( \frac{A\cdot v^4}{L} \right) \exp\left( -\frac{m}{2\cdot k\cdot T} \right) \left( v - v_f \right)^2$

// The factor of $10^{-6}$ is there to account for $dt$. Integrate uses the scaling of the wave because the scaling is in microseconds,

// to determine $dt$, but that is off from the true $dt$

// not seconds.

// again, the factors of $10^{-6}$ below are there to account for $dt$. Integrate uses the scaling of the wave because the scaling is in microseconds, not seconds.
\[ \text{di}_dL = (v/L)^{4-((m/(k*T)))*(v-vf)^2}*f*1e^{-6} \]
\[ \text{di}_dA = v^*(1/A)*f*1e^{-6} \]
\[ \text{di}_dvf = v^*(m/(k*T))*(v-vf)*f*1e^{-6} \]
\[ \text{di}_dT = v^*(m/(2*k*T^2))*(v-vf)^2*f*1e^{-6} \]

// Note that the derivatives below are not the *full* derivatives, but only the first part. They are incorporated into the full formulae below. See JRH, thesis for the full equations.

// In brief, they are x, where \( (dv/dy) = (x-vavg*(dFlux/dy))/Flux \) or \( (dE/dy) = (x-Eavg*(dFlux/dy))/Flux \), where \( y = L, T, vf \)

//

\[ dv_dvf = v^2*(m/(k*T))*(v-vf)*f*1e^{-6} \]
\[ dv_dT = v^2*(m/(2*k*T^2))*(v-vf)^2*f*1e^{-6} \]
\[ dE_dL = (v/L)^{0.5*m*v^2}*(6-(m/(k*T))*(v-vf)^2)*f*1e^{-6} \]
\[ dE_dT = v^3*(m^2/(4*k*T^2))*(v-vf)^2*f*1e^{-6} \]
\[ dE_dvf = v^3*(m^2/(2*k*T))*(v-vf)*f*1e^{-6} \]

// This for loop eliminates spurious error due to negative velocities

if \( (v[j]<0) \)
\[ \text{di}_dA[j]=0 \]
\[ \text{di}_dL[j]=0 \]
\[ \text{di}_dT[j]=0 \]
\[ \text{di}_dvf[j]=0 \]
\[ dv_dL[j]=0 \]
\[ dv_dT[j]=0 \]
\[ dv_dvf[j]=0 \]
\[ dE_dL[j]=0 \]
\[ dE_dT[j]=0 \]
\[ dE_dvf[j]=0 \]
endif

j++=1

while \( (j<254) \)

Integrate /T \text{di}_dL, \text{di}_dA, \text{di}_dvf, \text{di}_dT

Integrate /T \text{dv}_dL, \text{dv}_dvf, \text{dv}_dT

Integrate /T \text{dE}_dL, \text{dE}_dvf, \text{dE}_dT

// Due to the fact that the path length error is independent from the fit parameter uncertainties, it is taken into account separately.

\[ D_1[L][i]=\text{di}_dL[n] \]
\[ D_v[L][i]=(\text{dv}_dL[n]-v_avg*\text{di}_dL[n])/\text{flux} \]
\[ D_E[L][i]=(\text{dE}_dL[n]-E_avg*\text{di}_dL[n])/\text{flux} \]
\[ D_1[1+4*i]=\text{di}_dA[n] \]
\[ D_1[3+4*i]=\text{di}_dvf[n] \]
\[ D_1[4+4*i]=\text{di}_dT[n] \]
\[ D_v[3+4*i]=(\text{dv}_dvf[n]-v_avg*\text{di}_dvf[n])/\text{flux} \]
\[ D_v[4+4*i]=(\text{dv}_dT[n]-v_avg*\text{di}_dT[n])/\text{flux} \]
\[ D_E[3+4*i]=(\text{dE}_dvf[n]-E_avg*\text{di}_dvf[n])/\text{flux} \]
\[ D_E[4+4*i]=(\text{dE}_dT[n]-E_avg*\text{di}_dT[n])/\text{flux} \]

i+=1

While \( (i<\text{components}) \)

\[ \text{variable flux sigma} \]
variable \( v_{\text{avg} \sigma} \)
variable \( E_{\text{avg} \sigma} \)

\[
\text{Do}
\]
\[
\text{flux}_{\sigma}=0
\]
\[
\text{v}_{\text{avg} \sigma}=0
\]
\[
\text{E}_{\text{avg} \sigma}=0
\]
\[
\text{j}=0
\]
\[
\text{Do}
\]
\[
\text{j}+=1
\]
// This loop calculates all the diagonal and off-diagonal contributions of the covariance matrix to the final error in the three derived quantities flux, average velocity and average energy.

// First, take into account all factors involving \( d/dA \)
\[
\text{flux}_{\sigma}+=M_{\text{covar}}[(1+4*i)][j]*D_{I}[1+4*i]*D_{I}[i]
\]
\[
\text{v}_{\text{avg} \sigma}+=M_{\text{covar}}[(1+4*i)][j]*D_{v}[1+4*i]*D_{v}[j]
\]
\[
\text{E}_{\text{avg} \sigma}+=M_{\text{covar}}[(1+4*i)][j]*D_{E}[1+4*i]*D_{E}[j]
\]
// Next, all factors involving \( d/dv_f \)
\[
\text{flux}_{\sigma}+=M_{\text{covar}}[(3+4*i)][j]*D_{I}[3+4*i]*D_{I}[i]
\]
\[
\text{v}_{\text{avg} \sigma}+=M_{\text{covar}}[(3+4*i)][j]*D_{v}[3+4*i]*D_{v}[j]
\]
\[
\text{E}_{\text{avg} \sigma}+=M_{\text{covar}}[(3+4*i)][j]*D_{E}[3+4*i]*D_{E}[j]
\]
// Finally, all factors involving \( d/dT \)
\[
\text{flux}_{\sigma}+=M_{\text{covar}}[(4+4*i)][j]*D_{I}[4+4*i]*D_{I}[i]
\]
\[
\text{v}_{\text{avg} \sigma}+=M_{\text{covar}}[(4+4*i)][j]*D_{v}[4+4*i]*D_{v}[j]
\]
\[
\text{E}_{\text{avg} \sigma}+=M_{\text{covar}}[(4+4*i)][j]*D_{E}[4+4*i]*D_{E}[j]
\]

While (j<4*components)
\[
\text{flux}_{\sigma}+=(L_{\sigma}*D_{I}[i])^2
\]
\[
\text{flux}_{\sigma}+\sqrt{\text{abs(flux}_{\sigma})}
\]
\[
\text{fit\_stats\_uncert[1+3*i]}=\text{flux}_{\sigma}
\]
\[
\text{v}_{\text{avg} \sigma}+=(L_{\sigma}*D_{v}[j])^2
\]
\[
\text{v}_{\text{avg} \sigma}+\sqrt{\text{abs(v}_{\text{avg} \sigma})}
\]
\[
\text{fit\_stats\_uncert[2+3*i]}=v_{\text{avg} \sigma}
\]
\[
\text{E}_{\text{avg} \sigma}+=(L_{\sigma}*D_{E}[j])^2
\]
\[
\text{E}_{\text{avg} \sigma}+\sqrt{\text{abs(E}_{\text{avg} \sigma})}
\]
\[
\text{fit\_stats[3+3*i]}=\text{E}_{\text{avg} \sigma}*23.06/1.6e^{-19}
\]
\[
\text{fit\_stats\_uncert[3+3*i]}=\text{E}_{\text{avg} \sigma}*23.06/1.6e^{-19}
\]
\[
i+=1
\]

While(i<components)
\[
\text{Killwaves E\_weight velocity\_weight flux\_weight}
\]
\[
\text{KillWaves di\_dA di\_dvf di\_dT di\_dL v \ f}
\]
\[
\text{KillWaves dE\_dvf dE\_dT dE\_dL}
\]
\[
\text{KillWaves dv\_dvf dv\_dT dv\_dL}
\]

End

Function PofE(\text{TOF\_data\_fit}, \text{mass})

// Determines the translational energy distribution of the fit \text{TOF\_data\_fit} given a certain mass. The
// \text{TOF distribution is weighted by the Jacobian t^2/(mL) such that P(E)=t^2/(mL)*f(t)
// Alternatively in terms of velocity, P(E) = (L/mv^2)*f(t)

Wave \text{TOF\_data\_fit}; \text{Variable mass}
Wave parameter=parameter
Variable /G L
Duplicate /o TOF_data_fit velocity energy TOF_energy_transform

Variable dash=strsearch(NameOfWave(TOF_data_fit),"_fit",0)
if (dash==-1)
    String basename=NameOfWave(TOF_data_fit)
else
    basename=NameOfWave(TOF_data_fit)[0,dash-1]
endif
String TOF_energy=basename+"E"
String TOF_fit_energy=basename+_fit_E"
velocity=L/(x*1e-6)
energy=((0.5*(mass*1.66e-27)*velocity^2)/1.6e-19)*23.06
    // DELETE THE 23.06 TO GET eV!!
TOF_energy_transform=(L/(mass*velocity^2))*(TOF_data_fit-parameter[0])
duplicate /o energy $TOF_energy
duplicate /o TOF_energy_transform $TOF_fit_energy
KillWaves velocity, energy, TOF_energy_transform

Function Average_Wavelength()
//AT PRESENT, THIS PROPERTY IS NOT INTEGRATED INTO THE FITTING ALGORITHM; IT CAN
//BE CALLED SEPARATELY
//Deleted for v. 11_27_01_json - look in a previous version if needed
End

Function TOFuncert(TOFdata)
//Calculate standard deviation of each TOF data point for cross-correlation TOF data (See Appendix B of D. Gosalvez-Blanco, Ph.D. thesis, 1997) and create weighting wave for fitting algorithm.
Wave TOF_data
Wave fit_stats=fit_stats
Wave fit_stats_uncert=fit_stats_uncert
WaveStats /Q TOF_data
Variable total_counts=V_avg*V_npnts
fit_stats[0]=total_counts
fit_stats_uncert[0]=sqrt(total_counts)
Return sqrt(total_counts)
End

Function LayoutTOF(TOFdata)

****************************************************************************
//TABLES, GRAPHS, LAYOUTS
****************************************************************************
Function Layout_TOF(TOF_data)
Wave TOFdata
String TOFdata_fit=NameOfWave(TOFdata)+"_fit"
String TOFdata_energy=NameOfWave(TOFdata)+"_E"
String TOFdata_fit_params=NameOfWave(TOFdata)+"_params"
String TOFdata_fit_params_uncert=TOFdata_fit_params+"_uncert"
String TOFdata_fit_stats=NameOfWave(TOFdata)+"_stats"
String TOFdata_fit_stats_uncert=TOFdata_fit_stats+"_uncert"
String TOFdata_fit_sigma=TOFdata_fit_stats+"_sigma"

Preferences 0
Execute("Layout/W=(5.25,41.75,221.25,300.5) Graph0, Graph1, table_parameter, table_fit_stats")
Preferences 0
Textbox/N=txt0/F=0/A=LB/X=5.78/Y=92.95 "\F'Times\Z24"+NameOfwave(TOFdata)
Execute("layout_style()")

Window table_parameter(): Table
PauseUpdate; Silent 1 // building window...
Edit/W=(283.5,146,528.75,398.75) parameter_text,parameter,parameter_uncert
AppendToTable constraint
AppendToTable constraint_text
ModifyTable width(Point)=0,font(parameter_text)="Times New Roman",width(parameter_text)=92
ModifyTable title(parameter_text)="parameter",font(parameter)="Times New Roman"
ModifyTable alignment(parameter)=1,sigDigits(parameter)=4,width(parameter)=60,title(parameter)="value"
ModifyTable font(parameter_uncert)="Times New Roman",alignment(parameter_uncert)=1
digits(parameter_uncert)=4,sigDigits(parameter_uncert)=4,width(parameter_uncert)=50
ModifyTable title(parameter_uncert)="uncert",font(constraint)="Times New Roman"
ModifyTable alignment(constraint)=1,sigDigits(constraint)=3,width(constraint)=20
ModifyTable title(constraint)="hold?"
ModifyTable alignment(constraint_text)=1,width(constraint)=25
ModifyTable title(constraint_text)="constraint"
EndMacro

Window table_fit_stats(): Table
PauseUpdate; Silent 1 // building window...
Edit/W=(280.5,43.25,568.5,281) fit_stats_text,fit_stats,fit_stats_uncert
fit_stats_sigma is omitted
ModifyTable width(Point)=0,font(fit_stats_text)="Times New Roman",width(fit_stats_text)=110
ModifyTable title(fit_stats_text)="properties",font(fit_stats)="Times New Roman"
ModifyTable alignment(fit_stats)=1,sigDigits(fit_stats)=4,width(fit_stats)=59,title(fit_stats)="value"
ModifyTable font(fit_stats_uncert)="Times New Roman",alignment(fit_stats_uncert)=1
ModifyTable sigDigits(fit_stats_uncert)=4,width(fit_stats_uncert)=53,title(fit_stats_uncert)="uncert"
ModifyTable font(fit_stats_sigma)="Times New Roman",alignment(fit_stats_sigma)=1
ModifyTable sigDigits(fit_stats_sigma)=4,width(fit_stats_sigma)=47,title(fit_stats_sigma)="sigma"
EndMacro
Proc TOF_style(): GraphStyle
    PauseUpdate; Silent 1  // modifying window...
    ModifyGraph/Z mode[0]=3
    ModifyGraph/Z marker[0]=8
    ModifyGraph/Z lSize[1]=2
    ModifyGraph/Z
gb[0]=(0,0,0),rgb[1]=(36864,14592,58880),rgb[3]=(0,65280,0),rgb[4]=(0,0,65280),rgb[5]=(0,0,0)
    ModifyGraph/Z font="Times New Roman"
    Label/Z left "N(t)"
    Label/Z bottom "%times"time of flight (%times%s"
    ModifyGraph mirror=2, minor=1
EndMacro
Proc TOFstyleHz(): GraphStyle
    PauseUpdate; Silent 1  // modifying window...
    ModifyGraph/Z mode[0]=3
    ModifyGraph/Z marker[0]=8
    ModifyGraph/Z lSize[1]=2
    ModifyGraph/Z
gb[0]=(0,0,0),rgb[1]=(36864,14592,58880),rgb[3]=(0,65280,0),rgb[4]=(0,0,65280),rgb[5]=(0,0,0)
    ModifyGraph/Z font="Times New Roman"
    Label/Z left "N(t)"
    Label/Z left "Count Rate (Hz)"
    Label/Z bottom "%times"time of flight (%times%s"
EndMacro
Proc PoF_style(): GraphStyle
    PauseUpdate; Silent 1  // modifying window...
    if (max_components==1)
        ModifyGraph/Z mode[1]=3
        ModifyGraph/Z marker[1]=8
        ModifyGraph/Z rgb[0]=(65280,0,0),rgb[1]=(0,0,0)
    endif
    if (max_components==2)
        ModifyGraph/Z mode[2]=3
        ModifyGraph/Z marker[2]=8
        ModifyGraph/Z rgb[0]=(65280,0,0),rgb[1]=(0,0,0)
    endif
    if (max_components==3)
        ModifyGraph/Z mode[3]=3
        ModifyGraph/Z marker[3]=8
        ModifyGraph/Z
gb[0]=(65280,0,0),rgb[1]=(0,65280,0),rgb[2]=(0,0,65280),rgb[3]=(0,0,0)
    endif
    if (max_components==4)
        ModifyGraph/Z mode[4]=3
        ModifyGraph/Z marker[4]=8
    endif
1118. ModifyGraph/Z
   rgb[0]=(65280,0,0),rgb[1]=(0,65280,0),rgb[2]=(0,0,65280),rgb[3]=(0,0,0),rgb[4]=(0,0,0)
1119. endif
1120. if (max_components==5)
1121. ModifyGraph/Z mode[5]=3
1122. ModifyGraph/Z marker[5]=8
1123. ModifyGraph/Z
   rgb[0]=(65280,0,0),rgb[1]=(0,65280,0),rgb[2]=(0,0,65280),rgb[3]=(0,0,0),rgb[4]=(65280,0,0),rgb[5]=(0,0,0)
1124. endif
1125. ModifyGraph/Z font="Times New Roman"
1126. Label/Z left "P(E\text{\textit{trans}}M)"
1127. Label/Z bottom "\textit{F} Times\text{\textit{translational energy (kcal/mol)}}"
1128. Variable i=0
1129. Variable max_energy=1.3*fit_stats[3]
1130. //do
1131. // if (fit_stats[7+4*i]+3*fit_stats_sigma[7+4*i]>max_energy)
1132. // max_energy=fit_stats[7+4*i]+3*fit_stats_sigma[7+4*i]
1133. // endif
1134. // i+=1
1135. //while (i<max_components)
1136. SetAxis bottom 0,15
1137. EndMacro
1138.
1139. Proc LayoutStyle() : LayoutStyle
1140.   // modifying window...
1141. Variable/G components
1142. ModifyLayout/Z left[0]=84.6,top[0]=200,width[0]=432,height[0]=288,frame[0]=0,trans[0]=1
1147. ModifyLayout trans(Graph1)=0
1148. EndMacro
1149.
1150. Macro
   Append_Comments(m_e, res_deltaM, frequency, sets, sweeps_triggers, molecular_beam, scat_inc_beam, incident_angle, detection_angle, surface_temperature)
1151.   Variable m_e=NumVarOrDefault("gm\_e",38)
1152.   String res_deltaM=StrVarOrDefault("gres","3.5/0")
1153.   Variable frequency=NumVarOrDefault("gfrequency",280)
1154.   Variable sets=NumVarOrDefault("gsets",1)
1155.   String sweeps_triggers=StrVarOrDefault("gsweeps_triggers","5000x1")
1156.   String molecular_beam=StrVarOrDefault("gmolecular_beam","1% F2/Xe")
1157.   String scat_inc_beam
1158.   Variable incident_angle=NumVarOrDefault("gincident_angle",20)
1159.   Variable detection_angle=NumVarOrDefault("gdetection_angle",125)
1160.   Variable surface_temperature=NumVarOrDefault("gsurface_temperature",250)
1161.   Prompt m_e, "m/e"
1162.   Prompt res_deltaM, "resolution and delta M"
1163.   Prompt sets, "number of sets"
Prompt sweeps triggered, "number of triggers x sweeps"
Prompt molecular beam, "Molecular beam"
Prompt scat_inc beam, "Beam/detector geometry", Popup "scattered beam; incident beam"
Prompt incident angle, "Incident angle"
Prompt detection angle, "Detection angle"
Prompt surface temperature, "Surface Temperature"
Variable scattering_angle = detection angle - 90 - incident angle
Textbox/C/N=text I/F=0/A=LT/X=3.67/Y=6.93 "\f'Times" + molecular_beam
AppendText "\f'Times\f04Mass Spectrometer Settings"
AppendText "\f04Signal Averaging"
Variable scattering_angle = detection_angle - 90 - incident_angle
if (strlen(scat_inc_beam) == 14) //i.e., scattered beam
    AppendText "\f04Scattering Geometry"
    AppendText "\f04incident angle:" + num2str(incident_angle) + ", detection angle:" + num2str(detection_angle) + ", scattering angle:" + num2str(scattering_angle) + " K"
else
    AppendText "\f04Incident beam"
    AppendText "\f04Detection angle:" + num2str(detection_angle)
endif
Variable/G L, _sigma
AppendText "\f04Flight path:" + num2str(L) + " m, Ionizer length:" + num2str(2*_sigma) + " m"
Variable/G gm_e=m_e
String/G gres_deltaM=res_deltaM
Variable/G gfrequency=frequency
Variable/G gsets=sets
String/G gsweeps_triggers=sweeps_triggers
String/G gmolecular_beam=molecular_beam
String/G gscat_inc_beam=scat_inc_beam
Variable/G gincident_angle=incident_angle
Variable/G gdetection_angle=detection_angle
Variable/G gsurface_temperature=surface_temperature
EndMacro

// Functions to compact and uncompact TOF data have been removed because they were not used
-JRH 11/27/01
Appendix C: Data and Figure Sources

Chapter II:

Figure 1
Made in VectorWorks 9 by J.G. Lee. Copies of the drawings are found in the Big Machine drawing cabinet and electronically.

Figure 2
Made in VectorWorks 10. Copies of the drawing are found in the Big Machine drawing cabinet and electronically.

Figure 3
Made in VectorWorks 9 by J.G. Lee. Copies of the drawings are found in the Big Machine drawing cabinet and electronically.

Figure 4
Plot is made after analyzing singly ionized rare gas TOF spectra of incident beams of He (m/e = 4), Ne (m/e = 20), Ar (m/e = 40), Kr (m/e = 84) and Xe (m/e = 129) taken 3/14/13, 3/15/13 and 3/19/13.

Figure 5
Plot is made after analyzing singly ionized rare gas TOF spectra of incident beams of Ne (m/e = 20), Ar (m/e = 40), Kr (m/e = 84) and Xe (m/e = 129) taken 3/14/13, 3/15/13 and 3/19/13.

Figure 6
Plot is made after analyzing singly ionized rare gas TOF spectra of incident beams of He (m/e = 4), Ne (m/e = 20), Ar (m/e = 40), and Kr (m/e = 84) taken 3/14/13, 3/15/13 and 3/19/13.

Figure 7
Made in VectorWorks 9 by J.G. Lee. Copies of the drawings are found in the Big Machine drawing cabinet and electronically.

Figure 8
Made in VectorWorks 9 by J.G. Lee. Copies of the drawing are found in the Big Machine drawing cabinet and electronically.

Figure 9
Made in VectorWorks 9 by J.G. Lee. Copies of the drawing are found in the Big Machine drawing cabinet and electronically.

Figure 10
Copied from a drawing made by McGonigal. Copies of the drawing are found in the Big Machine drawing cabinet.
Figure 11
Made in VectorWorks 10. Copies of the drawing are found electronically.

Figure 12
Made in VectorWorks 10 by D.W. Rowlands. Copies of the drawing are found in the Big Machine drawing cabinet and electronically.

Figure 13
Made in VectorWorks 9 by J.G. Lee. Copies of the drawings are found in the Big Machine drawing cabinet and electronically.

Chapter III:

Figure 1
Made in Adobe.

Figure 2
\[ m/e = 66, 85, \theta_m = 0^\circ, \text{crystal rotated } 40^\circ \text{ after exposure so } \theta_d = 0^\circ, T_{Si} = 250 \text{ K, } T_{nozzle} = 27^\circ\text{C. Pure F}_2, P_{stag} = 225 \text{ Torr, mar1309j.tds} \]

Figure 3
5 experiments, all with \( \theta_{in} = 0^\circ, \theta_d = 180^\circ \) (incident beam), 75% F\(_2\)/Kr, \( T_{nozzle} = -75^\circ\text{C} \)
\[ P_{stag} = 67 \text{ Torr: } \text{feb0309g.rga} \]
\[ P_{stag} = 200 \text{ Torr: } \text{feb0309h.rga} \]
\[ P_{stag} = 300 \text{ Torr: } \text{feb0309i.rga} \]
\[ P_{stag} = 500 \text{ Torr: } \text{feb0309j.rga} \]
\[ P_{stag} = 600 \text{ Torr: } \text{feb0309k.rga} \]

Figure 4
2 experiments, both with \( \theta_{in} = 0^\circ, \theta_d = 180^\circ \) (incident beam), 75% F\(_2\)/Kr, \( P_{stag} = 300 \text{ Torr} \)
\[ T_{nozzle} = 27^\circ\text{C: } \text{feb0309d.rga} \]
\[ T_{nozzle} = -70^\circ\text{C: } \text{feb0309i.rga} \]

Figure 5
\( m/e = 40, \theta_{in} = 0^\circ, \theta_d = 180^\circ \) (incident beam), Pure Ar, \( P_{stag} = 0.50 \text{ Torr, } T_{nozzle} = 27^\circ\text{C. may2013c.tof} \)

Figure 6
\( m/e = 20, \theta_{in} = 0^\circ, \theta_d = 180^\circ \) (incident beam), Pure Ne, \( P_{stag} = 0.50 \text{ Torr, } T_{nozzle} = 27^\circ\text{C. may2113o.tof} \)

Figure 7
\( m/e = 40, \theta_{in} = 0^\circ, \theta_d = 180^\circ \) (incident beam), Pure Ar, \( P_{stag} = 0.50 \text{ Torr, } T_{nozzle} = 27^\circ\text{C. may2113b.tof} \)
Figure 8
m/e = 84, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), Pure Kr, \( P_\text{stag} = 0.50 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \).  
may2113m.tof

Figure 9
m/e = 129, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), Pure Xe, \( P_\text{stag} = 0.50 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \).  
may2213h.tof

Figure 10
Top: m/e = 122, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), 75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -70^\circ \text{C} \).  
Bottom: m/e = 122, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), 75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \).  
om2010d.tof  
jun0210d.tof

Figure 11
m/e = 122, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), 75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -69^\circ \text{C} \).  
om2010a.tof

Figure 12
m/e = 19, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 180^\circ \) (incident beam), 75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -69^\circ \text{C} \).  
om2010c.tof

Figure 13
m/e = 66, 85, \( \theta_\text{in} = 0^\circ \), crystal rotated 40° after exposure so \( \theta_\text{d} = 0^\circ \), \( T_\text{Si} = 250 \) K, \( T_\text{nozzle} = 27^\circ \text{C} \). Pure F\textsubscript{2}, \( P_\text{stag} = 225 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \).  
mar1309j.tds

Figure 14
m/e = 66, 85, \( \theta_\text{in} = 0^\circ \), crystal rotated 40° after exposure so \( \theta_\text{d} = 0^\circ \), \( T_\text{Si} = 250 \) K, \( T_\text{nozzle} = -60.5^\circ \text{C} \). 75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -70 \text{ to } -57^\circ \text{C} \).  
mar1709d.tds

Figure 15
m/e = 66, 85, \( \theta_\text{in} = 0^\circ \), crystal rotated 40° after exposure so \( \theta_\text{d} = 0^\circ \), \( T_\text{Si} = 250 \) K.  
Pure F\textsubscript{2}, \( P_\text{stag} = 225 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \):  
mar1309b-mar1309j.tds
75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -70 \text{ to } -57^\circ \text{C} \):  
mar0609b-mar0609r.tds

Figure 16
m/e = 38, \( \theta_\text{in} = 0^\circ \), \( \theta_\text{d} = 40^\circ \) (no crystal scattering), Pure F\textsubscript{2}, \( P_\text{stag} = 227 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \).  
om2010c.tof

Figures 17-22
m/e = 66, 85, \( \theta_\text{in} = 0^\circ \), crystal rotated 40° after exposure so \( \theta_\text{d} = 0^\circ \), \( T_\text{Si} = 250 \) K.  
Pure F\textsubscript{2}, \( P_\text{stag} = 225 \) Torr, \( T_\text{nozzle} = 27^\circ \text{C} \):  
mar1309b-mar1309j.tds
75% F\textsubscript{2}/Kr, \( P_\text{stag} = 300 \) Torr, \( T_\text{nozzle} = -70 \text{ to } -57^\circ \text{C} \):  
mar0609b-mar0609r.tds
Chapter IV:
All simulations were performed running the Python program fluorine_kt.py. It can be found using the Ceyer Lab Big Machine folder on Athena.

Figure 1:
Taken from

Figure 2:
Made using ChemBioDraw 13.0

Figures 3-5:
Data for plots are from Python program fluorine_11.py, Si Mass = 47, Si47.csv. Plotted in IgorPro

Figures 6-13:
Data for plots are from Python program fluorine_kt.py. $M_{Si} = 47; k_{Si} = 225 \text{ N/m}; M_X = 38$ or $167; v_{38} = 564.1 \text{ m/s}, v_{167} = 269.1 \text{ m/s}; \text{timestep} = 1 \times 10^{-16} \text{ sec}; \text{damping} = 0.05$. Plotted on IGORPro.
For Positions 1-4 for $F_2$: Si47RunkT1-Si47RunkT4
For Positions 1-4 for $XeF_2$: Si47RunkT5-Si47RunkT8

Figures 14-18:
All these figures were drawn using ChemBioDraw13 for each mode.

Figure 19:
Data for plots are from Python program fluorine_kT.py. $M_{Si} = 47; k_{Si} = 10, 50, 150, 225, 450 \text{ and } 850 \text{ N/m}; M_X = 38$ or $167; v_{38} = 564.1 \text{ m/s}, v_{167} = 269.1 \text{ m/s}; \text{timestep} = 1 \times 10^{-16} \text{ sec}; \text{damping} = 0.05$. Plotted on IGORPro.

Figure 20:

Figure 21:
Data for plots are from Python program fluorine_11.py. $M_{Si} = 75; k_{Si} = 10, 50, 150, 225, 450 \text{ and } 850 \text{ N/m}; M_X = 38$ or $167; v_{38} = 564.1 \text{ m/s}, v_{167} = 269.1 \text{ m/s}; \text{timestep} = 1 \times 10^{-16} \text{ sec}; \text{damping} = 0.05$. Plotted on IGORPro.

Figure 22:
Data for plots are from Python program fluorine_11.py. $M_{Si} = 94; k_{Si} = 10, 50, 150, 225, 450 \text{ and } 850 \text{ N/m}; M_X = 38$ or $167; v_{38} = 564.1 \text{ m/s}, v_{167} = 269.1 \text{ m/s}; \text{timestep} = 1 \times 10^{-16} \text{ sec}; \text{damping} = 0.05$. Plotted on IGORPro.

Figure 23:
Data for plots are from Python program fluorine_11.py. $M_{Si} = 150; k_{Si} = 10, 50, 150, 225, 450 \text{ and } 850 \text{ N/m}; M_X = 38$ or $167; v_{38} = 564.1 \text{ m/s}, v_{167} = 269.1 \text{ m/s}; \text{timestep} = 1 \times 10^{-16} \text{ sec}; \text{damping} = 0.05$. Plotted on IGORPro.
Figure 24:
Data for plots are from Python program fluorine_11.py. $M_{Si} = 206; k_{Si} = 10, 50, 150, 225, 450$ and 850 N/m; $M_X = 38$ or 167; $v_{38} = 564.1$ m/s, $v_{167} = 269.1$ m/s; timestep $= 1 \times 10^{-16}$ sec; damping $= 0.05$. Plotted on IGORPro.

Appendix A:

Figure 1
Made in VectorWorks 10. Copies of the drawing are found electronically.

Figure 2
Made in VectorWorks 10. Copies of the drawing are found electronically.

Figure 3
Made in VectorWorks 10. Copies of the drawing are found electronically.

Figure 4
Made in VectorWorks 10. Copies of the drawing are found electronically.
Appendix D: Curriculum Vitae

MICHAEL R. BLAIR

EDUCATION:

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
S.M. Physical Chemistry (January 2014)
GPA: 4.8/5.0

- Thesis: Role of Silicon Lattice Excitation as a Key to Plasmaless Etching
- Probed the reaction dynamics of Kr(F₂) and Xe(F₂) dimers with a Si(100)2x1 surface
to find that energy transfer to a surface is vital for plasmaless semiconductor etching.

FORDHAM COLLEGE AT ROSE HILL
B.S., Chemistry, Summa Cum Laude
GPA: 3.9/4.0

- Focused on electrochemistry at a silver surface.

EXPERIENCE:

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Research Assistant, Department of Chemistry
Cambridge, MA 2004 to Present

- Using an ultra high vacuum chamber to study the chemical dynamics of Si Etching
  with fluorinated noble gas dimers. An internal, rotatable line of sight mass
  spectrometer fitted with a pseudorandom chopper for time-of-flight analysis is used
  for data acquisition.
- Operating and maintaining two precisely coupled, triply differentially pumped
  molecular beam sources. The beams are used to expose the Si crystal to both
  reactive and noble gases.
- Familiar with the design and engineering of components to interface with the
  existing apparatus to add functionality as desired.
- Worked with the MIT Energy Initiative (MITEI) to design energy based problems
  and concepts for introductory chemistry and biology courses, along with mentoring
  undergraduates in a project-based energy course.

FORDHAM COLLEGE AT ROSE HILL
Undergraduate Researcher, Department of Chemistry
Bronx, NY 2002 to 2004

- Performed electrochemical catalysis experiments focusing on fuel cells.

UNIVERSITY OF ROCHESTER
NSF Research Experience for Undergraduates, Department of Chemistry
Rochester, NY Summer 2002

- Synthesized and characterized asymmetric molecules using chiral ligands as catalysts.

SKILLS

Experimental:

- Extensive knowledge in analytical chemistry
- Surface and thin film characterization
- Chemical Vapor Deposition (CVD)
- Cross-correlation time-of-flight
- Temperature Programmed Desorption
- Mass Spectrometry
- Helium atom diffraction
- Auger Electron Spectroscopy
- Argon ion sputtering
- Surface Enhanced Raman Spectroscopy (SERS)
- X-Ray Photoelectron Spectroscopy (XPS)
- Vacuum engineering
- Semiconductor etching
- Instrumental electronics.

**Computer:**
- Engineering using CAD
- Microsoft Office
- Data Analysis and Simulation using IgorPro
- Python

**AWARDS/ACTIVITIES:**

Phi Beta Kappa (Member – Academic Fraternity)  
Sigma Xi (Member - Academic Fraternity)  
Member, American Chemical Society  
Fordham Chemistry Club (President - 2002-2004)  
Leo K. Yanowski Award – Fordham University (2004)  
Bartender - Muddy Charles Pub at MIT (2004-Present)

**PUBLICATIONS:**

One first author (refereed),
One co-author (to be published)
Two conference presentations
Three co-author on presentation abstract

*(Publication titles available upon request)*