VERTICAL CHANNELING OF PYRIDINE MOLECULES EJECTED IN ION BOMBARDMENT EXPERIMENTS

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Recent secondary ion mass spectrometry experiments of organic molecules on metal surfaces show that the bonding geometry of the molecule on the surface is reflected in the polar angle distributions. Specifically, the polar distribution of pyridine molecules ejected from a σ-bonded configuration on a Ag{111} is narrower than the polar distribution of benzene molecules ejected from a π-bonded configuration. Classical dynamics calculations presented here identify a new channeling mechanism in which the σ-bonded pyridine molecules on the surface focus the ejection direction of other pyridine molecules.

The arrangement of atoms and molecules on surfaces has been shown to influence the angular distributions of ejected atomic and molecular species in keV ion bombardment experiments‡. The reason for this dependence is that there is a surface channeling mechanism that forces atoms to eject along open crystallographic directions where atom–atom repulsions are at a minimum [6–8]. These anisotropies have previously only been found in azimuthal angle distributions. In addition the high-energy secondary particles exhibit more azimuthal anisotropy than the low-energy secondary particles. The low-energy particles tend to eject after much of the momentum of the primary ion has dissipated within the crystal and destroyed parts of the initial surface order. High-energy particles, on the other hand, leave the crystal after only a few collisions have occurred, and thus more accurately reflect the symmetry of the surface.

Polar angle distributions of benzene and pyridine ions ejected due to ion bombardment of organic layers on Ag{111} exhibit features which indicate that a vertical channeling process is occurring [11]. For a Ag surface covered with a monolayer of benzene or exposed to 0.15 langmuir (L) of pyridine, the molecules are believed to be lying parallel to the surface. The polar angle distributions of $(M - H)^+$ ions ($C_6H_5^+$ for benzene) and $(M + H)^+$ ions ($C_5H_5NH^+$ for pyridine) are broad and exhibit a peak at $\theta = 20°$. The benzene polar angle distribution is reproduced in fig. 1a. On the other hand, for σ-bonded pyridine which is formed when Ag{111} is exposed to greater

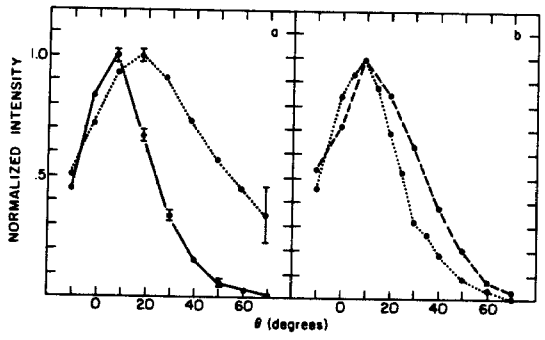

Fig. 1. Normalized polar angle distributions of molecular ions ejected from overlayers of organic molecules adsorbed on Ag{111} at 153 K. The polar angle is defined with respect to the surface normal. The experimental configuration and details are described in ref. [11]. (a) —— 4.5 L pyridine $(M + H)^+$; ... 2.5 L benzene $(M - H)^+$. (b) 4.5 L pyridine $(M + H)^+$, – – – 6–10 eV secondary ions; ... 3–7 eV secondary ions.

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‡ Over a hundred papers have appeared concerning this topic since 1956. For a review, see ref. [1]. See also refs. [2–10].

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than 0.15 L pyridine the polar angle distribution is sharper and peaks at $\theta = 10°$ (fig. 1a). It appears that the array of σ-bonded pyridine molecules provides a means of focusing the direction of ejection of the pyridine molecules. Further, the polar angle distribution of the high kinetic energy ions (6–10 eV) ejected from the σ-bonded pyridine structure is 20–30% wider than the distribution of the low kinetic energy ions (3–7 eV) as is shown in fig. 1b. This trend toward wider polar angle distributions for faster moving particles is counter to that observed for atom ejection.

A classical dynamics model has been used to elucidate important mechanisms of ejection of atoms and molecules from surfaces and to gain a fundamental understanding of the ion bombardment process [6–9]. Previous studies using this model predict that the geometry of the organic molecule on the surface, either π-bonded or σ-bonded, strongly influences the total yield of ejected molecules [12,13]. For the π-bonded benzene system, where the plane of the molecule is parallel to the surface, the calculated yield for C_6H_6 ejection is on the order of one molecule per incident ion. However, for the σ-bonded pyridine system, where the molecular plane is perpendicular to the surface, the calculations predict almost no molecular ejection. These predictions have been verified recently by experiments involving benzene and pyridine adsorbed on Ag{111} at 153 K [11], which clearly show that the molecular orientation affects the molecular ejection yield.

It is the purpose of this work to utilize the molecular dynamics calculations to understand, at least qualitatively, the changes that are observed in the angular and energy distributions of organic ions as their surface molecular orientation is altered. The emphasis of this study is to determine the mechanism by which the σ-bonded pyridine molecules are channeled into a vertical ejection direction and why the secondary ion energy dependence of the polar angle distribution is opposite to that observed in azimuthal angle distributions of atomic systems. Because of the relatively low yield of ejected pyridine molecules, the probable tilt of the pyridine molecules [13], and the spacing of the molecules on the surface it is unreliable in this case to make quantitative comparisons between the experimental results and the theoretical calculations. Our aim here is to determine the mechanistic reason for the apparent vertical channeling of the σ-bonded pyridine molecules. The details of the calculations have been described elsewhere [14]. In the model calculation presented here, the binding energy of a pyridine molecule to the surface is decreased from 1.8 to 0.9 eV as an arbitrary way to increase the number of ejecting pyridine molecules. This is also a more realistic value since pyridine only adsorbs on silver at temperatures considerably less than room temperature. The microcrystallite with the {001} face exposed has three layers of 145 metal atoms per layer. To remain consistent with previous calculations the metal atoms were given the mass of Ni, although the qualitative conclusions should be similar for Ag. Twenty-eight pyridine molecules are then placed on the surface in a $(\sqrt{2} \times 2\sqrt{2})R45°$ configuration. Even with the decreased binding energy and the increased number of pyridine adsorbates, the molecular ejection yield of σ-bonded pyridine is still lower by a factor of 3.2 than that of benzene. The primary ion is Ar^+ which bombards at 1 keV in a direction normal to the surface.

The calculations indicate that pyridine molecules initially σ-bonded perpendicularly to the surface are blocked by neighboring pyridine molecules when they exit from the surface at large polar angles. One example of how this blocking can significantly affect the trajectory of an ejecting pyridine molecule is illustrated in fig. 2. Only the species (one Ar^+ ion and two pyridine molecules) directly involved in this particular molecular ejection process are shown. In this example the metal substrate plays no direct role in ejecting the molecule. The grid lines are drawn between the nearest-neighbor atoms in the first plane of the microcrystallite. The elapsed time during the collision process is shown in fs. The initial positions of the atoms are drawn in fig. 2 (0 fs). At 33 fs the Ar^+ ion, which has backscattered from the surface, is colliding with 3 carbon atoms in the target pyridine molecule. The kinetic energy of the center of mass of this pyridine molecule is 11.6 eV and its molecular axis is oriented at a polar angle of $\theta = 66°$ from the surface normal. At 85 fs the ejecting pyridine molecule collides with a neighboring pyridine molecule and dissipates a fraction of its momentum. At the final stage of the sputtering process (120 fs), the pyridine molecule ejects molecularly, even though distorted, at a polar angle of $\theta = 31°$ with 1.40 eV of kinetic energy. Due to the blocking by a neighboring pyridine molecule, the polar angle of the ejected

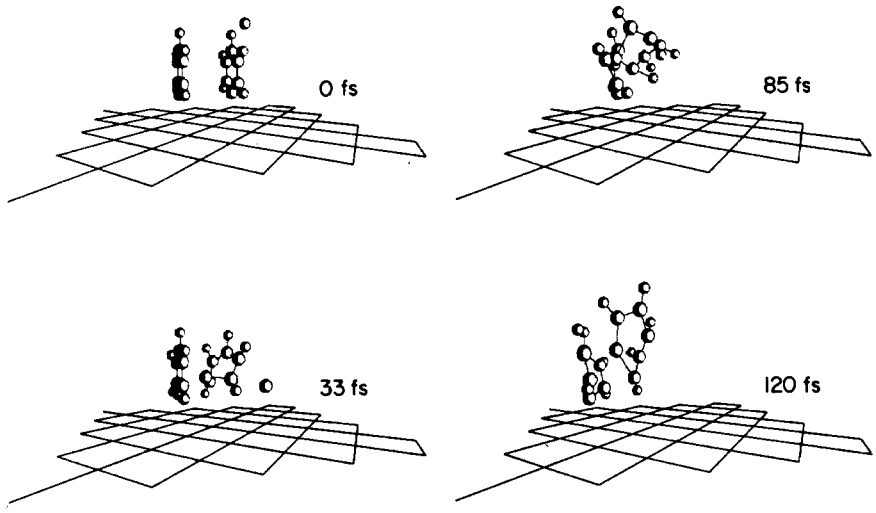

Fig. 2. Change of the ejection angle of a sputtered pyridine molecule (right one) due to the blocking by a neighboring pyridine molecule (left one). The labels are in fs. (0 fs) Initial positions of the atoms. (33 fs) The backscattered Ar^+ ion collides and ejects the pyridine molecule at a polar angle of $\theta = 66°$. (85 fs) The ejecting pyridine molecule is blocked by a neighboring pyridine molecule. (120 fs) Finally, the ejection polar angle is changed to $\theta = 31°$. Both the sputtered molecule and the blocking molecule are distorted.

pyridine molecule is altered from 66° to 31°. The walls created by pyridine molecules are not completely rigid as indicated by the distorted molecule shown on the left in the 120 fs frame. Therefore, a pyridine molecule ejecting with a large kinetic energy will not feel a strong enough force to channel it completely into the upward direction. The polar angle distribution of the high-energy ejected particles is thus broader than that of the low-energy ejected particles. This mechanism is distinct from that found with atom ejection. In this latter case, the energy dependence of the azimuthal distribution is related to the *time* of ejection and consequently to the amount of surface structure present when the atom ejects. Note that for the π-bonded benzene system, there are no channels to orient the ejecting molecules.

Although we do not feel it is appropriate, given the approximations in our scattering calculations, to make quantitative comparisons to experimental results, we did examine the calculated polar angle distributions. The benzene polar distribution is slightly broader than the pyridine one. The benzene distribution exhibits very little dependence on the energy of the secondary particles. For the σ-bonded pyridine distribution, the polar distribution of the particles with greater than 2 eV of kinetic energy is broader than that of the low-energy molecules. These qualitative trends are in line with the experimental observations.

In conclusion, a classical dynamics model has been utilized to identify the channeling mechanism that causes the narrow polar angle distribution of the molecular pyridine ions for σ-bonded pyridine on Ag{111}. The blocking by neighboring pyridine molecules affects the polar angles of ejected pyridine molecules and inhibits their ejection at high polar angles. As the result of these channeling effects, the polar angle distribution of the molecular ions for σ-bonded pyridine is much narrower than those for π-bonded benzene. The measurement of the molecular ejection yield and the polar angle distribution of the molecular ions appears to be a new approach for the study of the orientation of molecular systems where molecular channels influence the desorbing particle's trajectory.

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The factor 10^{-7} in the abscissa of fig. 2b should read 10^{-6}. The last two lines of the caption to fig. 2 should be replaced by "... $A_1 = 5.13 \times 10^{-21}$ and $A_2 = 1.22 \times 10^{-6}$." The last two lines of the caption to fig. 3 should be replaced by "... $P_{expr} = 0.56 \times 10^5$, $P_{calc} = 1.91 \times 10^5$."