

CLUSTERS DESORBED, EJECTED AND ABLATED FROM  
SOLID SURFACES

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Abstract. The microscopic mechanisms of desorption of molecules from solids are examined. The specific processes discussed are thermal desorption, ejection due to ion bombardment and ablative photodecomposition of polymers due to irradiation by 193nm laser light. A short movie depicting the ion bombardment events will be shown.

A number of physical processes can be responsible for the desorption, ejection, or ablation of material from a solid. The choice of technique depends on whether one is interested in merely removing the overlayer so that the surface is clean or whether one is monitoring the nature of the desorbed particles to obtain a better understanding of the adsorbed particles and their interaction with the surface. These techniques can also provide a means of synthesizing novel molecules or clusters. For example, in ion bombardment experiments on solid nitric oxide clusters of  $[\text{NO}(\text{N}_2\text{O}_3)_n]^+$  where  $n \leq 11$  have been observed to eject.<sup>(1)</sup> In this discussion we limit ourselves to three mechanisms of particle removal from solids. The first is thermal desorption, which provides a basis to which to compare the others. Ion bombardment experiments (sputtering, secondary ion mass spectrometry - SIMS, fast atom bombardment mass spectrometry - FABMS) are discussed in some detail. Finally, the mechanisms responsible for ablative photodecomposition of polymers at 193nm laser light are examined.

## THERMAL DESORPTION

A solid sample can be heated and material desorbs. (Eventually even the solid will vaporize.) Thermal desorption experiments are often performed such that the temperature of the sample increases at a constant rate. The amount and nature of the desorbed species are monitored as a function of the surface temperature. The temperature at which a particular molecule, e.g. CO, desorbs is a measure of the heat of desorption for the molecule. The timescale of the desorption process is milliseconds to seconds, thus the adsorbed molecule has sufficient time to

undergo many vibrational oscillations and absorb kinetic energy (heat) from the solid. Therefore, molecules which are thermally unstable will be broken up before they have time to desorb and be detected. This is in contrast to the ion bombardment experiments discussed next where the time scale for ejection is  $<.3 \times 10^{-12}$  seconds. In this case many large, thermally unstable molecules can be vaporized.

## EJECTION DUE TO ION BOMBARDMENT

The use of beams of ions with kinetic energies in the keV range has expanded as a means of getting large and novel clusters into the gas phase. Bombardment of tungsten results in ejection of metal clusters,  $W_n^+$ , where  $n \leq 12$ .<sup>(2)</sup> By preadsorbing oxygen on Ni(100) clusters of the type  $Ni_nO_m^{\pm}$  with  $n, m$  as large as 3 have been observed.<sup>(3)</sup> For systems with molecular CO adsorbed one observes clusters of the type  $Ni_nCO^+$  where  $n \leq 3$ .<sup>(4)</sup> Note that there is usually one carbonyl and several metal atoms. The nickel carbonyl that is synthesized by chemical means in  $Ni(CO)_4$ . We wish to address the question of how to relate these clusters to the original surface composition. As an example of the complexity of this question, bombardment of ice yields clusters of the type  $(H_2O)_nH^+$ <sup>(5)</sup>--obviously protons solvated with the original water molecules. Bombardment of solid nitric oxide (NO) only gives the clusters  $[NO(N_2O_3)_n]^{+1}$ <sup>(1)</sup>

We have been using a classical model to describe the ion bombardment event. This model can be used to look at the microscopic processes which are not accessible from experiments in order to give us further insight into the ejection mechanisms. Briefly, the theoretical model consists of approximating the solid and possible adsorbed molecules by a finite array of atoms.<sup>(6-15)</sup> Assuming a pairwise interaction potential among all the atoms, Hamilton's equations of motion are integrated to yield the positions and momenta of all particles as a function of time during the collision cascade. The final positions and momenta can be used to determine the experimental observables such as total yield of ejected particles, energy distributions, angular distributions and possible cluster formation. One advantage of the classical procedure is that one can monitor the collision events and analyze microscopic mechanisms of various processes.

From the classical dynamical treatment, it is possible to examine the cluster formation mechanism in detail and to provide semiquantitative information about cluster yields. In general, these calculations suggest that there are three basic mechanisms of cluster formation.<sup>(15,16)</sup> First, for systems with atomic identity such as metals, or atomic adsorbates on a solid, the ejected atoms can interact with each other in the near-surface region above the crystal to form a cluster by a recombination type of process.<sup>(6-8)</sup> The description would apply to clusters of the type  $M_nO_m$  observed in many types of SIMS experiments. In this case the atoms in the cluster do not need to arise from contiguous sites on the surface, although in the absence of long-range ionic forces the calculations indicate that most of them originate from

a circular region of radius - 5 angstroms. This rearrangement, however, complicates any straightforward deduction of the surface structure from the composition of the observed clusters. We have observed an Ar<sub>25</sub> cluster to eject from solid argon via this mechanism. (17)

A second type of cluster emission involves molecular species which can be as simple as carbon monoxide or as complicated as the dodecanucleotide. (18) Calculations have been performed for a series of organic molecules adsorbed on a Ni(001) surface to understand the mechanisms of molecular ejection. (11-13) The first molecules which have more than just a few atoms examined are benzene which  $\pi$ -bonds on a metal surface and pyridine which can either  $\pi$ -bond or  $\sigma$ -bond on a metal surface. Larger structures, whose size approach the diameter of bioorganic molecules, are naphthalene, biphenyl and coronene whose adsorption structures are unknown. In all cases we find that the molecular species may be ejected intact. From our theoretical calculations, three factors favor this process. First, a large molecule has many internal degrees of freedom and can absorb energy from an energetic collision without dissociating. Second, in the more massive framework of a large organic molecule, individual atoms will be small in size compared to a metal atom; thus, it is possible to strike several parts of the molecule in a concerted manner so that the entire molecule moves in one direction. Finally, by the time the organic molecule is struck, the energy of the primary particle has been dissipated so that the kinetic energies are tens of eVs rather than hundreds or thousands of eVs. These three factors are equally valid for the ejection of either carbon monoxide, benzene or coronene. However, in the cases of the larger molecules, we found that often 2-3 metal atoms would strike different parts of the molecule during the ejection process. The time for the molecules to eject after the primary particle has hit the sample is less than 200 femto-seconds. This intact ejection mechanism for molecules can be applied to molecular solids. Work in progress on the bombardment of ice shows that the water molecules can also eject intact. (19)

The final mechanism for cluster ejection is essentially a hydrid mechanism involving both intact ejection and recombination. In the case of CO on Ni<sub>3</sub>Fe, we find that the observed NiCO, Ni<sub>2</sub>CO and NiFeCO clusters form by a recombination of ejected Ni and Fe atoms with ejected CO molecules. There is apparently no direct relation between these moieties and linear and bridge-bond surface states. In the case of cationized species such as NiC<sub>6</sub>H<sub>6</sub><sup>+</sup> ions, we propose a reaction of the type



The presumption that the Ni supplies the charge is based on the fact that no C<sub>6</sub>H<sub>6</sub><sup>+</sup> is observed (20) and that the ionization potential of Ni is less than that of benzene.

This final hybrid mechanism may be responsible for the formation of the dimer ion of the dodecanucleotide<sup>(18)</sup> or of water clusters.<sup>(5)</sup> Each molecular unit ejects intact and then interacts with other molecules in the near surface region to form the cluster entities. The interpretation of the NO spectrum<sup>(1)</sup> is more difficult.

#### ABLATIVE PHOTODECOMPOSITION OF POLYMERS

The final mechanism of particle removal is a process termed ablative photodecomposition of polymers. When a pulse (~14 nsec halfwidth) of laser radiation of 193 nm wavelength with a fluence above a threshold value falls on a polymer film, the material at the irradiation site is spontaneously etched away to a depth of 1000Å or more.<sup>(21-23)</sup> Microscopic examination of the surface of the etched area shows no indication that the substrate has melted or flowed even in the case of polymers with a glass transition temperature as low as 100°C. Ablative photodecomposition is observed to occur in a variety of organic polymers at fluences as little as 10 mJ/cm<sup>2</sup>. The process has considerable potential as a "dry" etching step in the semiconductor industry and in certain medical applications. Here the focus of study is not so much what is coming off or even its relationship to the original structure. Rather it is the remaining sample with a clean and sharp pit region that is of interest. The results of this experiment are qualitatively different from other experiments thus one would suppose a different mechanism of ejection.

In our model the polymer is described by structureless monomer units held together by strong attractive interactions. After the laser light has struck the sample a few of the monomer units can react photochemically. We have simulated this process by allowing each monomer unit to undergo excitation from an attractive to a repulsive potential surface. This excitation produces a change in the volume that the monomers occupy. Given this configuration Hamilton's classical equations of motion for the particles are integrated in time. The important conclusion here is that this model predicts that the reacted monomer units ablate and that the remaining solid is not melted. It is conceivable that the impact of the explosion could have spread sideways and significantly damaged the crystal. The model has also predicted the average velocity and angular distribution of the ablated material. The corresponding experiments were subsequently performed<sup>(24,25)</sup> with the data in excellent agreement with the predictions from the calculations.<sup>(26)</sup>

#### FINALE

Three distinct processes of removal of material from a solid have been theoretically modeled. In each case the model gives a microscopic picture of the processes as well as predicting experimental observables.

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