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State-selective energy and angular resolved detection of neutral species ejected from keV ion bombarded C_6H_6/Ag{1 1 1}

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Abstract

We investigated the desorption of neutral benzene (C_6H_6) molecules and silver atoms from C_6H_6/Ag{1 1 1} upon bombardment by 8 keV Ar^+ ions. Using state-selective resonant ionization spectroscopy, substrate atoms sputtered in the ground and a high-lying metastable state, and ground-state and vibrationally excited molecules could be probed separately. The silver atom yield, kinetic energy and polar angle distributions were found to be modified upon benzene dosing. From these results, it was inferred that a large fraction of the metastable silver atoms de-excite during collisions with adsorbates. Also the ejection of benzene molecules depends strongly both on the internal energy of the molecules and the degree of coverage of the Ag surface. Up to monolayer thickness, the benzene molecules are mainly ejected during collisions with departing substrate particles. Molecules with higher internal energy leave the surface with a distribution shifted towards higher kinetic energies. At multi-layer coverages, a slow desorption mechanism becomes dominant. It is suggested that only benzene molecules vibrationally excited near the benzene–vacuum interface can survive the ejection process without de-excitation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Resonance ionization spectroscopy; Ion-beam desorption; Metastable atoms; Organic overlayers

1. Introduction

The impact of an energetic ion on a metallic substrate covered with an organic overlayer triggers a chain of events that finally leads to the ejection of both substrate atoms and intact adsorbate molecules. Such a desorption process is based on different mechanisms in which the properties of the incident particle, of the metal, and of the molecular overlayer contribute. An improved understanding of this complex interplay not only is of fundamental interest, but also could allow for the development of improved detection strategies for applications in molecular surface characterization based on ion beam desorption techniques [1,2].

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Recently, experimental evidence in combination with an increased understanding at a microscopic level gained from molecular dynamics simulations allowed different mechanisms that lead to the desorption of molecules from simple, well-defined systems to be discerned [3–5]. In this contribution we report on an experimental study in which highly sensitive resonant laser ionization spectroscopy was used to monitor quantum state-selectively both desorbed neutral molecules and atoms sputtered from the underlying substrate as a function of adsorbate coverage. Since excited atoms and molecules are sensitive to the chemical and physical environment, these results provide a means to compile a more detailed picture of the desorption process. As a model system we selected benzene physisorbed on the {1 1 1} planes of a cold clean silver crystal. This system is chosen because of a number of attractive attributes. Chemical reactions between the silver and the benzene which can modify the simple binary nature of the system can be largely neglected because of the inert nature of silver toward benzene. The system is reversible with temperature and highly reproducible. Moreover, the energy level system for both benzene and silver are well documented and their ultraviolet spectra are experimentally easily accessible.

Previously, non-resonant laser postionization was used to study the coverage-dependent molecular ejection from ion-bombarded C_6H_6/Ag{1 1 1} [3]. The results obtained from kinetic energy and angular distributions and the relative yield of neutral C_6H_6 molecules suggest that depending on the thickness of the overlayer, more than one mechanism is responsible for the ejection process. At low coverages, the desorption mechanism is largely a ballistic process: the C_6H_6 molecules are ejected upon collisions with the particles escaping from the underlying substrate. This ejection mechanism was confirmed in extensive molecular dynamics simulations performed on this system to gain insight at a molecular level [4]. As the coverage increases, intermolecular collisions in the overlayer gain importance in the desorption process. At multi-layer coverages yet another emission behavior is discerned that shifts the most probable kinetic energies of the desorbed particles to thermal values. Possible scenarios include desorption due to exothermic reactions between molecular fragments created by the impact of the primary projectile or due to local heating in a partially developed molecular collision cascade.

2. Experimental setup and procedures

The experimental setup to measure energy and angular resolved distributions of neutral (EARN) particles has been described elsewhere [6]. The experiments presented here are performed in an ultrahigh vacuum chamber (base pressure 1×10^{-10} Torr), equipped for low-energy electron diffraction (LEED). Desorption events are initiated by a 200 ns Ar^+ ion pulse focused to a spot with a diameter of 3 mm on the sample surface. The measurements are performed under static conditions with the primary ion dose kept at 10^{11} ions/cm^2 to limit the accumulation of surface damage as much as possible. The plume of desorbed particles is intersected about 1 cm in front of the sample by either one or two ribbon-shaped laser beams from pulsed Nd:YAG pumped dye laser systems. Typical output energies are of the order of 1 mJ in 6 ns pulses. Desorbed particles are subsequently mass selectively detected using a gated, position-sensitive microchannel plate detector.

Time-of-flight (TOF) density distributions are obtained by varying the delay between the moment of the ion pulse hits the sample and the ionizing laser pulse(s) arrive in front of the target. Energy distributions are obtained after coordinate transformation of the measured time distributions using the appropriate mass and surface to laser distance. For these experiments, the angle of incidence of the primary ions is 45° with respect to the surface normal and the photoions are collected within an angular range of ±20°. From the ion-impact positions on the detector, the distribution of the polar ejection angle of the sputtered particles can be calculated. Such EARN experiments are done with the primary ion beam at normal incidence.

Prior to the measurements, the Ag{1 1 1} single crystal is cleaned by many cycles of continuous ion bombardment and by annealing at 730 K until a sharp LEED pattern is obtained. Several freeze-pump-thaw cycles are performed to remove gaseous impurities from the benzene. Benzene is dosed onto the cold (120 K) Ag crystal by backfilling the chamber, and different coverages are obtained by controlling the pressure and the exposure period. All exposures are reported in Langmuirs (1 Langmuir (L) $= 1 \times 10^{-6}$ Torr s). Benzene is known to form ordered (3×3) flat overlayers on Ag{1 1 1} with 1 monolayer (ML) corresponding to an exposure of 5–7 L [7].

3. Results and discussion

3.1. Ionization schemes

State-selective detection of neutral silver atoms and benzene molecules was achieved by employing the appropriate resonant ionization scheme. The different ionization schemes are summarized in Fig. 1. To photoionize the Ag atoms we used two-photon two-color and one-photon one-color ionization schemes that were recently reported [8]. The $4d^{10}5s\ ^2S_{1/2}$ ground-state atoms (labeled Ag) were first excited into the $4d^{10}5p\ ^2P^o_{3/2}$ intermediate state and subsequently non-resonantly ionized by absorbing a second photon. The metastable atoms (Ag*) in the $4d^95s^2\ ^2D_{5/2}$ state are efficiently ionized by pumping them into the $4d^95s5p\ ^2D^o_{5/2}$ autoionizing state using only one photon. Resonant two-photon one-color photoionization of the ejected benzene molecules was achieved by pumping the 6^1_0 transition originating from the zero level of the molecular ground-state (C_6H_6), and the 6^0_1 transition starting from the first vibrationally excited state of the ν''_6 mode ($C_6H^*_6$), lying 0.1 eV above the molecular ground-state level [9].

3.2. Desorption of Ag substrate atoms

Previously, Berthold and Wucher have measured the population and energy and angular distributions of Ag and Ag* sputtered from polycrystalline foils [10,11]. They showed that Ag* ejected in the metastable $4d^95s^2\ ^2D_{5/2}$ state with an excitation energy of 3.75 eV above the ground-state contribute to an amazing 6% of the total flux of sputtered atoms. The angle-integrated energy distributions of the Ag* were found to fall off more steeply than those of the Ag. These results were partly explained as the resonant neutralization of a sputtered secondary ion containing a d-hole [12]. The same features were observed in our experiments on a clean single crystal, although the limited dynamical range of the detector did not allow us to determine the population partition.

The effect of the emission of silver atoms upon exposing the crystal with benzene was found to be dramatic. In Table 1 the yield, as obtained by integrating the total signal, is given for different

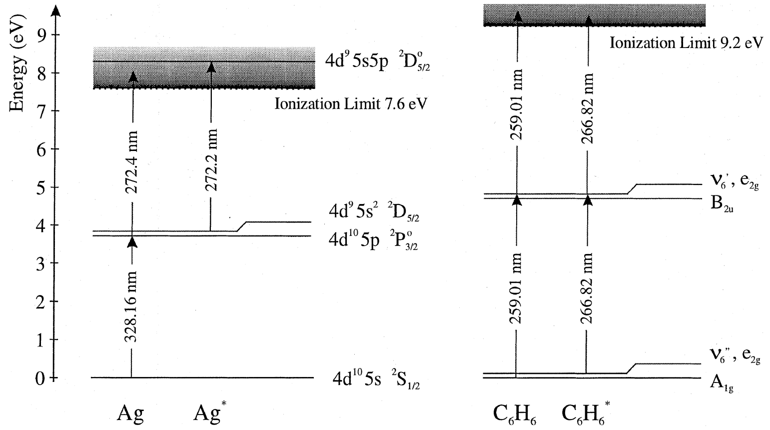

Fig. 1. Resonant ionization schemes used to detect Ag atoms in the ground (Ag) and high-lying metastable state (Ag*) and to detect C_6H_6 in the ground-state (C_6H_6) and the first vibrationally excited state of the ν''_6 mode of the electronic ground-state ($C_6H^*_6$).

Table 1
Yield of the ground-state (Ag) and metastable (Ag*) substrate atoms as function of benzene exposure of the crystal[a]

Exposure (L)	Ag (%)	Ag* (%)
0	100	100
3	70	30
7	50	20
50	34	20
100	11	7

[a] The yield is given relative to the yield obtained from a clean crystal.

exposures. Due to blocking by the adsorbate molecules, the yield decreases rapidly with increasing thickness of the overlayer. At low coverages, the yield from metastable atoms is more sensitive to the presence of benzene molecules on the crystal surface. The Ag and Ag* kinetic energy distributions integrated over all polar angles along the ⟨2 1 1⟩ azimuth are shown in Fig. 2. The distributions narrow and peak at lower kinetic energies when benzene is added to the surface. The energy distribution of the ground-state Ag atoms emitted from the clean Ag crystal has the characteristic features of a Thompson distribution [13]; however, we are currently in the course of making coverage-dependent molecular dynamics simulation studies using realistic potentials for both the silver atoms and the benzene molecules for the purpose of comparison to the experimental data. Also the energy-integrated angular distributions show a strong coverage-dependence as can be seen in Fig. 3. Both the Ag and Ag* angular distributions from a clean single crystal show a preferential ejection at a polar angle of about 35°. As the coverage of the benzene increases, the distribution broadens and shifts toward normal emission angles. However, this seems to be more pronounced for the Ag* (Fig. 3(a)).

The combined data can be interpreted as evidence that many substrate atoms are involved in collisions with the adsorbate molecules prior to escape [14]. These observations give additional evidence that the emission process of C_6H_6 is initiated by such collisions. The decrease in the yield due to blocking by benzene molecules is more effective for the Ag* because collisional quenching is among the possible de-excitation mechanisms for these atoms. The possibility of collisional quenching implies that a portion of the detected ground-state atoms left the surface in the metastable state but relaxed prior to detection. The possibility of quenching implies that both the kinetic energy and the polar-angle distribution contain a contribution from the de-excited Ag*. During the collisions with the organic-overlayer molecules, part of the kinetic energy of the Ag atoms will be exchanged thus shifting the kinetic energy distributions towards lower values. The preferential ejection of Ag atoms in the off-normal direction as observed in the polar-angle distributions is explained via channeling and blocking of the departing atoms by other first-layer atoms. Previously, the polar-angle distribution of ejected C_6H_6 molecules at low coverages was found to

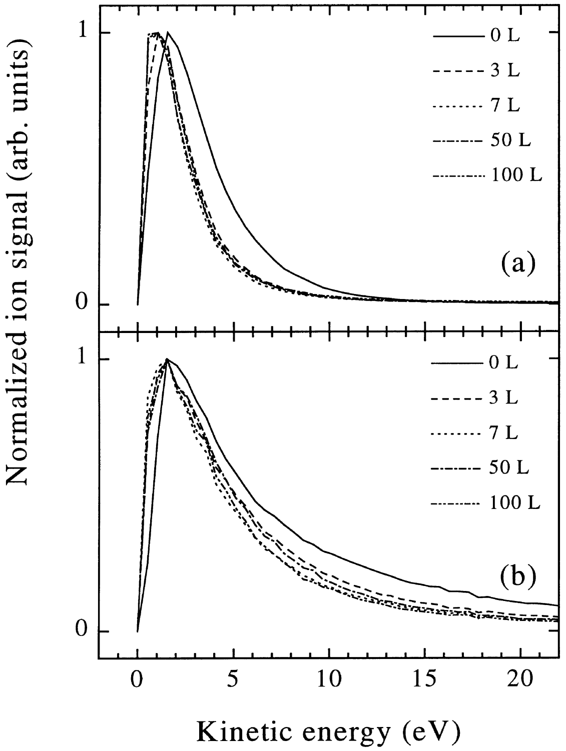

Fig. 2. Normalized kinetic energy distributions integrated over all polar angles, of silver atoms ejected from the substrate for a variety of benzene exposures, (a) distributions of Ag* and (b) Ag atoms.

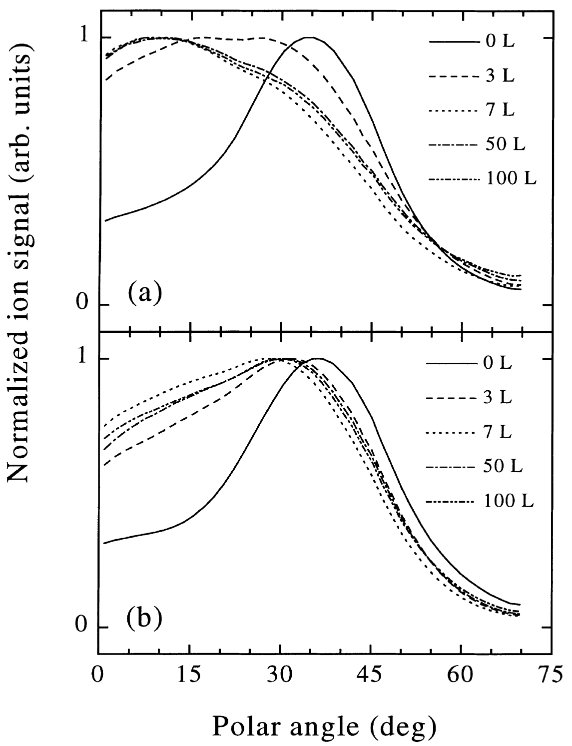

Fig. 3. Polar angle distributions integrated over all kinetic energies, of silver atoms ejected from the substrate for a variety of benzene exposures, (a) distributions of Ag* and (b) Ag atoms.

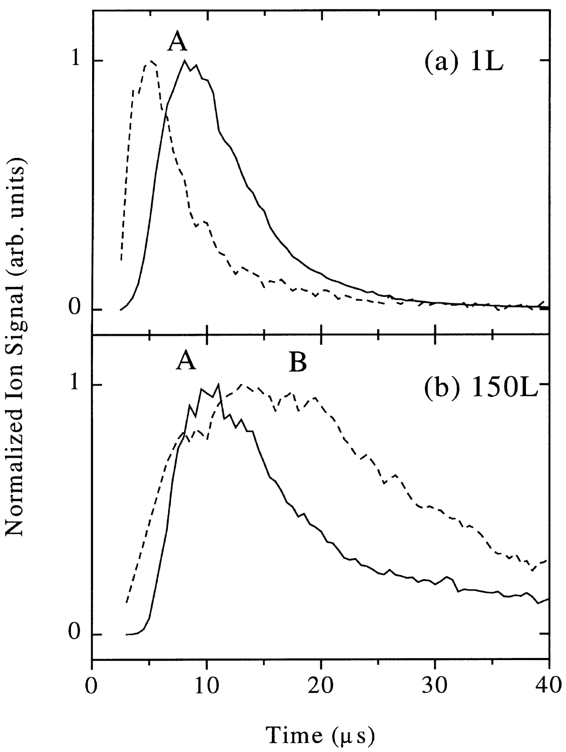

Fig. 4. State-selective time density distributions of neutral benzene molecules desorbed from C_6H_6/Ag{1 1 1} at (a) a submonolayer (1 L exposure) and (b) multi-layer coverage (150 L exposure). Solid lines represent the distributions obtained for C_6H_6 while the dashed lines show the distributions for $C_6H_6^*$.

include the same anisotropy [3]. Since the Ag*-distribution (Fig. 3(a)) is largely depleted of atoms ejected off-normally, it can be argued that these atoms did not survive a collision with a C_6H_6 molecule upon departure. Such de-excited Ag* atoms will be detected in the off-normal direction of the Ag polar-angle distribution. This might explain why this distribution shows more asymmetry even upon longer exposures. At higher coverages the shift of both distributions to a pronounced ejection in the normal direction is indicative that enough collisions with adsorbate molecules occur to largely randomize the trajectories of the ejected particles.

3.3. Desorption of benzene molecules

In Fig. 4, the time density distributions of desorbed C_6H_6 and $C_6H_6^*$ molecules are shown for a 1 L exposure (submonolayer coverage) and a 150 L exposure (multi-layer coverage). Both the width and the position of the peak depend strongly on the state in which the particle leaves the surface, as well as on the benzene coverage. Not surprisingly, the coverage-dependent desorption of C_6H_6 molecules bears great similarity with the results previously obtained by non-resonant ionization of ejected benzene molecules [3]. From these experiments, it was learned that a peak appearing at short flight times (labeled "A" in Fig. 4) was attributed to benzene molecules having a most probable kinetic energy of about 1 eV and desorbed by collisions with substrate particles. As the coverage increases, the number of less energetic intermolecular collisions grows resulting in a broadened TOF distribution that is peak-shifted towards longer flight times (lower kinetic energies). Finally, upon high exposures a pronounced second feature appears in the time distribution at large flight times (indicated by "B" in Fig. 4). This maximum is composed of benzene molecules that are emitted with a very low most probable kinetic energy of 0.04 eV. At intermediate coverages, such as the one presented here, both peak A and B are discernible, indicating that both desorption mechanisms are competing, while at very high coverages, only peak B is present [3].

The time distributions of the vibrationally excited $C_6H_6^*$ molecules allow for compiling a more detailed picture on the ejection mechanisms. At low coverages, the time distribution of $C_6H_6^*$ is found to be more narrow and to peak earlier compared to the C_6H_6 distributions. The corresponding kinetic energy distributions of molecules with a higher internal energy are thus shifted to a higher peak energy by about 0.5 eV. Previously, molecular dynamics simulations showed that the kinetic energies of the desorbed molecules are strongly correlated with their internal energies [4], leading to differences in the time distributions as we observed in our experiments. However, it remains unclear how such a small difference in internal energy (the vibrational state lies only 0.1 eV above the ground-state) can lead to such vastly different time distributions. The populations in more states, preferably in different vibrational modes, should be probed to rule out the possibility that the differences in the time distributions have a state-dependent origin.

At high coverages (Fig. 4(b)) the time distribution of the $C_6H_6^*$ is depleted from collisionally ejected molecules. A possible explanation for this observation is that in thick layers only the first few collisions between an escaping substrate atom and an adsorbate molecule are energetic enough to excite the molecule. Before this excited molecule can become detected, it has to travel through the thick molecular overlayer where intermolecular collisions are abundant. Collisional quenching or unimolecular decomposition are thus likely to occur. These experiments indicate that only $C_6H_6^*$ molecules created near the benzene–vacuum interface have a sufficiently high probability to survive de-excitation [15].

4. Summary

We used resonance ionization spectroscopy for the state-selective photoionization of neutral species desorbed from keV Ar^+ ion-bombarded C_6H_6/Ag{1 1 1}. The results allow us to compile a detailed picture of the desorption process in this model system. A substantial part of the substrate atoms were found to be sputtered into a very high-lying metastable state. The yield in this excited state was found to decrease rapidly as the amount of benzene covering the crystal surface increased. Also the kinetic energy and angular distributions were found to be modified upon dosing. The results indicate that a large fraction of the metastable silver atoms de-excite during collisions with the adsorbate molecules.

The benzene molecules exhibit a strong coverage-dependent desorption behavior. Up to monolayer coverage this process has a ballistic nature initiated by collisions between molecules in the overlayer and ejected substrate particles. Here, molecules with a higher vibrational energy have a kinetic energy distribution that has a larger peak energy compared to molecules desorbed in the ground level. When the benzene exposure increases to multi-layer coverages a second mechanism by which molecules are then desorbed with very low kinetic energies, will gain significance. Only excited benzene molecules created sufficiently close to the benzene-vacuum interface survive de-excitation during intermolecular collisions.

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