Environment-dependent desorption of benzene molecules

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Abstract. We have investigated the dependence of the 8 keV Ar\(^+\) ion beam-induced desorption of neutral benzene (C\(_6\)H\(_6\)) molecules on the local environment. The probed system was comprised of carefully constructed combinations of C\(_6\)H\(_6\) and sec-Butyl Alcohol (sBA) deposited on Ag(111). A pulsed 8 keV Ar\(^+\) ion beam at 45° incidence was used to stimulate the desorption of adsorbed molecules. Using state-selective resonant ionization spectroscopy and time-of-flight (TOF) mass spectrometry, C\(_6\)H\(_6\) molecules in the ground state and in the first level of a vibrationally excited state were probed. TOF distributions were measured versus the exposure of the sBA. The results show that the ejection of the C\(_6\)H\(_6\) depends strongly on both the internal energy and thickness of the formed layer. In general, as more sBA is added to the probed system, the TOF distributions tend to broaden and shift to higher times, and the relative C\(_6\)H\(_6\) yields diminish rapidly. The vibrationally excited C\(_6\)H\(_6\) is more sensitive to the addition of sBA, and an interpretation of the combined data suggests that the C\(_6\)H\(_6\) desorbed in an excited state originates from the organic/vacuum interface.

INTRODUCTION

When a surface is irradiated with energetic primary ions, molecules and atoms in a variety of charge and internal energy states are liberated from the surface [1]. Such a process is the basis for surface analytical techniques, such as secondary ion mass spectrometry [1,2]. However, the vast majority of the desorbed species are in a neutral charge state [2]. Because we use mass spectrometry to study the Ar\(^+\) ion stimulated-desorption, an efficient means of ionizing the desorbed neutral species must be employed to gain as much information about the desorption process as possible per primary ion. The utilization of laser postionization, especially when resonance-enhanced ionization schemes are used, provides an efficient means of generating ions [1]. The combination of time-of-flight mass spectrometry and laser postionization is a powerful method to study the interaction of energetic primary ions with surfaces and the desorption events that follow the impact of the primary ion.

The phenomena of the desorption of intact molecules from metals surfaces has been studied in the past using benzene (C\(_6\)H\(_6\)) adsorbed onto a Ag(111) surface that is subjected to 8 keV Ar\(^+\) ion bombardment [3]. Benzene was selected because it has
many attractive attributes that are conducive to such studies of molecular desorption [3]. Noticeable changes in the energy distributions were observed for both ground state benzene molecules (C\textsubscript{6}H\textsubscript{6}) and vibrationally excited benzene molecules (C\textsubscript{6}H\textsubscript{6}*\textsuperscript{\textdagger}) as the benzene exposure was increased [3]. In order to probe how the local chemical environment affects the desorption characteristics of the benzene molecules, additional experiments have been performed. These experiments consist of systematically making the system more organic in nature by depositing a sec-butyl alcohol (sBA) layer of increasing thickness on top of a monolayer of benzene on the Ag(111) surface. By varying the sBA layer thickness we can make the benzene layer closer or farther away from the organic/vacuum interface and effectively change the system from a thin organic film on a metal surface to one that is much more organic in nature. Moreover, an additional layer of benzene can be placed on top of the sBA layer so that a fresh sample of benzene is once again near the surface/vacuum interface. This final step probes the behavior of analyte molecules that are on an organic matrix and near the surface/vacuum interface.

**EXPERIMENTAL SETUP**

The experimental setup and procedure are described in detail elsewhere [4,5]. Several freeze-pump-thaw cycles are applied to both the benzene and the sBA before dosing either gas to remove dissolved contaminants. Before dosing the first monolayer of benzene, which is a 7L exposure (1L = 1x10\textsuperscript{-6} Torr sec), the single crystal of silver is sputter cleaned, annealed, and then cooled to 120 K and held at 120 K for the duration of the experiments. The exposures of benzene and of sBA were controlled by monitoring the chamber pressure and the dosing time.

The desorption process is initiated by bombarding the sample with an 8 keV, 200 ns Ar\textsuperscript{+} ion pulse. The Ar\textsuperscript{+} ion beam from which the pulses are derived is directed at the sample at 45\textdegree\ incidence and focused to a spot size of 3 mm. The primary ion dose is kept sufficiently low (∼10\textsuperscript{11} Ar\textsuperscript{+} ions/cm\textsuperscript{2}) in an attempt to minimize accumulated surface damage. Desorbed particles are detected by multiphoton ionization in combination with time-of-flight mass spectrometry. The postionization laser beam is focused to a ribbon shape about 1 cm above the crystal surface. As the time delay between the primary ion impact and laser ionization event is systematically varied, the density of the particles in the laser ionization volume is recorded as a function of time delay. Resonant two-photon one-color photoionization of the ejected benzene molecules is achieved by tuning the frequency-doubled output of Nd:YAG-pumped dye laser to drive the 6\textsuperscript{0} transition at 259.01 nm originating from the zero level of the molecular ground state, and the 6\textsuperscript{1} transition at 266.82 nm starting from the first quantum of the 7\textsuperscript{0} vibration [6].
RESULTS AND DISCUSSION

A generalized representation of the experimental sequence (A through C) used to make the system take on a more organic character is illustrated in Fig. 1. The first 7L exposure of benzene is applied to the surface to serve as a reference and so that the changes to the desorption characteristics of benzene as the benzene layer is systematically moved away from the surface/vacuum interface can be monitored. The layer of sBA creates an organic partition between the first monolayer of benzene and the vacuum. The layer of benzene on top of the sBA

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Figure 1. Illustration of the general experimental scheme. First, benzene (7L) is dosed (A) and spectra are obtained. Then, sec-butyl alcohol (sBA) is dosed (B) and spectra are obtained. Finally, an additional 7L of benzene is dosed (C) and spectra are taken.

Figure 2. Peak normalized time distributions for vibrationally excited benzene (TOP) and ground state benzene (BOTTOM). The distributions are for a variety of sBA exposures from 0L to 60L. The vibrationally excited benzene signal degrades more rapidly (as a function of sBA exposure) than the signal from the ground state benzene.

much less affected. These two findings suggest that as the benzene is moved farther from the surface/vacuum interface, the probability that benzene molecules in internally excited states will be desorbed and detected becomes smaller. As the benzene is buried
deeper in the organic matrix, the time distributions shift toward higher times, indicating that the presence of the organic matrix depletes the benzene molecules of translational energy as well.

Time distributions for the benzene layer applied to the top of the sBA layer are illustrated in Fig. 3 (step C). A significant finding from these plots is that the signal from the excited state benzene molecules is resurrected (TOP panel). In other words, as long as there are analyte molecules near the surface/vacuum interface, then some portion of the molecules can be desorbed and detected as internally excited molecules even as the system becomes more organic in nature. Another striking feature is that the time distributions of vibrationally excited molecules tend to shift to higher times and broaden more readily than do the distributions of the ground state molecules. Such an observation implies that the vibrationally excited molecules are desorbed with less translational energy than

\[ C_6H_6 \text{ Signal [arb. units]} \]

\[ \text{Time [? s]} \]

**Figure 3.** Peak normalized time distributions for vibrationally excited benzene (TOP) and ground state benzene (BOTTOM) from benzene deposited on top of the sBA layer. The sBA layers are from exposures ranging from 0L to 60L.

the ground state molecules as the system becomes one that resembles an organic matrix, as opposed to one resembling a thin organic film on a metal surface.

**CONCLUSIONS**

As the layer of analyte molecules becomes buried beneath an organic matrix, the time distributions for both excited state and ground state benzene molecules shift to higher times and broaden. Such changes indicate that the overlayer of the sBA tends to deplete the benzene molecules of translational energy. Because the \( C_6H_6^* \) signal is readily diminished by the presence of the sBA overlayer, it is reasonable to suggest that molecules buried deep in the organic matrix will not be desorbed and detected in an internally excited state. However, if analyte molecules are present near the surface/vacuum interface, then molecules in the ground state and internally excited
states may be desorbed. Molecules from the upper-most layer near the vacuum interface tend to be desorbed with less translational energy as the matrix progresses to one that is more organic.

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