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Desorption of silver atoms from benzene-covered Ag(1 1 1) by energetic Ar^+ bombardment

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Abstract

Experiments have been conducted to gain insight into the processes of desorption of neutral species from surfaces covered with organic molecules due to bombardment with keV particles. The system is comprised of benzene molecules adsorbed onto Ag(1 1 1) and bombarded with 8 keV Ar^+ ions. Molecular dynamics (MD) simulations of the same system have been performed. Results show that the presence of the benzene alters the yield, the kinetic energy distributions, and the angular distributions of the silver atoms. These changes of the desorption characteristics are the result of collisions between the Ag atoms and the benzene molecules adsorbed to the surface. As more benzene is adsorbed to the surface, the changes to the Ag atom desorption characteristics become more pronounced. The simulations reproduce the modifications to the Ag atom energy and angle distributions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The irradiation of a solid surface with energetic particles initiates a complex sequence of events. Following the impact of the energetic particle, desorption of atoms and molecules both in a variety of charge and internal energy states can occur [1]. Having detailed knowledge of the events causing the desorption is important for understanding and improving energetic ion beam-based surface sensitive analytical techniques, such as SIMS [2].

Experiments can be designed to obtain mass, energy and angle distributions of the species that are ejected in order to gain insight into the events leading to the desorption after the impact of the energetic particle. These experiments also guide and validate theoretical predictions from computer simulations. Ever-improving molecular dynamics (MD) computer simulations are a valuable asset for providing a microscopic picture of the complex

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events leading to atomic and molecular desorption [3]. This report discusses recent experiments and MD simulations of the energetic ion bombardment of benzene adsorbed to an Ag(1 1 1) surface.

The system of interest is benzene (C_6H_6) adsorbed onto an Ag(1 1 1) surface. The C_6H_6/Ag(1 1 1) system has many attractive features that make it an ideal candidate for studying energetic ion-stimulated molecular desorption from organic overlayers [4]. The inert nature of silver towards C_6H_6 largely prevents chemical reactions between the metal substrate and the adsorbate molecules, thus preserving a simple binary system for investigation. Moreover, the UV spectroscopy is well known for both the Ag atoms [5] and the C_6H_6 molecules [6]. Ground state and internally excited species of both Ag atoms and C_6H_6 molecules can be probed experimentally.

The C_6H_6/Ag(1 1 1) system has been studied in the past with both experiments [4] and MD simulations [7]. The finding from these experiments was that the C_6H_6 desorption mechanism changes as a function of C_6H_6 exposure. More recent experimental investigations using resonant postionization to probe specific quantum states of C_6H_6 molecules have been performed [8,9]. The energy distribution for vibrationally excited benzene molecules ($C_6H_6^*$) shifted to lower energies as a function of benzene exposure, but the energy distribution for ground state benzene molecules (C_6H_6) was less affected by the benzene exposure. These studies of the C_6H_6 desorption are complemented by investigations of Ag atom desorption characteristics as C_6H_6 molecules are adsorbed to an Ag(1 1 1) surface.

In order to discern the role that the departing substrate Ag atoms play in the desorption of benzene molecules, experiments using resonance enhanced multiphoton ionization of the Ag atoms in the atomic ground state have been performed. The presence of the organic overlayer affects the emission characteristics of the departing Ag substrate atoms, and these changes provide insight to desorption phenomena.

A detailed microscopic picture of the desorption phenomena is obtained from MD computer simulations of the energetic Ar-stimulated emission processes. To this end, MD simulations of Ar atom bombardment of a system comprised of C_6H_6 molecules on an Ag(1 1 1) surface have been conducted. In contrast to prior simulations based on 500 eV Ar atom bombardment [7], the simulations discussed here are based upon 5 keV Ar atom bombardment. The choice of using 5 keV Ar atoms, instead of 500 eV Ar atoms, is selected because it is in closer agreement to the experimental conditions of 8 keV Ar^+ ion bombardment. It has been shown that the higher kinetic energy introduces more higher action impacts that influence the kinetic energy distribution [10].

2. Methodology

The details of the instrumental system used to collect the experimental data have been described elsewhere [11]. In brief, the experiments are performed in a UHV chamber with a base pressure of 1×10^{-10} Torr equipped with low energy electron diffraction (LEED) and with laser postionization time-of-flight mass spectrometry. A 200 ns Ar^+ ion pulse, accelerated to 8 keV and focused to a 3 mm spot on the sample, initiates the desorption process. The angle of incidence is 0° for collecting energy and angle resolved distributions. Laser pulses from Nd:YAG pumped dye lasers are focused to a ribbon shape approximately 1 cm above the sample for postionizing a portion of the desorbed plume. The quantum state-specific laser postionization schemes are discussed in detail elsewhere [9]. The postionized particles are mass selectively detected on a gated, position sensitive MCP detector.

Both the Ag(1 1 1) surface and C_6H_6 gas are cleaned prior to dosing the C_6H_6 vapor [4,9]. After the crystal is cooled to 120 K, the chamber is filled with C_6H_6 vapor to a specific pressure for a certain time period to create a desired exposure, which is reported in Langmuir (L) units ($1\ \mathrm{L} = 1 \times 10^{-6}$ Torr·s). Benzene is reported to form a monolayer (ML) by a 5–7 L exposure [4,9] and to form an ordered monolayer in a (3×3) arrangement on Ag(1 1 1) by a 5 L exposure [12].

MD simulations of energetic Ar atom bombardment have been used to investigate the mechanisms of the desorption process. The detailed description of the method are found elsewhere [13]. In short, classical equations of motion are integrated to determine the position and velocity of each atom as a function of time. From the final positions and velocities of the atoms, experimentally observable properties, such as total yield, kinetic energy and angular distributions, are calculated.

The model system approximating the Ag(1 1 1) sample is represented by a microcrystallite composed of 5280 atoms arranged in 10 layers of 528 atoms each and is based on the crystal used earlier for modeling 5 keV Ar atom bombardment [10]. The organic overlayer is modeled by a (3 × 3) arrangement of 52 molecules placed parallel to the crystal surface above the hcp threefold sites. A less densely packed overlayer is modeled by 26 molecules in a (4 × 4) arrangement. A more densely packed overlayer is created by placing the C_6H_6 molecules in an approximately (2 × 2) arrangement. This case shall be referred to as "(2 × 2)" because not all the molecules can be placed exactly in the correct location for a true (2 × 2) arrangement. Moreover, a small number of the molecules in the equilibrated "(2 × 2)" overlayer do not lie parallel to the Ag(1 1 1) surface. In an effort to save computational time, a smaller microcrystallite is utilized for the "(2 × 2)" case. However, a (3 × 3) arrangement was also constructed on the smaller microcrystallite and the results compared quite favorably to those from the (3 × 3) arrangement on the larger microcrystallite detailed above. The final position of the benzene molecules is determined by allowing the system to equilibrate at 0 K using a generalized Langevin algorithm.

The 5 keV Ar atom is directed normal to the surface. A total of 1000 trajectories is calculated to sample the appropriate impact zone. Open boundary conditions are used so that energetic particles are allowed to escape the crystal. A purely repulsive Molière potential is used for the Ar–Ag, Ar–C and Ar–H interactions [14]. The Ag–Ag interactions are described by the MD/Monte Carlo corrected effective medium (MD/MC-CEM) potentials [15]. A Lennard–Jones potential function is used to describe the Ag–C_6H_6 interactions [7]. The Brenner potential for hydrocarbons is used to describe the C–C, C–H and H–H interactions [16,17]. This potential allows for chemical reactions and accompanying changes in atomic hybridization. A Molière function is attached to the repulsive wall of the Brenner potential to accommodate for energetic collisions [18]. Long-range interactions between C_6H_6 molecules are taken into account by the AIREBO potential [19].

3. Results and discussion

The experimental energy and polar angle distributions of ejected Ag atoms are shown in Figs. 1(A) and 2(A), respectively, as a function of ben-

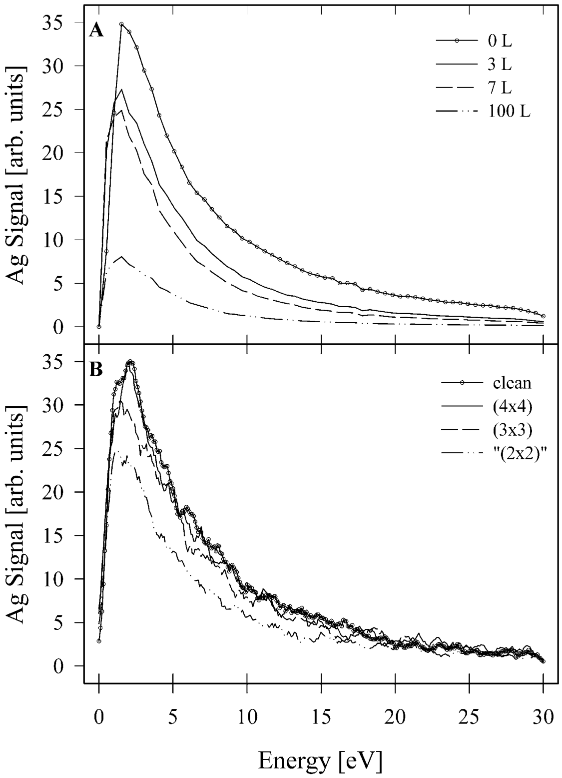

Fig. 1. Kinetic energy distributions for Ag substrate atoms. The experimentally obtained distributions for ground state Ag atoms for a variety of benzene exposures (panel A) are integrated over all polar angles. The 0 L exposure corresponds to a clean crystal surface. The Ag atom distributions for a variety of benzene coverages (panel B) from the simulations are angle integrated over all polar angles as well. The trace labeled clean is from a microcrystallite with no benzene adsorbed to the surface.

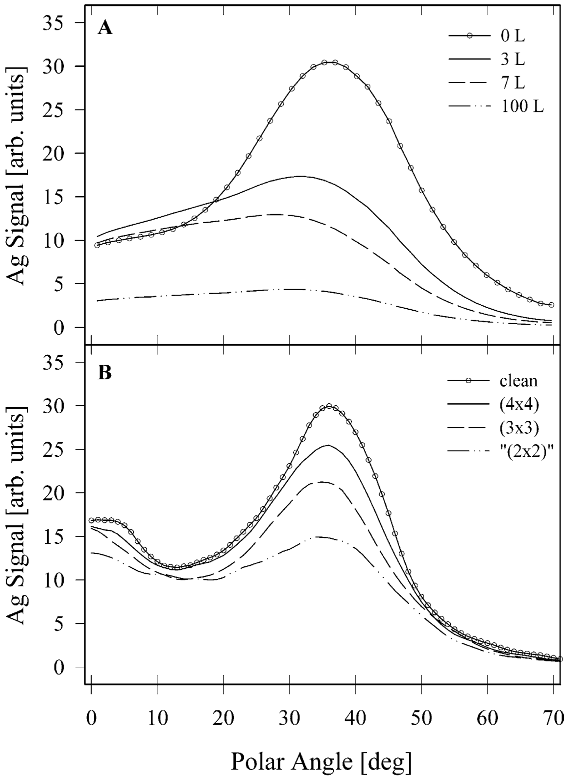

Fig. 2. Polar angle distributions for Ag substrate atoms. The experimentally obtained distributions for ground state Ag atoms for a variety of benzene exposures are in panel A. The 0 L exposure is from a clean crystal surface prior to the benzene exposures. The Ag atom distributions for a variety of benzene coverages from the simulations are illustrated in panel B. The trace labeled clean is from a microcrystallite with no benzene adsorbed to the surface.

zene exposure. Exposures nominally correspond to a sub-monolayer coverage (3 L) and approximately a monolayer coverage (7 L). The 100 L exposure results in multiple layers of benzene on the Ag(1 1 1) surface. The corresponding energy and polar angle distributions from the simulations are shown in Figs. 1(B) and 2(B).

The intensity of the energy distribution decreases as a function of coverage in both the experimental and calculated data. It is difficult to calibrate absolutely the experimental exposures with coverage, but the experimental distributions for the 3 and 7 L exposures are comparable with the distributions for the (3 × 3) and "(2 × 2)" coverages in the simulation. The intensity of the (4 × 4) in the calculated results is indistinguishable from that of the clean surface, a result consistent with previous investigations [20] of low coverages of adsorbates on surfaces. Concomitant with a decrease in the intensity with benzene coverage, there is also a small shift in the peak position to lower values.

The changes in the polar angle distributions as a function of coverage are consistent with the changes in the energy distributions. The experimental data for the 3 L and 7 L exposures and the data from the calculations for all coverages exhibit a decrease in the intensity of the peak at a polar angle of ~35° as the coverage increases. The intensity in the normal direction (polar angle of 0°) remains unaltered.

Although there are reports that a 5–7 L exposure of benzene on Ag(1 1 1) results in a monolayer [4,9] and that a 5 L exposure yields a (3 × 3) coverage [12], it appears from our comparisons that the 7 L exposure may correspond to a larger coverage. The distributions from the simulations with the (3 × 3) overlayer do not sufficiently attenuate the intensity of the energy distribution or the off-normal peak in the polar angle distribution.

4. Conclusion

We have examined a system composed of benzene adsorbed onto Ag(1 1 1) that is bombarded with 8 keV Ar$^+$ ions. In addition, MD simulations for 5 keV Ar atom bombardment of an overlayer of benzene on Ag(1 1 1) are performed. The simulations reproduce the experimentally observed shift in the Ag atom energy and angle distributions. The data from the simulations suggest that a monolayer of C_6H_6 molecules on an Ag(1 1 1) surface may be more densely packed on the surface than previously thought. Future simulations are planned for studying systems comprised of multilayers of benzene on Ag(1 1 1) in order to gain a deeper insight into the interplay between the departing substrate atoms and the adsorbed organic molecules. Modeling the energetic Ar atom bombardment of C_6H_6 multilayers on Ag(1 1 1) will also allow for the investigation into how the Ar-induced damage to the organic overlayer influences the emission characteristics, especially the polar angle distribution of the substrate atoms.

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