

## RESONANT POSTIONIZATION OF NEUTRAL SPECIES DESORBED BY keV Ar<sup>+</sup> BOMBARDMENT OF C<sub>6</sub>H<sub>6</sub>/Ag(111)

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### 1. Introduction

It is not well understood how intact molecules can be desorbed from a surface subsequent to a violent collision between a surface and massive particles having orders of magnitude more kinetic energy than the energy needed to hold an organic molecule together. In order to gain insight into such phenomena, a simple system consisting of benzene, C<sub>6</sub>H<sub>6</sub>, physisorbed onto cold Ag (111) is studied. Time-of-flight (TOF) and energy and angle resolved neutral (EARN) distributions are employed in this work.

This system is an ideal model system for such studies for a variety of reasons. Silver is unreactive toward benzene [1]; therefore, the system is reversible and reproducible for a variety of C<sub>6</sub>H<sub>6</sub> coverages. Furthermore, the possibility of chemical reactions between the adsorbate (C<sub>6</sub>H<sub>6</sub>) and the substrate (Ag) that could alter the binary nature of the system can be largely neglected. Another important attribute of this system is that both the (molecular) adsorbate and (atomic) substrate can be resonantly ionized. C<sub>6</sub>H<sub>6</sub> can be resonantly ionized by one-color two-step processes [2, 3]. Ag substrate atoms in the atomic ground state can be resonantly ionized with a two-color two-step process, while highly excited metastable Ag atoms, having 3.75 eV excitation energy, can be resonantly ionized with a one-color one-step process [4].

### 2. Experimental Setup

Details of the instrument used for these studies are provided elsewhere [5]. Prior to dosing the C<sub>6</sub>H<sub>6</sub> is purified by several freeze-pump-thaw cycles in order to remove dissolved gaseous impurities, and the Ag(111) is sputter cleaned, annealed, and then cooled to 120 K. The C<sub>6</sub>H<sub>6</sub> exposure is controlled by monitoring the chamber pressure as a function of time.

Desorption events are initiated by a 200 ns Ar<sup>+</sup> pulse accelerated to 8 keV and focused to a 3 mm spot. The Ar<sup>+</sup> dose is restricted to 10<sup>11</sup> Ar<sup>+</sup>/cm<sup>2</sup> to minimize surface damage. The angle of incidence is 45° for (TOF) experiments and 0° for EARN experiments. Desorbed particles are detected by multiphoton postionization and time

of flight mass spectrometry. A gated, position-sensitive microchannel plate detector is utilized to detect the postionized species and to discern angular information.

The output from a frequency doubled Nd:YAG pumped tunable dye laser is used for resonant photoionization of the species of interest. The dye laser output is focused to a ribbon about 1 cm in front of the sample. For ionizing  $C_6H_6$  ejected in the zero level of the molecular ground state 259.01 nm radiation is used, while 266.82 nm radiation will ionize vibrationally excited  $C_6H_6$  having one quantum in the  $\nu_6''$  vibrational mode [2, 3]. The output of two dye lasers, 328.2 nm and 272.4 nm, is used for probing Ag in the atomic ground state [4]. However, only a single photon of 272.2 nm radiation is needed to postionize Ag emitted in a highly excited metastable state,  $Ag^*$  [4].

### 3. Results and Discussion

The desorption of the  $C_6H_6$  is coverage dependant [1, 3]. In the low coverage regimes

the  $C_6H_6$  desorption process is largely ballistic in nature. However, in the very high coverage regime the mechanism appears to be thermal-like. The yields and the angle and energy distributions of the substrate atoms for a variety of  $C_6H_6$  exposures not only suggest the role that the substrate plays in the  $C_6H_6$  desorption, but also provide information concerning the effects of organic overlayers on the emission of substrate species.

The effect on the emission of Ag atoms by the addition of  $C_6H_6$  to the surface of the Ag crystal is found to be dramatic. The yield, which is determined by integrating the angle-integrated energy distributions, of the substrate atoms as a function of  $C_6H_6$  exposure decreases rapidly when about 7 L, or 1 ML, of  $C_6H_6$  is on the surface. The addition of  $C_6H_6$  to the surface differently affects the emission of the ground state and metastable state atoms. For instance, the addition of 7 L of  $C_6H_6$  will cut the ground state yield in half, while the metastable yield is reduced to 20% of the yield from a clean substrate. At multilayer coverages the yields slowly decrease to 11% and 7% at 100 L for the ground state and metastable state, respectively, when compared to the clean substrate. Since the metastable atoms are larger than the ground state atoms, they will have a higher probability of colliding with the organic overlayer. Through these collisions, they can undergo collisional deexcitation, and

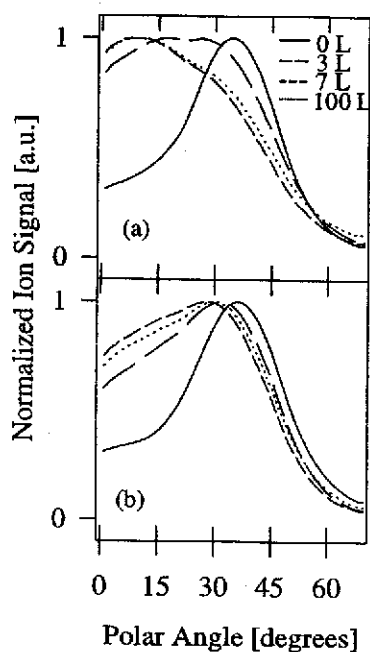


Fig. 1. Normalized energy-integrated polar angle distributions of the silver monomer subsequent to 8 keV  $Ar^+$  bombardment for a variety of benzene exposures. (a) Distributions of metastable atoms. (b) Distributions of ground state atoms.

therefore it is expected that the metastable yields would be more sensitive to the presence of the overlayer.

The energy-integrated angular distributions of Ag and Ag\* exhibit a coverage dependence. As the coverage of C<sub>6</sub>H<sub>6</sub> is increased, the prominent peak at 35° off-normal becomes shifted to the normal direction and is substantially broadened (Fig. 1). However, the shift is much more noticeable in the metastable case (Fig. 1a) than for the ground state (Fig.

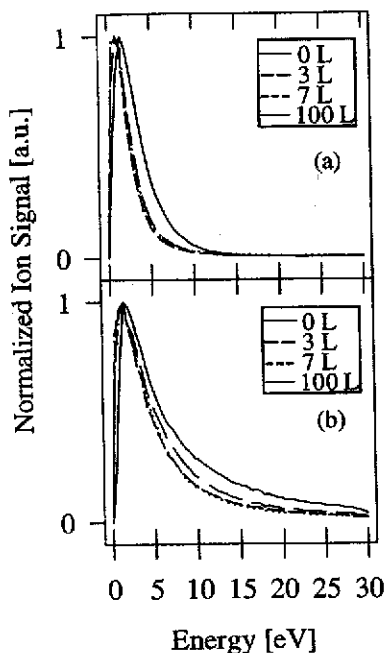


Fig. 2. Normalized angle-integrated kinetic energy distributions of the silver monomer subsequent to 8 keV Ar<sup>+</sup> bombardment for a variety of benzene exposures. (a) Distributions of metastable atoms. (b) Distributions of ground state atoms.

collisions between the silver atoms and C<sub>6</sub>H<sub>6</sub> molecules, which play a major role in the C<sub>6</sub>H<sub>6</sub> desorption at monolayer coverage, near the C<sub>6</sub>H<sub>6</sub>/vacuum interface are unimportant for multilayer samples. However, it appears that all of the major changes affecting the distributions of the substrate atoms occur in the submonolayer to monolayer regime, and the

1b). Because the Ag\* atoms can undergo collisional deexcitation, they may be detected as ground state Ag atoms, and not Ag\*. If this happens, then the off-normal peak in the Ag distribution will be bolstered by the deexcited Ag\* atoms, while the off normal peak in Ag\* distribution will diminish. The increased number of particles emitted in the normal direction may be caused by the randomized scattering as a result of the molecular adsorbate on the surface or possibly by an ion milling process whereby the incident primary ions create channels in the organic overlayer that are oriented largely perpendicular to the surface. It is through these channels that the substrate atoms preferentially travel away from the target.

The angle-integrated kinetic energy distributions of the Ag and Ag\* are also affected by the presence of the organic overlayers. Upon the addition of C<sub>6</sub>H<sub>6</sub> to the surface, the energy distributions tend to become more narrow (Fig. 2). A possible explanation for the observed trend is that the more translationally energetic silver atoms are more likely to impart some of their kinetic energy to the C<sub>6</sub>H<sub>6</sub> molecules, leading to the desorption of the C<sub>6</sub>H<sub>6</sub>, than the slower silver atoms. As a result, the detected Ag atoms will have reduced kinetic energy, and therefore will enhance the low energy portion of the energy distribution and make the energy distributions decay more rapidly.

Because the yield of the silver atoms is greatly diminished by 100 L of C<sub>6</sub>H<sub>6</sub> exposure, it stands to reason that direct

addition of multilayers of  $C_6H_6$  to the surface produces only subtle changes in the distributions of the substrate atoms.

#### 4. Conclusion

State selective TOF and EARN distributions of the adsorbate and substrate species allow for a detailed look at the processes leading to the desorption of atoms and of intact molecules subsequent to energetic particle bombardment of surfaces. The processes leading to the desorption of intact  $C_6H_6$  molecules are coverage dependant.

The addition of the organic overlayers on the Ag (111) dramatically affects the angle and energy distributions of the emitted silver atoms. In both cases of the ground state and metastable state atoms, the energy distributions tend to become more narrow after the surface has been exposed to  $C_6H_6$ . However, the changes are more pronounced in the  $Ag^*$  distributions than the Ag distributions. The angular distributions are also affected by the presence of the organic overlayers; however, the  $Ag^*$  atoms appear to be more affected than the Ag atoms. In both cases, the off-normal ejection peak associated with clean Ag (111) tends to shift toward the normal direction and also tends to broaden. The yields of both the Ag and  $Ag^*$  atoms initially tend to decay rapidly as a function of  $C_6H_6$  exposure, but initially the yields of the  $Ag^*$  atoms decay more rapidly than the Ag yields. However, beyond roughly 1 ML, the yields of both types of atoms tend to decay less rapidly. The trends observed in the angle and energy distributions and the yields of the Ag and  $Ag^*$  are generally similar. However, the trends of  $Ag^*$  seem to be more exaggerated than is observed for Ag, presumably because the larger  $Ag^*$  atoms can more readily collide with the overlayer molecules and deexcite.

#### Acknowledgements

The financial support of the National Science Foundation, the National Institutes of Health, the Office of Naval Research, and the Polish Committee for Scientific Research Fund and Maria Sklodowska-Curie Fund MEN/NSF-96-304 are gratefully acknowledged.

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