



Studies of gas-surface interaction dynamics with hyperthermal neutral beams
by Jianming Zhang

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of
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Abstract:

Hyperthermal neutral beams have been employed to study the gas-surface interaction dynamics for several systems, including initial reactions of hyperthermal atomic oxygen with a liquid hydrocarbon surface, collision-assisted erosion of polymers and graphite in an atomic oxygen environment, collision-assisted etching of Si in an atomic chlorine environment, and collision-induced desorption of Cl from a Si surface. Initial reactions between hyperthermal atomic oxygen and hydrocarbon surfaces involve gas-phase like H-atom abstraction to form OH and sequential H-atom abstraction to form H₂O. No volatile C-C bond breaking products were detected in the initial reactions. However, during the steady-state oxidation of polymers and graphite, volatile products of CO and CO₂ are produced, which are believed to account for a significant fraction of the mass loss of polymers or graphite that is observed under continuous atomic-oxygen attack. Exposure of these continuously-oxidized polymer or graphite surfaces to bombardment of hyperthermal inert species results in a dramatic increase in the production of CO and CO₂ and in the erosion rate of the surfaces. This synergism between energetic inert particles and chemically active species incident on surfaces is believed to be a generic effect. Both the production of volatile silicon chloride (SiCl_x, x =1-4) compounds and the Si etching rate are dramatically enhanced with the bombardment of energetic inert species on a continuously chlorinated Si surface. Mechanisms of this collisional effect involve chemical sputtering and chemically-enhanced physical sputtering. In our experiment, the latter mechanism is essentially synonymous with collision-induced desorption. Studies of collision-induced desorption of Cl from a chlorinated Si surface reveal that impulsive bimolecular collision between the incident collider and adsorbate is the dominant process. Although the details of these collisional mechanisms are complicated, the dynamical behavior of the ejected products may be described in terms of a simple kinematic picture in which an incident energetic particle collides with a localized region of the surface that has an effective mass. The studies of initial reactions between atomic oxygen and a saturated hydrocarbon surface and collisional enhancement in material removal under steady-state oxidation conditions are directly relevant to material erosion and degradation on spacecraft in the low Earth orbit environment.

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WITH HYPERTHERMAL NEUTRAL BEAMS

by

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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.

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ABSTRACT

Hyperthermal neutral beams have been employed to study the gas-surface interaction dynamics for several systems, including initial reactions of hyperthermal atomic oxygen with a liquid hydrocarbon surface, collision-assisted erosion of polymers and graphite in an atomic oxygen environment, collision-assisted etching of Si in an atomic chlorine environment, and collision-induced desorption of Cl from a Si surface. Initial reactions between hyperthermal atomic oxygen and hydrocarbon surfaces involve gas-phase like H-atom abstraction to form OH and sequential H-atom abstraction to form H₂O. No volatile C-C bond breaking products were detected in the initial reactions. However, during the steady-state oxidation of polymers and graphite, volatile products of CO and CO₂ are produced, which are believed to account for a significant fraction of the mass loss of polymers or graphite that is observed under continuous atomic-oxygen attack. Exposure of these continuously-oxidized polymer or graphite surfaces to bombardment of hyperthermal inert species results in a dramatic increase in the production of CO and CO₂ and in the erosion rate of the surfaces. This synergism between energetic inert particles and chemically active species incident on surfaces is believed to be a generic effect. Both the production of volatile silicon chloride (SiCl_x, x =1-4) compounds and the Si etching rate are dramatically enhanced with the bombardment of energetic inert species on a continuously chlorinated Si surface. Mechanisms of this collisional effect involve chemical sputtering and chemically-enhanced physical sputtering. In our experiment, the latter mechanism is essentially synonymous with collision-induced desorption. Studies of collision-induced desorption of Cl from a chlorinated Si surface reveal that impulsive bimolecular collision between the incident collider and adsorbate is the dominant process. Although the details of these collisional mechanisms are complicated, the dynamical behavior of the ejected products may be described in terms of a simple kinematic picture in which an incident energetic particle collides with a localized region of the surface that has an effective mass. The studies of initial reactions between atomic oxygen and a saturated hydrocarbon surface and collisional enhancement in material removal under steady-state oxidation conditions are directly relevant to material erosion and degradation on spacecraft in the low Earth orbit environment.

CHAPTER 1

INTRODUCTION

Atomic oxygen is considered to be a serious hazard to spacecraft in low Earth orbit (LEO).¹ At LEO altitudes, ranging from 200-700 km, the residual atmosphere is predominantly neutral atomic oxygen. The second most dominant component is molecular nitrogen, which has densities from a few per cent to more than 50% of those of atomic oxygen, depending on orbital altitude. At common LEO altitudes of 300-400 km, the number densities of atomic oxygen and molecular nitrogen are on the order of 10^9 and 10^7 cm⁻³, respectively.² Combining these densities with a spacecraft velocity of ~ 7.4 km s⁻¹ results in a flux of $\sim 10^{15}$ atoms cm⁻² s⁻¹ of O atoms and a flux of $\sim 10^{13}$ molecules cm⁻² s⁻¹ of N₂ molecules on ram surfaces.^{3,4} The average collision energies of O atoms and N₂ molecules on the ram surfaces of a spacecraft are ~ 450 and 790 kJ mol⁻¹, respectively. The ambient temperature of ~ 1000 K results in an energy spread (full width at half maximum) of 200 kJ mol⁻¹ (O atoms) and 350 kJ mol⁻¹ (N₂ molecules).^{3,5} Energetic collisions of O atoms with spacecraft surfaces can degrade materials through oxidation and erosion. The erosion mechanisms of polymeric materials on spacecraft are complex and involve initial reactions at the gas-surface interface as well as steady-state material removal processes. Although the production of CO and CO₂ through reactions of O atoms with polymer surfaces is responsible for most of material removal during steady-state exposure to the LEO environment, collisions of relatively inert molecular nitrogen may play an important role in accelerating the reaction rate.

Chapter 2 of this thesis describes an effort to understand the initial reaction mechanisms of hyperthermal atomic oxygen with hydrocarbon surfaces. A liquid hydrocarbon surface was used to provide the ability to study the reactions only at the initial steps. Chapters 3 and 4 describe the collisional effects of bombardment of inert energetic species on continuously-oxidized polymers and graphite surfaces. The collisional enhancement of the erosion rate under steady-state oxidation conditions is dramatic, and this synergism between energetic inert particles and chemically reactive species incident on a surface is believed to be a generic phenomenon, which is widely observed and analogous to processes occurring in ion-assisted etching in the semiconductor industry. Studies of collision-assisted etching of Si in an atomic chlorine environment are reported in Chapter 5. Results from Chapters 3-5 reveal that the collisional effect involves chemical sputtering and chemically-enhanced physical sputtering. In our experiment, the latter sputtering mechanism is essentially synonymous with collision-induced desorption. Details of a study of collision-induced desorption of Cl from Si surface are discussed in Chapter 6. A summary of this thesis is presented in Chapter 7.

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CHAPTER 2

REACTIVE AND INELASTIC SCATTERING DYNAMICS OF HYPERTHERMAL
OXYGEN ATOMS ON A HYDROCARBON SURFACEAbstract

The dynamics of the initial interactions of hyperthermal O atoms with a saturated hydrocarbon surface have been investigated by directing an O-atom beam at a continuously refreshed liquid squalane surface and monitoring energy and angular distributions of inelastically scattered O atoms and reactively scattered OH and H₂O. These products are formed through thermal and nonthermal processes. The inelastic scattering processes may be described in terms of the limiting cases of direct inelastic scattering (nonthermal) and trapping desorption (thermal). The initial step leading to production of volatile OH and H₂O is believed to be direct H-atom abstraction to form OH. Once formed, the OH may scatter directly into the gas phase before thermal equilibrium with the surface is reached, or it may undergo further collisions and reactions with the surface. These secondary interactions include trapping and desorption of OH and abstraction of a second hydrogen atom to form H₂O. Interactions that occur before thermal equilibrium with the surface can be reached lead to products that exit the surface at hyperthermal velocities, while those that occur in thermal equilibrium with the surface give products that leave the surface at thermal velocities given by the surface temperature. Direct, single collision, scattering events that produce O and OH are described with a kinematic picture that allows the determination of the effective surface mass encountered

by an incident O atom, the atom-surface collision energy in the center-of-mass frame, and the fraction of the center-of-mass collision energy that goes into translation of the scattered gaseous species and the recoiling surface fragment. Center-of-mass velocity flux maps for OH are indicative of a predominant reaction mechanism in which the H atom is stripped from the hydrocarbon with a nearly perpendicular O-H-C transition state, although some reactions appear to proceed through a more collinear transition state.

Introduction

The reactions of atomic oxygen with hydrocarbons have been studied extensively in both kinetics and dynamics during the past 40 years due to their essential role in many important chemistry fields, such as combustion, atmospheric chemistry. In the low Earth orbit (LEO) environment, the energetic collisions between spacecraft and atomic oxygen promote the oxidation and erosion of exposed polymer materials.¹⁻⁵ Studies of material degradation and durability under atomic oxygen attack have been performed in decades. Hydrocarbon polymers are particularly vulnerable to material loss in LEO, probably because the oxides of carbon (CO and CO₂) are volatile and can carry carbon away from the surface.⁶ The reactions of atomic oxygen with hydrocarbon molecules in the gas phase serve as models for the relatively unstudied reactions of atomic oxygen with a hydrocarbon surface.

The ground state oxygen atom O(³P) and the first electronic excited state oxygen atom O(¹D) react differently with the saturated hydrocarbons. O(³P) reacts with the saturated hydrocarbon by abstracting one hydrogen atom to form OH. In a crossed

molecular beam experiment that employed laser-induced fluorescence detection of OH product, the OH cold rotational state distributions implied that the abstraction reaction occurs only when $O(^3P)$ is collinear to a C-H bond.⁷ For $O(^3P)$ abstraction reaction, the exothermicities are -9.6, -29.3, and -43.1 kJ/mol, and the activation energies are 28.9, 18.8, and 13.8 kJ/mol for primary, secondary, and tertiary H-atom abstraction, respectively.⁷ More recent study⁸ confirmed the collinear configuration for $O(^3P)$ abstraction reaction and suggested that this constraint also applied to CH_4 and C_2H_6 . In a study of the reaction of $O(^3P)$ with cyclohexane clusters,⁹ Rudich and coworkers proposed that blocking of the abstraction reaction occurs when clusters are involved. Unlike $O(^3P)$ reactions, $O(^1D)$ can react with the saturated hydrocarbons by either H abstraction or insertion into a C-H bond. Luntz¹⁰ pointed out that the insert component dominates for small hydrocarbons (CH_4 , C_2H_6), while the abstraction component dominates for larger hydrocarbons [C_3H_8 , $C(CH_3)_4$]. For both insertion and abstraction mechanisms, the lifetime of the intermediate collision complex is enhanced by larger hydrocarbon molecules¹⁰ or by clusters.¹¹ The enhanced lifetime of the excited alcohol intermediate for the insertion reaction tends to stabilize the intermediate and leave it intact. While for the abstraction mechanism, the larger hydrocarbons and the longer lifetime of the intermediate increase the total probabilities of singlet-triplet surface crossing. Due to that the rotational distributions for $O(^1D)$ abstraction component is so similar to that produced by $O(^3P)$ reactions, $O(^1D)$ abstraction component is treated as the result of $O(^3P)$ reactions.¹⁰

The reactions of atomic oxygen with the liquid hydrocarbon surface have similar but different pathways than the reactions in the gas phase. The nature of the highly corrugated surface makes the gas-liquid interactions and reactions more complicated. A molecular beam study of collisions of Ne, CH₄, NH₃, and D₂O with glycerol and squalane¹² revealed that the impulsive energy transfer was extensive and depended only weakly on the type of gas or liquid. Both direct inelastic scattering and trapping desorption of the incident gases were observed. For the direct inelastic scattering, the gases appeared to undergo hard sphere-like collisions. While for trapping desorption processes, the thermal accommodation depended on the roughness and softness of hydrocarbons and the attractive forces between gases and liquids. The hard sphere-like collisions between the gas-liquid collisions were also observed in other experiments.¹³⁻¹⁵ In a comparison of a molecular dynamics computer simulations and the molecular beam scattering experiments for scattering of high-energy Xe atoms (180 kJ/mol) off liquid squalane, Lipkin *et al*¹⁴ reported that the instantaneous local structure of the liquid surface is highly corrugated. The out-of-plane scattering was extensive and the direct scattering can be interpreted in terms of contributions from single and multiple collision events. However, the single-collision hard-sphere model was successful in interpreting the data because the contributions of multiple collisions were more uniformly spread in final angle space. The assumption that single-collision events dominate in the direct inelastic scattering was also supported in a study of thermal roughing of liquid surface.¹⁶

Single collision processes can be described in the center-of-mass reference frame. Newton diagram and center-of-mass flux contour map have been widely used to describe

gas phase reactions.¹⁷ For the gas-surface interactions, simple Newton diagram can be constructed under the assumption that the surface collision partner of the incident particle is localized and has finite effective mass¹⁸⁻²⁰.

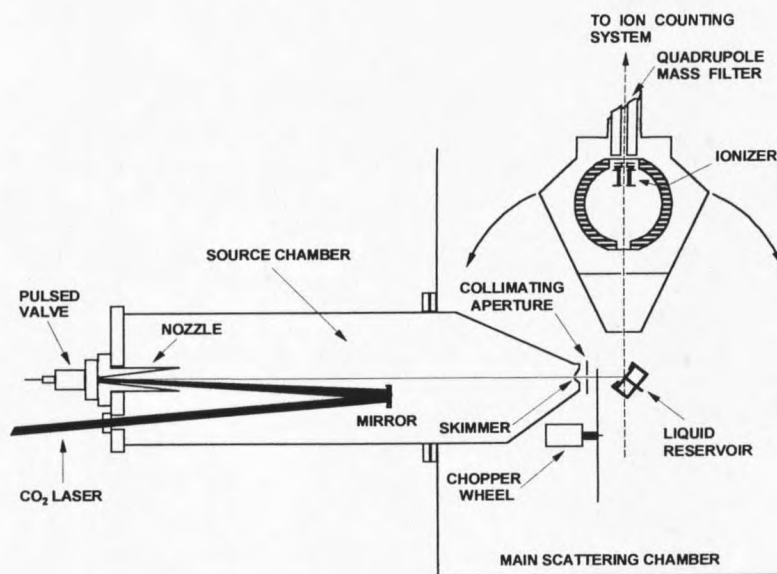


Figure 1. Schematic diagram of the laser-detonation hyperthermal beam source, the differentially-pumped scattering region containing the liquid surface, and the rotatable mass spectrometer detector.

In a previous study of reaction of atomic oxygen with liquid hydrocarbon surface²¹, two supersonic atomic oxygen beams with the average translational energies of 21 and 47 kJ mol⁻¹ were directed to a continuously refreshed squalane surface. O(³P) abstraction is the dominant mechanism to form volatile OH radical, where the hyperthermal OH product is formed through Eley-Rideal mechanism. A second product, H₂O, is formed by abstraction of a second hydrogen atom from the hydrocarbon chain by the primary OH product. In this paper, we present an investigation of the dynamics of the initial

interactions of hyperthermal O atoms with a squalane surface. Two atomic oxygen beams with the average translational energies of 297 and 504 kJ mol^{-1} were directed to the hydrocarbon surface. Inelastically and reactively scattered products were detected in a wide range of final angles (-13° - 85°).

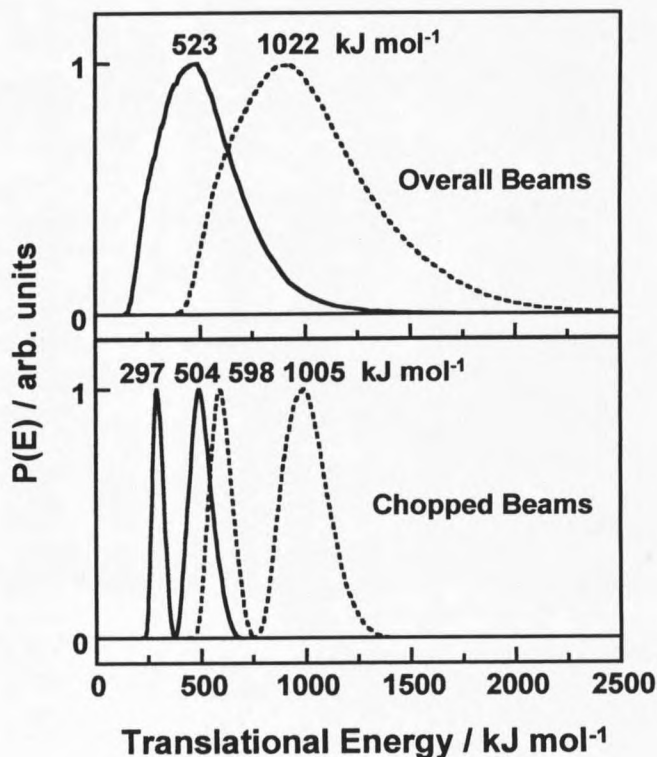


Figure 2. Translational energy distributions of atomic (solid curves) and molecular (dashed curves) oxygen components in the hyperthermal oxygen beams used. The overall beam distributions (top panel) were narrowed with the use of a chopper wheel, allowing the selection of the beam energies as shown (bottom panel).

Experimental Details

The experiments were performed with the use of a crossed molecular-beams apparatus^{22,23} coupled to a fast-atom beam source (see Fig. 1). A pulsed beam containing

hyperthermal oxygen atoms was directed at a saturated hydrocarbon surface, and a rotatable mass spectrometer detector was used to monitor scattered products. The surface and detector rotated about the same axis, with the surface normal rotating in the same plane as the detector. Reactively and inelastically scattered species that emerged from the surface were detected as a function of incident angle θ_i and final angle θ_f , with respect to the surface normal. For beam characterization, the surface was lowered out of the beam path, and the beam was directed into the detector.

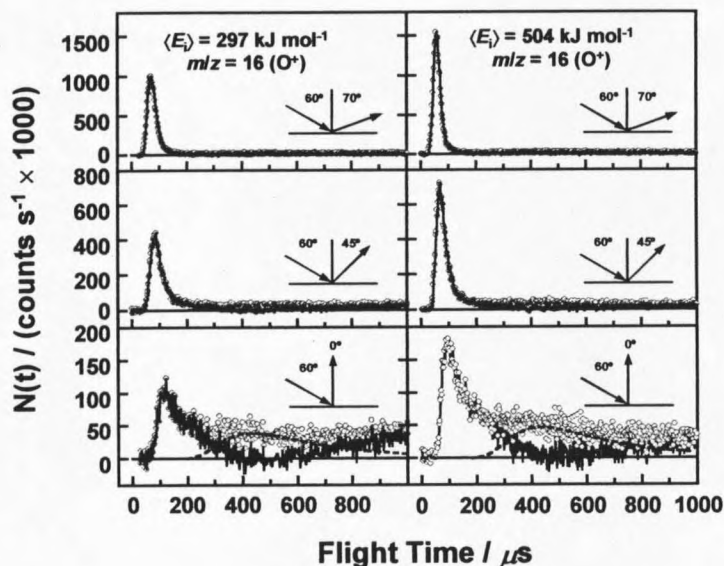


Figure 3. Representative time-of-flight distributions of scattered O atoms following impact with a squalane surface. The O-atom beams had average energies of 297 kJ mol^{-1} (left panel) and 504 kJ mol^{-1} (right panel) and impinged on the surface at an incident angle of 60° . The scattered O atoms were detected at three final angles: 70° , 45° , and 0° . The dashed curves represent the thermal (Maxwell-Boltzmann) components, and the solid curves represent the hyperthermal components, which come from the difference between the overall distributions (circle) and the thermal components.

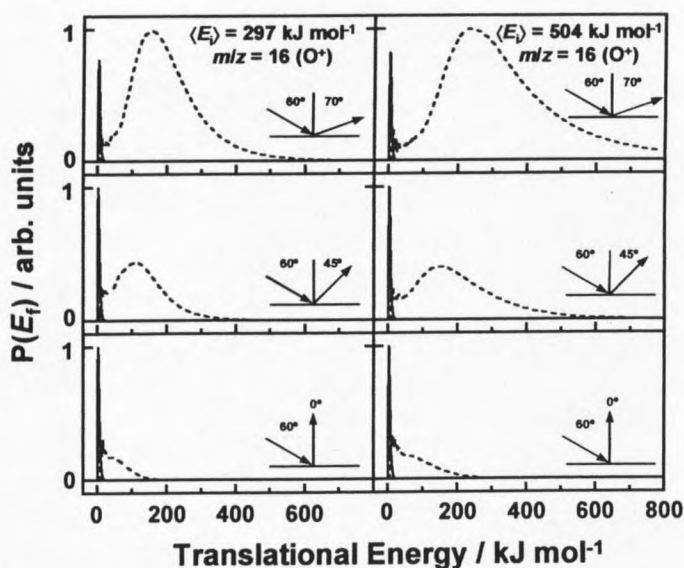


Figure 4. Translational energy distributions of scattered O atoms derived from the time-of-flight distributions shown in Figure 3. Each panel shows thermal (solid curves) and hyperthermal (dashed curves) components.

The beam source is based on the laser detonation source originally developed by Physical Sciences, Inc.²⁴ A piezoelectric pulsed valve²⁵ is used to inject a burst of oxygen gas, at 10-20 bars of pressure, into a 10-cm-long, water-cooled, gold-plated, copper nozzle. As the gas expands into the nozzle cone, a CO₂ TEA laser, with pulse energies in the range of 5 to 7 Joules, is fired, and the light is focused into the gas by means of a gold mirror placed 50 cm from the apex of the cone. The laser induces a breakdown in the gas and heats the resulting plasma to more than 20,000 K. The high-temperature, high-density plasma expands rapidly into the diverging cone following detonation and engulfs the remaining cold gas. The local densities in the nozzle are sufficient to permit efficient electron-ion recombination, but by the time the atoms formed in the plasma have cooled enough to recombine, the expansion is largely

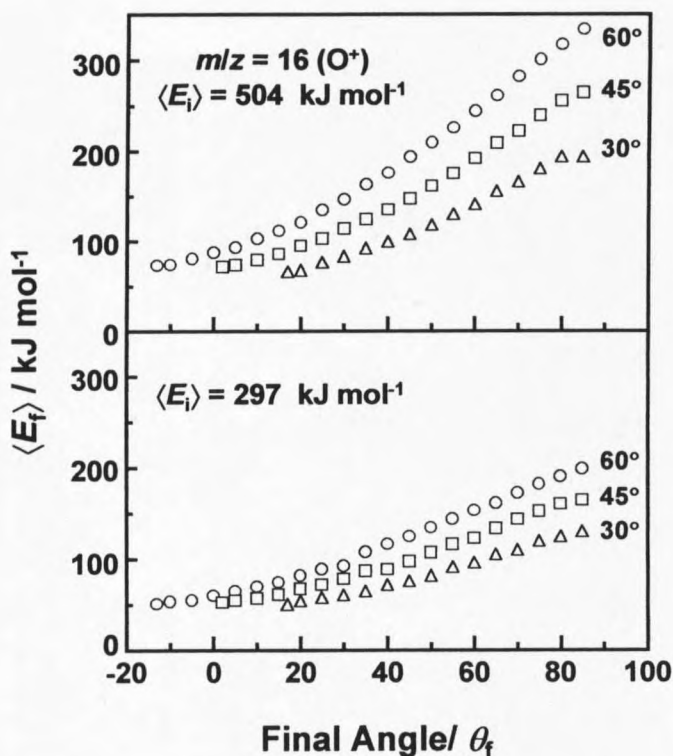


Figure 5 Average final translational energies of hyperthermal O as a function of final angle, corresponding to $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ (top panel) and $\langle E_i \rangle = 297 \text{ kJ mol}^{-1}$ (bottom panel) and to three incident angles, 60°, 45°, and 30°.

complete. The resulting beam consists predominantly of fast neutral atomic and molecular oxygen atoms, with a small ionic component ($\ll 1\%$). The beam is collimated with the use of a 3-mm-dia skimmer placed 80 cm from the apex of the nozzle cone. After the beam exits the source chamber through this skimmer, it is further collimated with a second 1.8-mm-dia aperture 2 cm downstream from the skimmer. The beam pulse has a broad velocity distribution, but because the pulse originates in a confined region of space, the laser detonation source is effectively a point source. Therefore, a single synchronized chopper wheel (slotted disk), placed 85 cm from the nozzle apex, is used to select a narrowed velocity distribution from the overall beam

pulse. The chopper wheel blocks all the light emitted by the source plasma and essentially all the residual ions, which travel at higher velocities than most of the atoms (or molecules) in the neutral beam pulse. The beam struck the target surface 7 mm past the chopper wheel, so the total distance from the nozzle apex to the surface was 92 cm. The estimated atomic oxygen flux at this distance from the source is $\sim 10^{14}$ atoms cm^{-2} pulse $^{-1}$, and the beam diameter is only marginally larger than the last defining aperture (1.8 mm). The pressure in the main chamber during the experiments was maintained near 2×10^{-7} Torr.

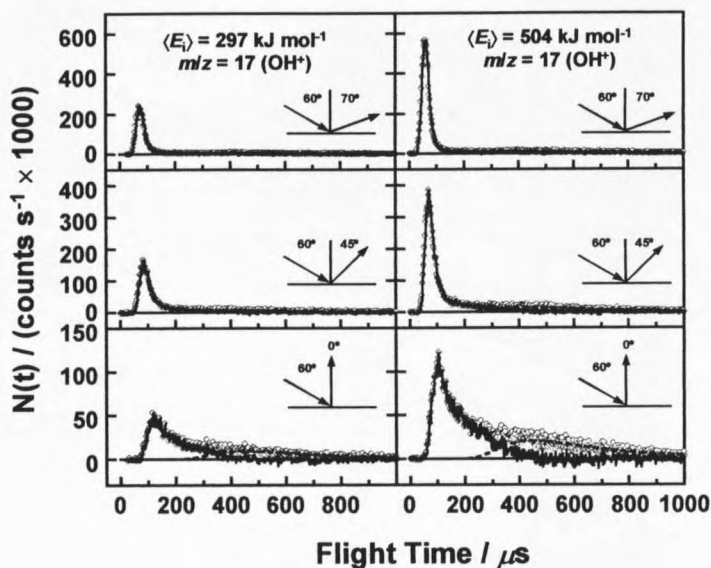


Figure 6. Representative time-of-flight distributions of reactively scattered OH following reaction of O-atoms with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol^{-1} . The incident angle of the beam was 60° and the detection angles were 70° , 45° , and 0° .

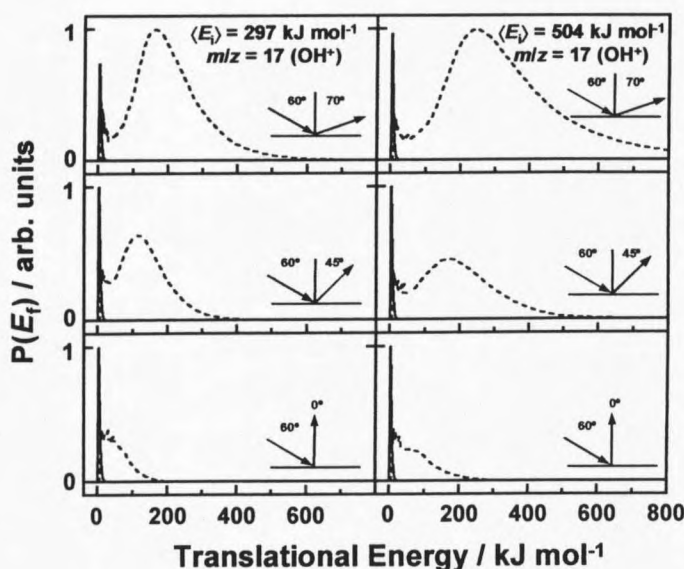


Figure 7. Translational energy distributions of reactively scattered OH derived from the time-of-flight distributions shown in Figure 6.

Characterization of the beam source was accomplished by measuring time-of-flight distributions of mass-selected species in the beam pulse. Translational energy distributions (probability density distributions as a function of translational energy) were derived by straightforward methods.²⁶ Figure 2 shows translational energy distributions of the atomic and molecular oxygen components in the overall beam pulse and the narrowed distributions which describe the two beams used in these experiments. The average atomic-oxygen translational energies of the two beams were 297 kJ mol^{-1} and 504 kJ mol^{-1} , and the ratios of the average translational energy E_i to the energy width ΔE_i (full width at half maximum) were 5.0 and 4.3, respectively. The ratios of the atomic oxygen concentration to molecular oxygen concentration in the beams, $[\text{O}]/[\text{O}_2]$, were 0.64 and 1.0, respectively. The translational energy and the $[\text{O}]/[\text{O}_2]$ ratio may be varied by adjusting the source operating conditions, most importantly the amount of gas in the

nozzle when the CO₂ laser fires. In order to verify that reactions of the molecular oxygen component in the beam did not contribute to the observed signals, another beam was created, which had an average O-atom translational energy of 504 kJ mol⁻¹ and a [O]/[O₂] ratio of 0.33.

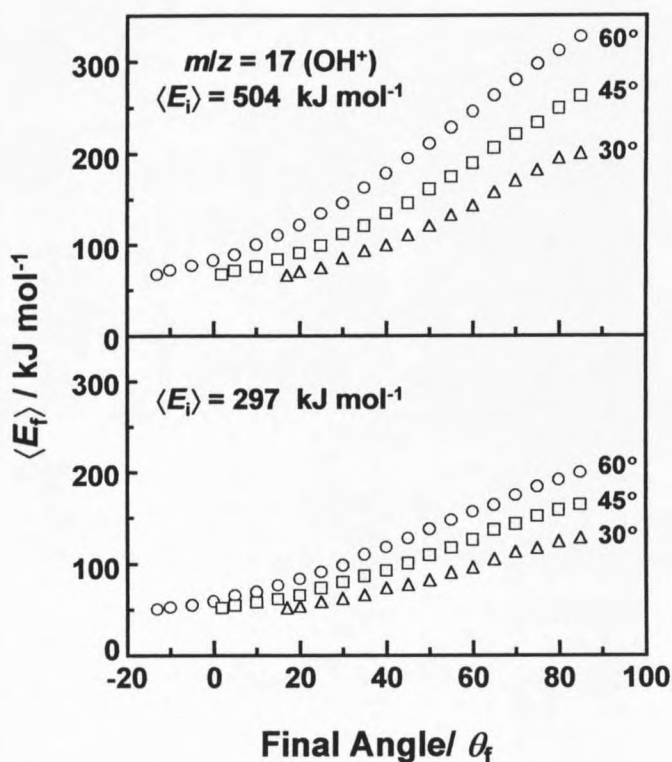


Figure 8. Average final translational energies of hyperthermal OH as a function of final angle, corresponding to $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ (top panel) and $\langle E_i \rangle = 297 \text{ kJ mol}^{-1}$ (bottom panel) and to three incident angles, 60°, 45°, and 30°.

The hyperthermal beams were directed at the surface of the saturated hydrocarbon squalane (2,6,10,15,19,23-hexamethyltetracosane), which is a liquid at room temperature with a vapor pressure of $\sim 2 \times 10^{-8}$ Torr. The squalane sample was degassed for more than

12 h before pouring it into a reservoir in the vacuum chamber. A continuously refreshed film of squalane was produced by rotating a polished stainless steel wheel through the liquid reservoir²⁷ held at 20°C. The surface of the film on the wheel was cleaned by passing the wheel by a sapphire scraper, leaving a fresh 100- μm -thick film on the wheel just one second before it was struck by the beam pulse. The wheel rotation rate was 0.25 Hz, while the repetition rate of the pulsed beam was 1.9 Hz. Therefore, each beam pulse encountered a fresh squalane surface.

Inelastic scattering signals were collected at mass-to-charge ratios (m/z) of 16 (O^+) and 32 (O_2^+). Reactive product signals were only detected at $m/z = 17$ (OH^+) and 18 (H_2O^+). Signals indicative of the possible reactive products, CO and CO_2 , were not observed. While it is possible that CH_3O might be produced, signals at $m/z = 30$ and 31 were roughly two orders of magnitude lower than the OH^+ signal, and they were barely discernable from the noise. H-atom and HO_2 product signals, if present, could not be detected because of high background signals at m/z ratios of 1 and 33. The focus of the experiment was thus on the time-of-flight (TOF) distributions that were collected at m/z ratios corresponding to O^+ , OH^+ , H_2O^+ , and O_2^+ , which were obtained for three incident angles (30°, 45°, and 60°) and a variety of final angles. Integrated counting rates fell in the ranges of 8×10^4 to 9×10^5 , 2×10^4 to 4×10^5 , 1×10^4 to 3×10^5 , and 2×10^5 to 2×10^6 counts s^{-1} for $m/z = 16, 17, 18$, and 32, respectively. Identical pairs of incident angles were used in the accumulation of data for both the lower- and higher-energy beams. For each incident angle and energy, TOF distributions were accumulated for 200 beam pulses at each final angle. The final angle was incremented until the entire (incident-angle-

dependent) angular range was covered. Then the increment direction was reversed, and the cycle was repeated until a total of four TOF distributions had been recorded for every final angle. The four distributions were then summed to yield a TOF distribution whose relative magnitude and shape were minimally affected by long-term drifts in the experimental parameters. The TOF distributions were corrected for the ion flight time from the Brink ionizer to the Daly ion counter, $3.47(m/z)^{1/2}$. The TOF distributions collected at $m/z = 16$ and 17 were also corrected for contributions from ionizer fragmentation of O_2 and/or H_2O . Time zero in the TOF distributions presented here corresponds to the time at which O atoms with the average translational energy of the pulse strike the surface.

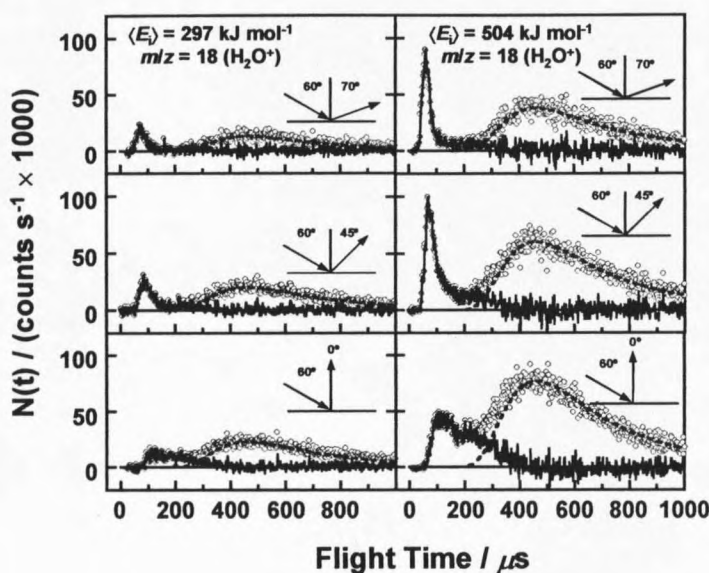


Figure 9. Representative time-of-flight distributions of reactively scattered H_2O following reaction of O-atoms with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol^{-1} . The incident angle of the beam was 60° and the detection angles were 70° , 45° , and 0° .

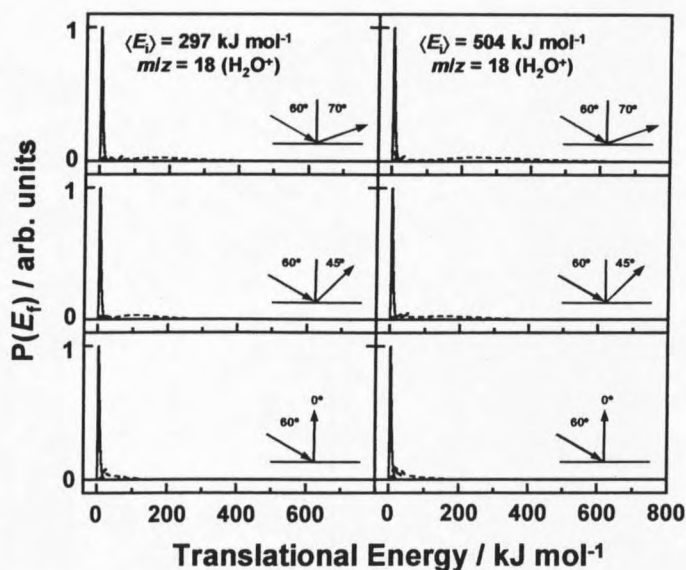


Figure 10. Translational energy distributions of reactively scattered H_2O derived from the time-of-flight distributions shown in Figure 9.

Results and Analysis

Dynamical Behavior Of Scattered Products

The most probable interaction of an oxygen atom (even with hundreds of kJ mol^{-1} of translational energy) with the squalane surface was non-reactive, or inelastic scattering. Figure 3 shows representative TOF distributions of O atoms that scattered from the squalane surface after impinging at an incident angle, θ_i , of 60° and average incident translational energies of 297 kJ mol^{-1} and 504 kJ mol^{-1} . These TOF distributions were collected at three different final angles, θ_f , as shown. The shapes of the signals depended on the incident and final angles. For a given incident angle, the signals generally increase with larger final angles, until the final angle becomes larger than 75° . In addition, the average final translational energy increases with increasing final angle, up to the

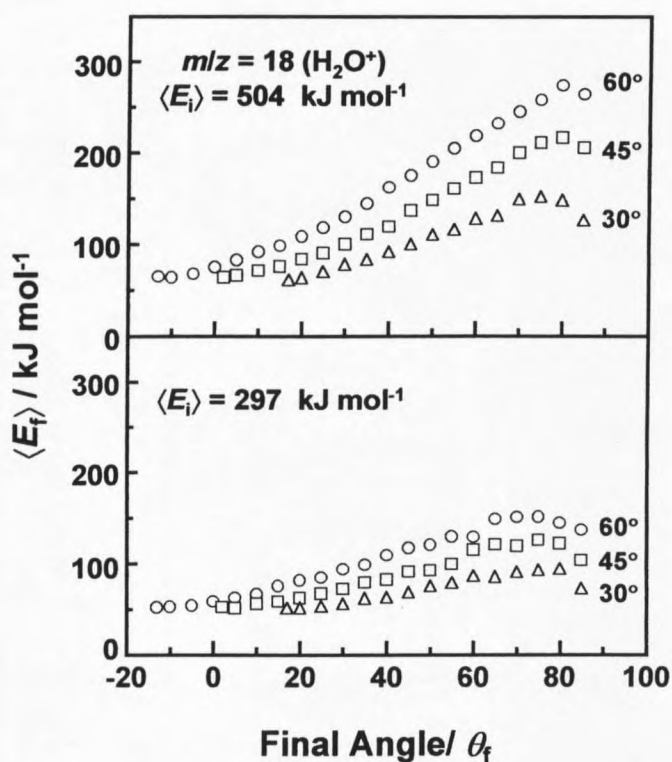


Figure 11. Average final translational energies of hyperthermal H_2O as a function of final angle, corresponding to $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ (top panel) and $\langle E_i \rangle = 297 \text{ kJ mol}^{-1}$ (bottom panel) and to three incident angles, 60°, 45°, and 30°.

maximum final angle observed, which was 85°. A tail at long flight times persists in the TOF distributions. Assuming O atoms exited the surface at velocities given by the surface temperature, the signal maximum would be predicted to occur at a flight time of 430 μs , which falls in the range of the persistent tail. It thus appears that a small fraction of incident O atoms lose essentially all their translational energy to the surface, while most O atoms scatter after losing only a fraction of their incident energy in the surface. As in our earlier studies of gas-surface scattering, we treated the non-reactive scattering in terms of two limiting cases, direct inelastic scattering (IS) and trapping desorption

(TD).^{18,21,28} The slower (TD) component was assumed to correspond to O atoms that came into thermal equilibrium with the surface and therefore exited the surface with a Maxwell-Boltzmann (MB) distribution of velocities. The difference between the overall TOF distribution and the assumed MB component was taken to be the TOF distribution of the second, hyperthermal component, which corresponds to products that exited the surface before thermal equilibrium was established.

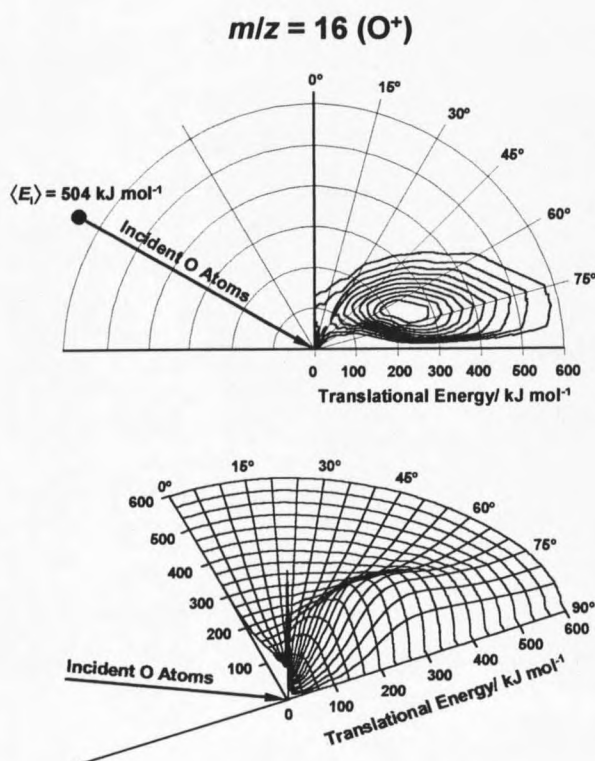


Figure 12. Contour map and mesh plot of translational energy distributions for inelastically scattered O atoms following impact with a squalane surface at $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$.

The process of deconvoluting the TOF distributions yielded probability density distributions as a function of final translational energy, which are commonly referred to

as translational energy distributions $P(E_t)$. The $P(E_t)$ distributions presented here were derived with the approximation that the incident beam was monoenergetic. While this approximation leads to derived $P(E_t)$ distributions that are slightly broader than they should be, the average energies of these distributions are accurate.²⁸ Figure 4 shows the translational energy distributions that were derived from the TOF distributions in Figure 3. The peak of each MB (or TD) energy distribution has been normalized to one, and the areas of each set of TD and IS distributions are proportional to the respective fluxes of O atoms that scatter by the two processes. The kinetic energy distributions for the IS component appear to be bimodal. The apparent non-zero probabilities of scattered translational energies above the average incident beam energies (297 or 504 kJ mol⁻¹) reveal the limitation of the monoenergetic beam approximation. The average energies of the O atoms which scattered directly (IS) at each final angle were calculated for each of the three incident angles and were plotted as a function of final angle as shown in Figure 5.

The dominant reactive product observed following O-atom collisions with a squalane surface was OH. Figure 6 shows representative TOF distributions of OH that scattered from the squalane surface after impinging O atoms struck the surface at an incident angle of 60° and average incident translational energies of 297 kJ mol⁻¹ and 504 kJ mol⁻¹. Both the shapes and the dependencies of these TOF distributions on final angle indicate scattering dynamics that are very similar to those of O-atom inelastic scattering. These distributions were deconvoluted in a procedure analogous to that used to deconvolute the TOF distributions for inelastically scattered O atoms. Translational energy distributions

that were derived from the TOF distributions in Figure 6 are presented in Figure 7. Average final energies obtained from the $P(E_f)$ distributions corresponding to OH products that exited the surface at greater-than-thermal (hyperthermal) translational energies are plotted in Figure 8 as a function of final angle. The average final energies of the hyperthermal OH product clearly increased with increasing final angle for all incident angles used. In addition, for a given set of incident and final angles, the final OH energy increased when the incident O-atom energy increased.

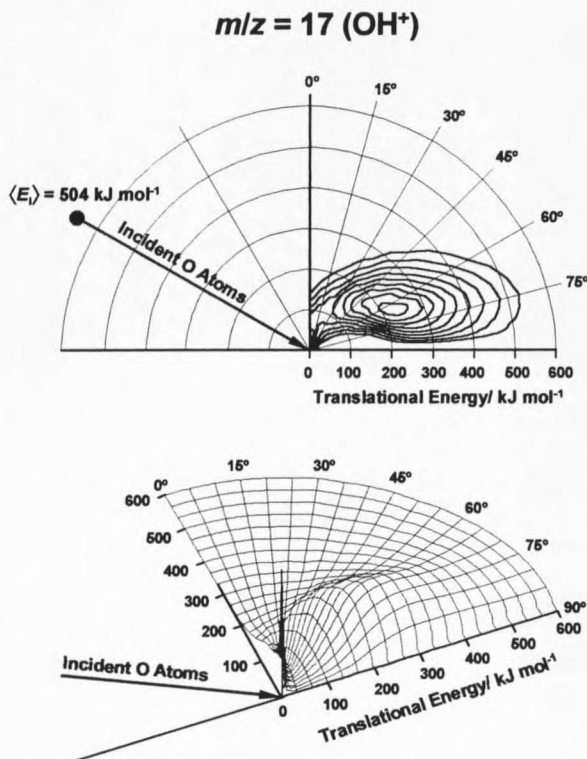


Figure 13. Contour map and mesh plot of translational energy distributions for reactively scattered OH following reaction of O-atoms with a squalane surface at $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$.

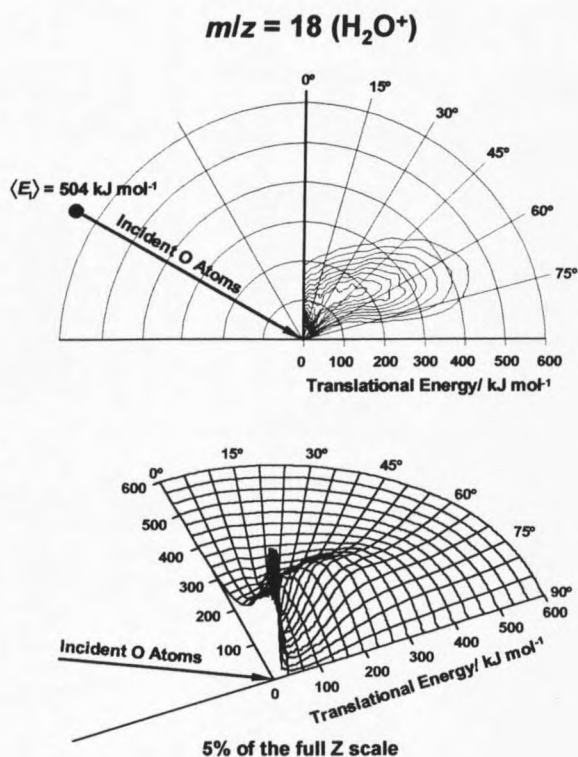


Figure 14. Contour map and mesh plot of translational energy distributions for reactively scattered H_2O following reaction of O-atoms with a squalane surface at $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$.

The other observed reactive product was H_2O . Figure 9 shows representative TOF distributions of H_2O produced from the interaction of O atoms with a squalane surface at an incident angle of 60° and average incident energies of 297 kJ mol^{-1} and 504 kJ mol^{-1} . The H_2O product TOF distributions have a prominent thermal component, suggesting that a large fraction of the H_2O molecules were released in thermal equilibrium with the surface. The hyperthermal component in the TOF distributions exhibited similar dynamical behavior as the hyperthermal O and OH signals: a trend toward shorter flight time and higher intensity for more grazing incidence collisions with more grazing final

angles. $P(E_f)$ distributions for the H_2O product were derived in the same manner as those for O and OH. The $P(E_f)$ distributions that were derived from the TOF distributions in Figure 9 are shown in Figure 10. These distributions indicate comparable fluxes of H_2O from thermal and non-thermal reaction pathways. Average final translational energies of the hyperthermal H_2O product as a function of final angle are displayed in Figure 11. While the trends are similar to those seen for the OH product (Figure 8), the H_2O hyperthermal products exit the surface at somewhat lower energies than the hyperthermal OH products do (for a given θ_i and θ_f).

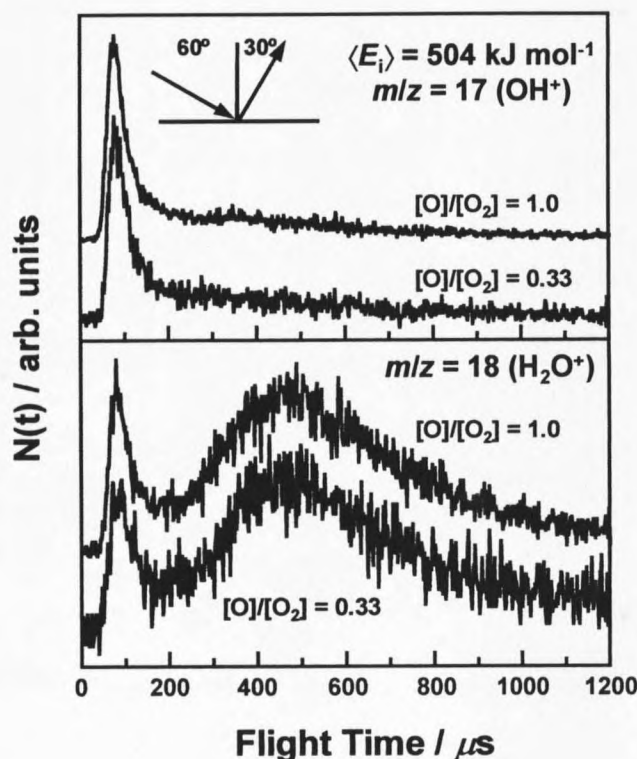


Figure 15. Time-of-flight distributions of OH and H_2O following impact with a squalane surface of two different atomic oxygen beams with different O/ O_2 ratios but same translational energy. Within the signal-to-noise and time resolution limitations of the data, the shapes of these distributions are identical.

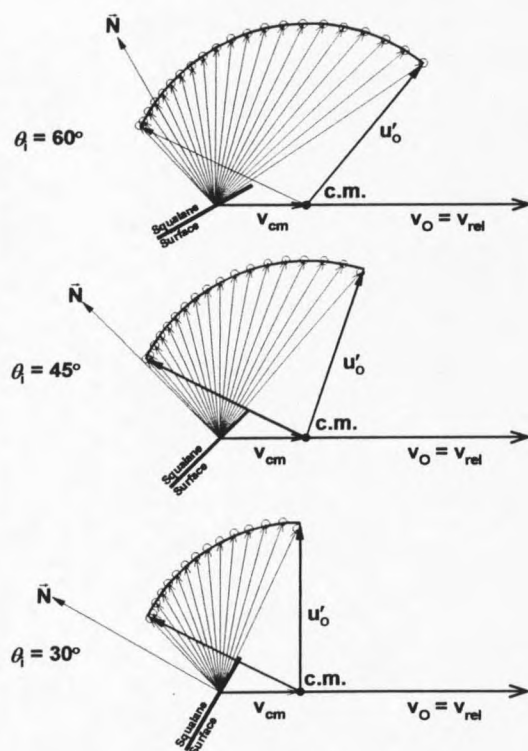


Figure 16. Newton diagrams for direct inelastic scattering of O atoms following impact with a squalane surface at $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ, 45^\circ$, and 30° .

Further manifestations of the dynamical behavior of the scattered products are reflected in the angular distributions of product flux. The combination of these angular distributions and the translational energy distributions provides a map of final energy and flux as a function of final angle. Such maps are represented in Figures 12-14 for the interactions of O atoms with a squalane surface at an average incident energy of 504 kJ mol^{-1} and an incident angle of 60° . Both thermal and hyperthermal product fluxes and energies are included in these maps. The hyperthermal product angular distributions are far from cosine, with maxima in the vicinity of the specular angle. On the other hand, the thermal products do follow a $\cos\theta_f$ distribution.

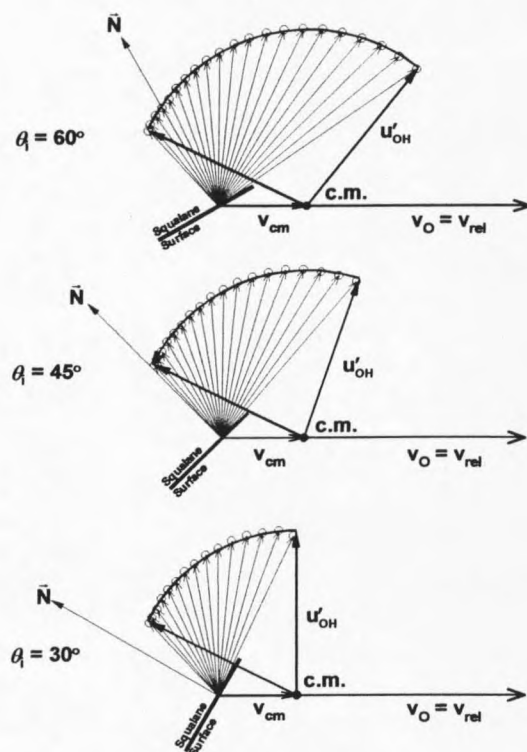


Figure 17. Newton diagrams for reactive scattering of OH (hyperthermal components) following impact of O atoms with a squalane surface at $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$, 45° , and 30° .

The possibility that the molecular oxygen component of the hyperthermal beam affected the observed reactive signals was investigated by varying the concentration ratio of O and O₂ in the beam. Figure 15 shows representative TOF distributions of OH and H₂O that were produced from the interaction of two different incident beams with the squalane surface. The beams had concentration ratios, [O]/[O₂], of 1.0 and 0.33. The shapes of the TOF distributions corresponding to impingement of each beam were identical. This same result was obtained for different [O]/[O₂] ratios in the lower energy beam, where the average translational energy of the atomic oxygen component was $\langle E_i \rangle =$

297 kJ mol⁻¹. The insensitivity of the TOF distributions of OH and H₂O with the [O]/[O₂] ratio in the incident beam suggests that only reactions involving atomic oxygen led to these observed products. The invariance of the observed products with incident beam conditions (for a given O-atom translational energy) also suggests that other potential byproducts in the hyperthermal beam did not play a role in the reactions that were probed. Enriching the beam in molecular oxygen should enhance the quenching of many excited-state species [e.g., O(¹D)] that might be formed in the nozzle. In addition, a change beam composition would be expected to result in a change in the small ionic fraction in the beam. As no change was observed in the TOF distributions of the reactive products when the beam composition was changed, it is likely that the key reactions that led to the observed products involved only atomic oxygen in its ground atomic state, O(³P).

Gas-Surface Interaction Kinematics

The dynamical behavior of the hyperthermal products suggests a gas-phase-like process where the incident O atom is viewed as interacting with a localized region of the surface. Simple Newton diagrams have been constructed for the interaction of energetic oxygen atoms with a squalane surface^{18,19} and for the interaction of energetic argon atoms with oxidized graphite and polyethylene surfaces.²⁰ These simple diagrams have been constructed with the use of average velocities of the incident atoms and scattered products. The Newton diagrams provide a picture of atom-surface scattering in the center-of-mass (c.m.) reference frame, with values derived for the effective surface mass, the c.m. collision energy, and the total c.m. energy that goes into translation of the

scattered volatile product and the recoiling surface fragment. Figures 16 and 17 show representative Newton diagrams for inelastically scattered O and reactive scattering of OH following impact of O atoms on the surface at an average incident energy of 504 kJ mol⁻¹. Tables 1 and 2 contain c.m. quantities that were derived from these diagrams and analogous diagrams for scattering with lower-energy O atoms. The average velocities of the hyperthermal H₂O product did not lead to a simple Newton diagram that could be fit by a circle in the c.m. reference frame (Figure 18); therefore, c.m. data were not derived for this reactive pathway.

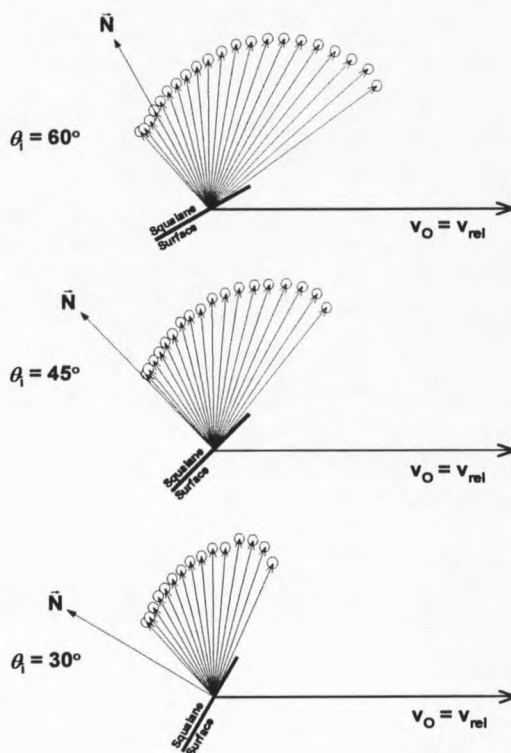


Figure 18. Newton diagrams for reactive scattering of H₂O (hyperthermal components) following impact of O atoms with a squalane surface at $\langle E_i \rangle = 504$ kJ mol⁻¹ and $\theta_i = 60^\circ$, 45° , and 30° .

Table 1. Center-of-mass quantities derived from a kinematic analysis of direct inelastic scattering of O atoms and reactive scattering of OH (hyperthermal components) following impact of O atoms with $\langle E_i \rangle = 504 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$, 45° , and 30° on a squalane surface.

Scattered Products	θ_i	m_s / amu	$\langle E_{\text{coll}} \rangle / \text{kJ mol}^{-1}$	$\langle E_T \rangle / \text{kJ mol}^{-1}$	$\langle E_{\text{int}} \rangle / \text{kJ mol}^{-1}$
$m/z = 16 (\text{O}^+)$	60°	39.1	357	244	113
	45°	41.1	362	236	126
	30°	45.1	371	212	159
$m/z = 17 (\text{OH}^+)$	60°	40.4	360	246	114
	45°	43.0	366	234	132
	30°	46.3	373	219	154

Table 2. Center-of-mass quantities derived from a kinematic analysis of direct inelastic scattering of O atoms and reactive scattering of OH (hyperthermal components) following impact of O atoms with $\langle E_i \rangle = 297 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$, 45° , and 30° on a squalane surface.

Scattered Products	θ_i	m_s / amu	$\langle E_{\text{coll}} \rangle / \text{kJ mol}^{-1}$	$\langle E_T \rangle / \text{kJ mol}^{-1}$	$\langle E_{\text{int}} \rangle / \text{kJ mol}^{-1}$
$m/z = 16 (\text{O}^+)$	60°	42.7	215	150	65
	45°	45.4	219	146	73
	30°	50.0	224	135	89
$m/z = 17 (\text{OH}^+)$	60°	43.6	217	156	61
	45°	46.9	221	150	71
	30°	53.4	228	136	92

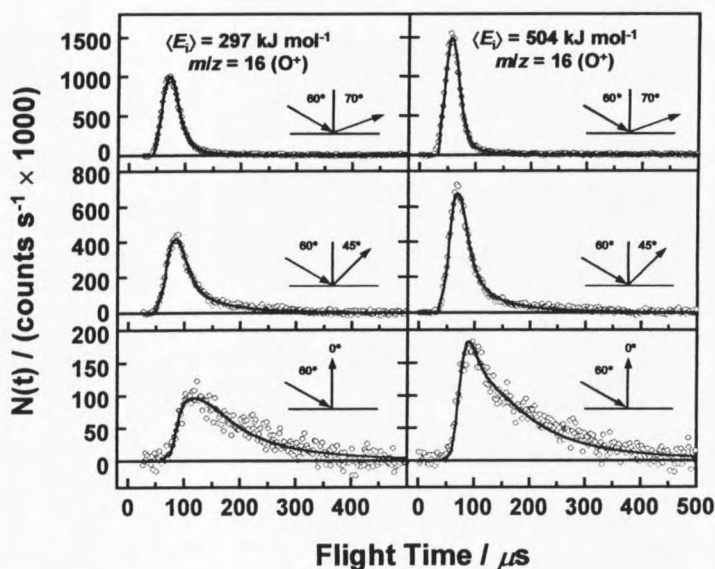


Figure 19. Forward convolution fit for hyperthermal components of time-of-flight distributions shown in Figure 3.

The assumption that the gas-surface interactions may be described by single collisions between an incident atom and a surface fragment suggests the use of a still more sophisticated analysis that is analogous to the treatment of data obtained in crossed molecular beams experiments. In such an analysis of gas-surface scattering, the interacting surface fragment is assumed to have the mass derived from the simple Newton diagrams and to be at rest in the laboratory frame, where it is assumed that thermal motion of the surface fragment is negligible compared with the high velocities of the incident O atoms. Center-of-mass translational energy distributions, $P(E_T)$, and angular distributions, $T(\theta_{cm})$, are generated from the laboratory TOF and angular distributions with the use of a forward convolution technique.²⁹⁻³¹ In our analysis, the c.m. angle, θ_{cm} , is referenced to the direction of the incident O-atom beam. As in the analysis described by Blank et al.,³¹ four separate sets of decoupled $T(\theta_{cm})$ and $P(E_T)$

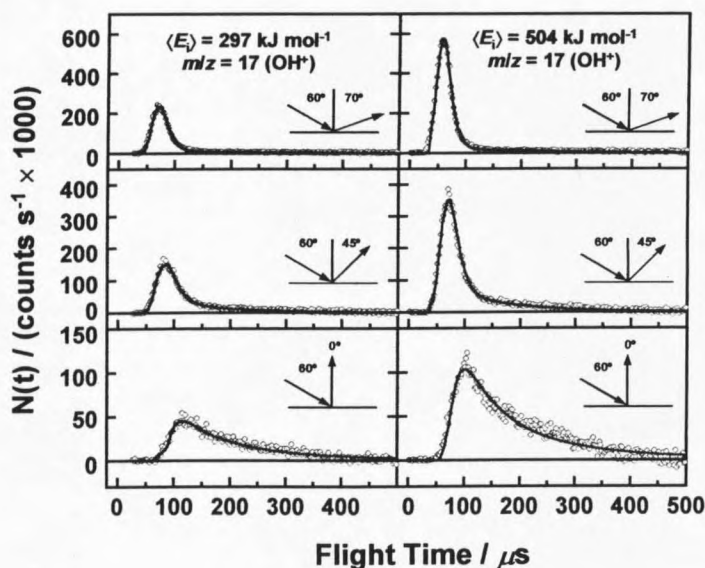


Figure 20. Forward convolution fit for hyperthermal components of time-of-flight distributions shown in Figure 6.

distributions were used, in order to account effectively for the coupling of the $T(\Theta_{\text{cm}})$ and $P(E_{\text{T}})$ distributions in the overall forward convolution fit to all the TOF distributions at all final scattering angles. Examples of TOF distributions (hyperthermal component only) and forward convolution fits are shown in Figs. 19 and 20, for scattered O and OH, respectively. The calculated TOF distributions shown in Figs. 19 and 20 are the “best-fit” TOF distributions obtained from the optimization of parameterized functions for the four separate sets of decoupled $T(\Theta_{\text{cm}})$ and $P(E_{\text{T}})$ distributions. Best-fit c.m. flux distributions, $I_{\text{cm}}(\Theta_{\text{cm}}, E_{\text{T}})$, yield distributions for the total energy released in translation, E_{T} , at various c.m. angles, Θ_{cm} (see examples in Figs. 21 and 22), and from this information, the average translational energy release as a function of c.m. angle may be obtained (Fig. 23). In addition, c.m. velocity flux maps may be obtained. Figure 24

shows such velocity flux maps for the case of O-atoms incident on a squalane surface at 60° with respect to the surface normal. The diagrams shown in Fig. 24 illustrate the nominal c.m. velocities of the incident O atom and interacting surface fragment, as well as the positions of the surface and center of mass. The c.m. product velocities vary widely, as a result of the velocity distribution in the incident O-atom beam. Thus, c.m. product velocities may be higher than the nominal c.m. velocity of the incident O atoms. Even though the only products that may be observed in the experiment are those that scatter from the surface, the c.m. flux distributions may be calculated at all c.m. angles once the best-fit functions are obtained. It appears from the flux maps that both O and OH scatter predominantly at small c.m. angles (forward direction) and that the velocity of these products tends to decrease at larger c.m. scattering angles. There is, however, a relatively small maximum at very large c.m. angles (backward direction), where the product velocity ceases to decrease or even increases slightly.

Discussion

The dynamical behavior of the TOF distributions of all scattered products is qualitatively similar to that observed in earlier studies of O-atom reactions with a squalane surface,^{18,21} where the incident O-atom translational energies were roughly one-tenth those used in the experiments described here. Thermal and non-thermal interaction/reaction pathways were indicated for all observed products. However, the relative fraction of hyperthermal products increased dramatically when the incident O-atom translational energy was increased. At the high incident translational energies

employed in the present experiment, non-thermal interactions overwhelmingly dominate the processes that lead to production of volatile O and OH from the surface, while non-thermal pathways to volatile H₂O become comparable in likelihood to thermal pathways. In all cases, the translational energies of the hyperthermal products increase with increasing incident O-atom energy, and their flux angular distributions have maxima far from the surface normal - toward the specular direction.

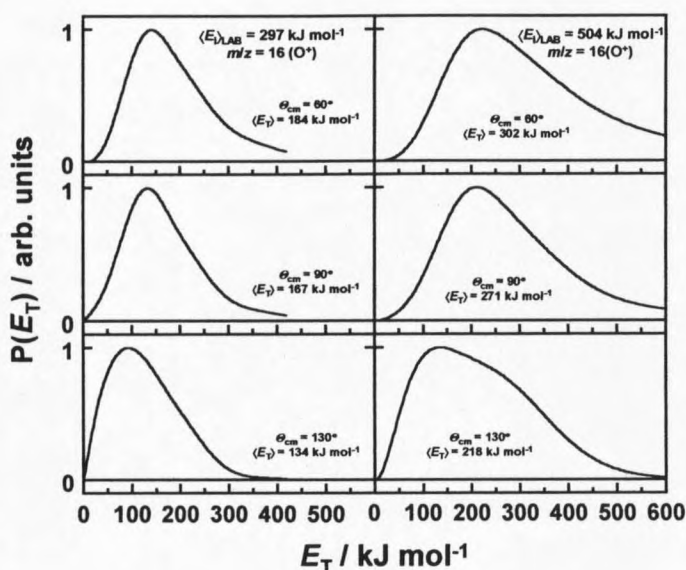


Figure 21. Center-of-mass (c.m.) translational energy distributions at three c.m. angles, 60°, 90°, and 130°, for direct inelastic scattering of O atoms following impact with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol^{-1} and $\theta_i = 60^\circ$ in the lab frame.

The dynamical behavior of the reactive product signals reveals the qualitative nature of the reactive pathways. Reactively scattered products with hyperthermal translational energies, scaling of product energy with incident reactant energy, and near-specular distributions of scattered product flux are hallmarks of an Eley-Rideal,³² or direct

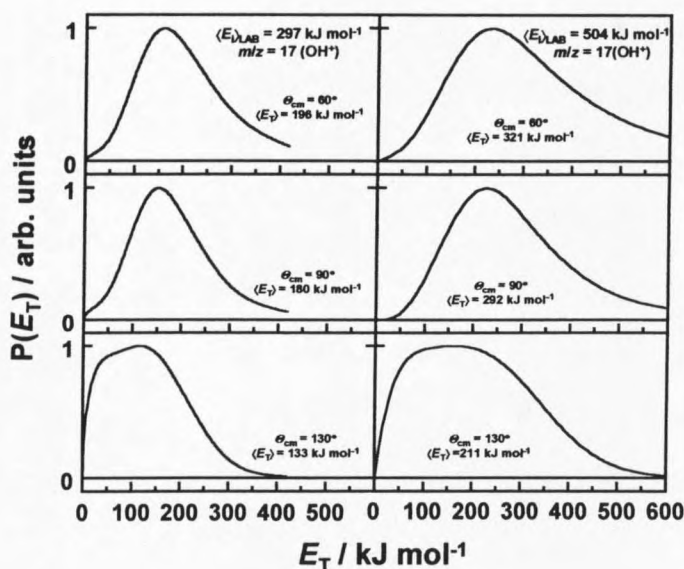


Figure 22. Center-of-mass (c.m.) translational energy distributions at three c.m. angles, 60°, 90°, and 130°, for reactive scattering of OH (hyperthermal components) following reaction of O atoms with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol⁻¹ and $\theta_i = 60^\circ$ in the lab frame.

abstraction, mechanism.³³ We therefore conclude that direct H-atom abstraction to form OH is the main source of volatile OH products when hyperthermal atomic oxygen encounters a squalane surface. The weak thermal OH signal suggests that a small fraction of the OH products become trapped and subsequently desorb in thermal equilibrium with the surface. If the incident O-atom becomes trapped, it is not likely to react if it is in the ground O(³P) state because the reaction barrier is too high.⁷ However, with a long residence time, thermalized O(³P) atoms may react with the hydrocarbon surface through a mechanism that involves triplet-singlet crossing of a long-lived collision complex and insertion of the O atom into a C-H bond to form an excited alcohol.^{9,11} Such reactions are not likely to yield volatile OH products, because the excited alcohol should be stabilized by the surface. Unlike the OH product, H₂O can

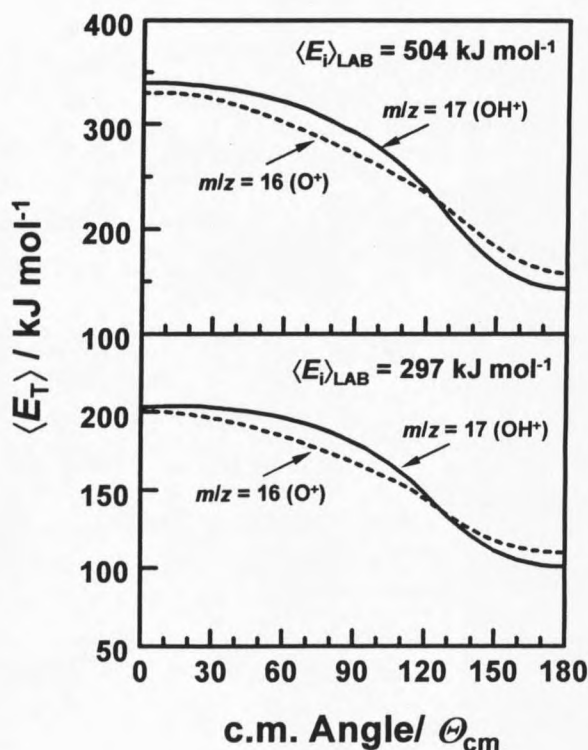


Figure 23. Center-of-mass (c.m.) average translational energy release as a function of c.m. angle for direct inelastic scattering of O atoms and reactive scattering of OH (hyperthermal components) following impact with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol^{-1} and $\theta_i = 60^\circ$ in the lab frame.

only be formed through a multiple collision process at the surface. The hyperthermal H_2O signal indicates a sequential process that occurs on a time scale too short for thermal equilibrium to be attained. The simplest such sequential process is a double-direct abstraction mechanism where an initially-formed OH radical abstracts a second hydrogen atom from another surface hydrocarbon segment. The substantial thermal H_2O signal also involves abstraction of two hydrogen atoms. A likely explanation is that the initially-formed OH radical becomes trapped on the surface and abstracts a hydrogen atom, thus producing H_2O which desorbs in thermal equilibrium with the surface. These

qualitative conclusions about the mechanisms of O-atom interactions with a saturated hydrocarbon surface are supported by recent theoretical work on the interaction of O atoms with an alkane thiol self-assembled monolayer surface at collision energies near 50 kJ mol⁻¹.³⁴

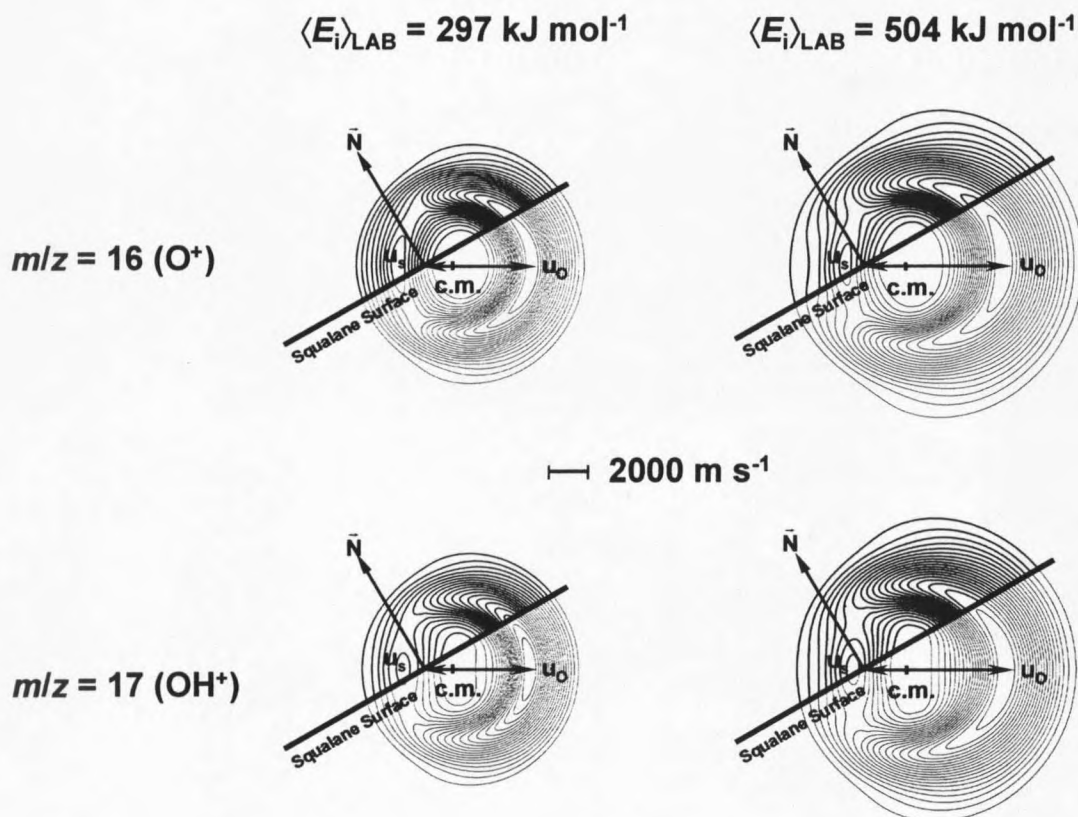


Figure 24. Contour maps of c.m. velocity distributions for direct inelastic scattering of O atoms and reactive scattering of OH (hyperthermal components) following impact of O atoms with a squalane surface at $\langle E_i \rangle = 297$ and 504 kJ mol⁻¹ and $\theta_i = 60^\circ$ in the lab frame.

The forward convolution technique that was used to derive c.m translational energy distribution, $P(E_T)$, and angular distribution, $T(\theta_{cm})$, takes into account the distribution of

c.m. collision energies resulting from the velocity distribution in the incident beam, but it does not account for the effect that the velocity distribution has on the distribution of times that O atoms encounter the squalane surface. Thus, "time zero" in all product TOF distributions is the time at which O atoms with the average velocity of the incident beam distribution strike the surface. Although the incident time distribution is relatively narrow, approximately 35 μ s at the base, the high-velocity products, especially from grazing collisions with the surface, arrive at the detector within tens of microseconds. Therefore, the apparent flight times of the scattered products will be significantly broadened over what they would be if the incident beam were monoenergetic. Both the laboratory translational energy distributions, $P(E_f)$, and the c.m. translational energy distributions, $P(E_T)$, are thus also broadened. The consequence for the c.m. velocity flux maps that have been derived is that the velocity range is unrealistically broad. Earlier work established, however, that the monoenergetic beam approximation did not alter the *average* energy of the translational energy distributions.²⁸ Even though the energy and velocity distributions derived in our analysis are too broad, they have the correct average energy and approximately the correct shape, therefore providing a semiquantitative picture of scattering in the c.m. reference frame.

The average c.m. translational energies (Fig. 23) that are derived from the forward convolution analysis are not constant with c.m. angle, yet the simple Newton diagrams that are derived from average final velocities in the laboratory frame suggest that c.m. translational energy is constant over the c.m. angular range accessible to the experiments (as evidenced by the constant c.m. product velocity). Nevertheless, the c.m. velocity

derived from the simple Newton diagram did result in the best fit to the data in the more sophisticated forward convolution analysis. It thus seems fortuitous that the average final product velocities in the laboratory frame just happen to lie on a circle about a point on the relative velocity vector and that this point yields a c.m. velocity that is consistent with a more sophisticated analysis. Apparently, the *average* product velocities as a function of final angle in the lab frame are not very sensitive to the details of the velocity flux distribution in the c.m. frame. This apparent insensitivity strengthens the conclusion from the simple Newton diagram for H_2O that the inability of the average final velocities to be fit by a circle reflects the fact that multiple collisions are required to produce H_2O .

The kinematic analysis of the hyperthermal O and OH signals implicitly assumes single-collision, or gas-phase-like, scattering between an incident O atom and an interacting surface fragment whose mass is near 40 amu (see Tables 1 and 2). The velocity and angular distributions of inelastically scattered O atoms mirror those of reactively scattered OH. This result is expected, given the similarity in mass of O and OH and the small exothermicities for OH formation (in the range 20-40 kJ mol^{-1} , depending on whether the H atom being abstracted is primary, secondary, or tertiary) compared to the c.m. collision energies. The c.m. product flux maps that are derived for OH appear somewhat similar to those obtained for H-atom abstraction from propane by Cl.³⁵ The asymmetry of the OH angular distributions in the forward and backward directions, the coupling of the $P(E_T)$ and $T(\theta_{\text{cm}})$ distributions, and the large fraction of the available energy that goes into translation are consistent with a direct reaction mechanism. Although our data do not directly probe scattering at small c.m. angles,

extrapolation of the fitted data suggests a strong propensity for OH products to be scattered into the forward direction. In addition, the products that scatter into the forward direction show very little change in momentum compared with the incident O atom, as the peak product velocities are close to the nominal c.m. velocity of the O-atom beam. As discussed earlier,³⁵ such forward scattering behavior in the abstraction of an H atom is indicative of a spectator/stripping mechanism, where the O-H-C angle is nearly perpendicular (large impact parameter) during the reaction. Even though collinear approach provides the largest fraction of the relative translational energy along the O-H-C reaction coordinate, the large c.m. collision energies in our experiments would still be expected to allow for a sufficient energy along the reaction coordinate to exceed the reaction barrier to OH formation at near perpendicular approach. Therefore, reaction by a spectator/stripping mechanism is a likely outcome. Sideways- and backward-scattered products may arise from more collinear collisions with C-H bonds on the surface (low impact parameters). The peak in the backward direction might thus be the result of backward recoil of OH after nearly collinear approach of an O atom with a C-H bond. In their studies of H-atom abstraction from propane by Cl, Blank et al.³⁵ identified two distinct mechanisms, a spectator/stripping mechanism resulting from large impact parameters and a mechanism leading to direct impulsive product recoil that results from low impact parameter collisions. At lower collision energies, the stripping mechanism pertained primarily to secondary hydrogens, but as the collision energy was increased, an increase in the stripping mechanism for primary hydrogen atoms was indicated. Our experiments cannot differentiate between abstraction of primary, secondary, or tertiary

hydrogen atoms; however, the O-atom-surface interaction likely occurs with primary H atoms, as the chain ends of squalane molecules are believed to be most prevalent at the surface of liquid squalane.³⁶ Because the scattering occurs on a surface, forward scattering would be expected to lead to secondary interactions, such as inelastic scattering, trapping desorption, and reaction. Hyperthermal OH products that come from secondary interactions may scatter over a wide angular range, possibly accounting in part for (1) the peak in the backward direction, (2) the production of thermal OH, and (3) the production of thermal and hyperthermal H₂O. As we do not know the extent to which secondary interactions of O or OH contribute to the observed product signals, the c.m. flux maps derived from the kinematic analysis must be regarded as approximate. A comparison between the observed gas-surface scattering dynamics and the results of a future experiment on the analogous gas-phase scattering dynamics of O + propane might add validity to the assumption that hyperthermal O and OH products result predominantly from single collisions of O atoms with a localized region of the squalane surface.

Conclusion

The dynamics of the interactions of hyperthermal atomic oxygen with the surface of a saturated hydrocarbon liquid, squalane, have been investigated. Pulsed beams containing high-velocity ($\sim 6\text{--}8\text{ km s}^{-1}$) O atoms were directed onto a squalane surface, and the volatile products, O, OH, and H₂O, were observed by mass spectrometry as a function of incident angle, final angle, and incident O-atom energy. All product time-of-flight distributions revealed thermal and non-thermal interaction channels. Direct inelastic

scattering, in which only a fraction of the initial translational energy is lost to the surface, is by far the most probable non-reactive interaction. Only a tiny fraction of incident O atoms appear to reach thermal equilibrium with the surface before desorbing. The most likely initial reaction is gas-phase-like H-atom abstraction to form OH, which often leads to scattered OH products with hyperthermal translational energies. An observed hyperthermal H₂O signal can be explained by a sequential direct H-atom abstraction mechanism involving initial formation of OH and subsequent abstraction of another hydrogen atom, with both steps occurring on a time scale too short for thermal equilibrium at the surface to be achieved. Thermal OH and H₂O products are believed to follow thermal accommodation of the initial OH product on the surface. Once the OH becomes accommodated on the surface, it may desorb thermally or abstract a hydrogen atom to form H₂O, which may also desorb thermally. We thus conclude that the first step toward volatile reaction products, whether thermal or hyperthermal, is a direct reaction to produce OH. The initial reactive and non-reactive events can be described in the center-of-mass (c.m.) reference frame with a use of a kinematic picture (Newton diagram) that allows the determination of the effective surface mass encountered by an incident O atom, the c.m. collision energy, and the fraction of the c.m. collision energy that is converted to internal energy in the surface and in the recoiling gaseous species. Center-of-mass product velocity flux maps of OH show predominantly forward scattering, which is indicative of H-atom abstraction by a spectator/stripping mechanism. Some OH flux is also scattered into the sideways and backward directions in the c.m. frame, suggesting a mechanism that proceeds through a more collinear O-H-C transition state.

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CHAPTER 3

COLLISION-ASSISTED EROSION OF HYDROCARBON POLYMERS IN
ATOMIC OXYGEN ENVIRONMENTSAbstract

Molecular beam-surface scattering experiments have been used to study the mechanisms of material removal when a hydrocarbon polymer surface erodes in the highly oxidizing environment of low Earth orbit or in a simulated space environment on Earth. During steady-state oxidation, CO and CO₂ are produced. Formation of these volatile species is believed to account for a significant fraction of the mass loss of a polymer that is under atomic-oxygen attack. The rate of production of CO and CO₂ is dramatically enhanced when a continuously-oxidized polymer surface is bombarded with Ar atoms or N₂ molecules possessing translational energies greater than 8 eV. The yield of volatile products from the surface appears to increase exponentially with collision energy of the inert atoms or molecules. Collisions of energetic inert species may accelerate the erosion of polymers in some exposure environments (e.g., in low Earth orbit, where N₂ may strike oxidized surfaces with collision energies greater than 8 eV, and in certain atomic-oxygen test facilities that subject oxidized surfaces to bombardment by O₂ molecules with average translational energies of approximately 10 eV.)

Introduction

The erosion mechanisms of polymeric materials on spacecraft in low Earth orbit (LEO) are complex and involve initial reactions at the gas-surface interface as well as steady-state material removal processes. Molecular beam-surface scattering experiments have shown that nonequilibrium processes dominate the first few scattering events when energetic oxygen atoms strike a hydrocarbon surface¹⁻⁵. Direct inelastic scattering, in which only a fraction of the initial translational energy is lost to the surface, is the most probable nonreactive interaction. The most probable initial reaction is gas-phase-like hydrogen-atom abstraction to form OH. Once formed, the OH may undergo further collisions with the surface, some of which yield H₂O. Radical sites generated on the hydrocarbon backbone will be susceptible to further reactions with incoming O atoms, neighboring parts of the polymer, or various other species present in the exposure environment. Ultimately, volatile carbon-containing products will carry mass away from the surface. CO and CO₂ are presumed to be important, if not dominant, carbon-containing-products when a polymer is continuously bombarded with O atoms⁶⁻¹¹. However, long-chain hydrocarbon fragments might desorb from the surface after enough chain-scission reactions have occurred¹². Little work has been done to quantify the fraction of carbon that leaves a surface in the form of hydrocarbon fragments, as opposed to CO or CO₂ molecules. Nevertheless, several experiments have confirmed the production of CO and CO₂ during O-atom bombardment of a polymer, and these products have been detected as important products even in experiments where hydrocarbon fragments were also observed¹².

Assuming the bulk of the mass loss during steady-state oxidation of a hydrocarbon polymer surface is the result of removal of carbon in the form of CO and CO₂, then the erosion rate might depend on the formation and/or removal rates of these species. A kinetic barrier to the removal of CO and CO₂ from the surface would then impede erosion, with the erosion rate being inversely related to the barrier height. If the rate of product removal from the surface were slower than the rate of formation of these products, then the material removal rate, not the reaction mechanisms, could dominate the erosion yield of a polymer. Alternatively, if a step in the formation of CO or CO₂ is relatively slow, then it would be the formation rate of CO and/or CO₂ and not the removal rate that would limit the erosion yield.

Energy transfer from collisions of energetic atoms or molecules with a surface that is under atomic oxygen attack might enhance either the formation or removal rate of CO and CO₂ at a surface. At orbital altitudes of ~300-400 km, the LEO environment subjects materials on the ram side of a spacecraft to collisions with atmospheric species that have an average impact velocity of $\sim 7.4 \text{ km s}^{-1}$.^{13, 14} The corresponding mean collision energies with ambient oxygen atoms and nitrogen molecules are ~4.5 eV and ~7.9 eV, respectively. The ambient temperature of approximately 1000 K results in a broad range of impact velocities, corresponding to collision-energy distributions whose widths (full width at half maximum) are ~2 eV (O atoms) and ~3.5 eV (N₂ molecules). In addition, an often-used source for simulation of atomic-oxygen-induced erosion in LEO is the laser-detonation source¹⁵⁻¹⁷, which exposes test samples to molecular oxygen with an average translational energy of ~10 eV at the same time it exposes the samples to atomic oxygen with an average translational energy of ~5 eV. The N₂ flux in the LEO environment and the O₂ flux in the ground-based

test environment are significant fractions of the O-atom flux, typically 5 to 50 percent¹⁸. It is possible that energetic collisions between O, O₂, or N₂ and an oxidized polymer surface might promote the formation and/or release of CO and CO₂ reaction products. In particular, the high collision energies of the relatively inert molecular species might enhance the production of reaction products from the surface. Collisions between rare-gas atoms, with translational energies of a few electron volts, and halogenated silicon surfaces have been shown to promote the ejection of silicon halides from the surface^{19,20}.

We have investigated the possibility of collision-induced production of CO and CO₂ from oxidized polymer surfaces. Hyperthermal beams of energy-selected Ar atoms or N₂ molecules were directed at continuously-oxidized polymer surfaces. Enhancement in the production of volatile CO and CO₂ was correlated with the impinging Ar atoms or N₂ molecules, indicating that collisions may indeed contribute to production of reaction products from an oxidized polymer surface. The collisional production of CO and CO₂ was strongly dependent on the incident energy of the colliding inert species.

Experimental Methods

The experiments were conducted with the use of a crossed molecular beams apparatus, which has been described previously²¹⁻²⁴. A schematic diagram of the configuration used for this experiment is shown in figure 1. A low-pressure RF discharge source was used to produce an effusive beam of atomic oxygen. This continuous beam was directed onto a polymer surface, resulting in slow oxidation and erosion. A second, pulsed beam of

hyperthermal Ar or N₂ was directed at the continuously-oxidized polymer surface. A hyperthermal beam containing atomic and molecular oxygen was also used for comparison. The angle between the effusive and hyperthermal sources was approximately 30°. Volatile CO and CO₂ products were monitored as a function of time after the hyperthermal pulse struck the surface, with the use of a rotatable mass spectrometer detector.

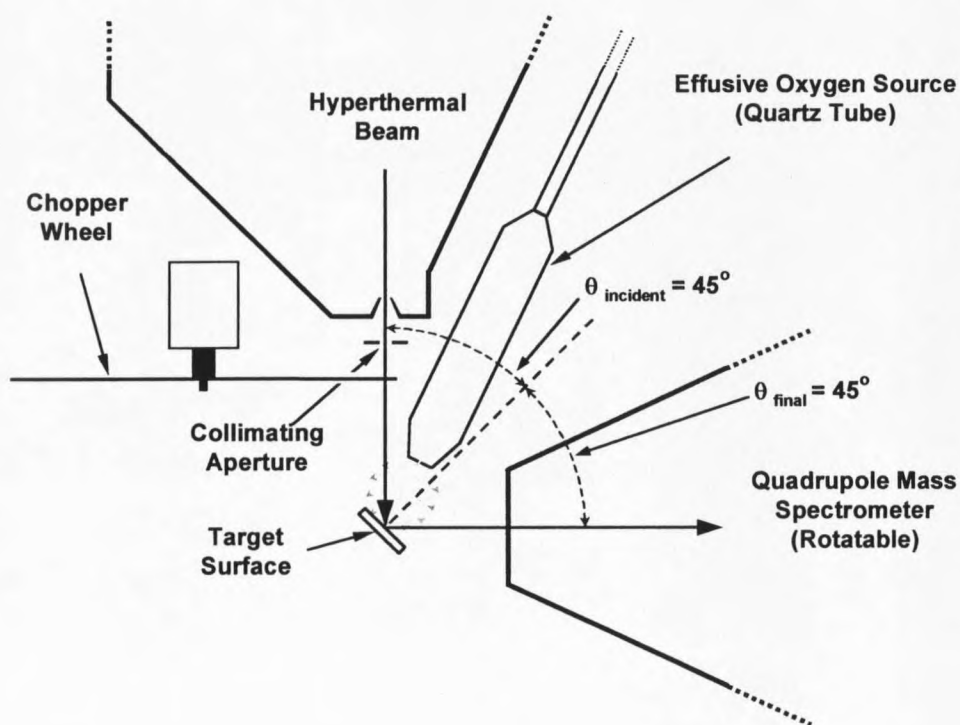


Figure 1. Schematic diagram of the interaction region, showing the orientation of the effusive plasma and hyperthermal beam sources, chopper wheel, target surface, and detector.

The sample surfaces were polystyrene and polyimide. Polystyrene samples were cut from a 0.93-mm-thick sheet obtained from Plaskolyte. The average molecular weight of the polystyrene was quoted by the manufacturer to be 100,000 g mol⁻¹. A polyimide film, with

the same chemical repeating unit as Dupont Kapton, was prepared by spin coating Dupont Pyralin onto a silicon substrate and curing the film at 300°C. The film thickness was approximately 1 μm . The samples were mounted on a manipulator such that the surface normal was contained in the plane of the detector rotation axis. The manipulator was positioned such that its rotation axis was coincident with the detector rotation axis, and this axis passed through the sample surface. The samples were thermally isolated, and the sample mount was electrically grounded. No heating was applied to the samples other than radiative heating from the RF plasma source, which increased the sample temperature less than 20°C from ambient.

The continuous effusive atomic oxygen beam was produced by an inductively coupled plasma. The O_2 precursor gas was fed into a 2.5-cm-diameter quartz tube and was maintained at 0.100 Torr. The plasma was operated at a power of 50 watts. Plasma products exited the quartz tube through a 0.50-mm-diameter orifice and were directed at the sample surface on the manipulator. The beam was characterized by aligning the detector with the plasma source and placing a chopper wheel (spinning slotted disk) in front of the detector to modulate the beam. The translational energy distributions of the O and O_2 components in the effusive beam were described well by Maxwell-Boltzmann distributions with temperatures of 465 K and 485 K, respectively. The fraction of atomic oxygen in the beam was 30 percent²⁵, and with the orifice a distance of 2.8 cm from the sample surface, the flux of O atoms on the surface was approximately $10^{15} \text{ atoms cm}^{-2} \text{ s}^{-1}$. With the filament of the electron-impact ionizer turned off, the number of ions in the O/ O_2 beam was

undetectable (within the noise of the detector). Thus the RF plasma effusive source provided a continuous neutral beam containing only atomic and molecular oxygen.

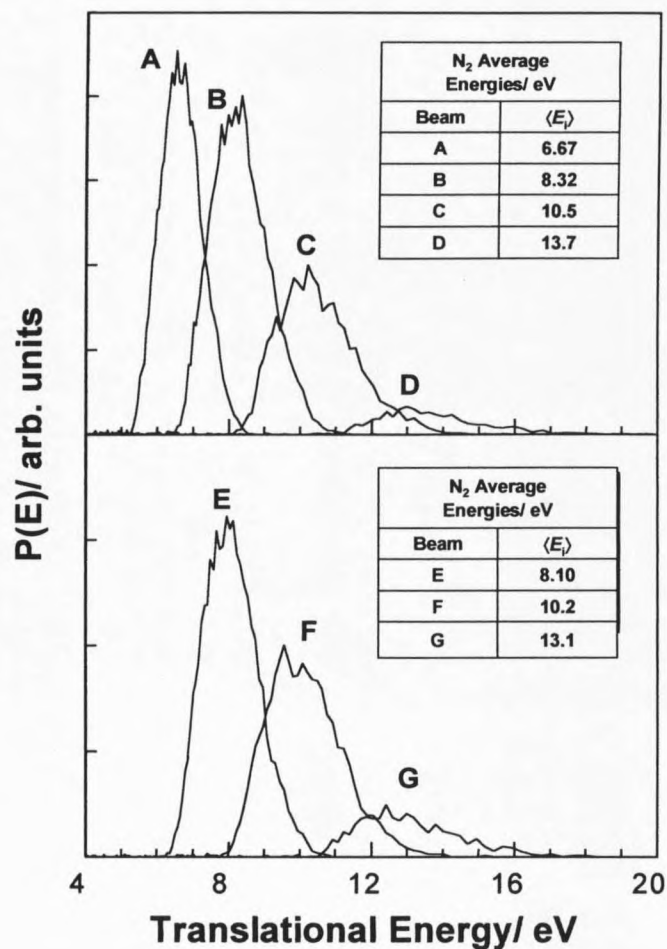


Figure 2. Translational energy distributions of the molecular nitrogen component of seven nitrogen beams used. Within each panel, the peak areas correspond to the relative flux of N_2 . The beams whose energy distributions are shown in the top panel (labeled A-D) were directed onto a polystyrene surface. The beams whose energy distributions are shown in the bottom panel (labeled E-G) were directed onto a polyimide surface.

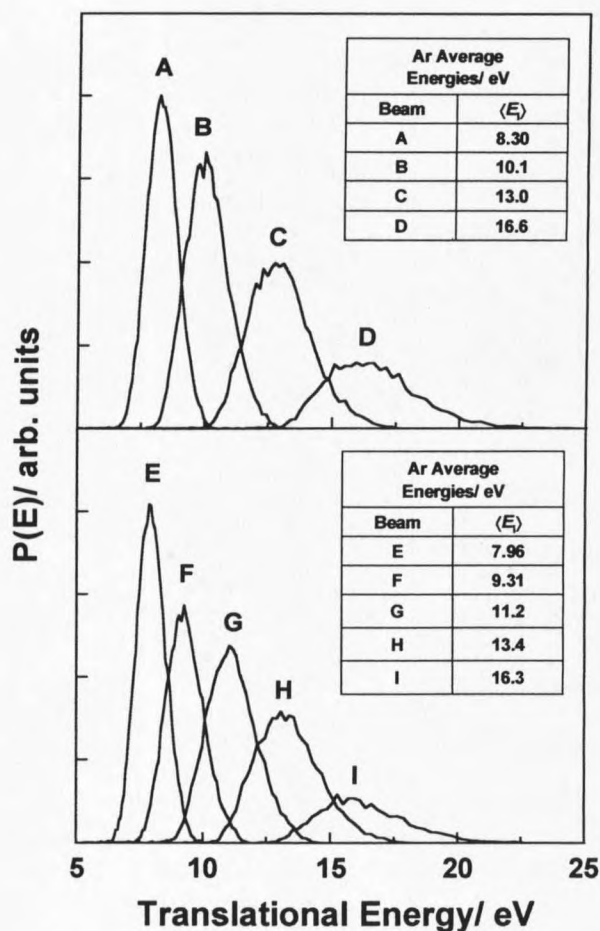


Figure 3. Translational energy distributions of nine Ar beams selected with the synchronized chopper wheel. Within each panel, the peak areas correspond to the relative flux of Ar. The beams whose translational energy distributions are shown in the top panel (labeled A-D) were directed onto a polystyrene surface. The beams whose energy distributions are shown in the bottom panel (labeled E-I) were directed onto a polyimide surface.

The hyperthermal beam source was a laser-detonation source, which has been described earlier^{15-17,21}. Argon, nitrogen, and oxygen were used as precursor gases. The two diatomic precursor gases were used to produce pulsed neutral beams containing N and N₂ in a molar ratio of approximately 20:80 or O and O₂ in a molar ratio of approximately 50:50. The

argon precursor gas yielded a pulsed beam of neutral argon atoms. The hyperthermal beam pulses originated effectively from a point source and had fairly broad translational energy distributions (full width at half maximum of approximately 7 eV for the molecular components and argon, and approximately 3 eV for the atomic O and N components). The beam pulses exited the differentially-pumped source chamber through a 3-mm-diameter skimmer and were chopped by a synchronized, velocity-selecting chopper wheel, which selected narrowed energy distributions from the overall beam pulses.

Time-of-flight (TOF) distributions of the incident beams were collected with the mass spectrometer and provided for the determination of the translational energy distributions of the atoms and molecules in the beams. The TOF distributions are proportional to the number density N of the detected species and are collected as a function of the flight time of the detected neutral species from the point of origin -- the hyperthermal beam source or the surface -- and the electron-bombardment ionizer of the detector. TOF distributions were converted to translational energy distributions with the use of the relationship, $P(E) \propto t^2 N(t)$. All translational energy distributions shown in this paper are probability density distributions, where the probability density $P(E)$ of finding a particular translational energy is plotted as a function of energy. The probability density $P(E)$ is proportional to the flux of the relevant species into the detector. By changing the synchronization of the chopper wheel, four different N/N₂ beams were created and were directed at a continuously-oxidized polystyrene surface. An additional experiment was conducted in which three different N/N₂ beams were directed at a continuously-oxidized polyimide surface. Normalized energy distributions of the N/N₂ beams are shown in figure 2. Four hyperthermal beams of Ar were

prepared and were directed at a continuously-oxidized polystyrene surface, and five Ar beams were directed at a continuously-oxidized polyimide surface. The normalized energy distributions for the Ar beams are shown in figure 3. Four different O/O₂ beams were created, with energy distributions shown in figure 4. These beams were directed at a continuously-oxidized polystyrene surface.

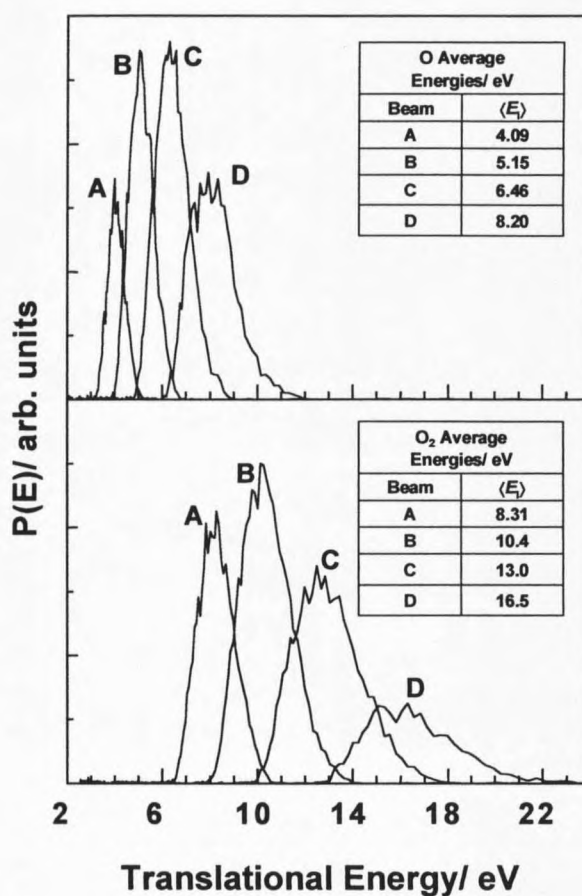


Figure 4. Translational energy distributions of the atomic and molecular components of the four O/O₂ beams that were used. For each beam, the peak areas of the O and O₂ distributions correspond to the relative fluxes of these components in the beam.

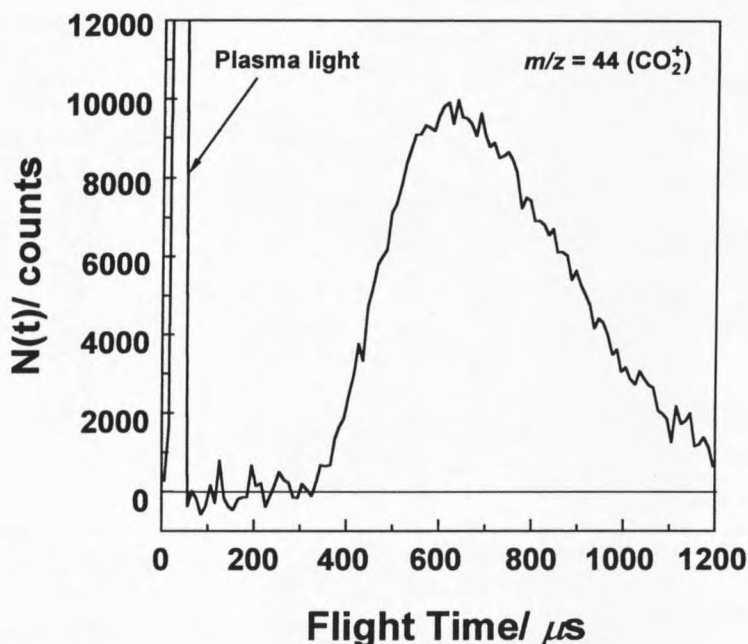


Figure 5. Time-of-flight distribution of CO_2 released from the surface during continuous thermal oxygen atom bombardment from the effusive plasma source. The large signal, labeled "Plasma light," arises from photoelectrons that were generated in the Daly-type ion counter from ultraviolet light emanating from the plasma source. The light signal, as well as the CO_2 signal, is modulated by a slotted-disk chopper wheel placed in front of the mass spectrometer detector.

Most product TOF distributions in these experiments were collected at a mass-to-charge ratio (m/z) of 44 (CO^+), and some distributions were collected at $m/z = 28$ (CO^+). Although both CO and CO_2 signals were detected with comparable intensities, the signal-to-noise ratios of the TOF distributions of CO_2 were significantly higher than those of CO because of the lower background in the detector at $m/z = 44$ as compared to $m/z = 28$. Thus, the quantitative data that are presented in this paper are focused on the CO_2 product. The behavior of the CO product signal is qualitatively similar.

TOF signals were averaged for 2,000 pulses of the hyperthermal O/O₂ beams and for 3,000 pulses (polystyrene) or 4,500 pulses (polyimide) of the hyperthermal N/N₂ beams. For hyperthermal Ar beam experiments, the TOF distributions were averaged for 3000 pulses (polystyrene) and for 1000 pulses (polyimide). The data that are presented here were collected with the incident angle of the hyperthermal beam and detection angle fixed at 45° with respect to the surface normal. However, additional data were collected at incident angles of 30° and 60°, while maintaining the angle between the hyperthermal beam and the detection axis fixed at 90°.

Results and Analysis

The continuous effusive beam of atomic and molecular oxygen from the plasma source oxidized and eroded the polymer surfaces. Evidence for the reaction of this effusive beam with the sample surfaces was seen in the detection of CO and CO₂ reaction products from the surfaces that were exposed to this beam and in the erosion of the samples after long-term exposure. TOF distributions of the CO and CO₂ products were monitored by placing a chopper wheel between the surface and detector. A representative TOF distribution of CO₂ produced from exposure of the polyimide to the effusive source is shown in figure 5. The shape of these distributions typically became constant within one hour of exposure, indicating that steady-state conditions had been reached. Such distributions reflect a Maxwell-Boltzmann (M-B) distribution of molecular speeds at the surface temperature, which is nominally room temperature. All data were collected after

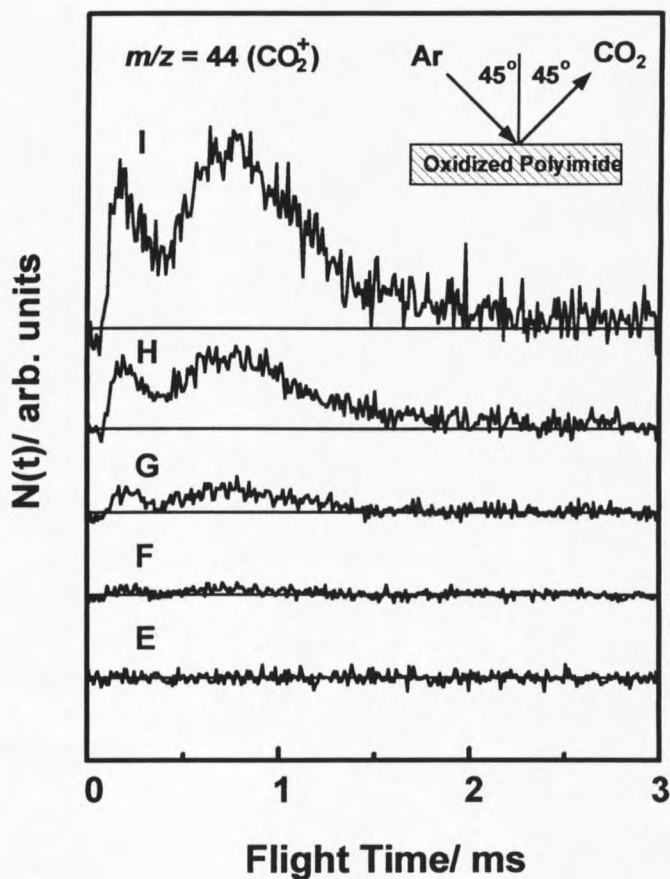


Figure 6. Time-of-flight distributions of CO_2 exiting a continuously-oxidized polyimide surface following exposure to pulses of five hyperthermal Ar beams (E-I) whose translational energy distributions are shown in figure 3.

the TOF distributions of CO_2 that were produced by exposure to the effusive source indicated that a steady-state oxidation/erosion condition had been reached. In a test experiment, a polyimide surface eroded about $1 \mu\text{m}$ after 16 hours of exposure to the effusive source. As the sample surfaces became eroded, they became increasingly roughened. In order to minimize the effect of surface roughness, all data were collected with fresh samples that were exposed to the effusive source for only a few hours. We

verified the negligible effect of surface roughening by checking the reproducibility of product TOF signals throughout the experiments.

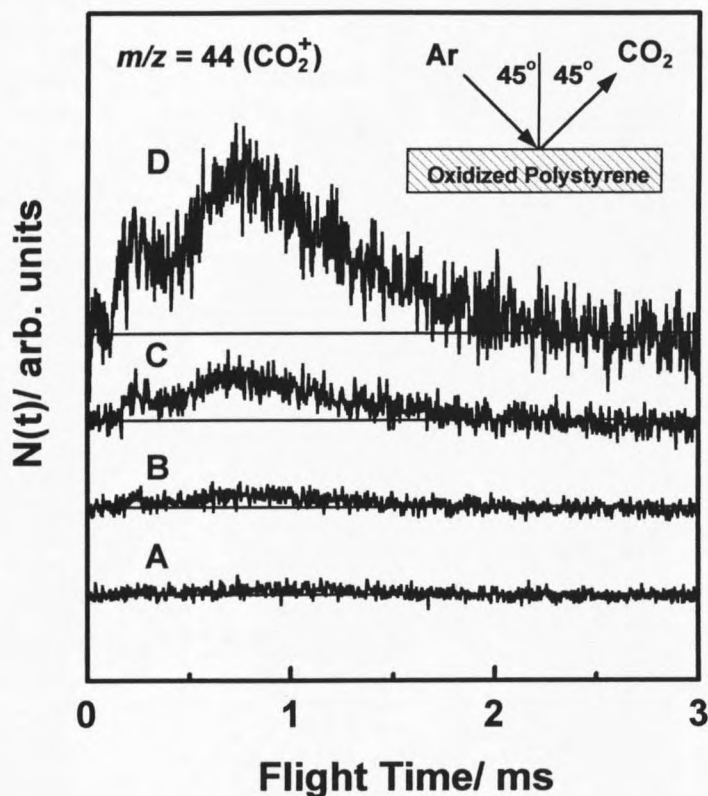


Figure 7. Time-of-flight distributions of CO_2 exiting a continuously-oxidized polystyrene surface following exposure to pulses of hyperthermal Ar beams (A-D) whose translational energy distributions are shown in figure 3.

Figure 6 shows TOF distributions of CO_2 following impingement of the five different Ar beams, whose energy distributions are shown in figure 3 (bottom panel), on a continuously-oxidized polyimide surface. The production of CO_2 from exposure to the effusive beam created a continuous background signal that was subtracted. The distributions in figure 6 are labeled with letters that relate each product TOF distribution to

its corresponding incident beam distribution (figure 3). Time zero in these distributions corresponds to the time at which the maximum intensity of the Ar beam pulse struck the surface. The product TOF distributions have been normalized to the integrated intensities of the respective incident beams. The TOF distributions are bimodal, indicating at least two mechanisms through which CO_2 leaves the surface following impact of the hyperthermal beam pulse. The slower (longer flight times) component corresponds to CO_2 molecules which exited the surface with a M-B distribution of molecular speeds corresponding to the surface temperature, while the faster (shorter flight times) component corresponds to CO_2 molecules which exited the surface with hyperthermal velocities. The average translational energy of the hyperthermal product signal was ~ 0.7 eV, and this energy was independent of incident Ar translational energy within the signal-to-noise limits of the data. As the incident Ar translational energy increased up to 16.2 eV, the intensity of the CO_2 product signal increased dramatically. The intensities of both the hyperthermal and thermal components increased at the same rate with increasing incident Ar translational energy.

TOF distributions of CO_2 produced by collisions of the four Ar beams, whose translational energy distributions are shown in the top panel of figure 3, with a continuously-oxidized polystyrene surface are shown in figure 7. The product signals have been normalized to the intensities of the corresponding incident beams. These TOF distributions are bimodal, with thermal and hyperthermal components, as seen in the TOF distributions in figure 6.

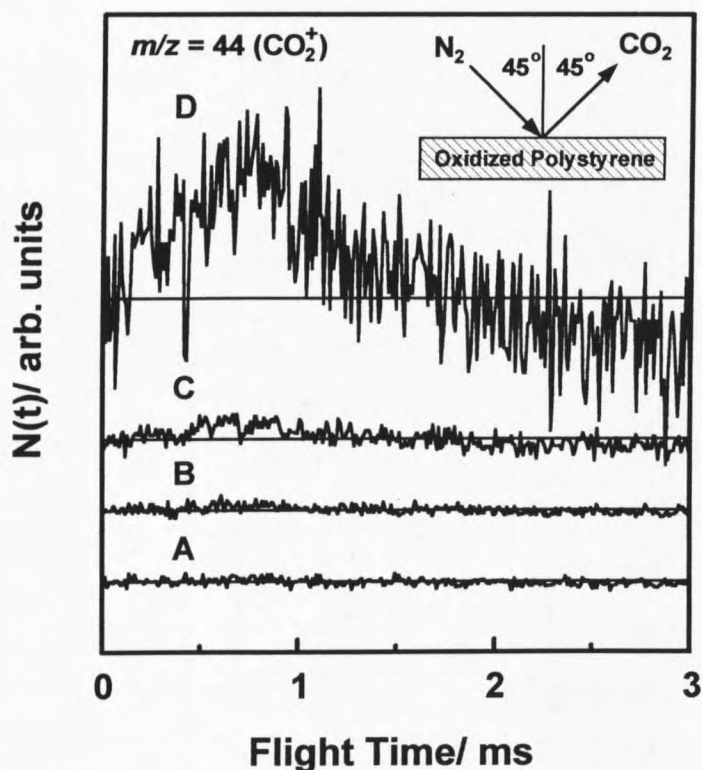


Figure 8. Time-of-flight distributions of CO_2 exiting a continuously oxidized polystyrene surface following exposure to pulses of each of the four hyperthermal nitrogen beams (A-D) whose translational energy distributions are shown in figure 2.

Figure 8 shows the TOF distributions of CO_2 produced by collisions of different N_2 beams (figure 2, top panel) with a continuously-oxidized polystyrene surface. The product signals were normalized to the integrated intensities of the N_2 components in the respective incident beams. The lowest N_2 beam translational energy of 6.67 eV did not produce any detectable CO_2 signal. Although the signal-to-noise ratios in these TOF distributions are lower than those in the distributions shown in figure 3 6 and 7, these distributions exhibit analogous thermal and hyperthermal components.

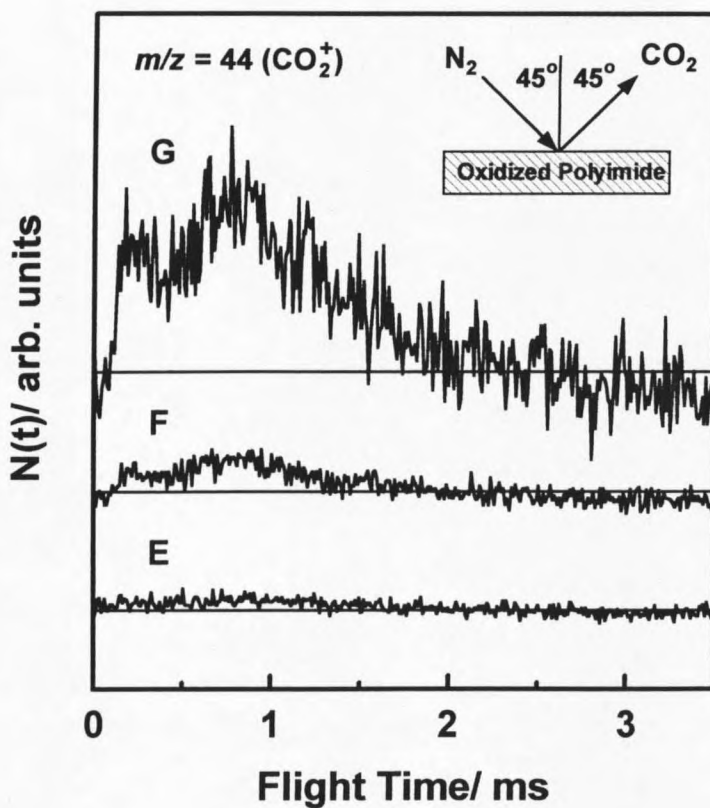


Figure 9. Time-of-flight distributions of CO_2 exiting a continuously oxidized polyimide surface following exposure to pulses of each of the three hyperthermal nitrogen beams (E-G) whose translational energy distributions are shown in figure 2.

The N_2 beams whose translational energy distributions are shown in the bottom panel of figure 2 were directed at a polyimide surface, and the corresponding TOF distributions of CO_2 are shown in figure 9. These distributions were normalized with respect to the intensity of the respective incident N_2 beams. Similar to other product TOF distributions, collisions of energetic N_2 with the polyimide surface also produced bimodal CO_2 signals.

We separated the two components of the bimodal distributions by assuming that the slower component corresponded to CO_2 molecules which exited the surface with a M-B

distribution of speeds corresponding to the surface temperature. Subtraction of the M-B component from the overall TOF distribution leaves the hyperthermal component, which corresponds to CO_2 molecules that exited the surface with energies much greater than thermal energies at the surface temperature. Figure 10 shows an example of the deconvolution of the bimodal TOF signal for the N_2 beam with $\langle E_i \rangle = 13.1$ eV impinging on a polyimide surface. A M-B distribution at 300 K provided a good fit to the slower component. The average energies of the hyperthermal component in figure 10 and the energies of the other hyperthermal components produced from energetic N_2 or Ar collisions, for both sample materials, are approximately the same (~ 0.7 eV).

TOF distributions of CO_2 that was produced from the collision of the pulsed hyperthermal O/O_2 beams with a continuously-oxidized polystyrene surface are shown in figure 11. The product TOF distributions were normalized to the integrated intensities of the O_2 component in the respective incident beams. These distributions have the same shape with or without concomitant exposure of the sample surface to the effusive source. However, the signals are ~ 30 percent larger with the additional exposure to the effusive source.

Figure 12 shows the relationship between the total integrated intensity of the CO_2 signal and the incident translational energy of the impinging species. The curves through each set of data points have an exponential form, underscoring the strong dependence of incident energy (of an inert atom or molecule) on CO_2 production from a continuously-oxidized surface.

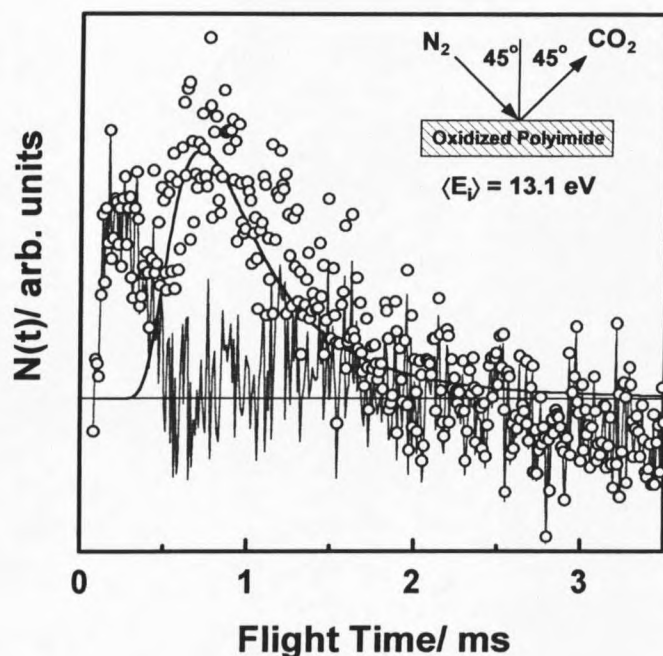


Figure 10. Deconvolution (into thermal and hyperthermal components) of the CO_2 time-of-flight distribution generated by exposure of a polyimide surface to hyperthermal nitrogen beam G (translational energy distribution shown in figure 2). The solid black curve represents the Maxwell-Boltzmann fit at the surface temperature to the thermal component. The solid gray curve represents the hyperthermal component, which comes from the difference between the overall distribution and the thermal component.

Discussion

The data demonstrate the existence of a collisional process that leads to ejection of CO_2 (and CO) from a continuously-oxidized polymer surface upon impingement of hyperthermal inert atoms or molecules and show that the rate of release of these carbon oxide molecules from the surface rises exponentially with incident translational energy above $\sim 8 \text{ eV}$. The fact that bombarding species of different mass give rise to the same energy threshold of 8 eV suggests that collision energy (as opposed to momentum)

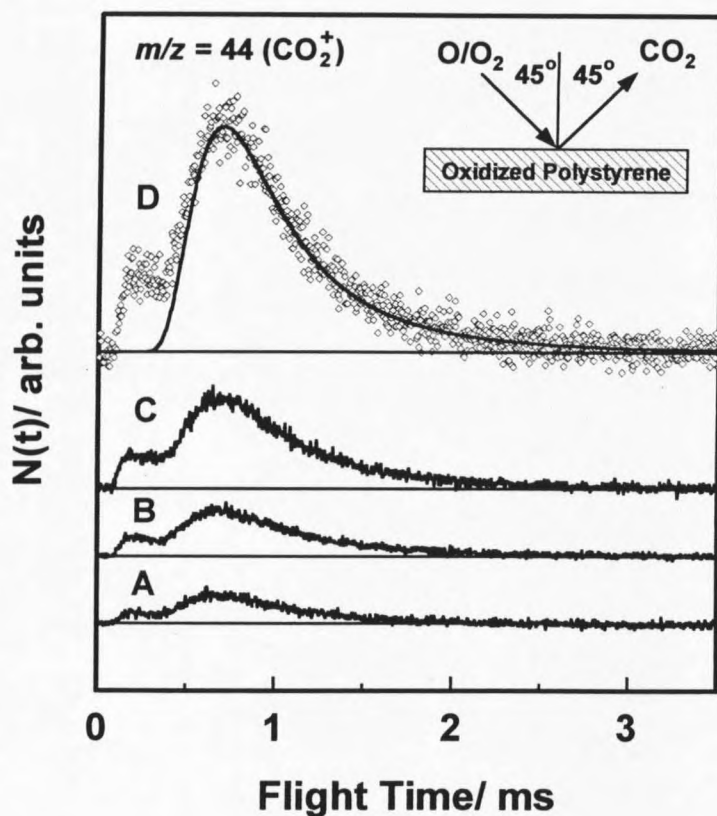


Figure 11. Time-of-flight distributions of CO_2 exiting a continuously oxidized polystyrene surface following exposure to pulses of each of the four hyperthermal oxygen beams (A-D) whose translational energy distributions are shown in figure 4. The solid curve in the distribution obtained with beam D is an example of a predicted time-of-flight distribution assuming the slower products exited the surface with a Maxwell-Boltzmann distribution of velocities given by the surface temperature (300°C).

governs the collisional production of reaction products from the surface. Although the data are not shown, the same exponential rise from a roughly 8 eV threshold is seen in the CO_2 signal intensity when the incident angle of the hyperthermal beam is 30° or 60° , instead of 45° . Thus, it appears that total energy, rather than normal energy, governs the collisional enhancement in the signal. This observation is consistent with an eroding surface that is

rough on a molecular scale. Energy transfer on such rough surfaces has been described in terms of gas-phase-like scattering from a moiety on the surface^{3, 26, 27}. The observed data exhibit distinct hyperthermal and thermal translational energy distributions, as has been seen in the OH and H₂O product translational energy distributions when hyperthermal atomic oxygen bombards a hydrocarbon surface that is rough on a molecular scale^{1, 2, 5}.

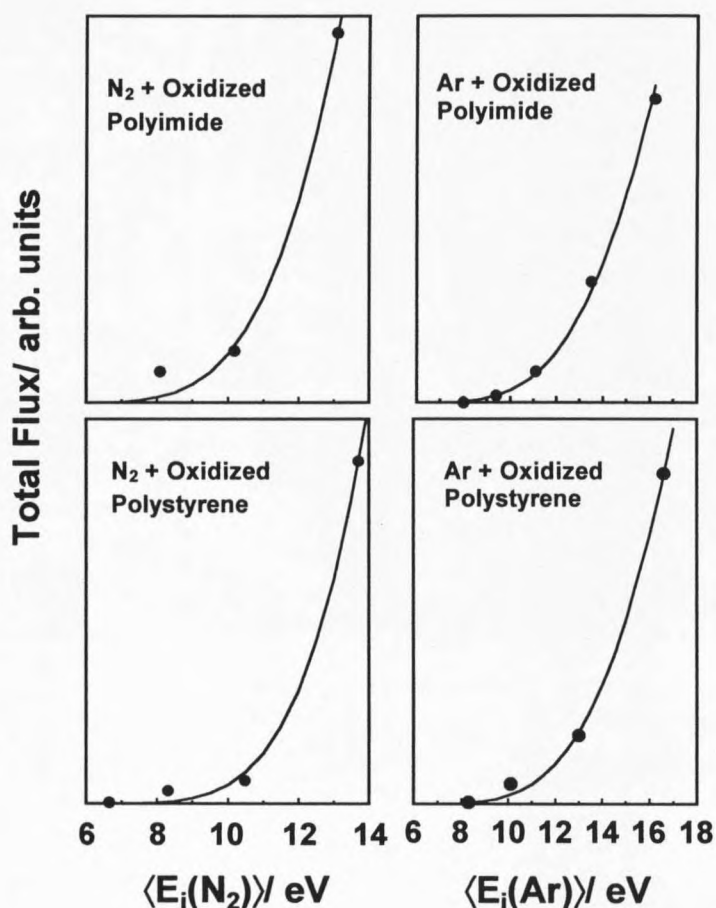


Figure 12. Total integrated intensities of CO₂ signal, obtained from the time-of-flight distributions shown in figures 6-9, as a function of incident hyperthermal Ar beam energy.

The enhancement in the rate of CO₂ release from the surface is significant. The CO₂ signals produced from collisions of energetic atoms or molecules with continuously-oxidized polymer surfaces have been observed to be as much as an order of magnitude greater than the background signal levels resulting from continuous exposure to O atoms from the effusive plasma source. The enhancement in the removal rate of CO₂ varies with incident energy and flux of the energetic inert species.

The increased removal rates of CO₂ (and CO) occur only during the hyperthermal pulse, which is estimated to contain somewhat less than 10^{14} inert particles cm⁻², or somewhat less than one tenth of a monolayer. Given this flux in the pulse, whose duration is ~ 100 μ s, it would take 10^{18} inert particles cm⁻² s⁻¹ to increase the steady-state removal rate of CO₂ (and CO) by an order of magnitude, provided the incident O-atom flux were high enough to maintain steady-state oxidation of the surface. If the collisional enhancement is linear with the flux of inert particles, the effect of high energy collisions on the erosion yield of a polymer under atomic oxygen attack would only be expected to be important (accounting for ejection of more than 10 percent of carbon-containing products from the surface) if the flux of energetic species onto the surface were on the order of 10^{16} inert particles cm⁻² s⁻¹, or approximately 10 monolayers per second. Thus, it appears from the scattering experiments that the flux of energetic species onto a continuously-oxidized surface would have to be relatively high in order to enhance significantly the erosion rate.

We tested this conclusion with a practical experiment in which we compared the erosion yield of polystyrene under exposure to the effusive plasma source with and without the addition of the pulsed hyperthermal Ar beam. In this experiment, the Ar beam pulse was not

chopped, so the entire beam pulse produced from the laser detonation source was allowed to strike the surface. The erosion yield was determined by placing a screen over the samples during exposure and measuring the etch depth of the exposed areas with a profilometer. The erosion yield when the Ar beam bombarded the sample in addition to the effluent from the effusive plasma source was approximately 30 percent higher than the erosion yield observed when only the effusive source was used to expose the surface. Presumably, only the high-energy tail of the Ar beam contributed significantly to the observed enhancement in the erosion yield. The flux of this part of the beam is estimated to be on the order of 10^{14} atoms $\text{cm}^{-2} \text{ s}^{-1}$. Apparently, the conclusion that a practical erosion yield would be unaffected by this average flux of energetic Ar atoms was erred. More work is needed to understand the nature of the collisional mechanisms, in order to make a more accurate assessment of the role of energetic collisions in the erosion of a polymer surface that is under simultaneous attack by atomic oxygen.

Collisional release of reaction products from surfaces undergoing etching has been observed in other studies. For example, in the etching of Si(100) with Cl_2 , Szabó et al.¹⁹ inferred that bombardment by energetic Ar atoms led to collision-induced desorption of a dominant etch product, SiCl_4 . A similar study concluded that collision-induced reaction on a fluorinated Si(100) surface by a 2-5 eV xenon beam produced etch products, detected at $m/z = 85$ (SiF_3^+), from a 480 K surface²⁰.

The collisional process that we have identified may be an important factor in material erosion in LEO. The second most dominant component of the LEO environment (after atomic oxygen) is molecular nitrogen, which can have densities from a few percent to more

than 50 percent those of atomic oxygen, depending on orbital altitude. At common orbital altitudes of 300-400 km, the N_2 density is typically 5-10 percent that of atomic oxygen, or roughly 2×10^7 molecules cm^{-3} . Combining this density with an impact velocity of 7.4 km s^{-1} results in a flux of N_2 molecules on ram surfaces of 1.4×10^{13} molecules $cm^{-2} s^{-1}$, about one tenth the estimated average flux of energetic Ar atoms in our erosion experiment. The average collision energy of N_2 on the ram surfaces of a spacecraft is ~ 7.9 eV, and the collision-energy distribution can reach up to 10 eV. In fact, approximately half the N_2 flux on a spacecraft collides with ram surfaces at impact energies above the 8 eV threshold where we have observed significant enhancement in the production of CO_2 and CO, although the majority of N_2 collisions will be close to the threshold energy. Given the relatively low N_2 flux at altitudes of 300 km and above, coupled with the fact that most collisions are expected to be near the energy threshold for assisting in production of CO and CO_2 from a surface, the role of collisions in assisting atomic oxygen in material removal from a polymer is expected to be minimal. However, collision-assisted erosion may become significant on the ram surfaces of a spacecraft at altitudes lower than 300 km. For example, the N_2 flux is approximately 3×10^{14} molecules $cm^{-2} s^{-1}$ on the ram surface of a spacecraft at an altitude of 250 km. The average flux of hyperthermal Ar atoms in the erosion experiment on polystyrene was on the same order as or lower than the N_2 flux on ram surfaces of spacecraft below 300 km. As we observed a 30 percent enhancement in erosion yield when the continuously-oxidized surface was simultaneously bombarded with hyperthermal Ar atoms, it is likely that N_2 in LEO also assists atomic oxygen in the erosion of spacecraft surfaces at

orbital altitudes below 300 km, where the flux of N_2 collisions above 8 eV is greater than 10^{14} molecules $cm^{-2} s^{-1}$.

Ground-based simulations of atomic oxygen effects in LEO may also include collisional processes. A laser-detonation source similar to the one employed in these experiments is often used to expose candidate spacecraft materials. With O_2 as a precursor gas in this source, we observed CO_2 product signals whose dynamical behavior was remarkably similar to the behavior of the signals that were generated with the combination of hyperthermal Ar or N_2 and a continuously-oxidized surface. It is therefore possible that O_2 in the hyperthermal O/O_2 beam acts to remove material through similar collisional processes. Perhaps, then, the heretofore unwanted molecular oxygen byproduct in the laser-detonation source is actually a desirable component that plays the role of N_2 collisions in ground-based simulations.

Conclusion

The role of energetic collisions in promoting material removal during steady-state erosion of a hydrocarbon polymer under atomic oxygen attack has been investigated by directing hyperthermal beams containing Ar, N_2 , and O_2 at continuously-oxidized polymer surfaces and monitoring the dynamical behavior of the CO_2 (and CO) reaction products. Significant production of CO_2 (and CO) from the continuously-oxidized surfaces was correlated with the impact of the hyperthermal, yet relatively inert, species with the surfaces, indicating a collisional process that assists in material removal from the surface. The

observation of an analogous collisional process for various hyperthermal species bombarding different oxidized polymer surfaces suggests that the collisional process is generic. The nature of this process is uncertain at this time and could involve an enhancement in the removal rate of CO_2 (or CO) products already residing on (or imbedded in) the surface and/or collision-induced reactions that lead to formation of CO_2 (and CO). The intensity of the CO_2 signal produced from the collisional process exhibited a strong dependence on gas-surface collision energy, increasing roughly exponentially with incident translational energy of the bombarding hyperthermal species in the range 8-16 eV. The identification of a collisional process that can assist in the material removal from a polymer under atomic oxygen attack adds a new variable to the study of erosion mechanisms on spacecraft in low Earth orbit and on sample surfaces in ground-based test facilities. Collisions of energetic species that are relatively inert might significantly enhance the rate of erosion of materials that are subjected to a highly oxidizing environment.

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CHAPTER 4

PRODUCTION OF VOLATILE CO AND CO₂ FROM OXIDIZED POLYETHYLENE
AND GRAPHITE SURFACES BY HYPERTHERMAL
ATOM-SURFACE COLLISIONS

Abstract.

Molecular beam-surface scattering experiments have been used to investigate the mechanisms of the enhancement in material removal rate (identified by the ejection of CO and CO₂) when continuously oxidized carbon or hydrocarbon surfaces are bombarded with inert particles (e.g., Ar atoms) possessing kinetic energies in the range 8-22 eV. Collisional enhancement in the material removal rate was observed to increase dramatically above an apparent threshold of ~8 eV. Although the details of the collisional mechanisms must involve complex sputtering processes, the dynamical behavior of the ejected CO and CO₂ may be described in terms of a simple kinematic picture in which an incident fast atom collides with a localized region of the surface that has an effective mass. Collisional, or sputtering, processes such as those identified in this study may be important in the erosion of materials in the low Earth orbital environment, as a result of highly energetic collisions of ambient N₂ with oxidized surfaces, and also in ground-based test facilities that subject oxidized surfaces to bombardment by O₂ molecules with very high translational energies.

Introduction

Energetic collisions between spacecraft surfaces and atomic oxygen in low Earth orbit (LEO) contribute to the oxidation and erosion of these surfaces. Carbon-based materials are particularly susceptible to erosion in LEO, presumably because the oxides of carbon are volatile and can carry carbon away from a surface¹⁻⁶. It has been proposed that collisions of energetic atoms or molecules with a surface under atomic oxygen attack might enhance the removal rate of material from a surface⁷. The LEO environment subjects materials on the ram side of a spacecraft to ~ 4.5 eV collisions with ambient O atoms and to ~ 8 eV collisions with ambient N₂ molecules. These collision energies are average values of relatively broad distributions (full width at half maximum ~ 3 -5 eV). The energies of these collisions are thus substantial, and the resulting energy transfer to the surface might help promote reactions at the surface or assist in the release of products from the surface.

The collisional release of reaction products from surfaces has been discussed in relation to semiconductor etching⁸, in which case ions are usually the energetic bombarding species. When an energetic ion collides with a surface, the collision results in a cascade of moving target atoms. The consequences of the collision cascade may include physical sputtering, back-scattering of the incident ion, ion-induced chemical reactions, production of lattice damage, etc. Two general ion-enhanced etching processes have been discussed for cases where the incident ions have relatively low kinetic energies (less than approximately 25 eV) that are not sufficient to induce physical sputtering of a pristine surface. One process is chemically-enhanced physical sputtering. In this

process, a weakly-bound molecule produced from concomitant chemical reactions is desorbed into the gas-phase because it has received enough kinetic energy (and momentum) from the collision cascade to overcome surface binding forces. A second process, chemical sputtering, refers to an interaction in which ion bombardment causes a chemical reaction to occur and thus creates a product that is weakly bound to the surface and may desorb into the gas phase. In addition to ion-surface collisions, atom-surface collisions have also been shown to enhance the removal rate of chemical species from semiconductor surfaces⁹⁻¹⁰.

We reported in an earlier study that collisions of energetic neutral species (Ar, N₂, and O₂) with continuously oxidized polymer surfaces can lead to the formation of volatile CO and CO₂ reaction products¹¹. Collision-assisted removal of reaction products from polymers is akin to sputtering processes that occur during ion-assisted etching of semiconductors, and these newly-identified processes may enhance the erosion rate of hydrocarbon and other carbon-based materials on spacecraft in LEO. The study reported here extends the earlier investigation of the phenomenology of the collisional processes by examining the dynamical behavior of the volatile CO and CO₂ products when hyperthermal beams of energy-selected Ar atoms are directed at continuously oxidized surfaces of polyethylene and highly oriented pyrolytic graphite (HOPG).

Experimental Methods

The experiments were conducted with the use of a crossed molecular beams apparatus, configured for studies of gas-surface interactions^{6, 11-13}. A schematic diagram

of the configuration used for this experiment is shown in figure 1. A low-pressure RF discharge source was used to produce an effusive beam of atomic oxygen. This continuous beam was directed onto a graphite or polymer surface, resulting in slow oxidation and erosion. A second, pulsed beam of hyperthermal Ar was prepared with the use of a laser detonation source¹⁴ and was simultaneously directed onto the continuously oxidized surface. The angle between the two beams was approximately 40°. Volatile CO and CO₂ products were monitored, with the use of a rotatable mass spectrometer, as a function of time after the hyperthermal pulse struck the surface.

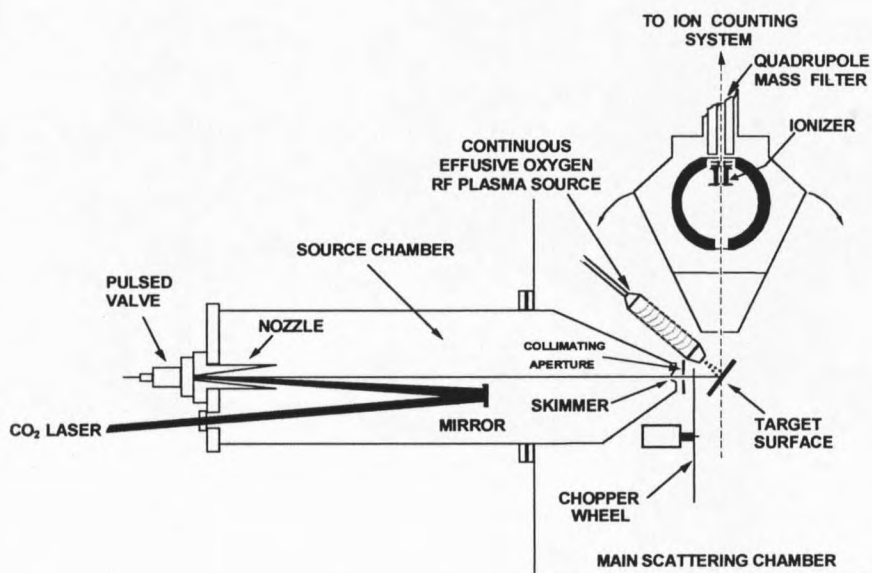


Figure 1. Schematic diagram of the experimental arrangement, showing the orientation of the effusive oxygen plasma and hyperthermal Ar beam sources, chopper wheel, target surface, and detector.

The sample surfaces were highly oriented pyrolytic graphite (HOPG, ZYA quality, basal plane) and low-density polyethylene. Surfaces of HOPG were prepared by cleaving

the sample (10 mm by 10 mm) in air with tape and immediately placing the sample into the vacuum chamber. Polyethylene samples were prepared by pressing low-density polyethylene beads between clean aluminum sheets and cutting this "sandwich" sheet into 10 mm by 8 mm rectangles. When a fresh sample was desired, the aluminum covering was removed, and the sample was placed immediately into the vacuum chamber. The samples were mounted on a manipulator such that the surface normal was contained in the plane of the detector rotation axis, and this axis passed through the sample surface. The sample mount was electrically grounded. No heating was applied to the samples other than radiative heating from the RF plasma source, which increased the sample temperature less than 20°C from ambient.

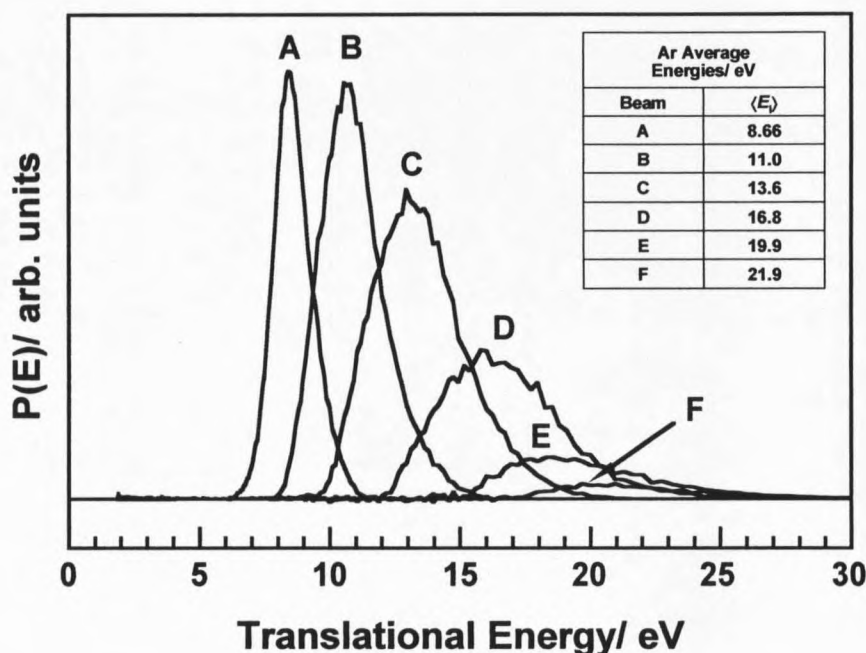


Figure 2. Translational energy distributions of six Ar beams selected with the synchronized chopper wheel. The peak areas correspond to the relative fluxes of Ar.

The effusive and hyperthermal beams were characterized as described earlier^{11, 15}. The effusive beam from the RF plasma source contained a mixture of atomic and molecular oxygen, with an atomic fraction of approximately 26 percent. The translational energy distributions of O and O₂ components in the effusive beam were described well by Maxwell-Boltzmann distributions at temperatures of 450 K and 600 K, respectively. The flux of O atoms onto the target surface was estimated to be 10^{15} atoms cm⁻² s⁻¹. Pulsed hyperthermal beams of Ar with relatively narrow energy distributions were prepared by adjusting the synchronization of a chopper wheel in order to select various portions of the broad hyperthermal beam pulse^{11, 15}. Six hyperthermal Ar beams were prepared and directed at the continuously oxidized HOPG and polyethylene surfaces. Translational energy distributions for the Ar atoms in the various beams selected are shown in figure 2. These distributions are normalized such that their areas are proportional to relative fluxes of Ar atoms in the beam pulse. The estimated flux of the highest-intensity Ar beam is $\sim 10^{14}$ atoms cm⁻² pulse⁻¹. The hyperthermal beam source was operated at a repetition rate of 2 Hz.

Time-of-flight (TOF) distributions were collected at mass-to-charge ratios (m/z) of 28 (CO⁺) and 44 (CO₂⁺). For the polyethylene surface, TOF distributions of 17 (OH⁺) and 18 (H₂O⁺) were also collected. However, the signal-to-noise ratios of the TOF distributions of OH⁺ and H₂O⁺ were significantly lower than those of CO⁺ and CO₂⁺. Therefore, the quantitative data that are presented in this paper pertain to the CO and CO₂ products. TOF distributions were typically averaged for 3,000 pulses of the hyperthermal beam for the HOPG experiment and 5,000 pulses for the polyethylene experiment. All

TOF distributions were collected after steady-state oxidation conditions had been established but before the surfaces became roughened through erosion. In other words, TOF distributions were collected under conditions where their shape remained constant. TOF distributions were collected at two angles of incidence ($\theta_i = 45^\circ$ and 60° , with respect to the direction of the hyperthermal beam and surface normal) and a variety of detection angles, θ_f . All TOF distributions shown here have been corrected for the ion flight time from the electron bombardment ionizer to the Daly ion counter, which was empirically determined to be $3.02(m/z)^{1/2} \mu\text{s}$. The TOF distributions of CO^+ have been corrected for the fragmentation of CO_2 in the ionizer.

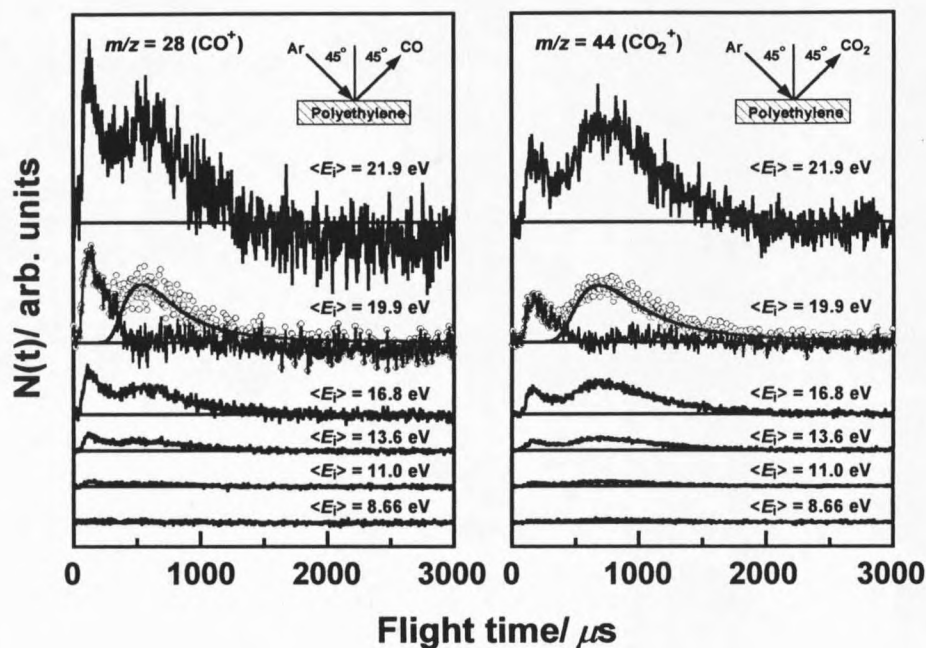


Figure 3. Time-of-flight distributions of CO and CO_2 exiting a continuously oxidized polyethylene surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 2. Deconvolution into thermal (long flight times) and hyperthermal (short flight times) components is illustrated in the distributions corresponding to $\langle E_i \rangle = 19.9$ eV.

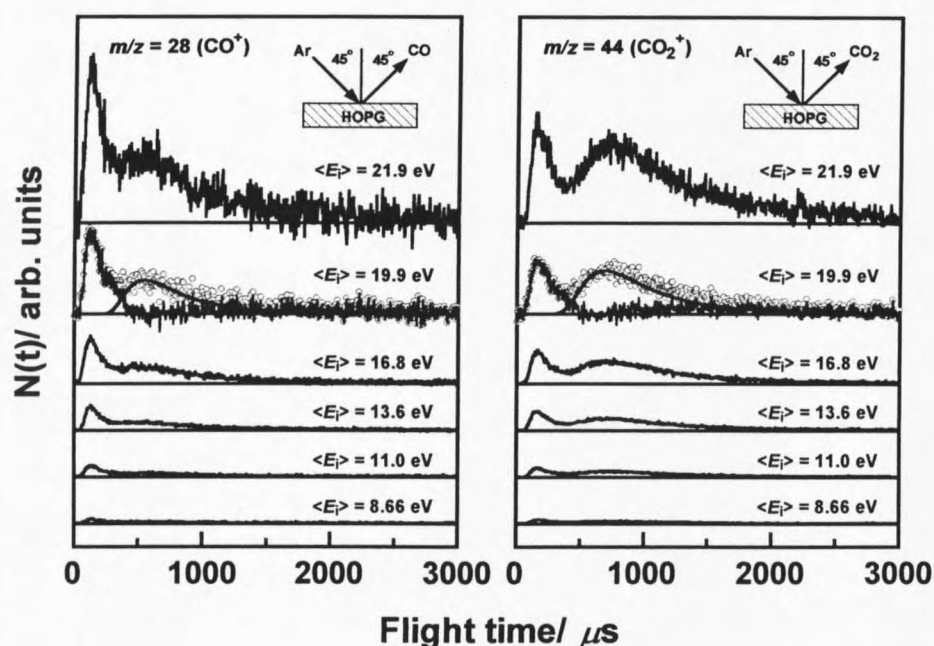


Figure 4. Time-of-flight distributions of CO and CO₂ exiting a continuously oxidized HOPG surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 2. Deconvolution into thermal (long flight times) and hyperthermal (short flight times) components is illustrated in the distributions corresponding to $\langle E_i \rangle = 19.9$ eV.

Results and Analysis

Dynamical Behavior of Product Signals

Figures 3 and 4 show representative TOF distributions of CO and CO₂ following impingement of the six different Ar beams on continuously oxidized polyethylene and HOPG surfaces, respectively. The continuous effusive beam from the oxygen plasma source reacted with the sample surfaces and generated a continuous background signal of CO and CO₂, which has been subtracted from the TOF distributions. Thus the TOF distributions represent only those products that are correlated with the hyperthermal Ar

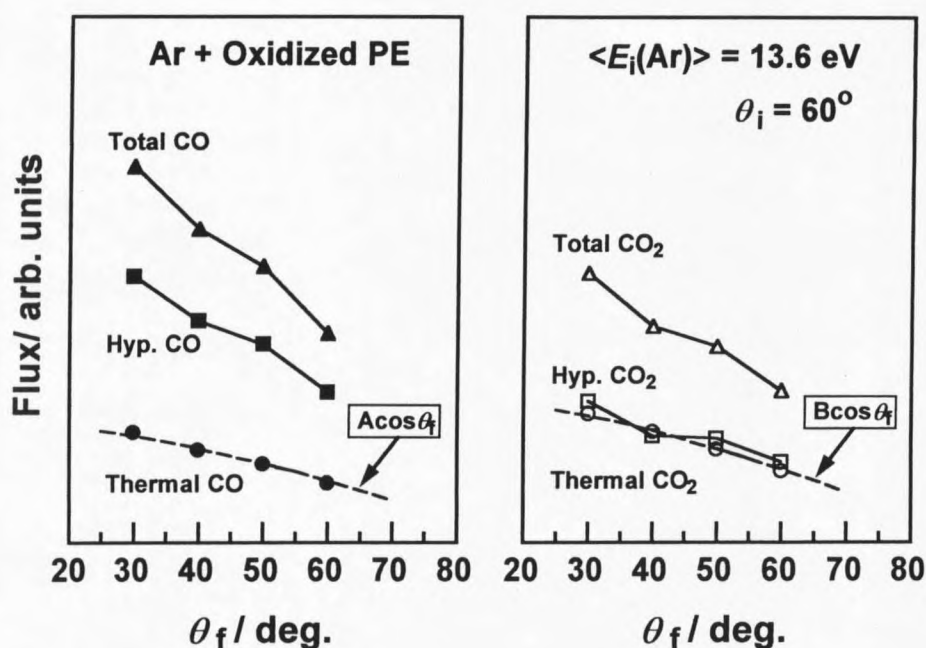


Figure 5. Angular distributions of scattered flux of thermal and hyperthermal CO and CO₂ (and their sums) following impingement of Ar atoms with $\langle E_i \rangle = 13.6$ eV and $\theta_i = 60^\circ$ on an oxidized polyethylene (PE) surface

pulses striking the surface. The TOF distributions have been normalized to the integrated intensities of the respective incident Ar beams. All signals are plotted on the same vertical scale so that the relative signals may be compared directly. The TOF distributions are bimodal, indicating at least two mechanisms through which the products leave the surface following impact of the hyperthermal beam pulse. The slower component corresponds to product molecules that exited the surface with a Maxwell-Boltzmann (MB) distribution at the surface temperature. The faster component corresponds to product molecules that exited the surface with hyperthermal velocities. One TOF distribution in each panel of figures 3 and 4 illustrates a deconvolution of the two components. The thermal product signals indicate a process in which all memory of

the incident hyperthermal beam energy is lost, while the hyperthermal product signals indicate a process in which memory of the energy of the incident hyperthermal beam is retained to some extent.

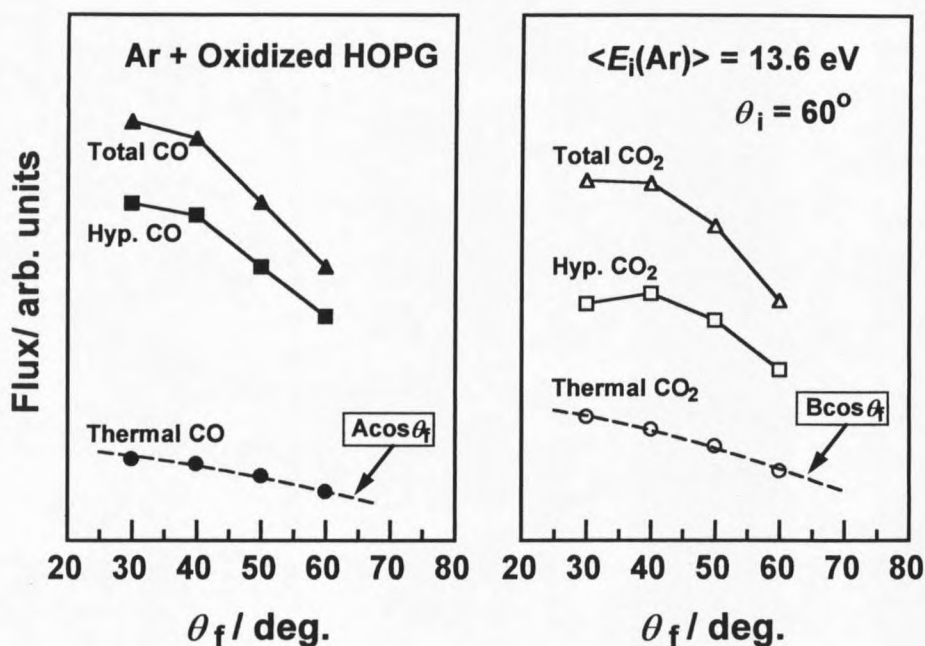


Figure 6. Angular distributions of scattered flux of thermal and hyperthermal CO and CO₂ (and their sums) following impingement of Ar atoms with $\langle E_i \rangle = 13.6$ eV and $\theta_i = 60^\circ$ on an oxidized HOPG surface.

Figures 5 and 6 show the angular distributions of scattered flux of thermal and hyperthermal CO and CO₂ following impingement of the Ar beam with $\langle E_i \rangle = 13.6$ eV and an incident angle, θ_i , of 60° . The thermal product signals follow a $\cos\theta_f$ distribution, while the hyperthermal product signals decrease with final angle according to functions that change somewhat more rapidly than $\cos\theta_f$ and that are believed to have maxima at angles offset slightly from the surface normal in the forward scattering direction. The

flux of hyperthermal products is generally larger than that of the thermal products except for the case of CO_2 products scattered from the oxidized polyethylene surface.

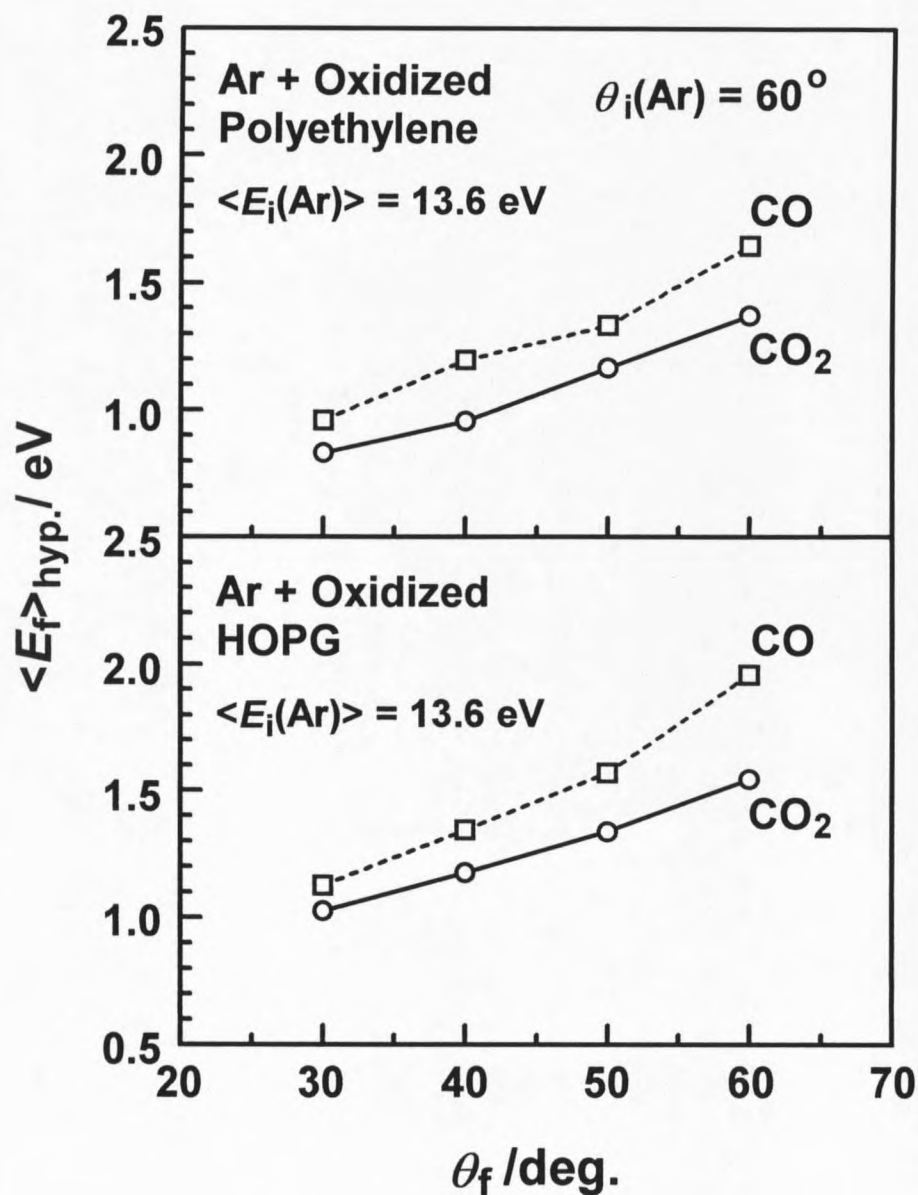


Figure 7. Average final energies of hyperthermal CO and CO_2 products as a function of final angle following impingement of Ar atoms with $\langle E_i \rangle = 13.6 \text{ eV}$ and $\theta_i = 60^\circ$ on oxidized polyethylene and HOPG surfaces.

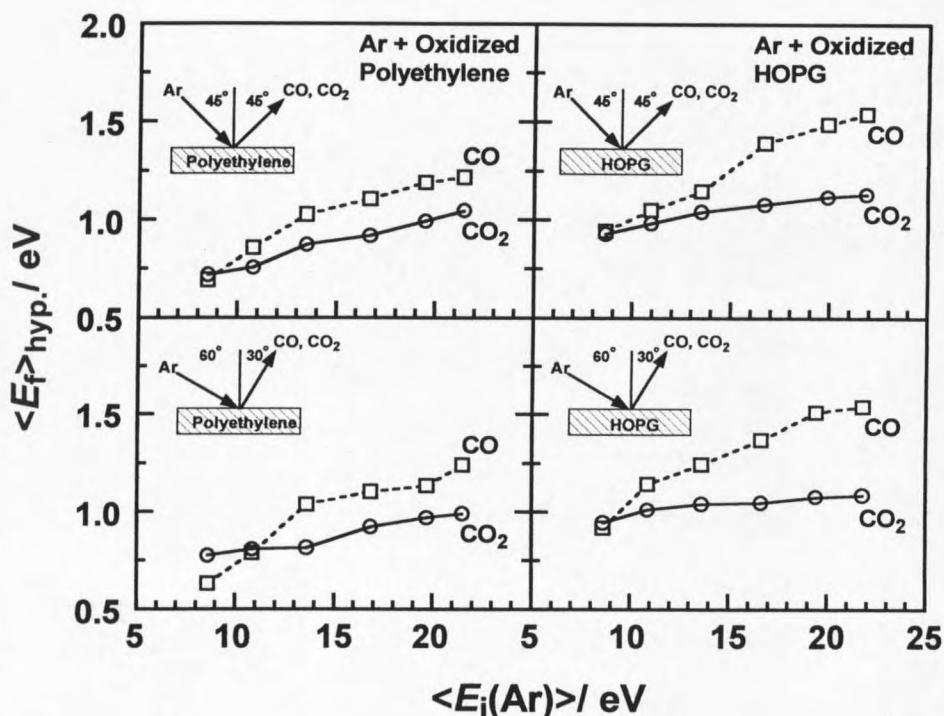


Figure 8. Average final energies of hyperthermal CO and CO₂ products as a function of average incident Ar-atom translational energy for two combinations of incident and final angles, as shown, on oxidized polyethylene and HOPG surfaces.

The average translational energies of the hyperthermal products increase with final angle and average incident Ar translational energy, as shown in figures 7 and 8, respectively. The hyperthermal CO and CO₂ translational energies are only a small fraction of the average incident Ar translational energy. Nevertheless, the fact that the product translational energies are hyperthermal and increase with increasing final angle and incident Ar translational energy suggests that some memory of the incident angle and translational energy of Ar beam is retained.

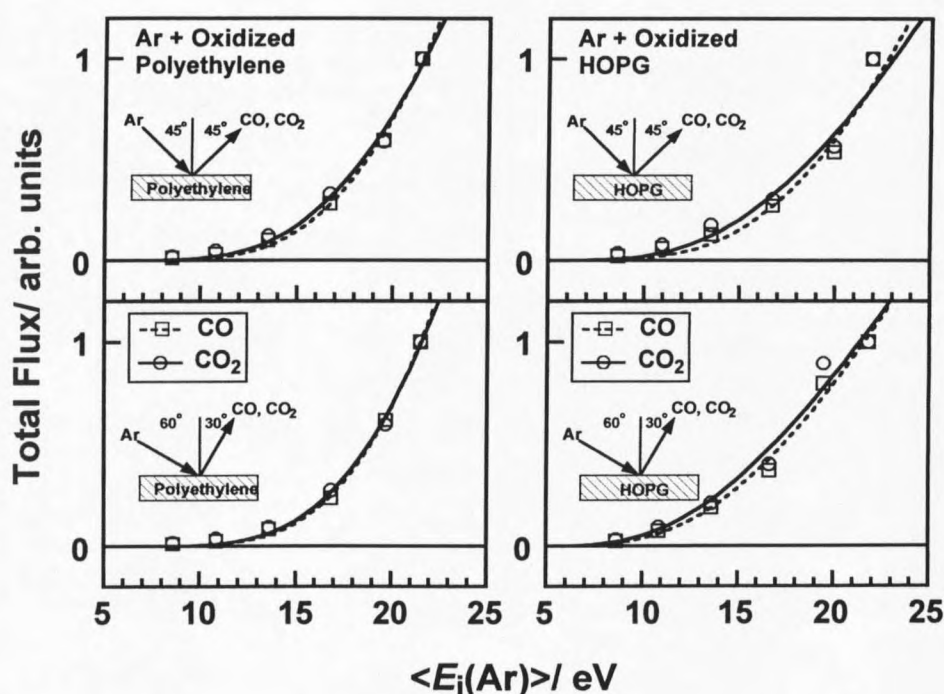


Figure 9. Total integrated intensities of CO and CO₂ products as a function of average incident Ar-atom translational energy for two combinations of incident and final angles, as shown, on oxidized polyethylene and HOPG surfaces.

Figure 9 shows the relationship between the total integrated flux of the product signals and the incident translational energy of the impinging Ar atoms. The dependencies of all products intensities from both surfaces at two sets of incident/final angles could be fit well with an arbitrary function of the form,

$$I(E_i) = Ae^{-B/\langle E_i \rangle}, \quad (1)$$

where values for the B parameter fall in the range 56 – 85 eV for HOPG and 87 – 109 eV for polyethylene. The magnitude of the A parameter depends on the units of the flux. The formation of CO and CO₂ products is clearly strongly dependent on the incident

energy. It appears that CO and CO₂ are produced from the oxidized surfaces when the incident translational energy of hyperthermal Ar is above ~8 eV.

Kinematic Analysis

The scaling of the hyperthermal CO and CO₂ product energies with final angle, δ_f , (figure 7) is reminiscent of the analogous behavior exhibited by reactively scattered (hyperthermal) OH products in the reaction of O atoms with a hydrocarbon surface¹⁵. In the latter reaction, it was shown that a Newton diagram could be used to describe the reactive scattering in the center-of-mass (c.m.) reference frame, where the incident O atom is viewed as interacting with a localized effective surface mass in a gas-phase-like process. Simple Newton diagrams for collisional production of CO and CO₂ from polyethylene and HOPG surfaces are shown in figures 10 and 11, respectively. These diagrams are constructed with the use of the average velocity of a beam of incident Ar atoms and the average final velocities of the scattered CO or CO₂ products. It is assumed that incident Ar atoms interact with a local region of the surface that is defined by an effective mass, m_{sX} . The localized region is capable of releasing CO or CO₂ from the surface. Because the effective surface moiety has finite mass and only thermal initial velocities, which are negligible compared to the velocity of the incident Ar atoms, the relative velocity, v_{rel} , between the incident Ar-atom beam and the surface is simply the velocity of incident Ar-atom beam. The c.m. velocity in the laboratory frame, $\bar{u}_{cm}$, has the same direction as the incident Ar-atom beam. We find that the velocity vectors corresponding to the average final velocities of the hyperthermal products (CO or CO₂)

lie on a circle whose center is a point on the relative velocity vector. This point corresponds to the tip of the c.m. velocity vector, $\vec{v}_{\text{cm}}$. Therefore, the mass of the effective surface moiety can be calculated:

$$m_{\text{sX}} = m_{\text{Ar}} \left(\frac{v_{\text{Ar}}}{v_{\text{cm}}} - 1 \right). \quad (2)$$

Once the mass of the effective surface moiety is known, other c.m. quantities may be calculated (refer to figure 12). The c.m. collision energy is

$$E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2, \quad (3)$$

where μ is the reduced mass between an incident Ar atom and the mass of the effective surface moiety. The total energy that goes into translation of the product, X , and of the center-of-mass of the recoiling Ar-surface fragment pair, $S_f\text{-Ar}$, is

$$E_{\text{T}} = \frac{1}{2} \mu' v_{\text{rel}}'^2 = \frac{1}{2} M \frac{m_{\text{X}}}{M - m_{\text{X}}} u_{\text{X}}'^2, \quad (4)$$

where the primes refer to post collision quantities, M is the total mass ($m_{\text{Ar}} + m_{\text{s}} + m_{\text{X}}$), m_{X} is the mass of the product (CO or CO₂), and u_{X}' is the product velocity in the c.m. frame. The difference between E_{coll} and E_{T} gives the total internal energy, E_{int} , after the initial collision. In this picture of scattering in the c.m. frame, the products are X (CO or CO₂), S_f , and Ar. Therefore, E_{int} includes contributions from the internal energies of the products [$E_{\text{int}}(X)$], the internal energy of the $S_f\text{-Ar}$ pair, and the energy required to create a product and remove it from the surface [$\Delta E(S_f\text{-}X)$]. Because the recoiling Ar atom and surface fragment are treated as one particle, $S_f\text{-Ar}$, the internal energy of the $S_f\text{-Ar}$ pair contains the internal excitation of the surface fragment, $E_{\text{int}}(S_f)$, and the relative

translational energy between m_s and Ar, $E_{\text{rel}}(S_f\text{-Ar})$. The quantity, $\Delta E(S_f\text{-}X)$, includes all chemical reactions that might be induced by the Ar-atom collision and may in principle be either negative or positive. The data do not provide sufficient information to allow us to determine the partitioning of E_{int} into its various possible contributions.

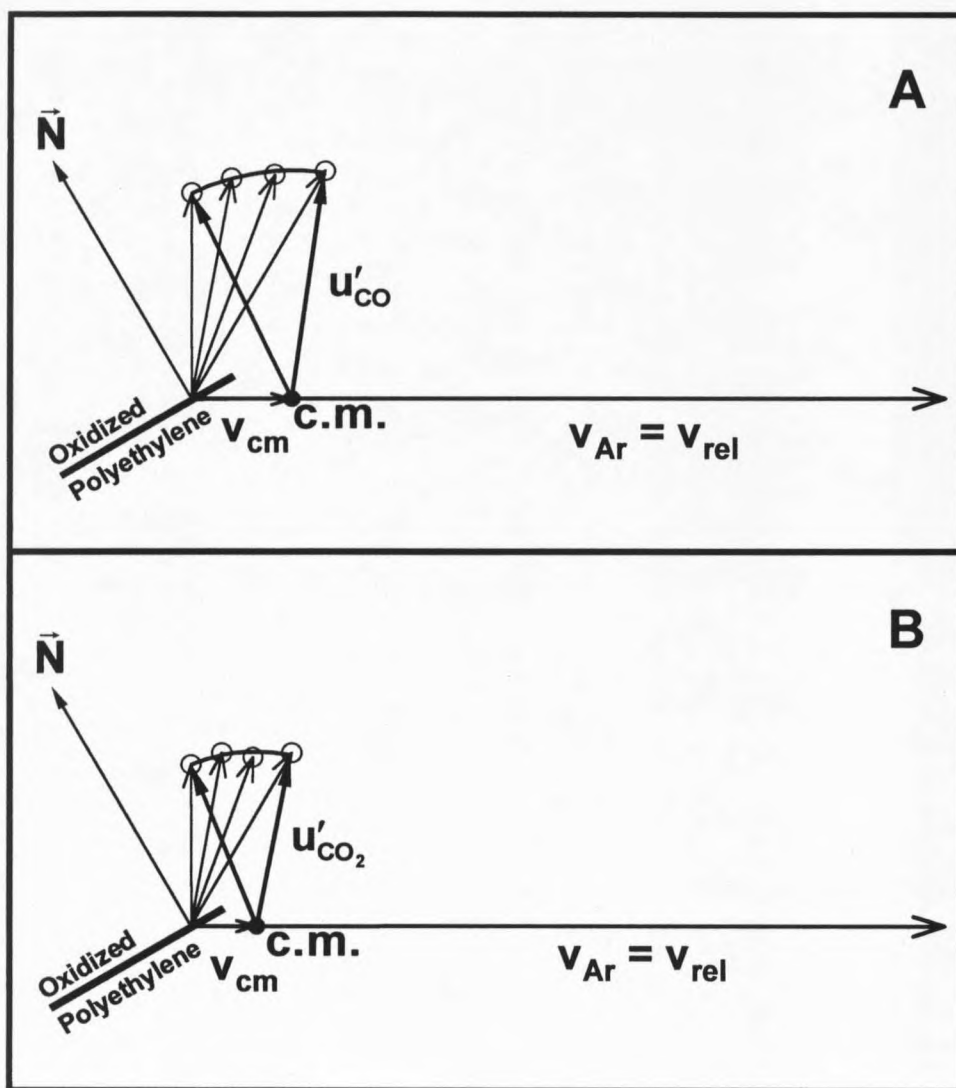


Figure 10. Newton diagrams for scattered hyperthermal CO and CO₂ following impingement of Ar atoms with $\langle E_i \rangle = 13.6$ eV and $\theta_i = 60^\circ$ on an oxidized polyethylene surface.

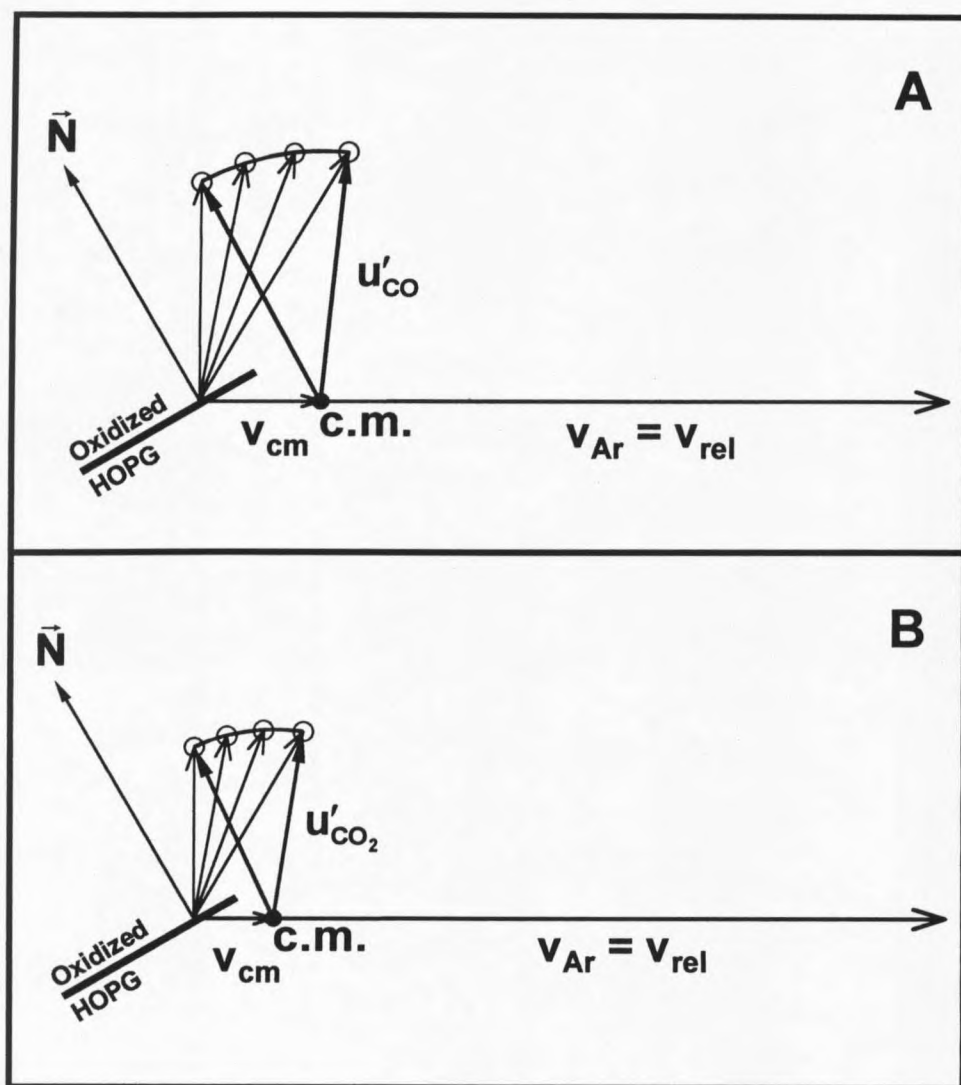


Figure 11. Newton diagrams for scattered hyperthermal CO and CO₂ following impingement of Ar atoms with $\langle E_i \rangle = 13.6$ eV and $\theta_i = 60^\circ$ on an oxidized HOPG surface.

Table 1 lists the quantities derived from the kinematic analysis of scattered hyperthermal CO and CO₂ from the oxidized polyethylene and HOPG surfaces. It should be noted that only the average velocities of the incident beam and of the scattered products were used to find the effective surface mass and other quantities derived from

the kinematic analysis. Therefore, the quantities in Table 1 should be considered to be rough and highly averaged.

Table 1. Center-of-mass quantities derived from a kinematic analysis of scattered hyperthermal CO and CO₂ following impingement of Ar atoms with $\langle E_i \rangle = 13.6$ eV and $\theta = 60^\circ$ on oxidized polyethylene (PE) and HOPG surfaces.

Collisional Event	m_{sX}/amu	$\langle E_{\text{coll}} \rangle/\text{eV}$	$\langle E_T \rangle/\text{eV}$	$\langle E_{\text{int}} \rangle/\text{eV}$
Ar + Oxidized PE (CO formation)	259	11.86	1.00	10.86
Ar + Oxidized PE (CO ₂ formation)	417	12.49	0.90	11.59
Ar + Oxidized HOPG (CO formation)	206	11.35	1.23	10.12
Ar + Oxidized HOPG (CO ₂ formation)	335	12.11	1.09	11.02

Discussion

The data show similar behavior to those found earlier for energetic Ar and N₂ colliding with oxidized polyimide and polystyrene surfaces¹¹. There is clearly a collisional process that leads to ejection of CO and CO₂ from an oxidized polymer or carbon surface upon impingement of hyperthermal inert atoms or molecules, and this process appears to be general. Regardless of the surface, incident inert particle, incident angle, or final angle, the production efficiency of volatile CO and CO₂ rises dramatically with Ar-atom incident collision energies above ~ 8 eV. The independence of the

threshold energy on the incident angle indicates that total energy, rather than the component of the incident energy normal to the surface, governs the collisional enhancement of the signal. This observation is consistent with an eroding surface that is rough and therefore strongly couples parallel energy with normal energy.

Atom scattering on rough surfaces has been viewed as a relatively localized gas-phase-like process that may be described by a binary collision model^{15, 16}. Our kinematic analysis suggests a related, three-body scattering, picture for collision-induced production of CO and CO₂ from a polymer or carbon surface. In this picture, an incident fast Ar atom interacts with the surface on such a short time scale that only a small region of the surface is involved in the collision, and this small region interacts with the colliding Ar atom with an effective mass. The effective surface masses (see Table 1) corresponding to production of CO were roughly 60 percent of those corresponding to the production of CO₂, suggesting that the interaction leading to CO is more localized than that leading to CO₂. In either case, the effective surface mass appears to contain tens of carbon atoms, so the interaction must involve the coupling of a large number of surface modes, or in other words, a "collision cascade." Even though the effective surface mass is relatively large, the kinematic analysis of the data implies that the energy associated with the motion of the center of mass of the two initial collision partners is conserved throughout the entire process that leads ultimately to the ejection of CO or CO₂ from the surface. Therefore, only the center-of-mass component of the incident Ar-atom energy, E_{coll} , is effective in the collisional production of CO or CO₂ from the surface. E_{coll} is the difference between the incident Ar-atom energy and the energy associated with the

motion of the center of mass. Approximately 90 percent of the c.m. collision energy (E_{coll}) is channeled into the quantity designated as E_{int} . The energy change, $\Delta E(m_s-X)$, associated with the production of gaseous CO or CO₂ is one of the four components of energy that comprise E_{int} (see figure 12). Although we are unable to assign a value to this energy change from our data, it will be some fraction of E_{int} , which in turn is a fraction of the incident Ar-atom energy, E_i . The observed threshold of $E_i \approx 8$ eV for the formation of volatile CO and CO₂ is therefore significantly higher than the actual energy required to produce these volatile species and remove them from the surface.

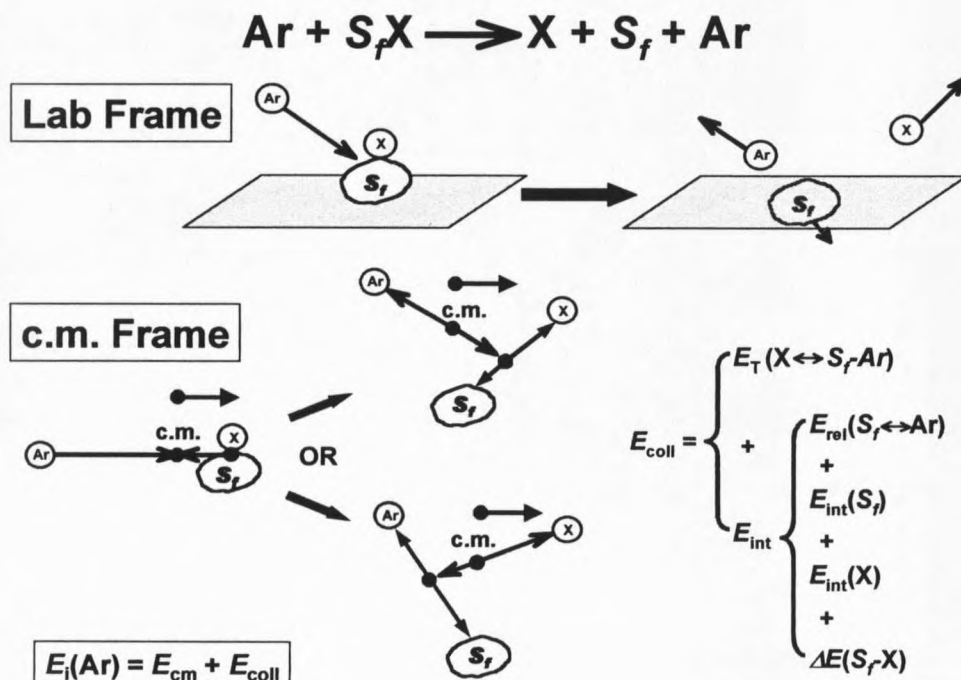


Figure 12. Pictorial representation of collision-induced ejection of product X in laboratory reference frame and in center-of-mass (c.m.) frame.

The dynamical behavior of the product signals indicates that CO and CO₂ may be produced through thermal and non-thermal channels. While the picture of a relatively localized gas-surface interaction has been developed from a consideration of only the hyperthermal product signal, the thermal signal appears to arise from the same initial mechanism because both the thermal and hyperthermal signals rise with incident Ar-atom energy in the same proportion. Assuming that thermal and hyperthermal mechanisms having, fortuitously, the same energy dependence may be discounted, we conclude that the thermal signals come from secondary processes that follow the primary energy-dependent processes. The hyperthermal signals may then be considered the key indicators of the initial interactions that lead to collisional production of CO and CO₂ from the surface.

The formation of volatile products from a surface that is bombarded with energetic atoms suggests a mechanism of sputtering, although physical sputtering is unlikely to be important at the incident Ar-atom energies employed in these experiments. The scaling of the hyperthermal product energy with incident energy and the increase in final energy of the hyperthermal products with increasing final scattering angle are consistent with a mechanism that has been discussed in terms of collision-induced desorption¹⁷. In our experiment, collision-induced desorption would be essentially synonymous with chemically-enhanced physical sputtering⁸. If the continuous oxidation of the surface produces CO and CO₂ molecules that are weakly bound to the surface or imbedded in the surface, then energy transfer from collisions of energetic Ar atoms could promote the removal of these species. Another mechanism, chemical sputtering⁸, is also consistent

with our results. In this case, the energy transferred to the surface from the incident atom may promote a chemical reaction that leads to the formation and desorption of volatile products. The products that are ejected from the surface via either sputtering mechanism may be desorbed during or after the collision cascade. Our data suggest the constraint that even during the complicated sputtering process, the energy associated with the motion of the c.m. of the incident Ar atom and effective surface mass is conserved throughout the process that liberates CO or CO₂ from the surface. During the collision cascade, much of the collision energy may be retained in the inelastically scattered Ar atom or deposited in the surface. In addition, some of the collision energy is required to produce and/or remove products from the surface. Hence, only a small fraction of the collision energy is likely to go into translation of the exiting products, as borne out by the data shown in figures 7 and 8. Products that are ejected from one surface site may scatter in directions such that they collide with another region of the surface and become trapped long enough to come into thermal equilibrium with the surface before desorbing, thus giving rise to a thermal population of volatile reaction products. This explanation of the thermal signal is supported by observations in our laboratory that the fraction of thermal product signal increases with increasing surface roughness. Products that scatter on a rougher surface would be expected to have a higher probability to undergo further collisions with the surface and become trapped. Regardless of the mechanism by which volatile CO and CO₂ products are formed, they may scatter directly into the gas phase, with hyperthermal translational energies, or they may become trapped momentarily and desorb thermally.

The collisional processes that we have identified may be regarded as a synergistic effect of the simultaneous bombardment of a surface by atomic oxygen and an energetic species. Collisions of Ar atoms, with translational energies in the range used for these experiments, are ineffective at producing volatile products from fresh polymer or HOPG surfaces. Under steady-state oxidation conditions, the production of volatile products may increase by more than an order of magnitude during exposure to collisions of fast inert atoms or molecules. If the source of atomic oxygen to the surface is turned off, collisions of energetic species with the surface will still produce CO and CO₂, but the intensities of these products will decay almost to zero over several hours of exposure. The collisional production of CO and CO₂ clearly requires both an oxidized surface and energetic particles with translational energies above ~8 eV. This synergistic effect may be important in LEO at altitudes below 300 km and in ground-based simulations of atomic oxygen effects on materials^{11, 15}. In the LEO environment, the second most dominant component after atomic oxygen is molecular nitrogen. Combining the N₂ density with the velocity of a spacecraft can result in a significant flux of energetic (> 8 eV) collisions of N₂ molecules on the ram surface. In ground-based simulations that employ a laser detonation source¹⁵, the O₂ in the hyperthermal O/O₂ beam typically has an average translational energy of ~10 eV and therefore may promote material removal through a collisional process.

Conclusion

The nature of the energetic collisions that promote material removal during steady-state erosion of polyethylene and HOPG under atomic oxygen attack has been investigated by directing hyperthermal beams of Ar at continuously oxidized surfaces of these materials and monitoring the dynamical behavior of the CO and CO₂ reaction products. Significant production of CO and CO₂ from the continuously oxidized surfaces was correlated with the impact of the hyperthermal Ar with the surfaces, indicating a collisional process that assists in material removal from the surface. These new data in combination with similar data from an earlier study suggest that the collisional process is generic. The origin of this process could involve an enhancement on the removal rate of CO or CO₂ reaction products already residing on or imbedded in the surface (chemically-enhanced physical sputtering) or collision-induced reactions that lead to formation of volatile CO and CO₂ (chemical sputtering). The dynamical behavior of the CO and CO₂ products in conjunction with a kinematic analysis, suggest a simple picture of the sputtering as an initial binary collision between an incident Ar atom and a localized region of the surface, which is followed by inelastic scattering of the Ar atom and breakup of the local surface moiety into an ejected CO or CO₂ molecule and a local collection of surface atoms that recoil as a group into the surface. The intensity of the CO and CO₂ signals produced from the sputtering process exhibited a strong dependence on Ar-atom-surface collision energy up to 22 eV, with an apparent threshold near 8 eV. The collisional processes that have been studied may be regarded as a synergistic effect in which collisions of energetic particles enhance the erosion rates of hydrocarbons and

carbon in atomic oxygen environments, such as those encountered by spacecraft in low Earth orbit or by candidate spacecraft materials in certain ground-based test facilities.

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CHAPTER 5

COLLISION-ASSISTED ETCHING OF Si IN AN
ATOMIC-CHLORINE ENVIRONMENTAbstract

Molecular beam-surface scattering experiments have been used to investigate the mechanisms of collision-assisted etching of Si when a Si surface is simultaneously exposed to an effusive beam of atomic chlorine and a hyperthermal beam of Ar atoms possessing translational energies in the range 780-2200 kJ mol⁻¹. Time-of-flight and angular distributions of silicon chloride (SiCl_x, x = 1-4) products were collected with a rotatable mass spectrometer detector. The intensity of the scattered products decreased with increasing chlorination. Time-of-flight distributions of these products exhibited two populations, one thermal and the other hyperthermal, which originated from same initial interaction mechanism. The thermal products have a measurable surface residence time, with lifetimes in the range of 65 to 700 μs. The Si etch rate is dramatically enhanced with the bombardment of energetic Ar atoms. The intensities of the etch products strongly depend on incident Ar translational energy. Dynamical behavior of the etch products indicates that the collisional mechanisms involve chemically-enhanced physical sputtering and chemical sputtering.

Introduction

Ion-assisted etching of semiconductors has been studied extensively^{1,2} due to its application in the fabrication of very large scale integrated circuits (VLSIs). The synergism between energetic ions and chemically active species incident on surfaces is responsible for the desired high anisotropic etching. In order for etching to occur, three sequential steps must occur¹: adsorption of chemically active species on the surface, product formation, and product desorption. The enhancement of etch rate by energetic ion bombardment must accelerate at least one of the three steps. Connelly and Flamm³ suggested that the first step is increased by ion bombardment via surface damage. Winters and Coburn¹ suggested that the second step is directly increased by collision-assisted product formation or chemical sputtering which produces a weakly bound species. The third step is increased via a mechanism that was first proposed by Mauer et al.⁴ and was called chemically-enhanced physical sputtering, in which the chemical reaction produces more weakly bound species on the surface but overcoming the surface binding energy is still the key process. For different systems, ion-enhanced etching could be dominated by surface damage, chemical sputtering, chemically-enhanced physical sputtering, or a combination of these mechanisms. Barone and Graves⁵ have compared the relative contributions of chemical and physical sputtering by performing molecular dynamics simulations for the system of Ar-ion bombardment of a fluorinated Si surface. In all of these mechanisms, the collision of an energetic ion with a surface must involve a cascade of moving target atoms, i.e., a collision cascade. De Vries and coworker⁶⁻¹¹ have conducted a series of studies of ion-assisted etching of Si and SiO₂, in which the

translational energy distributions of the sputtered products was explained by a collision cascade mechanism and the binding energies were calculated. A linear collision cascade mechanism was also suggested by Garrison *et al.*¹² in a molecular dynamics simulation of chemical sputtering of Si in a chlorine environment. In most of the studies of Si etching with halogens, ionization fragmentation from parent molecules often interferes with the interpretation of etching products. Recently, Leone *et al.*¹³⁻¹⁵ have employed a single-photon ionization time-of-flight mass spectroscopy (SPI-TOFMS) technique to examine the etching products in the system of ion-enhanced etching of Si with molecular chlorine.

The ion energy involved in most ion-assisted etching systems is typically on the order of hundreds to thousands of eV. This highly energetic ion bombardment leads to significant lattice damage and charge-associated damage due to charge buildup. Development of a damage-free etching has therefore drawn much attention, and many studies have focused on etching that uses a low energy neutral inert particle beam or halogen beams in the hyperthermal (1-20 eV) energy regime¹⁶⁻²¹. In the same energy regime, similar synergistic effects between energetic inert particles and chemically active species incident on surfaces has been observed in studies of collision-assisted erosion of hydrocarbon polymers and graphite in atomic-oxygen environments,^{22,23} in which the erosion rate was dramatically enhanced with the bombardment of energetic Ar atoms on the oxidized surfaces. This generic collisional enhancement in etching of Si and erosion of materials is relevant to the erosion of polymers in some exposure environments, such as low Earth orbit (LEO), where N₂ may strike oxidized spacecraft surfaces with collision

energies greater than 8 eV, and in certain atomic-oxygen test facilities that subject oxidized surfaces to bombardment of ~ 10 eV O_2 .^{22,23}

In this chapter, we report an investigation of collision-assisted etching of Si in an atomic-chlorine environment. When a Si surface is exposed to molecular chlorine, the Cl_2 molecule dissociates, and the resulting Cl atoms chemisorb on the Si surface, forming a Cl-passivated Si surface. This surface is inert to additional Cl_2 attack. However, when a Si surface is exposed to atomic chlorine, spontaneous etching will occur.^{24,25} Hyperthermal Ar atoms with translational energies of $780\text{--}2200$ kJ mol⁻¹ were directed at a Si surface that was under continuous attack from an effusive beam of chlorine atoms. Enhancement in the production of volatile etch products ($SiCl_x$, $x = 1\text{--}4$) was correlated with the bombardment of Ar atoms and was strongly dependent on the incident Ar energy, indicating that the etch rate of Si was dramatically increased by the collisions of energetic Ar atoms.

Experimental Methods

The experiment was conducted with the use of a crossed molecular beams apparatus,²⁶ configured for studies of gas-surface interactions using a hyperthermal beam source.²⁷ In addition to the hyperthermal beam source, a second, effusive beam of atomic chlorine was produced with a low-pressure RF discharge source. A schematic diagram of the experimental configuration is shown in figure 1. The details of this configuration and the hyperthermal beam source have been discussed previously.^{22,23,28} Briefly, the hyperthermal beam is a pulsed laser detonation source. Ar was used as the precursor gas.

A synchronized chopper wheel was used to select a narrowed portion of the overall Ar beam distribution. The silicon surface was exposed to the continuous atomic chlorine beam, resulting in chlorination and slow etching. At the same time, the pulsed hyperthermal Ar beam was directed at this chlorinated Si surface, which greatly enhanced the Si etching rate. The scattered products (SiCl_x , $x = 1-4$) were correlated with the impingement of the pulsed hyperthermal Ar beam, and they were monitored with the rotatable quadrupole mass spectrometer by collecting time-of-flight (TOF) distributions.

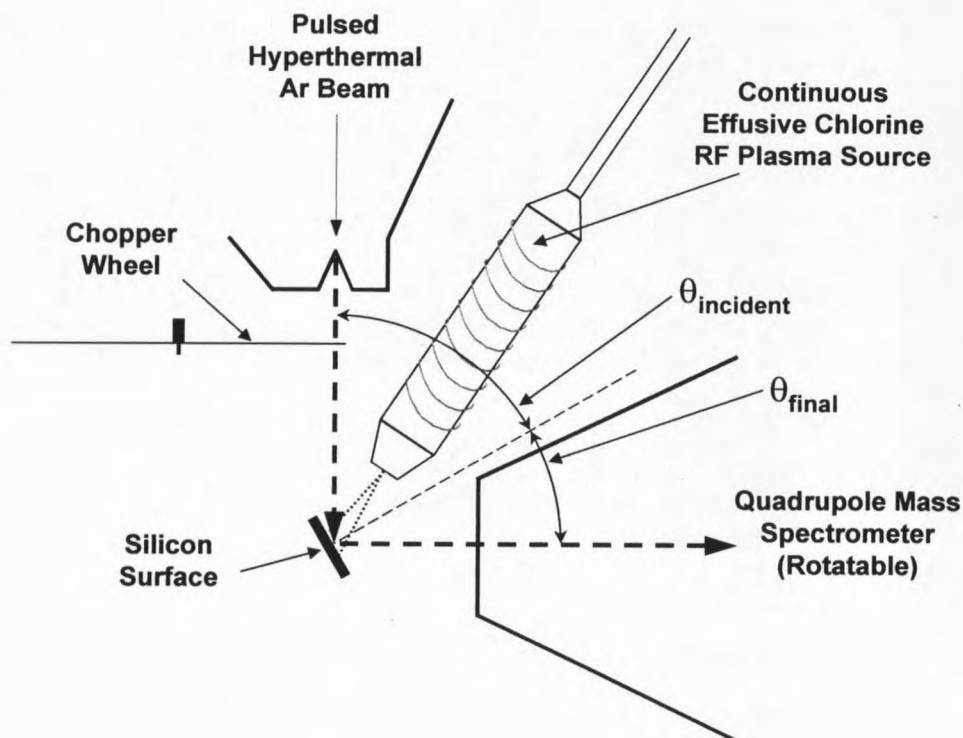


Figure 1. Schematic diagram of the interaction region, showing the effusive plasma and hyperthermal beam sources, chopper wheel, target surface, and detector.

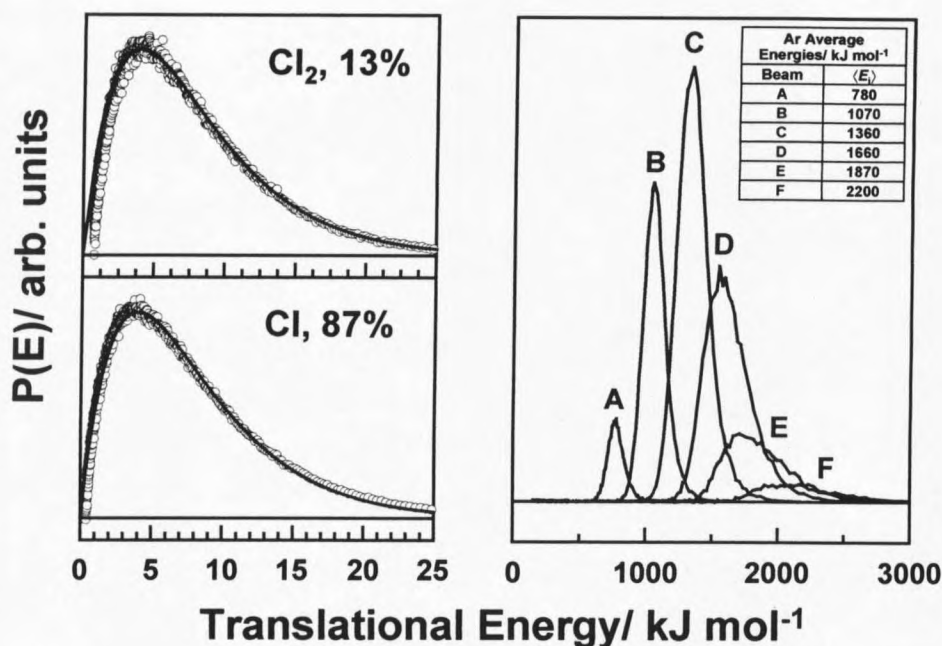


Figure 2. Translational energy distributions of the effusive chlorine plasma beam and six Ar beams that were used. The peak areas in the right panel correspond to the relative fluxes of Ar.

The sample surface was *p*-type Si(100), with resistance of 1-10 Ω cm. The sample cleaning procedure involved degreasing and HF dip.²⁹ The clean sample surface was immediately placed into the vacuum chamber. The hyperthermal beam incident angle, θ_i , and product detection angle, θ_f , are defined with respect to the surface normal. The sample mount was electronically grounded and was heated with a cartridge heater.

The continuous effusive atomic-chlorine beam was produced by an inductively coupled plasma and was characterized by aligning the detector with the plasma source and placing a chopper wheel in front of the detector to modulate the beam. The left panel of figure 2 shows the translational energy distributions of the Cl and Cl_2 components in the effusive beam. The data have been corrected for the ionization fragmentation of Cl_2

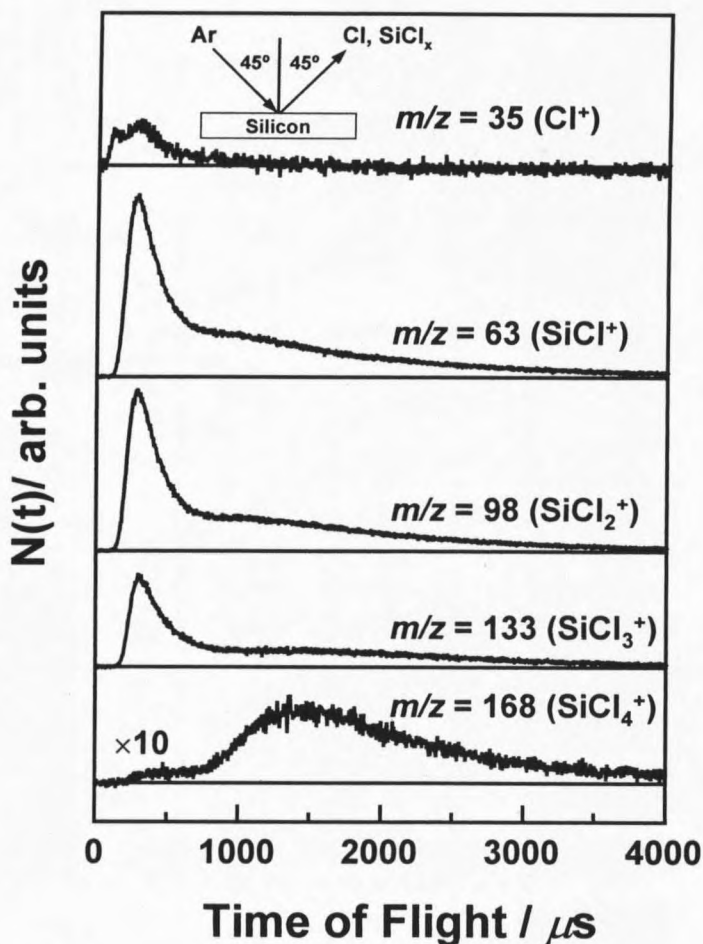


Figure 3. Representative TOF distributions of Cl and silicon chlorides (SiCl_x , $x = 1-4$) at a detection angle, θ_d , of 45° following impingement of Ar atoms with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ and $\theta_i = 45^\circ$ on a continuously-chlorinated Si surface. The scale on which the SiCl_4 signal is plotted has been multiplied by a factor of 10 relative to the others.

in the electron-impact ionizer. The difference of ionization cross sections between Cl_2 and Cl ^{30,31} was taken into account in the determination of the fraction of Cl and Cl_2 in the beam. The fraction of atomic chlorine in the beam was 87%, and the flux of atomic chlorine at the surface was $\sim 10^{15} \text{ atoms cm}^{-2} \text{ s}^{-1}$. Both Cl and Cl_2 translational energy distributions could be fit well with a Maxwell-Boltzmann (MB) distribution at a

temperature of 475 K. Ions in the Cl/Cl₂ beam were undetectable with the filament of the electron-impact ionizer turned off, which indicates that the RF plasma effusive source provided a neutral beam of atomic and molecular chlorine.

Six hyperthermal Ar beams were prepared with the use of the synchronized chopper wheel (figure 2). The average translational energies of the six beams were in the range 780-2200 kJ mol⁻¹. The translational energy distributions of the six Ar beams were normalized such that the areas are proportional to the relative fluxes of Ar atoms in the beams. The estimated flux at the surface for the highest Ar beam is about 10¹⁴ atoms cm⁻² pulse⁻¹. The Ar beams were operated at a repetition rate of 2 Hz.

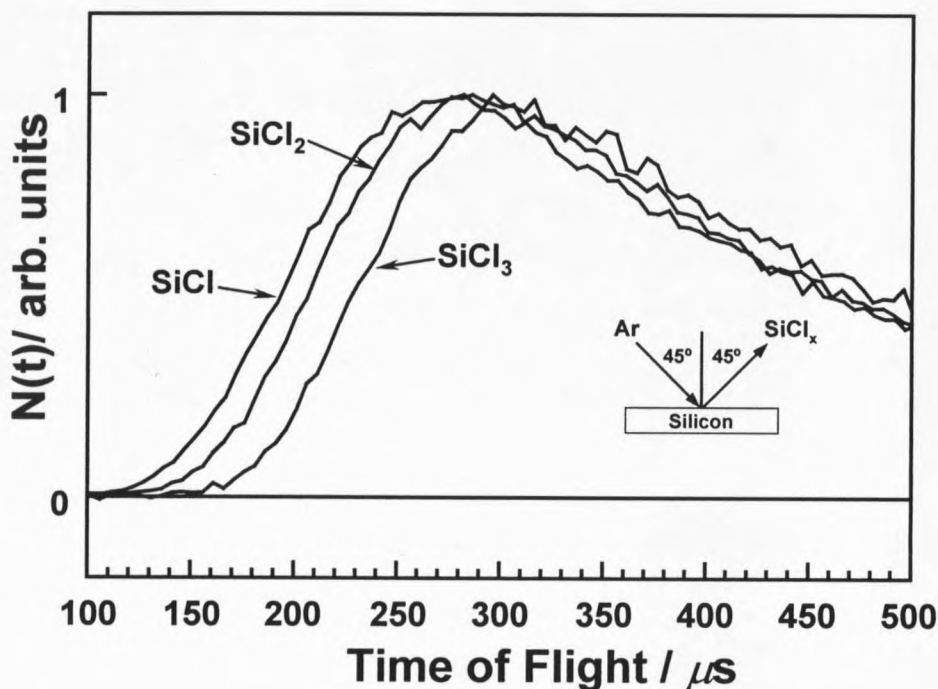


Figure 4. TOF distributions of SiCl, SiCl₂, and SiCl₃ at detection angle of 45° following impingement of Ar atoms with $\langle E_i \rangle = 1360$ kJ mol⁻¹ and $\theta_i = 45^\circ$ on continuously-chlorinated Si surface. Differences in flight time indicate the production of SiCl and SiCl₂, in addition to SiCl₃.

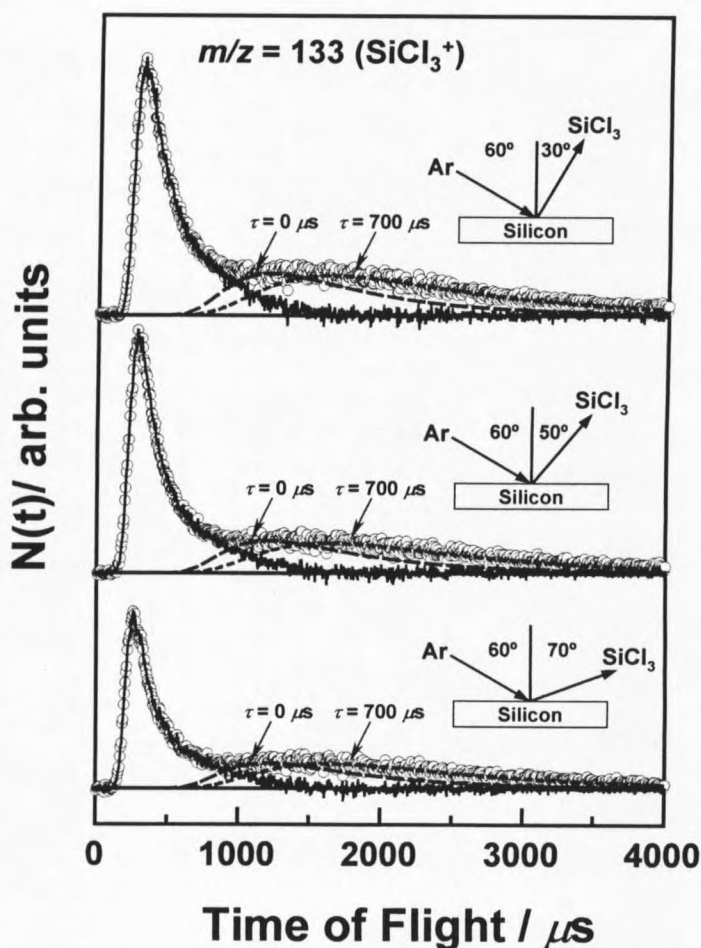


Figure 5. Representative TOF distributions of SiCl_3 following impingement of an incident Ar beam of $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ on continuously-chlorinated Si surface. The incident angle of the beam is 60° and the detection angles are 30° , 50° , and 70° . The distributions have been deconvoluted into hyperthermal (solid lines) and thermal (dashed lines) components. The short-dashed and long-dashed lines are M-B distributions with and without surface residence time, respectively.

TOF distributions were collected at mass-to-charge ratios (m/z) of 35 (Cl^+), 40 (Ar^+), 63 (SiCl^+), 98 (SiCl_2^+), 133 (SiCl_3^+), and 168 (SiCl_4^+). No detectable signal of Si ($m/z = 28$) was observed within the signal-to-noise limit of our data. TOF distributions were typically averaged for 1000 pulses of the hyperthermal beam. The angular and energy

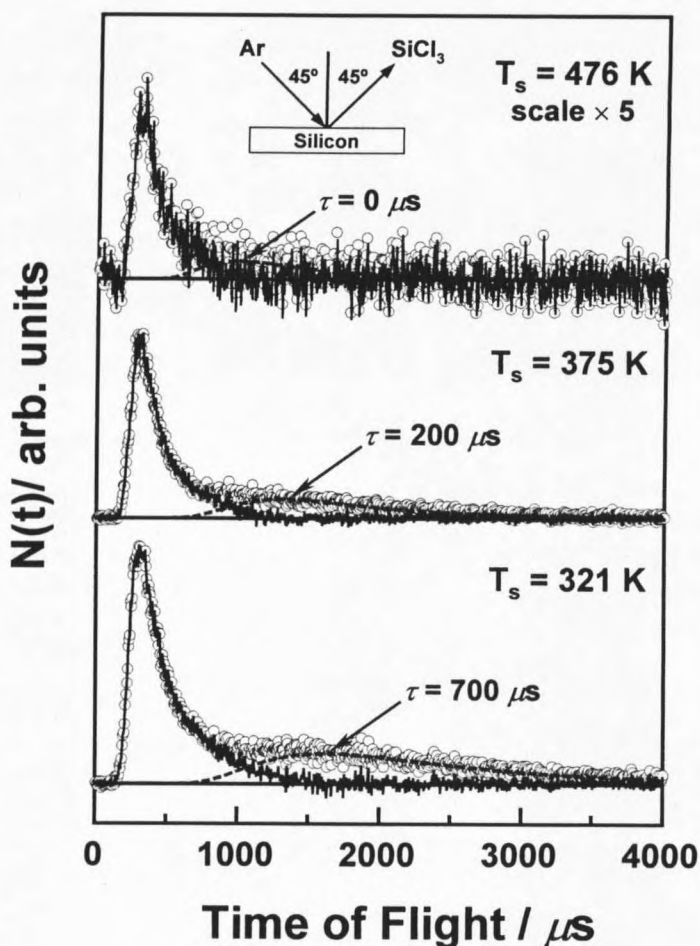


Figure 6. TOF distributions of SiCl_3 at a detection angle of 45° following impingement of Ar atoms with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ and $\theta_i = 45^\circ$ on a continuously-chlorinated Si surface at three surface temperatures, as shown.

dependencies of the scattered products were studied by collecting TOF distributions at different combinations of incident angle, detection angle, and incident Ar beam energy. For studies of angular dependence, incident Ar beams with $\langle E_i \rangle = 1360$ and 1660 kJ mol^{-1} were used, and TOF distributions were collected at two incident angles ($\theta_i = 45^\circ$ and $\theta_i = 60^\circ$) and a variety of detection angles. For studies of the energy dependence, TOF distributions were collected at two combinations of incident and detection angles, ($\theta_i =$

$45^\circ/\theta_i = 45^\circ$ and $\theta_i = 60^\circ/\theta_i = 30^\circ$) at six incident Ar energies. The surface temperature was maintained at 321 K for these angular and energy dependence studies. TOF distributions were also collected at surface temperatures of 375 K and 476 K for comparison. All the TOF distributions were collected under steady-state conditions, i.e., after the induction period and before the surface became roughened through etching. The TOF distributions of Cl and SiCl_x ($x = 1-3$) have been corrected for the fragmentation of SiCl_4 in the electron-impact ionizer. However, the ionization fragmentation patterns of the radicals, SiCl_3 , SiCl_2 , SiCl , were unable to be obtained. Therefore, only the quantitative data for SiCl_4 and SiCl_3 are presented in this article.

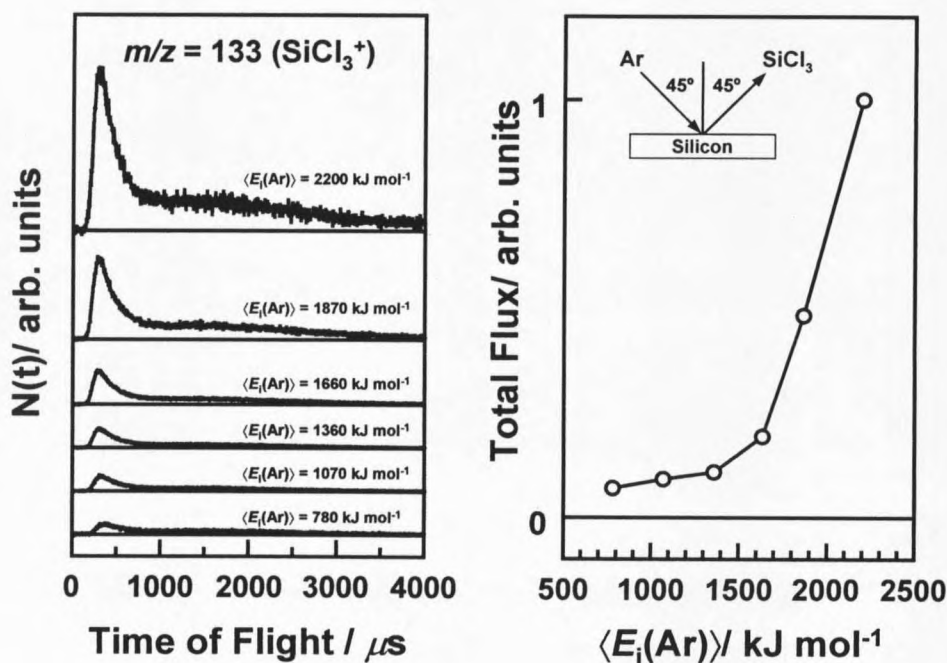


Figure 7. TOF distributions (left panel) and total integrated intensities (right panel) of SiCl_3 exiting a continuously-chlorinated Si surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 2. The incident angle of the Ar beams is 45° and the detection angle of SiCl_3 is 45° .

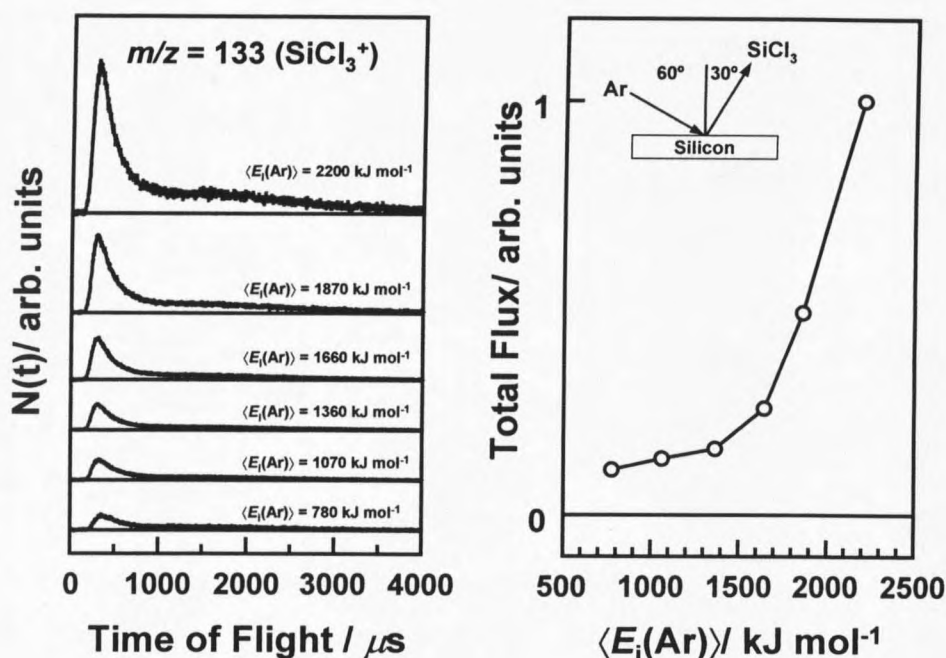


Figure 8. TOF distributions (left panel) and total integrated intensities (right panel) of SiCl_3 exiting a continuously chlorinated Si surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 2. The incident angle of Ar beams is 60° and the detection angle of SiCl_3 is 30° .

Results and Analysis

Figure 3 shows representative TOF distributions of scattered Cl and SiCl_x ($x = 1-4$) following impingement of the Ar beam with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ on a continuously-chlorinated Si surface. Background from ionizer fragmentation of Cl_2 in the continuous effusive chlorine beam scattered from Si surface has been subtracted from the Cl TOF distribution. The continuous effusive beam of atomic chlorine slowly etched the Si surface and generated a continuous background of SiCl_x , which has been subtracted from the SiCl_x TOF distributions. Thus all the TOF distributions represent only those scattered

products that are correlated with the hyperthermal Ar pulses striking the surface. The TOF distributions are plotted on the same scale (except for SiCl_4) so that the relative intensities can be compared directly. All the TOF distributions are bimodal. For SiCl_x , the fast components represent the scattered products that leave the surface with hyperthermal translational energies, and the slow components are the products that are first trapped on the surface momentarily and then desorb thermally. For the TOF distribution of Cl, the fast component indicates collision-induced desorption (CID) of Cl from the chlorinated Si surface, while the slow component is the result of ionizer fragmentation from SiCl_x products. Even though TOF distributions of SiCl_2 and SiCl were not corrected for the ionizer fragmentation from SiCl_3 (and SiCl_2), figure 4 clearly indicates that radicals of SiCl and SiCl_2 were ejected from the chlorinated Si surface. Note that figure 4 has been corrected for the differences in ion flight time from ionizer to the Daly ion counter.

Figure 5 shows the TOF distributions of scattered SiCl_3 at three detection angles following impingement of an Ar beam with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on the chlorinated Si surface. The TOF distributions have been deconvoluted into two components, hyperthermal (solid lines) and thermal (dash lines) components. The long-dashed lines are derived from simple MB distributions at surface temperature, which appear unable to fit the slow components.

The long tails of the slow components in the TOF distributions indicate that the trapped SiCl_3 radicals have some detectable surface residence time. The MB velocity distribution without surface residence time is expressed as the following equation:

$$f(v)dv \propto v^3 \exp\left(-\frac{mv^2}{2kT}\right)dv, \quad (1)$$

In terms of flux as a function of time, this function becomes

$$I(t)dt \propto \frac{1}{t^5} \exp\left(-\frac{mL^2}{2kTt^2}\right)dt, \quad (2)$$

where L is the length of the flight path and t is the flight time. Since the ionization efficiency of the electron bombardment ionizer is inversely proportional to velocity, the detected TOF distributions are number density distributions, so the detected MB distribution takes on the form:

$$N(t) \propto \frac{1}{t^4} \exp\left(-\frac{mL^2}{2kTt^2}\right). \quad (3)$$

When the trapped species has a surface residence time, its desorption time may vary. Assuming first order desorption kinetics (i.e., the desorption rate is inversely proportional to the surface coverage), the TOF form of the MB distribution is

$$N(t) \propto \int_0^t \frac{1}{(t-t_1)^4} \exp\left(-\frac{mL^2}{2kT(t-t_1)^2}\right) \exp\left(-\frac{t_1}{\tau}\right) dt, \quad (4)$$

where t_1 is the duration that the trapped species stays on the surface, and τ is the time constant. The short-dashed lines in figure 5 are the fitting of equation (5) with time constant of 700 μ s. Figure 6 shows the TOF distributions of scattered SiCl_3 at $\theta_f = 45^\circ$ at three surface temperatures following impingement of an Ar beam with $\langle E_i \rangle = 1360$ kJ mol^{-1} and $\theta_i = 45^\circ$ on the chlorinated Si surface. The time constant for surface residence and the overall intensity of SiCl_3 correlated with Ar beam pulses decrease with surface temperature.

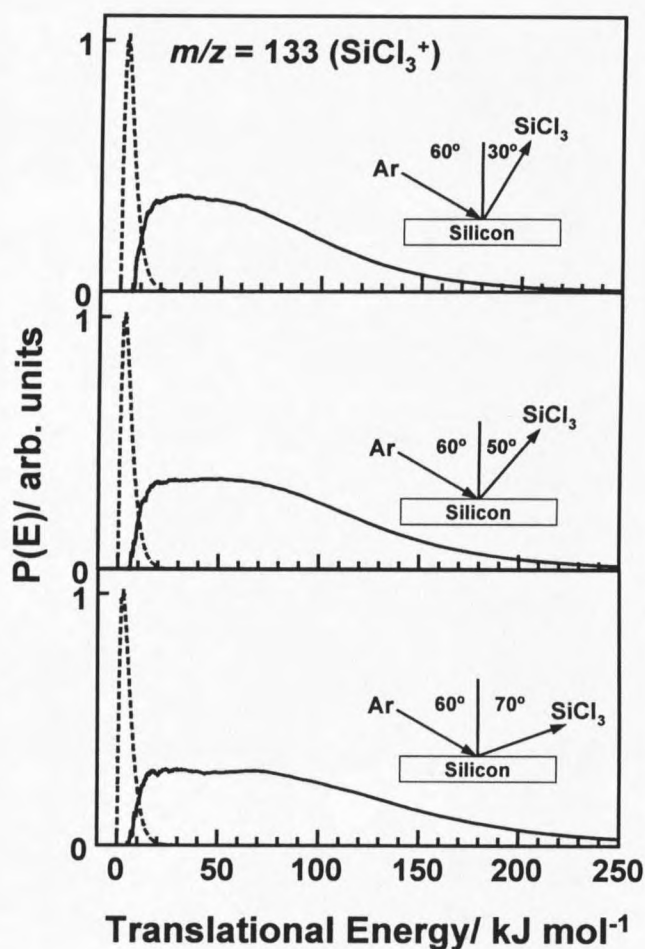


Figure 9. Translational energy distributions of SiCl_3 derived from the TOF distributions shown in Figure 5. The distributions contain hyperthermal (solid lines) and thermal (dashed lines) components, where thermal components are derived from MB distributions that take into account surface temperature and product residence time on the surface.

Figures 7 and 8 show the TOF distributions and the corresponding total integrated fluxes of scattered SiCl_3 at two combinations of incident and detection angles ($\theta_i = 45^\circ/\theta_f = 45^\circ$ and $\theta_i = 60^\circ/\theta_f = 30^\circ$) following impingement of six Ar beams on the chlorinated Si surface. The TOF distributions have been normalized to the integrated intensities of the respective incident Ar beams and are plotted on the same vertical scale so that the relative

intensities can be compared directly. The surface residence time constants for the thermal components are same ($700 \mu\text{s}$) for the six incident Ar beams. The total flux of the scattered SiCl_3 strongly depends on incident Ar translational energy.

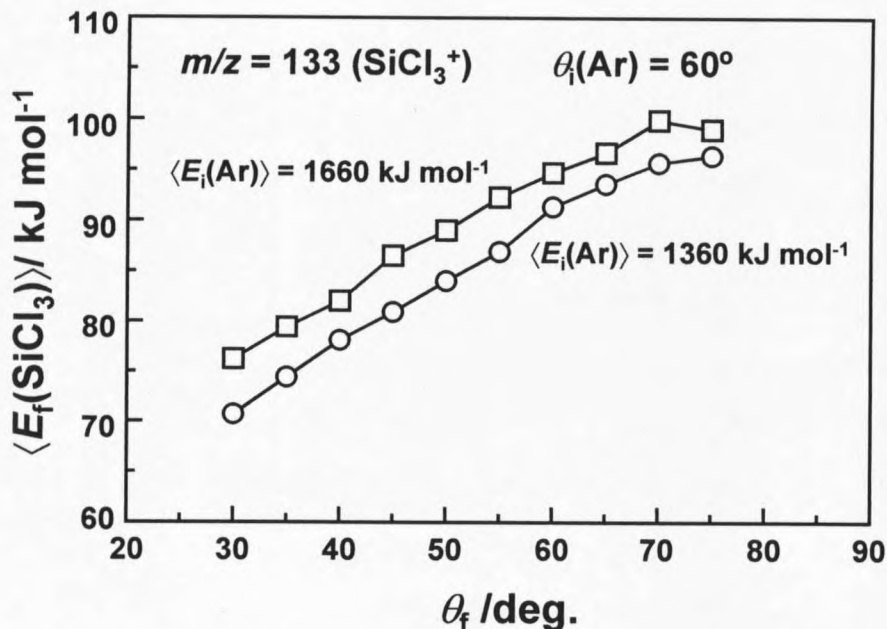


Figure 10. Average final translational energies of hyperthermal SiCl_3 as a function of detection angle following impingement of two Ar beams at $\theta_i = 60^\circ$ with $\langle E_i \rangle = 1360$ and 1660 kJ mol^{-1} on a continuously-chlorinated Si surface.

Figure 9 contains the translational energy distributions of scattered SiCl_3 derived from the TOF distributions shown in figure 5. The hyperthermal components are very broad and shift to higher energy when the detection angle is increased. The average translational energies of the hyperthermal components of scattered SiCl_3 increase with detection angle and incident Ar beam energy, as shown in figures 10 and 11, respectively. This observation indicates that some memory of the incident angle and the translational

energy of the Ar beam is retained. However, the average translational energy of scattered hyperthermal SiCl_3 is only about 6% of the incident Ar translational energy.

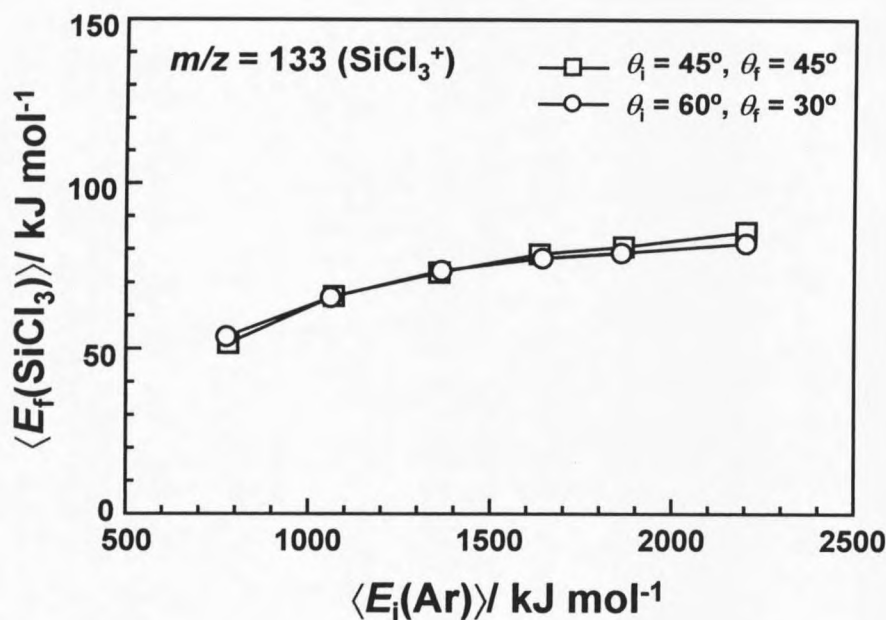


Figure 11. Average final translational energies of hyperthermal SiCl_3 as a function of average incident At-atom translational energy for two combinations of incident and final angles, as shown, on continuously-chlorinated Si surface.

The angular flux distributions of scattered SiCl_3 following impingement of Ar atoms with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ at incident angles of 45° and 60° on the continuously-chlorinated Si surface are shown in figure 12. While the thermal components follow a cosine distribution, the hyperthermal components are asymmetric to the surface normal and have maxima near the specular direction. The peak of flux of the scattered SiCl_3 occurs at roughly $\theta_f = 45^\circ$, regardless of incident angle. For the incident Ar beam of $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$, the contour map and mesh plot of the translational energy

distributions of scattered SiCl_3 at all the detection angles (30° to 75°) are shown in figure 13. The scattered SiCl_3 clearly shows forward scattering and increasing average translational energy with increasing detection angle.

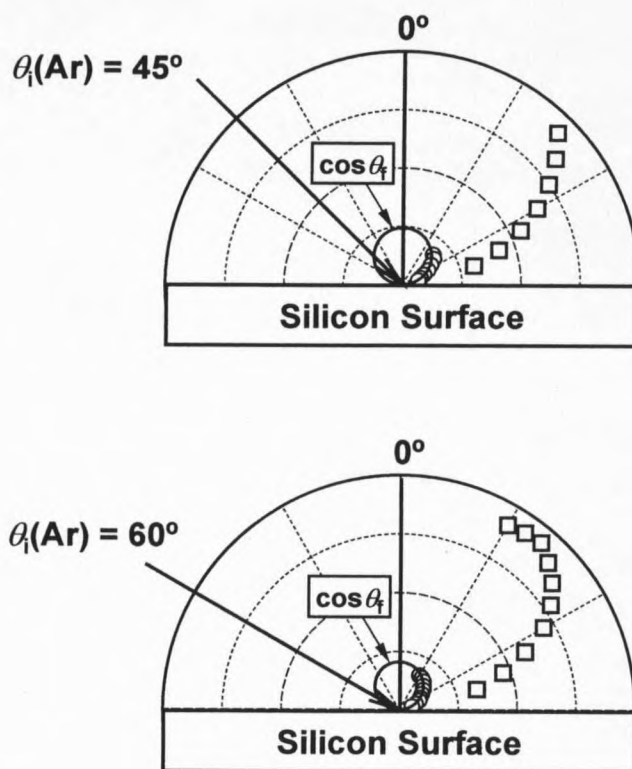


Figure 12. Angular distributions of SiCl_3 flux following impingement of Ar atoms with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ at two incident angles, $\theta_i = 45^\circ$ and 60° , on a continuously chlorinated Si surface. The thermal components (open circles) follow a cosine distribution (solid lines).

Discussion

The data clearly show a collisional process that enhances the production of silicon chloride and the etch rate of Si. Silicon chloride products (SiCl_x , $x = 1-4$) were formed, and the intensities of these chlorides decreased with increasing number of chlorine atoms,

indicating a process of sequential chlorination. The reaction processes involved in the etching of Si must incorporate three steps: (1) adsorption of Cl on an Si surface; (2) chemical reaction with Si to form an etch product; and (3) product desorption. The enhancement of Si etching by collisions of energetic Ar atoms is due to the acceleration of at least one of the three steps. In the energy range of incident Ar beams used in this experiment, acceleration of step (1) is expected to have no effect because the surface is in a steady-state of continuous chlorination at all times except during the relatively short Ar-atom pulse. Thus, Si etching must be enhanced via acceleration of steps (2) or/and (3). The observation that average energy of scattered hyperthermal products scales with incident Ar energy and detection angle indicates a direct collision process in which momentum transfer is dominant and some memory of the incident Ar atoms is retained. When an energetic Ar atom hits the surface, it encounters a localized surface moiety, so the interaction involves a cascade of moving target atoms, or in other words, a collision cascade. Two direct reaction mechanisms are possible for the formation of scattered hyperthermal products, chemically-enhanced physical sputtering and chemical sputtering.^{1,4} In chemically-enhanced physical sputtering, the chemical reactions produce more weakly bound products on the surface, thus lowering the binding energy. The sputtering yield is inversely proportional to the binding energy,³² so that the sputtering yield is enhanced. In this mechanism, the main role of the incident Ar atom is to remove products during the energetic collision cascade, i.e., increasing the rate of step (3). When Cl atoms adsorb and react with the Si surface, the binding energies of silicon chloride products (SiCl_x) are lower than that of Si atom.³³ In fact, using a linear collision

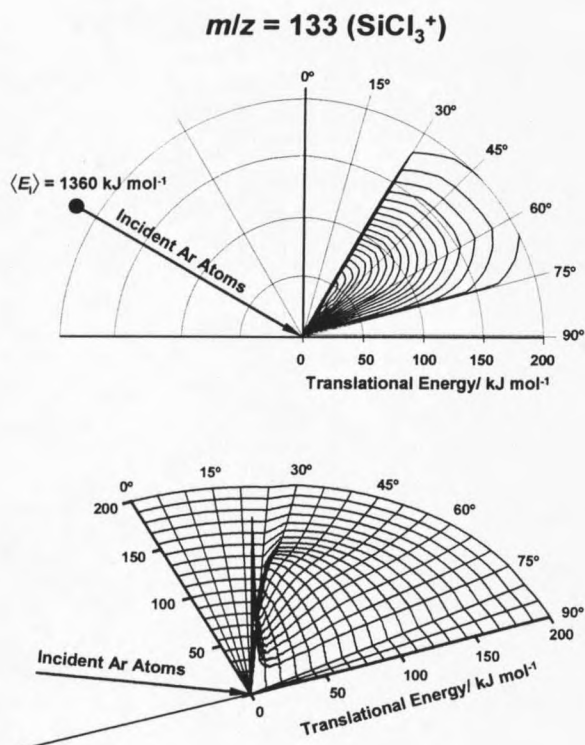


Figure 13. Contour map and mesh plot of translational energy distributions of SiCl_3 following impingement of Ar atoms with $\langle E_i \rangle = 1360 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on continuously-chlorinated Si surface.

cascade model,³² de Vries *et al.*^{7,8} have determined that the binding energy of SiCl and SiCl_2 on a Si surface are between 0.25 to 0.5 eV. In our experiment, chemically-enhanced physical sputtering is essentially synonymous with collision-induced desorption (CID), which was first used to explain the reaction mechanism of hyperthermal Cl with Si by Engel, *et al.*¹⁹ In the case of chemical sputtering, the energy transfer to the surface from the incident Ar atom may promote a chemical reaction and lead to product

formation and desorption. The key difference between chemically-enhanced physical sputtering and chemical sputtering is that for the latter case, the products are formed during the collision cascade. Thus in chemical sputtering process, the collisions of energetic Ar with the surface increase the rate of both steps (2) and (3).

The products that are ejected from the surface via either sputtering mechanisms may desorb during or after the collision cascade. When the products are ejected during the collision cascade, they may leave the surface with hyperthermal energies and thus contribute to the hyperthermal components of the products. The average translational energies of the hyperthermal components are only about 6% of the incident Ar translational energy, which indicates that most of the incident energy is retained in the inelastically scattered Ar atoms and deposited in the localized surface moiety to allow the reaction to occur and to overcome the binding energy to release the products. The small amount of translational energy in the desorbed hyperthermal products relative to the incident energy is a common phenomenon in ion assisted etching of semiconductors. This kind of energy partitioning is a consequence of significant bond breaking and formation during the collision cascade.¹ The products formed in the collision cascade may collide with another surface region and become trapped on the surface and reach thermal equilibrium and desorbed later, which leads to the thermal population of the products. Both thermal and hyperthermal signals are believed to originate from the same sputtering mechanism, which is supported by observations that the fractions of thermal signals remain unchanged for different incident Ar translational energies (figures 7 and 8).

The thermal components in the TOF distributions of scattered products clearly show a measurable surface residence time. However, the surface residence time shown in the TOF distributions is different from the duration that the trapped products stay on the surface before desorption. The surface residence time in the TOF distributions are relative to zero flight time, which is the instant at which Ar atoms with the average translational energy of the beam hit the surface. The apparent surface residence times in the TOF distributions are caused by a decrease of product surface coverage following impingement of Ar atoms on the surface. If the product surface coverage is not directly dependent on the collisions of Ar atoms, the desorbing rate will be constant. However, when the thermal desorption of products is caused by collisions of Ar atoms, the surface coverage will decrease after the collisions, and usually follows first order desorption kinetics. In our experiment, the measured 700 μ s surface residence time (SiCl_3 at T_s of 321 K) combined with the repetition rate of 2 Hz for Ar beam indicates that the product surface coverage went back to the initial level before the next pulse of Ar beam. The surface residence time thus depends on the formation and desorption rates of trapped products, particularly, the surface temperature, incident Ar translational energy, and binding energy.

The surface residence time decreases with increasing surface temperature (figure 6). This observation can be explained as follows. When the surface temperature is increased, the spontaneous etch rate of Si by the atomic chlorine beam alone increases while the Ar beam collisional enhancement becomes relatively less dominant. This can be seen in figure 6, where the intensity of SiCl_3 decreases with increasing surface temperature. The

thermal desorption rate of trapped SiCl_3 (without the help from collisions) will also increase with surface temperature, which makes the contribution from collisions of the Ar beam less important. At a certain surface temperature (some value less than 476 K), decrease of product surface coverage caused by collisions of Ar atoms becomes small enough that the surface residence time in the TOF distributions cannot be detected anymore. The surface residence time of SiCl_3 appears to be independent of the incident Ar beam energy in the range of our experiment, i.e., 780-2200 kJ mol⁻¹, which might be too small to cause measurable difference in surface residence time. In a study of Ar⁺-enhanced Si-Cl₂ reaction, Sawin *et al.*³⁴ observed that the surface residence time of SiCl_4 increased with increasing ion energy for a given Cl_2/Ar^+ ratio and increased with decreasing Cl_2/Ar^+ ratio for a given ion energy. They proposed that this observation was the result of a decrease in the amount of chlorine on and in the top layers of silicon. This explanation is consistent with ours because a lower surface concentration of chlorine will lead to greater depletion of products on the surface after the beam of Ar⁺ strikes the surface, which results in a longer surface residence time. The surface residence time of different products will be different due to different binding energies. The surface residence time of SiCl_4 at T_s of 321 K is 65 μs (data not shown), which is significantly less than 700 μs for SiCl_3 . The binding energy of SiCl_4 is significantly less than that of SiCl_3 ; thus the contribution from impingement of the Ar beam to the thermal desorption rate of SiCl_4 will be much less important, resulting a lower surface residence time.

The collisional enhancement of Si etching is significant and the rate of formation of etch products increases dramatically with increasing incident Ar translational energy

(figures 7 and 8). Similar behavior for different combinations of incident and detection angles indicates that the total incident energy, rather than the component of the incident energy normal to the surface, governs the collisional enhancement of the product signal. This observation is consistent with the rough etched surface, which strongly couples parallel energy with normal energy. In order to test the effect of collisional enhancement, we conducted a practical etching experiment in which the etch yield of an Si wafer under exposure to the effusive Cl plasma source with and without the addition of the pulsed hyperthermal Ar beam was compared. In this experiment, the entire Ar beam (unchopped) was allowed to strike the surface. The etch yield was determined by placing a screen over the samples during exposure and measuring the etch depth with a profilometer. The samples were exposed for 14 hours. The etch yield when the sample was exposed to both beams was approximately 7 times higher than the etch yield observed when only the effusive Cl beam was used to expose the sample. The collisional process may be regarded as a synergistic effect of the simultaneous bombardment of an eroding/etching surface and an energetic species, and this process appears to be general. Similar phenomena were observed in studies of collision-assisted erosion of polymers and graphite.^{22,23}

Conclusion

The mechanisms of collision-assisted etching of Si during steady-state etching conditions of Si surface under atomic chlorine attack have been investigated by directing hyperthermal Ar beams at a continuously chlorinated Si surface and monitoring the

dynamical behavior of the etch products. The silicon chloride products (SiCl_x , $x = 1-4$) were identified with the intensity decreasing with increasing extent of chlorination. Significant flux of these products was correlated with the impact of a hyperthermal Ar beam with the surface. TOF distributions of the products exhibited two populations, hyperthermal and thermal, which originated from same initial collisional mechanism. The origin of this process might involve chemically-enhanced physical sputtering and/or chemical sputtering. The thermal components of the products exhibit a measurable surface residence time, which is caused by the decrease of product surface coverage following impact of Ar atoms on the surface. When the surface is bombarded with energetic Ar atoms, the Si etching rate is increased dramatically and the intensity of the etch product signals strongly depends on incident Ar translational energy in the range 780-2200 kJ mol^{-1} . This collisional process is believed to be general and is regarded as a synergistic effect in which collisions of energetic particles enhance the etch rate.

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CHAPTER 6

COLLISION-INDUCED DESORPTION OF Cl CHEMISORBED ON Si(100)

Abstract

Molecular beam-surface scattering experiments have been used to investigate the mechanisms of collision-induced desorption (CID) of atomic chlorine that is chemisorbed on a Si(100) surface when a Cl-saturated Si surface is bombarded with Ar atoms possessing kinetic energies in the range 870-2200 kJ mol⁻¹. A corrugated potential energy surface from adsorbed Cl on Si surface governs the incident Ar translational energy accommodation to liberate Cl, in which a threshold energy of ~870 kJ mol⁻¹ is experimentally determined. Similar dynamical behavior in the inelastic scattering of Ar and CID of Cl indicates that the dominant mechanism of CID involves an impulsive bimolecular collision between Ar and adsorbed Cl. The collision process is described in terms of a simple kinematic picture by viewing the collision partner of the incident Ar as a localized region of the surface that has an effective mass and is capable of releasing Cl. When CID of Cl is viewed in the center-of-mass reference frame, the process is dominated by forward scattering that is due to large-impact-parameter collisions where the Ar atom approaches nearly perpendicular to the bond between the Cl atom and the surface. However, backward/sideways scattering of Cl in center-of-mass reference frame is also observed, which is caused by recoiling of Cl from small-impact-parameter collisions where the Ar atom approaches nearly collinear with the bond between the Cl atom and the surface.

Introduction

When a beam of energetic inert particles interacts with a surface, both desorption of adsorbate and substrate may occur. If the energy of the incident particles is equal to or slightly higher than the binding energy of the adsorbate, only desorption of adsorbate occurs. In this energy regime, typically less than 30 eV, no electronic or charge transfer processes are involved, so that the adsorbate desorbs as neutral particle. This process is commonly termed collision-induced desorption (CID). CID has drawn much attention in the past two decades because of its applications in high-pressure catalytic reactions^{1,2} and also as a means probing the potential energy surface (PES) of an adsorbate³⁻⁷. Recently, CID was observed to be an important pathway in collision-induced material removal by inert molecule/atom collisions in the low Earth orbit (LEO) environment and in certain ground-based test facilities.^{8,9}

The first quantitative description of the CID process was a theoretical study by Zeiri, *et al.*,¹⁰ who investigated CID of Xe from an Si surface. It has been suggested that angular and translational energy distributions of both the scattered incoming particle and the desorbing adsorbate may reveal information on binding energies and binding sites for adsorbates on surfaces. The first experimental observation of CID was the pioneering study conducted by Ceyer *et al.*,^{11,12} who investigated the desorption of CH₄ on Ni(111) by collisions with Ar atoms. A simple hard sphere/hard cube (HSHC) collision model was proposed to explain the dependence of the collision-induced cross section on incident angle and energy. In the HSHC model, the incident particle and adsorbate are treated as hard spheres, while the substrate is treated as a hard cube. Two types of collisions, direct

and mirror collisions, were proposed to contribute to the CID process. Direct collisions involve an initial collision between an incident particle and the adsorbate followed by a second collision between the adsorbate and substrate. For mirror collisions, the incident particle hits the substrate, rebounds back, and collides with adsorbate. Using the same model, Levis *et al.* were able to determine binding energies of adsorbates from threshold CID energies for a variety of adsorption systems.³⁻⁷ Cross sections for CID were measured as a function of incident energy, and the threshold energy for CID was extracted by extrapolating to zero cross section with a function that is commonly used in gas phase collision-induced dissociation studies. However, the knowledge of the effective surface mass of the substrate was required in order to calculate the binding energy. Other experimental studies of CID include systems of Xe-O₂/Pt(111),¹³ Ar(Xe)-O₂/Ag(001),^{2,14} and Xe-hydrocarbons/Au(111).¹⁵

Theoretical studies of CID have been investigated by several groups. Following the first theoretical study of CID of Xe from an Si surface, Zeiri and coworkers investigated the CID process for several adsorption systems, such as Ar-N₂/W(100),¹⁶ Xe-Ar/W(100),¹⁷ and Ar-N₂/Ru(001)¹⁸. In a combined experimental and theoretical study of CID of Xe from a Pt(111) surface, Kulginov *et al.*¹⁹ compared the results of a full molecular dynamics (MD) calculation to those of a simple HSHC model. Recently, Hase *et al.*²⁰ reported a classic trajectory simulation of CID of CH₄ from a Ni(111) surface and compared the results with the earlier experimental study conducted by Ceyer and coworkers.^{11,12} While in most cases, the HSHC model is capable of capturing most of the dynamics of CID processes, there are several observations and studies that show its

limitations. In a theoretical study of CID of N_2 from Ru(001), Romm *et al.*¹⁸ suggested that for systems with a corrugated adsorbate-substrate potential energy surface, the HSHC model is insufficient to explain the full dynamical picture of the CID event, such as the dependency of CID cross section and threshold energy on incident angle. The limited scope of the HSHC model is further demonstrated in the Ar(Xe)-O₂/Ag(001) system.^{2,14}

In all of the experimental and theoretical studies of CID processes, the dominant mechanism was determined to involve a direct (or impulsive), bimolecular collision between collider and adsorbate. Multiple collider-adsorbate collisions and mirror collisions were found to make relatively minor contributions. Depending on the PES of an adsorbate on the substrate, normal energy (smooth PES) or total energy (corrugated PES) accommodation during collisions may play a significant role in determining the CID cross section dependence on incident angle and energy.

In this article, we present an investigation of CID of Cl from an Si(100) surface. It is well known that when an Si surface is exposed to Cl₂ molecules, the Cl₂ molecules dissociate and the resulting Cl atoms chemisorb on the Si surface. For Si(100)-2×1 surface, it was found that Cl atoms saturate the dangling bonds of the surface Si symmetric dimer atoms in an off-normal direction in the equilibrium geometry and the binding energy of Cl on Si(100)-2×1 surface is 4.02 eV (388 kJ mol⁻¹).²¹ Hyperthermal Ar atoms with translational energies of 870-2200 kJ mol⁻¹ were directed at this chlorinated Si surface, and energy and angular distributions of inelastically scattered Ar and Cl produced by CID were studied. In this hyperthermal energy regime, collision-

induced etching of Si that is exposed to Cl_2 is insignificant. The similar dynamical behavior of Ar and Cl indicates that the dominant mechanism for the release of Cl involves impulsive, bimolecular collisions.

Experimental Methods

The experiments were performed with the use of a crossed molecular beams apparatus,²² which was coupled to a hyperthermal beam source^{23,24} and configured for studies of gas-surface interactions. The details of the apparatus and the experimental configurations were described previously.^{8,9,25} The sample surface was silicon and was dosed with molecular chlorine with the use of a continuous effusive beam of Cl_2 . Based on earlier studies, the chlorine molecules presumably dissociated and the resulting chlorine atoms were chemically adsorbed on the silicon surface. A second, pulsed beam of hyperthermal Ar was simultaneously directed onto the chlorinated silicon surface. Inelastic scattering (IS) of Ar and CID of Cl corresponding to hyperthermal Ar beam pulses were monitored with the use of a rotatable mass spectrometer.

The sample surface was Si(100) (*p* type, 1-10 Ω cm). The sample cleaning procedure involved 10 min. sonicating in trichloroethylene followed by 10 min. sonicating in ethanol (200 proof USP), a dip in nanopure water, followed by etching for 15 s in conc. HF (49%), a rinse in nanopure water, and finally a dip in ethanol. The clean sample was immediately placed into the vacuum chamber. The sample was mounted on a manipulator such that the rotation axis of the sample surface was coincident with that of the detector; thus the surface normal was contained in the plane formed by the incident

beam and detector axis. The incident angle of the hyperthermal Ar beam, θ_i , and the product detection angle, θ_f , are defined with respect to the surface normal. The sample was electronically grounded and was heated with a cartridge heater.

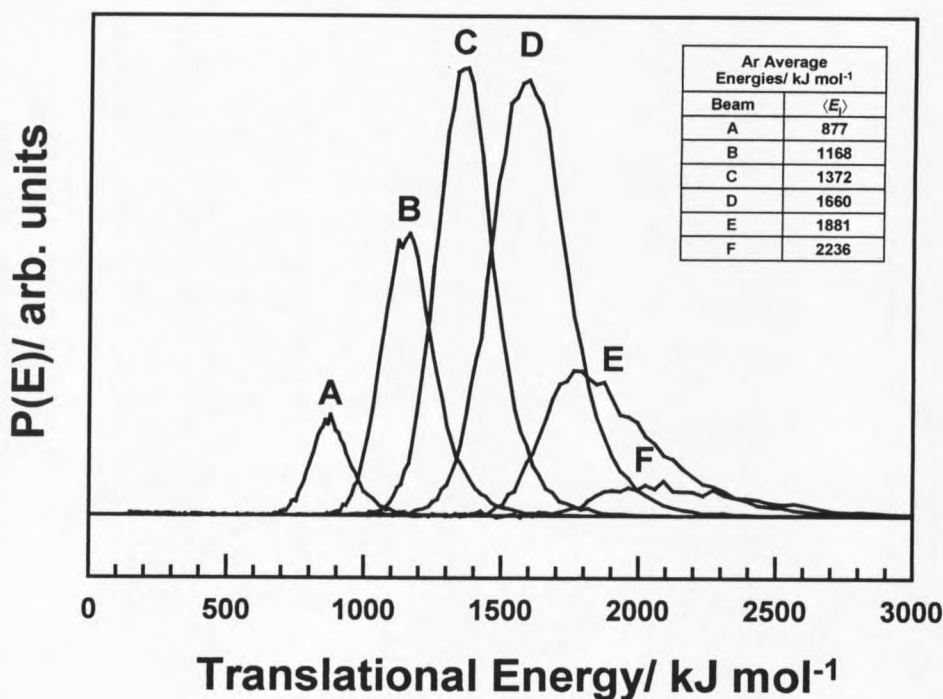


Figure 1. Translational energy distributions of six Ar beams that were used. The peak areas correspond to the relative fluxes of Ar.

Six pulsed hyperthermal Ar beams were prepared and directed at the chlorinated Si surface. The translational energy distributions for the Ar beams are shown in figure 1. The distributions are normalized such that the area of each distribution is proportional to the relative flux. At the sample surface, the estimated flux of the highest-intensity Ar beam is $\sim 10^{14}$ atoms cm⁻² pulse⁻¹. The hyperthermal Ar beams were operated at a repetition rate of 2 Hz, and the pulse width is in the order of 50 μ s. The flux of the

effusive chlorine molecules at the sample surface was estimated to be $\sim 10^{15}$ molecules $\text{cm}^{-2} \text{s}^{-1}$. Therefore, the duty cycle of the hyperthermal Ar beam is in the order of 10^{-4} , which indicates that the Si surface is saturated with Cl atoms before each pulse of Ar beam.

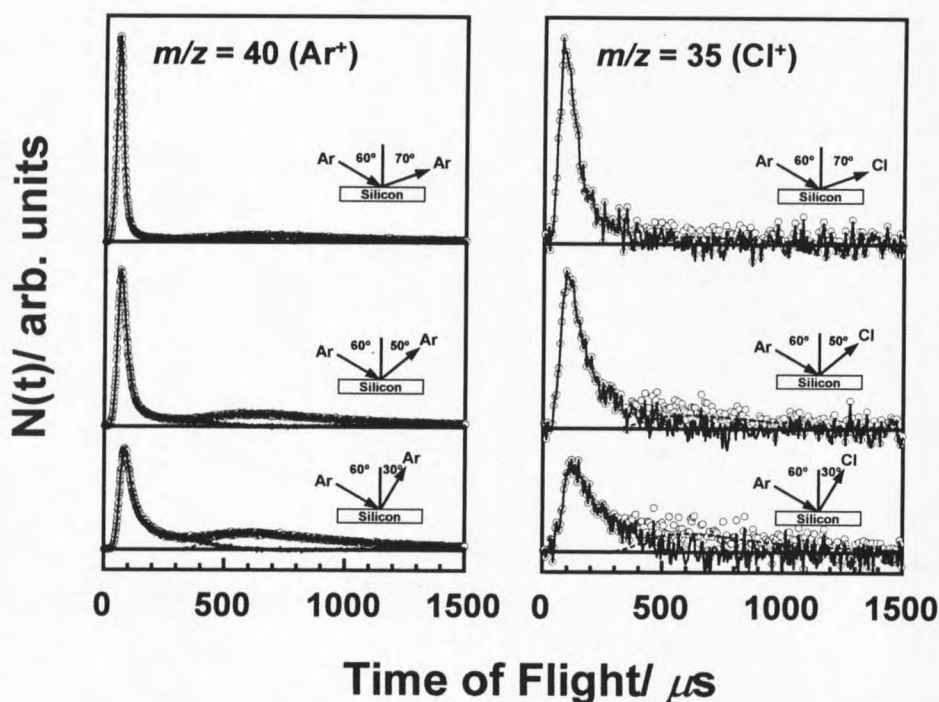


Figure 2. Representative TOF distributions of scattered Ar and desorbed Cl following impingement of an incident Ar beam with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ on the chlorinated Si surface. The incident angle of the beam is 60° and the detection angles, θ_f , are 70° , 50° , and 30° . The solid and dashed lines represent hyperthermal and thermal components, respectively.

Time-of-flight (TOF) distributions were collected at mass-to-charge ratios (m/z) of 35 (Cl^+) and 40 (Ar^+). Weak signals of silicon chloride (SiCl_x^+ , $x = 1-4$) products were also detected (more than 30 times weaker than Cl). Therefore, the contributions of ionizer fragmentation of SiCl_x to Cl are insignificant and not taken into account. Signals at m/z

of 28 (Si^+) were not observed within the signal-to-noise limit of the data. TOF distributions for Cl^+ and Ar^+ were typically averaged for 4,000 and 800 pulses of the hyperthermal beam, respectively. TOF distributions were collected at different combinations of incident/detection angle and incident energy. For studies of energy dependence, TOF distributions were collected at $\theta_i = 45^\circ/\theta_f = 45^\circ$, $\theta_i = 60^\circ/\theta_f = 30^\circ$, and $\theta_i = 60^\circ/\theta_f = 70^\circ$ at six incident Ar beam energies. Studies of the angular dependence employed incident Ar beams with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and 1660 kJ mol^{-1} ; TOF distributions were collected at two angles of incidence ($\theta_i = 45^\circ$ and $\theta_i = 60^\circ$) and a variety of detection angles. Studies of the energy and angular dependencies of CID of Cl were conducted at two surface temperatures, 60°C and 200°C . The data at these two temperatures are quantitatively similar. Therefore, only the data at surface temperature of 60°C are presented.

Results and Analysis

Dynamical Behavior of Product Signals

Figure 2 shows representative TOF distributions of Ar and Cl at an incident angle of 60° and three detection angles, following impingement of an Ar beam with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ on the Cl-saturated Si surface. For $m/z = 35$ (Cl^+), the continuous background of ionization fragmentation of Cl_2 scattered from sample surface has been subtracted from the TOF distributions. The overall TOF distributions are bimodal and have been separated into hyperthermal components (solid lines) and thermal components (dashed lines). The thermal components were assumed to follow Maxwell-Boltzmann (MB)

distributions at surface temperature. The TOF distributions have been normalized such that the relative intensity at different detection angles can be compared directly. Figure 3 shows the translational energy distributions that were derived from the TOF distributions in figure 2. The dashed lines are thermal components, while the solid lines are hyperthermal components. The thermal components indicate that all the memory of the energy and angle of the incident Ar beam is lost, while the hyperthermal components indicate that some memory of the incident Ar beam is retained. The hyperthermal components shift to shorter time (higher translational energy) as the detection angle increases. When the detection angle increases, the translational energy distributions of the hyperthermal components become bimodal.

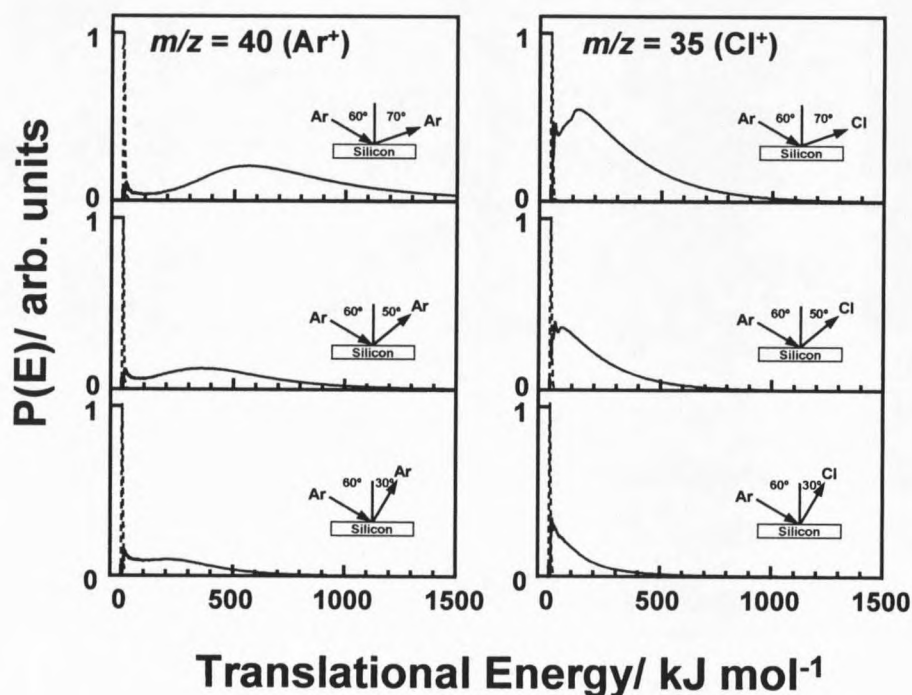


Figure 3. Translational energy distributions of scattered Ar and desorbed Cl derived from the TOF distributions shown in Figure 2. The distributions contain hyperthermal (solid lines) and thermal (dashed lines) components.

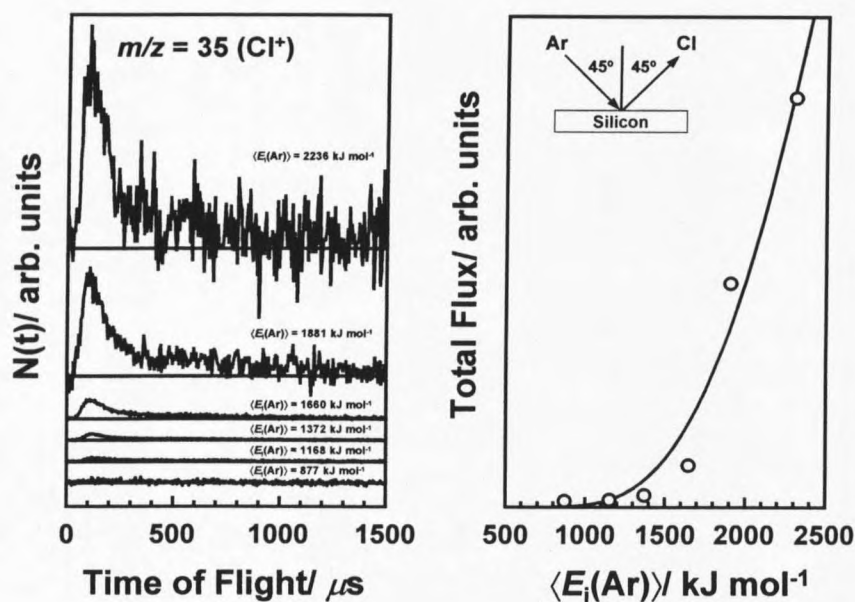


Figure 4. TOF distributions (left panel) and total integrated intensities (right panel) of desorbed Cl from chlorinated Si surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 1. The incident angle of the Ar beam is 45° and the detection angle of Cl is 45° . The solid line in the right panel has no physical significance and is only meant as a guide to the eye.

TOF distributions and the corresponding integrated fluxes at $m/z = 35$ (Cl^+) at two combinations of incident and detection angles ($\theta_i = 45^\circ/\theta_f = 45^\circ$ and $\theta_i = 60^\circ/\theta_f = 70^\circ$) following impingement of six Ar beams on a chlorinated Si surface are presented in figures 4 and 5. The TOF distributions have been normalized to the integrated intensities of the respective incident Ar beams and are plotted on the same vertical scale so that the relative signals can be compared directly. The flux of the scattered Cl strongly depends on the incident Ar translational energy. The dependency can be fit well with an arbitrary function of the form,

$$I(E_i) = Ae^{-B/\langle E_i \rangle}, \quad (1)$$

where values of parameter B fall in the range of 9300 – 12000 kJ mol⁻¹. The magnitude of parameter A depends on the units of the flux. It appears that the threshold translational energy of the incident Ar beam for the detection of CID of Cl from the Si surface is about 870 kJ mol⁻¹. Similar results (not shown) have also been observed for another combination of incident and detection angles ($\theta_i = 60^\circ/\theta_f = 30^\circ$).

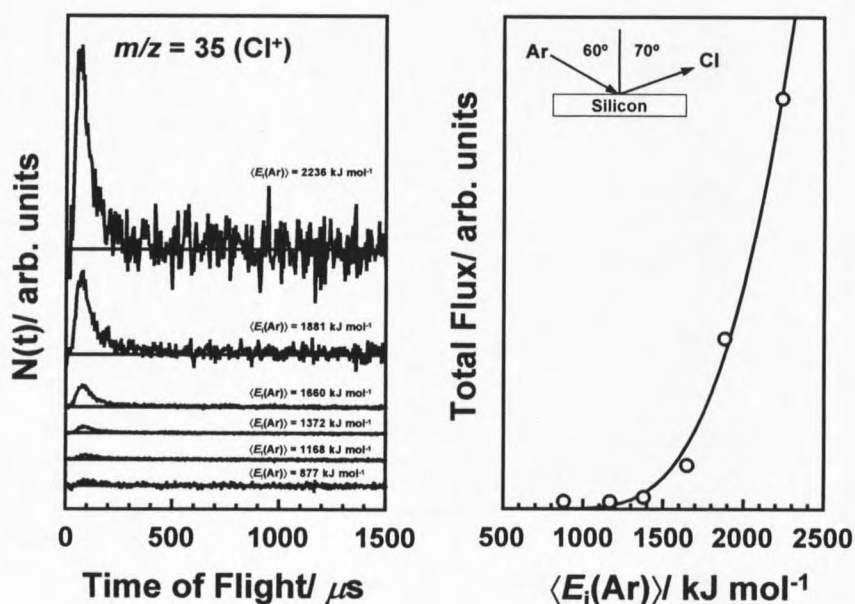


Figure 5. TOF distributions (left panel) and total integrated intensities (right panel) of desorbed Cl from chlorinated Si surface following impingement of six hyperthermal Ar beams whose translational energy distributions are shown in Figure 1. The incident angle of Ar beam is 60° and the detection angle of Cl is 70° . The solid line in the right panel has no physical significance and is only meant as a guide to the eye.

The average translational energies of scattered hyperthermal Ar and desorbed hyperthermal Cl increase with incident Ar translational energy and detection angle, as

shown in figures 6 and 7 respectively. Figure 6 indicates that the average translational energies of hyperthermal Ar or Cl are the same for two different combinations of incident and detection angles, $\theta_i = 45^\circ/\theta_f = 45^\circ$ and $\theta_i = 60^\circ/\theta_f = 30^\circ$, which have the same deflection angle, defined as $\chi = 180^\circ - \theta_i - \theta_f$. Figures 6 and 7 show that hyperthermal Ar has higher average translational energies than hyperthermal Cl. The observation that the average translational energies of scattered Ar and desorbed Cl are hyperthermal and increase with detection angle and incident Ar translational energy suggests that some memory of the incident angle and translational energy of the Ar beam is retained.

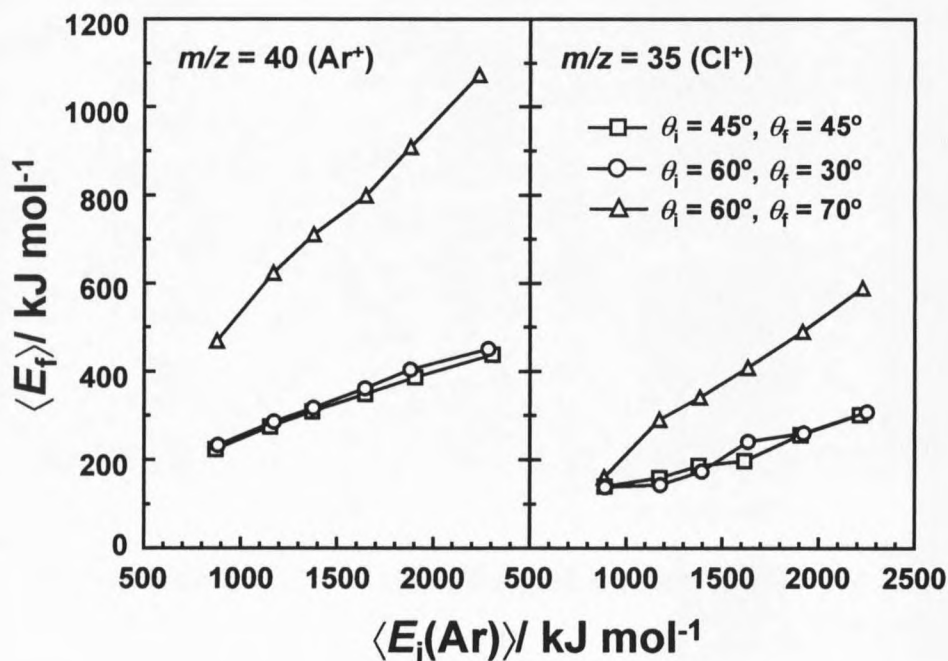


Figure 6. Average final energies of scattered hyperthermal Ar and desorbed hyperthermal Cl as a function of average incident Ar-atom translational energy for three combinations of incident and detection angles, as shown, on a chlorinated Si surface.

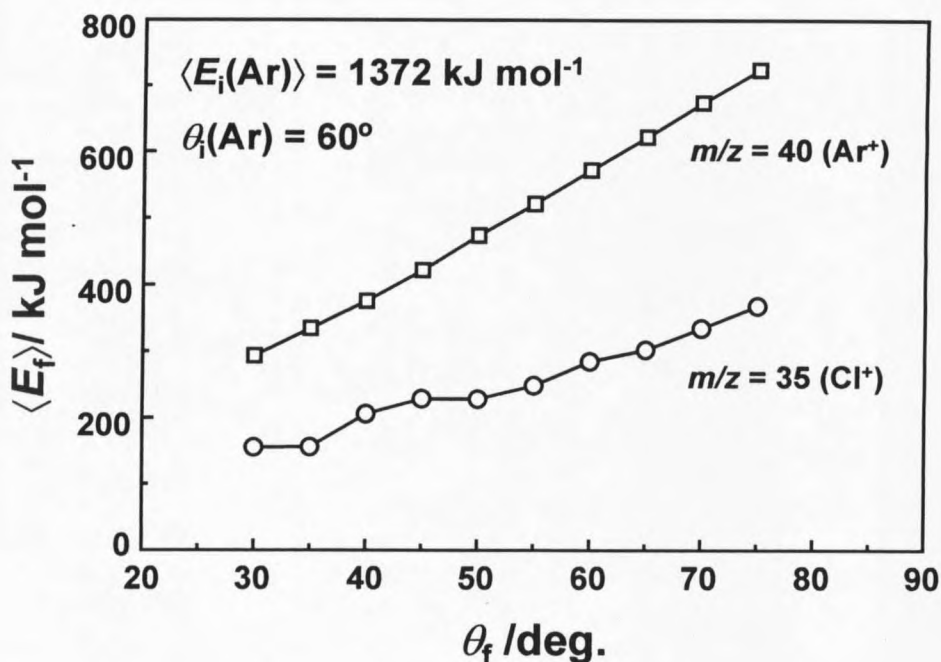


Figure 7. Average final energies of scattered hyperthermal Ar and desorbed hyperthermal Cl as a function of detection angle following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on a chlorinated Si surface.

Figure 8 shows the flux angular distributions of scattered hyperthermal Ar and desorbed hyperthermal Cl following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ at incident angles of 45° and 60° . The angular distributions show that the fluxes of Ar and Cl are asymmetric with respect to the surface normal. While the fluxes of scattered Ar have maxima near the specular directions, the fluxes of desorbed Cl have maxima near $\theta_f = 60^\circ$ for Ar incident at both 45° and 60° . For an incident Ar beam with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$, the contour maps and mesh plots of the translational energy distributions of scattered hyperthermal Ar and desorbed hyperthermal Cl at all the detection angles are shown in figures 9 and 10, respectively. At $\theta_i = 60^\circ$, the detection

angle range is from 30° to 75° . These views of scattered hyperthermal Ar and Cl clearly show forward scattering and increasing average final translational energy with increasing detection angle.

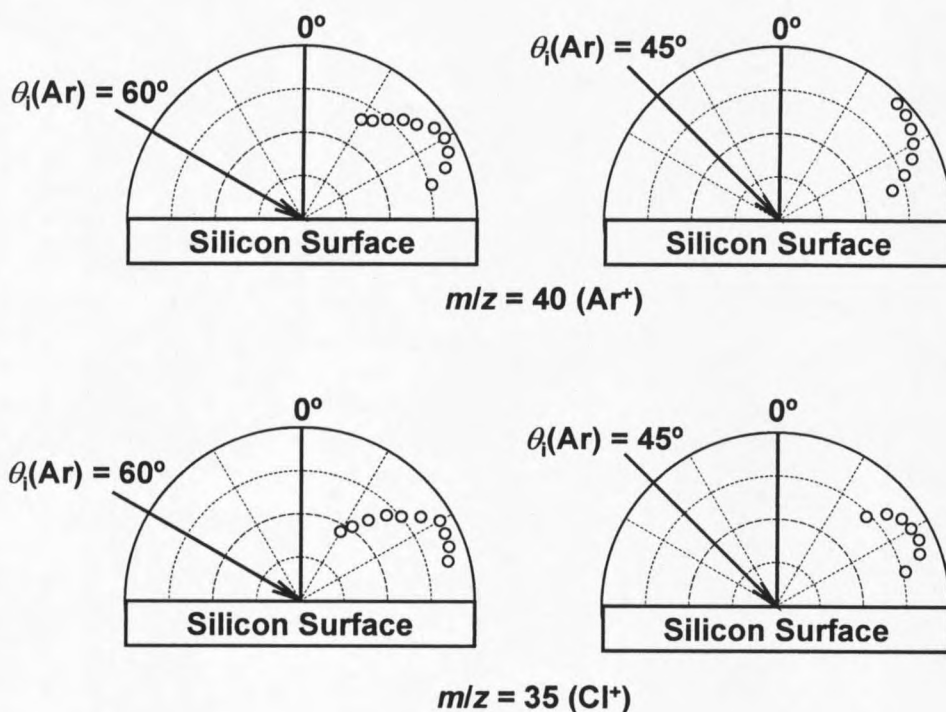


Figure 8. Angular flux distributions of scattered hyperthermal Ar and desorbed hyperthermal Cl following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ at incident angles of 60° (left) and 45° (right) on a chlorinated Si surface.

Kinematic Analysis

By analogy to the reaction of O atoms and Cl atoms with a squalane surface^{25,26} and the interactions of hyperthermal Ar with oxidized polyethylene and graphite surfaces to produce CO and CO₂,⁹ simple Newton diagrams can be constructed in order to represent the IS of Ar and CID of Cl from chlorinated Si surface in the center-of-mass frame. The

surface collision partner with which the incident Ar atom interacts is localized and has finite mass. Therefore, the gas-surface interaction can be viewed as a gas-phase-like interaction by treating the surface as a species with an effective surface mass and thermal initial velocities. Figure 11 shows the Newton diagrams of scattered hyperthermal Ar and desorbed hyperthermal Cl for an incident Ar beam of $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$. Table 1 lists the center-of-mass (c.m.) quantities derived from the kinematic analysis. As a comparison, c.m. quantities for an incident Ar beam of $\langle E_i \rangle = 1660 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ are also listed. The effective surface mass for IS of Ar is designated as m_s , while the effective surface mass for CID of Cl is designated as $m_{s\text{Cl}}$.

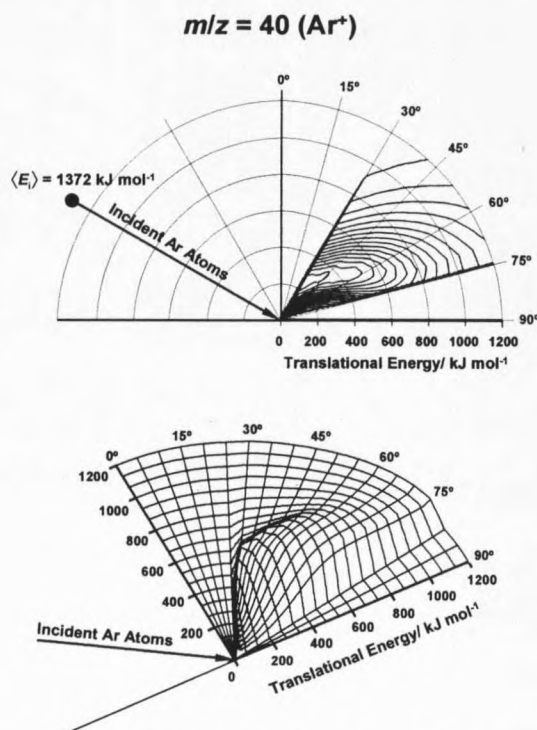


Figure 9. Contour map and mesh plot of translational energy distributions for scattered hyperthermal Ar following impact with a chlorinated Si surface. The Ar beam had an average translational energy of 1372 kJ mol^{-1} and impinged on the surface at an incident angle of 60° .

Table 1. Center-of-mass quantities derived from a kinematic analysis of scattered hyperthermal Ar (IS of Ar) and desorbed hyperthermal Cl (CID of Cl) following impingement of Ar atoms at $\theta_i = 60^\circ$ with $\langle E_i \rangle = 1372$ and 1660 kJ mol^{-1} on a chlorinated Si surface.

Collisional Event		m_s or m_{sCl} /amu	$\langle E_{coll} \rangle$ / kJ mol^{-1}	$\langle E_T \rangle$ / kJ mol^{-1}	$\langle E_{int} \rangle$ / kJ mol^{-1}
$\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ $\theta_i = 60^\circ$	IS of Ar	85	930	573	357
	CID of Cl	143	1070	210	860
$\langle E_i \rangle = 1660 \text{ kJ mol}^{-1}$ $\theta_i = 60^\circ$	IS of Ar	79	1098	688	410
	CID of Cl	133	1272	249	1023

The Newton diagram allows us to view the gas-surface interactions in the c.m. reference frame. C.M. angular distributions, $T(\theta_{cm})$, and translational energy distributions, $P(E_T)$, can be calculated from laboratory angular TOF distributions using a forward convolution technique. A computer simulation program, GMTHRASH, based on forward convolution method, was used to fit the hyperthermal components of the TOF distributions of scattered Ar and Cl. The details of the forward convolution method and the GMTHRASH program were discussed in Ref 27. Figure 12 shows the fitting results of this program for the hyperthermal components of TOF distributions shown in figure 2. Once $T(\theta_{cm})$ and $P(E_T)$ are known, contour map and mesh plot of c.m. flux, $P(u)$, can be constructed. The c.m. flux contour maps and mesh plots for IS of Ar and CID of Cl are shown in figures 13 and 14, respectively. The computer program treats the gas-surface

interactions as gas-phase-like processes, in which products can scatter in the directions of 360 degrees. However, in reality, products cannot scatter through the surface. In figures 13 and 14, thicker lines represent the observable scattering processes, while thinner lines represent scattering processes that cannot be observed due to the presence of the surface.

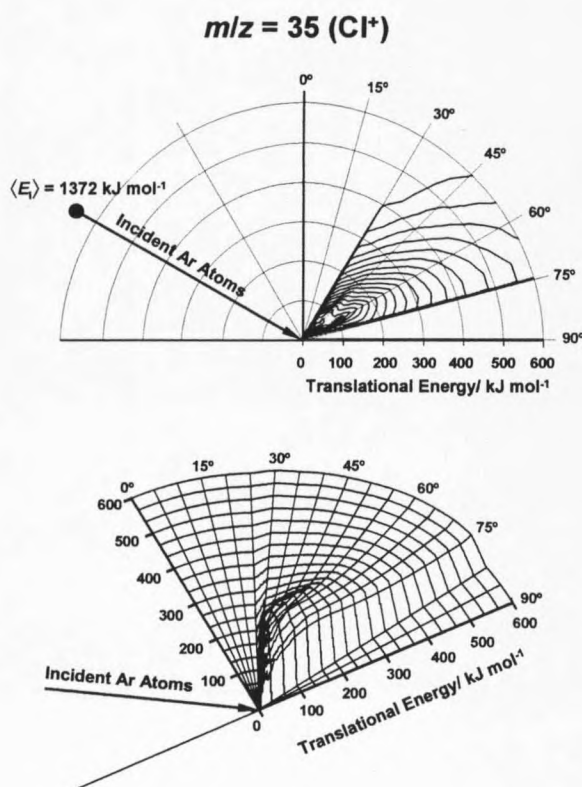


Figure 10. Contour map and mesh plot of translational energy distributions for desorbed hyperthermal Cl following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on a chlorinated Si surface.

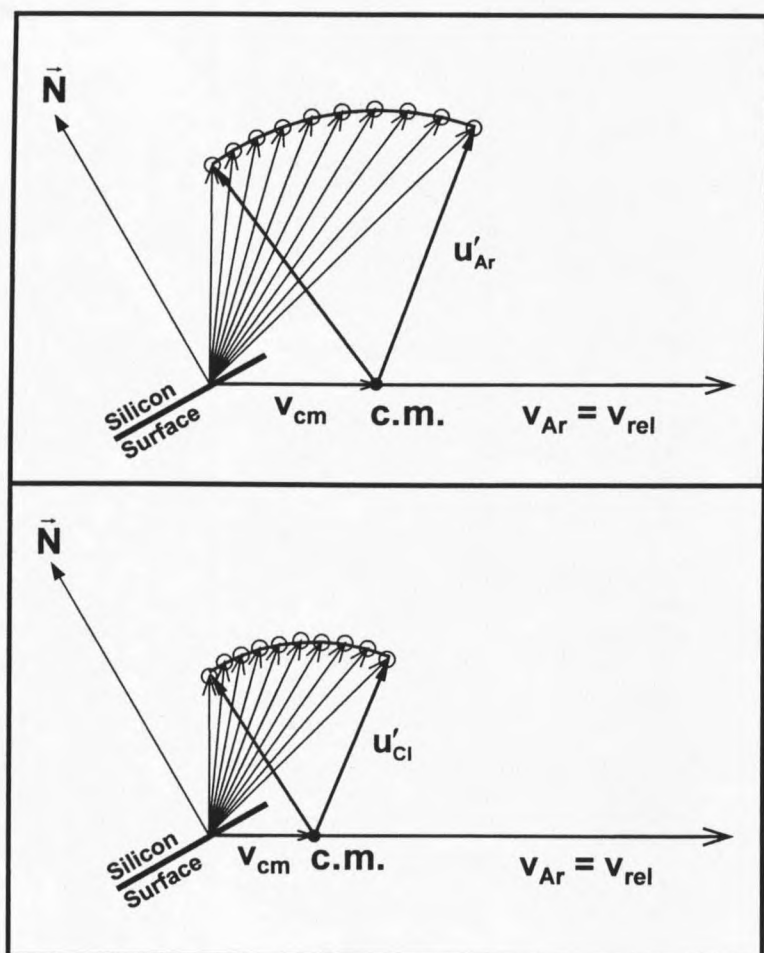


Figure 11. Newton diagrams for scattered hyperthermal Ar (upper panel) and desorbed hyperthermal Cl (lower panel) following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on a chlorinated Si surface.

Discussion

When a hyperthermal Ar atom hits the chlorinated Si surface, it will scatter back into the gas phase, while Cl may desorb or remain on the surface. We refer to the first case a “reactive collision”, while the second case is termed a “non-reactive collision”. Reactively and non-reactively scattered Ar atoms are indistinguishable in our experiment.

Thus all the data for IS of Ar are a mixture of reactive and non-reactive scattering. In a theoretical study of CID of N_2 from a W(100) surface,¹⁶ Zeiri found that the fraction of reactive collisions increased with incident energy and depended weakly on incident angle. He also found that the maximum fraction of reactive events was 38% for the highest incident energy, which was about 12 times higher than the binding energy of N_2 on W(100) surface. In our experiment, the highest incident Ar beam energy is less than 6 times of the binding energy of Cl on Si surface. In addition, the Ar-atom signal is 50-60 times that of Cl atoms, also suggesting that the Ar-atom signal is dominated by non-reactive collisions. Therefore, most of the scattered Ar atoms are believed to be the result of a non-reactive scattering channel.

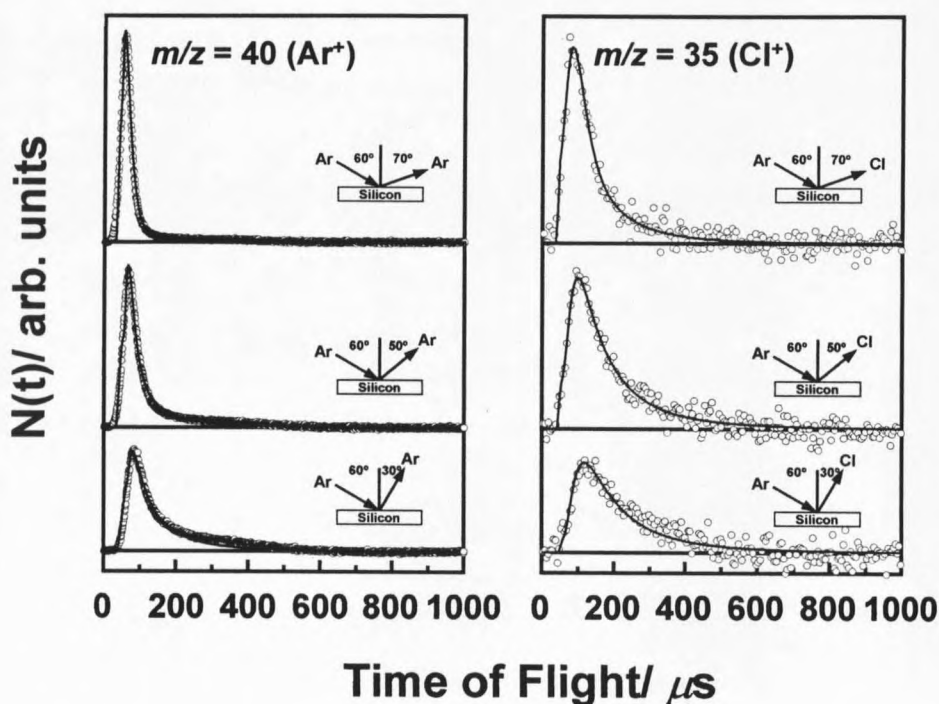


Figure 12. Computer simulation fitting results for hyperthermal components of TOF distributions shown in figure 2.

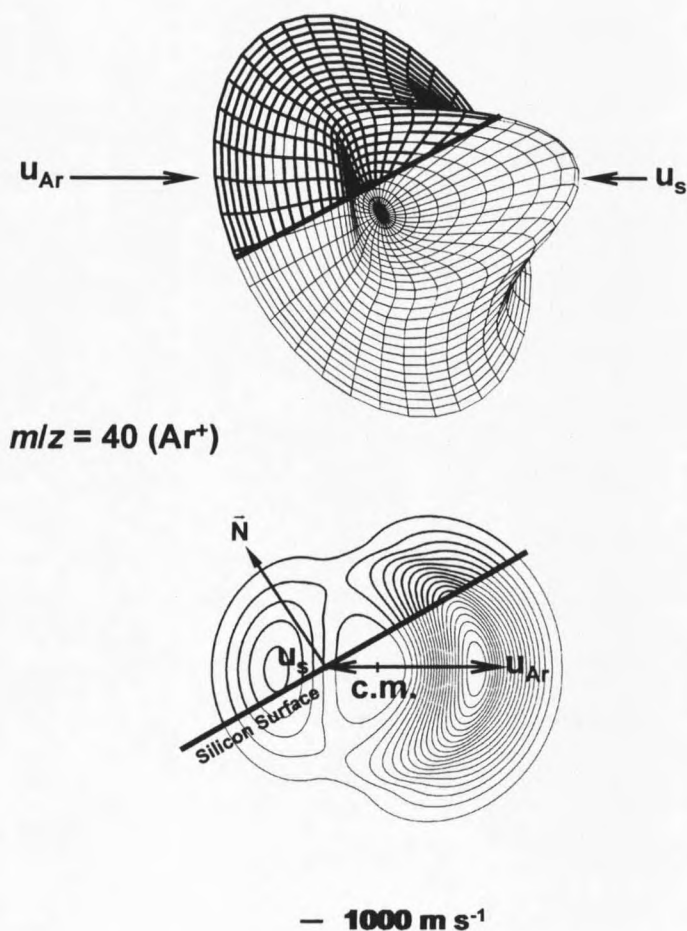


Figure 13. Center-of-mass contour map and mesh plot of velocity distributions for scattered hyperthermal Ar following impact with a chlorinated Si surface. The Ar beam had an average translational energy of 1372 kJ mol^{-1} and impinged on the surface at an incident angle of 60° .

When an Ar atom directly scatters back to the gas phase (reactive or non-reactive), it may retain hyperthermal translational energy, which gives rise to the hyperthermal component in the TOF distributions for Ar. If the incident Ar atom transfers most of the energy to substrate and/or Cl, it may become trapped on the surface, reach thermal equilibrium with the surface, and desorb, thus giving rise to a thermal population of

scattered Ar. In the case of CID of Cl, the desorbed Cl may have hyperthermal translational energies and directly scatter into the gas phase, or it may collide with another region of the surface and become trapped on the top of the adsorbate (not Si substrate) and desorb with thermal energies. These two possible processes give rise to two components (hyperthermal and thermal) of the desorbed Cl. If the desorbed Cl is trapped on the Si substrate, it will not desorb thermally because the binding energy of Cl on Si is two orders of magnitude higher than thermal energies at the surface temperature. Small fractions of thermal components shown in figure 2 indicate that collisional processes leading to hyperthermal components dominate the IS of Ar and CID of Cl.

Two mechanisms are possible in the production of desorbed Cl, direct reactive collisions and indirect reactive collisions. In the direct reaction pathway, the impulsive collision between Ar and Cl breaks the Cl-Si bond directly and causes Cl to desorb. In the indirect reaction pathway, mirror-like collisions¹² and a collision cascade type mechanism¹⁷ have been proposed. The mirror-like collisions involve the collision between Ar and the surface followed by collision between rebounded Ar and Cl. The collision cascade mechanism involves long range, surface mediated processes. In our study of CID of Cl from the chlorinated Si surface, the dangling bonds on the Si surface are saturated with Cl. In order for mirror-like collisions to occur, an Ar atom has to penetrate the Cl layer to collide with the substrate surface. Thus the possibility of Ar having enough remaining energy to liberate adsorbed Cl is small. In a theoretical study of CID of Ar from an Ar-monolayer-covered W(100) surface,¹⁷ the collision cascade

mechanism was found to have small possibility. Therefore, in our study, indirect reaction pathways are believed to be unimportant.

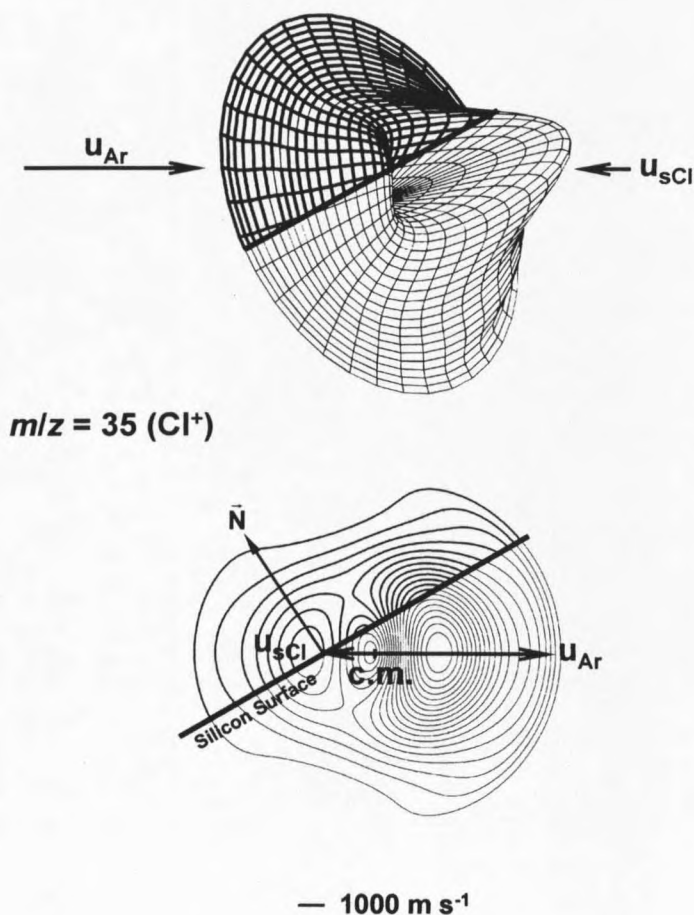


Figure 14. Center-of-mass contour map and mesh plot of velocity distributions for desorbed hyperthermal Cl following impingement of Ar atoms with $\langle E_i \rangle = 1372 \text{ kJ mol}^{-1}$ and $\theta_i = 60^\circ$ on a chlorinated Si surface.

The fact that most of Ar atoms scatter through a non-reactive channel, i.e., inelastic scattering, and the similarity between the dynamic behavior of IS of Ar and CID of Cl, leads us to conclude that desorption of Cl is mainly induced through a direct reactive

pathway. Figure 6 shows that the average translational energies of scattered hyperthermal Ar and desorbed hyperthermal Cl increase almost linearly with increasing incident Ar translational energy. Similar results were also observed in several theoretical studies of CID processes.^{10,16-19} The average translational energies of scattered hyperthermal Ar are always higher than those of desorbed hyperthermal Cl, which is reasonable given that most of the scattered Ar atoms come from non-reactive events. At combinations of incident and detection angles at $\theta_i = 45^\circ/\theta_f = 45^\circ$ and $\theta_i = 60^\circ/\theta_f = 30^\circ$ (open circles and squares in figure 6), about 20% of the translational energy is retained after Ar atoms scatter from the surface, while about 13% of the incident Ar translational energy is transferred to desorbed Cl. Most of the incident energy was deposited into the surface, part of which was used to overcome the binding energy of Cl on the Si surface. The angular dependence of desorbed Cl also supports the direct reactive pathway for CID of Cl. The average translational energies of scattered hyperthermal Ar and desorbed hyperthermal Cl increase with detection angle (figure 7), and the flux of scattered Ar and desorbed Cl peak at forward directions (figure 8). This fact combined with the observation of the scaling of average translational energy of desorbed Cl with incident Ar translational energy indicates that most of the angular and energy memory of the incident Ar atom is transferred to desorbed Cl after the reactive impulsive collision. An interesting feature in figure 8 is that the angle of maximum flux of scattered Ar depends on incident angle, i.e., the flux of scattered Ar peaks at near specular angles. However, the angle of maximum flux of desorbed Cl seems weakly dependent on incident angle. In fact, the flux of scattered Cl peaks at 60° for incident angles of both 45° and 60° . A

similar feature was observed in the theoretical studies of CID by Zeiri *et al.*^{16,18} They found that in the range of incident angle from 0° to 60° , the average polar angle of scattered collider increased with incident angle, while the average polar angle of desorbed adsorbate remained at about 70° for all the incident angles. This feature indicates that a large fraction of energy transferred to desorbed Cl during collision involves parallel components of the incident Ar translational motion. Normal components of the incident Ar translational motion are transferred to Cl to overcome the binding energy, while the parallel components are mostly retained.

Regardless of the incident angle and detection angle, the flux of desorbed Cl rises dramatically with incident Ar translational energies above a threshold of $\sim 870 \text{ kJ mol}^{-1}$ (figures 4 and 5). The independence of the threshold energy on incident angle indicates that total energy, rather than the normal component of the incident energy, governs the CID of Cl. This observation is consistent with the corrugated PES of chemisorbed Cl and Si surface. Such a corrugated PES efficiently couples parallel energy with normal energy so that total energy scaling is expected. Based on the HSHC model, Levis and coworkers have proposed a method to calculate binding energy from the threshold energy for CID.³⁻⁷ In the HSHC model, the collider and the adsorbate are treated as hard spheres, while the surface is treated as a hard cube. The CID process is pictured as two steps: collision between collider and adsorbate followed by collision of adsorbate with the surface. After the collision with the surface, the adsorbate desorbs only if the energy left is higher than the binding energy. The HSHC model is suitable for systems with relatively small binding energies, such as physisorption and some weak chemisorption

systems. For most chemisorption systems, such as the system studied in this article, the strong binding between adsorbate and surface makes it invalid that adsorbate and surface are treated separately. In fact, the strong chemical bond that is formed between Cl and Si when Cl is adsorbed on the Si surface makes Cl part of the surface.

When an Ar atom collides with the chlorinated Si surface, it actually interacts with a local region of the surface that has finite mass and is capable of releasing Cl. When no Cl is released (non-reactive collision), the collision is a typical two-body scattering process. However, for reactive collisions, the release of Cl makes the collision a three-body scattering process. The collision partner of Ar is a surface moiety, $S_f\text{-Cl}$, with an effective mass of m_{SiCl} . The collision products are Cl, Ar, and the effective surface moiety without Cl, designated as S_f . The scattered Ar and S_f can be treated together as a conceptual species, Ar/S_f , with the following properties: $m_{\text{Ar}/S_f} = m_{\text{Ar}} + m_{S_f}$, and $\vec{v}_{\text{Ar}/S_f} = \vec{v}_{\text{Ar}} + \vec{v}_{S_f}$. Thus, the three-body reactive scattering event can be viewed as a two-body scattering process:



The translational energy of the incident Ar atom may be separated into translational energy of the center-of-mass of Ar and $S_f\text{-Cl}$ and collision energy, E_{coll} , which is the total available energy for CID of Cl. Approximately 80% of E_{coll} is partitioned into a quantity designated as E_{int} . Three components comprise E_{int} : relative motion between recoiling Ar and S_f , internal energy of S_f , and dissociation energy of the Cl-Si bond, $D(\text{Si-Cl})$, which is the binding energy of Cl on Si surface. Although we are unable to assign a value to $D(\text{Si-Cl})$ from the experimental data, it will be some fraction of the incident Ar energy. In fact,

the $D(\text{Si-Cl})$ value of 388 kJ mol^{-1} (Ref. 21) is only 45% of the threshold energy of 870 kJ mol^{-1} .

As mentioned previously and shown in figure 6, the average translational energies of scattered hyperthermal Ar or desorbed hyperthermal Cl are the same for the same deflection angle. In fact, average fractional energy transfer, defined as $\frac{\Delta E}{E} = \frac{\langle E_i \rangle - \langle E_f \rangle}{\langle E_i \rangle}$, is a function of deflection angle, which is shown in figure 15. The open squares and circles are experimental data at incident angles of 45° and 60° , respectively. The kinematic analysis results allow us to gain a deeper insight into this relationship by using a soft-sphere model.^{25,26,28} The solid lines are calculated from the soft-sphere model, which is a modification of a hard-sphere model²⁹ by taking inelasticity into account. The soft-sphere model is given by the following equation:

$$\frac{\Delta E}{E} = \frac{2\mu_1}{\mu(\mu_1 + 1)^2} \left[\frac{\mu(\mu_1 + 1)}{2\mu_1} \left(\mu_0 + \mu_1 + \frac{E_{\text{int}}}{E_i} \right) - \mu_1 \cos^2 \chi \right. \\ \left. - \cos \chi \sqrt{\mu_1^2 \cos^2 \chi + \mu(\mu_1 + 1) \left(1 - \mu_0 - \frac{E_{\text{int}}}{E_i} \right)} \right] \quad (3)$$

where $\mu = \frac{m_f}{m_i}$, $\mu_0 = \frac{m_i}{m_{\text{eff}}}$, $\mu_1 = \frac{m_f}{m_{\text{eff}}}$. m_i is the mass of the incident Ar, m_f is the mass of scattered Ar or desorbed Cl, and m_{eff} is the effective surface mass, which is m_s for IS of Ar and m_{sCl} for CID of Cl. Equation (3) is a general form of a previously published soft-sphere model²⁸ for the case that scattered and incident species are different. Inelasticity of the collision process is taken into account in the term, E_{int}/E_i , which is determined experimentally as the value of $\langle E_{\text{int}} \rangle / \langle E_i \rangle$.

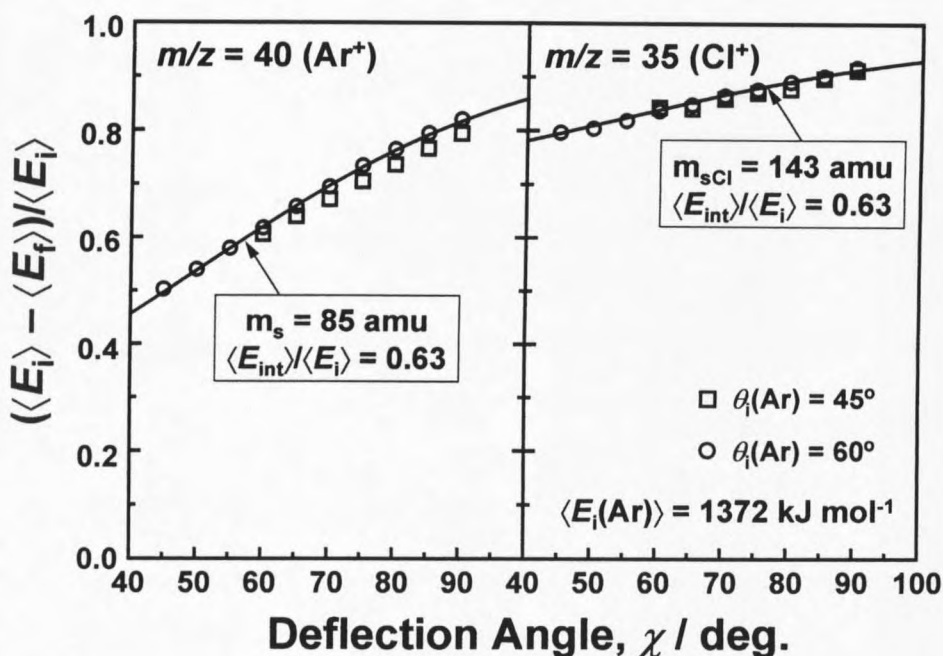


Figure 15. Average fractional energy transfer of scattered hyperthermal Ar and desorbed hyperthermal Cl as a function of deflection angle following impingement of Ar atoms with $\langle E_i \rangle = 1372$ kJ mol $^{-1}$ at incident angles of 45° and 60° on chlorinated Si surface. Circles and squares represent data points. Solid lines are the soft-sphere model predictions based on the effective surface mass and ratio of internal energy to incident energy, $\langle E_{\text{int}} \rangle / \langle E_i \rangle$, which are derived (see Table 1) from the kinematic analysis associated with the Newton diagrams in figure 11.

Our kinematic analysis (figure 11 and table 1) shows that the effective surface mass for IS of Ar is about 60% of that for CID of Cl. For reactively scattered Ar, the effective surface mass should be identical to that for CID of Cl. However, the scattered Ar is a mixture of reactive and non-reactive scattering with non-reactive scattering dominant. The interaction time between the Ar atom and the effective surface moiety is shorter for non-reactive scattering than for reactive scattering. Thus, the effective surface mass for non-reactive scattering of Ar is expected to be smaller than that for reactive scattering.

The effective surface mass is smaller for higher incident Ar energy (see Table 1) for the reason that the faster incident Ar atom has a shorter interaction time during the collision; thus the collision is more localized, which leads to smaller effective surface mass.

When the collision is viewed in the c.m. reference frame (figures 13 and 14), it shows two populations of scattering events, forward and backward/sideways scattering, which clearly indicate two distinct mechanisms that are responsible for the bimodality of the translational energy distributions of scattered hyperthermal Ar and desorbed hyperthermal Cl at higher detection angles (figure 3). For IS of Ar, forward scattering indicates large-impact-parameter collisions and a relatively weak interaction during the collision. Thus, only a small fraction of the translational energy of incident Ar is deposited to the effective surface moiety. Therefore, forward scattering of Ar are mainly non-reactive collision events. Backward/sideways scattering of Ar is correlated with head-on or small-impact-parameter collisions, which are mostly impulsive collisions and most efficient in energy transfer. Therefore, backward/sideways scattering of Ar is responsible for the CID of Cl. For the case of CID of Cl, the forward scattering is believed to be the result of large-impact-parameter collisions at non-collinear configurations of Ar-Cl- S_f , where most of the momentum and energy of Ar is transferred to Cl. On the other hand, backward/sideways scattering of Cl is due to small-impact-parameter collisions at near collinear configurations of Ar-Cl- S_f , following recoil of highly excited Cl at backward or sideways directions.

Conclusion

Collision-induced desorption of Cl from Si surface was studied by directing hyperthermal beams of Ar atoms at a Cl-covered Si surface and monitoring the dynamical behavior of scattered Ar and desorbed Cl. The collisional processes are divided into two channels, reactive collisions (release of Cl) and non-reactive collisions (Cl remains on the surface). The flux of desorbed Cl increases dramatically with incident Ar translational energy of above $\sim 870 \text{ kJ mol}^{-1}$, which is governed by total energy accommodation of the corrugated PES of adsorbed Cl on Si. TOF distributions of scattered Ar and desorbed Cl exhibit two populations, hyperthermal and thermal. The average translational energies of scattered hyperthermal Ar and desorbed hyperthermal Cl increase with incident Ar translational energy and detection angle. The flux angular distributions of IS of Ar and CID of Cl are asymmetric to the surface normal. The flux of scattered Ar peaks at specular angles, while the maximum-flux angle of desorbed Cl remains at 60° for incident angles of 45° and 60° . The similar dynamical behavior of IS of Ar and CID of Cl indicates that a direct impulsive collision is the dominant reaction pathway to induce desorption of Cl. The kinematic analysis suggests a simple picture of CID of Cl as an initial binary collision between an incident Ar atom and a localized region of the surface, which is followed by IS of the Ar atom and release of Cl from the local surface moiety. The kinematic analysis also allows us to view IS of Ar and CID of Cl in the c.m. reference frame, in which two populations of scattering events are observed: forward and backward/sideway scattering. Forward scattering of Ar is due to large-impact-parameter collisions, while backward/sideways scattering of Ar is due to small-

impact-parameter collisions, most of which are reactive collisions. For CID of Cl, forward scattering is caused by large-impact-parameter collisions at non-collinear Ar-Cl- S_f configurations. Backward/sideways scattering of Cl is due to small-impact-parameter collisions at near collinear Ar-Cl- S_f configurations following recoil of Cl in the backward/sideways directions.

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CHAPTER 7

SUMMARY

Hyperthermal neutral beams have been employed to study the gas-surface interaction dynamics for several systems, including initial interactions of hyperthermal atomic oxygen with a liquid hydrocarbon surface, collision-assisted erosion of polymers and graphite in atomic oxygen environments, collision-assisted etching of Si in atomic chlorine environments, and collision-induced desorption of Cl from an Si surface.

Non-equilibrium processes dominate the first few scattering events in the initial reactions between hyperthermal atomic oxygen and hydrocarbon surface. Direct inelastic scattering of O atoms, in which only a fraction of the initial translational energy is deposited to the surface, is the most probable non-reactive interaction. The most probable initial reaction is gas-phase like H-abstraction to form OH. Once formed, the OH may undergo further collisions with the surface, some of which yield H₂O. No volatile C-C bond breaking products were detected in the initial reactions. However, during steady-state oxidation conditions, volatile CO and CO₂ products are produced, which are believed to account for a significant fraction of mass loss of polymers or graphite that is under atomic-oxygen attack. When these continuously-oxidized surfaces were exposure to bombardment by hyperthermal N₂ or Ar above a threshold energy of $\sim 800 \text{ kJ mol}^{-1}$, production of CO and CO₂ and erosion rate of the surfaces are dramatically increased. The synergism between energetic inert particles and chemically active species incident on surfaces is believed to be a general effect, which is also observed in studies of collision-assisted etching of Si in atomic chlorine environments.

Production of volatile silicon chloride (SiCl_x , $x=1-4$) and the Si etch rate are dramatically enhanced with bombardment by energetic Ar atoms. The origin of this collisional effect could involve an enhancement in the removal rate of reaction products already residing on or imbedded in the surface (chemically-enhanced physical sputtering) or collision-induced reactions that lead to formation of volatile products (chemical sputtering). In our experiment, the former mechanism is essentially synonymous with collision-induced desorption. Studies of collision-induced desorption of Cl from an Si surface reveal that impulsive bimolecular collisions between an incident collider and an adsorbate are dominant. Although the details of these collisional mechanisms are complicated, the dynamical behavior of the ejected products may be described in terms of a simple kinematic picture in which an incident energetic particle collides with a localized region of the surface that has effective mass. The kinematic analysis allows us to view the interactions in the center-of-mass reference frame, which provides deeper insight into the interaction dynamics.

The studies of initial reactions between atomic oxygen and a hydrocarbon surface and collisional enhancement in material removal under steady-state oxidation conditions are closely relevant to the erosion of materials in the low Earth orbit environment, as a result of highly energetic collisions with ambient O atoms and N_2 molecules, and also in certain ground-based test facilities that subject oxidized surfaces to bombardment by O_2 molecules with high translational energies.

APPENDICES

APPENDIX A

SOFT-SPHERE MODEL

During a gas-surface scattering process, the incident particle encounters a localized surface moiety, which has finite effective surface mass. The incident particle may scatter back into the gas phase. If a reaction occurs during the collision, the reaction product may also scatter into the gas phase. The scattering process may be described as binary collision by assuming the incident particle and the effective surface moiety to be soft spheres. The soft-sphere model describes the fractional energy transfer, defined as $\frac{\Delta E}{E} = \frac{E_i - E_f}{E_i}$, as a function of deflection angle, defined as $\chi = 180^\circ - (\theta_i + \theta_f)$. E_i and E_f are the kinetic energies of incident and scattered particle, respectively. θ_i and θ_f are the incident and final angles with respect to the surface normal. The soft-sphere model is a modification of hard-sphere model,¹ which takes inelasticity into account. The term "soft sphere" indicates that the collision is inelastic, i.e., the kinetic energy is not conserved during collision. The term "hard sphere" indicates an elastic collision, in which the kinetic energy is conserved.

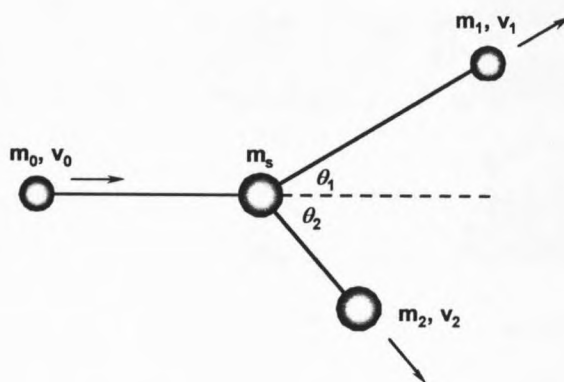


Figure 1. Binary collision process

Assume the following scattering scheme (Figure 1): the incident particle with mass m_0 and velocity v_0 collides with the effective surface moiety with mass m_s and zero initial velocity. The two post-collision products have masses of m_1 and m_2 and velocities of v_1 and v_2 . Momentum and energy must be conserved during the collision. Thus, we have the following equations:

$$m_0 v_0 = m_1 v_1 \cos \theta_1 + m_2 v_2 \cos \theta_2 \quad (1)$$

$$m_1 v_1 \sin \theta_1 = m_2 v_2 \sin \theta_2 \quad (2)$$

$$\frac{1}{2} m_0 v_0^2 = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + E_{\text{int}} \quad (3)$$

E_{int} is the energy that goes into the internal modes of the post-collision products. In figure 1, θ_1 is same as the deflection angle. The goal of the following derivation is to find the expression for fractional energy transfer, $\frac{\Delta E}{E} = \frac{E_i - E_f}{E_i}$, as a function of deflection angle, θ_1 .

Eq.(2) gives

$$v_2 = \frac{m_1 \sin \theta_1}{m_2 \sin \theta_2} v_1. \quad (4)$$

Substituting v_2 in Eq.(3) with Eq.(4) gives

$$\frac{m_1 v_1^2}{m_0 v_0^2} + \frac{m_1^2}{m_0 m_2} \cdot \frac{\sin^2 \theta_1}{\sin^2 \theta_2} \cdot \frac{v_1^2}{v_0^2} + \frac{E_{\text{int}}}{E_i} = 1 \quad (5)$$

Substituting v_2 in Eq.(1) with Eq.(4) gives the following derivations:

$$\cos \theta_2 = \frac{m_0 v_0 - m_1 v_1 \cos \theta_1}{m_2 v_2}$$

$$\begin{aligned}
\Rightarrow \sin^2 \theta_2 &= 1 - \frac{m_0^2 v_0^2 - 2m_0 m_1 v_0 v_1 \cos \theta_1 + m_1^2 v_1^2 \cos^2 \theta_1}{m_2^2 v_2^2} \\
\Rightarrow m_2^2 v_2^2 \sin^2 \theta_2 &= m_2^2 v_2^2 - m_0^2 v_0^2 + 2m_0 m_1 v_0 v_1 \cos \theta_1 - m_1^2 v_1^2 \cos^2 \theta_1 \\
\Rightarrow m_2^2 \sin^2 \theta_2 \frac{m_1^2 \sin^2 \theta_1}{m_2^2 \sin^2 \theta_2} v_1^2 &= m_2^2 \frac{m_1^2 \sin^2 \theta_1}{m_2^2 \sin^2 \theta_2} v_1^2 - m_0^2 v_0^2 + 2m_0 m_1 v_0 v_1 \cos \theta_1 \\
&\quad - m_1^2 v_1^2 \cos^2 \theta_1 \\
\Rightarrow m_1^2 \sin^2 \theta_1 v_1^2 &= \frac{m_1^2 \sin^2 \theta_1}{\sin^2 \theta_2} v_1^2 - m_0^2 v_0^2 + 2m_0 m_1 v_0 v_1 \cos \theta_1 - m_1^2 v_1^2 \cos^2 \theta_1 \\
\Rightarrow \frac{\sin^2 \theta_1}{\sin^2 \theta_2} &= \frac{1}{m_1^2 v_1^2} (m_1^2 v_1^2 + m_0^2 v_0^2 - 2m_0 m_1 v_0 v_1 \cos \theta_1) \quad (6)
\end{aligned}$$

Combining Eq.(5) and (6) gives

$$\begin{aligned}
\frac{m_1 v_1^2}{m_0 v_0^2} + \frac{m_1^2 v_1^2}{m_0 m_2 v_0^2} \cdot \frac{1}{m_1^2 v_1^2} (m_1^2 v_1^2 + m_0^2 v_0^2 - 2m_0 m_1 v_0 v_1 \cos \theta_1) + \frac{E_{\text{int}}}{E_i} &= 1 \\
\Rightarrow \frac{m_1 v_1^2}{m_0 v_0^2} + \frac{m_1^2 v_1^2}{m_0 m_2 v_0^2} + \frac{m_0}{m_2} - 2 \frac{m_1 v_1}{m_2 v_0} \cos \theta_1 + \frac{E_{\text{int}}}{E_i} &= 1 \\
\Rightarrow \frac{m_1}{m_0} \left(1 + \frac{m_1}{m_2} \right) \frac{v_1^2}{v_0^2} - \left(2 \frac{m_1}{m_2} \cos \theta_1 \right) \frac{v_1}{v_0} - \left(1 - \frac{m_0}{m_2} - \frac{E_{\text{int}}}{E_i} \right) &= 0 \quad (7)
\end{aligned}$$

In order to simplify the equation, the following symbols are defined:

$$\mu = \frac{m_0}{m_2}; \quad \mu_0 = \frac{m_1}{m_0}; \quad \mu_1 = \frac{m_1}{m_2}.$$

Thus, the solution of the value of v_1/v_0 from Eq.(7) is:

$$\frac{v_1}{v_0} = \frac{\mu_1 \cos \theta_1 + \sqrt{\mu_1^2 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) (1 - \mu - E_{\text{int}}/E_i)}}{\mu_0 (\mu_1 + 1)}.$$

The other solution of Eq.(7) is discarded due to negative value. Therefore, fractional energy transfer is derived as following:

$$\begin{aligned}
 \frac{\Delta E}{E} &= \frac{E_i - E_f}{E_i} = 1 - \frac{m_1}{m_0} \frac{v_1^2}{v_0^2} = 1 - \mu_0 \frac{v_1^2}{v_0^2} \\
 \Rightarrow \frac{\Delta E}{E} &= 1 - \mu_0 \left(\frac{\mu_1 \cos \theta_1 + \sqrt{\mu_1^2 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) (1 - \mu - E_{\text{int}}/E_i)}}{\mu_0 (\mu_1 + 1)} \right)^2 \\
 \Rightarrow \frac{\Delta E}{E} &= 1 - \frac{1}{\mu_0 (\mu_1 + 1)^2} \left[2\mu_1 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right) \right. \\
 &\quad \left. + 2\mu_1 \cos \theta_1 \sqrt{\mu_1^2 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right)} \right] \\
 \Rightarrow \frac{\Delta E}{E} &= \frac{2\mu_1}{\mu_0 (\mu_1 + 1)^2} \left[\frac{\mu_0 (\mu_1 + 1)^2}{2\mu_1} - \frac{\mu_0 (\mu_1 + 1)}{2\mu_1} \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right) - \mu_1 \cos^2 \theta_1 \right. \\
 &\quad \left. - \cos \theta_1 \sqrt{\mu_1^2 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right)} \right] \\
 \Rightarrow \frac{\Delta E}{E} &= \frac{2\mu_1}{\mu_0 (\mu_1 + 1)^2} \left[\frac{\mu_0 (\mu_1 + 1)}{2\mu_1} \left(\mu + \mu_1 + \frac{E_{\text{int}}}{E_i} \right) - \mu_1 \cos^2 \theta_1 \right. \\
 &\quad \left. - \cos \theta_1 \sqrt{\mu_1^2 \cos^2 \theta_1 + \mu_0 (\mu_1 + 1) \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right)} \right]
 \end{aligned}$$

Finally, changing θ_1 to χ gives the soft-sphere model equation:

$$\begin{aligned}
 \frac{\Delta E}{E} &= \frac{2\mu_1}{\mu_0 (\mu_1 + 1)^2} \left[\frac{\mu_0 (\mu_1 + 1)}{2\mu_1} \left(\mu + \mu_1 + \frac{E_{\text{int}}}{E_i} \right) - \mu_1 \cos^2 \chi \right. \\
 &\quad \left. - \cos \chi \sqrt{\mu_1^2 \cos^2 \chi + \mu_0 (\mu_1 + 1) \left(1 - \mu - \frac{E_{\text{int}}}{E_i} \right)} \right] \quad (8)
 \end{aligned}$$

For the case of inelastic scattering, the scattered particle is the same as the incident particle, which means $m_1 = m_0$, thus $\mu_1 = \mu$ and $\mu_0 = 1$. Eq.(8) simplifies to

$$\frac{\Delta E}{E} = \frac{2\mu}{(\mu+1)^2} \left[1 + \mu \sin^2 \chi + \frac{E_{\text{int}}}{E_i} \left(\frac{\mu+1}{2\mu} \right) - \cos \chi \sqrt{1 - \mu^2 \sin^2 \chi - \frac{E_{\text{int}}}{E_i} (\mu+1)} \right] \quad (9)$$

Making E_{int} equal to zero gives the hard-sphere model equation:

$$\frac{\Delta E}{E} = \frac{2\mu}{(\mu+1)^2} \left[1 + \mu \sin^2 \chi - \cos \chi \sqrt{1 - \mu^2 \sin^2 \chi} \right] \quad (10)$$

REFERENCES

- 1 J. Harris, in *Advances in Gas-Phase Photochemistry and Kinetics: Dynamics of Gas-Surface Interactions*, edited by C. T. Rettner and M. N. R. Ashfold (Royal Society of Chemistry, Cambridge, United Kingdom, 1991).

APPENDIX B

PRACTICAL ETCHING EXPERIMENTS

As discussed in Chapters 3-5, collisions with energetic Ar atoms with continuously oxidized polymers or graphite surfaces and a continuously chlorinated Si surface dramatically increase the erosion rate. When this erosion process is controlled by a patterned, protective mask, the process is considered etching. The collisional enhancement in the etching of a polymer or Si wafer under steady-state etching conditions with bombardment of energetic Ar atoms was tested with practical etching experiments.

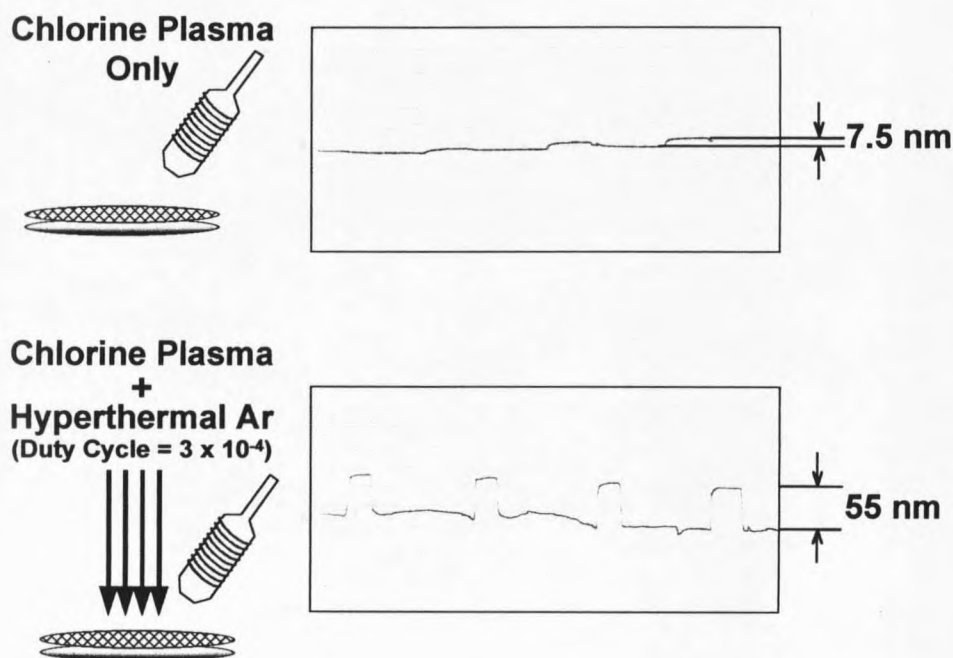


Figure 1. Etching depth of Si samples exposed to Cl plasma source with and without addition of hyperthermal Ar beam.

The polymer sample used in this experiment was polystyrene. The etch yield of polystyrene under exposure to the effusive O plasma source and the etch yield of an Si

wafer under exposure to the effusive Cl plasma source with and without addition of the pulsed hyperthermal Ar beam were compared. In this experiment, the entire Ar beam (unchopped) was allowed to strike the surface. The etch yield was determined by placing a screen over the samples during exposure and measuring the etch depth with a profilometer. The polystyrene and Si samples were exposed for 10 and 14 hours, respectively, in order to have good comparison. Si etching results are shown in figure 1. The etch yield of polystyrene (not shown) and Si wafer when the samples were exposed to both beams was approximately 1.3 (polystyrene) and 7 (Si) times of the etching yield observed when only the effusive plasma beams were used to expose the samples.

APPENDIX C

FORWARD CONVOLUTION METHOD AND
GMTHRASH PROGRAM

Forward convolution means the conversion from center-of-mass (c.m.) reference frame to lab reference frame. It begins with a trial c.m. flux distribution and forwardly convolutes to lab time-of-flight (TOF) distribution and compares with experimental data. This appendix briefly describes the forward convolution method followed by the Fortran code of the updated version of the GMTHRASH program. More details of the method and the original Fortran code can be found in references 1-4.

The following useful relations should be kept in mind in the derivation of the forward convolution method and the Fortran code. The symbols are listed as following:

P : probability density

I : Flux

A : area

t : flight time

v : velocity in lab frame

u : velocity in c.m. frame

θ : lab angle

Θ : c.m. angle

$$\frac{P}{A\Delta t} = I, \text{ so } P \propto I \quad (1)$$

$$P(v)dv = P(E)dE, \text{ so that } P(v) \propto vP(E) \quad (2)$$

Similarly, in c.m. frame, we have $P(u) \propto uP(E_T)$

$$N(v) \propto \frac{I(v)}{v} \text{ or } I(t) \propto \frac{N(t)}{t} \quad (3)$$

This is because the TOF distribution is number density distribution, which corresponds to a probability function divided by volume, while volume is proportional to velocity.

$$N(v)dv = \frac{P(v)dv}{V} = \frac{P(v)dv}{Av\Delta t}$$

$$N(v)dv = N(t)dt, \text{ so that } N(v) \propto t^2 N(t) \quad (4)$$

$$I(t)dt = P(E)dE, \text{ so that } P(E) \propto t^3 I(t)$$

$$\text{Thus, } P(E) \propto t^2 N(t) \quad (5)$$

$$N(t)dt = N(v)dv, \text{ thus } N(t) \propto \frac{N(v)}{t^2} \text{ or } N(t) \propto v^2 N(v) \quad (6)$$

$$\text{So, } N(t) \propto vI(v) \quad (7)$$

Derivation of the forward convolution method is shown as the following:

$$I_{Lab}(v, \theta)dv d\theta = I_{cm}(u, \Theta)du d\Theta$$

$$I_{Lab}(v, \theta) = I_{cm}(u, \Theta) \frac{du d\Theta}{dv d\theta} = \frac{v^2}{u^2} I_{cm}(u, \Theta). \quad (8)$$

This is called Jacobian transformation.

$$N_{Lab}(v, \theta) \propto \frac{v}{u^2} I_{cm}(u, \Theta)$$

$$N_{Lab}(t, \theta) \propto \frac{1}{u^2 t^3} I_{cm}(u, \Theta)$$

$$N_{Lab}(t, \theta) \propto \frac{1}{ut^3} I_{cm}(E_T, \Theta) \quad (9)$$

Eq. (9) and a trial $I_{cm}(E_T, \Theta)$ are used in the GMTHRASH program to calculate TOF distributions in lab frame and compare with experimental data. The trial $I_{cm}(E_T, \Theta)$ is iteratively adjusted until a best fit of the data is obtained. The fitting procedure

involves a non-linear least square procedure. In this program, c.m. energy and angular distributions are assumed to be completely separated:

$$I_{cm}(E_T, \Theta) = P(E_T)T(\Theta) \quad (10)$$

This is valid in reaction systems that have a long-lived intermediate complex, which means a weak coupling between $P(E_T)$ and $T(\Theta)$. However, in reactions that involve direct mechanisms, there is often strong coupling between them. This problem is solved by assuming the c.m. flux function consists of n sets of uncoupled $P(E_T)$ and $T(\Theta)$, each weighted by w_i .

$$I_{cm}(E_T, \Theta) = \sum_{i=1}^n w_i P_i(E_T) T_i(\Theta) \quad (11)$$

Four sets of uncoupled $P(E_T)$ and $T(\Theta)$ were required in the data analysis in Chapter 2, and three were required in the analysis whose results are presented in Chapter 6.

The input file for GMTHRASH is called input.txt. Output.txt and gmthrash.txt are the text output files that contain the information of the calculation process. Montof*.txt files are the TOF distributions, in which first column is flight time, second column is experimental data, third column is the calculated TOF data (sum of all channels), and the rest of the columns are TOF distributions calculated from each channel. Monpe*.txt and Montt*.txt are $P(E_T)$ and $T(\Theta)$, respectively, for each channel. Monbang.txt is the angular distribution, experimental and calculated sum of $N(t)$ at each lab angle.

If the c.m. plotting option is chosen, more files are created. Ave_et.txt and ave_u.txt are average E_T and u as a function of c.m. angle. Pe_angle*.txt files are $P(E_T)$ distributions at every 5 degrees of c.m. angle. Cont_e.txt and cont_u.txt are contour-map files for $P(E_T)$ and $P(u)$ distributions. The data are in three columns and in the XYZ

triplet format. Based on these data, one can create contour maps and 3D surface plots. Mesh_e_a.txt and mesh_e_r.txt are 3D trajectory files, in which the data are divided into a number of 3-columns, each 3-column is one trajectory. Mesh_e_a.txt contains angular trajectories, while mesh_e_r.txt contains radius trajectories. The same data format applies for mesh_u_a.txt and mesh_u_r.txt. T_theta.txt is total angular distribution, $T(\theta)$. If the option for plotting with surface is chosen, 125 more files will be created. This is for presentation purpose only, in which the whole $P(u)$ mesh plot is divided into two parts, above the surface and below the surface. The part above the surface is real, while the part below the surface is imaginary because of the presence of the surface. Due to different data lengths for different trajectories, each file contains only one trajectory. Thus, each trajectory has to be added together one by one, which is time consuming. Among the 125 files, surface_u.txt is the trajectory of the surface.

The code for GMTHRASH program is listed next. Some important and useful notes are written in the code, which is helpful in understanding the program. An example of input file with explanation is presented at the end.

Program GMTHRASH

```

c Version date: July, 2001
c
c This program is to calculate laboratory TOF and angular distributions of reactively
c scattered product and compare with experimental data. Input consists of beam
c parameters, trial energy distribution, trial angular distribution. Output can be contour
c map and mesh plot of velocity distributions in c.m. reference frame, angular data and
c calculated TOF data, or only tables of the calculated and experimental data.
c
c ***Featuring Simplex Optimization*** AGS march 1989
c (see Nelder and Mead, Computer Journal 1965, v.7 p308 or numerical recipes)
c
c Will optimize point form or rrkm p(e)
c Will optimize point form or legendre t(theta)
c Can accommodate up to ten different channels (6/21/01) with different product,
c reactant masses (reactant beam velocities must be the same for each channel)
c Weight of angular distribution in calculation of chisquare may be adjusted, and
c sections of tof may be excluded.
c Weighting of T( $\theta$ ) normalized correctly -- 12/26/94 AGS: Thanks, Miau
c
c ***Contains modified Newton subroutine and all other subroutines.***
c
c Has proper rrk form of p(e).
c Contains modifications of P. S. Weiss, May, 1984 and Feb. and Sept.-Nov., 1985
c and of G. Robinson, Nov. 1984.
c P(E) normalized as P(u), Jan., 1986
c Some minor modifications - AMS June 1986 mostly in subroutines of Newt1, Wate
c Mongo files; velocity selector option taken out May 87
c Free input format, no comments, area stuff taken out, 6/1/87
c Reduced product mass included in the Jacobian - but only for point form P(E)!
c Includes option to calculate data only using a cross section that is input and no
c experimental data, 9/87
c Calculated TOF scaled to measured TOF using least squares fit instead of integral,
c 2/23/88
c Maximum number of angles increased to 21, 3/15/88
c
c *****
c
common/chii/a(50),b(50),chis,dv,kplt,kdat,kcmp,p(2500,21,10),
1 pm(50),pc(2500,21,10),sum(10),sumf(50),
1 vl(2500),vz,xd(50),z,ww(10),nv,na,gb(10),chit

common/tnrm/tnorm(10)

```

```

common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1 ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1 np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1 tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

common/newton/al(4000,10),c(4000,10),c2(4000,10),cut(4000,10),cxmp,
c cymp,d(4000),fabg(4000,10),g1(10),g2(10),gamma,gg(10),hw1,hw2,
c ngam1,ngam2,ngrid,sr(2),thc(4000,10),vla(4000,10),vv(4000,10),
c v1,v2,vt(2),nvb(2),tm(10),pmass(10),hwidb(1)

common/tim/aab(50),abb,chnmn(5,21),chnmx(5,21),dl,ir,
c ktel,nch(50),ntb(50),of,pat,path,pmas,
c size,tat(500,50),tmin(5,21),tmxx(5,21),xion,xims,chin,
c idum(50),nto,igat

common/lege/kk,kpts,t,theta,to(51,10),chiwt
common/vels/alph,ivels,tmp,vs0,vsbeta,vsgam
common/int/almax,vel
common/opt/kdum1,knorm,kwarn,tsum,ngg(11),ngh(11),lop
common/trip/dia,dt,hz,sa,sb,time,trp(19),ttcm
common/weight/ef,ew(50),kwts,new,sig(50),kstp
common/area/area(10),rarea(4000,10),k(100),nibe(100),nopt
common/calcu/kcalc,zz,kopt
common/beamv/fb(50,2),vb(50,2)
common/cene/mp,cc,ss
dimension q(2),emax(10),ez(10),dden(10)
dimension pmax(10),hip(101,100),why(100),pbar(100)
dimension pn(120,10),th(120),tp(120),avge(10)
dimension po(51,10),pr(100),pr(100)
character*80 title
character*20 itemp
parameter(alpha=1.0,beta=0.5,gams=2.0,gang=1.05)
data q/3h no, 3hyes/
data rad/.0174533/
data fdeg/.0872665/

dimension ucont(600,600),econt(600,600),cau(600,600),cae(600,600)
dimension ux(600),uy(600),ex(600),ey(600)
dimension ux_r(300,200), uy_r(300,200), umesh_r(300,200)
dimension ux_a(200,300), uy_a(200,300), umesh_a(200,300)
dimension ex_r(300,200), ey_r(300,200), emesh_r(300,200)
dimension ex_a(200,300), ey_a(200,300), emesh_a(200,300)
dimension pet(250), pu(250), t_theta(200)

```

c Input 1: Title

```

        open(unit=7, file='input.txt', status='unknown')
        read(7,1000) title
1000  format(a80)

        open(unit=8, file='gmthrash.txt', status='unknown')
        write(8,1019) title
1019  format(1x,a80
      1  ,//,' laboratory to center of mass transformation program'
      1  , 'gmt10',/, ' version date: April 19, 1988',/))

```

c Input 2: Option list

```

        read(7,1003) kstp,kopt,kpts,kleg,ktim,kcmp,kwts,ksmo
      1  ,ktel,kwarn,kcalc,igat,ncn,lop
        read(7,1003) kcmplot, ksurface
1003  format(20i1)

```

c KMil uses Miller form for $T(\theta)$ (nleg=2, nang=0)

c Meanings of these options: (1 = yes, 0 = no)

c kstp: print Newton diagram information?

c kopt: optimized center of mass angular function?

c kpts: c.m. function, $P(E_T)$, in point form (RRK form not used)?

c kleg: print c.m. angular distribution?

c ktim: read in TOF of flight data? (Definitely yes!)

c kcmp: plot c.m. flux contour map? (This option has been deleted in the original program. The alternative plotting procedure is added at the end of the main program.)

c kwts: weighting of cross section?

c ksmo: smooth TOF data?

c ktel: create data file for plot?

c kwarn: skip cosine out of range warning? (This is used in calculating angles with Cosine Law)

c kcalc: calculate from input of cross section (no experimental data)?

c 'igat' is optimization output option:

c 1= suppress everything

c 2= show optimization progress for every 10 iteration

c 0= full output

c ncn: number of channels?

c lop: constraints applied for different channels.

c lop = 1 constrains $p(e)$ to be the same in both channels, $T(\theta)$ is reflected;

c for momentum-matched channels.

c kcmplot: calculate c.m. plot files? (including contour map, mesh plot, $P(E_T)$)

c distributions, $\langle E_T \rangle$)
 c ksurface: calculate mesh plot with surface in it? (The mesh plot is divided into
 c including two parts: upper and lower parts separated by surface. This is for
 c presentation purpose only. Notice: upper part is real, lower part is not.)

```

write(8,1203)
1203 format(' options:')
write(8,1216)q(kstp+1)
1216 format(' print newton diagram information? ',a3)
write(8,1204)q(kopt+1)
1204 format(' optimize center of mass angular function? ',a3)
write(8,1206)q(kpts+1)
1206 format(' energy distribution in point form? ',a3)
write(8,1208)q(kleg+1)
1208 format(' print center of mass angular distribution? ',a3)
write(8,1210)q(ktim+1)
1210 format(' number density (time) output? ',a3)
write(8,1214)q(kcmp+1)
1214 format(' plot center of mass flux contour map? ',a3)
write(8,1207)q(kwts+1)
1207 format(' weighting of cross sections? ',a3)
write(8,1209)q(ksmo+1)
1209 format(' smooth tof data? ',a3)
write(8,1121)q(ktel+1)
1121 format(' create data file for plot? ',a3)
write(8,1112) q(kwarn+1)
1112 format(' skip cosine out of range warning? ',a3)
write(8,1005) q(kcalc+1)
1005 format(' calculate only/no experimentaldata? ',a3)
write(8,*) ' number of channels:',ncn
write(8,2006) q(kcmplot+1)
2006 format('output c.m. contour and mesh plots? ', a3)
write(8,2007) q(ksurface+1)
2007 format('output c.m. contour and mesh plots with surface on? ', a3)

```

c Input the maximum value for c.m. velocity contour map (unit:10E4 cm/s) and # of
 c points

```
read(7,*) cm_u_max, n_cm_u
```

c Input the maximum value for c.m. E_T contour map (unit: kcal/mol) and # of points

```
read(7,*) cm_e_max, n_cm_e
```

c Input the number of angular divisions and the number of velocities/energies for the c.m.

c mesh plots. Notice: the mesh plot is not a real mesh. It's a combination of two

c groups of 3D trajectories, angular and radian.

```
read(7,*) na_mesh, nue
```

- c Input 3: 1) nvb(1): number of velocities in primary beam. For point form of incident beam, it's the number of points.
- c 2) nvb(2): number of velocities in secondary beam. For point form of incident beam, it's the number of points.
- c 3) number of beam intersection angles to be considered

```

read(7,*) nvb(1),nvb(2),ngam1,ngam2
if (ngam1.gt.7.or.ngam2.gt.7) then
    stop ' error: maximum ngam = 7 !!'
elseif (nvb(1).gt.50) then
    stop ' error: maximum nvb(1) = 50 !!'
elseif (nvb(2).gt.50) then
    stop ' error: maximum nvb(2) = 50 !!'
endif

```

- c Note: no error detected at execution time if ngam is set too large!!
- c Also: ngam should be odd!

- c Input 4: 1) mean beam intersection angle
- c 2) half width of primary and secondary beam

```

read(7,*) gamma,hw1,hw2

```

- c Input 5: beam parameters
- c Set ivels=1 for velocity selected beam.
- c hwidthb(1) is full width for velocity selected primary beam

```

read (7,*) ivels
if(ivels.eq.1) then
    read(7,*) hwidthb(1)

```

- c Input 6a: 1) velocity selector parameters and oven temperature

```

read(7,*) vs0,alph,vsbeta,vsgam,tmp
else

```

- c Input 7: primary nozzle beam parameters
- c Note: new option 4/88:
- c Input velocity distribution "manually". to do so, set s=0. and
- c read in distribution directly (does not have to be normalized)
- c vt(1): peak velocity, sr(1): speed ratio

```

read (7,*) vt(1),sr(1)
if (sr(1).eq.0.) then
    do 7321 i=1,nvb(1)

```

```

        read (7,*) vb(i,1),fb(i,1)
7321    continue
        endif
        endif

```

c Input 8: secondary nozzle beam parameters

```

        read (7,*) vt(2),sr(2)
        if (sr(2).eq.0.) then
            do 7322 i=1,nvb(2)
                read (7,*) vb(i,2),fb(i,2)
7322    continue
            endif

```

c Write beam conditions

c For velocity selected/nozzle primary beam; secondary nozzle beam:

```

        if(ivels .eq. 1) then
            write(8,1008) vs0,vsbeta,vsgam,alph
1008    format(7x,'v.s. param: pk vel,beta,gamma,alph:',5x,4f8.4)
            write(8,1014) tmp
1014    format(7x,'oven temperature = ',5x,f6.1)
            else
                write(8,1006) vt(1),sr(1)
1006    format(7x,'primary beam: peak velocity and speed ratio:',
1         5x,f8.4,5x,f8.4)
            endif
            write(8,1007) vt(2),sr(2)
1007    format(7x,'secondary beam: peak velocity and speed ratio:',
1         5x,f8.4,5x,f8.4)

```

c Write the number of velocities of of each beam to be averaged,
c reactant mases, product mass

```

23    write(8,1015) nvb(1),nvb(2)
1015    format(7x,'number of velocities averaged',7x,i4,5x,i4)

```

c Input 9: reactant masses

c Read in each product channel:

```
rel_w = 0
```

c rel_w is used to normalize rel(j).

```
do 81 j=1,ncn
```

```

      read(7,*) g1(j),g2(j)
c reactant masses for beam 1 and beam 2

```

```

      open(unit=10, file='output.txt', status='unknown')
      write (10,1009) g1(j),g2(j)
1009 format(7x,'reactant masses:',5x,2(f8.1,' amu  '))

```

c Input 10: channel weights

```

      read(7,*)rel(j)
c rel(j): weighting factor of this channel
      read(7,*)pmass(j)
c pmass: product mass
      write(8,*)' rel',j,'=' ,rel(j)
      pmas=pmass(j)
      nto=0
      gb(j) = pmas * (g1(j)+g2(j))/(g1(j)+g2(j)-pmas)
c gb(j) times u2 is ET

```

c Input 11: 1) number of legendre coefficients for center of mass angular distribution
c 2) option for use of 1)

c Input 11a-zz (optional)

c If center of mass angular intensities are to be input (no legendre coefficients, input the
c nleg angles for which intensity will be input.

```

      read(7,*)nleg(j),nang(j)
c nleg: number of terms of Legendre polynomial used
c nang(j): options for T( $\Theta$ ), nang(j) can be -1, 0, and 1. nang(j) = 1 means point form of
c T( $\Theta$ ); nang(j) = 0 or -1 means Legendre polynomial or miller form.
      if (nang(j).gt.0) then
        do 99 i=1,nleg(j)
99      read(7,*) to(i,j)
        to(nleg(j)+1,j)=0.
      endif

```

c Input 12a-z

c Legendre coefficients (or center of mass angular intensities) or Miller coeffs

```

      do 999 i=1,nleg(j)
999  read(7,*) po(i,j)
c The coefficients of each Legendre term is stored in po(i,j).
      po(nleg(j)+1,j)=0.
      if(nang(j).le.0)then
        write(8,1103)

```

```

1103  format(1x,'legendre coefficients')
      write(8,1104)(po(i,j),i=1,nleg(j))
1104  format(1x,5f8.3)
      endif

```

```

      write(8,1105)pmass(j)
1105  format(7x,'product mass = ',f10.3,' amu.')

```

c Input p(e) in point form

c Input 14 (optional): number of energies for which p(e) will be provided (maximum = 10)

```

      if (kpts.eq.1) then
c ET in point form, not RRK form.
      read(7,*) nen
      if (nen.le.0) stop ' number of energies must be positive !!'
      if (nen.gt.10) stop ' maximum number of energies = 10 !!'

```

c Input 15 (optional): 1) energy increment in p(e)

c 2) constant to be subtracted from collision energy

c 3) starting energy for p(e)

```

      read(7,*) den(j),ensub(j),enoff(j)
      write(8,1100)
1100  format(1x,'energy input')

```

c do for all energies (do loop to 994)

```

      do 994 i=1,nen

```

c Input 16a (optional): energies at which p(e)'s will be input

```

      read(7,*)en(i)
c en(i): collision energy, Ecoll.
      en(i)=en(i)-ensub(j)
      write(8,1101)en(i)
1101  format(1x,'collision energy: ',f10.3)

```

c Input 16b (optional) number of points in p(e) number i (max= 200)

```

      read(7,*)np(i,j)
c number of points
      npf(j)= np(i,j)
      if(npf(j).gt.200) then
        stop ' number of points in p(e) out of range !!'

```

end if

c Input 16c (optional): p(e) in point form

```

do 63 l=1,npf(j)
63  read(7,*) pe(l,i,j)

```

c Find peak in p(e)

```

peake(j) = 0.
jpeake(j) = 0
do 993 l=1,npf(j)
if(pe(l,i,j).le.peake(j)) go to 993
peake(j) = pe(l,i,j)
jpeake(j) = l
993  continue

```

c Normalize p(e) to unit area, and calculate mean energy

```

if(kopt.eq.0)then
c If kopt=1, the following few steps will be done later in optimization procedure.
area(j) = pe(1,i,j)
avge(j) = (pe(1,i,j)*enoff(j))
do 210 l=2,npf(j)
e(j) = enoff(j) + ((l-1) * den(j))
area(j) = area(j) + pe(l,i,j)
210  avge(j) = avge(j) + (pe(l,i,j) * e(j))

```

c Output number of points in p(e), energy increment, starting point of p(e), values of p(e),
c peak position and mean recoil energy from p(e),

```

write(8,1106) npf(j),den(j),enoff(j)
1106 format(1x,i5,' energies with a ',f9.5,' kcal/mole increment',
1  /,' starting at ',f9.5,' kcal/mole for the lowest value given.')
write(8,1102) (pe(l,i,j),l=1,npf(j))
1102 format(1x,20(/5f10.4))
write(8,212) (((jpeake(j)-1) * den(j)) + enoff(j))
1  ,(avge(j)/area(j))
212 format(/,' the peak of the p(e) is at ',f8.4,' kcal/mole.'
1  ,/,' the mean energy of the p(e) is at ',f8.4,' kcal/mole.',/)
area(j)=area(j)*den(j)
do 215 l=1,npf(j)
215  pe(l,i,j)= pe(l,i,j) /area(j)
c normalizes P(E) by area.
endif

```

```

994  continue
      if(nen.eq.1) then
        en(2)=800.
        np(2,j)=np(1,j)
        do 444 i=1,npf(j)
444   pe(i,2,j)=pe(i,1,j)
        endif
      else

```

c Get p(e) if not in point form

c Optional (13): read in RRK parameters: p, q, exo, b

```

      knorm=0
      read (7,*) (px(i,j),i=1,4)
      write(8,2000)(px(i,j),i=1,4)
2000  format(' rrk form for p(e) is used'
1     ,/, ' p = ',f7.3
1     ,/, ' q = ',f7.3
1     ,/, ' exo = ',f7.3
1     ,/, ' b = ',f7.3)
      enoff(j) = amax1(0.,px(4,j))

```

c amax1(x,y) is a built-in function.

```

      endif

```

c Close loop over product channels:

```

      ww(j)=gb(j)*.0023889

```

c When ww(j) times u^2 , the result is energy in kcal/mol. (u is in 10^4 cm/s)

```

      rel_w = rel_w + rel(j)

```

```

81    continue

```

```

      do 3456 j = 1, ncn

```

```

        rel(j) = rel(j)/rel_w

```

c normalizes rel(j).

```

3456  continue

```

c Input 17: 1) number of laboratory angles (to be input) for which the

c flux is to be calculated

c 2) number of velocities at each angle for which flux is to be calculated

```

      read(7,*)na,nv
      write(8,1220)na,nv
1220  format(' calculation is for ',i3,' angles ',i4
1     , ' velocities at each angle.')
      if(nv.gt.2500) stop ' maximum number of velocities (nv)=2500!!'

```

- c Input 18: 1) beginning velocity (in 1e04 cm/sec) in calculation
- c 2) increment in velocity in calculation

```
read(7,*)vz,dv
```

- c vz: beginning velocity
- c dv: velocity division. dv times nv is the maximum velocity that will be used to
- c calculate TOF distributions, which must be high enough to cover the whole range of
- c TOF. Also, dv should be sufficiently fine because it is the "resolution" that the program
- c calculates TOF distribution.

```
write(8,1221)vz,dv
```

```
1221 format(' starting with ',f7.3,' with ',f7.3,' spacing.')
```

```
do 7 iv=1,nv
```

```
7 vl(iv)=float(iv-1)*dv+vz
```

- c Input 18a (optional - only if kcalc=1)
- c cross section (z) to be used for calculation

```
if (kcalc.eq.1) read (7,*) zz
```

- c Input 19: 1) laboratory angle
- c 2) signal
- c 3) is there tof data at this angle (no = 1)

```
write(8,3000)
```

```
3000 format(' laboratory angular distribution'
```

```
1 ,/,5x,' angle    signal   tof at this angle?')
```

```
do 10 ia=1,na
```

```
read(7,*)aa,b(ia),idum(ia)
```

- c aa is the lab angle that relative to the incident direction of primary beam (beam 1)
- c b(ia) should be sum of N(t).

```
write(10,3001) aa,b(ia),q(2 - idum(ia))
```

```
3001 format(1x,f10.0,1x,f13.3,10x,a3)
```

```
a(ia)=aa*rad
```

- c changes the angle from degree to radian.

- c Read TOF data

```
if(ktim.eq.1.and.idum(ia).eq.0) then
```

- c Input 19a (optional): tof data options
- c 1) initial channel
- c 2) number of points
- c 3) dc value to be subtracted from each data point at this angle

```

        read(7,*) ntb(ia), nch(ia),dc
        write (8,2881) nch(ia),ntb(ia),dc
2881  format(' time of flight data: ',/,1x
1      ,i4,' points starting with'
1      , ' channel ',i4,'. '
1      ,/,1x,f14.6,' is to be subtracted from each point.')
        nit = nch(ia)

```

- c Input 19aa: option for excluding sections of tof from chi calculation
- c ir= number of sections excluded (max 10) 0 if none
- c then list min and max flight time (usec) of sections to be excluded

```

        read(7,*) ir
        if (ir.ne.0) then
            do 333 i=1,ir
333  read(7,*) tmin(i,ia),tmxx(i,ia)
c These two are time, not channel.
            endif
            write(8,*) ir, ' areas excluded from tof chi'
            write(8,*) ' excluded times:',(tmin(i,ia),tmxx(i,ia), i=1,ir)

```

- c Input 19b-z: tof data at angle aa
- c (if data are calculated only, no tof input)

```

        if (kcalc.ne.1) then
            read(7,*) (tdat(it,ia),it=1,nit)
c tdat stores TOF data.
            do 32 it=1,nit
32  tdat(it,ia) = tdat(it,ia) - dc
            write (8,2882) (tdat(it,ia),it=1,nit)
2882  format(256(8(1x,f9.0,:),/))
            endif
            endif
10  continue

```

```

        if(ktim.eq.1) then

```

- c Input 20: detector parameters
- c 1) ion flight time constant ($\Rightarrow$ ion flight time = $x_{ion}(\sqrt{\text{ion mass}})$))
- c 2) ion mass (amu)
- c 3) ionizer length (in cm)
- c 4) neutral flight path (in cm)
- c 5) dwell time per channel(usec)
- c 6) offset (usec)

```
read(7,*)xion,xims,size,path,time,of
```

c Input 21: TOF wheel parameters

- c 1) wheel speed
- c 2) wheel diameter
- c 3) wheel slit size (in mm)
- c 4) detector slit size (in mm)

```
read(7,*) hz, dia, sa, sb
```

```
call trap
```

```
path=path*100.
```

```
dl=size*5.
```

```
pat=path-size*50.
```

c Write detector parameters

```
write(8,1217)xion,xims,size,of
```

```
1217 format(' alpha = ',f6.3,/, ' ion mass = ',f6.1
```

```
1 ,/, ' ionizer = ',f4.2, ' cm',3x,'offset = ',f7.2)
```

```
write(8,1218)path/100.,time
```

```
1218 format(' product flight length = ',f6.2, ' cm'
```

```
1 ,5x,'time/channel = ',f3.0, ' usec')
```

```
write(8,1219) hz, dia, sa, sb
```

```
1219 format(/, ' wheel frequency = ',f7.2
```

```
1 , ' hz wheel diameter = ',f6.2
```

```
1 , ' cm',/, ' wheel slit = ',f6.2
```

```
1 , ' mm detector slit = ',f5.2, ' mm',/)
```

c If smoothing is to be done

```
if(ksmo.eq.1) then
```

c Input 22: number of channels for TOF smoothing

```
read(7,*)nm
```

```
nmh=nm/2
```

```
nm=nmh*2+1
```

```
write(8,1222)nm
```

```
1222 format(' perform a ',i5, ' channel smooth on the tof data.')
```

```
do 49 ia=1,na
```

```
if(idum(ia).ne.0)go to 49
```

```
nib=nmh+1
```

```
nit=nch(ia)-nmh
```

```
do 48 it=nib,nit
```

```

        sum(j)=0.
        nm=it-nmh-1
        do 47 n=1,nm
47      sum(j)=sum(j)+tdat(nm+n,ia)
48      tdat(it,ia)=sum(j)/nm
49      continue
        endif
        endif

```

c Input if optimization is to be done:

```
13      if(kopt.eq.1) then
```

c Input 23: parameters of optimization

- c 1) number of parameters to be fit
- c 2) maximum number of iterations
- c 3) option regarding what data to use for fit

```
        read(7,*)nopt,itmax,nto
```

- c use 1 as the value of nto. The value of nto will be changed in the program.
- c The meaning of nto is explained in subroutine ti.

c Weight of ang dist chi in determining total chi

```
        read(7,*)chiwt
```

- c Here, important note for χ^2 calculation in optimization. χ^2 can have two components:
- c difference in angular distribution and difference in each point of TOF.
- c $\chi^2 = \text{chiwt} * \text{SUM}(\text{square of difference in angular distribution}) +$
- c $\text{SUM}(\text{square of difference of each TOF point})$

```
        write(8,*) ' weight of ang dist chi is ', chiwt
        if((nto.ge.1).and.(ktim.eq.0)) nto=0
```

c Input 24: list of parameters to be varied

- c input is k(i) for i=1 to total number of parameters to vary
- c 1 to n are t(th)for chan 1 where n=nleg(1)
- c n+1 to m are p(e) for chan 1; m-n=# of points in p(e) or 4 if rrk
- c m+1 is rel(1)
- c m+2 to p is t(th) for chan2, etc

- c i is the index of the parameters that will be optimized.
- c k(i) is the real index of each parameter, starting from 1 to total number of parameters.
- c You can optimize certain parameteres by only inputting the correspoinding k(i)s.
- c See examples of input file.

```
read(7,*)(k(i),i=1,nopt)
```

c Input 25: radius of fit

```
read(7,*)radius
```

c Criterion of termination of optimization. Defined as difference in twp sequential steps
c divided by the sum.

```
endif
```

c (optimization input)

c Read energy weights if kwts=yes was specified.

c Inputs 26-28 optional

```
if (kwts.eq.1) then
```

c Read the number of cross sections to be entered

```
read(7,*)new
```

c Read the energy in kcal/mole, then the relative cross section

```
read(7,*)(ew(i),i=1,new)
```

```
read(7,*)(sig(i),i=1,new)
```

```
write(8,1001)
```

```
1001 format(///,'cross section weighting:!',/
```

```
1  , 'enery  relative cross section')
```

```
do 8 i=1,new
```

```
8  write(10,1002) ew(i),sig(i)
```

```
1002 format(1x,f6.2,10x,f10.4)
```

```
endif
```

c End of input

c**** calculate t(theta), fraction forward scattered (forw)

c (kk is set = 1 for call of eval: indicates that only t(theta)

c will be calculated)

```
kk=1
```

```
ca=0.
```

```
tsum=0.
```

```
ddt=fdeg/5.
```

c fdeg is the radian of 5 degree. So ddt is equal to 1 degree.

```

theta=-ddt/2.
do 219 j=1,ncn
tnorm(j)=0
do 219 i=1,180
theta=theta+ddt
call eval(po,j)

```

c Only t is returned because kk=1.

```

tnorm(j)=tnorm(j)+t*abs(sin(theta))
219 continue
do 21 j=1,ncn
rela(j)=rel(j)/tnorm(j)

```

c Weighting factor of each channel is changed to include T(theta) term.

```

write(10,*)j, tnorm(j) rela(j)='j,tnorm(j), rela(j)
do 21 i=1,180
theta=theta+ddt
call eval(po,j)
tsum=tsum+t*abs(sin(theta))*rela(j)
21 if(i.eq.901.and.j.eq.ncn) tsum90 = tsum
forw = tsum90 / tsum
tsum=tsum*ddt
kk=0

```

c kk is set to 0 after this.

c*** calculate and print newton diagram information

```

write(8,1242)
1242 format(' ')
do 7323 i=1,ncn
call newt1(i)
7323 continue

```

c Normalize the p(e) if rrk form is used

c ngrid and ec(ijk,j) are brought back from calling subroutine newt1(i). The following is
c a loop over total number of Newton diagrams, ngrid.

```

if(kpts.eq.0.and.kopt.eq.0) then
do 888 j=1,ncn
do 888 ijk=1,ngrid
et(j) = px(3,j)+ec(ijk,j)

```

c px(3,j) is the exothermicity.

c ec(ijk,j) is E_{coll}

c The energy increment will be: $e/1000$

```

de(j)=et(j)/1000.
area(j)=0.
e(j)=-de(j)/2.
do 889 i=1,1000
e(j) = e(j) + de(j)
if(e(j).gt.px(4,j)) then
pin = et(j) - e(j)
pin=(pin**px(2,j))*((e(j)-px(4,j))**px(1,j))
c RRK form of P(ET).
area(j)=area(j)+pin
endif
889 continue
rarea(ijk,j) = area(j) * de(j)
888 continue
endif

```

c*** Perform convolution over newton diagrams -> lab ang distr, and chi

```

kdum1=0
abb=0.

```

c Obsolete note: i'm using "z" to transfer the value of gb into subroutine chi for jacobian
c transformation, because g1 is changed in newt1 and z gets calculated only after all the
c transformations are done! when z comes back from chi it is the scalefactor!
c AMS 6/1/87

```

if(kopt.eq.0) call chi(po)

```

c c.m. to lab transformation is done in subroutine chi(po).

c *****optimization*****

```

if(kopt.ne.0)then
mpts=nopt+1
itt=0

```

c itt is the index number of iteration of optimization.

c Define sequence of parameters:

c i is the parameter index

c k(i) is the parameter number

c "nibe" is a flag calling for constraint of parameter to positive values.

```

do 4443 j=1,ncn+1

```

c The original program had a bug here, j was from 0 to ncn, which is not supported by

c Fortran due to 0 index of array element. It has been fixed in this following optimization

c steps and in the sunroutine param(po). J.Z. July, 2001.

```

      ngg(j)=0
      ngh(j)=0
4443  continue

```

c define p(e) array if rrk form:

```

      if(kpts.eq.0)then
      do 4343 j=1,ncn
      do 4343 i=1,4
      pe(i,1,j)=px(i,j)
      npf(j)=4
4343  continue
      endif

```

c Define parameters: poz(k(i)) is the set which will actually be varied by param routine.

```

      do 4944 j=2,ncn+1
      if(nang(j-1).le.0) then
      ngg(j)=ngh(j-1)+nleg(j-1)
c ngg(j) is Legendre coefficients of channel j.
c ngh(j) is the total number of parameters of channel j.
      ngh(j)=ngg(j)+npf(j-1)+1
c npf(j) is number of points in point form of ET. "1" is the last parameter, rel(j).
      else
      ngg(j)=ngh(j-1)+nleg(j-1)+nang(j-1)*nleg(j-1)
      ngh(j)=ngg(j)+npf(j-1)+1
      endif
4944  continue
      do 4444 i=1,nopt
      do 4444 j=2,ncn+1
      if(k(i).gt.ngh(j-1).and.k(i).le.ngg(j))then
      if(nang(j-1).le.0)then
      nibe(k(i))=0
      poz(k(i))=po((k(i)-ngh(j-1)),j-1)
      else
      if((k(i)-ngh(j-1)).le.nleg(j-1)) then
      poz(k(i))=alog(to(k(i)-ngh(j-1),j-1))
      else
      poz(k(i))=alog(po((k(i)-ngh(j-1)-nleg(j-1)),j-1))
      endif
      nibe(k(i))=1
      endif

```

c The above part is for Legendre coefficients.

else

if(k(i).lt.nggh(j).and.k(i).gt.ngg(j))then

if(kpts.eq.1)then

poz(k(i))=alog(pe((k(i)-ngg(j)),1,j-1))

c Point form of P(E_T).

nibe(k(i))=1

else

do 3434 m=1,2

if(k(i).eq.(ngg(j)+m))then

nibe(k(i))=1

poz(k(i))=alog(pe(m,1,j-1))

c p and q of RRK form.

endif

3434 continue

do 3435 m=3,4

if(k(i).eq.(ngg(j)+m))then

nibe(k(i))=0

poz(k(i))=pe(m,1,j-1)

c exo and b of RRK form.

endif

3435 continue

endif

endif

if(k(i).eq.nggh(j))then

poz(k(i))=alog(rel(j-1))

nibe(k(i))=1

endif

c rel(j).

endif

c poz(k(i)) contains the values of parameters. For values of p, q in RRK form, log values are used.

c poz(1) to poz(nleg) is Legendre coefficients. poz(nleg+1) to poz(m) is the parameters

c of RRK form or point form of E_T. poz(m+1) is rel(j).

c Close loops over channels and parameters:

4444 continue

c Initialize hip array which contains matrix of parameters:

c "gang" is the initial increment by which one parameter in each

c "hip" vector is varied.

do 5550 i=1,nopt

```

        hip(1,i)=poz(k(i))
        do 5550 j=2,mpts
            hip(j,i)=hip(1,i)
            if(j.eq.(i+1)) hip(j,i)=gang*hip(j,i)
c gang = 1.05 (in earlier part of main program)
5550 continue

```

c Initialize why array: "why" array contains values of chisq corresponding to each "hip"
c vector.

```

        do 5551 i=1,mpts
            chis=0.
            abb=0.
            do 5552 j=1,nopt
                poz(k(j))=hip(i,j)
5552 continue
            call param(po)

```

c For every row of hip matrix, param(po) is called and χ^2 is calculated.

```

        why(i)=chit
        print *, 'why', i, '=', why(i)
        write(8,*) 'why', i, '=', why(i)
        write(10,*) 'why', i, '=', why(i)
5551 continue

```

c Begin optimization

c ihi: index of highest why
c inhi: index of second highest why
c ilo: index of lowest why

```

5001 ilo=1
        if(why(1).gt.why(2))then
            ihi=1
            inhi=2
        else
            ihi=2
            inhi=1
        endif
        do 5002 i=1,mpts
            if(why(i).lt.why(ilo)) ilo=i
            if(why(i).gt.why(ihi))then
                inhi=ihi
                ihi=i
            else if(why(i).gt.why(inhi))then
                if(i.ne.ihi) inhi=i

```

```
endif
5002 continue
```

c output control: meaning of igat is explained in the input section of the main program.

```
if(igat.ne.1)then
if(igat.eq.2)then
igle=int(itt/10)
igle=igle*10
if(igle.eq.itt)go to 5902
go to 5903
endif
```

c When igat = 2, output at each 10 iteration:

```
5902 print*, 'after iteration #',itt, ' , best parameters are:'
print *, ' chisquare=',why(ilo)
write(8,*) 'after iteration #',itt, ' , best parameters are:'
write(8,*) ' chisquare=',why(ilo)
write(10,*) 'after iteration #',itt, ' , best parameters are:'
write(10,*) ' chisquare=',why(ilo)
do 5133 j=1,nopt
if (nibe(k(j)).eq.1)then
write(10,*)k(j), ' =',exp(hip(ilo,j))
else
write(10,*)k(j), ' =',hip(ilo,j)
endif
5133 continue
5903 endif
c !(output)
```

c Check tolerance and increment iteration number:

```
rtol=2.*abs(why(ihi)-why(ilo))/(abs(why(ihi))+abs(why(ilo)))
if(rtol.lt.radius)go to 5999
if(itt.eq.itmax) go to 5999
itt=itt+1

do 5003 j=1,nopt
pbar(j)=0.
5003 continue
```

c Begin simplex manipulation:

```
do 5005 i=1,mpts
```

```

    if(i.ne.ihj)then
    do 5004 j=1,nopt
    pbar(j)=pbar(j)+hip(i,j)
5004  continue
    endif
5005  continue
    do 5006 j=1,nopt
    pbar(j)=pbar(j)/nopt
    pr(j)=(1.+alpha)*pbar(j)-alpha*hip(ihj,j)
    poz(k(j))=pr(j)
5006  continue
    call param(po)
    ypr=chit
    if(ypr.le.why(ilo))then
    if(igat.eq.0)write(10,*)' good reflection'
    do 5008 j=1,nopt
    prr(j)=gams*pr(j)+(1.-gams)*pbar(j)
    poz(k(j))=prr(j)
5008  continue
    call param(po)
    ypr=chit
    if(ypr.lt.why(ilo)) then
    if(igat.eq.0)write(10,*)' good expansion'
    do 5017 j=1,nopt
    hip(ihj,j)=prr(j)
5017  continue
    why(ihj)=ypr
    else
    if(igat.eq.0)write(10,*)' failed expansion'
    do 5018 j=1,nopt
    hip(ihj,j)=pr(j)
5018  continue
    why(ihj)=ypr
    endif
    else if(ypr.ge.why(inhj))then
    if(ypr.lt.why(ihj))then
    if(igat.eq.0)write(10,*)' reflection replaces high point'
    do 5019 j=1,nopt
    hip(ihj,j)=pr(j)
5019  continue
    why(ihj)=ypr
    endif
    if(igat.eq.0)write(10,*)' try intermediate point'
    do 5021 j=1,nopt
    prr(j)=0.5*(hip(ihj,j)+pbar(j))

```

```

    poz(k(j))=pr(j)
5021  continue
    call param(po)
    ypr=chit
    if(ypr.lt.why(ihi))then
    if(igat.eq.0)write(10,*)' intermediate point accepted'
    do 5022 j=1,nopt
    hip(ihi,j)=pr(j)
5022  continue
    why(ihi)=ypr
    else
    do 5024 i=1,mpts
    if(i.ne.ilo)then
    if(igat.eq.0)write(10,*)' contract around minimum'
    do 5023 j=1,nopt
    pr(j)=0.5*hip(i,j)+0.5*hip(ilo,j)
    poz(k(j))=pr(j)
    hip(i,j)=pr(j)
5023  continue
    call param(po)
    why(i)=chit
    endif
5024  continue
    endif
    else
    if(igat.eq.0)write(10,*)' middling reflection accepted'
    do 5025 j=1,nopt
    hip(ihi,j)=pr(j)
    poz(k(j))=pr(j)
5025  continue
    why(ihi)=ypr
    endif
    go to 5001
5999  continue

```

c Type out current parameter values after iteration and end optimization

```

print *, ' optimized fit parameters are:'
write(8,*)' optimized fit parameters are:'
write(10,*)' optimized fit parameters are:'
print *, ' chisquare=',why(ilo)
write(8,*)' chisquare=',why(ilo)
write(10,*)' chisquare=',why(ilo)
do 5132 j=1,nopt
if(nibe(k(j)).eq.1)then

```

```

        write(8,*) k(j),'=',exp(hip(ilo,j))
        write(10,*) k(j),'=',exp(hip(ilo,j))
        print*,k(j),'=',exp(hip(ilo,j))
        else
        print*,k(j),'=',hip(ilo,j)
        write(8,*)k(j),'=',hip(ilo,j)
        write(10,*)k(j),'=',hip(ilo,j)
        endif
5132  continue
      nto=0
      endif
c It's a long if-endif loop!
c ! End optimization

c*** Begin output

      if(kleg.eq.1) then
      kk = 1
      ca = 0.
      theta = 0.

c Write out final center of mass angular distribution
      write(8,1120)
1120  format(' angle',5x,'leg(a)')
      do 54 i=1,37
      do 53 j=1,ncn
      call eval(po,j)
      t=t*rela(j)
53    tr=tr+t
      the = theta/rad
      write(8,1119) the,tr
1119  format(2x,f4.0,4x,f7.3)
54    theta = theta + .0872665
      kk = 0
      endif

c Write exp. and calc. lab angular distributions

      write(8,991) 12
      write(8,992)
      do 57 ia=1,na
      a(ia)=a(ia)/rad
      write(8,1993)a(ia),b(ia),sumf(ia),xd(ia),sumf(ia)/z
57    continue
991  format(1x,a1,/, ' product angular distribution')

```

```

992  format(' lab angle',5x,'expt int',6x,'calc intensity'
1    ,3x,'difference',6x, 'unscaled data')
1993 format(2x,f6.1,6x,f8.0,8x,f11.3,6x,e10.3,6x,f11.6)
      if(ktel.eq.1)then

```

c Create angular distribution data file for plotting program

```

      open (unit=9, file='monbang.txt', status='unknown')
      write (9,1339) (a(ia),b(ia),sumf(ia),ia=1,na)
1339  format(1x,f6.1,f10.0,f10.0)
      close (unit=9)
      endif
      write(8,1240) 12,z,(100.*forw)
1240  format(1x,a1,/, ' nominal cross section: 1.000'
1    ,/, ' integrated cross section = ',e10.4
2    ,/,1x,f5.1, '% forward scattered.')
      if(ktim.ne.0) call ti
      do 95 i=1,na
95    a(i)=a(i)*rad

```

c Point form p(e): for printer plot*****

```

      do 666 j=1,ncn
      pmax(j)=0.
      if(kpts.eq.1) then
      npf(j)=np(1,j)
      emax(j)=(npf(j)-1)*den(j) + enoff(j)
      dden(j)=emax(j)/100.
      ez(j)=-dden(j)
      pe(npf(j)+1,1,j)=pe(npf(j),1,j)
      do 92 i=1,101
      ez(j)=ez(j)+dden(j)
      pn(i,j) = 0.
      f = ((ez(j) - enoff(j)) / den(j)) + 1.0
      kf = int(f)

```

c If ez is below the threshold energy enoff, p(e)=0

```

      if(kf.le.0) go to 92
      f = f - kf
      pn(i,j) = pe(kf,1,j)+f * (pe(kf+1,1,j)-pe(kf,1,j))
92    pmax(j) = amax1(pmax(j),pn(i,j))

```

c Point form: for tellagraff files****

```

      pmax1=0.

```

```

do 920 l=1,npf(j)
920  if (pmax1.lt.pe(l,1,j)) pmax1 = pe(l,1,j)
do 921 l=1,npf(j)
921  pe(l,1,j) = pe(l,1,j)/pmax1
else

```

c RRK form of $p(e)$ ****

```

ijk=mp
emax(j)=ec(mp,j)+px(3,j)
dden(j)=emax(j)/100.
e(j)=-dden(j)
do 120 i=1,101
e(j)=e(j)+dden(j)
call energy(j)
pn(i,j)=pin
pmax(j)=amax1(pmax(j),pin)
120  continue
if (ktel.eq.1) e(j)=-dden(j)
endif

```

c create data file of normalized $p(e)$

```

if (ktel.eq.1)then
if(j.eq.1) open(unit=9, file='monpe1.txt', status='unknown')
if(j.eq.2) open(unit=9, file='monpe2.txt', status='unknown')
if(j.eq.3) open(unit=9, file='monpe3.txt', status='unknown')
if(j.eq.4) open(unit=9, file='monpe4.txt', status='unknown')
if(j.eq.5) open(unit=9, file='monpe5.txt', status='unknown')
if(j.eq.6) open(unit=9, file='monpe6.txt', status='unknown')
if(j.eq.7) open(unit=9, file='monpe7.txt', status='unknown')
if(j.eq.8) open(unit=9, file='monpe8.txt', status='unknown')
if(j.eq.9) open(unit=9, file='monpe9.txt', status='unknown')
if(j.eq.10) open(unit=9, file='monpe10.txt', status='unknown')
endif
if (kpts.eq.1) then
e(j)=0.
do 959 l=1,npf(j)
write (9,1011) (e(j)+enoff(j)),pe(l,1,j)
959  e(j)=e(j)+den(j)
else
do 196 i=1,101
pn(i,j)=pn(i,j)/pmax(j)
e(j)=e(j)+dden(j)
196  write (9,1011) e(j), pn(i,j)

```

```

endif
if(ktel.eq.1) close (unit=9)
666 continue

```

```

1011 format(2x,f6.2,2x,f6.2)
c Printer plot of t(theta) and p(e)

```

```

      if (kpts.eq.1) then
      do 121 j=1,ncn
      do 121 i=1,101
121   pn(i,j)=pn(i,j)/pmax(j)
      endif
      tmax=0.
      kk=1
      pif=.0314159
      theta=-pif
      do 122 i=1,101
      theta=theta+pif
      th(i)=theta/rad
      do 9876 j=1,ncn
      call eval(po,j)
9876   tp(i)=t+tp(i)
122    tmax=amax1(tmax,tp(i))
      do 123 i=1,101
123    tp(i)=tp(i)/tmax

```

```

c Plot p(e) and t(theta)

```

```

c Data file for t(theta)

```

```

      if (ktel.eq.1)then
      kk=1
      pif=.0314159
      do 9800 iiii = 1 , ncn
      theta=-pif
      write(itype,9801)iiii
9801  format('montt',i1,'.txt')
      open(unit=9,file=itype,status='unknown')
      theta = -pif
      do 9802 i=1,101
      theta=theta+pif
      th(i)=theta/rad
      call eval(po,iiii)
      write(9,1238) 57.3*theta,t
1238  format(1x,f6.1,f14.3)

```

```

9802  continue
      close(9)
9800  continue
      endif

      emax(j)=emax(j)/5.
      write(8,1247)(emax(j)*(i-1),i=1,6)
1247  format(8x,f6.2,5(14x,f6.2))
      kk=0
      close(8)
      close(10)

```

c Begin c.m. contour and mesh plot calculation.

```
if(kcmplot .eq. 1) then
```

c Plot c.m. velocity and E_T contour maps.

```

      kk = 0
      u_step = cm_u_max/n_cm_u
      e_step = cm_e_max/n_cm_e

      do 6660 i = 1, n_cm_u
        ux(i) = -u_step*(n_cm_u - i + 1)
        uy(i) = -u_step*(n_cm_u - i + 1)
6660    continue

      ux(n_cm_u + 1) = 0
      uy(n_cm_u + 1) = 0

      do 6661 i = 1, n_cm_u
        ux(n_cm_u + 1 + i) = u_step*i
        uy(n_cm_u + 1 + i) = u_step*i
6661    continue

      do 6662 i = 1, n_cm_e
        ex(i) = -e_step*(n_cm_e - i + 1)
        ey(i) = -e_step*(n_cm_e - i + 1)
6662    continue

      ex(n_cm_e + 1) = 0
      ey(n_cm_e + 1) = 0

      do 6663 i = 1, n_cm_e

```

```

        ex(n_cm_e + 1 + i) = e_step*i
        ey(n_cm_e + 1 + i) = e_step*i
6663  continue

        pumax = 0
        pemax = 0

        do 6664 i = 1, (2*n_cm_u+1)
        do 6664 ii = 1, (2*n_cm_u+1)
            uu = abs(ux(i))*abs(ux(ii)) + abs(uy(ii))*abs(uy(ii))
            u = sqrt(uu)
            ca = ux(i)/u
            cau(i,ii) = ca

            putemp = 0
            do 6665 j = 1, ncn
            e(j) = gg(j)*uu
            do 6665 ijk = 1, ngrid
            call eval(po,j)
            pan = rela(j)*pin*gb(j)/(6.28319*tsum)
            putemp = putemp + (fabg(ijk,j)*u*pan)
6665  continue

            ucont(i,ii) = putemp
            pumax = amax1(pumax, putemp)
6664  continue
            if(pumax .eq. 0) pumax = 1

            do 6666 i = 1, (2*n_cm_e+1)
            do 6666 ii = 1, (2*n_cm_e+1)
                eee = sqrt(abs(ex(i))*abs(ex(ii)) + abs(ey(ii))*abs(ey(ii)))
                ca = ex(i)/eee
                cae(i,ii) = ca

                petemp=0
                do 6667 j = 1, ncn
                e(j) = eee
                do 6667 ijk = 1, ngrid
                call eval(po,j)
                pan = rela(j)*pin*gb(j)/(6.28319*tsum)
                petemp = petemp + (fabg(ijk,j)*pan)
6667  continue

                econt(i,ii) = petemp
                pemax = amax1(pemax, petemp)

```

```

6666 continue
      if(pemax .eq. 0) pemax = 1

      open(unit=19, file='cont_u.txt', status='unknown')
      open(unit=18, file='cont_e.txt', status='unknown')

c      Write the data to file: in the XYZ triplet format!

      do 6668 ii = 1, (2*n_cm_u+1)
      do 6668 i = 1, (2*n_cm_u+1)
      if((ii .eq. n_cm_u+1) .and. (i .eq. n_cm_u+1)) ucont(i,ii) = 0
      ucont(i,ii) = ucont(i,ii)/pumax
      write(19,*) 100*ux(i), 100*uy(ii), ucont(i,ii)
6668 continue

      do 6669 ii = 1, (2*n_cm_e+1)
      do 6669 i = 1, (2*n_cm_e+1)
      if((ii .eq. n_cm_e+1) .and. (i .eq. n_cm_e+1)) econt(i,ii) = 0
      econt(i,ii) = econt(i,ii)/pemax
      write(18,*) 4.186*ex(i), 4.186*ey(ii), econt(i,ii)
6669 continue

      close(19)
      close(18)

```

c Plot c.m. velocity and E_T mesh maps (use the same ranges as the contour maps)

c Angle is from 0 to 360 degree.

```

      kk = 0
      u_step = cm_u_max/nue
      e_step = cm_e_max/nue

      a_step = 2*3.14159/na_mesh
      pu_max = 0
      pe_max = 0

      do 6670 i = 1, nue+1
      u = (i-1)*u_step
      eet = (i-1)*e_step
      do 6670 ia = 1, na_mesh+1
      ca = cos((ia-1)*a_step)
      sa = sin((ia-1)*a_step)
      ux_r(i, ia) = u*ca
      uy_r(i, ia) = u*sa
      ex_r(i, ia) = eet*ca

```

```

    ey_r(i, ia) = eet*sa
    putemp = 0
    petemp = 0
    do 6671 j = 1, ncn
    e(j) = gg(j)*u*u
    do 6111 ijk = 1, ngrid
    call eval(po,j)
    pan = rela(j)*pin*gb(j)/(6.28319*tsum)
    putemp = putemp + (fabg(ijk,j)*u*pan)
6111 continue
    e(j) = eet
    do 6112 ijk = 1, ngrid
    call eval(po,j)
    pan = rela(j)*pin*gb(j)/(6.28319*tsum)
    petemp = petemp + (fabg(ijk,j)*pan)
6112 continue
6671 continue
    pu_max = amax1(pu_max, putemp)
    pe_max = amax1(pe_max, petemp)
    umesh_r(i, ia) = putemp
    emesh_r(i, ia) = petemp
6670 continue

    do 6672 ia = 1, na_mesh+1
    ca = cos((ia-1)*a_step)
    sa = sin((ia-1)*a_step)
    do 6672 i = 1, nue+1
    u = (i-1)*u_step
    eet = (i-1)*e_step
    ux_a(ia, i) = u*ca
    uy_a(ia, i) = u*sa
    ex_a(ia, i) = eet*ca
    ey_a(ia, i) = eet*sa
    putemp = 0
    petemp = 0
    do 6673 j = 1, ncn
    e(j) = gg(j)*u*u
    do 6113 ijk = 1, ngrid
    call eval(po,j)
    pan = rela(j)*pin*gb(j)/(6.28319*tsum)
    putemp = putemp + (fabg(ijk,j)*u*pan)
6113 continue
    e(j) = eet
    do 6114 ijk = 1, ngrid
    call eval(po,j)

```

```

pan = rela(j)*pin*gb(j)/(6.28319*tsum)
petemp = petemp + (fabg(ijk,j)*pan)
6114 continue
6673 continue
pu_max = amax1(pu_max, putemp)
pe_max = amax1(pe_max, petemp)
umesh_a(ia, i) = putemp
emesh_a(ia, i) = petemp
6672 continue

if(pu_max.eq. 0) pu_max = 1
if(pe_max.eq. 0) pe_max = 1
do 6674 i = 1, nue+1
do 6674 ia = 1, na_mesh+1
umesh_r(i, ia) = umesh_r(i, ia)/pu_max
emesh_r(i, ia) = emesh_r(i, ia)/pe_max
umesh_a(ia, i) = umesh_a(ia, i)/pu_max
emesh_a(ia, i) = emesh_a(ia, i)/pe_max
6674 continue

open(unit=17, file='mesh_u_a.txt', status='unknown')
open(unit=16, file='mesh_u_r.txt', status='unknown')
open(unit=15, file='mesh_e_a.txt', status='unknown')
open(unit=14, file='mesh_e_r.txt', status='unknown')

```

c Mesh plots here means 3D trajectory plots. Mesh plots files are in numbers of XYZ
c columns. Columns 1-3 are xyz of the first 3D curve; columns 4-6 are xyz of second 3D
c curve; and so on. Files with name *_a.txt are the 3D curves for different angles, while
c files with name *_r.txt are for different radius.

```

do 6675 ia = 1, na_mesh+1
write(17, 6676) ((ux_r(i, ia)*100, uy_r(i, ia)*100,
1 umesh_r(i, ia)), i = 1, nue+1)
write(15, 6676) ((ex_r(i, ia)*4.186, ey_r(i, ia)*4.186,
1 emesh_r(i, ia)), i = 1, nue+1)
6675 continue
6676 format(300(f9.2, 1x, f9.2, 1x, f7.4, 1x))

do 6677 i = 1, nue+1
write(16, 6678) ((ux_a(ia, i)*100, uy_a(ia, i)*100,
1 umesh_a(ia, i)), ia = 1, na_mesh+1)
write(14, 6678) ((ex_a(ia, i)*4.186, ey_a(ia, i)*4.186,
1 emesh_a(ia, i)), ia = 1, na_mesh+1)
6677 continue
6678 format(200(f9.2, 1x, f9.2, 1x, f7.4, 1x))

```

```
close(17)
close(16)
close(15)
close(14)
```

```
if(ksurface .eq. 1) then
```

c Output the 3D curve for presenting the surface, assuming incident angle of 60 degree.

```
theta_i = 60
theta_max = (90 - theta_i)*3.1415926535/180
theta_min = 3.1415926535 - theta_max
aaaa = c(mp,1)
bbbb = cm_u_max
cccc = aaaa*cos(theta_max) + sqrt(bbbb*bbbb -
1 aaaa*aaaa*sin(theta_max)*sin(theta_max))
x_max = cccc*cos(theta_max) - aaaa
cccc = aaaa*cos(theta_min) + sqrt(bbbb*bbbb -
1 aaaa*aaaa*sin(theta_min)*sin(theta_min))
x_min = -cccc*cos(theta_max) - aaaa

x_step = (x_max - x_min)/nue
open(unit=111, file='surface_u.txt', status='unknown')

do 9655 i = 1, nue+1
xu = x_min + x_step*(i-1)
yu = (xu + aaaa)*tan(theta_max)
u = sqrt(xu*xu + yu*yu)
ca = xu/u

putemp = 0

do 9654 j = 1, ncx
e(j) = gg(j)*u*u
do 9654 ijk = 1, ngrid
call eval(po,j)
pan = rela(j)*pin*gb(j)/(6.28319*tsum)
putemp = putemp + (fabg(ijk,j)*u*pan)
9654 continue
putemp = putemp/px_max
write(111,*) xu*100, yu*100, putemp
9655 continue
close(111)
```

- c Output c.m. velocity mesh plot (use the same ranges as the contour maps)
 c which is divided into upper and lower parts due to the presense of the surface.

```

a_surf_min = acos(x_max/cm_u_max)
a_surf_max = acos(abs(x_min)/cm_u_max) + 3.1415926535

do 6695 ia = 1, na_mesh

  write(ityp,1089)ia
1089  format('mesh_up_r',i2,'.txt')
      open(unit=9,file=ityp,status='unknown')
      write(ityp,1099)ia
1099  format('mesh_down_r',i2,'.txt')
      open(unit=10,file=ityp,status='unknown')

  ca = cos((ia-1)*a_step)
  tana = tan((ia-1)*a_step)

  if(((ia-1)*a_step .ge. a_surf_min) .and.
1   ((ia-1)*a_step .le. a_surf_max)) then

    x0 = c(mp,1)*tan(theta_max)/(tana - tan(theta_max))
    y0 = (x0 + c(mp,1))*tan(theta_max)
    u = sqrt(x0*x0 + y0*y0)
    putemp = 0
    do 445 j = 1, ncn
      e(j) = gg(j)*u*u
      do 445 ijk = 1, ngrid
        call eval(po,j)
        pan = rela(j)*pin*gb(j)/(6.28319*tsum)
        putemp = putemp + (fabg(ijk,j)*u*pan)
445   continue
      putemp = putemp/pu_max

c The first point of the mesh_up_r curve.
      write(9,*) x0*100, y0*100, putemp

    endif

    do 915 i = 1, nue+1
      if(uy_r(i,ia) .gt. (tan(theta_max)*(ux_r(i,ia)+aaaa))) then
        write(9,*) ux_r(i,ia)*100, uy_r(i,ia)*100, umesh_r(i,ia)
      else
        write(10,*) ux_r(i,ia)*100, uy_r(i,ia)*100, umesh_r(i,ia)
      endif

```

915 continue

if(((ia-1)*a_step.ge. a_surf_min) .and.

1 ((ia-1)*a_step.le. a_surf_max))

1 write(10,*) x0*100, y0*100, putemp

c The last point of the mesh_down_r curve.

close(9)

close(10)

6695 continue

do 6697 i = 1, nue+1

write(itemp,1079)i

1079 format('mesh_up_a',i2,'.txt')

open(unit=9,file=itemp,status='unknown')

write(itemp,1069)i

1069 format('mesh_down_a',i2,'.txt')

open(unit=10,file=itemp,status='unknown')

u = u_step*(i-1)

a_ = 1 + tan(theta_max)*tan(theta_max)

b_ = 2*tan(theta_max)*tan(theta_max)*c(mp,1)

c_ = c(mp,1)*c(mp,1)*tan(theta_max)*tan(theta_max) - u*u

delta = b_*b_ - 4*a_*c_

if(delta.ge. 0) then

x1 = (-b_ + sqrt(delta))/(2*a_)

y1 = (x1 + c(mp,1))*tan(theta_max)

ca = x1/u

putemp1 = 0

do 446 j = 1, ncn

e(j) = gg(j)*u*u

do 446 ijk = 1, ngrid

call eval(po,j)

pan = rela(j)*pin*gb(j)/(6.28319*tsum)

putemp1 = putemp1 + (fabg(ijk,j)*u*pan)

446 continue

putemp1 = putemp1/pu_max

c The first point of the mesh_up_a curve.

write(9,*) x1*100, y1*100, putemp1

x2 = (-b_ - sqrt(delta))/(2*a_)

```

y2 = (x2 + c(mp,1))*tan(theta_max)
ca = x2/u
putemp2 = 0
do 447 j = 1, ncn
e(j) = gg(j)*u*u
do 447 ijk = 1, ngrid
call eval(po,i)
pan = rela(j)*pin*gb(j)/(6.28319*tsum)
putemp2 = putemp2 + (fabg(ijk,j)*u*pan)
447 continue
putemp2 = putemp2/pu_max

```

c The first point of the mesh_down_a curve.
 write(10,*) x2*100, y2*100, putemp2

```

a_min = acos(x1/u)
if(y2 .gt. 0.) then
a_max = acos(x2/u)
else
a_max = 3.1415926535 + acos(abs(x2)/u)
endif

```

```

do 96 ia = 1, na_mesh+1
if(((ia-1)*a_step .ge. a_min).and.((ia-1)*a_step .le. a_max)) then
write(9, *) ux_a(ia,i)*100, uy_a(ia,i)*100, umesh_a(ia,i)
else
if((ia-1)*a_step .ge. a_max)
1 write(10, *) ux_a(ia,i)*100, uy_a(ia,i)*100, umesh_a(ia,i)
endif
96 continue

```

```

do 94 ia = 1, na_mesh
if((ia-1)*a_step .le. a_min)
1 write(10, *) ux_a(ia,i)*100, uy_a(ia,i)*100, umesh_a(ia,i)
94 continue

```

c The last point of the mesh_down_a curve.
 write(10,*) x1*100, y1*100, putemp1

c The last point of the mesh_up_a curve.
 write(9,*) x2*100, y2*100, putemp2

```

else
do 91 ia = 1, na_mesh
write(10, *) ux_a(ia,i)*100, uy_a(ia,i)*100, umesh_a(ia,i)

```

```
91    continue
      endif
```

```
      close(9)
      close(10)
```

```
6697 continue
```

```
      endif
```

c Create output files for c.m. ET and T(theta). (use the same ranges as contour maps)

c Energy step is $cm_e_max/200$, angle step is 5 degree.

c Angle is from 0 to 180 degree.

```
e_step = cm_e_max/200
u_step = cm_u_max/200
a_step = 0.017453*5
```

```
kk = 0
```

```
open(unit=21, file='ave_et.txt', status='unknown')
open(unit=22, file='ave_u.txt', status='unknown')
```

```
do 6679 ia = 1, 37
  pe_max = 0
  pu_max = 0
  ca = cos((ia-1)*a_step)
```

```
do 6680 i = 1, 201
  eet = (i-1)*e_step
  u = (i-1)*u_step
  petemp = 0
  putemp = 0
```

```
do 6681 j = 1, ncn
  e(j) = eet
  do 6115 ijk = 1, ngrid
    call eval(po,j)
    pan = rela(j)*pin*gb(j)/(6.28319*tsum)
    petemp = petemp + (fabg(ijk,j)*pan)
```

```
6115 continue
```

```
  e(j) = gg(j)*u*u
  do 6116 ijk = 1, ngrid
    call eval(po,j)
    pan = rela(j)*pin*gb(j)/(6.28319*tsum)
    putemp = putemp + (fabg(ijk,j)*u*pan)
```

```

6116 continue
6681 continue

      pe_max = amax1(pe_max, petemp)
      pet(i) = petemp
      pu_max = amax1(pu_max, putemp)
      pu(i) = putemp
6680 continue

      iaa = (ia-1)*5
      write(itemp, 6682) iaa
6682 format('pe_angle', i3, '.txt')
      open(unit=133, file=itemp, status='unknown')

      ave_temp_e = 0
      sum_temp_e = 0
      ave_temp_u = 0
      sum_temp_u = 0

      if(pu_max.eq. 0) pu_max = 1
      if(pe_max.eq. 0) pe_max = 1
      do 6683 i = 1, 201
      pet(i) = pet(i)/pe_max
      pu(i) = pu(i)/pu_max
      eet = e_step*(i-1)
      u = u_step*(i-1)
      write(133, *) eet*4.186, pet(i)

c Calculate average ET and u for the up limit which is corresponding to beam energy.
c This is different for different c.m. angle.
c Note: when doing invert, the upper limit for calculating <E> is beam energy.
c Vbeam and Vcm are taken as the one of canonical newton diagram.
c (It's same for all the channels.)
c      ei = 504
c <Ei> in the unit of kJ/mol
c      aaaa = 0.01*sqrt(2*ei*1000000/pmass(1))
c velocity in 1e4 cm/s
c      bbbb = c(mp,1)
c      cccc = -bbbb*ca + sqrt(aaaa*aaaa - bbbb*bbbb + bbbb*bbbb*ca*ca)
c      limit_e = gg(1)*cccc*cccc
c      limit_u = cccc

c      if(eet.lt. limit_e) then

      ave_temp_e = ave_temp_e + 4.186*eet*pet(i)

```

```

sum_temp_e = sum_temp_e + pet(i)

c      endif
c      if(u .lt. limit_u) then

ave_temp_u = ave_temp_u + 100*u*pu(i)
sum_temp_u = sum_temp_u + pu(i)

c      endif
6683  continue

close(133)

if(sum_temp_e .eq. 0) sum_temp_e = 1
if(sum_temp_u .eq. 0) sum_temp_u = 1
write(21, *) (ia-1)*5, ave_temp_e/sum_temp_e
write(22, *) (ia-1)*5, ave_temp_u/sum_temp_u
6679  continue

close(21)
close(22)

c Output T(theta)
kk = 1
t_max = 0
a_step = 3.14159/180

do 6684 ia = 1, 181
theta = (ia-1)*a_step

do 6685 j = 1, ncn
call eval(po,j)
t_theta(ia) = t_theta(ia)*rela(j) + t
6685  continue

t_max = amax1(t_max, t_theta(ia))
6684  continue

if(t_max .eq. 0) t_max = 1
open(unit=134, file='t_theta.txt', status='unknown')
do 6686 ia = 1, 181
write(134, *) ia-1, t_theta(ia)/t_max
6686  continue

close(134)

```

endif

stop
end

c Main program ends here. The following is subroutines

c*****

SUBROUTINE chi(po)

c Vversion date: march 17, 1988

c Modified by Paul S. Weiss, AMS

c *** program to smooth p(e) and p(t) over the newton diagrams.

c *** compares calculated lab angular distr with experimental and

c *** finds the chi-square value.

c Note use of v/u transformation, due to use of number density detector and p(u).

c Facility for dealing with photodissociation removed. 1/86, psw

c Includes option of only calculating data with given z (cross section)

```

common/chii/a(50),b(50),chis,dv,kplt,kdat,kcmp,p(2500,21,10),
1 pm(50),pc(2500,21,10),sum(10),sumf(50),
1 vl(2500),vz,xd(50),z,ww(10),nv,na,gb(10),chit

```

```

common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1 ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1 np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1 tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

```

```

common/newton/al(4000,10),c(4000,10),c2(4000,10),cut(4000,10),cxmp,
1 cymp,d(4000),fabg(4000,10),g1(10),g2(10),gamma,gg(10),hw1,hw2,
1 ngam1,ngam2,ngrid,sr(2),thc(4000,10),vla(4000,10),vv(4000,10),
1 v1,v2,vt(2),nvb(2),tm(10),pmass(10),hwidb(1)

```

```

common/opt/kdum1,knorm,kwarn,tsum,ngg(11),ngh(11),lop
common/trip/dia,dt,hz,sa,sb,time,trp(19),ttcm
common/calcu/kcalc,zz,kopt
dimension po(51,10)
dimension ct(4000)

```

```

      x=0.
      y=0.
      qdvsq = 0.25 * dv * dv
c square of half dv
      do 30 ia=1,na
      sumt=0.
      sumf(ia)=0.
      do 301 j=1,ncn
      gb(j)=ww(j)
c contains mass of product. See more explanation in next page.
      sum(j)=0.
      do 27 ijk=1,ngrid
      tt=thc(ijk,j)-a(ia)
c thc is the angle between primary beam and  $v_{cm}$ . a(ia) is the lab angle, between primary
c beam and product detection direction.
c So, tt is the angle between  $v_{cm}$  and the direction at which the product is detected.
      ct(ijk)= cos(tt)
27      continue
      do 29 iv=1,nv
      v=vl(iv)
c v is the lab velocity (see input 18). v is not from experimental data, as opposite, v is
c used to calculate TOF data.
      vsq = v * v
      fc=0.
      f=0.
      do 28 ijk=1,ngrid
c loop over every Newton diagram
      uu=c2(ijk,j)+v*(v-2.* c(ijk,j)*ct(ijk))
c uu is the square of c.m. velocity
c c2 is square of  $v_{cm}$ 
c c is  $v_{cm}$ 

c There has been a problem at statement 22 with floating zero divide. A fix is to see if u
c is too small, and if so, to increase it to some minimal value. i have chosen to use one
c half the velocity increment as the minimum value. note that uu is the square of the
c center of mass velocity, and that dvsq = .25 * dv * dv, was calculated above to
c streamline program execution (vsq, and vvsq also).
c P. S. Weiss, 6 nov. 1985

      if(uu.lt.(qdvsq)) uu = qdvsq
      e(j) = gg(j) * uu
c e(j) is  $E_{coll}$ 

c If the center of mass energy is lower than the offset (the first non-zero value of the
c p(e)), skip all subsequent calculations and go on to the next newton diagram

```

```

      if(e(j).lt.enoff(j))then
      go to 28
      endif
      u = sqrt(uu)
      aa = vsq+vv(ijk,j)*(vv(ijk,j)-2.*v*cos(a(ia)+al(ijk,j)))
c vv is the primary beam velocity in lab frame
c al considers beam spread

22      ca=(uu+v1a(ijk,j)*v1a(ijk,j)-aa)/(2.*v1a(ijk,j)*u)
c ca is cosine of c.m. angle.

c Print warning if cosine of angle out of range then correct situation (unless option set to
c skip printing this, kwarn=1 or kdum1=1)

      if((ca.le.1.).and.(ca.ge.-1.)) go to 280
      if((kdum1.ne.0).or.(kwarn.ne.0)) go to 275
      write(10,8888) ca,u,v,ijk
275      if(ca.lt.-1.) ca = -.999999
      if(ca.gt.1.0) ca = .999999
280      if(u.lt.cut(ijk,j)) u = cut(ijk,j)
c cut might be the minimum value of u.

c Obtaining signal in lab frame at given angle

      call eval(po,j)
c returns with pin = P(E)T(Θ)

c Note: changes made by AMS 6/87

c Starting from rick buss version which normalizes p(e) (vs. u(u) in paul weiss version)
c the reduced product mass "gb" is introduced here since it appears as part of the
c Jacobian and is obviously not the same for different reaction channels! only after the
c data are properly converted into the lab frame, the scaling is done (i.e. factor z
c determined)

c Note: "unscaled data" in the angular distribution output is the data for unity total cross
c section transformed to the laboratory system. Also: if kcalc=1 no experimental data
c are used, but instead calculation of output data values is done using a given z (cross
c section)

c T(theta) is also normalized: tsum has been calculated right after input, pin=p(e)*t(theta)
c -> pin/(2*pi*tsum)

c 3/88: previously dv was not taken into account when normalizing

```

c p(e) - see main routine for changes!

```

      pan=pin*gb(j)/(6.28319*tsum)
c pan is I(ET, Θ) in c.m. frame
      if(kcmp.ne.0) fc = fc + (fabg(ijk,j) * u * pan)
c fc is I(u, Θ) in c.m. frame.
      f = f + fabg(ijk,j)*vsq/u*pan
c f is P(v) in lab frame
c 28 is loop over ngrid
c Here, fc and f are summed over all the Newton diagrams. fabg is the weight of each
c Newton diagram.
28      continue
      p(iv,ia,j)=f
      if(kcmp.ne.0) pc(iv,ia,j) = fc
      sum(j)=sum(j)+f/v
c f/v, which is P(v)/v, is P(E) or N(v)
c 29 is loop over velocities
29      continue
      sum(j)=sum(j)*dv
c Here, it seems N(v)*dv, which is equal to N(t)dt.
      sum(j)=sum(j)*rela(j)
      sumt=sumt+sum(j)
c 301 is loop over channels
301      continue
      sumf(ia)=sumt
c So, sumf is actually sum of N(t) because dt is constant (dwell time).
      x=x+sumt*b(ia)
      y=y+sumt*sumt
c 30 is loop over angles
30      continue
      kdum1=1

```

c Changes by p. weiss 5/84

```

      if(y.ne.0.) go to 2000
      y = 0.0001
      write(10,2100)
2100  format(' ***** error *****'
1      ,/, ' y = 0 in subroutine chi'
2      ,/, ' calculated distribution is everywhere zero.')
2000  z=x/y
      if (kcalc.eq.1) z=zz
      chis=0.

```

c Calc. and expt. angular distributions are written in the main program after optimization
 c (GR,11/84)

```

      do 40 ia=1,na
      sumf(ia)=sumf(ia)*z
      if (kcalc.ne.1) then
      xd(ia)=b(ia)-sumf(ia)
      chis=chis+xd(ia)*xd(ia)
      else
      b(ia)=0.
      xd(ia)=0.
      endif
40    continue
      if(kopt.eq.0)then
      write(10,1117)chis
c  chis is chi square. It doesn't have any meaning. When only one lab angle has data, chis
c  is 0, which doesn't make any sense. See xd(ia) calculation.
      print 1117, chis
      endif

      if(z.ne.0.) go to 2200
      write(10,2210)
2210  format(' warning -- z=0. z is the normalizing factor for the'
1     ,/, ' comparison of experimental and calculated data.',/)
2200  continue
      return
1117  format(' chisquare = ',e16.10)
8888  format(' warning: cos(cm angle)=',f8.5,', v cm=',f7.4
1     ,', v lab=',f7.4,', newt diag #',i3)
      end

```

c*****

SUBROUTINE energy(j)

c Version date: march 30, 1988
 c AMS, Gary Robinson, Paul S. Weiss, Rick Buss, *et al.*
 c Subroutine energy calculates the p(e) from RRKM parameters:
 c p, q, exothermicity, and b as follows:

$$c \quad P(E) = (E_{Total} - E)^q (E - b)^p$$

$$c \quad E_{Total} = E_{coll} + \text{exothermicity}$$

- c The $p(e)$ is actually calculated in reduced energy because
- c for sharp distributions, the exponents p and q can grow large.

```

common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1  ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1  np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1  tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

```

```

common/area/area(10),rarea(4000,10),k(100),nibe(100),nopt

```

- c This version only evaluates $p(e)$

```

      if(e(j).lt.px(4,j).or.rarea(ijk,j).eq.0.) then
        pin=0.
      else
        et(j) = px(3,j) + ec(ijk,j)
c Exothermicity +  $E_{coll}$ 
        pin = (et(j) - e(j))
        if(pin.le.0.) then
          pin=0.
        else
          pin = pin ** px(2,j)
          pin = pin * (e(j) - px(4,j)) ** px(1,j)
          pin = pin / rarea(ijk,j)
        endif
      endif
      return
end

```

c*****

SUBROUTINE eval(po,mcn)

- c Version date: march 22, 1988

- c Modified by paul s. weiss, ams

- c In case of point-form $p(e)$: $p(e)$ scaled for every collision energy

- c Evaluates the product $p(e)t(\theta)$ for a given cm angle and velocity.

```

common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1  ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1  np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1  tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

```

```

common/lege/kk,kpts,t,theta,to(51,10),chiwt
common/cene/mp,cc,ss
dimension y(11),po(51,10),pol(51)
data rad/.0174533/
c kk is a flag!
c kk=1: t(theta) only
c nang=0: use legendre coefficients
c kpts=0: rrk-form of energy

c***** calculate t(theta)

      do 9874 i=1,nleg(mcn)
9874   pol(i)=po(i,mcn)
      if(nang(mcn).gt.0) then
      if(kk.eq.0) then
      cc=acos(ca)/rad
      else
      cc=theta/rad
      endif
      if(nang(mcn).eq.2.and.cc.gt.90.)cc = 180. - cc
      do 4 i=1,nleg(mcn)
4       if(cc.ge.to(i,mcn))k=i
      t=pol(k)+(pol(k+1)-pol(k))*(cc-to(k,mcn))/
1       (to(k+1,mcn)-to(k,mcn))

c If legendre coefficients or miller are used (nang=0), begin here

      else
      if(nang(mcn).eq.0) then
      cc=ca
      if(kk.ne.0)cc=cos(theta)
      call legpol(cc,y,nleg(mcn)-1)
      t=0.
      do 1 i=1,nleg(mcn)
      t=t+pol(i)*y(i)
1       continue
      endif

c Miller form of t(theta)
c
      if(nang(mcn).lt.0) then
      if(kk.eq.0) then
      cc=acos(ca)
      else
      cc=theta

```

```

endif
calph=cos(pol(1))
calphp=cos(pol(2))
tempval=sqrt((sin(cc)*sin(cc))-calph*calph-calphp*calphp
1 +2*calph*calphp*ca)
valmin=1/pol(3)
if(tempval.gt.valmin) then
  t=1/tempval
else
  t=pol(3)
endif
endif
endif

```

- c If the center of mass angular function is less than 0 at this angle, reset it to 0, and set
 c product of $p(e)*t = 0$

```

if(t.le.0.) then
  t = 0.
  pin = 0.
  return
endif
endif

```

- c If only $t(\theta)$ is to be evaluated return otherwise continue to calculate $p(e)*t(t)$
 c product

```

if(kk.ne.0)return

```

c***** calculate $p(e)$

- c If the energy is less than the offset of $p(e)$, $p(e)=0$, and skip evaluation

```

if(e(mcn).lt.enoff(mcn)) then
  pin=0.
  return
endif

```

- c If rrk from is used, calculate $p(e)$ with subroutine energy

```

if(kpts.eq.0) then
  call energy(mcn)
  pin=pin*t
  return
endif

```

c New section 3/22/88, AMS:

- c If only one $p(e)$ is given ($nen=1$), get different $p(e)$ -distributions by scaling the curve as
 c input by $e(tot)=e(avl)+e(coll)$ - consequently normalization factor also changes -> use
 c different $p(e)$ s for different collision energies!

```

if (nen.eq.1) then
  eavl=float(np(1,mcn)-1)*den(mcn)+enoff(mcn)-ec(mp,mcn)
  alpha=(eavl+ec(mp,mcn)-enoff(mcn))/(eavl+ec(ijk,mcn)-enoff(mcn))
  beta=enoff(mcn)*(1.-alpha)
  ecorr=e(mcn)*alpha + beta

```

c as below:

```

n=int((ecorr-enoff(mcn))/den(mcn))
f=((ecorr-enoff(mcn))/den(mcn))-n
n=n+1
if (n.ge.np(1,mcn)) then
  pin=0.
  return
endif
pp=pe(n,1,mcn)-(pe(n,1,mcn)-pe(n+1,1,mcn))*f
pin=pp*alpha*t
1234 format(9(1x,e8.3))
return
endif

```

c f is the fraction that e is between the two adjacent points in $p(e)$

```

n = int((e(mcn) - enoff(mcn))/den(mcn))
f = ((e(mcn)- enoff(mcn))/den(mcn)) - n
n=n+1

```

c Assumes first element of $p(e)$ is for $e=enoff + 0$. kcal.

c jump to 8 if no interpolation between different $p(e)$'s needed

```

do 6 ne=1,max(2,nen)
6  if(ec(ijk,mcn).lt.en(ne))go to 7
   go to 8
7  if(ne.eq.1)go to 8

```

c Interpolate between points in $p(e)$ to have correct energy

```

me=ne-1
if((n.ge.np(ne,mcn)) .or. (n.ge.np(me,mcn))) then
  pin=0.
  return
endif

```

```

pb=pe(n,me,mcn)-(pe(n,me,mcn)-pe(n+1,me,mcn))*f
pa=pe(n,ne,mcn)-(pe(n,ne,mcn)-pe(n+1,ne,mcn))*f

```

c Interpolate between p(e)s for collision energies above and below
 c the one calculated here

```

      pp=pa+(pb-pa)*(ec(ijk,mcn)-en(me))/(en(ne)-en(me))
      go to 10
8      if(n.ge.np(ne,mcn)) then
      pin=0.
      return
      endif

```

c Interpolate between points in p(e) to have correct energy

```

      pp=pe(n,ne,mcn)-(pe(n,ne,mcn)-pe(n+1,ne,mcn))*f
10     pin=pp*t
      return
      end

```

c*****

SUBROUTINE legpol (x,y,n)

c *** evaluates Legendre polynomial of degree m.

```

      dimension y(11)
c up to 11 terms of Legendre polynomial

```

```

      m = n + 1
      y(1) = 1.
      y(2) = x
      if (m.lt.3) return
      do 1 i=3,m
      r= float(i-2)
      y(i)= (2.*r+1.)*x*y(i-1)/(r+1.)-r*y(i-2)/(r+1.)
1      continue
      return
      end

```

c*****

SUBROUTINE newt1(mcn)

c Modified version of newton that allows for primary beam to be velocity selected. G.

- c Robinson, nov. 1984 (after D. Neumark's corrections to coupled.for)
- c Some cleanup and comments by AMS - 8/86
- c Changed treatment of non-90deg-newton-diagrams: treat both beam divergences separately AMS, 3/88
- c The so-called 'mean beam intersection angle' is never used in GMT. It was assumed the intersection angle be 90 deg. -- Miau
- c The velocity selected beam option was taken out by someone at some point. i have no intention to put it back in the program in this release. -- Miau

```

common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1  ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1  np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1  tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

common/newton/al(4000,10),c(4000,10),c2(4000,10),cut(4000,10),cxmp,
1  cymp,d(4000),fabg(4000,10),g1(10),g2(10),gamma,gg(10),hw1,hw2,
1  ngam1,ngam2,ngrid,sr(2),thc(4000,10),vla(4000,10),vv(4000,10),
1  v1,v2,vt(2),nvb(2),tm(10),pmass(10),hwidb(1)

```

```

common/vels/alph,ivels,tmp,vs0,vsbeta,vsgam
common/int/almax,vel
common/weight/ef,ew(50),kwts,new,sig(50),kstp
common/beamv/fb(50,2),vb(50,2)
common/cene/mp,cc,ss
real sum

```

```

dimension gam(50),fg(50)
data con1,rad/.00119503,.0174533/

```

- c con1 has to do with conversion to kcal
- c (velocity is in 100 m/s, mass is in gm)

```

data slit,ddet/2.,145./

```

```

v1=nvb(1)

```

```

nv1=float(nv1)/2
f(aint(fnv1).eq.fnv1.and.ivels.eq.1) nv1=nv1+1

```

- c This forces nv1 to be odd

```

nv2=nvb(2)
g=g1(mcn)+g2(mcn)
g2(mcn)=g2(mcn)/g

```

```

    gfac=con1*g1(mcn)*g2(mcn)
    tm(mcn)=g-pmass(mcn)
    gg(mcn)=con1*pmass(mcn)*g/tm(mcn)
c  gg*u2 = Ecoll
    g1(mcn)=g1(mcn)/g
    g12=g1(mcn)*g2(mcn)*2
    g11=g1(mcn)*g1(mcn)
    g22=g2(mcn)*g2(mcn)

    if(ivels.eq.1) then
    print *, 'sorry - this option has been taken out!'
    print *, 'you have to change your input data!'
    stop

    else
    lf=1
    endif

```

c Velocity distributions of nozzle beams

```

    do 12 l=lf,2
    nvl=nv1
    if (l .eq. 2) nvl=nv2
    s=sr(l)
    if(s.ne.0.)then

```

c s, sr: speedratio
 c vt: peak velocity (input!) - this is the peak of the TOF (number-density, time space!)
 c distribution - see Krajnovich, thesis, appendix, eq. (17), pg 273

 c pk: this is the peak of the number density distribution, in velocity space:
 c $v^{**2} \exp((v/\alpha - s)^{**2})$ expressed as velocity/alpha.

 c fnorm is a normalization factor for the weights of the velocities over which you want to
 c average; such that the most probable velocity has fb=1.

```

    alpha=vt(l)*2./(s+sqrt(s**2+8.))
    pk=(s+sqrt(s**2+4.))/2
    fnorm=exp((pk-s)**2)/pk**2

```

c The velocities over which the program averages (array vb) are chosen as equally
 c spaced, extending further out in the distribution, the larger the number requested; in the
 c limit of very large numbers, the first und last velocity have a probability (array fb) of
 c about .1. If you want to include velocities in a larger range, replace the factor 3.33022
 c (= 4*sqrt(ln2))

```

dv=5./float(nvl+1)
nh=nvl/2+1
do 22 i=1,nvl
  r=pk+float(i-nh)*dv
  vb(i,l)=alpha*r
  fb(i,l)=fnorm*r**2*exp(-(r-s)**2)
22  continue
  else
  fnorm=0.
  do 9999 i=1,nvl
    if(fb(i,l).gt.fnorm)fnorm=fb(i,l)
9999 continue
  do 8888 i=1,nvl
    fb(i,l)=fb(i,l)/fnorm
8888 continue
  endif
12  continue
  ngam=ngam1*ngam2
  ngrid=nv1*nv2*ngam
  if(ngrid.gt.4000) then
  write(10,9100) ngrid
  stop
  endif

```

c The goal of the do (4) loop is to calculate all the Newton diagram info, that is fill the c arrays al,vv,ec,c,c2,cut,thc,vla,fabg and to find the canonical newton diagram (see c below)

c ijk indexes the newton diagrams

```

fnp=0.
ijk=0
k=0
nh1=ngam1/2+1
fnh1=nh1
nh2=ngam2/2+1
fnh2=nh2
do 4 k1=1,ngam1
  al1=float(k1-nh1)*hw1/fnh1
  fg1=1.
  if(hw1.ne.0.) fg1=1.-abs(al1)/hw1
  do 4 k2=1,ngam2
    al2=float(k2-nh2)*hw2/fnh2
    fg2=1.

```

```

if(hw2.ne.0.) fg2=1.-abs(al2)/hw2
k=k+1
fg(k)=fg1*fg2

```

c In the following statement, we assumed the intersection angle to be 90 deg., maybe it should be changed to gamma instead. -- Miao

c Drawing a Newton diagram is helpful to understand the following code.

```

gm k=(90.+al1+al2)
gam(k)=gm k
gm k=gm k*rad
cg = cos(gm k)
sg = sin(gm k)
do 4 i=1,nv1
v1=vb(i,1)
c velocity of beam 1
do 4 j=1,nv2
v2=vb(j,2)
c velocity of beam 2
ijk=ijk+1
al(ijk,mcn)=al1*rad
vv(ijk,mcn)=v1
vrels = v1*v1+v2*(v2-2.*v1*cg)
vrel=sqrt(vrels)
v1a(ijk,mcn) = vrel*g2(mcn)
c2(ijk,mcn)=g11*v1*v1+g22*v2*v2+g12*v1*v2*cg
c c2 is square of vcm
c(ijk,mcn)= sqrt(c2(ijk,mcn))
cut(ijk,mcn)=c(ijk,mcn)*slit/ddet

```

c New inclusion 3/88 AMS:

```

c
sinb=sg*v2/vrel
cosb=sqrt(1-sinb*sinb)
tgth=v1a(ijk,mcn)*sinb/(v1-v1a(ijk,mcn)*cosb)
thc(ijk,mcn)=atan(tgth)-al(ijk,mcn)

```

c ef is needed in case wate is called: for the input, it's the collision energy of the current

c newton diagram {ijk} in the output, however, it's the weight!

```

ef=vrels*gfac
ec(ijk,mcn)=ef
c Ecoll

```

c Obtain crosssection weighting stored in ef.

```

if(kwts.eq.0) then
  ef=1.
else
  call wate
endif

```

c Remember: fabg(ijk) is the weight of the newton diagram ijk

c fmp keeps track of the newton diagram with the largest weight (the "canonical"

c Newton diagram: its number is mp, the corresponding v1 (v2) has index imp (jmp) etc)

```

fabg(ijk,mcn)=fb(i,1)*fb(j,2)*fg(k)*vrel*ef
if(fmp.gt.fabg(ijk,mcn)) go to 4
fmp=fabg(ijk,mcn)
mp=ijk
imp=i
jmp=j
4 continue

```

c Some values for the canonical newton diagram: mp, ss, cc are in common block /cene/

c cxmp, cymp are part of common block /newton/

```

v1=vb(imp,1)
v2=vb(jmp,2)
cxmp=g1(mcn)*v1
cymp=g2(mcn)*v2
cc=(c2(mp,mcn)+v1a(mp,mcn)*v1a(mp,mcn)-v1*v1)/
1 (2.*c(mp,mcn)*v1a(mp,mcn))
ss=sin(acos(cc))

```

c Normalize the weights of the newton diagrams to sum up to 1.

```

sum=0.
do 65 ijk=1,ngrid
  sum=sum+fabg(ijk,mcn)
65 continue
do 67 ijk=1,ngrid
  fabg(ijk,mcn)=fabg(ijk,mcn)/sum
67 continue

```

c Print out newton diagram info

```

if (kstp.ne.0) then
  write(10,1000)
  ijk=0

```

```

do 8 k=1,ngam
do 8 i=1,nv1
do 8 j=1,nv2
ijk=ijk+1
t=thc(ijk,mcn)/rad
write (10,1001) vb(i,1),fb(i,1),vb(j,2),fb(j,2),gam(k)
1 ,fg(k),fabg(ijk,mcn),t,c(ijk,mcn),ec(ijk,mcn)
8 continue
endif
t=thc(mp,mcn)/rad
write(10,1002) v1,v2,t,c(mp,mcn),ec(mp,mcn),ngrid
1000 format(1x,4x,'vel1 f1',5x,'vel2 f2',4x,'gamma fg'
1 ,4x,'f12g',6x,'thc',5x,'vcm',4x,'ecol')
1001 format(1x,3(f8.2,f5.2),f8.4,3f8.2)
1002 format(//,'canonical:',/,1x,f8.2,5x,f8.2,26x,3f8.2
1 ,/,10x,i5,' newton diagrams')
9100 format(//,' *****'
1 ,/, ' error -- too many newton diagrams (ngrid = ',i5,')'
2 ,/, ' *****',/)
return
end

```

c*****

SUBROUTINE param(po)

c Redefines parameters for optimization and calls chi and ti to calculate chisquare

```

common/chii/a(50),b(50),chis,dv,kplt,kdat,kcmp,p(2500,21,10),
1 pm(50),pc(2500,21,10),sum(10),sumf(50),
1 vl(2500),vz,xd(50),z,ww(10),nv,na,gb(10),chit

common/tnrm/tnorm(10)
common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1 ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1 np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1 tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

common/newton/al(4000,10),c(4000,10),c2(4000,10),cut(4000,10),cxmp,
1 cymp,d(4000),fabg(4000,10),g1(10),g2(10),gamma,gg(10),hw1,hw2,
1 ngaml,ngam2,ngrid,sr(2),thc(4000,10),vla(4000,10),vv(4000,10),
1 v1,v2,vt(2),nvb(2),tm(10),pmass(10),hwidb(1)

common/tim/aab(50),abb,chnmn(5,21),chnmx(5,21),dl,ir,
1 ktel,nch(50),ntb(50),of,pat,path,pmas,

```

```

1 size,tdat(500,50),tmin(5,21),tmxx(5,21),xion,xims,chin,
1 idum(50),nto,igat

```

```

common/lege/kk,kpts,t,theta,to(51,10),chiwt
common/opt/kdum1,knorm,kwarn,tsum,ngg(11),ngh(11),lop
common/area/area(10),rarea(4000,10),k(100),nibe(100),nopt
dimension po(51,10),avge(10)
data fdeg/.0872665/

```

```

chis=0.
abb=0.
do 8500 j=2,ncn+1
do 8500 i=1,nopt
nn=k(i)-ngh(j-1)

```

c Legendre polynomial

```
nm=k(i)-ngg(j)
```

c P(E), RRK or point form, and rel(j)

```

if(k(i).gt.ngh(j-1).and.k(i).le.ngg(j))then
if(nibe(k(i)).eq.0)then

```

c From here to line 812 is for Legendre coefficients.

```

po(nn,j-1)=poz(k(i))
if(lop.eq.1)then
nfrc=2.*(int(nn/2.))
if(nfrc.eq.nn.and.j.eq.2)then
po(nn,2)=-1.*po(nn,1)
else
po(nn,2)=po(nn,1)
endif
endif
else
if(nn.le.nleg(j-1))then
to(nn,j-1)=exp(poz(k(i)))
else
po(nn-nleg(j-1),j-1)=exp(poz(k(i)))
endif
if(lop.eq.1.and.j.eq.2)po((nleg(1)-nn+1),2)=po(nn,1)
812 endif
else

```

```
if(k(i).gt.ngg(j).and.k(i).lt.ngh(j))then
```

c From here to line 8502 is for rrk form.

```

if(kpts.eq.1)then
pe(nm,1,j-1)=exp(poz(k(i)))
if(lop.eq.1.and.j.eq.2)pe(nm,1,2)=pe(nm,1,1)
lse
do 8501 m = 1,2

```

```

    if(k(i).eq.ngg(j)+m)then
    pe(m,1,j-1)=exp(poz(k(i)))
    if(lop.eq.1.and.j.eq.2)pe(m,1,2)=pe(m,1,1)
    endif
8501 continue
    do 8502 m=3,4
    if(k(i).eq.ngg(j)+m)then
    pe(m,1,j-1)=poz(k(i))
    if(lop.eq.1.and.j.eq.2)pe(m,1,2)=pe(m,1,1)
    endif
8502 continue
    endif
    endif
    if(k(i).eq.ngg(j))rel(j-1)=exp(poz(k(i)))
c for rel(j)
    endif
8500 continue
    if(kpts.eq.0)then
c From here to line 8881 is for RRK form
    do 5721 i=1,4
    do 5721 m=1,ncn
    px(i,m)=pe(i,1,m)
5721 continue
    do 8881 j=1,ncn
    do 8881 ijk=1,ngrid
    et(j) = px(3,j)+ec(ijk,j)
    de(j)=et(j)/1000.
    area(j)=0.
    e(j)=-de(j)/2.
    do 8891 i=1,1000
    e(j) = e(j) + de(j)
    if(e(j).gt.px(4,j))then
    pin = et(j) - e(j)
    pin=(pin**px(2,j))*((e(j)-px(4,j))**px(1,j))
    area(j)=area(j)+pin
    endif
8891 continue
    rarea(ijk,j) = area(j) * de(j)
8881 continue
    else
c From here to line 2152 is for point form of P(E).
    do 2152 j=1,ncn
    area(j) = pe(1,1,j)
    avge(j) = (pe(1,1,j)*enoff(j))
    do 2101 l=2,npf(j)

```

```

    e(j) = enoff(j) + ((l-1) * den(j))
    area(j) = area(j) + pe(l,1,j)
    avge(j) = avge(j) + (pe(l,1,j) * e(j))
2101  continue
    area(j)=area(j)*den(j)
    do 2151 l=1,npf(j)
    pe(l,1,j)= pe(l,1,j) /area(j)
2151  continue
    en(2)=800.
    np(2,j)=np(1,j)
    do 4441 i=1,npf(j)
    pe(i,2,j)=pe(i,1,j)
4441  continue
2152  continue
    endif
    kk=1
    ca=0.
    tsum=0.
    ddt=fdeg/5.
    theta=-ddt/2.
    do 4219 j=1,ncn
    tnorm(j)=0
    do 4219 i=1,180
    theta=theta+ddt
    call eval(po,j)
    tnorm(j)=tnorm(j)+t*abs(sin(theta))
4219  continue
    do 4321 j=1,ncn
    rela(j)=rel(j)/tnorm(j)
    do 4321 i=1,180
    theta=theta+ddt
    call eval(po,j)
4321  tsum=tsum+t*abs(sin(theta))*rela(j)

    tsum=tsum*ddt
    kk=0
    chis=0.
    chit=0.
    ab=0.
    call chi(po)
c returns with chi square for sum of N(t), angular distribution.
    if(nton.ne.0) call ti
    if(nton.gt.1)chis=0.
    chis=chis*chiwt
    chit=chis+abb

```

c abb is in subroutine ti. It's chi square for TOF points.

```

      if(kpts.eq.1)then
      do 2751 j=1,ncn
      do 2751 l=1,npf(j)
      pe(l,l,j)= pe(l,l,j)*area(j)
2751  continue
      endif
      return
      end

```

c*****

SUBROUTINE ti

c Version date: march 24, 1988

c Modified by Paul S. Weiss and Gary Robinson and Barbara Balko

c AMS

c Calculates TOF distributions

c In a modification of ??/85 calculated TOF's are scaled to experimental angular
c distribution value.

c In a further modification 2/23/88 measured TOF's are scaled to calculated tof's in a
c least square fit (rather than just making the integrals equal)

c If kcalc=1: use a given cross section (zz) to only calculate TOF-data; no experimental
c input!

```

      common/chii/a(50),b(50),chis,dv,kplt,kdat,kcmp,p(2500,21,10),
      cpm(50),pc(2500,21,10),sum(10),sumf(50),
      cvl(2500),vz,xd(50),z,ww(10),nv,na,gb(10),chit

```

```

      common/val/ca,de(10),den(10),e(10),en(10),enoff(10),et(10),
1     ijk,jpeake(10),nang(10),ncn,nleg(10),px(4,10),
1     np(50,10),pan,pin,peake(10),poz(100),rel(10),rela(10),
1     tem(51),nen,ec(4000,10),pe(200,10,10),ensub(10),npf(10)

```

```

      common/tim/aab(50),abb,chnmn(5,21),chnmx(5,21),dl,ir,
1     ktel,nch(50),ntb(50),of,pat,path,pmas,
1     size,tat(500,50),tmin(5,21),tmxx(5,21),xion,xims,chin,
1     idum(50),nto,igat

```

```

      common/trip/dia,dt,hz,sa,sb,time,trp(19),ttcm
      common/calcu/kcalc,zz,kopt

```

```

dimension pt(2500,50,10),pp(560,10),ppsh(560,10),
1  ppp(560),ppsht(560),tmf(556),ppmax(10)

dimension ffcmm(10)
character*12 montof
integer itemp

c nto=0 <=> output
c nto=0 <= no optimization
c (in which case ti is called only once, when it's time to output data)

c nto>0 <=> optimization; calculate chisquare for tof in each iteration, but no output
c after iterations are done, nto is set = 0 so that at the last call output will be done

abb=0.
if(nton.eq.0) then
c nto was set to 0 at input 10 (when no optimization)
write(8,1113)
endif
off=(xion*sqrt(xims)+of)/time
ib=0
itemp = 0
do 55 ia=1,na
abc=0.
if(idum(ia).ne.0)go to 55
itemp = itemp + 1
c*** calculate n(t) ****
nit=nch(ia)
do 131 n=1,nit
ppsht(n)=0.
131 continue
do 20 j=1,ncn
do 33 iv=1,nv
pt(iv,ia,j)=p(iv,ia,j)*vl(iv)
c This means N(t)lab = P(v)*v

33 continue
if(nton.eq.0) write(8,1114) 12,a(ia)
ppmax(j)=0.
c*** smooth tof data over ionizer length
do 44 n=1,nit
chan=(float(ntb(ia)+n)-1.5-off)*time
pp(n,j)=0.
pa=pat
do 44 i=1,21

```

```

      v=pa/chan
      if(v.lt.vz)go to 44
      nn=int((v-vz)/dv)+1
      if(nn.ge.nv)go to 44
      pp(n,j)=pp(n,j)+pt(nn,ia,j)+
1      (pt(nn+1,ia,j)-pt(nn,ia,j))*((v-vz)/dv-nn+1)
c pp is N(t)
      pa=pa+dl
44      continue
c*** smooth tof data over wheel slit function
c*** ttcn=tt: from "trap"***
      do 88 n=1,nit
      ppsht(n,j)=.0
      tcn=n-ttcn
      do 779 m=1,19
      tcn=tcn+dt
      l=int(tcn)
      if(l.le.0.or.l.ge.nit)go to 779
      tfcn=tcn-l
      ffcn(j)=pp(l,j)+(pp(l+1,j)-pp(l,j))*tfcn
      ppsht(n,j)=ppsht(n,j)+ffcn(j)*trp(m)
779      continue
88      continue
      do 2776 n=1,nit
      ppsht(n,j)=ppsht(n,j)*rela(j)
      ppsht(n)=ppsht(n)+ppsht(n,j)
      if(ppmax(j).lt.ppsht(n)) ppmax(j)=ppsht(n)
c ppsht is N(t) now. Sum over channel
2776      continue

c      *****
c      Commented this line!
c      ppmax(j) = 0 means that the calculated N(t) is 0 everywhere for that channel.
c      This line will mislead the chi_square calculation!!!
c      J. Z - 7/13/01
c      if(ppmax(j).eq.0.)go to 55
c      *****

20      continue

c Normalize experimental tof intensity to angular distribution intensity

c chnmn,chnmx are bounds of parts of tof not weighted into chisquare
c chin is (binary) weighting factor

```

```

x=0.
xy=0.
xx=0.
t=0.
if(kcalc.eq.1)then
do 99 it=1,nit
x=x+ppsht(it)
99  continue
za=0.
ad = sumf(ia)/x
else
do 19 it=1,nit
xy=xy+ppsht(it)*tdat(it,ia)
xx=xx+ppsht(it)*ppsht(it)
t=t+tdat(it,ia)
19  continue
za=b(ia)/t
c Zero of N(t) is fixed here!
if(xx .ne. 0) then
ad = za*xy/xx
c ad is the scaling factor to normalize calculated TOF with experimental data.
else
ad = 1
endif
c ad is a normalizatin factor. When N(t) is 0, the value of ad will not matter.
endif
ab=0.
if(nton.ne.0)then
do 12 it=1,nit
aa=ppsht(it)*ad-tdat(it,ia)*za
chin=1
if (ir.ge.1) then
do 102 i=1,ir
chnmn(i,ia)=ntb(ia)+off+(tmin(i,ia)/time)
chnmx(i,ia)=ntb(ia)+off+(tmxx(i,ia)/time)
if(it.ge.chnmn(i,ia).and.it.le.chnmx(i,ia))then
chin=0
else
chin=1.0
endif
102  continue
endif
12  ab=ab+(aa*aa)*chin
abb=abb+ab
c abb is chi square.

```

```

ib=ib+1
aab(ib)=ab
else

```

c Output of data file for plotting

```

      if (ktel.eq.1) then
      if(itemp.lt.10)then
      write(montof,9999)itemp
9999  format('montof,i1,'.txt')
      else
      write(montof,8888)itemp
8888  format('montof,i2,'.txt')
      endif
      open(unit=9,file=montof,status='unknown')
      endif
      write (8,1115)
      do 3113 it=1,nit
      tmf(it)=(ntb(ia)+it-1.5-off)*time
      ppp(it)=ppsht(it)*ad
c ad is the normalization factor. See last page.
      do 111 j=1,ncn
      ppsh(it,j)=ppsh(it,j)*ad
111   continue
      write(8,1116)tmf(it),tdat(it,ia)*za,ppp(it)
3113  continue
      if(ktel.eq.1)then
      do 3114 it = 1 , nit
      write(9,1122)tmf(it),tdat(it,ia)*za,ppp(it),
1      (ppsh(it,j),j=1,ncn)
3114  continue
      endif
      do 1920 it=1,nit
      aa=ppp(it)-tdat(it,ia)*za
      abc=abc+aa*aa

1920  continue
      if(igat.eq.0)then
      print *, ' angle:',ia,' tof chi=',abc
      write(8,*) ' mong tof chi=',abc
      write(10,*) ' mong tof chi=',abc
      endif
      write (8,1919)ad,za
1919  format(' calc norm=',e11.5,' exp norm=',e11.5)
      endif

```

```

      close(9)
55      continue

```

```

      return
1113  format(////,' velocity distribution')
1114  format(1x,a1,' angle=',f6.2)
1115  format(' time  ',5x,' expt',9x,' calc')
1116  format(2x,f6.1,4x,f15.3,4x,f15.3)
c Format 1122 is for 6 channels
1122  format(2x,f6.1,12(2x,f11.3))
      end

```

c*****

SUBROUTINE wate

```

c Version date: august 1986
c Revised by paul s. weiss, ams

```

c *** Calculates weights for the energy dependence of the cross section.

```

c
      common/weight/ef,ew(50),kwts,new,sig(50),kstp
      n=0
      do 4 i=1,new
      if(ef.lt.ew(i))go to 4
      n=i
4      continue
      if(n.eq.0.or.n.eq.new)go to 5
      ef=sig(n)+(sig(n+1)-sig(n))*((ef-ew(n))/(ew(n+1)-ew(n)))
      return

```

c If there was a newton diagram outside the range of weights, print an error message

```

5      write(10,1111)
      ef=1.0
      return

```

```

1111  format(' caution, collision energy is outside range of weights')
      end

```

c*****

SUBROUTINE trap

```

common/trip/dia,dt,hz,sa,sb,time,trp(19),tt
data it/10/
data pi,con/3.14159265,100000./
t=con/(pi*dia*hz*2.*time)
tt=t*(sa+sb)
sa=amin1(sa,sb)
dt=tt*.1
ta=tt-sa*t*2.
trp(10)=1.0
sum=.5
d=0.
do 5 i=1,9
  j=i+it
  d=d+dt
  if(d.le.ta)go to 4
  trp(j)=(d-tt)/(ta-tt)
  trp(it-i)=trp(j)
  go to 3
4   trp(j)=1.0
   trp(it-i)=1.0
3   sum=sum+trp(j)
5   continue
   sum=.5/sum
   do 6 i=1,19
6   trp(i)=trp(i)*sum
   return
end

```

Example of Input File

O + Squalane

01001000110240 (The meaning of these options are explained in the code and in the gmthrashtxt output file. Here, we choose to run optimization, input TOF data, output plot, skip cosine out of range warning, show optimization progress for every 10 iteration, and use 4 channels.)

11 (First "1" means we want c.m. contour and mesh plot output, second "1" means to output mesh plot presenting the surface. Put 0 is we don't want them.)

100 100 (Maximum value for c.m. $P(u)$ contour map in unit of 10^4 cm/s (first "100") and number of points to calculate (second "100").)

150 100 (Maximum value for c.m. $P(E)$ contour map in unit of kcal/mol ("150") and number of points to calculate ("100").)

36 25 (The number of angular divisions ("36") and the number of velocities/energies ("25") for c.m. mesh plots.)

25 1 1 1 (Number of velocities or data points (should be odd) for primary ("25") and second ("1") beam, and number of beam intersection angles to be considered (last two "1").)

90. 1.0 1.0 (Mean beam intersection angle ("90") and half width of primary and secondary beam (two "1.0").)

0 (Value for ivels, "0" means it's not a velocity selected beam.)

79.24 0 (Peak velocity ("79.24") in 10^4 cm/s and speed ratio for primary beam. "0" speed ratio means point form of beam. Input format is v and P(v) as the following data. Number of points is 25, see row of "25 1 1 1".)

69.21875	0.002623926
70.3125	0.051828167
71.40625	0.148037645
72.5	0.27972279
73.59375	0.433942394
74.6875	0.594490206
75.78125	0.742735737
76.875	0.859962473
77.96875	0.930561926
79.0625	0.945212234
80.15625	0.903036448
81.25	0.811925106
82.34375	0.686747741
83.4375	0.545899362
84.53125	0.407228395
85.625	0.284588741
86.71875	0.185952123
87.8125	0.113362477
88.90625	0.064335852
90	0.033911435
91.09375	0.016562095
92.1875	0.00747665
93.28125	0.0031121
94.375	0.001191452
95.46875	0.000418496

0.01 20 (Peak velocity ("0.01") in 10^4 cm/s and speed ratio ("20") for secondary beam.)

16. 39.1 (Masses of primary beam ("16.") and secondary beam ("39.1").)

8.0435976E-02 (Relative weight of this channel)

16 (Product mass)

3 0 (Three terms for c.m. angular function ("3") and use Legendre function ("0").)

1.1009885E-04 (Coefficient/weight of first term of c.m. angular function)

1.4393915E-04 (Coefficient/weight of second term of c.m. angular function)

-3.4172676E-04 (Coefficient/weight of third term of c.m. angular function)

5.566140 4.984050 0 0 (Parameters for RRK form, p, q, exo, b, respectively)

(The following three paragraphs are for the other three channels.)

16. 39.1
9.2569061E-02
16
3 0
2.3733759E-04
-4.1085033E-04
2.8865982E-04
1.778512 4.938462 -6.9921210E-02 0

16. 39.1
0.4742024
16
3 0
5.862406
1.674541
-3.070670
4.101728 12.29501 145.9369 0

16. 39.1
0.4550481
16
3 0
1.154232
1.919351
0.8942742
1.941377 11.96690 443.2889 0

6 500 (Number of lab angles ("6") and number of points ("500") of velocity that will be used to calculate TOF data.)

0.1 0.2 (Starting velocity ("0.1") and velocity step ("0.2") for velocities that will be used to calculate TOF data. Unit: 10^4 cm/s)

35 26359.97133 0 (Lab angle ("35") respective to direction of primary beam; sum of $N(t)$ "26359.97133". "0" means there are TOF data at this angle.)

1 50 0 (Starting channel ("1"); number of TOF points at this angle ("50"); and offset ("0"))

0 (Number of channels excluded in calculating chi square)

(The following is 50 points of TOF data. The number of points can be up to 500.)

17.27128
16.46128
42.03529

98.53329
197.4073
310.9392
409.5814
649.3713
754.7773
992.2094
1285.683
1442.922
1676.247
1743.755
1823.595
1878.503
1704.998
1759.42
1550.69
1540.74
1178.402
1021.615
869.8414
675.2073
585.0713
456.9054
285.3013
244.8573
227.6793
134.5693
119.3873
90.81729
61.89729
78.36128
32.44128
24.48328
48.83328
62.29729
33.56728
47.37729
25.72329
28.03528
23.68529
12.72328
24.99728
8.031281
15.07328
3.613281

20.80729
23.22928

(The following is for other lab angles. For simplicity, they don't have data points.)

40 36958.81023 1

45 42745.15202 1

50 44267.73276 1

55 45844.45358 1

110 19680.09997 1

115 19517.54997 1

0.0 16.0 1.0 33.9 2. 0 ("0.0": ion flight time constant. Because this has been taken care of, so 0 is chosen. "16.0": product mass; "1.0": ionizer length in cm; "33.9": neutral flight path in cm; "2.": dwell time in μ s; "0": offset in μ s. This is very important when the first data point of input TOF data is not 1 μ s. For example, if the input TOF data starts with 20 μ s, this offset should be -20 to correct this.)

5000. 17.8 3 4.0 ("5000": Wheel speed in Hz; "17.8": wheel diameter in cm; "3": wheel slit in mm; "4.0": detector slit in mm.)

29 5000 1 ("29": number of parameter to optimized; "5000": maximum of iteration number; "1": option regarding what data to use for fit, choose 1)

0 (Weight of angular distribution chi square)

1 2 3 4 5 6 7 8 (Here it means all the parameters of first channel will be optimized. "1, 2, 3" are three Legendre coefficients; "4, 5, 6, 7" are p, q, exo, and b for RRK form; "8" is rel(j) of first channel.)

9 10 11 12 13 14 16 (Parameters of second channel that will be optimized. Notice that "15" is missing because we don't want to optimize it, which is b of RRK form of second channel.)

17 18 19 20 21 23 24 (Parameters of third channel. "22" is missing, which means that exo of third channel is fixed.)

25 26 27 28 29 30 31 (Parameters of 4th channel. "32" is missing, which means that rel(4) is fixed.)

(Notice that the number of parameters listed above must be equal to "29".)

0.0 (Tolerance for terminating optimization)

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