MOLECULAR BEAM STUDIES OF HYPERTHERMAL ATOMIC OXYGEN
AND ARGON INTERACTIONS WITH POLYMER SURFACES
AND GAS-PHASE MOLECULES

by

Amy Leigh Brunsvold

A dissertation submitted in partial fulfillment
of the requirements for the degree
of
Doctor of Philosophy
in
Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana
April 2007
APPROVAL

of a dissertation submitted by

Amy Leigh Brunsvold

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Timothy K. Minton

Approved for the Department of Chemistry

David J. Singel

Approved for the Division of Graduate Education

Carl A. Fox
STATEMENT OF PERMISSION TO USE

In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this dissertation is allowable only for scholarly purposes, consistent with “fair use” as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this dissertation should be referred to ProQuest Information and Learning, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted “the exclusive right to reproduce and distribute my dissertation in and from microform along with the non-exclusive right to reproduce and distribute my abstract in any format in whole or in part.”

Amy Brunsvold
April 2007
ACKNOWLEDGEMENTS

First, I would like to thank Prof. Timothy Minton; without him, this work would not be possible. His unending encouragement, patience, and support have given me the courage to complete this research. Meetings of the “Late Night Data-Taking Club” were never the same after Donna Garton graduated. I am eternally grateful to her for teaching me how to use the machine, analyze data, and for being a good friend. Jianming Zhang, Hari Upadhyaya, and Russ Cooper were the best lab mates anyone could ask for. I hope that Russ stays true to the “X-Beam 4 Life!” I thank all of my friends who were either a phone call away, or up for a night out. Thanks also to Bill Hostetler for the many interesting conversations about science and life. Many thanks to my professors from Central College; Cathy Haustein, Dan Bruss, Louis Zaffiro, Viktor Martisovits, and Mark Mills for their guidance, support, and friendship. I am grateful to Zonta International for granting me an Amelia Earhart Fellowship and to the Montana Spacegrant Consortium. Finally, I would like to express my most sincere gratitude to my parents, David and Sara, and my brother, Matthew.
## TABLE OF CONTENTS

LIST OF TABLES........................................................................................................... viii

LIST OF FIGURES ......................................................................................................... ix

ABSTRACT.................................................................................................................... xix

1. INTRODUCTION ......................................................................................................1
   - The Low-Earth-Orbital Environment .................................................................1
   - Materials Degradation in LEO ................................................................. 2
   - Materials Modifications to Protect from Atomic Oxygen Attack ......................4
   - Synergistic Effects on Materials ................................................................. 5
   - Rocket Plume Interactions with Ambient Species in Leo .....................................6
   - Ground-Based Studied for Simulating the Leo Environment ...............................7
   - Scope of this Thesis .......................................................................................7
   - References .....................................................................................................9

2. EXPERIMENTAL METHODS ....................................................................................13
   - Laser Detonation Source ..............................................................................13
   - Sample Exposures to Hyperthermal Beam .....................................................16
   - Beam-Surface Scattering Studies ....................................................................17
   - Crossed-Molecular Beams Scattering Experiments .........................................18
   - Hyperthermal Beams and Scattered Products: Time-of-Flight Distributions ........21
   - Crossed-Beams Experiments: Center-of-Mass Laboratory Transformation ..........23
   - References ....................................................................................................25

3. AN INVESTIGATION OF THE RESISTANCE OF POSS POLYIMIDE TO
   ATOMIC-OXYGEN ATTACK .............................................................................27
   - Introduction ....................................................................................................27
   - Experimental Details .....................................................................................29
     - Synthesis of a POSS Polyimide Polymer .......................................................29
     - Exposure of Polymer Samples to a Hyperthermal O-Containing Beam ..........30
     - Surface Profilometry ...............................................................................33
     - Atomic Force Microscopy .........................................................................33
TABLE OF CONTENTS - CONTINUED

X-Ray Photoelectron Spectroscopy .................................................................33
Results and Analysis .......................................................................................34
Discussion ..........................................................................................................40
Conclusion ..........................................................................................................47
References ..........................................................................................................49

4. BEAM-SURFACE SCATTERING STUDIES OF THE INDIVIDUAL AND COMBINED EFFECTS OF VUV RADIATION AND HYPERThERMAL O, O₂, OR ARGON ON FEP TEFLOn® SURFACES ..........................................................51

Introduction .....................................................................................................51
Experimental Details .........................................................................................55
Preparation of FEP Teflon® Sample .................................................................55
Vacuum Ultraviolet Light Irradiation .................................................................56
Hyperthermal Gas-Surface Interactions ............................................................58
Results ...............................................................................................................62
VUV Light Alone ..............................................................................................62
Ar + FEP Teflon® ..............................................................................................63
Ar + VUV Light + FEP Teflon® .........................................................................65
O/O₂ + FEP Teflon® ..........................................................................................66
O/O₂ + VUV Light + FEP Teflon® .....................................................................69
Discussion ...........................................................................................................71
Conclusion ..........................................................................................................79
References ..........................................................................................................81

5. DYNAMICS OF BEAM-SURFACE SCATTERING OF HYPERThERMAL O, O₂, OR ARGON WITH FLUORINATED SURFACES .............................................84

Introduction .....................................................................................................84
Experimental Details .........................................................................................87
FEP Teflon® Surface .........................................................................................87
Perfluoropolyether (PFPE) Surface .................................................................87
Results and Analysis .........................................................................................89
Dynamics of Beam-Surface Scattering from an FEP Teflon® Surface ..............89
Dynamics of Beam-Surface Scattering from PFPE Surface .........................90
Discussion ...........................................................................................................101
Conclusion ..........................................................................................................104
References ..........................................................................................................106
# Table of Contents - Continued

6. CROSSED-BEAMS STUDY OF THE DYNAMICS OF HYPERTHERMAL COLLISIONS BETWEEN AR AND ETHANE ...........................................109
   - Introduction ...............................................................................................................109
   - Experimental Details .................................................................................................112
   - Results and Analysis .................................................................................................115
   - Discussion: Comparison of Experiment and Theory ................................................121
     - Dependence of Energy Transfer on Collision Geometry ............................................124
   - Conclusion ................................................................................................................127
   - References ..................................................................................................................130

7. CROSSED-BEAMS STUDY OF THE INTERACTIONS OF O($^3P$) WITH CARBON MONOXIDE .........................................................135
   - Introduction ...............................................................................................................135
   - Experimental Details .................................................................................................139
   - Theoretical Details .....................................................................................................144
   - Results and Analysis .................................................................................................145
     - Inelastic Scattering ................................................................................................145
     - Reactive Scattering .................................................................................................149
   - Discussion .................................................................................................................153
     - Inelastic Scattering ................................................................................................155
     - Reactive Scattering .................................................................................................157
     - Energy Partitioning .................................................................................................160
   - Conclusion ................................................................................................................161
   - References ..................................................................................................................166

8. EXCITATION FUNCTION FOR THE O($^3P$) + H$_2$O $\rightarrow$ HO$_2$ + H REACTION .................................................................168
   - Introduction ...............................................................................................................168
   - Experimental Details .................................................................................................171
   - Results and Analysis .................................................................................................179
   - Discussion .................................................................................................................180
   - Conclusion ................................................................................................................188
   - References ..................................................................................................................189

9. CONCLUSION .............................................................................................................191
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>39</td>
</tr>
</tbody>
</table>

3.1 Surface atomic concentrations (in percent) determined from XPS survey scans . . . 39
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Neutral composition of the Earth’s upper atmosphere (Roble, in <em>The Upper Mesosphere and Lower Thermosphere: A Review of Experiment and Theory</em>, Geophysical Monograph 87, pp 1 -21, 1995) ..................................1</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic diagram of the laser detonation source used to create hyperthermal neutral beams ..........................................................14</td>
</tr>
<tr>
<td>2.2</td>
<td>Representative atomic oxygen beam time-of-flight distributions. The overall beam distribution (dashed line) was narrowed with the use of a synchronized chopper wheel with a rotation rate of 300 Hz (solid line) ..........15</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic diagram of apparatus configuration for sample exposures including hyperthermal beam source, sample mount, and rotatable mass spectrometer .................................................................16</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic diagram of the crossed molecular beams apparatus, configured for gas-surface scattering experiments showing the hyperthermal beam source, the target surface, and the rotatable mass spectrometer detector ..........18</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic diagram of the crossed-molecular beams apparatus, showing the hyperthermal beam source, the crossed, gas-phase source, and the rotatable mass spectrometer detector .................................................................19</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic representation of the POSS polyimide polymer used in these studies. The letter, R, indicates cyclopentyl .........................................................30</td>
</tr>
<tr>
<td>3.2</td>
<td>Translational energy distributions of atomic and molecular oxygen in the hyperthermal beam .................................................................................................31</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>3.3</td>
<td>(a) Etch depth measurements for 0, 10, and 20 wt% POSS polyimide as a function of O-atom fluence, represented by etch depth of the Kapton H witness samples and (b) etch rates of POSS samples (derivatives of curves in figure 3.3a)</td>
</tr>
<tr>
<td>3.4</td>
<td>AFM images (10 x 10 µm) of (a) 0 wt%, (b) 10 wt% and (c) 20 wt% POSS polyimide surfaces after exposure to atomic oxygen fluences of 0.0, 3.8×10¹⁹, 1.6×10²⁰, and 4.1×10²⁰ O atoms cm⁻². The z scales for all images are the same, with a full scale of 500 nm. Root mean square roughness values are shown above each corresponding image</td>
</tr>
<tr>
<td>3.5</td>
<td>High resolution XPS spectra of C(1s) line for 0 wt% POSS polyimide. 6, 30, and 100 k pulses correspond to Kapton-equivalent O-atom fluences of ~1×10¹⁹, 3.8×10¹⁹ and 1.6×10²⁰ O atoms cm⁻², respectively</td>
</tr>
<tr>
<td>3.6</td>
<td>High resolution XPS spectra of C(1s) line for 20 wt% POSS polyimide. 6, 30, and 100 k pulses correspond to Kapton-equivalent O-atom fluences of ~1×10¹⁹, 3.8×10¹⁹ and 1.6×10²⁰ O atoms cm⁻², respectively</td>
</tr>
<tr>
<td>3.7</td>
<td>High resolution XPS spectra of Si(2p) line for 20 wt% POSS polyimide. 6, 30, and 100 k pulses correspond to Kapton-equivalent O-atom fluences of ~1×10¹⁹, 3.8×10¹⁹ and 1.6×10²⁰ O atoms cm⁻², respectively</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic representation of FEP (fluorinated ethylene propylene) Teflon®</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic diagram of the crossed molecular beams apparatus, configured for gas-surface scattering experiments showing the hyperthermal beam source, the target surface, the D₂ lamp, and the rotatable mass spectrometer detector</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.3</td>
<td>Translational energy distributions of O, O$_2$, and Ar beams selected with synchronized chopper wheel.</td>
</tr>
<tr>
<td>4.4</td>
<td>Mass spectrum of volatile products detected when an FEP Teflon$^\circledR$ surface was exposed to unfiltered D$_2$ lamp 50 cm away.</td>
</tr>
<tr>
<td>4.5</td>
<td>Time-of-flight distributions of scattered C$_m$F$_n$ fragments following exposure of pristine FEP Teflon$^\circledR$ surface to hyperthermal beam with $\langle E_i \rangle = 12.6$ eV. The incident and detection angles were both 60° with respect to the surface normal</td>
</tr>
<tr>
<td>4.6</td>
<td>Energy dependences of Ar-induced CID products detected at CF$^+$, CF$_2$$^+$, and CF$_3$$^+$</td>
</tr>
<tr>
<td>4.7</td>
<td>Energy dependence of Ar-induced CID product (CF$_3$) with and without exposure to D$_2$ lamp placed 12.7 cm away. The incident and detection angles were both 60° with respect to the surface normal</td>
</tr>
<tr>
<td>4.8</td>
<td>Energy dependence of CID product detected at $m/z = 50$ with incident Ar and O/O$_2$ beams. The incident energy refers to Ar and O$_2$.</td>
</tr>
<tr>
<td>4.9</td>
<td>Time-of-flight distributions of O-containing products following exposure of pristine FEP Teflon$^\circledR$ surface to hyperthermal O/O$_2$ beams with three sets of energies. The incident and detection angles were both 60° with respect to the surface normal</td>
</tr>
<tr>
<td>4.10</td>
<td>Time-of-flight distribution of O-containing CID products following bombardment of FEP Teflon$^\circledR$ surface by O/O$_2$ beam with and without exposure to filtered D$_2$ lamp. The average O and O$_2$ beam energies were 6.3 and 12.6 eV, respectively. The incident and detection angles were both 60° with respect to the surface normal</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES - CONTINUED**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.11</td>
<td>Energy dependence of O/O\textsubscript{2}-induced CID product with and without exposure to D\textsubscript{2} lamp placed 12.7 cm away. The incident and detection angles were both 60° with respect to the surface normal.</td>
</tr>
<tr>
<td>5.1</td>
<td>Schematic diagram of the crossed molecular beams apparatus, configured for gas-surface scattering experiments showing the hyperthermal beam source, the liquid reservoir, and the rotatable mass spectrometer detector.</td>
</tr>
<tr>
<td>5.2</td>
<td>Angular distributions of Ar-induced CID products detected at CF\textsuperscript{+}, CF\textsubscript{2}\textsuperscript{+}, and CF\textsubscript{3}\textsuperscript{+}.</td>
</tr>
<tr>
<td>5.3</td>
<td>Time-of-flight distributions (TOF) of inelastically scattered Ar atoms from FEP Teflon\textsuperscript{®} with (E_i) = 12.7 eV. The open circles are the collected TOF distributions, the red lines are the Maxwell-Boltzmann (MB) fits to the thermal components, and the solid black lines are the hyperthermal components which was found by subtracting the MB distributions from the collected TOF distributions.</td>
</tr>
<tr>
<td>5.4</td>
<td>Average final translational energies of hyperthermal CF\textsubscript{3} as a function of detector angle following impingement of an Ar beam at (\theta_i = 60°) with (E_i) = 12.7 eV on a continuously refreshed PFPE surface.</td>
</tr>
<tr>
<td>5.5</td>
<td>TOF distributions of scattered C\textsubscript{m}F\textsubscript{n} fragments following exposure of continuously refreshed PFPE to hyperthermal Ar beam with (E_i) = 14.7 eV. The incident and detection angles were both 60° with respect to the surface normal. For the signals detected at (m/z = 31) and 50, the MB distribution was assumed to be from the neutral CF\textsubscript{3} product.</td>
</tr>
<tr>
<td>5.6</td>
<td>Energy dependence of CID products with incident Ar (top) and O/O\textsubscript{2} beams (bottom) impinging from continuously refreshed PFPE surface. The incident and detection angles were both 60° with respect to the surface normal.</td>
</tr>
<tr>
<td>5.7</td>
<td>Angular distributions of Ar-induced CID products detected at CF\textsuperscript{+}, CF\textsubscript{2}\textsuperscript{+}, and CF\textsubscript{3}\textsuperscript{+}. The open circles represent the Ar atoms which scattered from the surface with hyperthermal velocities and the solid circles represent those which desorbed with thermal velocities.</td>
</tr>
</tbody>
</table>
5.8 a) Angular distribution and b) energy and flux distributions for the inelastically scattered Ar when \(<E_i> = 12.7 \text{ eV}\). The open circles in (a) represent the Ar atoms which scattered from the surface with hyperthermal velocities and the solid circles represent those which desorbed with thermal velocities. ...........................................................................99

5.9 Energy and flux distributions of Ar-induced CID products detected at \(\text{CF}^+\) and \(\text{CF}_2^+\).........................................................................................................100

6.1 Translational energy distributions of the narrowed hyperthermal Ar beams used in the experiments. The nominal center-of-mass collision energy (\(E_{\text{coll}}\)) for Ar + ethane collisions is shown above the distribution for each beam...............................................................................114

6.2 Comparison of the ionizer fragmentation pattern of room temperature ethane (cross-hatched bars) and the fragmentation pattern of inelastically scattered ethane (solid bars)........................................................................................................116

6.3 Representative time-of-flight distributions of ethane scattered from Ar. The circles correspond to the experimental data and the solid lines are the forward convolution fits to the data..................................................................................117

6.4 Laboratory angular distributions for scattered ethane. The symbols are obtained by integrating the time-of-flight distributions shown in Fig. 4, and the dotted lines are derived from the forward convolution of the best-fit c.m. translational energy and angular distributions (see Figs. 7 and 8) ....................................................................................................................119

6.5 Newton Diagram for collisions of Ar + ethane at \(E_{\text{coll}} = 3.3 \text{ eV}\), where Ar has a velocity of 6050 m s\(^{-1}\) and the ethane beam velocity is 800 m s\(^{-1}\). The shaded region indicates the range of laboratory angles examined. The larger, solid circle represents the recoil velocities of elastically scattered ethane. The smaller, dashed circle represents the recoil velocities of scattered ethane when 85% of the collision energy goes into translation.................................................................120
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6</td>
<td>Center-of-mass translational energy distributions derived from experiment</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>(solid curves) and from theoretical calculations (dotted curves)</td>
<td></td>
</tr>
<tr>
<td>6.7</td>
<td>Experimental (top) and theoretical (bottom) center-of-mass</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>angular distributions of relative flux for ethane scattered in the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>backward hemisphere</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>(a) Probability distributions for the distance between Ar and the center</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>of mass ethane RSH at the trajectories’ inner turning point. (b) Probability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>distributions for the angle formed between the RSH distance and the C–C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>axis ARSH at the turning point of the trajectories. The calculations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pertain to backward hemisphere scattering of ethane in hyperthermal Ar +</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ethane collisions at $E_{\text{coll}} = 6.6$ eV.</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Calculated potential energy curves of the ground singlet state of CO$_2$</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>($^1A'$), and the three lowest triplet states, $^3A'$, $^13A''$, and $^23A''$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at an OCO angle of 120° and where one of the CO bond distances of 1.2 Å is</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fixed and the other is varied. The curves show these states</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at $C_s$ geometries to their O+CO dissociation limits, as a function of $r_{\text{CO}}$</td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>Translational energy distributions of atomic and molecular oxygen in the</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>hyperthermal beam</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>Newton Diagram for collisions of O($^3P$) with C$^{18}$O at $E_{\text{coll}}$</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>= 3.6 eV, where O has a velocity of 8100 m s$^{-1}$ and the C$^{18}$O beam</td>
<td></td>
</tr>
<tr>
<td></td>
<td>velocity is 800 m s$^{-1}$. The shaded region indicates the range of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>laboratory angles examined. The solid circles represent the recoil</td>
<td></td>
</tr>
<tr>
<td></td>
<td>velocities of elastically scattered C$^{18}$O and $^{16}$O. The dashed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>circles represent the maximum recoil velocities of scattered $^{16}$OC (blue)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and $^{18}$O (red)</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>Time-of-flight distributions of inelastically scattered O and C$^{18}$O</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>following collisions $&lt;E_{\text{coll}}&gt;$ = 3.6 eV. The circles are the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>experimental data. The red (O) and blue (C$^{18}$O) solid curves are the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>forward-convolution simulations of the data, derived from the c.m. angular</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and translational energy distributions of corresponding colors in Figure 7.6</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>Laboratoy angular distributions of O atoms and C\textsuperscript{18}O molecules which scattered inelastically with $&lt;E_{\text{coll}}&gt; = 3.6$ eV. The black symbols with error bars are the experimental data, and the line-connected colored symbols are the forward convolution fits to the data, derived from the c.m. angular and translational energy distributions of corresponding color in Figure 7.6. The error bars are estimated from fitting the experimental TOF distributions with a modified Gaussian function and finding maximum and minimum acceptable fits by adjusting the Gaussian parameters. The integrated ranges of these fits are shown as error bars.</td>
<td>147</td>
</tr>
<tr>
<td>7.6</td>
<td>Center-of-mass angular and translational energy distributions for the inelastic scattering of O from C\textsuperscript{18}O at $&lt;E_{\text{coll}}&gt; = 3.6$ eV, used in the forward-convolution fit of the laboratory TOF and angular distributions for $m/z = 16$ (O$^+$) and 30 (C\textsuperscript{18}O$^+$). These distributions were obtained from QCT calculations for O (blue) and C\textsuperscript{18}O (red).</td>
<td>148</td>
</tr>
<tr>
<td>7.7</td>
<td>Center-of-mass velocity-flux maps for the C\textsuperscript{18}O product, derived from the angular and translational energy distributions shown in Figure 7.6.</td>
<td>150</td>
</tr>
<tr>
<td>7.8</td>
<td>Time-of-flight distributions of reactively scattered $^{16}$OC following reaction of O($^3P$) with C\textsuperscript{18}O at $&lt;E_{\text{coll}}&gt;$ = 3.6 eV. The circles are the experimental data. The blue and red solid curves are the forward-convolution simulations of the data, derived from the c.m. angular and translational energy distributions of corresponding colors in Figure 7.10.</td>
<td>152</td>
</tr>
<tr>
<td>7.9</td>
<td>Laboratory angular distribution (black symbols with error bars) of the $^{16}$OC product from the reaction of O($^3P$) with C\textsuperscript{18}O at $&lt;E_{\text{coll}}&gt;$ = 3.6 eV. The error bars are estimated from fitting the TOF distributions with a modified Gaussian function and finding maximum and minimum acceptable fits by adjusting the Gaussian parameters. The integrated ranges of these fits are shown as error bars. The colored curves are the forward-convolution simulations to the data, derived from the c.m. angular and translational energy distributions of corresponding color in Figure 7.10.</td>
<td>153</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES - CONTINUED

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.10</td>
<td>Center-of-mass angular and translational energy distributions for reactive scattering of O($^3P$) from C$^{18}$O at $\langle E_{\text{coll}} \rangle = 3.6$ eV, used in the forward-convolution fit of the laboratory TOF and angular distributions for $m/z = 28$ ($^{16}$OC$^+$). The distributions shown in blue were obtained from QCT calculations and those shown in red were determined by the experiment.</td>
</tr>
<tr>
<td>7.11</td>
<td>Center-of-mass velocity-flux maps for the $^{16}$OC product from a) experimental and b) theoretical translational energy and angular distributions.</td>
</tr>
<tr>
<td>7.12</td>
<td>Internal energy distributions (derived from Figures 7.6 and 7.10) for carbon monoxide products.</td>
</tr>
<tr>
<td>7.13</td>
<td>Calculated cross sections for O + CO collisions at 8 km s$^{-1}$ collision speed (77.9 kcal mol$^{-1}$) showing the contribution from each final CO(v,j) state as a function of the final translational energy of collision products. (a) reactive channel, (b) inelastic channel, (c) inelastic channel minus the CO(v=0,j) product contributions. The numbers in the figures indicate the thresholds for the CO(v) product vibrational levels. In (b), the contribution from CO(v=0) below the CO(v=1) threshold extends above the axis limit, and so is not visible in the figure.</td>
</tr>
<tr>
<td>7.14</td>
<td>Calculated vibrationally resolved cross sections for O + CO collisions at 3, 4, 5, 6, 7, 8, 9, 10 km s$^{-1}$ collision speeds. (a) reactive collisions; (b) inelastic collisions. The numbers in the figure refer to the collision speed.</td>
</tr>
<tr>
<td>7.15</td>
<td>Calculated ro-vibrationally resolved cross sections for O + CO collisions at 8 km s$^{-1}$ collision speed (77.9 kcal mol$^{-1}$). ○, CO(v=0); □, CO(v=1); △, CO(v=2); ◇, CO(v=3). (a) reactive channel, (b) inelastic channel. The CO(v=0) inelastic cross section has been multiplied by $10^3$ in order to fit on the scale.</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>8.1</td>
<td>170</td>
</tr>
<tr>
<td>8.2</td>
<td>172</td>
</tr>
<tr>
<td>8.3</td>
<td>174</td>
</tr>
<tr>
<td>8.4</td>
<td>175</td>
</tr>
<tr>
<td>8.5</td>
<td>176</td>
</tr>
<tr>
<td>8.6</td>
<td>176</td>
</tr>
<tr>
<td>8.7</td>
<td>178</td>
</tr>
<tr>
<td>8.8</td>
<td>182</td>
</tr>
<tr>
<td>8.9</td>
<td>183</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>8.10</td>
<td>Trajectories of O($^3P$) + H$_2$O with collision geometries that may lead to HO$_2$ + H where a) the HO$_2$ is scattered in the forward direction with respect to incident O atom and b) the HO$_2$ is scattered in the backward direction, with little internal excitation</td>
</tr>
<tr>
<td>8.11</td>
<td>Theoretically calculated center-of-mass (c.m.) velocity flux maps for reactive scattering of HO$<em>2$ from O($^3P$) at $E</em>{\text{coll}} = 70$ kcal mol$^{-1}$ (top), 115 kcal mol$^{-1}$ (center), and 160 kcal mol$^{-1}$ (bottom)</td>
</tr>
</tbody>
</table>
ABSTRACT

O atoms and N\textsubscript{2} molecules in the outer atmosphere of the Earth collide with spacecraft surfaces and various gases that are released from space vehicles. The high relative velocity of the collisions promotes high reaction probability and large energy transfers, leading to materials degradation and chemiluminescent reactions, which may interfere with the mission of the vehicle. The work presented in this thesis uses sophisticated molecular beam and surface science techniques to study materials degradation and individual reactive and inelastic collisions in an effort to understand the complex chemistry and physics that are characteristic of space vehicle interactions with Earth’s upper atmosphere. A new space-durable polymer, polyhedral oligomeric silsesquioxane polyimide, has been identified. When exposed to atomic oxygen, this polymer forms a protective SiO\textsubscript{2} layer on its surface. Beam-surface scattering experiments showed that collision-induced dissociation becomes an important gas-surface process when the translational energy of the incident atom or molecule is greater than 8 eV. Experiments on the dynamics of gas-phase collisions at hyperthermal collision energies found that inelastic collisions may transfer large amounts of energy into internal degrees of freedom. The scattering dynamics of the reactive \textsuperscript{16}OC product from the \textsuperscript{16}O(\textsuperscript{3}P) + C\textsuperscript{18}O \rightarrow \textsuperscript{16}OC + \textsuperscript{18}O reaction were quite unexpected, with \textsuperscript{16}OC predominantly forward scattered. Experiments on the reactions of O(\textsuperscript{3}P) with H\textsubscript{2}O demonstrated the occurrence of a previously unobserved reaction pathway, O(\textsuperscript{3}P) + H\textsubscript{2}O \rightarrow HO\textsubscript{2} + H, with a barrier determined to be \textasciitilde2.6 eV. These studies of hyperthermal processes with molecular beam techniques have enabled us to identify a promising new material and to understand the detailed collision dynamics in model gas-surface and gas-phase systems. In each case, the experiments have revealed new chemical or energy transfer processes that were not considered earlier. These previously unknown processes reveal trends in hyperthermal collisions that will undoubtedly be critical to the planning and design of missions that put space vehicles in contact with the outer reaches of the Earth’s atmosphere.
INTRODUCTION

The Low-Earth-Orbital Environment

The International Space Station (ISS), the Hubble Space Telescope (HST), the space shuttle, and many private and government satellites orbit in the altitude range of 200-600 km above the Earth. This region of the Earth’s upper atmosphere is commonly referred to as low Earth orbit (LEO). Atomic oxygen is the most abundant species in LEO and is created by the dissociation of molecular oxygen into atomic oxygen by ultraviolet radiation from the sun. The average atomic-oxygen density is approximately $10^9$ cm$^{-3}$ at a typical space shuttle altitude of $\sim 300$ km.\textsuperscript{1-6} Most of the oxygen atoms (more

![Figure 1.1. Neutral Composition of the Earth’s Upper Atmosphere (Roble, in The Upper Mesosphere and Lower Thermosphere: A Review of Experiment and Theory, Geophysical Monograph 87, pp 1 – 21, 1995.)](image)
than 99.99 \%) are in the ground, \text{O}^3(\text{P})\), electronic state.\textsuperscript{5} The few additional O atoms are in the first excited electronic state, \text{O}^1(\text{D}). While atomic oxygen is the predominant neutral species in the ambient atmosphere in LEO, molecular nitrogen (N\textsubscript{2}), molecular oxygen (O\textsubscript{2}), and He are present, but with much lower number densities.\textsuperscript{5} Figure 1.1 illustrates the neutral composition of the LEO environment. Oxygen ions (O\textsuperscript{+}) are the most common charged species present in LEO, but with a number density 10\textsuperscript{-4} times that of atomic oxygen.\textsuperscript{5,7,8}

**Materials Degradation in LEO**

As space vehicles travel through LEO, their ram surfaces collide with the residual atmosphere with relative velocities of \sim 7.4 \text{ km s}\textsuperscript{-1}.\textsuperscript{1-3} The ram surfaces experience atomic oxygen fluxes of about 10\textsuperscript{15} O atoms cm\textsuperscript{-2} s\textsuperscript{-1} (\sim 1 monolayer s\textsuperscript{-1}), with the collisions equivalent to \sim 4.5 \text{ eV} O atoms colliding with spacecraft surfaces. These energetic collisions can lead to surface degradation of spacecraft and were first observed on early space shuttle flights when post-flight analyses on polymer surfaces were conducted. Some of the atomic-oxygen-induced effects included loss of surface gloss and transparency, mass loss, and oxidation.\textsuperscript{9-12}

Incident atoms and molecules may also scatter from a spacecraft surface without reaction and may lead to surface degradation though high-energy inelastic collisions. Inelastic scattering of molecules heavier than O atoms (such as N\textsubscript{2}) from spacecraft surfaces result in larger collisions energies and therefore may degrade surfaces more easily. As shown in the insert in Figure 1, at LEO altitudes in the 100-200 km range, the number density of N\textsubscript{2} is almost equal to that of O atoms.\textsuperscript{5} The high relative velocities
lead to gas-surface collisions with many electron volts of collision energy in the center-of-mass reference frame. The energy associated with these hyperthermal collisions is in excess of many bond dissociation energies and may help promote materials degradation by allowing barriers to reaction or to collision-induced dissociation (CID) to be overcome.\textsuperscript{2,13-15} Therefore, collisions of spacecraft surfaces with N\textsubscript{2} molecules may result in CID and might be responsible for some of the detrimental effects on surfaces exposed to the residual atmosphere in LEO.

Organic polymers are commonly used on spacecraft as thermal control and structural materials, but they are susceptible to erosion from reactions with oxygen atoms in low Earth orbit. The phenomenology of polymer erosion has been investigated extensively in space- and ground-based exposure environments.\textsuperscript{6,13,16} Kapton® is an organic polyimide that is used extensively for space applications because of its desirable mechanical and thermal properties. The erosion yield of Kapton® H in a space environment is very well-characterized and has an agreed upon value of $3.00 \times 10^{-24}$ cm\textsuperscript{3} O-atom\textsuperscript{-1}, and is used frequently as a calibration standard for determining the O-atom fluence for a particular space mission, or for ground-based studies.\textsuperscript{13,17} Another material commonly used on spacecraft is FEP (fluorinated ethylene propylene) Teflon®. Compared to hydrocarbons, FEP Teflon® degrades very slowly when exposed to atomic oxygen.\textsuperscript{18} However, it has been reported that FEP Teflon® erodes more dramatically under the combined exposure of atomic oxygen and vacuum ultraviolet (VUV) light.\textsuperscript{19}
Materials Modification to Protect from Atomic Oxygen Attack

Inorganic oxide surface coatings, such as SiO$_2$, are generally used to protect polymers from atomic oxygen attack in LEO$^{20}$ Kapton® surfaces that were coated with silicon dioxide have exhibited erosion yields as low as a few tenths of one percent of the erosion yield of unprotected Kapton®. While the coating itself resists atomic oxygen attack, defects as the result of poor adhesion, micrometeoroid or debris impact, materials handling, and imperfect coating application process can allow oxygen atoms to attack the underlying polymer and give a finite erosion yield to the material.

An approach superior to simply coating a surface with an O-atom-resistant material is to modify the structure of a material in order to make it inherently resistant to atomic oxygen. Ion implantation has been used to insert elemental ions (e.g. Ai$^+$ and Al$^+$) just below the surface of a polymer.$^{21,22}$ Atomic oxygen reacts with the Si or Al and forms a passivating layer of SiO$_2$ or Al$_2$O$_3$. Another approach has been to develop new polymers (e.g., phosphine oxide polymers) that have the ability to form a passivating oxide layer when exposed to atomic oxygen.$^{23}$

A specifically promising approach to the production of space-survivable polymers is to incorporate polyhedral oligomeric silsesquioxanes (POSS) into a polymer structure into a polymer structure that is known to have desirable functional qualities. These nanoscopic cages have typical diameters of ~1.5 nm and can be copolymerized, grafted, and blended into traditional polymers systems.$^{24-27}$ Studies of the erosion resistance of POSS polyimide are part of this thesis research.
Synergistic Effects on Materials

Spacecraft in LEO are also exposed to high levels of radiation, including light with wavelengths in the vacuum ultraviolet (VUV) region. The VUV spectrum consists of radiation with wavelengths below 200 nm, including the Lyman-α emissions of atomic hydrogen at 121 nm. The Hubble Space Telescope (HST) and other spacecraft flying in LEO use thermal blankets to provide protection from solar heating. A material extensively used as a thermal blanket is FEP Teflon®. Studies on the effects of atomic oxygen and VUV radiation on the surface of FEP Teflon® have reported that the surface erodes only under the combined exposure of VUV light and atomic oxygen, and atomic oxygen alone has only a minor, if any, effect on the erosion. FEP Teflon® is optically transparent in the visible region of the spectrum, but below 300 nm the absorbance begins to rise slowly. The absorption spectrum for PTFE (polytetrafluoroethylene) Teflon® has been reported and shows that there is a strong absorption at 161 nm corresponding to the transition from the HOMO levels for the C-C and C-F bonds to a conduction band. PTFE Teflon® and FEP Teflon® are both fluorocarbons and their absorption spectra should be assumed to be similar. When there is spectral overlap between the VUV radiation present in LEO and the absorption spectrum of Teflon®, degradation of the surface can occur.

In addition to reactions with atomic oxygen and photodissociation, another mechanism that may be important in FEP Teflon® degradation in LEO is collision-induced dissociation (CID). Although several studies have added to our understanding of
the role of VUV light and its synergistic effects with atomic oxygen (see, for example, Refs. 19, 29-39), virtually nothing is known about the relative importance of CID.

A major problem in ground-based studies used to determine fluoropolymer erosion rates from atomic oxygen exposure is that creating these high-energy collisions is not a trivial task. In order to create gas-surface interactions with the same relative velocities as those observed in LEO, a beam of hyperthermal (~7.4 km s\(^{-1}\)) atomic oxygen, in its ground, \(^3P\), state can be directed at a surface. Prior to the work described in this thesis, all ground-based studies on the mechanisms of FEP Teflon\(^\text{®}\) degradation in simulated LEO environments have been conducted with either thermal atomic oxygen, or with hyperthermal atomic oxygen sources that have not been well-characterized and may contain a variety of other components (e.g. ions, radiation) that complicate the observed erosion rates.\(^{32,33}\)

**Rocket Plume Interactions with Ambient Species in LEO**

In addition to O-atom-surface interactions in LEO, atomic oxygen (and molecular nitrogen) also collide with exhaust plume streams at relative velocities in the vicinity of ~7.4 km s\(^{-1}\).\(^{40}\) These high relative velocities lead to gas-phase collisions with many electron volts of collision energy in the center-of-mass reference frame and may lead to large energy transfers and unusual reactions that only become important at hyperthermal collision energies. Water vapor, carbon dioxide, and carbon monoxide and their reaction or collision products are the most important combustion product molecules in rocket plumes that emit near IR radiation.\(^{40}\) The expected rocket plume signatures can be
predicted with models that incorporate accurate data on the dynamics of, for example, hyperthermal O-atom interactions.

**Ground-Based Studies for Simulating the LEO Environment**

Space-based studies of the effects of the space environment are costly and can be difficult to interpret because of the lack of control over all parameters. In order to simulate the interactions of hyperthermal atomic oxygen with spacecraft (surfaces and exhaust gases), ground-based experiments are employed so that individual parameters may be controlled. Laboratory studies of the interactions of O atoms with spacecraft surfaces and plumes have been conducted using a variety of atomic–oxygen environments, including plasmas and atomic beams. The high chemical reactivity of atomic oxygen makes it difficult to create a completely pure atomic oxygen beam source, because all of the methods that have been developed have byproducts (IR and UV light, ions, electrons, O₂, etc.). A review of a variety of atomic oxygen sources may be found in Ref. 13. One of the most well-characterized hyperthermal O-atom sources is the laser detonation source that is used in the experiments presented in this thesis. This source will be described in detail in Chapter 2 of this thesis.

**Scope of this Thesis**

The types of experiments presented in this thesis scan a wide range from exposures of new types of materials to atomic oxygen, to gas-surface scattering studies with hyperthermal beam energies, to crossed-molecular beams experiments. Theoretical calculations by Prof. George Schatz at Northwestern University and his former post-
doctoral researcher, Prof. Diego Troya (who is now a professor at Virginia Tech) have been performed on many of the systems in this thesis and compared to our experimental results. Dr. Matthew Braunstein from Spectral Sciences, Inc has also provided theoretical calculations, with have been compared to the experimental results presented in Chapter 7 of this thesis. Throughout this thesis, many of the theoretical results and comparisons will be shown, but all calculations were done by collaborators outside MSU and none were done by the author.

Chapter 3 discusses the survivability of a novel polymer material when exposed to a hyperthermal O-atom beam. Chapters 4 and 5 summarize a gas-surface scattering study of the effects of hyperthermal collisions on fluorinated surfaces, such as FEP Teflon®. Chapter 6 is an investigation of energy transfer in inelastic collisions of hyperthermal Ar atoms with ethane molecules in a crossed-molecular beams experiment. Crossed-molecular beams studies for simulating interactions of spacecraft exhaust gases with atomic oxygen in the LEO environment will be presented in the remaining chapters. Interactions (both reactive and inelastic) of O(3P) with carbon monoxide molecules at hyperthermal collision energies will be presented in Chapter 7. Chapter 8 focuses on hyperthermal collisions of atomic oxygen with water.
References


EXPERIMENTAL METHODS

Laser Detonation Source

A laser detonation source, originally developed by Physical Sciences, Inc.\textsuperscript{1,2} is used to create neutral beams of atoms or small molecules with hyperthermal translational energies. The precursor gas (such as O\textsubscript{2} or Ar in these experiments), with a backing pressure of 500 psig, is injected into a 10 cm, water-cooled, gold-plated copper nozzle with the use of a piezoelectric valve\textsuperscript{3} at a repetition rate of 2 Hz. Then, a 7 J pulse\textsuperscript{-1} CO\textsubscript{2} laser fires and enters the source chamber through a ZnSe window (AR coating at 10.6 microns) and is focused into the conical apex with a gold mirror. This high energy laser pulse induces a breakdown of the gas and heats the resulting plasma to more than 20,000 K. The remaining cold gas is engulfed by the detonation wave and ultimately creates a beam of neutral species (either O and O\textsubscript{2} in the oxygen beam or Ar) due to efficient ion-electron recombination in the nozzle as the plasma cools. A schematic diagram of the laser detonation source is shown in Figure 2.1. The average energy of the atomic oxygen in the beam can range from 3-6 eV and the atomic fraction can vary from 25-98 percent, depending on the conditions of the source. The average energy of the Ar beam can range from 5-15 eV. Alignment of a rotatable mass spectrometer detector with the beam axis is used to characterize the beam source.
In order to accurately simulate the O atom reactions that occur in LEO, it is important that the laser detonation source creates atomic oxygen in its ground electronic state, O\( (^3P) \). A recent crossed-molecular beams experiment on the reaction \( O + H_2 \rightarrow OH + H \) was conducted in our laboratory and a relative excitation function (flux as a function of collision energy) of the OH product was found.\(^4\) Dynamics calculations, both quasiclassical trajectories and time dependent quantum mechanical wave packet methods, were carried out by Schatz, \emph{et al.} for the same reaction. The calculations on the triplet-only potential energy surfaces matched the experimental results and therefore it has been determined that the OH signal was the result of \( O(^3P) \) reacting with \( H_2 \). They have concluded that the hyperthermal O atoms beam could be, at most, 1.0 percent \( O(^1D) \). Therefore, we are confident that the laser detonation source used in this experiment produced \( O(^3P) \), and that the experiments in this thesis may be used to simulate the
effects of the LEO environment where hyperthermal O atoms are known to be in their ground electronic state.

Figure 2.2 shows a representative temporal profile of the atomic oxygen in the overall hyperthermal beam pulse, with “time zero” corresponding to the point in time when the oxygen atoms are created. The overall pulse is very broad, so in order to narrow the time (and velocity) width of the beam pulse, a synchronized chopper wheel is used. The chopper wheel is placed in the main scattering chamber of the apparatus. The rotation rate was 300 Hz in the experiments described in this thesis. The narrowed O-atom beam pulse that was selected with the synchronized chopper wheel is shown as the solid curve in Figure 2.2.

Figure 2.2. Representative atomic oxygen beam time-of-flight distributions. The overall beam distribution (dashed line) was narrowed with the use of a synchronized chopper wheel with a rotation rate of 300 Hz (solid line).
Sample Exposures to Hyperthermal Beam

The crossed-molecular beams apparatus used in our laboratory can be configured to perform a variety of types of experiments. For the types of experiments described in Chapter 3 of this thesis, a sample mount is placed in the hyperthermal O-atom source chamber of the apparatus so that samples placed in the mount are exposed to the beam.\textsuperscript{5,6} Figure 2.3 is a schematic diagram of the apparatus configured for sample exposures. It illustrates the hyperthermal beam source and the sample mount. After the samples are exposed to the beam, they are removed from the chamber and their surfaces are examined by a variety of techniques. Screens are placed over the samples so that a profilometer can determine erosion yields of the samples by measuring the step heights between protected

![Figure 2.3. Schematic diagram of apparatus configuration for sample exposures including hyperthermal beam source, sample mount, and rotatable mass spectrometer.](image-url)
areas and exposed areas on the surface. Atomic force microscopy (AFM) is used to measure the surface roughness of the samples before and after exposure to hyperthermal atomic oxygen. Chemical composition changes on the surface can be measured with the use of X-ray photoelectron spectroscopy (XPS). These measurements are all performed \textit{ex situ} and after the samples have been exposed to air.

\textbf{Beam-Surface Scattering Studies}

While sample exposure experiments are useful in learning how a material degrades in a simulated low-Earth-orbital environment, beam-surface scattering studies allow us to gather information about the mechanism of degradation by monitoring products that scatter from the surface in “real-time” experiments. A sample is placed in the main scattering chamber of the apparatus on a manipulator such that the hyperthermal beam strikes the surface and products that scatter as a result are detected by a rotatable mass spectrometer detector as a function of incident beam impingement angle, arrival time to the detector, and the final (or detector) angle.\textsuperscript{7,8} The apparatus configured for beam surface scattering studies is shown in Figure 2.4.
Crossed-Molecular Beams Scattering Experiments

The apparatus can also be configured for crossed-molecular beams scattering experiments, whereby the hyperthermal beam is crossed at 90° by another gas-phase beam. The crossed-molecular beams apparatus is based on an apparatus originally designed by Y. T. Lee for studying bimolecular collision dynamics. Figure 2.5 is a schematic diagram of the machine configured for crossed-molecular beams experiments. A piezoelectric pulsed valve is often used to produce pulsed beams of molecules (such as
ethane and CO, which are presented in this thesis) that were collided with the hyperthermal beam. The orifice of the nozzle has a diameter of 1 mm. The beam enters the main scattering chamber though a 5-mm-diameter skimmer into a differentially pumped region and through a 2.5 mm-diameter aperture located 3 cm from the interaction region of the two beams. Timing is crucial to these types of experiments because the two beams must reach the interaction region at the same time. A timing diagram and further

Figure 2.5. Schematic diagram of the crossed molecular beams apparatus, showing the hyperthermal beam source, the crossed, gas-phase source, and the rotatable mass spectrometer detector.
discussion of the timing of the experiments can be found in Ref. 15. The velocities of the supersonic beams can be roughly estimated with the use of the formula:16

\[ v = \sqrt{\frac{2k_B T}{m} \left( \frac{\gamma}{\gamma - 1} \right)} \]

where \( T \) is the temperature of the nozzle, \( m \) is the mass of the species, and \( \gamma = \frac{C_p}{C_v} \).

While this calculation provides only an estimate and may have up to a ±15% error, the errors in this estimation are negligible when calculating the collision energy for the colliding species. For example, to calculate the collision energy of a hyperthermal beam of O atoms with a supersonic beam of CO molecules,

\[ E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2 \]

where \( \mu \) is the reduced mass of the colliding species and \( v_{\text{rel}} \) is the relative velocity of the species in the laboratory. If the velocity for a CO beam is calculated using the estimation described above, at 298 K, the CO molecules are predicted to have an average velocity of ~840 m s\(^{-1}\). A collision (90° crossing angle) of an oxygen atom with a velocity of 8000 m s\(^{-1}\) and a CO molecule traveling at 840 m s\(^{-1}\) would have an average collision energy of 3.42 eV. But, an error of ±15% in the velocity estimation of the CO beam would lead to only a ±0.01 eV error in the calculation of the collision energy. This amount of error is negligible compared to other errors in the experiment, including the uncertainties in the hyperthermal beam velocity.

For the experiment on the O + H\(_2\)O reaction discussed in Chapter 8 of this thesis, a continuous, effusive beam source was implemented. Continuous beams have the advantage over pulsed beams in that there are no errors due to inadequate overlap of the
beam pulses in the interaction region. In addition, effusive beams have well-known velocity distributions that can be described as a Maxwell distribution, and are not likely to produce dimers. However, continuous beams do not have the high peak intensities of pulsed beams, and they typically increase the overall pressure in the main scattering chamber to a higher extent because the gas is continuously entering the machine. A continuous beam of gaseous water was created by using the water vapor above a reservoir of liquid water. For the experiment described in Chapter 8, an effusive beam of water was used by allowing the water vapor above a liquid water reservoir to enter the apparatus and form a molecular beam in the vacuum of the main scattering region. The vapor pressure of the water was adjusted by changing the temperature of the liquid water. A cluster of small capillaries with a total diameter of 2.5 mm was placed at the end of the tube, roughly 4 mm from the crossing region of the two beams. More details about the design of the water source will be given in Chapter 8.

Hyperthermal Beams and Scattered Products: Time-Flight-Distributions

A quadrupole mass filter is used to select the mass of product species after they are ionized with a Brink-type electron impact ionizer, and then the ions are counted with a Daly-type ion counter. A multichannel scalar is used to accumulate the ions as a function of their arrival time to the detector. The number density of the neutral species is reflected in the number of ions generated in the electron-impact ionizer, so the mass spectrometer detector measures number density distributions as a function of their arrival time, or time-of-flight (TOF) distributions.
The collected TOF distributions include a number of time delays because the multichannel scalar is triggered by the same pulse that triggers the opening of the pulsed valve. For TOF distributions of the constituents in the beam that are collected with the detector aligned with the beam, the laser delay (delay after the precursor gas valve is opened and the laser is fired) and the ion flight time from the ionizer to the Daly ion counter are subtracted from the collected TOF distribution to give the flight time of the neutral constituents to the ionizer. The ion flight time has been found to be $2.44(m/z)^{1/2}$, where $m/z$ is the mass-to-charge ratio.\textsuperscript{11,15} The time-corrected TOF distributions can then be converted to velocity or translational energy distributions by knowing the distance the species has traveled. The distance from the cone to the ionizer is 128.66 cm when the instrument is configured for gas-surface interactions or 132.66 cm for crossed-molecular beams experiments.

Products that scatter from either a stationary surface or a colliding gas species are detected with the rotatable mass spectrometer detector as a function of scattering angle and arrival time to the detector. Therefore, measured TOF distributions of the scattered products include the laser delay, the ion flight time of the detected species, the flight time of the neutral species to the ionizer, and the flight time of the hyperthermal beam pulse to the interaction region (either the surface or the other gas-phase beam). The delays are subtracted so that the distributions correspond to the time it takes the neutral products to arrive at the detector that is 33.66 cm from the interaction region. TOF distributions, or number density distributions $N(t)$, at a fixed detector position are integrated to give laboratory angular distributions, $N(\Theta)$, where $\Theta$ is the laboratory angle with respect to the hyperthermal beam axis. The laboratory angle is defined as zero for the hyperthermal
beam direction. For crossed-beams experiments, a positive angular direction is the rotation toward the other gas-phase beam. For beam surface experiments, laboratory angular distributions are collected as a function of final scattering angle with respect to the surface normal.

Crossed-Beams Experiments: Center-of-Mass to Laboratory Transformation

From the laboratory TOF and angular distributions, c.m. translational energy and angular distributions are derived by a forward convolution method. In this method, the c.m. scattered flux per unit solid angle, \( I_{\text{cm}}(E, \theta) \), is typically assumed to be separable into the product of two functions: a c.m. translational energy distribution, \( P(E) \), and a c.m. angular distribution, \( T(\theta) \), where \( E \) is the total product translational energy and \( \theta \) is the c.m. scattering angle. Trial \( P(E) \) and \( T(\theta) \) distributions are iteratively adjusted until optimum fits to all laboratory distributions are obtained. Uncertainties in the derived \( P(E) \) and \( T(\theta) \) distributions are determined by observing the maximum variation in these distributions that can still produce the observed laboratory TOF and angular distributions acceptably well. In order to allow for easy manipulation of the \( P(E) \) and \( T(\theta) \) distributions, parameterized functions are commonly used. However, when theoretically calculated c.m. translational energy and angular distributions are available, they can be used to help guide the analysis and can be directly used in the forward convolution as point-form functions. In Chapter 6, the \( P(E) \) distributions were based on the RRK form, \( P(E_T) = (E_T - B)^p (E_{\text{avail}} - E_T)^q \). A Legendre polynomial function, with adjustable weighting of each of the polynomial terms, can be used to describe the \( T(\theta) \) distribution.
An eleven-term Legendre polynomial was used in Chapter 6. Legendre polynomials are found using Rodrigues’ formula:

\[ T_k(\theta) = \frac{a_k}{2^k k!} \frac{d^k}{d(\cos(\theta))^k} \cos^2(\theta) - 1^k, \]

where \( k = 0, 1, 2, \ldots, 10 \) (for an 11-term Legendre polynomial), \( a_k \) are the weighting coefficients, and the \( T(\theta) \) is found by summing over all the terms. The computer program used to carry out the center-of-mass to laboratory transformation is the MSU XBEAM Program, Version 2.2.\(^{11,15,22}\)
References


AN INVESTIGATION OF THE RESISTANCE OF POSS POLYIMIDE TO
ATOMIC-OXYGEN ATTACK

Introduction

Kapton and other polyimides are ubiquitous on spacecraft. However, like all hydrocarbon-based polymers, polyimides erode in the highly oxidative environment of low-Earth orbit (LEO). Coatings of inorganic oxide (e.g., SiO₂) are typically used to mitigate this problem. Kapton surfaces that are coated with SiO₂ have been shown to exhibit erosion yields as low as a few tenths of one percent of the erosion yield of unprotected Kapton. Although the SiO₂ coating itself is resistant to O atoms in LEO, defects in the coating will permit O atoms to attack the underlying polymer and undercut the coating, thus giving a finite erosion yield to the material. Defects are the inevitable result of imperfect coating application processes, poor adhesion, material handling, thermal expansion mismatch between the coating and the substrate, and micrometeoroid or debris impacts. Coatings of high integrity may be prepared by taking advantage of atomic oxygen in LEO to react with silicon-containing moieties that have been chemically bonded to a polymer surface. Upon atomic-oxygen attack, the treated surface will react to form a protective SiO₂ layer. Regardless of the initial quality of a coating, however, it will eventually develop defects in LEO and become compromised. An approach superior to simply coating a surface is to modify the structure of a material in order to make it inherently resistant to atomic oxygen. One approach is to use ion implantation to insert elemental ions (e.g., Si⁺ and Al⁺) into the surface of a polymer.
atoms will react with the Si or Al in the surface to form a passivating layer of SiO$_2$ or Al$_2$O$_3$. Another approach is to develop new polymers (e.g., phosphine oxide polymers) that have the ability to form a passivating oxide layer when exposed to atomic oxygen.\textsuperscript{6} These approaches that utilize the oxide-producing nature of species in the bulk of the polymer have the advantage over coatings that they can self heal in the event of a crack or micrometeoroid impact, because the exposed fresh surface will quickly oxidize and restore the passivating layer. An alternative to ion implantation or the development of an entirely new material is to create a mixed inorganic/organic polymer, consisting of nanoscopic inorganic particles chemically bound to or blended with the chains of an existing polymer that is known to have desirable functional properties. If the inorganic phase of the material were effective at establishing a passivating layer at the surface and if the organic phase retained its functional properties, then a general approach to protecting currently employed polymers from O atoms in the LEO environment would simply be the incorporation of inorganic nanoparticles into the polymer formulation. The arduous task of finding totally new materials that could simultaneously resist the harsh effects of the LEO environment and perform a desired function could thus be alleviated, if not circumvented altogether.

A specifically promising approach to the production of space-survivable polymers is to incorporate polyhedral oligomeric silsesquioxanes (POSS) into a polymer structure, thereby creating an inorganic/organic hybrid polymer. POSS frameworks consist of a three-dimensional inorganic cage structure, with a Si:O ratio of 2:3, surrounded by tailorable organic groups.\textsuperscript{7,8} These POSS cages are nanoscopic in size, with typical dimensions of $\sim$1.5 nm. Functional groups on the POSS monomers allow them to be
copolymerized, grafted, and blended into traditional polymer systems. The POSS nanostructures can be dispersed throughout the polymer matrix, and completely transparent hybrid polymers can be synthesized even with high POSS loadings. The properties of the polymer can be controlled and tailored by changing the weight percentage of POSS that is incorporated. Studies of mechanical properties of POSS polyimides have concluded that the inclusion of POSS into the polyimide systems does not compromise the thermal and mechanical properties of the pure polyimide. In addition, the incorporation of POSS in a polymer affords the possibility of making the bulk material resistant to atomic oxygen attack. Gonzalez and co-workers have shown that POSS polymers form a surface silica layer upon exposure to atomic oxygen.\textsuperscript{9,10} This layer may protect the underlying material from further attack. In order to evaluate the ability of POSS polymers to resist atomic-oxygen attack and to develop an understanding of the nature of the passivating layer, we have investigated the behavior of a POSS-modified polyimide material (shown in Figure 3.1) that was exposed for varying durations to an atomic oxygen environment. Various surface analytical techniques were used to characterize samples of POSS polyimides before and after exposure to a beam containing hyperthermal O atoms.

**Experimental Details**

**Synthesis of a POSS polyimide polymer**

Polyimides with the same chemical formula as Kapton were synthesized by our collaborators at Edwards Air Force Base in the Materials Applications Branch Space and Missile Propulsion Division by using condensation polymerization of 4,4´-
oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N’-dimethylacetamide (DMAc) solvent. POSS nanostructures were incorporated into the backbone of the Kapton-equivalent polyimide polymer to create 10 and 20 wt% POSS-polyimide films (see Figure 3.1).

Figure 3.1. Schematic representation of the POSS polyimide polymer used in these studies. The letter, R, indicates cyclopentyl.

Exposure of Polymer Samples to a Hyperthermal O-Containing Beam

Sample exposures were performed with a pulsed beam, operating at a repetition rate of 2 Hz and containing hyperthermal atoms that were generated with the use of a laser-detonation source that was previously described in Chapter 2. Time-of-flight distributions, collected with the use of the mass spectrometer detector, have allowed us to identify the major constituents of the beam and to derive translational energy
distributions for these constituents. Experiments on this apparatus have also enabled us to learn additional details about the constituents of the beam.

The hyperthermal beam contains neutral atomic and molecular oxygen, with only a tiny ionic component (<0.01%). Translational energy distributions for the O and O$_2$ components of the beam are shown in Figure 3.2. Average translational energies for atomic and molecular oxygen were 4.93 and 8.42 eV, respectively, with the energy widths (FWHM) of the atomic and molecular oxygen components being approximately 3.6 and 6.0 eV, respectively. The mole fraction of atomic oxygen in the beam was approximately 70 percent. A recent crossed-beams reactive scattering experiment/theory comparison on the reaction, O + H$_2$, has shown that the O atoms in the hyperthermal beam are in their ground O($^3P$) state. A similar study on the reaction of the O/O$_2$ beam with CH$_4$, indicates that the molecular oxygen in the beam is in its ground O$_2$ ($^3\Sigma_g^-$) state.

![Figure 3.2. Translational energy distributions of atomic and molecular oxygen in the hyperthermal beam.](image)
The hyperthermal O-containing beam was directed at samples mounted 40 cm from the apex of the conical nozzle. Two samples each of 0, 10, and 20 wt% POSS polyimide were cleaned by rinsing with a solution of 25% ethanol and 75% trichloroethylene and placed in a sample mount. One of each type was covered with an etched, stainless steel mesh disk (0.48 inch diameter, 0.003 inch thick) in order to mask areas of the surfaces and thus facilitate step height measurements between etched and unetched regions. The other samples were left unmasked to provide large exposed areas in anticipation of subsequent analyses by x-ray photoelectron spectroscopy (XPS). For every exposure, a masked Kapton H reference sample was placed in the center of the sample mount in order to use the step height measurements to calculate the Kapton-equivalent O-atom fluence. The nominal position of the sample mount was a few degrees off the beam axis; thus the beam impingement angle on a given sample fell in the range one to ten degrees from the surface normal. The exact impingement angle on a sample depended on its position on the sample mount. Each sample thus experienced a very slightly different fluence, but the samples were always placed in the same position in the sample mount in order to ensure consistency in relative measurements. Samples were exposed at ambient temperatures (~300 K) to 6000, 30,000, 50,000, 100,000, 150,624, 250,000, and 395,000 pulses of the hyperthermal beam, corresponding to Kapton-equivalent atomic-oxygen fluences of ~1×10^{19}, 3.83×10^{19}, 7.23×10^{19}, 1.63×10^{20}, 2.44×10^{20}, 4.10×10^{20}, 8.47×10^{20} O atoms cm^{-2}, respectively. On average, each beam pulse contained about 1.75×10^{15} O atoms, with a mean translational energy of 4.9-5.0 eV. All samples were handled in ambient air after exposure, and the etch depth, surface
topography, and surface chemistry of the samples were probed by various techniques as described below.

**Surface Profilometry**

The step height measurements between the masked and exposed areas of the samples were obtained with the use of a Dektak³ (Veeco Metrology Group, Santa Barbara, CA) surface profilometer. Scan lengths ranged from two to four microns, and scan speeds were slow to medium. The etched-mesh screens used to cover the samples had a wire thickness of 100 µm, with approximately square open areas that were 500 µm wide. Average step heights for the masked samples were obtained from 30 different step height measurements on each sample.

**Atomic Force Microscopy**

TappingMode™ AFM images were collected in ambient conditions on a MultiMode Nanoscope III (Digital Instruments, Santa Barbara, CA). Silicon tips with a resonant frequency of approximately 300 kHz were used, and the scan rate was in the range of 0.5 to 1.0 Hz.

**X-Ray Photoelectron Spectroscopy**

XPS spectra were obtained with the use of non-monochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Sample charging shifted the XPS lines to higher binding energies by 0.5 to 3 eV. In the present study, this shift was corrected by assuming that the binding energy of the lowest C(1s) component is 285.0 eV for the unexposed polyimide (0 wt% POSS) sample. (Note that
the binding energy scale was calibrated with the use of an Ag(3d$_{5/2}$) line at 368.25 eV as a reference.)

**Results and Analysis**

Figure 3.3a shows the results of step height measurements for 0, 10, and 20 wt% POSS polyimide films that were exposed to various numbers of hyperthermal O-atom beam pulses. Step heights (or etch depths) of POSS samples are plotted in Figure 3.3a as a function of the step height of the Kapton H reference sample for each exposure. For Figure 3.3b, the step heights of each of the 0, 10, and 20 wt% POSS polyimide films were divided by the corresponding step height of the Kapton H reference sample, and the result is plotted against the Kapton H step height. Figure 3.3b thus gives the rate of change of the step height (proportional to erosion rate) of the POSS samples as a function of exposure duration. The Kapton H reference sample has an accepted erosion yield in the LEO environment of $3.00 \times 10^{-24} \text{ cm}^3 \text{ O-atom}^{-1}$ and may be used to calculate the Kapton-equivalent fluence of each exposure (shown at the top of the plot in Figure 3.3), as well as the Kapton-equivalent erosion yields of the POSS samples. The erosion yield of the 0 wt% POSS sample appeared to increase linearly with fluence, so the 0 wt% POSS data in Figure 3.3a were fit by a simple linear regression. After an initial rapid increase with fluence that etched 12.3 $\mu$m of Kapton H ($4.10 \times 10^{20} \text{ O atoms}^2$). These data were fit well by the functional form, $y = ax^b$, where the parameter, $a$, was found to be $0.24 \mu m^{1/b}$ for 10 wt% POSS and $0.14 \mu m^{1/b}$ for 20 wt% POSS polyimide, and the respective $b$ parameters were 0.59 and 0.43. The erosion rates, shown in Figure 4b, were found by taking the derivatives of the functions used to fit the erosion yield data ($dy/dx =$...
The derivative functions indicated that the 10 and 20 wt% POSS polyimides reached erosion rates, after 395,000 beam pulses, of 3.7 and 0.98 percent, respectively, those of Kapton H.

AFM images (10×10 µm) obtained from 0, 10, and 20 wt% POSS polyimide films after exposure to Kapton-equivalent atomic-oxygen fluences of 0, 3.8×10¹⁹, 1.6×10²⁰, and 4.1×10²⁰ O atoms cm⁻² are shown in Figure 3.4. Before exposure, all samples were smooth, with root mean square roughness values of approximately 2.5 nm. With increasing exposure fluence, the surface topography changed dramatically. The 0 wt% polyimide control became increasingly rough with increasing exposure fluence and formed features similar to those typically observed on eroded Kapton H[11]. The 10 wt% POSS polyimide surface also became increasingly rough with increasing exposure fluence, but to a much lesser extent than the 0 wt% POSS polyimide surface. The 20 wt% POSS polyimide surface became even less rough than the 10 wt% POSS polyimide surface. Both the 10 wt% and 20 wt% POSS polyimide surfaces continued to roughen slowly as the fluence increased.

The elemental composition of the 0, 10, and 20 wt% POSS polyimide samples was determined by XPS survey spectra obtained before and after exposure to the hyperthermal beam. Table 1 shows the surface elemental composition for samples that were exposed to a variety of fluences (beam pulses). For the 0 wt% POSS surface, the carbon atomic concentration decreased somewhat with fluence, while the oxygen atomic concentration essentially doubled. Both the carbon and oxygen atomic concentrations tended toward steady-state values as the exposure duration increased. The decrease in the carbon atomic concentration was much more dramatic for the 10 and 20 wt% POSS
Figure 3.3. (a) Etch depth measurements for 0, 10, and 20 wt% POSS polyimide as a function of O-atom fluence, represented by etch depth of the Kapton H witness samples and (b) etch rates of POSS samples (derivatives of curves in Figure 3.3a.)
samples. Likewise, the increase in oxygen atomic concentration was also more dramatic for the POSS-containing samples than for the 0 wt% POSS samples. The rate of change in the atomic concentrations decreased sharply with exposures above 6 kpulses. The key difference in the surface composition of the POSS samples as opposed to the 0 wt% POSS samples was the presence of silicon. The silicon atomic concentrations on the surfaces of pristine POSS polyimides were very low, only a few percent. However, upon exposure to atomic oxygen, the Si atomic concentration rose rapidly to roughly constant values around 25 percent. At the highest exposure fluence, the Si:O ratio was ~1:2.

High resolution XPS spectra of the C(1s) and Si(2p) peaks corresponding to unexposed and exposed samples of 0 and 20 wt% POSS samples are shown in Figures 3.5, 3.6, and 3.7. The high resolution C(1s) line shape for the unexposed 0 wt% POSS sample (Figure 3.5) is typical for pristine Kapton. Upon exposure to O atoms, the “valley” between the hydrocarbon peak at 285 eV and the C=O peak near 288.8 eV became somewhat less pronounced, indicating the formation of carbon in more oxidation states than were originally present. The C(1s) line shape for the 20 wt% POSS sample surface (Figure 3.6) changed much more dramatically upon exposure to the O-atom beam than did the C(1s) line shape of the 0 wt% POSS sample. And the chemical structures associated with polyimide appeared to be lost. Figure 3.7 shows that the significant oxygen atomic concentration that is apparent from the survey spectra (table 1) is mainly accounted for in the spectrum of the Si(2p) line. The Si(2p) line shifted from a binding energy of 102.3 eV, corresponding to Si$_2$O$_3$, for the unexposed 20 wt% POSS sample to a binding energy of nearly 104 eV, corresponding to SiO$_2$, after this sample was exposed to binding energy of nearly 104 eV, corresponding to SiO$_2$, after this sample was exposed to
Figure 3.4. AFM images (10×10 μm) of (a) 0 wt%, (b) 10 wt%, and (c) 20 wt% POSS polyimide surfaces after exposure to atomic oxygen fluences of 0.0, 3.8×10^{19}, 1.6×10^{19}, and 4.1×10^{20} O atoms cm^{-2}. The z scales for all images are the same, with a full scale of 500 nm. Root mean square roughness values are shown above each corresponding image.
Table 3.1. Surface atomic concentrations (in percent) determined from XPS survey scans.

100 kpulses of the O-atom beam. And the chemical structures associated with polyimide appeared to be lost. Figure 3.7 shows that the significant oxygen atomic concentration that is apparent from the survey spectra (Table 1) is mainly accounted for in the spectrum of the Si(2p) line. The Si(2p) line shifted from a binding energy of 102.3 eV, corresponding to Si₂O₃, for the unexposed 20 wt% POSS sample to a binding energy of nearly 104 eV, corresponding to SiO₂, after this sample was exposed to 100 kpulses of the O-atom beam. It thus appears that at the surface, the POSS in the polymer was oxidized essentially to SiO₂. Further evidence of the oxidation of silicon is seen in the high resolution spectrum of the O(1s) line (not shown). The peaks in the O(1s) spectra for the 10 and 20 wt% POSS polyimides shifted from 532 eV to 533 eV after exposure to O atoms, again indicating that silicon near the surface was oxidized to SiO₂. The carbon

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure (beam kpulses)</th>
<th>Kapton-equivalent atomic oxygen fluence ($10^{30}$ O atoms cm⁻²)</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>N</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>72</td>
<td>19.5</td>
<td>1</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>69</td>
<td>20</td>
<td>2</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>69</td>
<td>24</td>
<td>1</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>55</td>
<td>36</td>
<td>0</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>10 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>77</td>
<td>16</td>
<td>2</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>73</td>
<td>18.5</td>
<td>5</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>48</td>
<td>30</td>
<td>19</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>20</td>
<td>56</td>
<td>23.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>20 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>70</td>
<td>20</td>
<td>6</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>66</td>
<td>24</td>
<td>7</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>20</td>
<td>54</td>
<td>25</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>12</td>
<td>60</td>
<td>26</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
content of the surface layer that was probed by XPS (~5-8 nm thick) was reduced to 12 atomic percent after exposure to 100 k pulses. This small amount of carbon may be the result of organic contamination or carbon from the polymer that was either in the passivating surface layer or in the unmodified polymer beneath it. Nevertheless, after the 100 k pulse exposure, the surface of the 20 wt% POSS polyimide had become almost entirely SiO₂.

Discussion

The incorporation of POSS into the chemical structure of a Kapton-like polyimide clearly leads to a hybrid material that is largely resistant to atomic-oxygen attack. The erosion rates of the 10 and 20 wt% POSS samples were found to be as low as 3.7 and 0.98 percent, respectively, of the erosion rate for Kapton H, at the highest exposure fluence used in this study (Kapton-equivalent O-atom fluence of 8.47×10²⁰ O atoms cm⁻²). The erosion rates for the POSS-containing samples decreased rapidly with O-atom exposure and appeared to reach a near steady state at the higher fluences, suggesting the O-atom-induced formation of a passivating layer that ultimately limits the erosion rate to a low but finite steady-state value. The microscopic surface topography of the exposed and unexposed samples, as probed by atomic force microscopy, supports what is suggested by the erosion-yield measurements. The 0 wt% POSS (i.e., pure polyimide) material becomes very rough upon exposure to the O-atom beam, indicating significant erosion. In contrast, the POSS-containing polyimide films show minimal roughening with exposure (see Figure 3.4). Nevertheless, even the POSS-containing samples exhibit some increase in surface roughness when exposed to increasing O-atom fluences. Apparently,
the erosion yields of the POSS-containing polymers, while greatly reduced, do not go to zero with the formation of a passivating later, although higher POSS loading in the hybrid material increases the O-atom resistance of the passivating layer that is formed. The XPS data also indicate the formation of a passivating layer, and they provide insight into the chemical nature of this layer. Upon exposure to the O-atom beam, the carbon atomic concentration at the surface of the POSS-containing polymers decreased dramatically, with concomitant large increases in the oxygen and silicon atomic concentrations (see Table 1). These observations suggest that the organic component of the surface was eroded away and was replaced by oxides of silicon. Also, the formation of a passivating layer was indicated by the reduction in the rate of change in the various surface atomic concentrations as the exposure fluence increased. High resolution XPS spectra (Figure 3.7) show that, as the O-atom exposure fluence increased, the silicon that was present transformed from a suboxide of silicon, which has the stoichiometry of POSS (i.e., Si$_2$O$_3$), to fully oxidized silicon (SiO$_2$). This observation leads to the conclusion that the passivating layer is SiO$_2$, which would be expected to protect the underlying material from O-atom attack.$^{1,2}$ Unlike an SiO$_2$ coating that is applied to the surface, the passivating layer could be restored if a defect developed, because POSS material in the bulk would react with incident O atoms to create more SiO$_2$. 
Figure 3.5. High resolution XPS spectra of C(1s) line for 0 wt% POSS polyimide. 6, 30, and 100 kpulses correspond to Kapton-equivalent O-atom fluences of \( \sim 1 \times 10^{19} \), \( 3.8 \times 10^{19} \) and \( 1.6 \times 10^{20} \) O atoms cm\(^{-2}\), respectively.
Figure 3.6. High resolution XPS spectra of C(1s) line for 20 wt% POSS polyimide. 6, 30, and 100 k pulses correspond to Kapton-equivalent O-atom fluences of \(~1 \times 10^{19}\), \(3.8 \times 10^{19}\) and \(1.6 \times 10^{20}\) O atoms cm\(^{-2}\), respectively.
Figure 3.7. High resolution XPS spectra of Si(2p) line for 20 wt% POSS polyimide. 6, 30, and 100 k pulses correspond to Kapton-equivalent O-atom fluences of $\sim 1 \times 10^{19}$, $3.8 \times 10^{19}$ and $1.6 \times 10^{20}$ O atoms cm$^{-2}$, respectively.
It should be noted that all XPS spectra were collected after the exposed samples had been removed from the vacuum system and had been in contact with air. Earlier studies on the effect of air exposure on the surface chemistry of polyimide surfaces that were oxidized in an atomic-oxygen environment have shown significant differences in the XPS spectra collected in situ as compared with the XPS spectra collected after air exposure. In two cases, the surface oxygen atomic concentration was found to decrease with increasing O-atom fluence while the samples were held under vacuum, and after exposure to air, the surface oxygen atomic concentration on these samples was found to increase. In another case, however, the surface oxygen atomic concentration was found to increase with O-atom fluence while the polyimide was held under vacuum, and then, after air exposure, the surface oxygen atomic concentration decreased somewhat. These earlier studies used much lower O-atom exposure fluences than does the present study. Although air exposure may affect the surface chemistry of an organic polymer, such as a polyimide, we do not believe that reactions of air with freshly oxidized surfaces will significantly affect our results and conclusions. Certainly, the 0 wt% POSS polyimide control samples may be altered by air exposure after they have been oxidized by the hyperthermal beam, so the observed oxygen atomic concentrations for this material may be somewhat in error. In addition, the surface of a POSS-containing sample that was exposed to O-atom fluences too low to erode much of the organic component of the surface and promote significant oxidation of the POSS near the surface would be expected to be affected by subsequent air exposure. Nevertheless, if the O-atom fluence is high enough to generate an SiO₂-containing layer that protects the surface from hyperthermal O-atom attack, then air would not be expected to react with this passivated
surface and lead to an alteration of the surface chemistry. We estimate that the passivation layer is largely developed before 100,000 pulses of the hyperthermal beam have struck the surface. Thus, the XPS spectra reported here should be accurate for the POSS samples that were exposed to 100,000 and 250,000 pulses of the O-atom beam (1.63×10^{20} and 4.10×10^{20} O atoms cm^{-2}, respectively), because these spectra show that the surfaces (especially of the 20 wt% POSS polyimide) largely consisted of silicon and oxygen in a ratio suggestive of SiO2.

Even though a predominant SiO2 layer is apparently formed when a POSS-containing polyimide is exposed to the O-atom beam, both POSS materials used in this study still eroded somewhat, with ultimate steady-state erosion rates of approximately one to four percent that of Kapton H. The fact that the erosion persists even with the steady-state passivating layer fully developed suggests that the surface is not completely passivating. Nevertheless, this study is the first of its kind to explore the erosion yields of POSS-containing polyimides that are exposed to hyperthermal atomic oxygen in a simulated LEO environment. And this initial study demonstrates an O-atom resistance for a POSS-containing polyimide (20 wt% POSS) that is comparable to the O-atom resistance of SiO2-coated Kapton, which is the current state of the art. Other formulations may yield hybrid POSS/polyimide materials with even more O-atom resistance without changing the basic functionality of the polyimide phase. Possible approaches are changing the bonding of POSS to the polymer chains, increasing the POSS loading, or improving the uniformity in the distribution of POSS throughout the polymer bulk.
Conclusion

The resistance of hybrid inorganic/organic polymers to hyperthermal atomic-oxygen attack in a simulated low-Earth orbital environment has been investigated by various surface analytical techniques. These hybrid polymers contain polyhedral oligomeric silsesquioxane (POSS, with silicon-oxygen stoichiometry Si$_2$O$_3$) nanoparticles that are chemically bound to Kapton-like polyimide chains through organic functional groups on the POSS particles. The results indicate that the POSS-containing polyimide formed a passivating layer, which largely resisted atomic-oxygen attack. Measurements of etch depth showed a dramatic reduction in the erosion yield of POSS polyimide versus that of Kapton H. The 20 wt% POSS polyimide sample exhibited erosion rates as low as ~1 percent those of Kapton H. Atomic Force Microscopy (AFM) images showed that the surface of the 0 wt% polyimide control sample became very rough with atomic oxygen exposure, while the 20 wt% POSS polyimide surface became much less rough. X-ray photoelectron spectroscopic (XPS) analysis tracked the evolution of the surface chemistry with increasing O-atom exposure fluence. With increasing exposure of the POSS polyimide, the organic carbon concentration at the surface decreased, and the surface silicon further oxidized from Si$_2$O$_3$ to SiO$_2$. All the data are consistent with an erosion mechanism in which the organic component of the surface erodes and the inorganic component oxidizes to SiO$_2$. A passivating layer containing SiO$_2$ apparently grows with time and becomes increasingly resistant to atomic oxygen attack. Although the passivation layer still allows a small amount of erosion to occur, these early results
indicate enormous promise for the use of POSS polyimide as a “drop-in” replacement for Kapton on spacecraft that operate in the LEO environment.
References


16. Theoretical calculations suggest that the reaction, \( \text{O}_2(\Delta_g) + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{CO} \), proceeds with a reasonably large cross section of \( \approx 2 \) a.u. at hyperthermal collision energies [G C Schatz, personal communication]. We have conducted a crossed-beams study of the reactions of our \( \text{O/O}_2 \) beam with \( \text{CH}_4 \), and, while we have observed products that are indicative of an \( \text{O}(^3P) \) reaction, such as \( \text{OH} \) and \( \text{OCH}_3 \), we have detected no \( \text{H}_2\text{O} \). Therefore, we conclude that there is no excited \( \text{O}_2(\Delta_g) \) in the hyperthermal beam and that the \( \text{O}_2 \) present is in its ground \( ^3\Sigma_u^- \) state.


BEAM-SURFACE SCATTERING STUDIES OF THE INDIVIDUAL AND COMBINED EFFECTS OF VUV RADIATION AND HYPERTHERMAL O, O₂, OR ARGON ATOMS ON FEP TEFLON® SURFACES

Introduction

Surfaces of spacecraft traveling in low Earth orbit (LEO) are exposed to an environment containing atomic oxygen, electromagnetic radiation, ions, electrons, and high-energy charge particles. Atomic oxygen and molecular nitrogen are the major constituents in the residual atmosphere at LEO altitudes,¹² and they collide with spacecraft surfaces at relative velocities of ~7.4 km s⁻¹.³ These high relative velocities lead to gas-surface collisions with many electron volts of collision energy in the center-of-mass reference frame. The energy associated with these hyperthermal collisions is in excess of many bond dissociation energies and may help promote materials degradation by allowing barriers to reaction or to collision-induced dissociation (CID) to be overcome. High fluxes of vacuum ultraviolet (VUV) radiation might contribute to the degradation of materials through various photochemical mechanisms. The VUV spectrum includes radiation with wavelengths below 200 nm, including the Lyman-α line of atomic hydrogen (121 nm).⁴⁻⁵ Fluorinated ethylene propylene (FEP) Teflon® (see Figure 4.1) is commonly used as a thermal blanketing material on space vehicles to provide protection from solar heating.⁴ Thermal blankets generally consist of a thin film (5 mils) of FEP Teflon® with a reflective silver coating (~0.1-0.2 µm thick) on one surface. After
exposure to the low-Earth-orbital environment, however, FEP Teflon® is susceptible to erosion and cracking, thereby reducing the effectiveness of the thermal control.

Various NASA missions, including the Long Duration Exposure Facility (LDEF) satellite and the Hubble Space Telescope (HST), have shown evidence of severe FEP Teflon® degradation after exposure in LEO.9-13 One of the functions of LDEF was to provide information on the long-term effects of the space environment on materials used for space applications. The LDEF satellite remained in space for 69 months and experienced one-half of a solar cycle. FEP Teflon® was placed in various locations aboard the LDEF satellite to explore the effects of specific environments. One sample was placed on the leading edge surface and therefore experienced a LEO environment consisting of O atoms, VUV light, N₂ molecules, and other constituents in the

Figure 4.1. Schematic representation of FEP (fluorinated ethylene propylene) Teflon®.
atmosphere. Another FEP Teflon® sample was placed on the trailing edge of the satellite so that the sample was exposed only to VUV radiation, but not O atoms or N₂ molecules. After the LDEF satellite was retrieved from space, the samples were examined by a variety of surface analysis techniques, such as atomic force microscopy (AFM). AFM images obtained from pristine FEP Teflon® and the samples exposed in various positions on LDEF had quite different surface topographies, indicating that the erosion mechanisms of FEP Teflon® may have been different on the samples placed on the leading and trailing edges of LDEF. Although it is known that the FEP Teflon® surfaces exhibit differing erosion mechanisms, the exact mechanisms have remained unknown.

Many theories have been proposed to explain the erosion and deterioration of the mechanical properties of FEP Teflon® in LEO. It has been reported that FEP Teflon® erodes under the combined exposure of VUV light and atomic oxygen, while the erosion by atomic oxygen alone is negligible.⁶⁻⁸ Gindulyte and coworkers¹⁴,¹⁵ supported this assertion by proposing (with the use of the ab-initio methods and density functional theory) that collisions with O(^3P) species in LEO have enough collision energy to degrade fluorocarbon materials, regardless of exposure to VUV radiation. On the contrary, Koontz et. al.⁶ reported results that appeared to demonstrate that FEP Teflon® showed little or no reactivity with atomic oxygen in the absence of VUV, but even low levels of VUV can alter the reactivity of the material with atomic oxygen. Skurat et. al.¹⁶ have suggested that it is only VUV light that is responsible for FEP Teflon® degradation in LEO. They have proposed a mechanism whereby VUV radiation breaks C–C and C–F bonds until smaller fragments of the chain exist and are formed and become volatile, thereby carrying mass away. A preliminary study on the gas-phase reaction of O(^3P) +
C₃F₈ \((E_{\text{coll}} \sim 5 \text{ eV})\) done in our laboratory showed no evidence of oxygen-containing products, indicating that a direct reaction with atomic oxygen is unlikely. This result is consistent with theoretical calculations by Troya and Schatz on the reaction of atomic oxygen with perfluororethane, where they observed very low reaction probabilities at collision energies below 6 eV.\(^{17}\) The mechanistic details of FEP Teflon\(^{®}\) erosion in LEO and in simulated LEO environments have been difficult to determine. Although several studies have added to our understanding of the role of VUV light and its synergistic effects with atomic oxygen (see, for example, Refs. 6-8, 16, 17-22), virtually nothing is known about the relative importance of CID. A recent quasiclassical trajectory (QCT) study of energy transfer and CID in hyperthermal Ar + CH₄ and Ar + CF₄ collisions has been done by Troya.\(^{23}\) The results indicate that the cross section of Ar + CF₄ collisions where enough energy is transferred into internal energy of the CF₄ molecule to break the C–F bond is almost one order of magnitude larger than the cross section to transfer energy above the dissociation limit of the CH₄. In addition, the QCT results indicate that fluorination of an alkane molecule greatly enhances the energy transfer from the translational energy of the Ar atom to internal modes of the alkane molecule. In this case, fluorinated hydrocarbons may be more susceptible to erosion though a CID mechanism than hydrogenated hydrocarbons. Another study by Troya et. al. on the interactions of Ar + C₂H₆ and C₂F₆, indicated that Ar can break C–C bonds much more easily than C–F or C–H bonds at collision energies that are accessible in LEO.\(^{24}\)

In order to develop an understanding of the erosion mechanisms of FEP Teflon\(^{®}\) in a LEO environment, we have conducted a beam-surface scattering experiment that probed products scattered from an FEP Teflon\(^{®}\) surface that was bombarded by various
combinations of hyperthermal O atoms, O₂ molecules, hyperthermal Ar atoms, and VUV light. The use of Ar to study hyperthermal collisions with FEP Teflon® provides for a model system that restricts the possible interactions to collisional processes only. This beam-surface scattering experiment is this first of its kind to separate the effects and identify volatile reaction or collisional products of hyperthermal atomic oxygen, VUV radiation, and CID on the surfaces of FEP Teflon®.

Experimental Details

The experiments were conducted with the use of a crossed-molecular beams apparatus, configured for gas-surface interactions. A laser detonation source was used to create hyperthermal beams of O, O₂, and Ar that were directed at an FEP Teflon® surface. A rotatable mass spectrometer detector identified volatile products that scattered from the surface as a function of the incident O, O₂, or Ar beam translational energy. Volatile products were also detected when VUV light continuously irradiated a FEP Teflon® surface. Finally, volatile products that emerged from the FEP Teflon® surface were monitored while a hyperthermal beam of O, O₂, or Ar was directed onto the simultaneously VUV-irradiated surface.

Preparation of FEP Teflon® Sample

One side of a 1-inch-diameter FEP Teflon® sample was chemically altered with a surface etchant (Tetraetch) and bonded to a 1-inch-diameter Si substrate with a thermally conductive, silver filled, adhesive (Ablebond 70-1). The adhesive was cured in air with a maximum curing temperature of 473 K. When mounted in the sample manipulator, the
backside of the silicon substrate was in contact with the metal surfaces that were kept in thermal equilibrium on the heated mount by resistive heating. It was very important to have the backside of the entire FEP Teflon® completely bonded to the silicon substrate so that thermal conductivity over the entire sample was achieved. After an initial overnight bakeout (up to 373 K) of the prepared sample, the temperature of the sample was held at 343 K throughout the experiment.

Vacuum Ultraviolet Light Irradiation

A 30 watt deuterium lamp (Hamamatsu) provided VUV radiation mainly in the wavelength range of 115-200 nm, with light extending to ~400 nm. Figure 4.2 is a schematic diagram that illustrates the position of the D₂ lamp in the apparatus. When investigating the effects of VUV irradiation alone on the surface of FEP Teflon®, the lamp was used without filtering and the distance between the lamp and the sample was 50 cm. Spectral and intensity information about the D₂ lamp was provided by Joyce Dever from NASA Glenn.²⁸ When the lamp was at this distance, the sample surface experienced an irradiance of ~3 suns. When the entire spectrum of the D₂ lamp was used, high background signals were detected from molecules desorbing from the surface walls of the apparatus and from scattered VUV light that entered the detector. While optically transparent in the visible region, FEP Teflon® absorbs strongly at 161 nm,⁵ which corresponds to a transition from the HOMO levels for the C-C and C-F bonds to a conduction band in the polymer. Therefore, for the experiments where beam-surface scattering was conducted in addition to VUV light exposure, the light was filtered. The
filter was a band-pass filter, with a transmission peak at 161 (±2.5) nm and a full width at half maximum of 20 nm. The filter was used to narrow the wavelength range and reduce the overall background in the chamber. In this configuration, the lamp was placed 12.7 cm from the surface of the sample with the entire sample exposed to the VUV light. The

Figure 4.2. Schematic diagram of the crossed molecular beams apparatus, configured for gas-surface scattering experiments showing the hyperthermal beam source, the target surface, the D₂ lamp, and the rotatable mass spectrometer detector.
filter transmitted ~12% of the total irradiance and therefore the sample surface experienced an irradiance of ~0.5 suns. Although the photon flux in these experiments was less than the irradiance of one sun, the filtered wavelength range of the lamp that corresponded to the maximum absorbance of the FEP Teflon® may be comparable to the effective photon flux in space. To investigate the effect of VUV light exposure alone on a pristine FEP Teflon® surface, the sample was irradiated with continuous VUV radiation and TOF distributions of the products that emerged from the surface were detected at a variety of \( C_nF_m \) fragment mass-to-charge ratios with the mass spectrometer.

Hyperthermal Gas-Surface Interactions

The gas-surface experiments were conducted with pulsed beams, operating at a repetition rate of 2 Hz and containing hyperthermal O, O\(_2\), or Ar atoms. The pressure in the main chamber was maintained at \(~1 \times 10^{-7}\) Torr throughout the experiment.

Figure 4.3 shows representative translational energy distributions of the narrowed (chopped) O and O\(_2\) beams used in these experiments. The translational energies of the O and O\(_2\) in the hyperthermal oxygen beam ranged from 4.5 to 6.3 eV and 9.0 to 12.6 eV, respectively. The atomic oxygen and molecular oxygen in the beams were in their ground electronic states, O(\(^3P\)) and O\(_2\)(\(^3\Sigma^-\)), respectively.\(^{29}\) The mole fraction of atomic oxygen in the beam was 50 to 80 percent, with high energy beams having a higher O atom mole fraction. A hyperthermal beam of Ar (Figure 4.3) was also created with the laser detonation source and was used to investigate the CID mechanism. The average translational energies of the Ar beam used in this experiment ranged from 7.6 to 12.7 eV.
The hyperthermal beam struck the FEP Teflon® target surface (placed ~95 cm from the apex of the nozzle) about 7 cm past the chopper wheel. The FEP Teflon® sample was mounted on a manipulator such that the surface normal was contained in the plane of rotation of the detector. The manipulator was positioned such that its rotation axis was coincident with the detector’s rotation axis, and this axis passed through the sample surface. The samples were thermally isolated, and the sample mount was electrically grounded. The temperature of the sample was held at 343 K throughout the experiment which was hot enough to keep the surface clean (i.e., gas-phase molecules in the apparatus did not “stick” to the surface) but below the glass transition point (~523 K).

Three pristine FEP Teflon® samples were used in these experiments and beam-surface scattering studies were conducted under the following conditions: 1) VUV light alone, 2) O/O₂ + FEP Teflon® then O/O₂ + VUV + FEP Teflon®, and 3) Ar + FEP Teflon® then Ar + VUV + FEP Teflon®.

Time-of-flight distributions of the scattered products from the surface were collected as a function of arrival time in the detector. When the hyperthermal oxygen beam was directed at the sample, inelastically scattered products were detected at mass-to-charge ratios \((m/z)\) of 16 (O⁺) and 32 (O₂⁺), and other products that exited the surface were detected at \(m/z = 19\) (F⁺), 47 (CFO⁺), 50 (CF₂⁺), and 69 (CF₃⁺), as a function of the translational energy of the incident beams. After obtaining TOF spectra from products that scattered from the surface after impingement of the hyperthermal O/O₂ beam, the D₂ lamp was turned on and TOF distributions were also collected with simultaneous exposure to VUV light and hyperthermal O/O₂ at the same mass-to-charge ratios. TOF
data for other C<sub>m</sub>F<sub>n</sub> fragments, as well as possible O-containing products, were investigated and collected.

For the hyperthermal Ar beam experiments, TOF distributions were collected for inelastically scattered products at \( m/z = 40 \) (Ar\(^+\)) and reactively scattered products at \( m/z = 31 \) (CF\(^+\)), 50 (CF\(_2^+\)), and 69 (CF\(_3^+\)) as a function of the translational energy of the incident Ar atoms.

After collecting TOF spectra for the collisionally dissociated products, TOF distributions of volatile products that formed after simultaneous exposure to VUV radiation and hyperthermal Ar atoms were collected. For both the hyperthermal O/O\(_2\) and Ar beams, the TOF signals were collected for 200 pulses for the inelastically scattered beams and 1000 pulses for the scattered products at each energy starting from low energy to high energy, then the direction was reversed and the process was repeated until four TOF distributions at each \( m/z \) and incident beam energy were collected. The TOF distributions for inelastically scattered products were thus accumulated for a total of 800 beam pulses each, and the TOF distributions for other products were accumulated for 4000 beam pulses each.
Figure 4.3. Translational energy distributions of O, O₂, and Ar beams selected with synchronized chopper wheel.
Results

VUV light alone

FEP Teflon® that was exposed to the unfiltered VUV light alone yielded volatile reaction products that were detected with a mass spectrometer (see Figure 4.4). The detected C_mF_n fragment with the highest intensity was the CF_3 product. However, dissociative ionization may cause the higher mass fragments to divide into a variety of lower mass fragments. It is therefore difficult to identify the parent ion signals. Evidence of signals detected at C_mF_n mass-to-charge ratios is indicative of a C–C bond.

Figure 4.4. Mass spectrum of volatile products detected when an FEP Teflon® surface was exposed to unfiltered D_2 lamp 50 cm away.
breakage mechanism that can occur by a photochemical process when the incident photon energy is ~7.7 eV.

\( \text{Ar} + \text{FEP Teflon}\)

Figure 4.5 shows representative TOF distributions for a variety of \( C_m F_n \) products that scattered from the surface when the incident angle, \( \theta_i \), and final angle, \( \theta_f \), were both 60° and with the highest beam energy used in these experiments (\( \langle E_i \rangle (\text{Ar}) = 12.7 \) eV). “Time zero” in these distributions corresponds to the time at which the Ar beam pulse struck the surface. The only detectable \( C_m F_n \) fragments were F, CF, CF\(_2\), and CF\(_3\). Because the signals detected at \( m/z = 19 \) (F\(^+\)) were quite weak, it was difficult to distinguish them from the overlapping signal coming from mass leakage from inelastically scattered Ar, which could be detected at Ar\(^{2+}\) (\( m/z = 20 \)). Comparison of the TOF distributions for \( m/z = 19, 31, \) and 50 shows that the shapes of the distributions have both hyperthermal and thermal components. The fast peak corresponds to products that leave the surface with hyperthermal translational energies because the incident Ar atoms interact with the surface on a time scale too short for thermal equilibrium to be reached. The slower part corresponds to thermal products that desorb from the surface at energies determined by a Maxwell-Boltzmann (MB) distribution at the surface temperature (343 K). The TOF distribution for \( m/z = 69 \) also appears to have two components, but the relative intensities of the peaks are quite different from the distributions for the other \( C_n F_m \) fragments. There is also a small hyperthermal component present in the TOF distributions, but there is a long, slow, tail that extends longer than the time predicted for a simple MB distribution at \( m/z = 69 \). This may be due to ionizer fragmentation of much
larger $C_mF_n$ fragments that are leaving the surface at thermal energies. Even though no obvious signals were detected at large (up to $m/z = 200$) $C_mF_n$ fragments, ionizer fragmentation is very likely, and thus the signal from the parent mass would be detected at a smaller fragment. Because there can be a variety of sizes of the parent molecules fragmenting to CF$_3$, the slow distribution is likely the result of many overlapping MB distributions and becomes quite broad.

Figure 4.5. Time-of-flight distributions of scattered $C_mF_n$ fragments following exposure of pristine FEP Teflon® surface to hyperthermal beam with $<E_i> = 12.6$ eV. The incident and detection angles were both 60° with respect to the surface normal.
The TOF distributions of CF, CF₂, and CF₃ produced by collisions with the five energy-selected Ar beams were converted to product flux distributions with the use of the relationship, \( \text{flux}(\theta) \propto \Sigma N(t)/t \). The product signals varied with incident beam energy in part because the flux in the corresponding Ar beam varied. Therefore, product signals were normalized to the intensities of the inelastically scattered Ar atoms from the corresponding incident beams. Figure 4.6 shows the relationship between the total integrated intensity of the product signals and the incident translational energy of the impinging Ar atoms. The lowest energy beam, with an average translational energy of 7.6 eV, did not produce any detectable CID products. The shapes of the curves through each set of data points are the same, indicating that a similar mechanism leads to the production of these fragments.

**Ar + VUV + FEP Teflon®**

The energy dependences of the CF₃ product with and without VUV light are compared in Figure 4.7. There is an obvious enhancement of the signal indicating that there is a synergistic effect between a CID mechanism and VUV light. The integrated CF₃ flux of the VUV-exposed FEP Teflon®, at the highest incident Ar beam energy, is ~8.5 times that of the integrated flux of the CF₃ product scattered from the surface that did not experience VUV light. The scattered CID product signal increased significantly when VUV light was present, suggesting that VUV light plays an important synergistic role in the mass loss of FEP Teflon® not only by creating reactive sites but also by producing relatively light fragments that can be dislodged from the surface by energetic gas-surface collisions.
TOF distributions of $m/z = 19$ (F$^+$), 47 (CFO$^+$), 50 (CF$_2^+$), and 69 (CF$_3^+$) were collected when the incident angle, $\theta_i$, and final angle, $\theta_f$, were both 60° with the highest beam energy used in these experiments ($<E_i>(O) = 6.4$ eV and $<E_i>(O_2) = 12.8$ eV).

The observed TOF distributions exhibit hyperthermal and thermal translational energy

O/O$_3$ + FEP Teflon$^\text{®}$

Figure 4.6. Energy dependences of Ar-induced CID products detected at CF$^+$, CF$_2^+$, and CF$_3^+$. 
distributions, as was seen before in the Ar + FEP Teflon® beam-surface scattering experiment. CID products were observed at \( m/z = 19, 50, \) and 69 when the beam energy had an average translational energy of at least ~4 eV (O atoms) and ~8 eV (O\(_2\) molecules). We assumed that the product is CF\(_3\), but due to ionizer fragmentation, signals were detected at \( m/z = 19 \) and 50. We were unable to distinguish an \( m/z = 31 \) (CF\(^+\)) signal from mass leakage from inelastically scattered O\(_2\) molecules. As previously shown in the Ar + FEP Teflon® experiment, there was an energy threshold for a CID

Figure 4.7. Energy dependence of Ar-induced CID product (CF\(_3\)) with and without exposure to D\(_2\) lamp placed 12.7 cm away. The incident and detection angles were both 60° with respect to the surface normal.
mechanism. These products were not observed until the impinging Ar atoms had an average translational energy of ~8 eV. Therefore, collisions of energetic O atoms (up to 6.4 eV) with the surface cannot induce CID from FEP Teflon®. Hence, in the O/O₂ + FEP Teflon® beam-surface scattering experiment, the O₂ molecules in the beam must be responsible for the release of products from the surface through CID. This conclusion is supported by the integrated flux of the CF₃ product as a function of the impinging beam energy, which has the same shape regardless of whether the impinging species are Ar atoms or O₂ molecules, as shown in Figure 4.8.

One obvious difference in the O/O₂ + FEP Teflon® beam-surface scattering experiment is the presence of an O-containing product detected when the incident O₂ molecules had translational energies of 12.6 eV (Figure 4.9). The weak, but still quite apparent, signal detected at m/z = 47 (CFO⁺) indicates that an O-atom reaction is occurring at the surface. The CFO⁺ signal was much weaker than the CₘFₙ product signals, but it still appears that energetic collisions of the ~12.6 eV O₂ species in the beam create radical sites at the surface with which the O atoms in the beam may react, but O atoms alone (with translational energies up to 6.4 eV) do not react to form volatile products.
When the surface of an FEP Teflon® sample was exposed to a hyperthermal beam of O/O₂ and simultaneous VUV irradiation, the CF O signal was enhanced, as seen in Figure 4.10. The scattered CID product was also enhanced in the present of VUV light. A comparison of the dependence of total integrated flux of the CID products as a function of the translational energy of the incident O₂ molecules with and without VUV light is shown in Figure 4.11. The flux of the CID product was normalized to the intensities of the corresponding O₂ beams. The integrated CF₃ flux of the VUV-exposed FEP Teflon®, at the highest incident Ar beam energy, is ~8.5 times that of the integrated flux of the CF₃
product scattered from the surface that did not experience VUV light. The scattered CID product signal increased significantly when VUV light was present, suggesting that VUV light plays an important synergistic role in the mass loss of FEP Teflon® not only by creating reactive sites but also by producing relatively light fragments that can be dislodged from the surface by energetic gas-surface collisions.

Figure 4.9. Time-of-flight distributions of O-containing products following exposure of pristine FEP Teflon® surface to hyperthermal O/O₂ beams with three sets of energies. The incident and detection angles were both 60° with respect to the surface normal.
Discussion

There are many processes that may lead to the ejection of CID products from an FEP Teflon® surface after a beam of hyperthermal Ar atoms or a hyperthermal beam containing O atoms and O2 molecules impinged on the surface. The rate at which these products leave the surface increases exponentially with incident translational energies above ~8 eV, regardless of the mass of the bombarding species. Vacuum ultraviolet radiation may break bonds at an FEP Teflon® surface through photodissociation. There
appeared to be an induction period of ~30 minutes after the lamp was turned on before the CmFn fragments were detected with the mass-spectrometer detector.

Photoinduced degradation and surface embrittlement due to VUV exposure alone has been observed in previous ground-based studies. The production of carbon-containing products leaving the surface is consistent with a type of mechanism where C–C bonds are broken at the surface by high energy photons that are absorbed by the material and then volatile, carbon-containing products leave the surface. In the proposed mechanism, the high energy photons (up to 11 eV) create volatile fragments by “chewing” away at the surface.

Figure 4.11. Energy dependence of O/O₂-induced CID product with and without exposure to D₂ lamp placed 12.7 cm away. The incident and detection angles were both 60° with respect to the surface normal.
surface until pieces of the polymer chain desorb from the surface. While the largest CₙFₙ fragment signal was detected at m/z = 69 (CF₃⁺), many other fragments were detected at larger mass-to-charge ratios (up to 200 amu) and at m/z = 31 (CF⁺) and 50 (CF₂⁺). While it should be assumed that a fraction of the signals detected at m/z = 31 and 50 may be ionizer fragments of the CF₃⁺ parent ion, they, and the signals present at larger CₙFₙ fragments, may either be ionizer fragments of even larger species (which were outside of the detection range for this apparatus) or volatile products that left the surface completely intact. The experiment did not have the sensitivity to distinguish between these possibilities. Similarly, the signal detected at m/z = 69 (CF₃⁺) may arise from –CF₃ groups desorbing from the surface after bond breakage from VUV irradiation and from the fragmentation during ionization of larger CₙFₙ fragments. Regardless, VUV light may degrade FEP Teflon® surfaces through a mechanism where high energy photons break bonds and produce fragments of the polymer which carry mass away from the surface.

As a model system for studying a CID mechanism, the hyperthermal interactions of Ar atoms with FEP Teflon® were investigated. The use of Ar atoms isolates the interactions only to collisional processes. The results suggest that when Ar atoms have translational energies greater than ~8 eV, volatile products may form and leave the surface. The product TOF distributions have a prominent thermal component suggesting that a large fraction of the CID products are in thermal equilibrium with the surface. The hyperthermal component of the TOF distributions is explained by CID products that exit the surface before the Ar atoms reach thermal equilibrium with the surface. Because it seems that both the hyperthermal and thermal signals have the same energy dependence,
they likely originate from the same process. The thermal CID products must come from directly-formed products which become trapped, and then desorb from the surface. The hyperthermal CID products, or those formed through a direct interaction, may be described in terms of a gas-phase process where an incident Ar atom interacts with a localized region on the surface. Both scenarios involve high-energy Ar atoms breaking bonds at the surface to allow C\textsubscript{m}F\textsubscript{n} fragments to become dislodged and carry mass away from the surface.

The QCT study on CID of Ar with methane and perfluoromethane reveals information about the threshold for CID in the c.m. reference frame.\textsuperscript{23} The dissociation energy for a C–F bond is 5.7 eV, and the calculated c.m. collision energy for Ar + CF\textsubscript{4} collisions that generate CF\textsubscript{4} molecules with internal energy above the C–F dissociation limit is ~6 eV. In the case of CID in collisions of Ar + CH\textsubscript{4}, the threshold for internal excitation of the CH\textsubscript{4} molecule above the C–H dissociation energy (4.8 eV) is ~7 eV. These results indicate that the probability of collision-induced dissociation in fluorinated alkanes may be much larger than that in hydrogenated alkanes, mainly because there is a high probability of transferring large amounts of energy in these collisions. While the theoretically calculated values for the threshold energy in the c.m. reference frame are lower than the experimentally observed incident translational energy threshold, the c.m. collision energy in the experiment is dependent on the size of the interaction region on the surface (i.e., the reduced mass of the system). In the case of gas-surface scattering, no all of the translational energy in the Ar or O\textsubscript{2} molecules would be expected to be available because the c.m. collision energy is dependent on the reduced mass of the
system and there are many degrees of freedom at the surface where the translational energy can be dispersed.

While the number density of Ar atoms present in LEO is only $10^{-5}$ that of the number density of O atoms, N$_2$ molecules have comparable number densities to O atoms in LEO and may have an important role in the degradation of FEP Teflon$^\text{®}$. At a typical spacecraft orbiting altitude of 300 km, the number density of N$_2$ is about one-tenth that of the number density of atomic oxygen. However, at lower LEO altitudes in the range of 100-300 km above the Earth, molecular nitrogen is as abundant at atomic oxygen (recall Figure 1.1). N$_2$ molecules are almost twice as heavy as O atoms and therefore the energy associated with collisions of N$_2$ with FEP Teflon$^\text{®}$ is almost twice as large. Consequently, while collisions of O atoms with spacecraft surfaces are equivalent to 4.5 – 5 eV O atoms striking the surface, energetic collisions of N$_2$ molecules are equivalent to, on average, ~7.9 eV N$_2$ molecules impinging on the surface, and the energy distribution can reach up to 10 eV. The experimental results presented in this thesis indicate that FEP Teflon$^\text{®}$ can degrade when species that possess ~8 eV or more of translational energy are directed onto the surface, regardless of the momentum of the species. A typical N$_2$ number density at an altitude of 200 km is on the order of $10^9$, which corresponds to a flux of approximately $10^{15}$ N$_2$ molecules cm$^{-2}$ s$^{-1}$ on ram surfaces of spacecraft when the average relative velocity between a spacecraft and ambient nitrogen molecules is ~7.4 km s$^{-1}$.

When the O/O$_2$ beam was directed at a pristine FEP Teflon$^\text{®}$ surface, we observed O-containing products, but only when the beam contained O atoms with 6.3 eV and O$_2$ molecules with ~12.6 eV of translational energy (see Figure 4.10). It thus appears that O
atoms alone do not react directly with FEP Teflon®, at least when they possess up to \( \leq 6.3 \text{ eV} \) of translational energy. This result is consistent with theoretical calculations by Troya and Schatz\(^{17}\) on the reactions of atomic oxygen with perfluoroethane, where they observed very low reaction probabilities at collision energies below 6 eV. We cannot ignore the possible role of \( \text{O}_2 \) molecules in the results shown in Figure 4.10, because the \( \text{O}_2 \) translational energy is twice that of atomic oxygen, leading to the possibility that collisions of \( \text{O}_2 \) could create reactive radical sites through collision-induced dissociation (CID). While a pure atomic oxygen beam (no molecular oxygen) is nearly impossible to create using the aforementioned laser detonation source, this study is the first of its kind to illustrate synergism between energetic collisions (greater than \( \sim 8 \text{ eV} \) incident translational energy) and atomic oxygen. These observations contradict previous work by Banks \textit{et. al.} where they observed degradation of FEP Teflon® when the surface was exposed to a plasma containing \textit{thermal} \( (0.04 \text{ eV}) \) atomic oxygen.\(^{15}\) While a plasma environment consists predominantly of ground-state, thermal O atoms, it also subjects sample surfaces to intense ultraviolet radiation and high energy ions.\(^{30}\) They have claimed that the O atoms went though a “tortuous path” which eliminated any ions and VUV light that was created in the plasma so that the surfaces experiment only thermal atomic oxygen. Their related quantum mechanical theoretical calculations estimated the activation energy for the chain-breaking reactions of \( \text{O}^{(3P)} \) with various \( \text{C}_m\text{F}_n \) mass fragments on a fluoropolymer chain is \( \sim 2.9–3.3 \text{ eV} \) in the c.m. reference frame, which, depending on the effective surface mass (i.e. the size of the localized region on the surface with which the O-atom interacts), may correspond to much larger incident translational energies, such as seen in our threshold of \( \sim 8 \text{ eV} \) for the incident translational
energy of the Ar atoms or O\textsubscript{2} molecules. However, from their experiments they observed FEP Teflon\textsuperscript{®} erosion and concluded that a high energy tail of atomic oxygen in their plasma might be responsible for erosion in FEP Teflon\textsuperscript{®}. Regardless, their plasma source has not been well-characterized and the electronic state and the concentration of ions and VUV light have not been quantified. Consequently, their results may be affected by the other components present in the plasma, and the degradation due to ground-state O atoms may not be well-represented. Recently, a beam-surface scattering study of atomic oxygen ($E_T \sim 0.1 \text{ eV}$) with semifluorinated SAMs has been conducted by Fairbrother, et. al.\textsuperscript{31} The only reaction products that were observed were at the film/substrate interface and not with C–F or C–C bonds in the chains, so they concluded that thermal O atoms do not react with semifluorinated SAMs. On the other hand, experiments in their laboratory on atomic oxygen impinging on alkanethiolate SAMs surfaces produced oxygen-containing reaction products from C–H or C–C bonds in the chains.

In both hyperthermal Ar and O/O\textsubscript{2} scattering from an FEP Teflon\textsuperscript{®} surface, the scattered product signals (CID and reactive) were greatly enhanced in the presence of simultaneous VUV irradiation. It appeared that an induction period of \sim 30 minutes was needed before significant enhancement (and stability) of the product signal was seen. This is in agreement with a previous study.\textsuperscript{16} However, after the lamp was turned on for 2-3 hours and then turned off, the intensity of the CID and reactive (with O/O\textsubscript{2} beams) product signals remained the same for at least three hours, even without VUV light irradiating the surface. That may mean that once FEP Teflon\textsuperscript{®} is exposed to VUV light in LEO for an extended period, the synergistic effect with CID with N\textsubscript{2} molecules or reaction with atomic oxygen may continue to be enhanced.
In the experiments described in this thesis, no O-containing product was observed with VUV light only. Small signals for O-containing products were observed for the O/O₂ + FEP Teflon® system, but only when the O₂ incident translational energy was ~12.6 eV, which may create radical site with which atomic oxygen may react. However, for the O/O₂ + VUV + FEP Teflon® system, the O-containing product signal when \( <E_i(O_2)> = 12.6 \text{ eV} \) was enhanced by more than a factor of 5. Therefore, it appears that if VUV light can create radical sites on the surface, atomic oxygen can react and the increase in the erosion rate with the addition of atomic oxygen is not negligible.

We have clearly shown that there is a synergistic effect between atomic oxygen and VUV light in the degradation of FEP Teflon®. We have also identified CID as a new degradation mechanism and have shown that it is also enhanced in the presence of VUV light and/or atomic oxygen. The relative importance of the synergistic effects has been difficult to determine based on our data. For instance, when scattered VUV light enters the detector, photoelectrons can be formed and will contribute to a background signal that makes it difficult, if not impossible, to distinguish between products that scatter from the surface. In the mechanism proposed by Skurat et al.,¹⁶ they suggest that FEP Teflon® undergoes erosion by VUV radiation that is not significantly influenced by hyperthermal atomic oxygen bombardment. While this is difficult for us to confirm or disprove in our experiments, it has been shown in previous space- and ground-based experiments that when FEP Teflon® is exposed to VUV light alone, an embrittled layer is formed, presumably, as the result of chain scission and subsequent cross-linkage.³²,³³ However, when FEP Teflon® was exposed to the space environment on the ram side of LDEF to VUV light, atomic oxygen, and molecular nitrogen, the surface was deeply etched, which
was quite different than that of the FEP Teflon® exposed to VUV only. Therefore, synergistic effects must be responsible for FEP Teflon® degradation. Ions have been suggested as another synergistic effect,\textsuperscript{34} which is a possibility (especially at high altitudes in LEO), but this scenario is not necessary to use as an explanation for FEP Teflon® degradation because we have clearly shown the synergistic effects between CID and VUV, atomic oxygen and VUV, and CID and atomic oxygen. In any case, the relative importance of each mechanism will most likely depend on the exact mission environment.

Conclusion

Molecular beam-surface scattering experiments on FEP Teflon® and provide insight into the mechanisms by which fluorocarbon materials erode in the low Earth orbital environment. Atomic oxygen, even with translational energies in the vicinity of 5 eV, is not expected to react with FEP Teflon® with high enough probability to account for the erosion of this material in LEO. Energetic collisions of N\textsubscript{2} may break bonds through CID, and VUV light may break bonds through photodissociation. While either of these processes alone has the potential to erode FEP Teflon®, the erosion rate will increase significantly if they are present together. Furthermore, the combination of atomic oxygen with CID and VUV light opens another erosion pathway: chemical reaction of atomic oxygen with reactive sites where bonds have been broken. The combination of O-atom flux, VUV flux, and nature and flux of energetic collisions will determine the details of the degradation mechanism and therefore the rate of FEP Teflon® erosion in low Earth
orbit. Other interactions that were not probed in our experiments would also be expected to contribute if they can lead to bond breakage in the polymer. Hence, the degradation mechanism will depend strongly on the exact mission environment.
References


28. Joyce Dever from NASA Glenn has used the same model of the D₂ lamp used in our experiments and had the lamp calibrate at NIST to determine the irradiance of the lamp and its comparison to the sun.


DYNAMICS OF BEAM-SURFACE SCATTERING OF HYPERTHERMAL O, O₂, OR ARGON WITH FLUORINATED SURFACES

Introduction

In gas-phase interactions, for three-atom system, A + BC, the following channels may be important at high collision energies:¹

\[
\begin{align*}
A + BC &\rightarrow A + BC \quad \text{(inelastic scattering)} \\
&\rightarrow AB + C \quad \text{(reactive scattering)} \\
&\rightarrow AC + B \quad \text{(reactive scattering)} \\
&\rightarrow A + B + C \quad \text{(collision-induced dissociation)}
\end{align*}
\]

When the center-of-mass collision energy is more than twice the dissociation energy of BC, it is difficult to form either stable AB or AC and the CID channel becomes important. Theoretical studies and statistical methods have modeled CID mechanisms in the gas-phase to complement experimental observations of CID.¹⁻³

CID mechanisms at surfaces have been observed previously with thermal collisions resulting in dissociative chemisorption and desorption and in thermal and hyperthermal collisions of ions with surfaces.⁴⁻⁷ There have been many studies of dissociative scattering of small polyatomic ions from single-crystal surfaces⁸,⁹ and models have been proposed to explain these processes.¹⁰,¹¹ For ion-surface scattering, two mechanisms have been proposed: (1) impulsive scattering in which translational-to-internal energy transfer occurs and (2) dissociation through an electron transfer process. In thermal collisions, the translational energy of the impinging molecules is insufficient in breaking bonds, so in this case, the observed dissociation is driven by electronic
processes close to the surface. However, at hyperthermal translational energies, momentum transfer from the impinging species to the surface can create CID products.\textsuperscript{12}

Dissociative scattering of CF\textsuperscript{+}, CF\textsubscript{2}\textsuperscript{+}, and CF\textsubscript{3}\textsuperscript{+} ions from liquid PFPE (perfluoropolyether) surfaces in the 0.1 – 5 KeV energy range has been studied in detail previously.\textsuperscript{13,14} It was shown that the ions dissociate through impulsive collisions, where the ions scatter off the –CF\textsubscript{3} groups in the PFPE in single collision events with the scattering dynamics resembling gas-phase scattering.\textsuperscript{14} A number of gas-surface studies have measured very detailed aspects of the dynamics of neutral noble gases and liquid surfaces,\textsuperscript{15-18} and hydrocarbon self-assembled monolayers (SAMs),\textsuperscript{19-21} and related theoretical simulations.\textsuperscript{22-25} The collision energy in the beams of rare gases employed in gas-surface experiments has been usually constrained to a maximum of \(\sim 0.8\) eV for the case of incident Ar atoms. The recent development of hyperthermal, neutral Ar beams\textsuperscript{26-28} has opened new avenues for the understanding of CID. As described in the previous chapter, beam-surface scattering experiments were conducted to probe products which scattered from FEP Teflon\textsuperscript{®} surfaces that were bombarded by various combinations of atomic and molecular oxygen, argon atoms, and VUV light. The results indicated that, while O atoms do not react with a pristine FEP Teflon\textsuperscript{®} surface, VUV light or highly energetic collisions of O\textsubscript{2} or Ar may break bonds and create radical sites where O atoms may react. In addition, these highly energetic collisions may break bonds at the surface and allow for non-reactive products to emerge from the surface in a collision-induced dissociation (CID) mechanism.

In order to investigate more thoroughly the dynamics of energetic collisions of O, O\textsubscript{2}, or Ar with FEP Teflon\textsuperscript{®} surfaces, hyperthermal oxygen and argon beams were
directed at an FEP Teflon® surface and time-of-flight and angular distributions of the scattered products were monitored as a function of incident beam energy and incident and final scattering angles. As shown in Chapter 4, the main scattered CID products were found at $m/z = 31$ (CF$^+$), 50 (CF$_2^+$), and 69 (CF$_3^+$), but their nearly identical energy dependences indicated that the primary neutral CID product is CF$_3$ which undergoes fragmentation in the electron-bombardment ionizer. Also, the incident energy dependence on the product scattered flux was similar for both incident O$_2$ and Ar beams. Therefore, the hyperthermal Ar beam was directed at the FEP Teflon® surface and signals detected at $m/z = 31$ (CF$^+$), 50 (CF$_2^+$), and 69 (CF$_3^+$) were monitored as a function of final scattering angle.

As the beam-surface scattering experiment was conducted, the pulsed hyperthermal beam impinged on the FEP Teflon® surface on the same location on the sample throughout the experiment. One concern is that the CID products are formed not because of single collision events where one high-energy collision breaks a bond(s) at the surface to create volatile CID products, but because many collisions are required to induce CID. To limit the scattering events to initial interactions (single collisions) only, a continuously refreshed liquid polyfluoropolyether (PFPE) surface was used as a model surface to understand the dynamics of initial hyperthermal O, O$_2$, or Ar interactions with a fluorocarbon surface.
Experimental Details

The experiments were performed with the crossed-molecular beams apparatus configured for beam-surface scattering studies that was described in detail in Chapter 2. A pulsed beam of Ar atoms produced in the laser detonation source was directed at an FEP Teflon® surface and a PFPE surface in separate experiments.

**FEP Teflon® Surface**

A hyperthermal Ar beam with a nominal energy of 12.7 eV was directed at an FEP Teflon® sample, which was prepared in the same way as described in Chapter 4, with an incident angle ($\theta_i$) of 60 degrees. Volatile products which exited the sample surface were detected by the rotatable quadrupole mass spectrometer detector, whose electron bombardment ionizer was 33.7 cm from the surface. Products were detected as a function of arrival time in the ionizer and exit angle with respect to the surface normal. For the results reported here, the arrival-time distributions (which are proportional to number density distributions) were converted to flux distributions and the flux was integrated to give total relative flux detected at a particular mass-to-charge ratio and detection angle. TOF distributions were collected at 18 detector angles from -10 degrees to 75 degrees in 5 degree increments. TOF distributions were accumulated for 4000 beam pulses at each final angle.

**Perfluoropolyether (PFPE) Surface**

The structure of PFPE (Krytox 1625) has a structural formula given by $\text{F[CF(CF$_3$)CF$_2$O]$_{27(\text{ave})}$CF$_2$CF$_3$.}$ PFPE is an inert liquid with a vapor pressure of $\sim 3 \times 10^{-11}$
Torr at 278 K. The PFPE sample was heated (343 K) and degassed under a rough vacuum for more than 24 hours before placing it in a container in the vacuum chamber. A continuously refreshed film was produced by a technique used in our lab previously. A polished stainless-steel wheel is rotated through the liquid reservoir held at 293 K. A 100-μm-thick film is formed by passing the wheel by a sapphire scraper. The wheel rotation rate was 0.25 Hz and the repetition rate of the pulsed beam was 2 Hz, so each beam pulse encountered a fresh PFPE surface. Figure 5.1 shows a schematic diagram of the liquid reservoir and the apparatus configured for beam-surface scattering. A synchronized chopper wheel was used to select a relatively narrow distribution of velocities from the overall beam pulse. The hyperthermal beams were directed at the surface of PFPE and scattered products were detected as a function of flight time to the detector, initial beam translational energy, and exit angle with respect to the surface normal. Relative intensities for each mass-to-charge ratio at a given detector angle and incident beam energy are derived from TOF distributions collected for a total of 2000 beam pulses. The angular distributions were determined by obtaining product flux as a function of final scattering angle. The angular range studied in this experiment was -10° to 80° with respect to the surface normal.
Results and Analysis

Dynamics of Beam-Surface Scattering from an FEP Teflon® Surface

Figure 5.2 shows the angular distributions of \( m/z = 31 \) (CF\(^+\) 50 (CF\(_2\)\(^+\) and 69 (CF\(_3\)\(^+\)) that scattered from the FEP Teflon\(^\circledR\) surface after a beam containing 12.7 eV Ar atoms impinged on the surface with an incident angle of 60°. The final scattering angles were from -10° to 80° with respect to the surface normal. All of the C\(_m\)F\(_n\) fragments have
similar angular distributions and with the maxima of the product flux at the specular angle. The TOF distributions for the CID products had hyperthermal and thermal components, but the signals were quite weak and it was difficult to distinguish between products that exited the surface with hyperthermal velocities and those which desorbed from the surface in thermal equilibrium from the surface. Therefore, the product angular distributions are product flux as a function of angle, where both the hyperthermal and thermal flux components were included in the flux determination. An angular dependence study of the scattered CID products when the O/O$_2$ beam impinged on an FEP Teflon® surface was not conducted for three main reasons: (1) CID product signals were weak when the O/O$_2$ beam was used and an investigation of the angular dependence would not be feasible, (2) from the previous chapter, we are confident that O$_2$ and Ar induce similar CID mechanisms, and (3) the only O-containing product (CFO) that was seen with the O/O$_2$ beam had very weak scattering signals even when $<E_i>(O_2) = 12.6$ eV, so an angular dependence of this scattered product was deemed too difficult for the current study.

Dynamics of Beam-Surface Scattering from PFPE Surface

The most probable interaction of hyperthermal Ar with the PFPE surface was inelastic scattering. Figure 5.3 shows TOF distributions of Ar atoms that scattered from the PFPE surface after impinging on the surface with an average incident translational energy of 12.7 eV and with an incident angle of 60°. These TOF distributions were collected at a variety of final angles (see above) and three are shown as representative
angles to discuss the scattering trend. The signals increase with larger final angles, but the shapes of the signals depend on the final angles. There are two obvious components in the TOF distributions; a sharp peak at fast arrival times to the detector and a broader peak at longer arrival times, corresponding to slower products. This trend has been observed many times before in gas-surface scattering experiments and can be explained by two mechanisms: direct inelastic scattering (IS) and trapping desorption (TD). The slower signal corresponds to Ar atoms which became “trapped” at the surface, reached thermal equilibrium with the surface, and then desorbed with a Maxwell-
Figure 5.3. Time-of-flight distributions (TOF) of inelastically scattered Ar atoms from PFPE with $<E_i> = 12.7$ eV. The open circles are the collected TOF distributions, the red lines are the Maxwell-Boltzmann (MB) fits to the thermal components, and the solid black lines are the hyperthermal component which was found by subtracting the MB distributions from the collected TOF distributions.
Boltzmann (MB) distribution of velocities. The difference of the overall TOF distributions (shown in Figure 5.3 as open circles) and the TD component (red line) is taken to be the hyperthermal component which corresponds to products that scatter directly without reaching thermal equilibrium with the surface. The TOF distributions were then converted to translational energy distributions at a particular scattering angle. Figure 5.4 shows the average translational energies of the hyperthermal CF$_3$ products scattered at each final angle as a function of final angle. As shown, the average final translational energy increases with final scattering angle for the hyperthermal products.

![Figure 5.4. Average final translational energies of hyperthermal CF$_3$ as a function of detector angle following impingement of an Ar beam at $\theta_i = 60^\circ$ with $<E_i> = 12.7$ eV on a continuously refreshed PFPE surface.](image-url)
Figure 5.5 shows arrival-time distributions of several volatile products that were formed when a hyperthermal Ar beam ($<E_i>$ = 12.7 eV) was directed at the continuously refreshed PFPE surface when the incident and detection angles were both 60° with respect to the surface normal. The signals in these distributions of $C_mF_n$ fragments confirm the existence of a CID mechanism under these conditions, and the CID products appear to be relatively low-mass fragments, which have mass-to-charge ratios of 69 amu or less. This observation is consistent with the CID products that scattered from the surface of FEP Teflon® after hyperthermal Ar atoms impinged upon the surface, with the shapes of these TOF distributions very similar to those of Ar inelastic scattering. The TOF distributions were therefore separated in the same manner as that used in the case of Ar inelastic scattering.

In the case of Ar scattering from an FEP Teflon® surface, the product signals detected at $m/z = 31$ (CF⁺) and 50 (CF₂⁺) were assumed to be ionizer fragments of the neutral CF₃ CID product. As further evidence for this conclusion, the thermal components of the TOF distributions were fit well with a MB distribution assuming that the product mass was 69 amu. A feature present in the TOF distribution collected at $m/z = 69$ (CF₃⁺) is the very broad peak at ~ 3 ms. This may be evidence for “evaporation” of larger molecular fragments of PFPE that may fragment during ionization, which has been observed previously in our lab for interactions of hyperthermal O atoms with squalane.³⁰,³¹ While a MB distribution of velocities could be used to explain this (and give an average molecular weight fragment), the analysis is quite complicated and ambiguous because of the large variety of masses of the fragments that would be
Figure 5.5. TOF distributions of scattered $C_mF_n$ fragments following exposure of continuously refreshed PFPE to hyperthermal Ar beam with $<E_i> = 12.7$ eV. The incident and detection angles were both 60° with respect to the surface normal. For the signals detected at $m/z = 31$ and 50, the MB distribution was assumed to be from the neutral CF$_3$ product.

Possible. However, an “average” mass of an “evaporative” product was determined to be $\sim 500$ amu.

Figures 5.6 and 5.7 show the dynamical behavior of the $C_mF_n$ product signals detected. Figure 5.6 shows the dependence of scattered product signal on incident Ar and O$_2$ translational energy. Figure 5.7 shows the angular distributions of the detected signals when the Ar beam had an average translational energy of 12.7 eV and impinged on the surface with an incident angle of 60° with respect to the surface normal. The energy dependence shows that a CID mechanism becomes important when the incident beam
energy is greater than ~8 eV, which is similar to the energy dependence of CID when the target surface was FEP Teflon®. The angular distributions have two components: (1) thermal products whose angular distributions resemble a cosine distribution of intensities about the surface normal and (2) hyperthermal products which have angular distributions with maxima near the specular angle, which are far from a cosine distribution. The similar angular and energy dependencies of these signals is yet another indication that the primary neutral CID product is CF₃ which undergoes fragmentation in the electron-bombardment ionizer.

Figure 5.8 shows the dynamical behavior for the inelastically scattered Ar atoms from the PFPE surface. Figure 5.8a shows the product angular dependence and Figure 5.8b shows the energy and flux distributions. The hyperthermal component has maxima near the specular angle, with most of the Ar atoms scattering from the surface with very little change in translational energy.

The energy and flux distributions of the CF₃ CID product [collected at m/z = 31 (CF⁺) and 50 (CF₂⁺)] are shown in Figure 5.9. Both thermal and hyperthermal products are included in these distributions. The hyperthermal product angular distributions have maxima near the specular angle while the thermal products follow a cos θₑ distribution. The distributions are similar for both products and indicate, once again, that the distributions obtained are ionizer fragments of the primary CF₃ product, and not formed directly after hyperthermal Ar atoms impinged on the surface.
Figure 5.6. Energy dependence of CID products with incident Ar (top) and O/O$_2$ beams (bottom) impinging from continuously refreshed PFPE surface. The incident and detections angles were both 60° with respect to the surface normal.
Figure 5.7. Angular distributions of Ar-induced CID products detected at CF\(^+.\) CF\(_2^+.\) and CF\(_3^+.\) The open circles represent the Ar atoms which scattered from the surface with hyperthermal velocities and the solid circles represent those which desorbed with thermal velocities.
Figure 5.8. a) Angular distribution and b) energy and flux distributions for inelastically scattered Ar when $<E_i> = 12.7 \text{ eV}$ The open circles in a) are the Ar atoms which scattered from the surface with hyperthermal velocities and the solid circles are those which desorbed with thermal velocities.
Figure 5.9. Energy and flux distributions of Ar-induced CID products detected at CF\(^+\) and CF\(_2\)\(^+\)
In the case of both fluorinated surfaces examined in this study (FEP Teflon® and PFPE), products emerged from the surface when a hyperthermal O₂ or Ar beam with at least ~8 eV of translational energy impinged on the surface. These products were formed in a CID mechanism that was evident by the TOF distributions collected at a variety of CₘFₙ fragments. While product signals were detected at a variety of CₘFₙ fragments, m/z = 31(CF⁺), 50 (CF₂⁺) and 69 (CF₃⁺) had very similar dynamical behaviors, including product angular and energy dependencies, and therefore the signals detected at m/z = 31 and 50 were assumed to be the result of fragmentation of the parent ion, CF₃⁺, in the ionizer. A CID mechanism may occur even under a single collision, as demonstrated by the formation of CID products when hyperthermal Ar or O₂ impinged on a continuously refreshed PFPE liquid surface. The TOF distributions for the CID products that emerged from the PFPE liquid surface has two distinct features: one sharply peaked component at fast flight times corresponding to products that emerged from the surface with hyperthermal velocities and one slower, broader feature corresponding to products that were in thermal equilibrium with the surface and desorbed with a Maxwell-Boltzmann distribution of velocities. The relative fraction of hyperthermal products increased dramatically when the incident Ar-atom or O₂-molecule translational energy increased. Also, at a fixed incident scattering angle, the fraction of hyperthermal products to thermal products was highest near the specular angle. The thermal CID products must come from directly formed products which become trapped on the surface, and then desorb from the surface. Because the incident energy threshold to form CID products is ~8 eV, the
thermal CID products cannot originate from trapped Ar or O₂ molecules that interact with the surface. The hyperthermal CID products, or those formed through a direct interaction, may be described in terms of a gas-phase process where an incident Ar or O₂ molecule interacts with a localized region on the surface.

While it has been determined that O atoms do not react with a pristine FEP Teflon® surface, VUV light or highly energetic collisions of O₂ or Ar may break bonds and create radical sites where O atoms may react, as shown in Chapter 4. The signals detected at \( m/z = 47 \) (CFO⁺) are the result of an O-atom (or possibly an O₂ molecule) reacting with a radical site present on the FEP Teflon® surface that was formed either after a higher energy O₂ molecule or VUV radiation broke a bond (or bonds) at the surface. This O-containing product was only obvious when the incident O₂ beam energy was \( \sim 12.6 \) eV.

When the target fluorocarbon surface was PFPE, a very obvious signal was detected at \( m/z = 47 \) (CFO⁺) when a hyperthermal argon beam was used. The previous analysis of the reaction of atomic oxygen with a radical site present on the surface does not apply here, however, as there was no atomic oxygen present in the hyperthermal beam and the continuously refreshed PFPE surface would not form the same type of exposed radical sites after hyperthermal Ar atoms impinged on the surface as in the FEP Teflon® surface. But, unlike in the FEP Teflon®, the structure of PFPE contains O atoms which must be responsible for the observable signal at this mass-to-charge ratio. The structure and composition of the PFPE surface created in this method has been the subject of many extensive studies. There is experimental support from beam-surface scattering experiments of noble gas atoms from a PFPE surface, with much lower
incident translational energies than hyperthermal, that the collisions are hard-sphere-like with the surface covered by protruding –CF_n (n=1-3) groups.^{16,29} Cooks and co-workers^{35} conducted reactive ion scattering experiments which suggested scattering from a surface covered by –F and –CF_3 groups. Also, angle-resolved photoelectron spectroscopies (ARPES) measurements^{36-38} illustrate a PFPE surface that is predominantly composed of –CF_3 groups. All of these experiments lead to the conclusion that a surface structure of PFPE surface created in this manner is one in which the O atoms lie beneath the topmost layer and are shielded by the –CF_n groups. The theory is that the molecule rearranges itself by forming the outermost layer of the liquid with the CF_3 side- and end-groups. One of the main reasons that PFPE was chosen for the current experiments described in this thesis is while PFPE contains atomic oxygen (and FEP Teflon® does not), the presence would be negligible because it would not be on the outermost layer of the surface. But in the experiments presented herein, an oxygen-containing product was formed after hyperthermal Ar atoms impinged on the surface, which may contradict the theory that the oxygen atoms present on PFPE are completely buried under the outermost layer. However, further analysis of the ARPES measurements of the PFPE surface indeed show a presence of O (1s) at the surface of PFPE, but at a much lower concentration than the -CF_n groups.^{37,38} It has been suggested that below 100 eV, an ion beam samples only the first atom layer and in ARPES experiments the electrons, with about 1000 eV of kinetic energy, have an escape depth of about 30-60 angstroms in organic materials.^{38} Therefore, the O atoms may be buried only a few angstroms beneath the surface. The experiments described in this thesis are the
only experiments performed to this date where a hyperthermal, *neutral* species impinged upon a PFPE surface.

Further inspection of the TOF spectrum collected for the CFO product reveals many different features. Just as in the case of inelastically-scattered Ar and the CID products, there is a thermal component to the distribution that matches well the distribution of CFO products exiting the surface with a MB distribution of velocities determined by the surface temperature and the product mass. There is also a broader, even slower peak present in the TOF distribution which could be explained by assuming that the signal detected at $m/z = 47$ is an ionizer fragment of a larger parent ion that exits the surface with a much slower MB distribution of velocities. This may be caused by the presence of much larger fragments of PFPE “evaporating” and then fragmenting in the electron-bombardment ionizer to $m/z = 47$ (CFO$^+$). This peak would be difficult to fit by assuming that only a single parent ion is responsible for this signal because many different sizes of evaporative products may fragment to this product. This is very similar to the large, slow signal detected at $m/z = 69$ (CF$_3^+$).

**Conclusion**

The dynamics of beam-surface scattering studies of hyperthermal oxygen and argon interactions with fluorinated surfaces have been investigated. Pulsed beams of Ar atoms and O/O$_2$ molecules were directed on FEP Teflon® and continuously refreshed liquid PFPE surfaces and volatile products were detected with a rotatable mass spectrometer detector as a function of incident beam translational energy, incident angle,
and final scattering angle. While the most probably interaction is inelastic scattering, collision-induced dissociation can occur to eject CF$_3$ molecules from the surface. The time-of-flight distributions of both inelastically scattered and CID products show evidence of hyperthermal and thermal interaction channels. Gas-phase-like interactions can lead to CID products leaving the surface with hyperthermal translational energies. Thermal CID products arise from direct dissociation followed by trapping at the surface. Once the product reaches thermal equilibrium with the surface, it may desorb with a MB distribution of translational energies. Therefore, the first step in creating volatile CID products is a direct dissociation to create CF$_3$, which can exit the surface with hyperthermal or thermal translational energies.
References


CROSSED-BEAMS STUDY OF THE DYNAMICS OF HYPERTHERMAL COLLISIONS BETWEEN AR AND ETHANE

Introduction

Collisional energy transfer has long been of interest to the molecular dynamics community. During the last two decades, much of the effort that has driven the understanding of collisional energy transfer has been devoted to the characterization of the mechanisms whereby a highly vibrationally excited molecule loses energy in collisions with a room temperature bath gas.\(^1\)\(^2\) Most of the experiments and simulations have used noble gases as collisional partners, because their closed-shell nature prevents reactions that would complicate the examination of energy transfer. The gas-phase organic molecules most commonly used in these experiments are aromatic hydrocarbons such as benzene, perfluorobenzene, toluene, azulene, and pyrazine.\(^3\)\(^-\)\(^{16}\) Classical trajectory calculations have often accompanied experiments in order to aid in the understanding of the microscopic mechanisms of energy transfer.\(^17\)\(^-\)\(^{27}\) Statistical theories\(^28\)\(^,\)\(^{29}\) and approximate quantum scattering calculations\(^30\)\(^,\)\(^{31}\) have also been used to model collisional energy transfer in such systems. (For a detailed review of theory and experiments up to 1995, see Refs. 32 and 33.) Additional theoretical research on collisional energy transfer involving highly vibrationally excited gas-phase molecules with Ar include studies of Ar + propane,\(^34\) Ar + water,\(^35\) and Ar + fullerenes.\(^36\)

This wealth of research on gas-phase collisional energy transfer has recently been complemented by a number of gas-surface studies involving noble gases and condensed-
phase hydrocarbons. Nathanson and coworkers characterized experimentally the
dynamics of collisions of molecules and rare-gas atoms with liquid surfaces,\textsuperscript{37-40} whereas
Sibener and coworkers\textsuperscript{41,42} and Morris and coworkers\textsuperscript{43-47} have measured very detailed
aspects of the dynamics of rare-gas collisions with hydrocarbon self-assembled
monolayers. Most of the simulations of rare-gas scattering on self-assembled monolayers
have been conducted by Hase and coworkers.\textsuperscript{48-51} We have also studied inelastic
scattering of ground-state atomic oxygen, O(\textsuperscript{3}P), on liquid hydrocarbon surfaces\textsuperscript{52-54} and
hydrocarbon self-assembled monolayers.\textsuperscript{55}

A distinction between these gas-surface experiments and the gas-phase experiments mentioned above is the source of initial excitation. Gas-phase organic molecules have been prepared with high internal excitation by absorption of light. On the other hand, in gas-surface experiments the total energy available comes from the collision energy of the atoms or molecules that strike the hydrocarbon surface. While it has been possible to introduce large amounts of energy (up to \(\sim 50,000\) cm\(^{-1}\) or \(\sim 6.2\) eV) in a gas-phase molecule by laser excitation, the collision energy in the beams of rare gases employed in gas-surface experiments has been usually constrained to a maximum of about \(\sim 0.8\) eV (for the case of incident Ar atoms).

The recent development of hyperthermal Ar beams\textsuperscript{56-58} has opened new avenues for the understanding of collisional energy transfer. In this chapter, a study of collisional energy transfer will be presented, making use of a hyperthermal Ar beam in experiments whose interpretation is augmented with molecular dynamics simulations. The novelty of this study is that by crossing the Ar beam with a gas-phase hydrocarbon (ethane) beam, we can examine energy transfer from initial translation to internal excitation of the target
gas-phase hydrocarbon molecule \((T \rightarrow V', R')\), thereby complementing earlier work on energy transfer from vibrational degrees of freedom to relative motion of the colliding partners and rotation of the initially excited molecule \((V \rightarrow T', R')\).

Aside from its importance to the fundamentals of collisional energy transfer, the present work is important to understanding hyperthermal collisions on and around space vehicles that travel through the upper atmosphere. Atomic oxygen and molecular nitrogen in the residual atmosphere collide with spacecraft surfaces and exhaust streams at relative velocities of \(\sim 7.8 \text{ km s}^{-1}\). These high relative velocities lead to gas-surface and gas-phase collisions with many electron volts of collision energy in the center-of-mass reference frame.\(^{52,59}\) The energy associated with these hyperthermal collisions is in excess of many bond dissociation energies and may help promote materials degradation through collision-induced dissociation or reaction.\(^{56,57}\) And in gas-phase hyperthermal collisions, inelastic energy transfer may lead to highly excited products which can radiate and contribute to the signature of an exhaust stream.\(^{60,61}\) The number density of Ar at 100 km altitude is about two orders of magnitude smaller than that of atomic oxygen or molecular nitrogen. However, the use of Ar to study energy transfer in hyperthermal collisions with ethane provides for a model system that restricts the possible interactions to elastic and inelastic scattering (in the range of collision energies explored in this work).
Experimental Details

The experiments were performed with the use of a crossed-molecular beams apparatus equipped with a fast-atom beam source. A pulsed hyperthermal Ar beam (operating at a repetition rate of 2 Hz) was created by a laser detonation source that is based on an original design by Physical Sciences, Inc. The Ar beam passed through a 1.0-cm-diameter aperture into a differential pumping region and then into the main scattering chamber through a 2.5-cm-diameter collimating aperture located 96 cm from the apex of the conical nozzle. A synchronized chopper wheel, located ~98 cm from the nozzle, was used to select a narrow portion of the overall beam pulse. Nominal velocities selected were in the range 5200 – 7500 m s\(^{-1}\). The velocity widths of the beams were dependent on the average velocity of the pulse that passed through the chopper wheel, the wheel rotation rate (400 Hz), the wheel diameter (17.8 cm), and the width of the slots in the wheel (1.5 mm). The velocity widths (full width at half maximum) of the narrowed beams varied from ~180 m s\(^{-1}\) to ~340 m s\(^{-1}\), with beams of higher velocity having broader velocity distributions. The Ar beam was crossed at a 90° intersection angle by a pulsed beam of ethane molecules, produced by a supersonic expansion through a pulsed valve. The ethane beam passed through a 7-mm-diameter skimmer and a 1.2-mm-diameter aperture before crossing the Ar beam. The crossing region of the two beams was 99 cm from the apex of the conical nozzle of the Ar source and 12 cm from orifice of the ethane pulsed valve source. A rotatable mass spectrometer detector, with an electron-impact ionizer, a quadrupole mass filter, and a Daly-type ion counter, was used to characterize the Ar beams and monitor the products that scattered inelastically from the
crossing region of the two beams. The distance from the crossing region to the ionizer was 33.7 cm. Number density distributions, \( N(t) \), [also known as time-of-flight (TOF) distributions] for scattered species were collected as a function of their arrival time at the ionizer of the detector. TOF distributions collected at different detector angles were integrated to give laboratory angular distributions, \( N(\Theta) \).

The laboratory angle, \( \Theta \), is defined with respect to the direction of the hyperthermal Ar beam in the laboratory, with \( \Theta = 0^\circ \) corresponding to the direction of the Ar beam and the positive rotation direction toward the ethane beam.

The hyperthermal Ar beam was characterized by collecting TOF distributions of Ar as a function of the flight time from the nozzle apex to the ionizer, with the detector aligned along the hyperthermal beam axis. These number density distributions of the Ar beam have allowed us to derive translational energy distributions, \( P(E) \), for the three Ar beams used in the experiments. Average Ar translational energies were 5.7 eV, 7.6 eV, and 11.6 eV.

The ethane beam velocity was estimated to be 800 m s\(^{-1}\) based on the average mass of the beam and the nozzle temperature (~298 K).\(^6^6\) The validity of this estimated velocity was confirmed in the analysis by noting that the average velocities of scattered products were constant in the center-of-mass reference frame. The velocity width of the ethane beam was not considered in these experiments, because the velocity of the Ar beam was an order of magnitude higher and the spread in Ar velocities was a large fraction of the velocity of the ethane beam. The velocity width of the Ar beam thus dominated the distribution of Ar-ethane collision energies.
Figure 6.1 shows translational energy distributions for the narrowed hyperthermal Ar beams used in the experiments. The nominal center-of-mass collision energy \( E_{\text{coll}} \) for Ar + ethane collisions is shown above the distribution for each beam.

Figure 6.1 shows translational energy distributions for the narrowed Ar beams. The collision energies in the center-of-mass (c.m.) reference frame were derived from the velocity distribution of the three Ar beams selected and the nominal velocity of the ethane beam. The average experimental collision energies were 2.6 eV, 3.3 eV, and 5.0 eV.

The experiments focused on ethane molecules that scattered backward with respect to their initial direction (in the c.m. frame) after colliding with Ar atoms. The range of laboratory detection angles accessible in the experiments was \(+5^\circ\) to \(+50^\circ\). TOF distributions of ethane were collected at increments of \(5^\circ\) in this range. The electron impact ionization of ethane molecules produced ionizer fragments which were observed
at mass-to-charge ratios ($m/z$) of 30 ($C_2H_6^+$), 29 ($C_2H_5^+$), 28 ($C_2H_4^+$), 27 ($C_2H_3^+$), and 15 ($CH_3^+$). Internal excitation of the inelastically scattered molecules altered the fragmentation pattern from that of room temperature ethane (see Figure 6.2), but the dominant mass fragment remained $m/z = 28$. We thus collected laboratory TOF distributions for scattered ethane at this mass-to-charge ratio. For each of the three c.m. collision energies, TOF distributions were accumulated for 500 beam pulses at the ten laboratory detector angles, starting with $5^\circ$ and going up to $50^\circ$. Then the angular direction was reversed, and the cycle was repeated until a total of four TOF distributions had been collected for each angle. The four distributions were summed to produce TOF distributions that were accumulated for a total of 2000 beam pulses. Laboratory angular distributions were obtained by integrating the TOF distributions for each of the ten laboratory angles. The scattered flux of ethane varied by less than a factor of two over the entire laboratory angular range. At a “middle” laboratory angle of $25^\circ$, the integrated count rates for $m/z = 28$ were $4.65 \times 10^5$, $10.2 \times 10^5$, and $3.66 \times 10^5$ counts s$^{-1}$, for c.m. collision energies of 2.6, 3.3, and 5.0 eV, respectively.

Results

Representative TOF and angular distributions for scattered $C_2H_6$ are shown in Figures 6.3 and 6.4, respectively. Time zero in the TOF distributions represents the time at which the peak intensity of the Ar pulse crossed the ethane beam. The duration of the interaction between n Ar atoms and ethane molecules was determined by the temporal width of the Ar beam pulse, which was ~15 µs (full width at half maximum) at the beam
Figure 6.2. Comparison of the ionizer fragmentation pattern of room temperature ethane (cross-hatched bars) and the fragmentation pattern of inelastically scattered ethane (solid bars).
Figure 6.3. Representative time-of-flight distributions of ethane scattered from Ar. The circles correspond to the experimental data and the solid lines are the forward convolution fits to the data.
crossing region. From the laboratory TOF and angular distributions, c.m. translational energy and angular distributions were derived by a forward convolution method.\textsuperscript{67-69} In this method, the c.m. scattered flux per unit solid angle, $I_{\text{cm}}(E, \theta)$, is typically assumed to be separable into the product of two functions: a c.m. translational energy distribution, $P(E)$, and a c.m. angular distribution, $T(\theta)$, where $E$ is the total product translational energy and $\theta$ is the c.m. scattering angle. Trial $P(E)$ and $T(\theta)$ distributions are iteratively adjusted until optimum fits to all laboratory distributions are obtained. Uncertainties in the derived $P(E)$ and $T(\theta)$ distributions are determined by observing the maximum variation in these distributions that can still produce calculated laboratory TOF and angular distributions acceptably well. In order to allow for easy manipulation of the $P(E)$ and $T(\theta)$ distributions, parametrized functions are commonly used. The $P(E)$ distributions were based on the RRK form.\textsuperscript{69} An eleven-term Legendre polynomial function, with adjustable weighting of each of the polynomial terms, was used to describe the $T(\theta)$ distribution.

Best-fit c.m. translational energy and angular distributions are shown in Figure 6.6 and 6.7, respectively. For Ar-ethane collisions at all three c.m. collision energies investigated, the peak of the translational energy distributions of the inelastically scattered products is ~84-91 percent of the collision energy. The angular distributions show that the scattered flux of C$_2$H$_6$ varied only slightly from c.m. angles of 180\degree (directly backward) to 80\degree (sideways).
Figure 6.4. Laboratory angular distributions for scattered ethane. The symbols are obtained by integrating time-of-flight distributions shown in Figure 6.3, and the dotted lines are derived from the forward convolution of the best-fit c.m. translational energy and angular distributions (see Figures 6.5 and 6.7.)
An example of a Newton diagram for collisions of Ar atoms and ethane molecules with $E_{\text{coll}} = 3.3$ eV is shown in Figure 6.5. This diagram shows recoil velocities for elastically scattered ethane (solid circle) and for inelastically scattered ethane when 85 percent of the collision energy goes into translation (dashed circle). The shaded region shown on the Newton diagram indicates the range of laboratory angles used for the experiment. As can be seen, the laboratory detection angles are primarily sensitive to ethane molecules that scatter into the backward hemisphere in the c.m. frame – i.e., opposite to their original direction, or parallel to the direction of the incident Ar atoms.

![Newton Diagram for collisions of Ar + ethane at $E_{\text{coll}} = 3.3$ eV](image)

Figure 6.5. Newton Diagram for collisions of Ar + ethane at $E_{\text{coll}} = 3.3$ eV, where Ar has a velocity of 6050 m s$^{-1}$ and the ethane beam velocity is 800 m s$^{-1}$. The shaded region indicates the range of laboratory angles examined. The larger, solid circle represents the recoil velocities of elastically scattered ethane. The smaller, dashed circle represents the recoil velocities of scattered ethane when 85% of the collision energy goes into translation.
Discussion: Comparison of Experiment and Theory

Figure 6.6 compares experimental and calculated product translational energy distributions for $E_{\text{coll}} = 2.6$, 3.3 and 5.0 eV. For the two lower collision energies explored, the peaks of the calculated and experimental distributions overlap and the widths of the distributions agree, within the experimental error bars, which are ±0.1 eV.

Figure 6.6. Center-of-mass translational energy distributions derived from experiment (solid curves) and from theoretical calculations (dotted curves).
However, when $E_{\text{coll}} = 5.0$ eV the agreement is not quite quantitative. The calculated distribution is shifted to lower translational energies and is significantly broader than the experimental distribution.

There are several reasons why the agreement between theory and experiment may diverge as the collision energy increases. Higher collision energies involve regions of the surface that might not be as well calibrated as those at lower energy. Errors in both the inter- and intra-molecular terms used in the calculations are possible, as is the QM/MM separation into intramolecular and intermolecular potentials. Although their intermolecular potential seems well calibrated, it should be noted that their calculations span a very large range of energies which makes it difficult to generate an accurate fit of the multidimensional potential energy surface. So it is possible that the excessively larger energy transfer observed in the calculations comes from a too steep intermolecular potential at higher energies. Intermolecular potential fitting issues have been encountered numerous times in earlier calculations.\textsuperscript{70}

Regarding angular distributions, there is agreement between the trends seen in the experiments (Figure 6.7 top) and in the calculations (Figure 6.7 bottom). The backward-hemisphere angular distributions are rather isotropic, and the cross sections decrease for increasing collision energy in both theory and experiment.

Overall, there is consistent agreement between theory and experiment in both angular and translational energy distributions. For large collision energies, the calculations seem to overestimate the energy transfer to ethane, and this error seems to be tied to inaccuracies in the potential energy surface.
Figure 6.7. Experimental (top) and theoretical (bottom) center-of-mass angular distributions of relative flux for ethane scattered in the backward hemisphere.
Dependence of Energy Transfer on Collision Geometry

Here we focus our attention on describing the mechanisms by which large amounts of energy are transferred from reagent translational energy to product vibrational energy in hyperthermal collisions of Ar with ethane. Following an earlier convention, Prof. George Schatz and Prof. Diego Troya have performed an analysis of the geometry of the collisions at the inner turning point of each trajectory. This turning point is the point at which the distance from Ar to the ethane molecule center of mass (which we call RSH hereafter) reaches a global minimum. To gain additional insight the angle formed between the RSH vector (the vector connecting Ar with the center of mass of ethane) and a vector which lies along the the C-C internuclear axis (we refer to this angle as ARSH, hereafter) was examined. Figure 6.8 displays the probability distributions of RSH [Figure 6.8(a)] and ARSH [Figure 6.8(b)] for trajectories yielding backward hemisphere scattering at $E_{\text{coll}} = 6.6$ eV and for different amounts of vibrational excitation of the ethane product. It should be noted that the distributions of ARSH are symmetric with respect to 90 degrees (perpendicular approach of Ar to the C-C axis) as a result of the symmetry of ethane (i.e., approaches to one of the CH$_3$ moieties are symmetrically equivalent to approaches to the other moiety).

We distinguish three different general approaches that lead to three different degrees of vibrational excitation. The trajectories that yield ethane with a vibrational energy below 0.25 eV show a peak in the RSH distributions at large values (~5 a.u.) and peaks in the ARSH distributions at 0 and 180°. These trajectories correspond to approach of Ar to ethane in which collinear Ar-C-C arrangements are explored in the vicinity of
Figure 6.8. (a) Probability distributions for the distance between Ar and the center of mass of ethane –RSH at the trajectories’ inner turning point. (b) Probability distributions for the angle formed between the RSH distance and the C–C axis –ARSH at the turning point of the trajectories. The calculations pertain to backward hemisphere scattering of ethane in hyperthermal Ar + ethane collisions at $E_{\text{coll}} = 6.6$ eV.
turning point. Such “head-on” collisions hinder energy transfer from initial translation to product vibration. Trajectories in which ethane is produced with vibrational energy in the 0.25-1.0 eV range have an RSH distribution that peaks at smaller values (~3.8 a.u.) and an ARSH distribution that peaks at 90°. Approaches in which Ar comes close to the center of mass of ethane with ARSH angles close to 90° at the turning point are those in which Ar penetrates the ethane potential perpendicularly to the C-C axis. Therefore, it can be inferred that “side-on” collisions promote vibrational excitation to a larger extent than head-on collisions do. The largest amount of energy transfer is produced in trajectories with turning points at RSH values near 4.75 a.u. and ARSH angles of about 50° (or 130°). In these “bent” approaches of Ar to the C-C axis, Ar usually interacts very strongly with one of the hydrogen atoms, which becomes “sandwiched” between the incoming Ar atom and a C atom. The H-atom sandwiched between the impinging Ar and the hydrocarbon moiety escapes the highly repulsive interactions through bending H-C-C motions in or out of the Ar-H-C-C collision plane. Large stretching motion of the C-H bond associated with the impact of the Ar atom follows, as well as substantial H-C-C and H-C-H′ bending excitation. If H escapes the collision plane through out-of-plane motions, there is energy transfer to CH₃-CH₃ internal rotation that is enough to surmount the CH₃-CH₃ internal rotation barrier. This is consistent with previous studies of the involvement of these internal rotors in deactivation through collisional energy transfer for highly excited linear alkane molecules interacting with noble gases.³⁴

This mechanism for large energy transfer just discussed is reminiscent of earlier descriptions of the microscopic mechanisms of supercollisions in which large amounts of vibrational energy are transferred to product translational energy in collisions of highly
excited molecules with room temperature noble gases. A similar mechanism has been discussed in connection with the photodissociation of Ar-H-X (X=Cl, F) complexes. A “cage effect” or “squeezed atom effect” was found to diminish the amount of relative translation between the recoiling H and X species after an activation period in which H “rattles” between Ar and X. The mechanisms for large energy transfer in both deactivation of highly-excited molecules and in photodissociation involve complexes in which an H atom oscillates between a bath gas atom and a heavy atom several times. In the present case all collisions are direct, and large energy transfer is produced in collisions in which H is sandwiched between the hyperthermal Ar and the hydrocarbon. Significant internal excitation is produced as the H recoils from this repulsive environment.

**Conclusion**

Collisional energy transfer has been examined in hyperthermal collisions of Ar with ethane by a combination of crossed-molecular beams scattering experiments and classical trajectory calculations. Unlike most of the previous studies, we consider collisions in which the energy available for transfer enters the system as reagent relative translation rather than internal excitation of the molecular reagent. These hyperthermal processes lead to collisions that at low impact parameters produce backward scattering and a very substantial $T\rightarrow V', R'$ energy transfer in single events, with 10-20 percent of the initial collision energy being diverted to ethane degrees of freedom (for an average over backward scattered collisions), and up to 80% transferred in the most extreme trajectories. Classical trajectory calculations based on an earlier *ab initio*-fitted Ar-ethane
intermolecular potential and the MSINDO Hamiltonian for the ethane intramolecular potential have been used to gather insight about the microscopic mechanisms that promote large energy transfer. Analysis of trajectories that lead to energy transfer of more than 50% of the available energy indicates that such a large energy transfer occurs when an H atom is sandwiched between the incoming Ar atom and the rest of the hydrocarbon moiety and escapes the Ar-C axis through large H-C-C bending motions. This type of collision facilitates energy transfer by making a large amount of the repulsive potential energy accumulated in the vicinity of the trajectory’s turning point delivered to ethane internal energy (torsions, bends, rotation). This description is similar to supercollision mechanisms that have been described in earlier energy transfer studies.

The results of this study may be relevant to the interactions of space vehicles with the ambient environment in the upper atmosphere. The possibility of large energy transfers in single hyperthermal collisions suggests that gas-phase species exhausted from a rocket may become highly excited by inelastic collisions with atmospheric atomic oxygen and molecular nitrogen. The internally excited rocket exhaust species may then radiate in the infrared, which would make up a component of a rocket plume signature. In addition to gas-phase collisions, gas-surface collisions occur between the outer materials (often polymers) of a spacecraft and ambient O atoms and N\textsubscript{2} molecules. The relative velocities are comparable to those used in the studies described herein. Center-of-mass collision energies with a heavy surface may be as high as 10 eV, and large energy transfers in the gas-surface collisions may result in collision-induced dissociation. Collision-induced dissociation would produce radical sites that would make a polymeric
material much more susceptible to atomic-oxygen attack. Thus, strongly inelastic collisions may act synergistically with atomic oxygen to degrade spacecraft materials.
References


A CROSSED-BEAMS STUDY OF THE INTERACTION OF O($^3P$) WITH CARBON MONOXIDE

Introduction

Interest in collisions of O($^3P$) with CO has spanned four decades. Many experiments have been conducted on the vibrational relaxation of diatomic molecules by chemically active atoms at a range of temperatures using discharge flow or shock tube methods.$^{1,2}$ The O($^3P$) + CO interaction is important in the kinetics of the chemical laser, where vibrationally hot CO is produced from O + CS.$^3$ O($^3P$) atoms that do not react with CS can efficiently quench the vibrationally excited CO(v=1) molecules, indicating that O($^3P$) plays an important role in CO gas discharge chemical lasers.$^4$ O($^3P$) + CO has been suggested to be an important step in the initiation of shock waves, either by forming an excited intermediate, CO$_2^*$, that reacts with O$_2$ in an oxygen substitution reaction.

The photodissociation of CO$_2$ has been studied with photofragment translational spectroscopy, and it has been found that CO$_2$ molecules dissociate via two channels after excitation in the 140-170 nm wavelength range:

$$\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}^1D$$

$$\rightarrow \text{CO} + \text{O}^3P$$

with a branching ratio (determined both by 157 nm excitation$^5$ and with molecular beam photofragmentation spectroscopy$^6$) of 94% O($^1D$) and 6% O($^3P$). Although there is only a 6% probability of forming O($^3P$) from the photodissociation of CO$_2$, the existence of a triplet channel reveals a great deal about the dynamics of dissociation and the relationship
to the electronic structure of the CO$_2$ parent molecule. The pathway to form O($^3P$) is a
direct and fast dissociation process, while the O($^1D$) is formed when the transition state is
highly bent.$^6$

As described in the first chapter of this thesis, carbon monoxide is a major
combustion product present in rocket plumes. Gas-phase interactions of rocket plumes
traveling at $\sim$8 km s$^{-1}$ and ground state atomic oxygen in LEO lead to collision energies
with many electron volts in the center-of-mass (c.m.) reference frame. The two reactions
between O($^3P$) and CO that lead to a diatomic product are:

$$
O(^3P) + CO \rightarrow C + O_2 (\Delta H_{r,0^\circ} = 11.1 \text{ eV}) \quad (1)
$$

$$
O(^3P) + CO \rightarrow OC + O (\Delta H_{r,0^\circ} = 0) \text{ (reactive)} \quad (2)
$$

$$
O(^3P) + CO \rightarrow CO + O (\Delta H_{r,0^\circ} = 0) \text{ (inelastic)} \quad (3)
$$

where in (2) an the incoming O-atom is exchanged with the O-atom on CO (reactive
channel) and in (3) the incoming O-atom inelastically scatters from the target CO. At a
relative velocity of 8 km s$^{-1}$, the c.m. collision energy of O + CO is $\sim$3.4 eV. The
collision energy distribution between CO exhaust gas and O in the upper atmosphere
extends to a maximum of $\sim$5 eV. Therefore, the only channels that are accessible at the
collision energies relevant to LEO are (2) and (3). Upschulte and Caledonia$^7$ have
measured the infrared spectrum of vibrationally excited CO following collisions between
atomic oxygen and CO at relative velocities of $\sim$8 km s$^{-1}$, and they reported a cross
section for vibrational excitation of CO of $7.3 \times 10^{-17}$ cm$^2$. From their measured spectra
they concluded that the CO molecules were highly vibrationally excited, up to
CO(v=11).. However, in this study they were unable to distinguish between CO that was formed in an oxygen substitution reaction and CO that was inelastically scattered from atomic oxygen. In addition, they were unable to detect CO(v=0) or to map out the dynamics of the O + CO interactions. A space-based study by Green and coworkers\textsuperscript{8} where emission was detected after CO and NO gases were released on orbit, where relative collision velocities between O and CO were about 8 km s\textsuperscript{-1}, determined that bright infrared emissions in both fundamental and overtone vibrational bands observed for CO and NO resulted from the highly energetic interaction of the released gases with the residual atmospheric gases. They estimated the cross section to create internally excited CO(v) from collisional processes to be on the order of 10\textsuperscript{-16}-10\textsuperscript{-18} cm\textsuperscript{2}, in rough agreement with the results of Upschulte and Caledonia.

Braunstein and coworkers\textsuperscript{9} have computed the potential energy surfaces of the three lowest electronic triplet states of CO\textsubscript{2}(\textit{3}A\textsuperscript{'} state and two \textit{3}A\textsuperscript{''} states), which lead to O(\textit{3}P) + CO(\textit{1}\Sigma\textsuperscript{+}). In addition, they ran classical trajectories on these surfaces. Figure 7.1 shows the calculated potential energy curves of the ground singlet state of CO\textsubscript{2}(\textit{1}A\textsuperscript{'} state) and the three lowest triplet states, with the OCO bond angle equal to 120°. The energy shown here is a function of one of the CO bond lengths, while fixing the other CO bond length at 1.2 Å. The barrier to O-atom exchange (2) is 0.2 eV. Although coupling to the singlet ground state is spin-forbidden from the three lowest-lying triplet states, the singlet potential energy surface (which includes the ground state of CO\textsubscript{2}) crosses the triplet surface and leads to a higher dissociation limit, with products, O(\textit{1}D) + CO(\textit{1}\Sigma\textsuperscript{+}), about 2 eV above the dissociation limit that leads to O(\textit{3}P) + CO(\textit{1}\Sigma\textsuperscript{+}). With sufficient spin-orbit coupling between the triplet and singlet states, intersystem crossing (ISC) is possible.
However, there have been very few experimental studies indicating that ISC is important in reactions with ground state O atoms, at any collision energy.\textsuperscript{10-12} If the triplet CO\textsubscript{2} intermediate in the title reaction does couple to the singlet potential energy surface, the dynamics of the system involving motion on the singlet and triplet surfaces will be different than those involving only the low-lying triplet potential energy surfaces, and thus the calculations done on the triplet surfaces only may not be enough to describe the system.

Figure 7.1. Calculated potential energy curves of the ground singlet state of CO\textsubscript{2} (\textsuperscript{1}A'), and the three lowest triplet states, \textsuperscript{3}A', \textsuperscript{1}3A'', and \textsuperscript{2}3A'', at an OCO angle of 120\textdegree and where one of the CO bond distances of 1.2 Å is fixed and the other is varied. The curves show these states at Cs geometries to their O+CO dissociation limits, as a function of \textit{r}_{CO}. 

\begin{center}
\includegraphics[width=\textwidth]{figure7.1.png}
\end{center}
While much was revealed about energy transfer in hyperthermal collisions of O(3P) with CO through the IR emission experiments and the theoretical calculations, the dynamical behavior of the products were not investigated in the earlier experiment and some aspects of the dynamics (e.g., differential reaction cross sections) were not investigated in the theoretical calculations. In this chapter, a crossed-molecular beams study of O(3P) + CO collisions conducted at a hyperthermal collision energy of 3.6 eV is described. Isotopic substitution was used to distinguish between the reactive channel, \(^{16}\text{O} + \text{C}^{18}\text{O} \rightarrow \text{^{16}OC} + {^{18}\text{O}}\), and the inelastic channel, \(^{16}\text{O} + \text{C}^{18}\text{O} \rightarrow \text{^{16}O} + \text{C}^{18}\text{O}\). We investigated the dynamics of these two pathways, including the disposal of energy in the products and the angular distributions of the scattered products. Quasiclassical trajectory (QCT) calculations by Dr. Matt Braunstein were used to aid in the interpretation of the results, and the possibility of intersystem crossing at these collision energies was explored. The excellent agreement between the experiment and theory on the O(3P) + C\(^{18}\text{O}\) system at \(<E_{\text{coll}}>= 3.6\text{ eV}\) provided a good verification of the accuracy of the current theoretical methods.

**Experimental Details**

The experiments were performed with the use of a crossed-molecular beams apparatus equipped with a fast-atom beam source\(^{13-17}\). General details about the experimental apparatus and details of the analysis can be found in Chapter 2 of this thesis and an earlier paper.\(^{15}\) A pulsed beam of oxygen atoms beam was crossed at right angles with a pulsed, supersonic beam of C\(^{18}\text{O}\) gas. Products that scattered from the interaction
region were detected with a rotatable mass spectrometer detector that measured number density distributions as a function of arrival time, $N(t)$, which are also called time-of-flight (TOF) distributions. Laboratory angular distributions, $N(\Theta)$, are determined by integrating the TOF distributions. $\Theta$ is the angle of the scattered product with respect to the O-atom beam. These data are collected in the laboratory reference frame, so a forward convolution method$^{18-20}$ is employed to derive center-of-mass (c.m.) quantities from the. The details of the analysis methods were described in Chapter 2.

The hyperthermal beam used in the experiment had an average translational energy of 5 eV (Figure 7.2), and the mole fraction of atomic oxygen in the beam was approximately 98 percent. The hyperthermal O-atom beam was crossed at a 90° intersection angle by a pulsed beam of isotopically-labeled carbon monoxide molecules (C$^{18}$O). The C$^{18}$O (Isotec, Sigma Aldrich) was 98.7% C$^{18}$O, with the remainder (1.3%) being C$^{16}$O. A supersonic expansion of carbon monoxide was created with a piezoelectric pulsed valve from a stagnation pressure of 10 psig C$^{18}$O. The C$^{18}$O beam passed through a 5-mm-diameter skimmer and a 3-mm-diameter aperture before crossing the O-atom beam. The distance between the nozzle and skimmer was 9.2 cm, and the distance from the skimmer to the 3-mm-diameter aperture was 2.8 cm. From the aperture, the beam traveled 1.5 cm to the crossing point of the two beams. The C$^{18}$O beam velocity was estimated to be 800 (±80) m s$^{-1}$. The velocity of the carbon monoxide beam was an order of magnitude lower than the O atom beam and the velocity width of the carbon monoxide beam was not considered in these experiments. The crossing region of the two beams was located 99 cm from the apex of the conical nozzle of the O-atom source and 13 cm from the orifice of the C$^{18}$O pulsed valve source.
The average collision energy in the c.m. reference frame was derived from the average velocity of the O-atom beam and the nominal velocity of the carbon monoxide beam using the equation, \( E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2 \), where \( \mu \) is the reduced mass and \( v_{\text{rel}} \) is the relative velocity of the O atoms and the C\(^{18}\)O molecules. The average collision energy in this experiment was 3.6 eV, and the width of the collision energy distribution (FWHM) ranged from 3.0 to 4.3 eV. A Newton diagram for collisions of O atoms and carbon monoxide with \( E_{\text{coll}} = 3.6 \) eV is shown in Figure 7.3. This diagram shows maximum recoil velocities inelastically-scattered C\(^{18}\)O (blue solid circle) and \(^{16}\)O (blue dashed circle). It also shows maximum recoil velocities for the reactively scattered \(^{16}\)OC (red circle).

![Figure 7.2. Translational energy distributions of atomic and molecular oxygen in the hyperthermal beam.](image)
solid circle) and $^{18}$O products (red dashed circles). The shaded region shown on the Newton diagram indicates the range of laboratory angles used for the experiment: +6° to +54°.

The experiments were sensitive to the reactively-scattered $^{16}$OC molecules ($m/z = 28$), inelastically-scattered $^{18}$O molecules ($m/z = 30$), and inelastically-scattered O atoms ($m/z = 16$). Signals from $m/z = 32$ ($O_2^+$) were used to correct the $m/z = 16$ data for the contribution of cracking $O_2$ to $O^+$ on the ionizer. Low scattering signals combined with high background levels of water in the detector at $m/z = 18$ made it impossible to detect the reactive $^{18}$O product. TOF distributions were collected for 2000 beam pulses for $m/z = 28$ ($^{16}$OC$^+$) and 30 ($^{18}$O$^+$), and 200 beam pulses for 16 ($O^+$), and 32 ($O_2^+$) at each laboratory angle. The laboratory angle was adjusted in 2° increments until the entire angular range was covered. Then the increment direction was reversed and the cycle was repeated until a total of four TOF distributions had been collected for each product at each detector. Because this process lasted more than 35 hours, it was important to sum the TOF distributions collected in this manner to account for long-term drifts in the experimental parameters. At a representative laboratory angle of 10°, the integrated count rates were $8.5 \times 10^6$ counts s$^{-1}$ for $m/z = 30$ ($^{18}$O$^+$), $1.2 \times 10^8$ counts s$^{-1}$ for $m/z = 16$ ($O^+$), and $2.5 \times 10^7$ counts s$^{-1}$ for $m/z = 28$ ($^{16}$OC$^+$).
Figure 7.3. Newton Diagram for collisions of O($^3P$) with C$^{18}$O at $E_{\text{coll}} = 3.6$ eV, where O has a velocity of 8100 m s$^{-1}$ and the C$^{18}$O beam velocity is 800 m s$^{-1}$. The shaded region indicates the range of laboratory angles examined. The solid circles represent the recoil velocities of elastically scattered C$^{18}$O and $^{16}$O. The dashed circles represent the maximum recoil velocities of scattered $^{16}$OC (blue) and $^{18}$O (red)
Theoretical Details

Dr. Matt Braunstein’s theoretical methods are based on calculated potential surfaces and quasi-classical trajectory (QCT) calculations on these surfaces, as described in their earlier paper on O(3\textit{P}) + CO.\textsuperscript{9} They used the same surfaces, and they extended the QCT calculations to generate new cross-section results that could be compared directly with hyperthermal experimental data discussed in this chapter. The new work provides extensive results that separate the reactive and inelastic cross sections. The new results also use at least an order of magnitude more trajectories per collision energy than their previous work for better statistical convergence.

Figure 7.1 shows the basic features of the relevant potentials. Collisions of O(3\textit{P}) + CO(1\textit{Σ}\textsuperscript{+}) lead to three electronic stats of CO\textsubscript{2}, all triplets: a single 3\textit{A}\textsuperscript{′} state and two 3\textit{A}\textsuperscript{′′} states. The five nearby singlet states, which can only participate through weak spin-orbit interactions, lead to O(1\textit{D}) and CO(1\textit{Σ}\textsuperscript{+}), about two eV above the O(3\textit{P})+CO(1\textit{Σ}\textsuperscript{+}) threshold. One of these five singlet states leads to the 1\textit{Σ}\textsuperscript{g}\textsuperscript{+} ground state of CO\textsubscript{2} about 5.5 eV below the O(3\textit{P}) + CO(1\textit{Σ}\textsuperscript{+}) threshold. Spin-orbit interactions that could mix the singlet and triplet states were ignored in the calculations.

The \textit{ab-initio} calculations were performed at the (12 electron, 10 orbital) CASSCF-MP2 level, with a modest 631+G(d) basis set and the use of the electronic structure code GAMESS. The three lowest triplet potential surfaces were used to generate cross sections at several fixed collision energies, separating contributions into reactive collisions, where the incoming O-atom is exchanged with the O-atom belonging to the target CO, and non-reactive, inelastic collisions where the incoming O-atom is not
exchanged with the O-atom belonging to the target CO. All calculations were performed with $^{12}$C and $^{16}$O atom masses for the target CO and $^{16}$O for the incoming O-atom. The CO mass used in the calculations is therefore different from the present measurements which use $^{16}$O + $^{12}$C$^{18}$O. However, at relative collision velocities of ~8 km s$^{-1}$, we believe differences in results due to different $^{12}$C$^{16}$O and $^{12}$C$^{18}$O masses to be much smaller than other approximations made in the present calculations. All calculations were done with the CO in the ground vibrational state and rotational temperature of 300 K.

Experimental Results

Inelastic Scattering

Figure 7.4 shows TOF distributions for $m/z = 16$ (O$^+$) and 30 ($^{18}$O$^+$) collected at five laboratory detector angles. Signals detected at $m/z = 16$ were corrected for the contribution of O$_2$ cracking to O$^+$ in the ionizer. Figure 7.5 shows laboratory angular distributions for atomic oxygen and $^{18}$O inelastic scattering. The curves in Figures 7.4 and 7.5 are forward convolution fits to the laboratory angular distributions for the O product (red) and the $^{18}$O product (blue), based on the corresponding c.m. translational energy and blue and red angular distributions in Figure 7.6. These c.m. distributions were obtained from QCT calculations conducted on the triplet potential energy surfaces, and they accurately predict the laboratory distributions, as shown in Figures 7.4 and 7.5.
Figure 7.4. Time-of-flight distributions of inelastically scattered O and C\textsuperscript{18}O following collisions $<E_{\text{col}}>$ = 3.6 eV. The circles are the experimental data. The red (O) and blue (C\textsuperscript{18}O) solid curves are the forward-convolution simulations of the data, derived from the c.m. angular and translational energy distributions of corresponding colors in Figure 7.6.
The $^{16}\text{O}$ product is forward scattered and the $^{18}\text{O}$ is backward scattered with respect to the incoming $\text{O}$ atoms. As can be seen in the Newton diagram (Figure 7.3), the laboratory detection angles are primarily sensitive to $^{18}\text{O}$ molecules that scatter into the backward hemisphere in the c.m. reference frame with respect to the direction of the incident $\text{O}$ atoms, so only the corresponding angular range in the c.m. angular distributions that was accessible in experiment was used in the forward convolution.

Figure 7.5. Laboratory angular distributions of $\text{O}$ atoms and $^{18}\text{O}$ molecules which scattered inelastically with $<E_{\text{coll}}>$ = 3.6 eV. The black symbols with error bars are the experimental data, and the line-connected colored symbols are the forward convolution fits to the data, derived from the c.m. angular and translational energy distributions of corresponding color in Figure 7.6. The error bars are estimated from fitting the experimental TOF distributions with a modified Gaussian function and finding maximum and minimum acceptable fits by adjusting the Gaussian parameters. The integrated ranges of these fits are shown as error bars.
Figure 7.6. Center-of-mass angular and translational energy distributions for the inelastic scattering of O from C\textsuperscript{18}O at $<E_{\text{coll}}>$ = 3.6 eV, used in the forward-convolution fit of the laboratory TOF and angular distributions for m/z = 16 (O$^+$) and 30 (C\textsuperscript{18}O$^+$). These distributions were obtained from QCT calculations for O (red) and C\textsuperscript{18}O (blue).
The experiments were sensitive to C\textsuperscript{18}O and O scattered from 0-120 degrees and 0-80 degrees, respectively, in the c.m. reference frame. The calculated translational energy distribution, which predicts the observed data very well, predicts that, on average, about 85% of the available energy (3.6 eV) is released in translation in the inelastic channel. Velocity-flux maps derived from the sets of translational energy and angular distributions in Figure 7.6 are shown in Figure 7.7.

A second inelastic scattering channel, O\textsubscript{2} + C\textsuperscript{18}O → C\textsuperscript{18}O + O\textsubscript{2} was observed and could be identified as a small, fast shoulder in the TOF distributions collected at m/z = 30 (C\textsuperscript{18}O\textsuperscript{+}). When the signals from the fast peak were integrated at all laboratory detection angles, an angular distribution that is consistent with inelastic scattering of C\textsuperscript{18}O from O\textsubscript{2} was uncovered. Therefore, for all of the TOF distributions collected at m/z = 30 (C\textsuperscript{18}O\textsuperscript{+}), two peaks were found and only the slower peak, corresponding to the C\textsuperscript{18}O scattering inelastically from \textsuperscript{16}O, was used to gather dynamical information about the inelastic channel. Although the hyperthermal beam in our experiment had only a very small amount of O\textsubscript{2}, the inelastic cross section for O\textsubscript{2} + C\textsuperscript{18}O is almost twice that for O + C\textsuperscript{18}O, so the contribution to the inelastic scattering signal detected at m/z = 30 (C\textsuperscript{18}O\textsuperscript{+}) is not negligible.

**Reactive Scattering**

TOF and laboratory angular distributions collected at m/z = 28 (\textsuperscript{16}OC\textsuperscript{+}) at five laboratory angles are shown in Figures 7.8 and 7.9, respectively. Center- of-mass angular
Figure 7.7. Center-of-mass velocity-flux maps for the a) C^{18}O and b) \textsuperscript{16}O products, derived from the angular and translational energy distributions shown in Figure 7.6.
and translational energy distributions for the \(O(\text{^3P}) + C^{18}\text{O} \rightarrow ^{16}\text{OC} + ^{18}\text{O}\) reaction were obtained from the QCT calculations and are shown in blue in Figure 7.10. These c.m. distributions were used in the forward-convolution procedure to predict laboratory TOF and angular distributions shown in blue in Figures 7.8 and 7.9. The predicted TOF distributions match the experimental distributions fairly well, but the predicted laboratory angular distribution is not quite a perfect match to the experimental distribution. To improve the fit to the observed data, a translational energy distribution (based on an RRK form\(^{10}\)) and a point-form angular distribution was created (shown in red in Figure 7.10); the new fits are shown the red curves in Figures 7.8 and 7.9. The theoretical and experimental results both indicate that about 60% of the available energy is released in translation and the \(^{16}\text{OC}\) product is predominantly forward scattered. Theoretical calculations predict a small increase in the amount of scattering of \(^{16}\text{OC}\) at the most backward angles, near 180°, but that angular region is outside the limits of the sensitivity in the experiment. As seen in the Newton diagram in Figure 7.3, the experiment is sensitive to \(^{16}\text{OC}\) scattered from 0-120 degrees in the c.m. reference frame. A velocity-flux map, shown in Figure 7.11 illustrates the forward scattering of \(^{16}\text{OC}\), where a broad range of translational energy is channeled into the product. This figure compares the theoretically predicted c.m. velocity-flux map for \(^{16}\text{OC}\) with that determine from the experiment. Although similar, there are small differences between the two results that are statistically different.
Figure 7.8. Time-of-flight distributions of reactively scattered $^{16}\text{OC}$ following reaction of O($^3P$) with C$^{18}\text{O}$ at $<E_{\text{coll}}>$ = 3.6 eV. The circles are the experimental data. The blue and red solid curves are the forward-convolution simulations of the data, derived from the c.m. angular and translational energy distributions of corresponding colors in Figure 10.
Discussion

The results indicate that inelastic and reactive scattering of O($^3P$) from C$^{18}$O at a hyperthermal collision energy ($<E_{\text{coll}}>$ = 3.6 eV) have very different dynamics, even though the products are chemically identical. The experimental results have been used to test the predictions of QCT calculations performed on the three lowest-lying triplet surfaces. The dynamics of the inelastic and reactive scattering pathways are discussed below.

![Figure 7.9. Laboratory angular distribution (black symbols with error bars) of the $^{16}$OC product from the reaction of O($^3P$) with C$^{18}$O at $<E_{\text{coll}}>$ = 3.6 eV. The error bars are estimated from fitting the TOF distributions with a modified Gaussian function and finding maximum and minimum acceptable fits by adjusting the Gaussian parameters. The integrated ranges of these fits are shown as error bars. The colored curves are the forward-convolution simulations to the data, derived from the c.m. angular and translational energy distributions of corresponding color in Figure 10.](image-url)
Figure 7.10. Center-of-mass angular and translational energy distributions for reactive scattering of O($^3P$) from C$^{18}$O at $<E_{\text{coll}}>$ = 3.6 eV, used in the forward-convolution fit of the laboratory TOF and angular distributions for $m/z = 28$ ($^{16}$OC$^+$). The distributions shown in blue were obtained from QCT calculations and those shown in red were determined by the experiment.
Inelastic Scattering

Experimental results showed that oxygen atoms scatter from C\textsuperscript{18}O with little change in direction and translational energy and which are in good agreement with QCT calculations. The O atoms are predominantly forward scattered and the C\textsuperscript{18}O molecules are predominately backward scattered in the c.m. reference frame. The c.m. translational energy distribution for the oxygen atoms has a maximum near the c.m. collision energy in both the experimental and QCT results, implying little internal energy transfer on average. By using the translational energy distribution and the available energy, the product internal energy distribution, $P(E_{\text{int}})$, can be derived. The C\textsuperscript{18}O product internal energy distribution, shown in Figure 7.12, indicates that on average, ~15\% of the available energy is transferred into internal energy of the product. However, the high energy tail in the distribution indicates that a small fraction of collisions (15-20\%) can transfer more than ~1 eV of energy into internal energy of the C\textsuperscript{18}O, equivalent to C\textsuperscript{18}O (v=5). A smaller fraction (~5\%) of C\textsuperscript{18}O molecules can have more than ~3 eV of internal energy after single O(^3P) + C\textsuperscript{18}O collisions with $<E_{\text{coll}}>$ = 3.6 eV, corresponding to C\textsuperscript{18}O (v=11). It should be noted that C\textsuperscript{18}O detected in the experiment can only come from collisions of O atoms with C\textsuperscript{18}O molecules that lead to C\textsuperscript{18}O scattering in the backward direction with respect to its initial approach, as seen in the Newton diagram (Figure 7.3). While the majority of collisions lead to C\textsuperscript{18}O scattered with very little change in initial direction, even a small percentage of the collisions that occur with low impact parameters could transfer more energy into internal energy of the products than would glancing collisions with large impact parameters.
Figure 7.11. Center-of-mass velocity-flux maps for the $^{16}$OC product from a) experimental and b) theoretical translational energy and angular distributions.
Reactive Scattering

In the case of reactive scattering, the experimental results clearly showed that that $^{16}$OC can be formed from collisions with O atoms with $<E_{\text{coll}}>$ = 3.6 eV. The $^{16}$OC product appears to be mostly forward scattered in the c.m. reference frame with, on average, 60% of the available energy released in translation. Theoretically calculated center-of-mass angular and translational distributions (Figure 7.10) that were used in the forward-convolution procedure for predicted laboratory TOF and angular distributions gave results that were very similar to the experimental results, but they were not in quantitative agreement. The experimental c.m. angular distribution, shown in red in Figure 7.10a, more accurately predicted the observed data. However, the slight disagreement in the c.m. angular distributions may not be significant, as it can be attributed to the known errors in the calculations at small c.m. angles, where the range of impact parameters was limited. The theoretical and experimental c.m. translational energy distributions were quite similar both in the shape of the distributions and average translational energy release in the reaction. The good agreement with the calculations, which were performed only on the two low-lying triplet potential energy surfaces, suggests that intersystem crossing does not play a major role in the dynamics of O($^3P$) + CO collisions. The absence of intersystem crossing was also a conclusion in the measurements of the excitation functions for O($^3P$) + H$_2$ → OH + H, and O($^3P$) + CH$_4$ → OCH$_3$ + H, and in the dynamics of the reaction O($^3P$) + D$_2$ → OD + D, even though theoretical calculations suggested that triplet-singlet intersystem crossing might have been possible for these reactions.
Figure 7.12. Internal energy distributions (derived from Figures 7.6 and 7.10) for carbon monoxide products.
When examining the trajectories, it appears that most of the reactions of \( O(3P) + C^{18}O \) that lead to the \( ^{16}OC \) product proceed through a low-impact-parameter collision, or “hard hits” where the O atom transfers large amounts of translational energy into internal energy of the \( ^{16}OC \) product, and tends to scatter in the forward direction with respect to the initial direction of the O atom. This resembles the dynamics observed in previous studies where forward-scattering of a product indicated a “stripping” mechanism, in which reaction occurs through high-impact-parameter. However, a typical characteristic of stripping mechanisms is very little energy transfer in the collision, which is quite different than the observed dynamics for this reactive channel. While, on average, 60% the available energy is released in translation, the translational energy distribution is quite broad and has an appreciable tail that extends to low translational energies. The c.m. internal energy distribution of the reactively scattered \( ^{16}OC \) product, shown in Figure 7.11a, was found by subtracting the c.m. translational energy distribution from the available (collision) energy. On average, about 40% of the available energy is channeled into internal excitation of the \( ^{16}OC \) product, but a high fraction of collisions can lead to very highly internally excited products. In fact, \(~20\%\) of the collisions of \(^{16}O(3P) + C^{18}O\) at \(\langle E_{\text{coll}}\rangle = 3.6\) eV can lead to \(^{16}OC\) with more than \(~3\) eV of internal excitation. On average, most of the \(^{16}OC\) products are formed with internal energies corresponding to \(v = \sim 5, 6\) levels, but a non-negligible fraction of the products are formed with internal energies corresponding to \(v=11\) or higher.

The presence of the small, backward-scattered component in the calculated c.m. angular distribution (blue line, Figure 7.11b) suggests that a portion of the collisions may lead to \(^{16}OC\) scattering with a different mechanism than that described above. Products
that scatter in the backward direction with respect to the initial direction of the O atoms and with large amounts of internal excitation are indicative of a low impact parameter collision. Reactive collisions with low impact parameters would most likely lead to \(^{16}\text{OC}\) that is more internally excited than the \(^{16}\text{OC}\) products formed with more “glancing” collisions, but in the experiments it is impossible to tell how the energy is partitioned into internal excitation and which collision geometries lead to the most internal energy transfer.

**Energy Partitioning**

The experimental and theoretical results indicated a large amount of internal excitation (corresponding to vibrational quantum states up to \(v\sim11\), and even slightly higher) in both reactively and inelastically scattered carbon monoxide products. Theoretical calculations have given rovibrationally resolved translational energy distributions for the products (Figure 7.13). Cross sections as a function of vibrational excitation in the products are shown in Figure 7.14 and indicate that for both the reactive and inelastic channels, vibrational and rotational excitation of the nascent carbon monoxide molecule are inversely proportional. This trend is in agreement with previous experimental studies of reactive triatomic collisions, and for experimental and theoretical studies on inelastic triatomic collisions. Regardless, products formed in any vibrational level can transfer a large fraction of the available energy into rotational energy of the products, especially in lower vibrational quantum states. Figure 7.15 shows that the reactive and inelastic rovibrationally resolved cross sections extend to \(j\sim100\). The \(\sigma(0,j)\) inelastic cross section peaks at much lower rotational quantum numbers and
has a much larger magnitude, reflecting the different dynamics of pure rotational excitation which occurs at large impact parameters. The maxima for the inelastic $\sigma(v=1-3,j)$ cross sections occur for lower rotational quantum numbers as the vibrational levels increase, reflecting the fact that less energy is available for rotation as the vibrational excitation increases.

The current experimental and theoretical results reveal similar limits to the amount of internal excitation in scattered CO to what was reported in the IR emission experiment conducted by Upschulte and Caledonia. They concluded that collisions of O($^3P$) with CO at $E_{\text{coll}} = 3.4$ eV can produce CO in vibrational levels up to $v=11$, while our crossed-beams study of O($^3P$) with C$^{18}$O at $<E_{\text{coll}}>$ = 3.6 eV verified that both the inelastic product, C$^{18}$O, and the reactive product, $^{16}$OC, may be in vibrational levels of $v=11$ or greater.

Conclusion

Crossed-molecular beams methods and theoretical calculations have been used to investigate the interactions of O($^3P$) with carbon monoxide at an c.m. collision energy of 3.6 eV. Inelastic scattering experiments of $^{16}$O($^3P$) + C$^{18}$O $\rightarrow$ C$^{18}$O + $^{16}$O indicate that oxygen atoms scatter from C$^{18}$O with relatively large impact parameters and lead to forward scattering with very little change in direction and translational energy. Roughly 85% of the available energy is released in translation, with the remaining 15% in internal excitation of the inelastically scattered products. The inelastically-scattered C$^{18}$O molecules scatter mainly in the backward direction, with respect to the O atoms, or the forward direction with respect to the initial approach of C$^{18}$O. The reactive channel, $^{16}$O($^3P$) + C$^{18}$O $\rightarrow$ $^{16}$OC + $^{18}$O, created $^{16}$OC products that were mostly forward scattered.
Figure 7.13. Calculated cross sections for O + CO collisions at 8 km s⁻¹ collision speed (77.9 kcal mol⁻¹) showing the contribution from each final CO(v,j) state as a function of the final translational energy of collision products. (a) reactive channel, (b) inelastic channel, (c) inelastic channel minus the CO(v=0,j) product contributions. The numbers in the figures indicate the thresholds for the CO(v) product vibrational levels. In (b), the contribution from CO(v=0) below the CO(v=1) threshold extends above the axis limit, and so is not visible in the figure.
Figure 7.14. Calculated vibrationally resolved cross sections for O + CO collisions at 3, 4, 5, 6, 7, 8, 9, 10 km s$^{-1}$ collision speeds. (a) reactive collisions; (b) inelastic collisions. The numbers in the figure refer to the collision speed.
with theoretical calculations predicting a small amount of collisions leading to $^{16}$OC scattered in the sideways and backward direction. The $^{16}$OC product formed in this reactive channel had ~40%, on average, of the available energy transferred into internal excitation, with many collisions channeling ~80% or more of the available energy into internal modes of the product. The scattering behavior of the $^{16}$OC was indicative of low-impact-parameter collisions between the hyperthermal oxygen atoms and the C$^{18}$O molecules leading to forward-scattered $^{16}$OC. The presence of intersystem crossing was investigated, but the agreement between the observed
dynamics and the calculations on the triplet-only surface suggest that the effects of intersystem crossing are negligible.
References


EXCITATION FUNCTION FOR THE O(3\textit{P}) + H\textsubscript{2}O \rightarrow \textit{HO}_2 + \textit{H} REACTION

Introduction

Hyperthermal interactions of O(3\textit{P}) with H\textsubscript{2}O(\textit{X} \textsubscript{1}\textit{A\textsubscript{1}}) occur in the vicinity of space vehicles that travel through the Earth’s residual atmosphere at altitudes higher than \(~\sim\~\)100 km. H\textsubscript{2}O is a major outgassing product from spacecraft, and it may be released from manned spacecraft by waste water dumps. H\textsubscript{2}O is also a main component of rocket exhaust gas and therefore may exit maneuvering engines and other propulsion systems at velocities that may exceed 3000 m s\textsuperscript{−1}. O(3\textit{P}) atoms dominate the residual atmosphere of the Earth at altitudes from \(~\sim\~\)150 km to 700 km. Thus, as space vehicles travel at orbital or suborbital velocities of \(~\sim\~\)8 km s\textsuperscript{−1}, ambient O(3\textit{P}) atoms collide with expelled H\textsubscript{2}O molecules at high relative velocities. A relative velocity of \(~\sim\~\)8 km s\textsuperscript{−1}, for example, yields collisions of O(3\textit{P}) with H\textsubscript{2}O with a center-of-mass (c.m.) collision energy of 2.8 eV. The high-energy collisions between O(3\textit{P}) and H\textsubscript{2}O may give rise to infrared (IR) radiation resulting from internally excited products, and if the collision energy is high enough, ultraviolet (UV) emission may be observed from electronically excited products, such as OH(\textit{A\textsubscript{2}\Sigma\textsuperscript{+}}). The importance of the IR and UV emission from hyperthermal O(3\textit{P}) + H\textsubscript{2}O collisions in the vicinity of space vehicles has motivated a number of space-based and laboratory experiments, as well as theoretical studies, of the inelastic and reactive pathways. The work to date has focused on three important pathways: O(3\textit{P}) + H\textsubscript{2}O[\textit{X} \textsubscript{1}\textit{A\textsubscript{1}} (\nu_1\nu_2\nu_3,JK)] \rightarrow O(3\textit{P}) + H\textsubscript{2}O[\textit{X} \textsubscript{1}\textit{A\textsubscript{1}} (\nu_1'\nu_2'\nu_3',J'K')]\textsuperscript{5−8}, OH(\textit{X\textsubscript{2}\Pi}) + OH(\textit{X\textsubscript{2}\Pi})\textsuperscript{1,7,9−11} and OH(\textit{A\textsubscript{2}\Sigma\textsuperscript{+}}) + OH(\textit{X\textsubscript{2}\Pi})\textsuperscript{12,13}. Additional pathways on H\textsubscript{2}O\textsubscript{2} triplet potential energy
An energy diagram for various possible triplet reactions is shown in Figure 1. H-atom abstraction to produce OH($X^2\Pi$) + OH($X^2\Pi$) is the lowest energy reactive channel, but at hyperthermal collision energies greater than $\sim 60$ kcal mol$^{-1}$, two additional channels become accessible: a molecular channel to form H$_2$(1$\Sigma^+_g$) + O$_2$(3$\Sigma^-_g$) and an H-atom elimination reaction to form H(2$S$) + HO$_2$(2$A'$). At very high collision energies, $>100$ kcal mol$^{-1}$ (such as those that might occur when a rocket engine is fired into the ram direction of a spacecraft), fragmentation into three bodies or electronic excitation of OH may occur. H-atom elimination has been observed in studies of hyperthermal O-atom reactions with CH$_4$ and HCl, yet the importance of analogous H-atom elimination has not been investigated in earlier studies of O + H$_2$O collisions. In fact, the reaction of O($^3P$) with H$_2$O to produce H + HO$_2$ has never been observed experimentally, presumably because of the large reaction endothermicity.

We have undertaken experimental and theoretical studies of the hyperthermal collisions of O($^3P$) + H$_2$O($X^1A_1$) with special attention to the H-atom elimination reaction. We have observed this reaction in a crossed-beams experiment and have measured the relative excitation function in the region of the energy threshold for the reaction (48–80 kcal mol$^{-1}$). The experimental relative excitation function has been compared with the excitation calculated by direct dynamics calculations. The calculations provide detailed information on the dynamics of O($^3P$) collisions with H$_2$O that are not accessible in the experiment.
Figure 8.1. Energy diagram for the possible reaction channels in the reaction of O($^3P$) with H$_2$O. The horizontal line at the top shows the experimentally accessible energy range. from thermochemical data: (a) from References 15 and 17 (b) from References 1, 20, and 21 (c) from Reference 15 (d) from Reference 16 (e) from current work (f) from Reference 14 (g) from Reference 16 (h) from Reference 12.
Experimental Details

The experiments were performed with the crossed-molecular beams apparatus and the hyperthermal atomic-oxygen beam source that have been described in Chapter 2. Figure 8.2 shows a schematic diagram of the apparatus configured for crossed-beams studies of O + H₂O collisions. A pulsed hyperthermal beam containing ~90\% O(^3P) and ~10\% O₂(^3Σ_g⁻) was produced with a laser detonation source. This beam passed through two regions of differential pumping and entered the main scattering chamber, where it crossed a continuous beam of H₂O molecules. Products that scattered from the crossing region were detected with a rotatable mass spectrometer detector. In order to prepare hyperthermal O-atom beams with relatively narrow and variable velocity distributions, a synchronized chopper wheel was used to select a portion of the overall hyperthermal pulse. The nominal velocity of the O-atom beam could be varied by adjusting the synchronization between a photodiode on the chopper wheel and the initiation of the hyperthermal pulse. The chopper wheel was 17.8 cm diameter and rotated at 400 Hz. It had three equally spaced slots, each 1.5 mm wide, and it was placed about 97 cm from the apex of the conical nozzle and 2 cm from the axis of the H₂O beam. The mass spectrometer detector was used to monitor the hyperthermal O-atom beam, and the velocity distributions in the O-atom beam pulses were determined by the time-of-flight method.

The only substantial difference between the current experiment and the earlier experiments is the source of H₂O molecules. A beam of H₂O was formed by allowing pure H₂O vapor, at a stagnation pressure of ~2.2 Torr, to expand into the scattering
chamber through a cluster of capillary tubes. A stainless steel reservoir containing nanopure H$_2$O was held in a temperature-controlled water bath, held at –10 °C. A schematic and picture of the water source are shown in Figures 8.2 and 8.3, respectively. The water was degassed in three freeze-pump-thaw cycles. A 1.0-cm-long cluster of ~60 capillaries (each 0.3 mm OD, with a total cluster diameter of 2.5 mm) was glued with Torr-Seal® into the end of stainless steel tube leading from the H$_2$O reservoir to the apparatus and can be seen in Figures 8.4 and 8.5. The cluster was positioned such that the end of the cluster was perpendicular to and 5 mm from the axis of the hyperthermal

Figure 8.2. Schematic diagram of the crossed-beams apparatus with water source.
O-atom beam. The H$_2$O beam which exited the cluster thus crossed the hyperthermal O-atom beam at a nominal angle of 90º. The center of this crossing region contains the axis of rotation of the rotatable mass spectrometer detector. The cross-sectional diameter of the O-atom beam at the crossing region was defined to be ~3.0 mm by a skimmer. The diameter of the H$_2$O beam at the crossing region was not well defined, but it is assumed that the majority of the intensity of the beam lay within a diameter of 3 mm as a result of the focusing effect of the cluster. Although the H$_2$O beam was continuous, the hyperthermal O-atom beam was pulsed at a repetition rate of 2 Hz. The flux of O atoms at the crossing region is estimated to be $\sim$10$^{14}$ atoms cm$^{-2}$ pulse$^{-1}$, with the pulse width at the crossing region being ~20 µs long (full width at half maximum). The flux of H$_2$O at the crossing region was not measured, but it might be as high as $\sim$10$^{19}$ molecules cm$^{-2}$ s$^{-1}$. Although the H$_2$O flux was relatively high, there were still relatively few molecules in the crossing region during the O-atom pulse, and multiple collision events in the crossing region were determined from a variety of tests to be negligible.
Figure 8.3. Schematic diagram of the water source.
Figure 8.4. Picture of water source connected to crossed-molecular beams apparatus.
Figure 8.5. Picture of capillary cluster at the end of the water vapor source line.

Figure 8.6. Picture of the interaction region of the water source with capillary cluster (at left) and the O-atom beam (at right). Note: the chopper wheel for the O-atom beam is not shown in this picture.
The H$_2$O beam was characterized by mounting the chopper wheel in front of the entrance to the detector and aligning the detector with the beam axis. Time-of-flight (TOF) distributions of $m/z = 18$ (H$_2$O$^+$) were collected, and other mass-to-charge ratios (e.g., $m/z = 36, 35$) characteristic of dimers or clusters were scanned for signal. No evidence of H$_2$O dimers or clusters was found. The measured TOF distributions were used to determine the velocity distribution of the H$_2$O beam. The average velocity was $\sim 600$ m s$^{-1}$, and the velocity width (FWHM) was 450 – 800 m s$^{-1}$.

Time-of-flight distributions of eight atomic-oxygen beams selected with the synchronized chopper wheel were collected with the detector aligned with the hyperthermal beam axis. From each TOF distribution, a velocity distribution of the hyperthermal O atoms was derived, which, in turn, allowed the determination a collision-energy distribution in the c.m. reference frame for O + H$_2$O. The c.m. collision energy distributions corresponding to the eight O-atom beams used in the experiment are shown in Figure 8.6. TOF distributions of inelastically and reactively scattered products were collected as a function of flight time from the crossing region of the two beams to the ionizer, which was 33.66 cm away. The relative fluxes of scattered products were derived using the relationship, $\text{flux}(\Theta) \propto \Sigma N(t)/t$, where $\Theta$ is the laboratory detector angle with respect to the atomic-oxygen beam. For each nominal c.m. collision energy, the detector was placed so that it was aligned with the velocity vector corresponding to the center-of-mass of the O + H$_2$O system. The TOF distributions were thus collected with a laboratory angle, $\Theta$, that varied from 6$^\circ$ to 7$^\circ$. Reactively scattered products were detected at $m/z = 33$ (HO$_2^+$), with integrated count rates from $\sim 0$ counts s$^{-1}$ to $5.0 \times 10^7$ counts s$^{-1}$. Inelastically scattered products were detected at $m/z = 16$ (O$^+$) and 32 (O$_2^+$),
with integrated count rates in the ranges $5.6 \times 10^8 - 1.1 \times 10^9$ and $8.2 \times 10^8 - 1.0 \times 10^9$ counts s$^{-1}$, respectively. The $m/z = 32$ TOF distributions were used to correct the $m/z = 16$ TOF distributions for the contribution to the $m/z = 16$ distributions that comes from dissociative ionization of O$_2$ in the electron bombardment ionizer. This correction is 11 percent of the signal detected at $m/z = 32$. Each corrected TOF distribution collected at $m/z = 16$ was integrated with the appropriate velocity weighting to give relative flux, and this flux, which is proportional to the flux of the incident O-atom beam, was used to normalize the integrated flux of the HO$_2$ signal observed with the corresponding collision energy.

Figure 8.7. Collision energy distributions for O($^3P$) + H$_2$O collisions. The distributions correspond to eight atomic oxygen beam velocity distributions created with the used of a synchronized chopper wheel rotating at 300 Hz.
Results and Analysis

Figure 8.8 shows TOF distributions of the inelastically scattered O and reactively scattered HO$_2$ corresponding to the eight average center-of-mass collision energies from 50.7 to 78.4 kcal mol$^{-1}$. The scattered HO$_2$ flux increased with collision energy, but part of this increase reflected the increasing O-atom flux with the velocity of the hyperthermal beam. Therefore, the HO$_2$ flux was normalized to the flux of the O atoms at the corresponding c.m. collision energy. The integrated flux of the HO$_2$ product as a function of c.m. collision energy is shown in Figure 8.9 as the pink triangles. The threshold experimental threshold for the reaction has been determined to be 60 ± 5 kcal mol$^{-1}$.

The HO$_2$ excitation functions derived from the direct dynamics calculations are also shown in Figure 8.9. Note that the experimental excitation function has been normalized such that its shape can be compared with the excitation calculated with the B3LYP/6-31G level of theory. This level of theory happened to yield a reaction barrier (59.5 ± 3.5 kcal mol$^{-1}$) that was very close to the experimentally observed threshold. The excitation function derived from the UMP2/6-31-G direct dynamics calculations has the same shape as that derived from the B3LYP/6-31G calculations (although the UMP2/6-31-G calculations were done at fewer collision energies), but the barrier is shifted to a higher energy (87.2 ± 3 kcal mol$^{-1}$). The calculations predict a maximum in the HO$_2$ excitation function at collision energies near 115 kcal mol$^{-1}$, well beyond the range of experimentally accessible collision energies. Similar behavior was observed in direct dynamics calculations of the ClO excitation function in the hyperthermal reactions of
O(3\(^3\)P) with HCl to produce ClO + H. The decrease in the cross section for production of ClO at collision energies above 110 kcal mol\(^{-1}\) was explained by fragmentation of highly internally excited ClO. An analogous explanation applies to the HO\(_2\) excitation function: at high collision energies, HO\(_2\) may fragment to H + O\(_2\) or OH + H (see Figure 8.1). The excitation function calculated for the H atom that is initially eliminated follows the HO\(_2\) excitation function up to ~110 kcal mol\(^{-1}\) and then it continues to increase dramatically while the HO\(_2\) excitation function decreases (see Figure 8.9). This result supports the conclusion that HO\(_2\) dissociates following initial H-atom elimination at high collision energies.

**Discussion**

The O(3\(^3\)P) + H\(_2\)O → HO\(_2\) + H reaction pathway has been observed for the first time with the crossed-molecular beams technique and the energy dependence of the scattered HO\(_2\) product was compared with theoretical calculations. The energy threshold for the reaction was experimentally measured to be 60 ± 5 kcal mol\(^{-1}\). The experimental excitation function matches the calculated excitation function very well over the range of collision energies studied. The observed threshold appears to be slightly higher than the reaction endoergicity, although the experimental error would almost support the conclusion of little or no barrier above the endoergicity of the reaction. The theoretical barriers were calculated with different levels of theory, UMP2/6-31G and B3LYP/6-31G, and were found to be 59.5 ± 3.5 kcal mol\(^{-1}\) and 87.2 ± 3 kcal mol\(^{-1}\), respectively. The UMP2/6-31G level overestimates the barrier by more than ~25 kcal mol\(^{-1}\), while the B3LYP/6-31G excitation function matched the experimental excitation function very
The good match between the theoretical and experimental excitation functions suggests that the reaction only occurs on the triplet surfaces, so there is no need to invoke singlet surfaces to explain, for example, signals below the $\Delta E$ for the reaction.

The theoretical calculations can provide information about the reaction mechanism and the effect of collision geometry on the reaction. The theoretical excitation function in Figure 8.9 shows that the differential cross section for the HO$_2$ product increases up to $\sim$110 kcal mol$^{-1}$ and then begins to decrease as the collision energy increases. This is reminiscent of an earlier theoretical study on the reaction $\text{O}^{(3}\text{P}) + \text{HCl} \rightarrow \text{ClO} + \text{H}$ where the excitation function of the ClO product showed a similar trend.$^{19}$ Direct dynamics calculations on the $\text{O}^{(3}\text{P}) + \text{HCl}$ reaction at hyperthermal collision energies found that the differential cross section for the ClO product increased from threshold to its maximum around $E_{\text{coll}} \sim$110 kcal mol$^{-1}$ and then decreased. At high collision energies, only a small range of trajectories lead to stable HO$_2$. In order to explain the shape of the excitation function, we suggest a few reaction mechanisms. When the O atom approaches the water molecule with the sandwiched hydrogen far from the O-O axis (Figure 8.10a), it appears that as the c.m. collision energy increases, the translational energy of the eliminated H atom is unaffected. Therefore, the kinetic energy of the H-atom in the c.m. frame is only weakly coupled to the c.m. collision energy. Conservation of energy and momentum require that the excess available energy is partitioned into the internal energy of the recoiling HO$_2$ product, which tends to increase with increasing collision energy. But, examination of the cross section for HO$_2$ as a function of collision energy shows an increase to $\sim$110 kcal mol$^{-1}$, and then it decreases
Figure 8.8. Time-of-flight distributions of inelastically-scattered O-atoms (top) and reactively scattered HO$_2$ molecules (bottom). Eight TOF distributions were collected for both products corresponding to eight center-of-mass collision energies.
Figure 8.9. Experimental and theoretical excitation functions (cross section vs. collision energy) for the $\text{O}^3P + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{H}$ reaction. Triangles show the experimental results. The circles connected with a dashed line represent B3LYP/6-31G results and the squares connected with the solid line represent the UMP2/6-31G results. The diamonds connected with the dotted line represent the cross section as a function of collision energy for the dissociation of the HO$_2$ product (HO$_2$ $\rightarrow$ O$_2$ + H).
as the collision energy increases further. This can be explained by a mechanism in which the HO₂ product becomes so highly internally excited that it is too unstable and subsequently dissociates into O₂ + H. Therefore, the theoretically calculated excitation function shows the decrease in cross section for the HO₂ product when the calculated internal energy exceeds its dissociation energy (ΔfH°[HO₂ → O₂ + H] = 101.38 kcal mol⁻¹). In the recent theoretical study of O(^3P) scattering from HCl at hyperthermal collision energies, the calculations found that the H atom had ~43.8 kcal mol⁻¹ of translational energy. If we assume that the eliminated H atom in this system has a similar translational energy, HO₂ would be expected to begin to fragment to O₂ + H when the c.m. collision energy is ~90-115 kcal mol⁻¹. These fragmentations can be understood as “failed” HO₂ reactions. The cross section as a function of c.m. collision energy for the fragmentation of the HO₂ product is shown as a dotted line in Figure 8.9.

On the other hand, if the O atom approaches the water molecule that is oriented such H atom closest to the incoming hyperthermal O atom can experience a large force from both of the O atoms so the H atom can carry away a larger amount of translational energy when it is eliminated (Figure 8.10b). The H atom is then scattered in the backward direction with respect to the initial O atom direction and the relatively stable HO₂ product can scatter in the forward direction. HO₂ molecules that are still present at high c.m. collision energies may be formed from this type of mechanism where the HO₂ product is formed with insufficient internal energy to dissociate.

The angular distributions of the HO₂ product are therefore different when the collision energy is increased. Figure 8.11 shows theoretically calculated c.m. velocity
flux maps for the HO\(_2\) product when the c.m. collision energy is 70, 115, or 160 kcal mol\(^{-1}\). When the collision energy is 70 kcal mol\(^{-1}\) (just above the threshold for the reaction), the HO\(_2\) product is almost completely backward-scattered. When the c.m. collision energy is 115 kcal mol\(^{-1}\), the HO\(_2\) product is still scattered mainly in the backward direction, but a small fraction of HO\(_2\) molecules can scatter in the forward direction with respect to the direction of the incident oxygen atom. These forward-scattered HO\(_2\) molecules may correspond to collisions where the hydrogen atom in the water molecule closest to the incoming oxygen atom is eliminated quickly, leaving the HO\(_2\) product to be formed internally cold. At the highest c.m. collision energy explored in the theoretical calculations, almost all of the HO\(_2\) molecules scatter in the sideways to forward direction. Nearly all of the HO\(_2\) molecules formed in this collision energy range
must be formed in this manner. The cross section for HO$_2$ fragmentation is so large at these high collision energies that failed reactions dominate, also shown in the c.m. velocity flux map (Figure 8.11) by the lack of any backward scattered HO$_2$ products.

It should be noted that the calculated cross sections for the O($^3P$) + H$_2$O → HO$_2$ + H reaction are roughly 10 – 20 percent those for the O($^3P$) + H$_2$O → OH + OH for the collision energy range of 70 – 160 kcal mol$^{-1}$. This is quite different than in the case of the O($^3P$) + HCl reaction, where the cross section of the H-elimination channel was similar to, even larger than, the magnitude of the cross section for the H-abstraction channel when $E_{\text{coll}} \sim 115$ kcal mol$^{-1}$. In both cases, the H-elimination channel to form either HO$_2$ or HCl favors small impact parameters and backward scattering of the product while the H-abstraction channel prefers large impact parameter collisions.

We considered the possibility of H$_2$ + O$_2$ in the calculations. And we observed that this reaction almost never occurs because the transition state is improbable to access. HO$_2$ is clearly a significant reaction product at collision energies above 60 kcal mol$^{-1}$. It can be formed internally hot, so this species will be a source of radiation in addition to OH in the O + H$_2$O reaction.
Figure 8.11. Theoretically calculated center-of-mass (c.m.) velocity flux maps for reactive scattering of HO$_2$ from O($^3P$) at $E_{\text{coll}} = 70$ kcal mol$^{-1}$ (top), 115 kcal mol$^{-1}$ (center), and 160 kcal mol$^{-1}$ (bottom).
The O($^3P$) + H$_2$O $\rightarrow$ HO$_2$ + H excitation function was measured in a crossed-beams experiment and compared with direct dynamics quasiclassical trajectory results. The experimental barrier was found to be $\sim$60 ± 5 kcal mol$^{-1}$, which matched well the theoretically calculated threshold at the B3LYP/6-31G level. The shape of the theoretical differential cross section of the HO$_2$ product as a function of collision energy (70 – 160 kcal mol$^{-1}$) can be explained by an increase in the cross section as the collision energy increases with fragmentation (HO$_2$ $\rightarrow$ O$_2$ + H) becoming important at the highest energies. However, at high collision energies, some of the trajectories indicate that HO$_2$ products can be formed with low levels of internal excitation and show dynamical trends that are quite different than products that are formed at energies just above the reaction threshold. At collision energies just above the threshold (up to 70 kcal mol$^{-1}$ eV), the HO$_2$ is scattered mainly in the backward direction. When the collision energy is greater than 110 kcal mol$^{-1}$ eV, some of the HO$_2$ begins to dissociate, and is displayed as a decrease in the theoretically calculated cross section. Above $\sim$110 kcal mol$^{-1}$, the HO$_2$ that survives may be formed in a different mechanism where the product is formed with little internal energy and scatters in the forward hemisphere with respect to the initial direction of the atomic oxygen.
References


CONCLUSION

As space vehicles travel through Earth’s outer atmosphere, their surfaces and exhaust gases collide with ambient O atoms or N\textsubscript{2} molecules. These energetic collisions can lead to surface degradation and to highly internally excited products that can radiate and contribute to the signature of an exhaust stream. The six distinct experiments presented in this thesis explored a variety of interactions of molecular beams with polymer surfaces and gas-phase molecules, each representing interactions that may occur in the vicinity of space vehicles that travel in or through Earth’s residual atmosphere at altitudes of 100—700 km. The process of studying these interactions of relevance to space vehicles has led to a wealth of new insight into the fundamental dynamics of hyperthermal gas-surface and gas-phase collisions.

The resistance of a novel inorganic/organic hybrid polymer, POSS polyimide, to atomic oxygen attack was investigated. These POSS/polyimide hybrid polymers are Kapton\textsuperscript{®}-like polymers containing POSS nanoparticles that are chemically bound into the polymer chain. Samples of these POSS polyimides, as well as polyimide controls, were exposed to a hyperthermal O-atom beam. Exposed and unexposed surfaces were characterized by surface profilometry, atomic force microscopy, and x-ray photoelectron spectroscopy. The data indicate that the POSS-containing polyimides have significantly lower erosion yields than Kapton, because they form a surface SiO\textsubscript{2} layer, which passivates the surface and protects the underlying polymer from further O-atom attack.
These results suggest promise for the use of a POSS polyimide polymer as a replacement for Kapton on spacecraft operating in the low-Earth orbital environment.

Beam-surface scattering experiments probed products which scattered from FEP Teflon® surfaces that were bombarded by various combinations of atomic and molecular oxygen, argon atoms, and VUV light. The incident energy of the beams was tunable and controlled by a synchronized chopper wheel. A filtered deuterium lamp provided a source of VUV light. Volatile products that exited the surfaces were measured with a rotatable mass spectrometer detector. It appears that while O atoms do not react with a pristine FEP Teflon® surface, VUV light or highly energetic collisions of O₂ or Ar may break bonds and create radical sites where O atoms may react. In addition, the dynamics of scattered products after impingement of hyperthermal beams of O, O₂, or Ar on fluorinated surfaces (FEP Teflon® and a PFPE liquid) was investigated. While the most probable interaction is inelastic scattering, collision-induced dissociation can occur to eject CF₃ molecules from the surface. The time-of-flight distributions of both inelastically scattered and CID products show evidence of hyperthermal and thermal interaction channels. Gas-phase-like interactions can lead to CID products leaving the surface with hyperthermal translational energies. Thermal CID products can arise from direct dissociation followed by trapping at the surface. Once the product reaches thermal equilibrium with the surface, it may desorb with a Maxwell-Boltzmann distribution of translational energies. Therefore, the first step in creating volatile CID products is a direct dissociation to create CF₃, which can exit the surface with hyperthermal or thermal translational energies.
Crossed-molecular beams experiments and classical trajectory calculations were used to study the dynamics of Ar + ethane collisions at hyperthermal collision energies. Experimental time-of-flight and angular distributions of ethane molecules that scattered into the backward hemisphere (with respect to their original direction in the center-of-mass frame) were collected and translational energy distributions, derived from the time-of-flight distributions, revealed that a substantial fraction of the collisions transfer abnormally large amounts of energy to internal excitation of ethane. The flux of the scattered ethane molecules increased only slightly from directly backward scattering to sideways scattering. Theoretical calculations show angular and translational energy distributions which are in fairly good agreement with the experimental results. These calculations have been used to examine the microscopic mechanism for large energy transfer collisions (“supercollisions”). Collinear (“head-on”) or perpendicular (“side-on”) approaches of Ar to the C–C axis of ethane do not promote energy transfer as much as bent approaches, and collisions in which the H atom is “sandwiched” in a bent Ar···H–C configuration lead to the largest energy transfer.

A crossed-molecular beams experiment was used to study the dynamics of O(3P) + CO collisions at a hyperthermal collision energy of $<E_{\text{coli}}> = 3.6$ eV. A rotatable mass spectrometer detector was used to monitor inelastically and reactively scattered products as a function of velocity and scattering angle. From these data, center-of-mass (c.m.) translational energy and angular distributions were derived for two channels: inelastic and reactive scattering. Isotopically labeled C$^{18}$O was used to distinguish the reactive channel ($^{16}$O + C$^{18}$O → $^{16}$OC + $^{18}$O) from the inelastic channel ($^{16}$O + C$^{18}$O → C$^{18}$O + $^{16}$O). The reactive $^{16}$OC molecules scattered predominantly in the forward direction –
i.e., in the same direction as the reagent O atoms in the c.m. frame. The c.m. translational energy distribution of the reactively scattered $^{16}$OC and $^{18}$O was very broad, indicating that $^{16}$OC can be formed with a wide range of internal energy. The average internal excitation of the $^{16}$OC product was 40 percent of the available energy. The c.m. translational energy distributions for inelastically scattered C$^{18}$O and $^{16}$O products indicated that an average of 15 percent of the collision energy went into internal excitation of C$^{18}$O, although a small fraction of the collisions transferred nearly all the collision energy into internal excitation of C$^{18}$O. The experimental results were compared with results of quasiclassical trajectory calculations that took into account interactions on the three low-lying triplet potential energy surfaces but did not allow for coupling to the singlet surface. The theoretical calculations produced c.m. translational energy and angular distributions for both channels which closely match the experimentally determined distributions for the reactive channel and which are in quantitative agreement for the inelastic channel. We concluded from the good agreement between experiment and theory that intersystem crossing between triplet and singlet surfaces is unimportant in hyperthermal O + CO collisions. The theoretical calculations, which were validated by the experimental results, were used to derive internal state distributions of scattered CO products and to probe in detail the interactions that lead to the observed dynamical behavior.

Reactions of O($^3P$) with H$_2$O were also studied at hyperthermal collision energies by the crossed-beams technique. A unique water source was designed and built to create a beam of gas-phase water molecules that were crossed with beams of hyperthermal O atoms. The results represent the first experimental observation of the
reaction to produce HO$_2$ + H. The excitation function (relative cross section as a function of collision energy) for the reaction O($^3P$) + H$_2$O → HO$_2$ + H was measured, and the barrier for this reaction was found to be $\sim$60 kcal mol$^{-1}$. The shape of the measured excitation function compared favorably with those of theoretical excitation functions calculated by Dr. Jon Camden and Prof. George Schatz of Northwestern University.

The results of these studies are relevant to the interactions of spacecraft with the ambient O or N$_2$ present in the outer atmosphere of the Earth. Chemical species present in the contamination cloud that surrounds a spacecraft or in rocket exhaust streams may react with O atoms or become highly internally excited by inelastic collisions with O and/or N$_2$. Internally excited products may then radiate in the infrared, which might interfere with a mission. Our results suggest that common energy transfers of 10-20 percent and uncommon energy transfers as high as 50 percent should be taken into account when attempting to model hyperthermal gas-phase processes in the vicinity of a spacecraft. In addition to gas-phase collisions, gas-surface collisions occur between the external materials (often polymers) of a spacecraft and ambient O atoms and N$_2$ molecules. The relative velocities are comparable to those used in the studies described herein. Center-of-mass collision energies may be as high as 10 eV, and large energy transfers in gas-surface collisions may result in collision-induced dissociation (CID). CID may produce radical sites that would make a polymeric material much more susceptible to atomic-oxygen attack. Thus, highly inelastic collisions may act synergistically with atomic oxygen to degrade spacecraft materials.