

State-selective laser photoionization of neutral benzene molecules ejected from keV ion bombarded C₆H₆/Ag{111}

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Abstract. One-color two-photon ionization spectroscopy was used to probe state-selectively neutral benzene molecules desorbed from a benzene overlayer physisorbed on a Ag{111} surface upon 8 keV Ar⁺ bombardment. Time distributions were measured for benzene molecules ejected in the zero level of the molecular ground state and in the first state of the ν_6^+ vibration. These distributions are found to show a strong dependence both on the internal energy of the ejected molecules and the degree of coverage of the Ag surface. Up to monolayer coverages, benzene molecules are ejected by direct collisions with Ag particles sputtered from the underlying substrate. Molecules with higher internal energy leave the surface with a distribution shifted towards lower flight times. At multilayer coverages, a second, thermal-like ejection mechanism gains significance. It is suggested that only molecules excited near the benzene-vacuum interface, survive the ejection process without being deexcited.

INTRODUCTION

Analytical techniques based on ion beam induced desorption of molecules are routinely used for the surface-analysis of complex chemical and biological systems (1). Up to now, it is still poorly understood how *intact* molecules can be desorbed from a surface upon bombardment with primary ions with kinetic energies which are many orders of magnitude higher than the energy contained in the chemical bonds. In this work, we study the desorption of *neutral* benzene molecules from a cold Ag{111} surface during keV Ar⁺ ion bombardment. Benzene/Ag{111} provides a model system in which the organic molecules are physisorbed on a fairly unreactive metallic surface. The C₆H₆ exposure can be varied from submonolayer to multilayer coverages in order to probe the influence of the local molecular environment on the desorption process. Moreover, the energy level scheme for benzene is well known and its ultraviolet spectrum is experimentally easily accessible. We used resonant one-color two-step

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photoionization to detect selectively neutral benzene molecules in the zero level and in the first vibrationally excited state of the molecular electronic ground state. To our knowledge, these are the first experiments where the desorption process of neutral benzene molecules from molecular overlayers is state-selectively monitored.

EXPERIMENTAL SETUP

The experimental setup and procedure are described in detail elsewhere (2). In short, benzene was adsorbed on a clean Ag{111} surface cooled to 120 K. Several freeze-pump-thaw cycles were applied before dosing to remove dissolved contaminants from the benzene. The benzene exposure was controlled by monitoring the chamber pressure and the dosing time.

The desorption process was initiated by bombarding the sample with an 8 keV, 250 ns Ar⁺ pulse, at 45° incidence, focused to a spot with a diameter of 3 mm. The primary ion dose was kept sufficiently low so as to eliminate effects of surface damage. Desorbed particles were detected by multiphoton ionization in combination with time-of-flight mass spectrometry using a gated microchannel plate detector. The mass spectrum showed prominent peaks at m/z 54 (C₄H₄ fragment), 78 (molecular C₆H₆), 108 (Ag) and 216 (Ag₂). The laser beam was focused to a ribbon shape approximately 1 cm above the crystal surface. The density of the particles in the laser ionization volume was recorded as function of time by systematically varying the time delay between the primary ion and laser pulses. Resonant two-photon one-color photoionization of the ejected benzene molecules was achieved by tuning the frequency-doubled output of a Nd:YAG pumped dye laser to drive the 6₀¹ transition at 259.01 nm originating from the zero level of the molecular ground state, and the 6₀¹ (266.82 nm) and 6₁¹₀ (260.37 nm) transitions starting from the first vibrationally excited state of the ν_6^+ mode (3,4).

RESULTS AND DISCUSSION

In Fig. 1 the time density distributions are shown both for molecules ejected in the ground and the excited state upon 8 keV Ar⁺ bombardment of C₆H₆/Ag{111} at a submonolayer (Fig. 1a) and a multilayer (Fig. 1b) coverage of the surface. The width and the position of the maximum of the time distributions are strongly dependent on the benzene coverage. We first discuss the distributions for molecules ejected in the *zero level of the molecular electronic ground state*. Since most molecules leave the surface in this state, it is not unexpected that their time distributions are very similar to those obtained when the desorbed molecules are non-resonantly photoionized (i.e. not state selective) (2). At submonolayer coverage the peak in the time distribution (labeled as A in Fig. 1) corresponds to benzene molecules that leave the surface with kinetic energies of about 1 eV. As the coverage increases to a complete monolayer, the most probable kinetic energy of the ejected molecules decreases to 0.25 eV. These results, in combination with experimentally obtained angular distributions and molecular dynamics simulations (5), indicate that the ejection process at these coverages is largely ballistic in nature. As the primary ion hits the sample, a collision

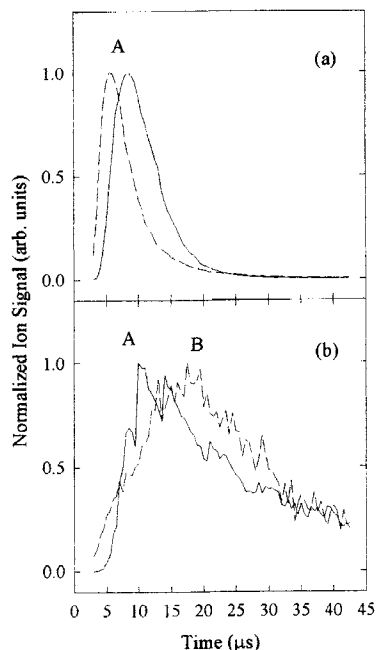


FIGURE 1. State-selective time density distributions of neutral benzene molecules desorbed from $C_6H_6/Ag\{111\}$ upon 8 keV Ar^+ bombardment at (a) 1L exposure, resulting in a submonolayer coverage of the Ag crystal surface and (b) 200 L exposure yielding a multilayer coverage. The solid line represents the distributions obtained for molecules ejected in the zero level of the molecular ground state, while the dashed line shows the distributions for vibrationally excited molecules.

molecules from $C_6H_6/Ag\{111\}$ from a microscopic point of view (5).

The time distributions obtained for vibrationally excited molecules desorbed from thick organic overlayers show almost solely a peak corresponding to molecules departing with low kinetic energies. The mechanisms that govern slow desorption might thus favor the emission of vibrationally excited molecules. Alternatively, since molecules with high kinetic energies are predominantly created near the Ag surface by collisions with substrate particles, the absence of these fast molecules from the time distributions might be indicative that only molecules that get excited close to the benzene-vacuum interface have a sufficiently large probability to survive the process in that vibrationally excited state. Collisional quenching or unimolecular decomposition of the molecules before detection are among the possible deexcitation mechanisms.

cascade in the Ag crystal is initiated and the benzene molecules are ejected by direct collisions with the departing Ag particles. As the thickness of the organic overlayer increases, a second maximum (peak B in Fig. 1b) appears in the time distribution. This maximum corresponds to benzene molecules that desorb from the surface with an extremely low kinetic energy of about 0.04 eV. With increasing coverage, the importance of prompt ejection of benzene molecules by substrate originating particles decreases while other mechanisms become more likely. Plausible scenarios include desorption of the molecules due to exothermic reactions between molecular fragments created by the impact of the primary particle or the ejection upon collisions between molecules and fragments.

The time distributions of benzene molecules ejected in the *vibrationally excited state* show that these molecules are more sensitive to underlying ejection mechanisms. At low coverages, the time distributions of the excited molecules are narrower and peak earlier compared to the one for molecules ejected in the ground state. The kinetic energy distributions are thus shifted to higher energies for molecules with higher internal energies. These experiments confirm the trend predicted by molecular dynamics simulations that have delineated the ejection mechanisms of

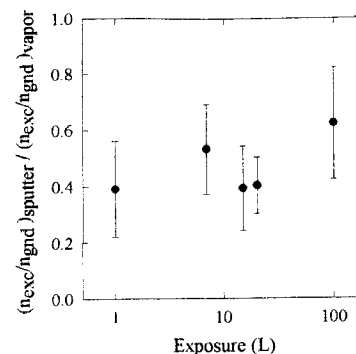


FIGURE 2. Ratio of the relative benzene populations on the vibrationally excited state (n_{exc}) to the ground state (n_{gnd}) for the ion induced desorption from $C_6H_6/Ag\{111\}$ and the vapor phase, as function of the benzene exposure.

sputter experiment and the vapor phase population ratio is shown in Fig. 2 as function of the benzene exposure. Within the accuracy of the measurement, no real trend can be observed. With increasing coverage, the reduction of the population of the excited state induced by substrate originating particles seems to be compensated by molecules excited by phenomena occurring primarily in the organic overlayer.

In conclusion, we have proven that state-selective time distributions of neutral benzene molecules ejected from keV bombarded $C_6H_6/Ag\{111\}$ can be determined. In combination with molecular dynamics simulations, these experiments provide insight to the underlying ejection mechanisms. Future experiments will be performed to determine state-selective angular distributions of desorbed benzene at coverages low enough to retain the $\{111\}$ character of the crystal surface.

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