

Mechanisms of Organic Molecule Ejection in SIMS and FABMS Experiments

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A classical dynamics model is used to investigate nuclear motion in solids due to bombardment by energetic atoms and ions. Of interest are the mechanisms of ejection and cluster formation of molecular species where we have predicted intact ejection of benzene-C₆H₆, pyridine-C₅H₅N, naphthalene-C₁₀H₈, biphenyl-C₁₂H₁₀ and coronene-C₂₄H₁₂. The results presented here show that the energy distributions of the parent molecular species, e.g., benzene, are narrower than those of atomic species, even though the ejection processes in both cases arise from energetic nuclear collisions. The bonding geometry also influences the ejection yield and angular distribution. The specific case of π -bonded and σ -bonded pyridine on a metal surface is discussed with comparisons between the calculated results and experimental data. These calculations provide a means of interpreting SIMS, FABMS and possibly even PDMS experimental data.

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. These mechanisms are shown schematically in Figure 1 and have been discussed in detail elsewhere [1,2]. Of particular interest here is the ejection of species that were originally molecules on the surface, e.g., benzene-C₆H₆, pyridine-C₅H₅N, naphthalene-C₁₀H₈, biphenyl-C₁₂H₁₀, and coronene-C₂₄H₁₂. Here the calculations indicate that there can be intact ejection. From our theoretical calculations, three factors favor this process [3,4]. 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 femtoseconds. 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 also eject intact [5].

For metal-organic clusters such as the Ni₂C₆H₆ species shown in Figure 1 the calculations indicate that a hybrid mechanism involving intact ejection and recombination is operative. This final hybrid mechanism may be

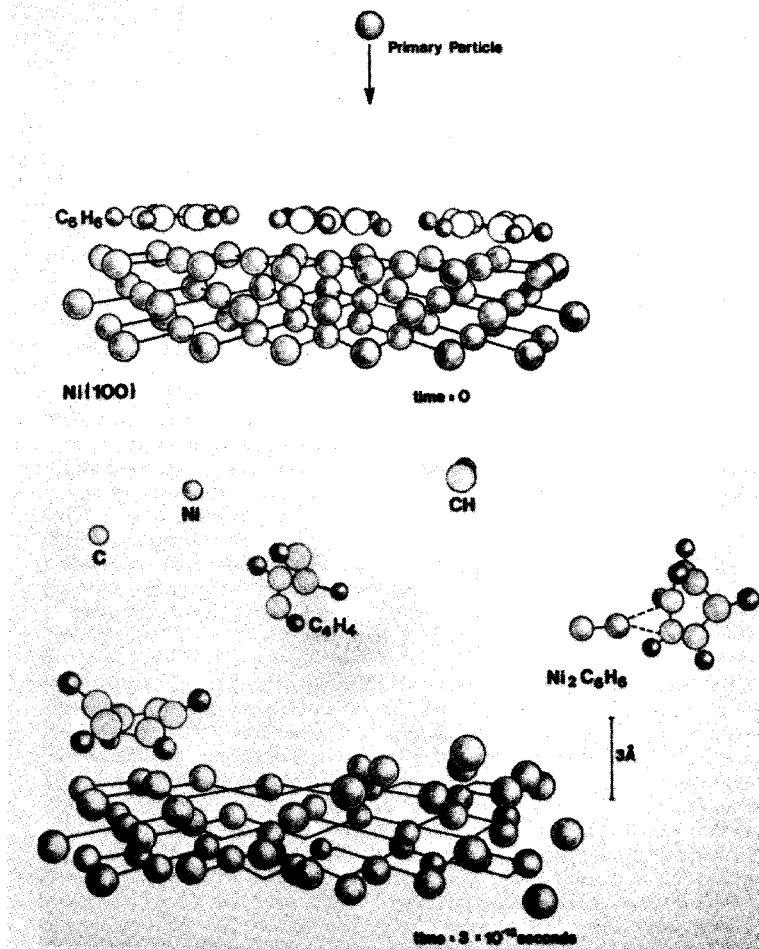


Fig.1 Before and after drawings of one ion bombardment event

responsible for the formation of the dimer ion of the dodecanucleotide [6] or of water clusters [7].

The energy distributions of atomic species ejected in bombardment experiments are characterized by a peak at 1-5eV and a high energy tail that goes approximately as E^{-n} where $n \approx 2$. This distribution is characteristic of a non-equilibrium collision cascade. The energy distributions of the parent molecular species are much narrower, however, and often terminate at ~ 10 eV [2,8]. Since the molecular species are ejecting during the same collision cascade as the metal ions and on the same timescale, one would expect the distribution of collision energies that cause ejection to be the same for the metal atoms and the organic molecules. However, the energetic collisions with the molecular species can and do cause fragmentation. Thus the energetic molecules are depleted. The fragments then should have a distribution at higher energies. These trends are confirmed by both our

calculations and recent experiments of benzene adsorbed in Ag{111}[2,8]. It is tempting to use the energy distributions of the ejected particles as a key to understanding the mechanisms responsible for the desorption. Care must be taken, however, as collision cascades can give rise to very different energy distributions depending on the nature of the species.

It is of interest to compare the ejection mechanisms for molecules bonded to the surface with different orientations. In benzene, the interaction with the surface is shared among six carbon atoms via the π -electron cloud. In pyridine, however, the bonding occurs almost totally through the nitrogen atom while the remainder of the molecule is pointing away from the surface. The most striking difference between the two cases is that the computed yield of molecular species for the pyridine system is extremely low [4]. The reasons for the major difference in yields for these two structures are clear from an analysis of the trajectories that lead to molecular ejection of pyridine. Very simply, pyridine ejection requires the specific cleavage of a N-metal bond during a single collision. When a carbon atom is struck, the molecule either stays on the surface or tends to dissociate. There appears to be no efficient modes of transferring the energy of collisions with the molecule into translation away from the surface. Obviously the original structure of the organic molecules, then, affects the ejection and fragmentation processes. One would not necessarily expect similar spectra from a sample of a monolayer of organic molecules on a metal, a liquid, or an ordered solid. These orientational effects have recently been confirmed in SIMS measurements of pyridine and benzene adsorbed on Ag{111} [9]. In this system the benzene π -bonds to the surface while the pyridine π -bonds at low coverages but rearranges at higher coverages to σ -bond to the surface. The intensity of the AgC_6H_6^+ ion monotonically increases as the benzene coverage on the silver surface is increased to one monolayer. The $\text{AgC}_5\text{H}_5\text{N}^+$ and $\text{C}_5\text{H}_5\text{NH}^+$ ion intensities, however, initially increase and then decrease as the molecule rearranges on the surface, and finally increase again as the pyridine coverage is increased to one monolayer.

Acknowledgment

The interaction with those who have supplied the experimental data, D. W. Moon, R. J. Bleiler, E. J. Karwacki and N. Winograd, has greatly helped in solidifying many of the ideas presented here. I thank them for many stimulating conversations. The financial support of the National Science Foundation, the Office of Naval Research, the A. P. Sloan Foundation and the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

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