

Desorption Mechanism of Benzene from $C_6H_6/Ag(111)$ using keV Ion Bombardment and Laser Postionization

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Abstract. Laser postionization of neutral benzene sputtered from $C_6H_6/Ag(111)$ has been performed to investigate the mechanisms that lead to desorption of molecules from surfaces. The velocity time of flight (TOF) distributions of neutral benzene were measured after 8 keV Ar^+ bombardment. Two components are present in the distributions. For sub-monolayer and monolayer coverages a low TOF, high kinetic energy (1.14 - 0.25 eV) peak dominates the distribution, whereas for multilayer coverages a high TOF, low kinetic energy (0.04 eV) peak dominates. The intensity of the high TOF peak increases with bombardment time for desorption from multilayers of benzene. The results indicate that a collision cascade in the metal initiates the benzene ejection from thin overlayers of benzene on Ag(111). An ion beam induced chemical change is proposed to occur in thick benzene overlayers.

INTRODUCTION

Ion beam induced desorption techniques have found useful applications in molecular surface characterization of organic and biological systems (1). Of fundamental interest is the interaction of ion beams with organic solids and the mechanisms that lead to molecular desorption (2,3). It is well known that a collision cascade leads to ejection of atomic species in the case of metals and semiconductors. The mechanism by which the primary ion beam dissipates energy into the substrate to lead to the ejection of molecules is still not very well understood. The present study focuses on desorption induced by ion bombardment of benzene adsorbed on Ag(111). Since the sputtering of Ag(111) is well investigated a submonolayer to multilayer coverage of benzene on Ag(111) provides a simple model system to study desorption mechanisms from molecular

overlayers. To our knowledge, these are the first measurements obtained for neutral benzene molecules desorbed from monolayer films.

EXPERIMENTAL

Benzene was adsorbed on a clean Ag(111) surface cooled to 120 K. Gases dissolved in benzene were removed by several freeze-pump-thaw cycles before dosing. The benzene coverage was controlled by monitoring the chamber pressure and the dosing time.

An 8 keV, 220 ns Ar^+ pulse focused to a 3 mm spot on the sample initiated the desorption process. Ejected neutral molecules were detected after multiphoton ionization with a 6 ns laser pulse at 266 nm. The laser beam was focused to a ribbon shape approximately 1 cm above the sample. The time of flight of neutral benzene molecules from the surface to the laser plane was recorded by varying the delay between the ion pulse and the laser pulse. The ionized molecules were then detected by time of flight mass spectrometry using a gated microchannel plate detector. The experimental setup has been described in detail previously (4).

The angle of incidence of the primary ion beam was 45° and the signal was detected normal to the surface over an angular range of $0^\circ \pm 20^\circ$. The postionization mass spectrum had peaks at m/z 52 (C_4H_4 fragment), 78 (molecular C_6H_6), 108 (Ag) and 216 (Ag_2). The distributions were recorded by monitoring m/z 78 for benzene and m/z 216 for silver dimer. The silver monomer distributions were not recorded as they have contributions from dimers fragmenting in the laser plane.

RESULTS AND DISCUSSION

The velocity TOF distributions of neutral benzene desorbed after 8 keV Ar^+ bombardment of $\text{C}_6\text{H}_6/\text{Ag}(111)$ are shown in Figure 1 for various exposures. The distributions have a striking dependence on the benzene coverage. A low TOF component (peak A) is present at low coverage and a high TOF component (peak B) becomes dominant at higher coverage. At extremely low coverage the benzene distributions look similar to that of silver. This result implies that benzene desorption at low TOF occurs due to direct collisions between the substrate and overlayer species. As the benzene overlayer is increased from sub-monolayer to monolayer coverage (1L - 5L), peak A shifts towards a higher time of flight. This corresponds to a peak shift in the kinetic energy distribution from 1.14 eV to 0.25 eV. As the benzene coverage increases collisions between the overlayer molecules become significant and a part of the primary energy is deposited into various internal degrees of freedom, thereby decreasing the kinetic

energy of the molecules. Increase in benzene coverage also changes the surface binding energy which leads to the shift in the kinetic energy peak.

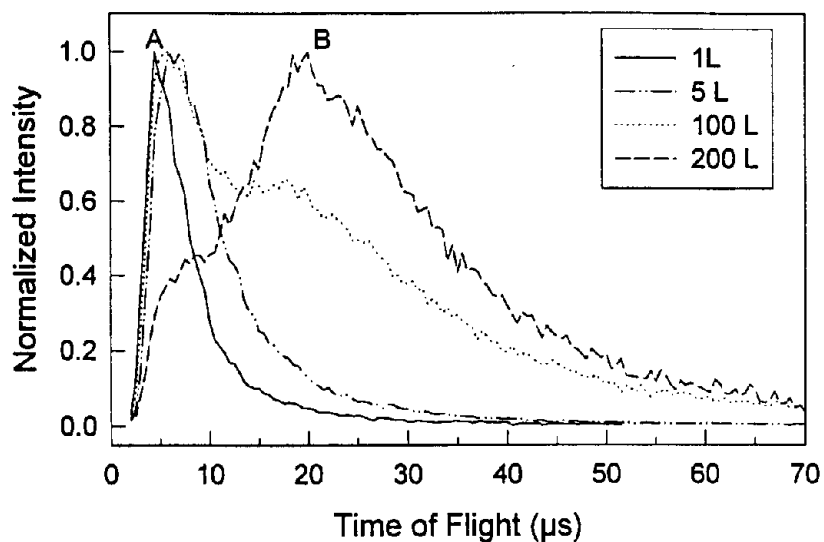


Fig. 1. The velocity time of flight distribution of neutral benzene for various exposures (1 L = 1×10^{-6} torr • sec).

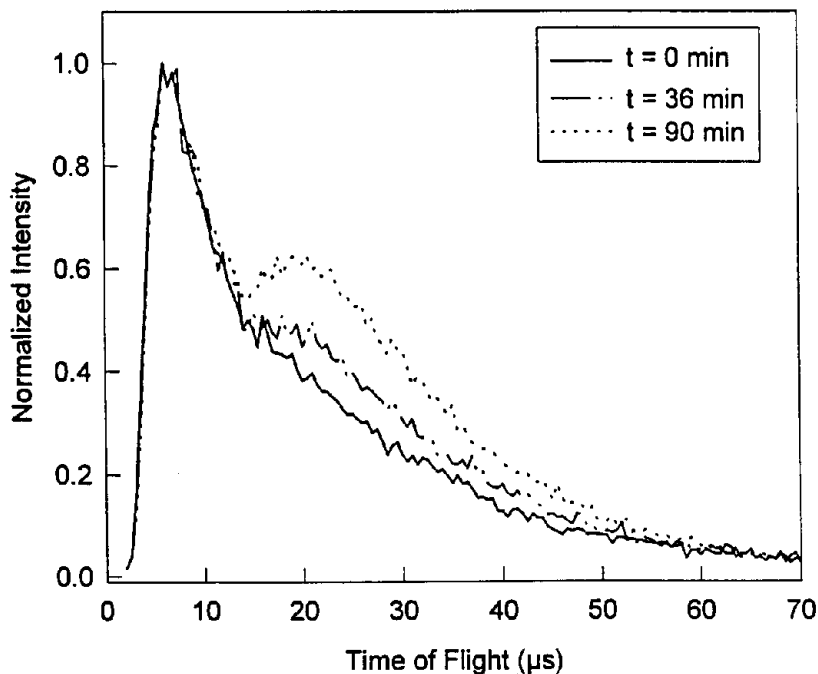


Fig. 2. The velocity time of flight distribution of neutral benzene (90 L exposure) as a function of bombardment time

As the thickness of the benzene layer is further increased a very low kinetic energy peak (0.04 eV) emerges in the distribution (peak B in Fig. 1). The two components coexist, with an increase in peak B intensity as the benzene overlayer becomes thicker. On the other hand, the intensity of the silver as well as the low TOF peak of benzene decreases for higher exposures, and at 800 L only the high TOF peak is present. At this point no silver signal is seen in the mass spectrum. This clearly indicates that desorption at extremely low kinetic energies from multilayer coverages of benzene is not initiated by direct collisions from the substrate. Although it is tempting to ascribe the low kinetic energy component to a thermal desorption process, the Boltzmann distribution fit temperature (575 K) does not match the experimental surface temperature (120 K).

Another interesting feature, as shown in Figure 2, is that the TOF distributions depend not only on benzene coverage but also on the bombardment time. The intensity of the high TOF component increases with prolonged ion bombardment. The rate of change of the signal intensity increases as the benzene overlayer becomes thicker. After moving the ion beam to a new sample spot the signal intensity reverts to its original value. This implies that a local chemical or physical change in the sample induced by the ion beam results in desorption at these extremely low kinetic energies. Earlier studies have shown that electron beam impact of benzene overlayers on Ag(111) leads to the formation of phenyl fragments which desorb as biphenyl upon increasing the sample temperature (5). It is possible that a similar process initiated by the ion beam results in the ejection of biphenyl or larger aromatic molecules from the surface which eventually fragment into benzene in the laser plane.

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