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Molecule Liftoff from Surfaces

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ABSTRACT

Molecular dynamics simulations have been used to model the kiloelectronvolt particle bombardment of organic layers on metal substrates such as occurs in the analytical techniques of secondary ion mass spectrometry and fast atom bombardment mass spectrometry. Vignettes of insights gained from the simulations along with comparisons to experimental data are presented in this Account. Topics include intact molecular ejection vs fragmentation, prediction of reaction pathways, influence of the substrate, and quantitative predictions of energy and angular distributions.

I. Introduction

Imagine playing billiards with balls representing atoms held together by breakable springs as in an organic molecule. At the end of the billiard game, it is easy to

envision only atoms or fragments of molecules with no remaining intact components left on the billiard table. This scenario sounds quite logical even to those who have been examining energetic particle bombardment of solids for decades. An animation of the sequence of events that occurs when a kiloelectronvolt particle beam bombards a surface is shown in Figure 1. The incident particle, SF₅ (red spheres) in this scenario, bombards a Si substrate (silver spheres) with an adsorbed layer of biphenyl molecules (gold spheres). A collision cascade develops in which many atoms are displaced from their initial positions; that is, the rack of balls is breaking up. In Figure 1c, two individual H atoms are shown ejecting. By the time step shown in Figure 1d, several intact biphenyl molecules are lifting off the surface toward the vacuum, where they can be detected and their properties measured.

Is this game of billiards with sticky balls merely a playground for computational chemists or is there some practical utility? Mass spectrometric analysis of large organic and biological molecules is hampered because these molecules often decompose upon heating, the conventional method of vaporizing the molecules for detection. By using energetic particles or even photons, however, large molecules can be lifted off¹ the surface intact, as shown in Figure 1d. An example of a spectrum from this highly destructive process is shown in Figure 2 for cyclosporin A initially adsorbed on a Ag surface. For ion, atom, or photon bombardment, the analytical techniques are secondary ion mass spectrometry (SIMS), fast-atom bombardment mass spectrometry (FABMS),^{2,3} and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry,⁴ respectively. Although the experimental techniques are quite mature, the interrelationships between the motions in the solid that result in liftoff of intact molecules and the final experimental spectra remain elusive. It is tempting to describe SIMS, FABMS, and MALDI as similar processes. After all, in each technique an energized beam is used to deposit energy in the substrate, considerable motion in the substrate gives rise to the liftoff of molecules to be analyzed, and the final mass spectra are often quite similar. The physics of liftoff, however, is different. SIMS and FABMS can be described

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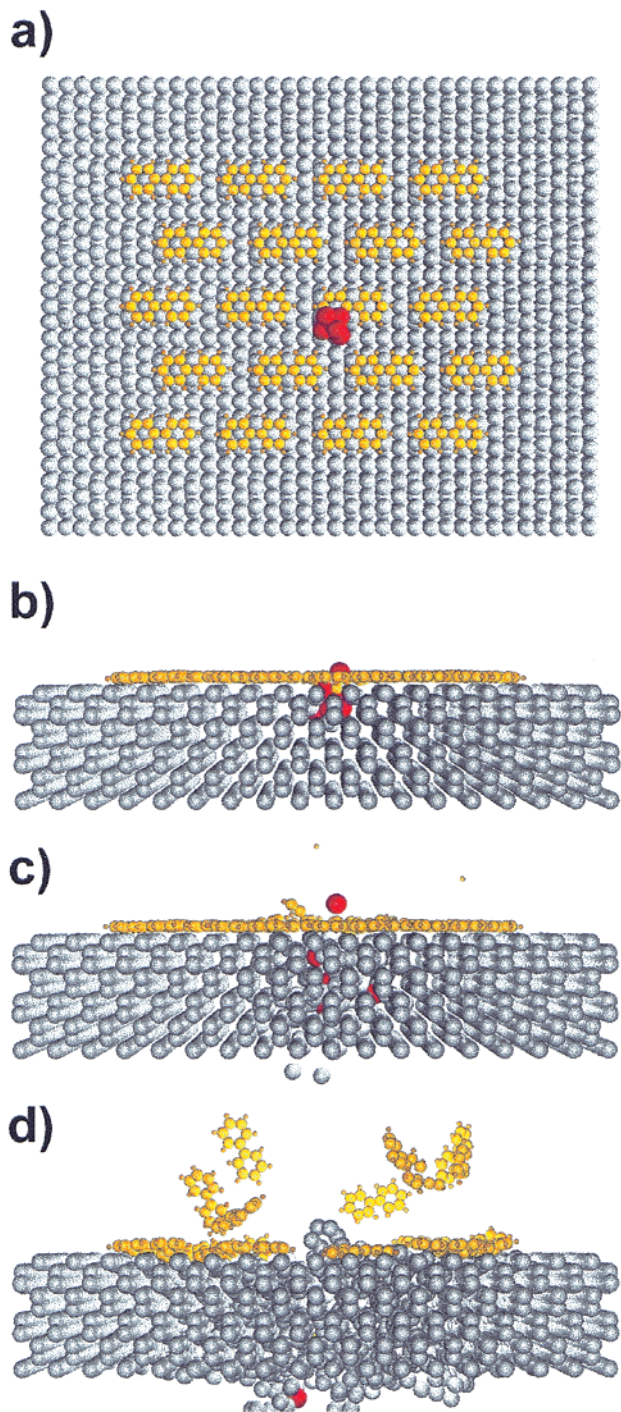


FIGURE 1. Collision cascade and ejection occurring for SF_5 bombardment at 600 eV of a layer of biphenyl molecules on $\text{Si}\{001\}$ - (2×1) . The Si atoms are represented by silver spheres, the C and H atoms by large and small gold spheres, and the S and F atoms by red spheres. The top frame is a top-down view of the initial system, and the lower frames are later time snapshots. The total elapsed time is 3 ps. This particular simulation has 2966 atoms and took ~ 20 min of CPU time.

by a collision cascade or a sophisticated pool game with sticky balls, as shown in Figure 1. In MALDI there is a collective effect of a large number of molecules that gives rise to the liftoff of biological molecules entrained in the plume of the matrix molecules. In this Account, we restrict

ourselves to the SIMS/FABMS process, as we have described the MALDI events in a recent publication.⁵

Molecular systems investigated experimentally by SIMS/FABMS include adsorbed films on a metal substrate, molecular solids, polymers, or even biological cells. In this Account, we focus on thin organic layers on metal substrates as they are used for analytical purposes,^{6a} are intriguing from a fundamental viewpoint, and are computationally tractable. First, the bombardment of submonolayers of organic molecules adsorbed on metals gives rise to a high-yield production of parent molecules (designated as M) attached to metal cations and fragments up to 10 000–12 000 amu.^{6,7} In addition, the yield of other molecular ions, including M^+ , $(\text{M} + \text{H})^+$, and $(\text{M} - \text{H})^-$, and the ratio between the yield of parents and the yield of fragments are enhanced by the presence of the metal when compared to those of a neat sample of organic molecules.^{8,9} This increase of the useful signal arising from large organic species, also observed for neutral molecules,¹⁰ is due not only to the increase of the ionization probability but also to the mechanistic peculiarities of the sputtering process itself.

One successful approach for understanding collision cascades or atomic motions after bombardment by very energetic particles is molecular dynamics (MD) computer simulation.^{11,12} One of the predictions of the MD simulations for atomic solids is that the ejection of particles due to the collision cascade predominantly occurs on the subpicosecond time scale. This fast time scale opens the possibility for large organic and biological molecules being ejected without reaching thermal equilibrium and decomposing. Can MD simulations therefore be used to understand organic SIMS, where the ejected species are molecular ions and molecular ion fragments? Certainly describing the chemical specificity of fragmentation, formation of ions, and possible electronic effects in the collision cascade is beyond the capability of classical mechanics. On the other hand, some experimental data indicate that collision cascades play a major role in the ejection of molecules.^{9,13,14} Regardless of the importance of phenomena we cannot model, there must be a collision cascade present. Thus, we charge forth to see what experimental quantities can be explained with pure classical mechanics. This Account presents vignettes of insights gained from the simulations along with comparisons to experimental data. We hope that by the end of the Account, it will be clear that MD simulations do indeed describe many of the essential events in the ejection of molecules due to energetic particle bombardment.

Briefly, the MD approach involves integrating the classical equations of motion for all the particles in the solid.^{15,16} The results of the simulation provide the positions and velocities of all the atoms in the system as a function of time. From the final velocities, measurable quantities such as energy and angular distributions can be calculated. From the time development of the atomic positions, a microscopic picture of the important motions can be visualized. In addition, the microscopic mechanisms can be identified with specific quantities that can

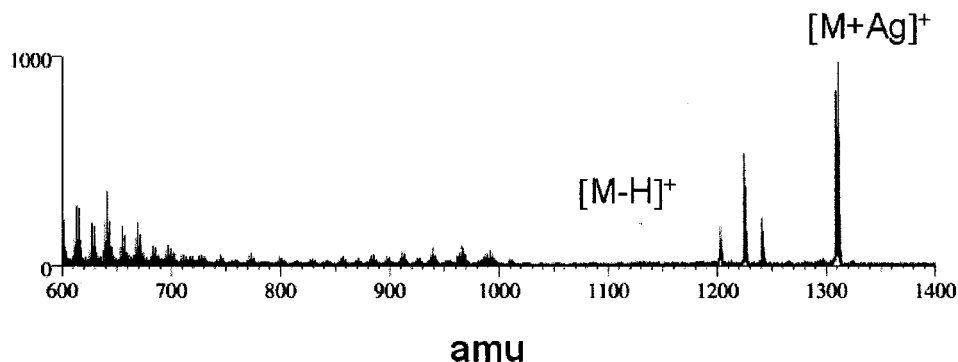


FIGURE 2. Experimental mass spectrum of cyclosporin A (designated M) on Ag. Peaks at 1225 and 1241 amu are $[M + Na]^+$ and $[M + K]^+$, respectively. Peaks between 600 and 1000 amu are unidentified. Reprinted with permission from ref 6d. Copyright 1999 Surface Spectra, Ltd.

be measured. The MD approach needs as input a force field or interaction potential among the atoms. A great advance in the past decade has been the development of many-body potentials for describing extended systems.¹⁷ For example, the Brenner potential initially developed¹⁸ for modeling chemical vapor deposition of diamond films has provided insight into a number of different reactive scenarios involving hydrocarbon systems.¹⁶

II. Results

The simulations provide mechanistic insights into the bombardment process as well as predictions of quantitative distributions of the ejected species. In the following discussion, we first explain the concepts of intact ejection, fragmentation, and reactions and relate these concepts to experimental results. Next, we discuss quantitative comparisons of the results from simulations to experimental energy and angular distributions of ejected molecules.

For monolayers of organic molecules adsorbed on a substrate, two types of bonding configurations have been examined. The first geometry is one in which the molecules have multiple contact points on the surface. Examples of such systems include benzene on Ni^{19,20} and Ag,^{21,22} biphenyl on Cu^{23,24} and Si,²⁵ coronene on Ni,²⁶ and ethylene on Ni.²⁷ The second bonding configuration is one in which there is one primary contact point to the substrate. Examples of these systems include pyridine on Ni,^{20,28} ethylidyne and similar molecules on Pt,^{29–33} alkanethiol chains on Au,^{34,35} and phenyl rings on graphite.³⁶ Of note is that in general the simulations have been performed for incident particle energies between ~500 and ~5000 eV. Exemplary references have been chosen for comparison to experimental data.

Intact Molecular Ejection vs Fragmentation. How do molecules eject with sufficiently low internal energy that they reach the detector intact? Sometimes, in fact, the parent molecules do not appear in the spectrum. In this case, are the molecules not being ejected intact or is there merely a detection problem such as might result from low ionization efficiency. The answer to the question about intact ejection depends on the bonding arrangement of the molecule to the substrate.

(a) Systems with Multiple Contacts to the Substrate.

The predominant ejection mechanism for molecules with multiple contact points to the surface is one in which several substrate atoms hit different parts of the molecule, resulting in a cooperative uplifting of the intact unit.^{19–21,23,26,27} This process is illustrated in Figure 3 for a polystyrene tetramer on Ag. The imparted upward energy to the molecule in this case comes from several gentle collisions rather than one violent collision. Of course, if the collisions are more energetic, fragmentation may occur. In some cases, there are even collisions in which one substrate atom can eject the intact molecule.

Ejection of a molecule from the substrate requires that there be momentum directed toward the vacuum above the surface. The momentum of the primary particle, on the other hand, is initially aimed into the solid. Is there some way to enhance the chances of several substrate atoms moving upward underneath the molecule on the surface? One approach to coordinating subsurface motion uses polyatomic projectiles^{37–40} such as metal or SF₅⁺ clusters. Our calculations clearly show that the polyatomic projectiles, in fact, do increase the probability of having several substrate atoms cooperatively uplift a molecule from the surface.^{23–25}

(b) Upright Chains. Two scenarios have been observed for intact molecular ejection of upright chains on a surface, as shown in Figure 4.^{20,30,32,35} In one case, another particle must specifically move between the bottom atom in the adsorbate molecule and the metal substrate. This motion tends to be a low-probability event, and consequently there is relatively little intact molecular ejection. Second, a particle may strike the middle of the adsorbed molecule, and if the binding energy to the solid is sufficiently small, then the molecule ejects intact.³¹ If the binding energy is large, however, such collisions usually break a bond within the molecule, thus creating a fragment such as the C₃H₇ fragment (turquoise) shown in Figure 4. This fragmentation can be initiated by collisions with the primary particle, a substrate atom, or even other chain fragments (pink).^{30,35} The calculations predict that the top portion of the chain is clipped off and ejected most frequently. For alkane chains such as shown in Figure 4, the predominant fragments are of the type C_nH_{2n+1}.

How does this mechanistic insight help in the interpretation of experimental data?

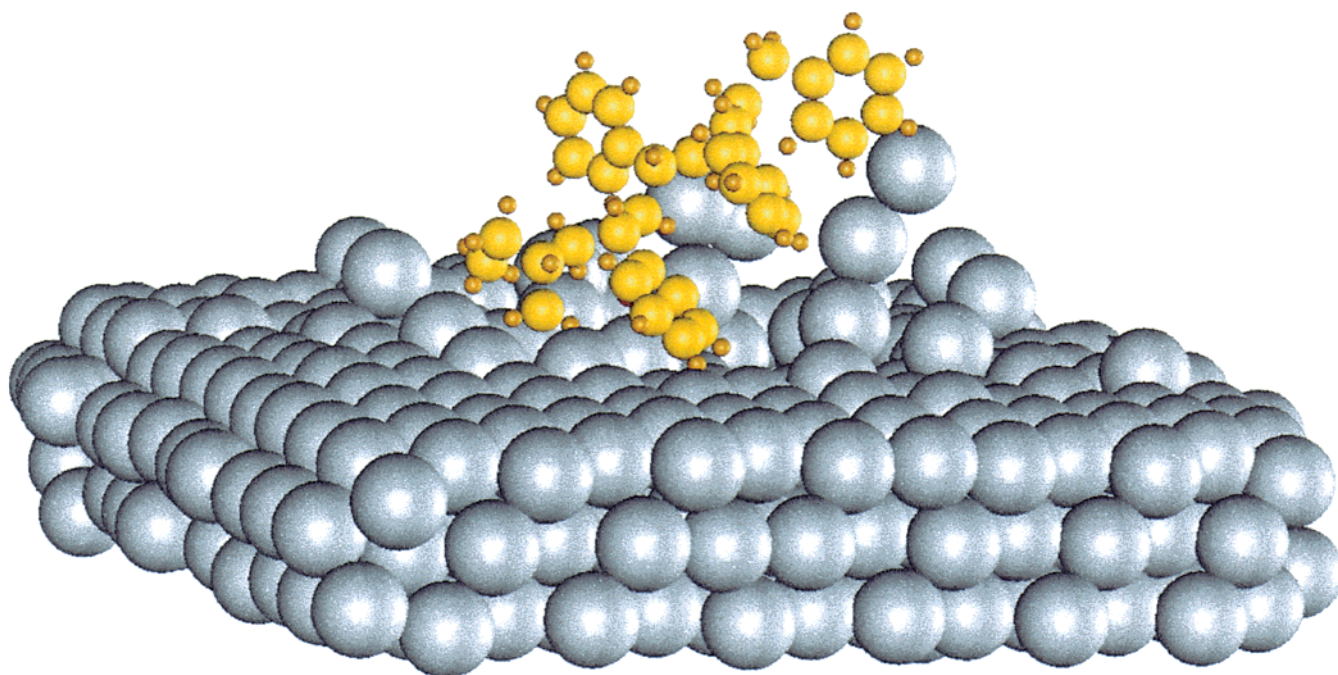


FIGURE 3. Cooperative uplifting mechanism for a polystyrene tetramer on Ag. The Ag atoms are represented by silver spheres and the C and H atoms by large and small gold spheres. Many atoms, including other PS tetramers, are omitted for visual clarity.

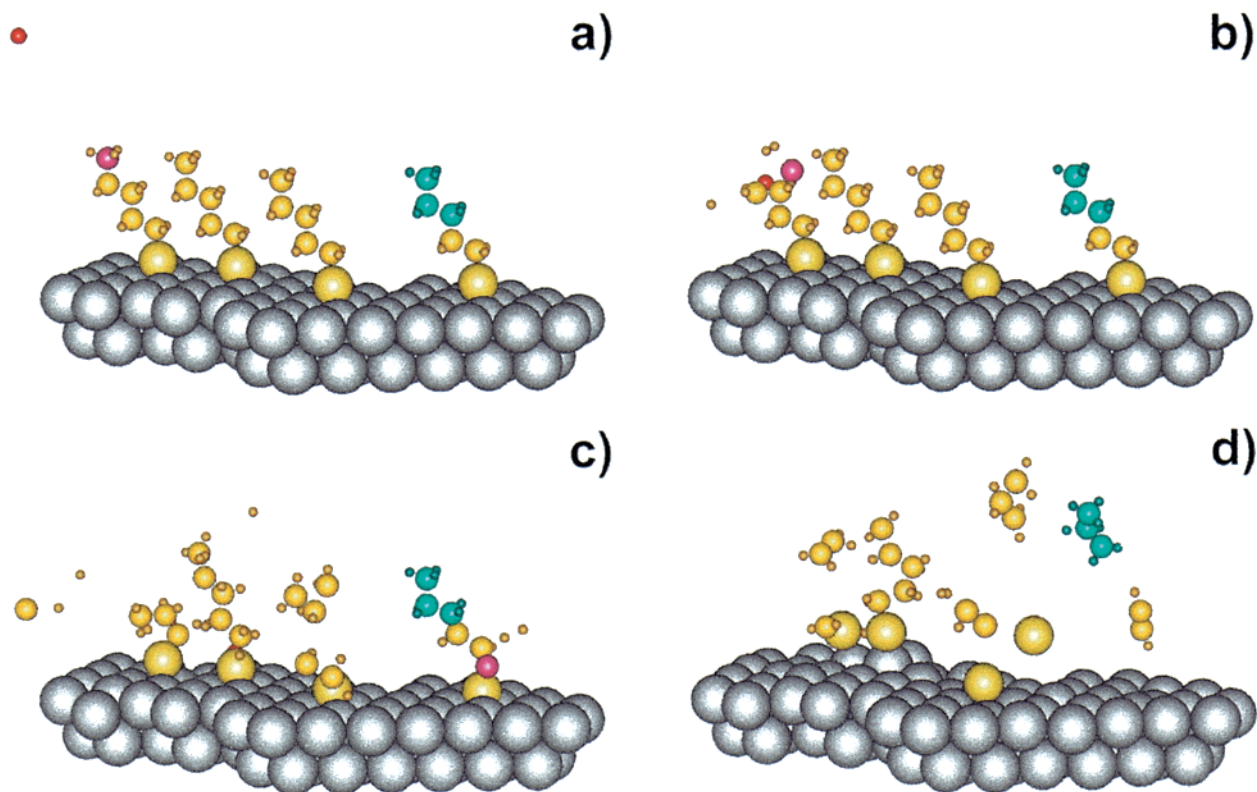


FIGURE 4. Clipping of a C_3H_7 fragment (turquoise spheres) by a C atom (pink sphere) fragment. The system consists of alkanethiol chains (gold spheres for all the S, C, and H atoms) on Au (silver spheres). The red sphere represents the incident Ar projectile. Many atoms, including several chains, are omitted for visual clarity. In addition to the C_3H_7 fragment, an acetylene molecule is present at the right of frame d.

(i) The bonding geometry of pyridine on Ag is coverage dependent. At a low coverage it π -bonds with the surface, while at a higher coverage it σ -bonds in an upright configuration.⁴¹ Concomitant with the geometry change from π -bonded to σ -bonded, the parent molecule intensity

in SIMS decreases⁴² in accordance with the prediction from the simulation.²⁰ In addition to the change in yield, there is also a change in angular distribution that is both measured experimentally and predicted by the simulations.²⁸

(ii) Although the spectrum shown in Figure 2 exhibits peaks that are characteristic of the parent molecule, the dominant peak for ethylidyne, C–CH₃, and propylidyne, C–CH₂–CH₃, on Pt⁴³ and for propylidyne on Ru⁴⁴ is not the parent peak. Rather, fragments such as CH₃⁺ and C₂H₃⁺ dominate the spectrum. In contrast, by monitoring the SIMS signals as a function of temperature, it was shown for a Fischer–Tropsch methanation reaction on Ni that the signals of CH₃⁺, CH₂⁺, and CH⁺ are reflective of their presence on a surface.⁴⁵ The simulations clearly resolve the appearance or nonappearance of the parent molecule for these systems. For molecules with only one carbon atom, there are not many fragmentation pathways, and thus the whole molecule dominates the spectrum.³² When a second carbon group is added, clipping off the top part of the chain becomes most probable.

(iii) How tightly a molecule is bound to the surface will influence the ejection yield.³¹ This concept has been demonstrated in SIMS experiments of femtomole quantities of small peptides on polystyrene beads.⁴⁶ The parent molecule is undetectable when covalently bonded to the bead. When clipped with trifluoroacetic acid vapor into a noncovalent, physisorbed state prior to the bombardment process, the parent signal of the peptide is easily observed.

(iv) Dipalmitoyl phosphatidylcholine (DPPC) can be made to orient either heads-up or tails-up by choice of a suitable substrate.⁴⁷ The experimental results clearly show that a fragment characteristic of the tail group appears in the SIMS spectrum when the DPPC is oriented tails-up, whereas a fragment characteristic of the headgroup is absent. When the DPPC is oriented heads-up, the reverse situation appears in the SIMS spectrum. When the phospholipid is lying sideways, both fragments are observed. This experiment clearly confirms the predictions of the simulations.

(v) The experimental spectra^{6b} of alkanethiols adsorbed on metal surfaces exhibit a series of peaks of the type C_nH_{2n+1}⁺, again in accordance with the results from the simulations.³⁵ Other features of SIMS spectra of alkanethiols on metal surfaces will be discussed below.

Reactions. The violent collision process initiated by energetic particle bombardment induces chemical reactions in the system. Predicting reaction pathways, however, stretches the bounds of the approximations of classical dynamics and the assumed interaction potential. It is possible, however, to gain certain insights into these processes by carefully selecting the model system and by imposing some discretionary judgment on the analysis. For example, mechanistic pathways appear that may be beyond the known capability of the potential but are sufficiently prevalent in the simulations or are so chemically intuitive that they simply cannot be ignored. Specifically, using the Brenner potential in MD simulations of diamond surfaces, a β-scission reaction for carbon insertion into the surface dimer bond was predicted.⁴⁸ Although the mechanism was speculative at the time, the prediction has been shown to be quite feasible by traditional organic chemistry methodology on small-molecule analogues of the diamond surface structure.^{49,50}

(i) The ability to predict reaction pathways is a powerful new aspect of the MD technique. Examples of such reactions include an H abstraction reaction²⁹ to form H₂, and CH₃ abstraction of an H atom to form CH₄.^{30,33} Of course, if the molecule is sufficiently large, then there might be reactions between different regions of the same molecule, as shown in Figure 5, where a C₇H₆ fragment (turquoise) from a polystyrene tetramer abstracts an H atom (pink) from a neighboring site to form C₇H₇. Curiously, a reaction between a free H atom moving sideways along the surface and a free CH₃ radical to form CH₄ has also been observed.³⁰

These proposed reaction mechanisms result from one primary particle impact on the surface and not from prior collision events. How do these reactions relate to the experimental spectra? The C₇H₇⁺ cation is observed in the experimental spectrum of polystyrene oligomers as well as high-molecular-weight polystyrene, and it cannot be explained solely by straightforward gas-phase unimolecular rearrangement.⁵¹ In a recent study of bombardment of organic and inorganic targets, numerous peaks in the spectra are observed that are attributed to a recombination process or “manufacturing” of ions.⁵² Perhaps most of the molecules formed via abstraction-type reactions are neutral and it will take postionization experiments⁵³ to detect these products. In any event, reactions between two molecules or two portions of the same molecule are too prevalent in the simulations to dismiss as artifacts.

(ii) The simulations identify unimolecular reactions that occur on both subpicosecond and microsecond time scales. In tens of femtoseconds,³⁰ an ethylidyne, C₂H₃, species that has been hit by a metal substrate atom can rearrange and spit out an H atom to form acetylene, C₂H₂. Acetylene and ethylene are also predicted to form in the simulations of alkanethiol chains³⁵ and polyethylene films.^{54,55} These stable, neutral species are generally not observed in SIMS spectra but have been observed in postionization studies of polymer films.^{6c} High yields of C_nH_{2n+1} from direct fragmentation are predicted,³⁵ in agreement with experimental data on a number of systems.⁶ The experimental results, however, consistently exhibit a companion peak of C_nH_{2n-1}⁺.^{6b} We suggest, then, that these ions form during the microsecond flight to the detector via the reaction C_nH_{2n+1}⁺ → C_nH_{2n-1}⁺ + H₂.⁵¹

(iii) The parent molecule in the experiments is often observed attached to a metal cation,⁷ as shown in Figure 2. There is naturally a desire to conclude that the metal atom and organic molecules were adjacent on the surface before desorption. In experiments of mixed thiolate (M and M') overlayers on Au, AuMM' clusters might be interpreted as arising from adjacent M and M' molecules.^{56,57} The simulations consistently predict that the metal atom in AuM clusters is not necessarily the metal atom closest to the molecule on the surface.^{20,34,35} The AuM molecule is formed from Au and M moieties that were originally within 6 Å of each other on the surface, with less than a quarter of the Au atoms coming from the 3-fold binding site of the thiolate chain.^{34,35} On the other hand, for the clusters of the type AuM₂, the simulations

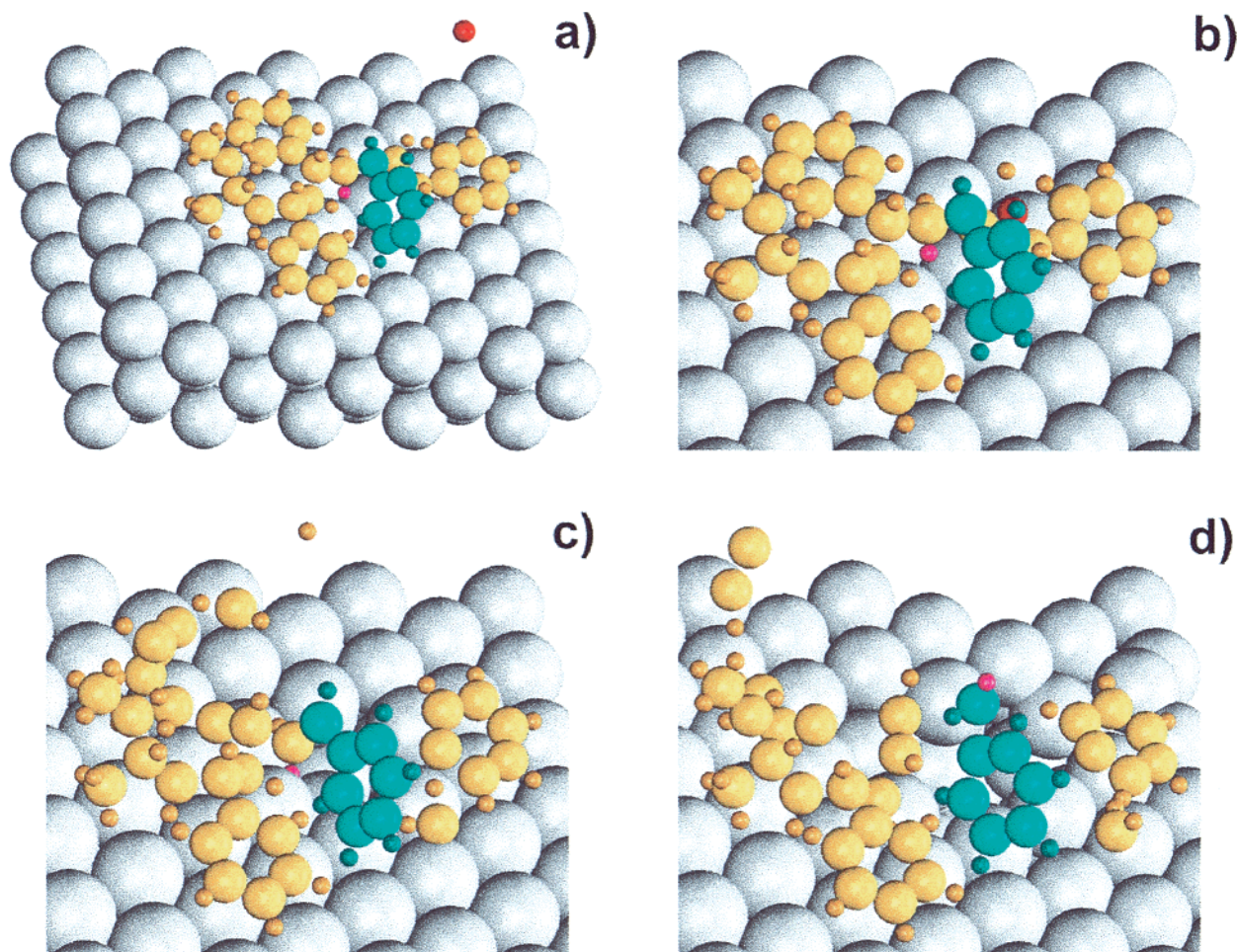


FIGURE 5. Abstraction of an H atom (pink sphere) by a C_7H_6 fragment (turquoise spheres) to give C_7H_7 . The molecule is a polystyrene tetramer. The red sphere represents the incident Ar projectile.

predict that over 90% of the thiolate molecules were adjacent to each other on the surface before desorption.

(iv) The formation of numerous minor fragments that have not been mentioned above are predicted by the simulations. There is also a plethora of minor peaks seen in most experimental spectra. In the study of alkanethiols on Au, some of these peaks are discussed in more detail.³⁵ Currently, interpretation of the significance of some of the minor fragments and reaction products is beyond the scope of the MD approach.

Substrate Influence. There are several ways that the substrate can enhance or inhibit the ejection process. The relevant properties identified to date include opacity and mass of the substrate as well as the binding energy to the molecule of interest to the substrate, as discussed above. It is becoming increasingly clear that the interplay between the substrate and the incident particle is more complex than originally thought. Continued developments, both experimentally and theoretically, are expected in this arena.

(i) The opacity of the substrate influences how effectively the incident particle can initiate a collision cascade underneath the surface. For example, primary beams of polyatomic cluster ions appear to enhance the parent molecule signal over atomic projectiles.^{37–40} The

first explanations of the important physics behind this phenomenon revolved around the nature of the cluster beam and the fact that it could enhance the cooperative uplifting of molecules from the surface, as discussed above. Our simulations clearly predict, however, that the openness of the substrate is also a factor in the yield enhancement.²⁵ For an open lattice such as Si, the incident SF_5 projectile can penetrate beneath the top Si layer and break up within the solid, as shown in Figure 1. Consequently, the S and F atoms are in a position to induce upward momentum for ejecting molecules. For close-packed lattices like Cu, on the other hand, the SF_5 molecule tends to be dissociated by the surface layer and cannot induce as much upward momentum below the surface-bound molecules.

(ii) The mass of the substrate can also influence the ejection of organic molecules from surfaces. Simulations of Ar bombardment of pentylidyne on both Pt and diamond clearly show that the heavier substrate greatly enhances the ejection of the organic species.^{31,33} The Pt atoms are able to turn around part of the momentum of the incident Ar projectile in order to effectively eject the organic molecules. In contrast, the Ar projectile plows through the light C substrate. Certainly, it is well known that parent molecule ion yields can be enhanced by

adsorbing the molecules on metal substrates.^{6a} According to experiments conducted with increasing coverage of organic molecules on metal substrates, the enhancement is due not only to the cationization process⁷ but also to the nature of the collision cascade in the substrate.^{10,58}

Energy and Angular Distributions. Philosophically, we believe that it is imperative to perform reality checks on the simulations by comparison to detailed experimental data. The more detailed the data, the more rigorous the test of the robustness of the computational model. In this regard, measurements of energy and angular distributions of ejected neutral species as measured with multiphoton resonance ionization techniques⁵³ have provided excellent benchmarking studies for the simulations of atomic ejection events.^{11,12} In this final section, a combined experimental and computational investigation of the energy and angular distributions of benzene molecules ejected from a Ag{111} surface is presented.^{21,22}

The system investigated is 0.2 monolayer of benzene adsorbed on Ag{111}.⁵⁸ The measured and calculated energy distributions for C₆H₆ molecules are shown in Figure 6a. The molecular distribution is much narrower and lacks the high-energy tail that typifies metal atom distributions. The molecules that might have had high kinetic energies are, in general, struck so hard that they dissociate.

The comparison between the experimental and calculated energy distributions of the C₆H₆ molecules shown in Figure 6a is quite good, especially for energies less than 4 or 5 eV. The small discrepancies at higher energies arise because there is a correlation between kinetic energy and internal (e.g., vibrational) energy in the molecule, as shown in Figure 6b. These highly excited molecules will decompose unimolecularly before reaching the detector tens of microseconds later. As explained in other articles,^{21,30,35,59} a value of 5 eV is chosen for the maximum allowable internal energy for benzene molecules to have in order to reach the detector. The calculated energy distribution without the highly excited benzene molecules shown in Figure 6a exhibits a much more favorable comparison to the experimental distribution. The data shown in Figure 6b suggest that molecules with low internal energies should have a kinetic energy distribution that peaks at a lower value than that of molecules with high internal energies.²¹ An experiment that state-selects the ejected species by postionization has been performed to verify the correlation of internal energy with kinetic energy, and the prediction of the simulation is quite clearly followed.²²

The polar angle distributions along one azimuthal direction from both the experiment and the calculation are shown in Figure 7a.²¹ The angular distribution exhibits two peaks. One peak is in the direction normal to the surface, and the other one is off normal at a polar angle of about 40°. Shown in Figure 7b is the calculated energy-resolved angular distribution along the same azimuthal direction. Clearly, the normal peak has particles with low kinetic energies, and the off-normal peak has higher kinetic energies. The higher energy ejection events in the

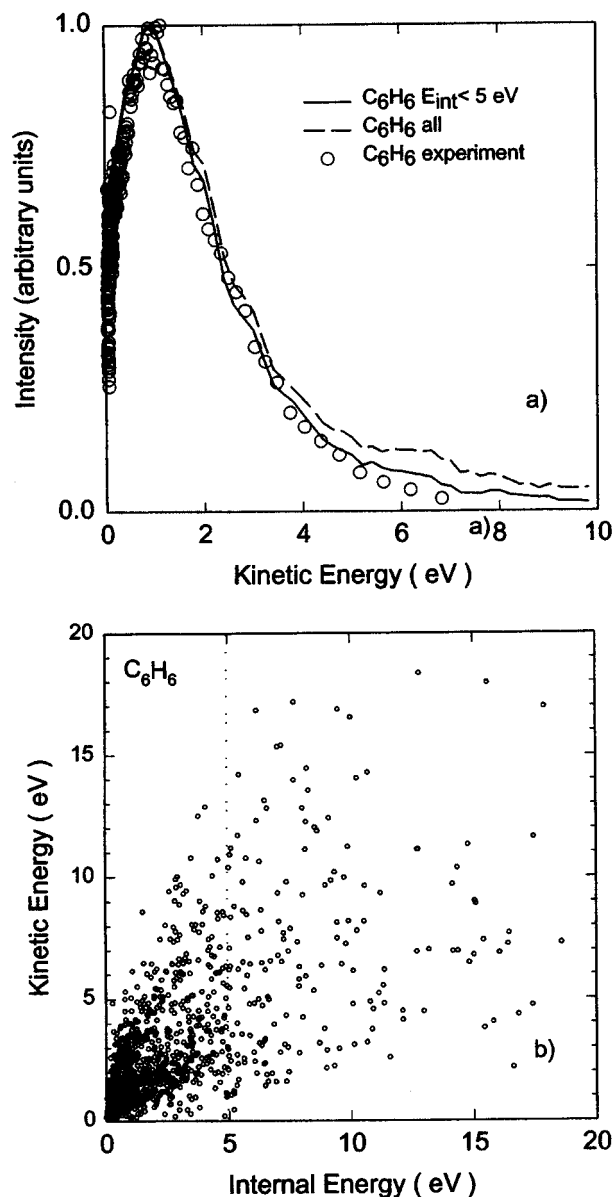


FIGURE 6. Energy distributions of C₆H₆ molecules. (a) Kinetic energy distributions. (b) Scatter plot correlating the kinetic energies with the internal energies. Reprinted with permission from ref 21. Copyright 1999 American Chemical Society.

off-normal direction result primarily from collisions of the benzene molecule with only one Ag atom, which also preferentially ejects in the same direction. The molecules that eject in the normal direction, on the other hand, are energized by the cooperative uplifting mechanism discussed above with two Ag atoms.

III. Prospects for the Future

These studies of modeling energetic particle bombardment of organic films were initially undertaken as a calculated risk. Certain of the predictions from the calculations have been confirmed by experimental data, including cooperative uplifting of molecules, clipping of the tops off of chains, abstraction reactions, and enhancement of molecular ejection due to polyatomic projectiles

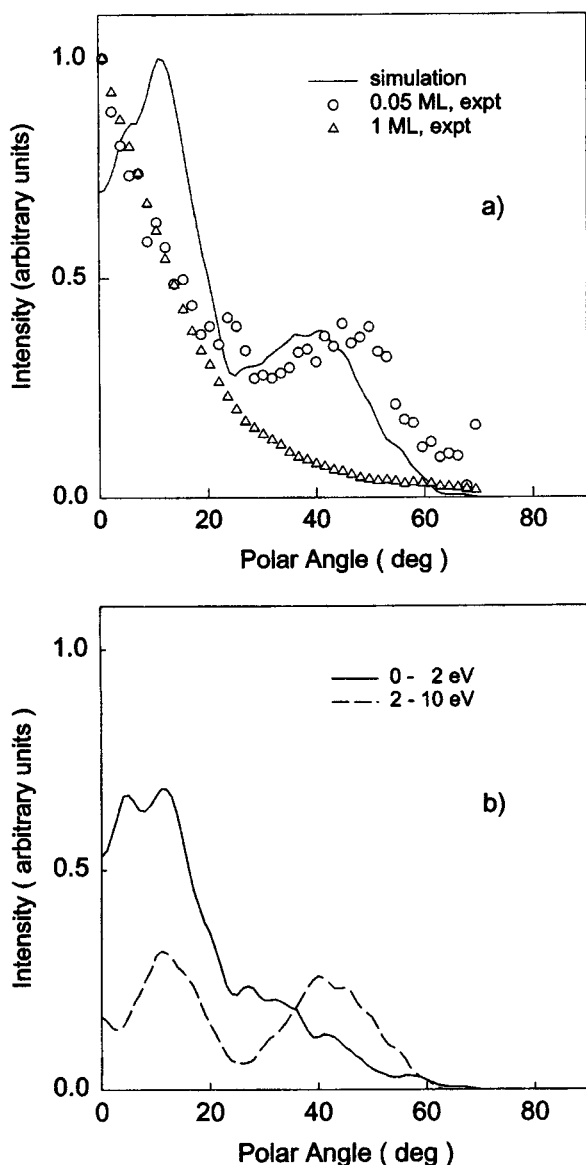


FIGURE 7. Polar angle distribution of C_6H_6 molecules. (a) Experimental distributions. (b) Calculated energy resolved angular distributions. Reprinted with permission from ref 21. Copyright 1999 American Chemical Society.

because of the openness of the substrate. Specific reaction mechanisms, including those involving unimolecular decay products however, are still not possible to predict.

A key aspect for future calculations, then, is to continue to refine the model so that it becomes feasible to predict larger portions of the mass spectrum. Part of this goal involves incorporation of ionization processes that are still problematic to model. Finally, it is essential to extend these ideas to the study of the condensed films of organic molecules, polymers, and biochemicals that are critically important to a wide community of experimentalists. Henceforth we move in this direction.

We are indebted to several collaborators in these investigations. The late Don E. Harrison, Jr., helped get us started in this field. Nick Winograd and his group have provided experimental data that inspires us to continually improve the model. Don Brenner

performed the initial simulations on *ice*⁶⁰ and developed the hydrocarbon potential that made these simulations possible. Ramona Taylor, Susanna Liu, John C. Vickerman, Reema Chatterjee, Zbigniew Postawa, and numerous undergraduate students at College of Charleston have provided the results that make this article possible. The financial support (B.J.G.) of the Chemistry Division of the National Science Foundation is deeply appreciated. The National Science Foundation through the MRI and CRIF programs and IBM through the Selected University Research program provided the computers. K.D.K. acknowledges support from the National Science Foundation, the Petroleum Research Fund, and the Research Corporation. The Penn State Center for Academic Computing staff have been most gracious in helping us efficiently use the IBM SP computer and develop graphics for animation and presentation.

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