

## FUNDAMENTAL ASPECTS OF MOLECULAR DESORPTION IN SIMS

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### 1. Introduction

Mechanisms of molecular desorption from ion-bombarded surfaces are still not well-understood. Elucidation of these mechanisms is, of course, essential to maximizing the information content of the SIMS signal. To determine the important physical and chemical processes that lead to desorption, our laboratory has concentrated on measuring the energy and angle-distributions of ejected neutral molecules[1]. This information is then compared when possible to molecular dynamics computer simulations of the ion-bombardment event[2]. The comparison is important since these types of calculations provide a molecular-level view of the atomic motion in the solid that leads to the ejection process, and if the calculated trajectories agree with the measured trajectories, then we feel confident that the picture presented by the computer is a realistic one. In this report, results from several different systems are examined. The results yield a rather confusing picture associated with a variety of desorption mechanisms that yield diagnostic trajectory information. These include sputtering by collision cascades and momentum transfer, various thermal desorption mechanisms and mechanisms involving electronic processes. Moreover, the type of bonding between the adsorbate and the substrate strongly influences the nature of the fragmentation pattern associated with the SIMS spectra. Although complex, these factors contribute to a framework about which a more general understanding can emerge.

### 2. Results and discussion

The first example is the case of a fraction of a monolayer of benzene adsorbed onto Ag{111}. For this situation, we have already shown that the kinetic energy (KE) distribution of benzene molecules peaks at a value of about 1 eV and is similar in appearance to the Ag KE distribution[1]. Molecular dynamics calculations match up very well with the experimental ones if molecules calculated to contain more than 5 eV are removed from consideration[2]. These molecules, it is assumed, would undergo unimolecular decay on the way to the detector. For this situation, the desorption mechanism is clearly initiated by a collision cascade of Ag atoms, and the theory works very well.

For multilayers of benzene on Ag, the situation changes dramatically. The KE distribution peaks at 0.04 eV, and takes on a Maxwell-Boltzmann appearance with a fit temperature that is much greater than the substrate temperature (500K vs 120K). Bombardment with  $H_2^+$  projectile ions does not result in the ejection of molecules, indicating that momentum transfer is a critical part of the process. At present, these data support the notion that there is a molecular collision cascade in the multilayer film which involves

vibrational and rotational excitation of the molecules and exothermic reactions of fragments formed in the cascade. These events can cause local heating of the substrate and emission of molecules with effective temperatures higher than the macroscopic surface temperature. Molecular dynamics calculations are not yet available to test these ideas, although our formalism is presently being adapted to allow this type of modeling.

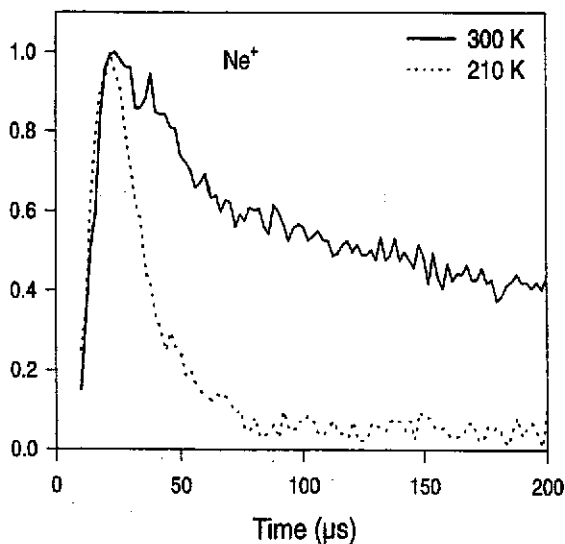


Fig. 1. TOF distribution of the neutral tryptophan fragment at  $m/z$  130 using 8 keV  $\text{Ne}^+$  projectiles as a function of surface temperatures.

A third type of molecular desorption is represented by a sample made of pellets of tryptophan[3]. In this case, we monitor a neutral tryptophan fragment at  $m/z$  130 after bombardment with 8 keV  $\text{Ne}^+$  ions at 300 K and 210 K surface temperatures. As seen in Figure 1, the TOF distributions at both surface temperatures have a well-defined peak close to 20  $\mu\text{s}$ . This value corresponds to a KE of about 0.1 eV, a value similar to that seen for benzene ice. At 300 K, however, the TOF distribution exhibits a continuous emission of molecular fragments that persists for longer than 200  $\mu\text{s}$  after bombardment. Note that this emission is not observed when the sample is cooled to 210 K. A possible explanation of this effect is that energy is stored in

some kind of electronically excited state for a time after excitation. Deexcitation may involve a radiationless decay transferring KE to the solid matrix. Tryptophan is known to have a long-lived triplet state, which would be quenched at lower temperatures. It will be interesting to see if other systems exhibit such unusual effects, or if there is simultaneous light emission associated with these materials.

For all of the above cases, the molecules are only weakly bonded to their substrates. In many cases, there are strong covalent bonds between the adsorbate and the substrate that can dramatically alter the energy dissipation pathways. A prototypical example involves the desorption of organic molecules covalently attached to polystyrene spheres. This is a very important practical situation since these spheres are used to create large combinatorial libraries associated with drug discovery research. As shown in Figure 2, we find that the TOF-SIMS spectra of stearic acid attached to a polystyrene surface using the chemical linker shown in the figure exhibits only fragment ions associated with the bead itself. After a brief exposure to a vapor of trifluoroacetic acid (TFA) and chloromethane, however, the molecular ion at  $M+\text{H}^+$  and the fragment at  $M-\text{OH}^+$  are clearly visible. This treatment cleaves the covalent bond, allowing the stearic acid molecule to rest comfortably on the polystyrene surface. This type of result was also predicted by early MD simulations where it was reported that molecules strongly chemisorbed on Pt surfaces were more readily fragmented than were

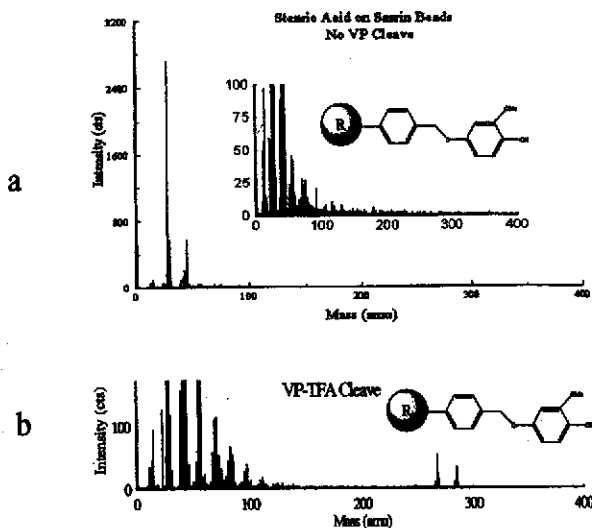


Fig. 2. TOF-SIMS spectra of stearic acid attached to a polystyrene resin (R) by a sasrin linker as shown. The beads in (a) are untreated and in (b) are exposed to TFA vapor for five minutes.

To prepare a film with the tailgroup pointing away from the surface, a  $\text{SiO}_2/\text{Si}$  substrate was pulled through a layer of DPPC on a water subphase. This substrate presents a polar surface that preferentially binds the lipid headgroup. To prepare a film with the headgroup pointing away from the surface, a  $\text{C}_{16}$  alkane thiol monolayer on gold was inserted through a layer of DPPC on the same water subphase. The TOF-SIMS results illustrated in Figure 3 provide a clear verification of this principle. In fact, the main headgroup fragment ion at  $m/z$  184 and the tailgroup hydrocarbon fragment ion at  $m/z$  311 provide enough contrast such that imaging phospholipid domains becomes feasible.

### 3. Conclusions

Here we have compared the sputtering behavior of a variety of classes of molecules to attempt to identify the key physical and chemical properties that influence the mechanism of desorption. Perhaps the important point at this stage of understanding is that we have identified many factors that can be involved, and that as much as possible needs to be known about the system before predictions of SIMS spectra can be made. Our efforts have focused on the role of the nuclear motion, leaving ionization effects for future studies. However, it is clear that a better understanding of the events associated with the molecular collision cascade will offer a better chance at predicting *a priori* how a system will respond to ion bombardment.

physisorbed molecules[4]. The principle obviously imparts broad implications to TOF-SIMS measurements including detection of small biomolecules bound to receptor sites, antibody-antigen interactions as well as surface adsorption studies in general.

Finally, we consider how the orientation of the molecule influences the mechanism of desorption. The initial molecular dynamics simulations of organic molecule desorption predicted that the tops of long chain molecules would be preferentially removed from the surface[4]. To test this prediction, we constructed oriented Langmuir-Blodgett films of phosphatidylcholine dipalmitoyl (DPPC) such that either a headgroup or a tailgroup is forced toward the air-film interface[5].

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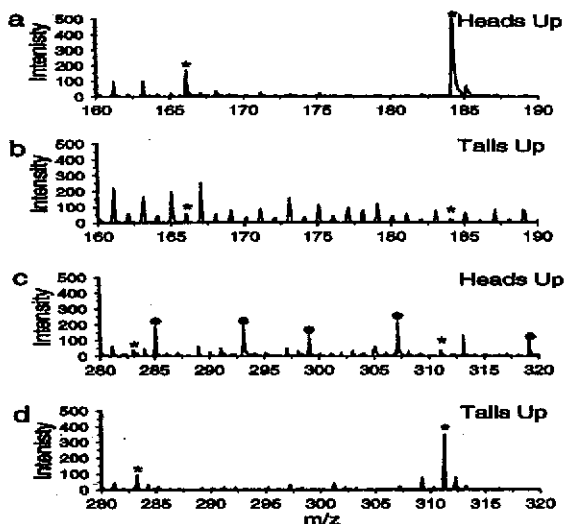


Fig. 3. TOF-SIMS spectra of DPPC LB film prepared with the headgroup exposed to the beam (a and c) and the tailgroup exposed to the beam (b and d). The labeled peaks (•) refer to mass peaks from the substrate or peaks which change with orientation (\*).

## References

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