

Local electronic structural effects and measurements on the adsorption of benzene on Ag(110)

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The adsorption of benzene on the Ag(110) surface has been investigated using low-temperature scanning tunneling microscopy (STM). We found that benzene molecules preferentially adsorb above step edges at 66 K, leaving the terraces free of molecules. The preference for the step edge adsorption is attributed to the Smoluchowski effect enhancing the empty states to which charge is donated from the π orbitals of the benzene. However, only the $[1\bar{1}0]$ step edges are decorated. We attribute this to the presence of the band gap that exists at the $[001]$ step edge, reducing the Smoluchowski effect—the charge transfer across step edges—and thus the adsorption on these steps. We have also explored the deposition of additional benzene onto this surface at 4 K, where benzene populates a weak adsorbed state. A saturated monolayer of these species arranges hexagonally, commensurate along one direction with the Ag surface. These overlayers present interesting transparency effects in the STM images. The transparency is highly dependent upon changes in the tip-sample distance and is believed to be due to dielectric screening of the Ag orbitals by the benzene.

The scanning tunneling microscope (STM) is particularly useful for elucidating the atomic-scale nature of adsorbate/substrate systems because it simultaneously probes both topographic and electronic features. Numerous studies have yielded insight into the physical and electronic structural effects for benzene, a weak nucleophile, interacting with metal surfaces.^{1–10}

It has been demonstrated both theoretically¹⁰ and experimentally^{1,6,7} that benzene at dilute coverage is capable of adsorbing at a variety of surface sites. Yoshinobu *et al.* found that on Pd(110) at 100 K, molecules adsorbed on terraces demonstrated no special affinity for step edges.⁷ In contrast to this, but similar to work described here, Weiss and co-workers have studied benzene on Cu(111) and have found that at high enough temperatures benzene molecules preferentially bind at all step edges.^{1–4} Our results indicate that benzene molecules prefer even more specific binding sites on Ag(110) than previously found for other surfaces.

Experiments by Somorjai and co-workers have shown that benzene alone does not form well-ordered monolayers on the close-packed Rh(111) (Ref. 5) and Pt(111) (Ref. 11) surfaces. At high coverage, benzene was reported to form a $c(4\times 2)$ overlayer on Pd(110).⁷ Our observations of benzene overlayers on Ag(110) are considerably different from these systems.

Electronic structures and properties of the adsorbate, surface, and surface defects such as steps control the physical preferences and characteristics of adsorbed molecules.^{3,12} By using the STM to image benzene on Ag(110), we have been able to elucidate the electronic effects that influence the system.

In the present experiment, benzene was deposited on Ag(110), first at 66 K, and subsequently at 4 K. Scanning tunneling microscopy was used to determine the binding site preferences of benzene at low coverage, to elucidate the lattice structure of benzene at high coverages, to illustrate the electronic effects present at step edges, and to reveal the characteristics of the decay of electronic states into the vacuum.

Experiments were performed in a low-temperature ultrahigh-vacuum STM (Ref. 13) with the capability of raising the temperature in a controlled manner up to 80 K.¹⁴ The Ag(110) samples were cleaned by repeated cycles of Ar⁺ sputtering and annealing. After this, they were transferred to the microscope chamber, which was kept at 4 K. The bare silver surface was imaged at this temperature before dosing to confirm its cleanliness. A natural defect density on the order of 10^{-2} defects/nm² was observed. The surface was exposed to benzene by backfilling the main, room-temperature chamber and allowing the molecules to reach the sample. The STM was used to calibrate the coverage at each dosing temperature, although all the images presented were acquired at 4 K.¹⁵

After an initial benzene dose at 66 K, only molecules decorating the $[1\bar{1}0]$ step edges were observed in STM images. As seen in Fig. 1, molecules adsorb only at the end of the silver close-packed atomic rows, which form the $[1\bar{1}0]$ steps. At these sites, benzene adsorbs either isolated or in small rows parallel to the step; these molecules do not act as nucleation sites for any further growth at this temperature, even after additional similar doses of benzene vapor. It is apparent from these images that the terraces and the $[001]$ steps remain completely free of molecules.

These results indicate that the sites at the end of the close-packed rows are the only active sites for the adsorption of benzene at 66 K. The benzene molecules are above the step risers [see the schematic view in Fig. 1(c)], and at typical tunneling conditions ($V=500$ mV, $I=0.1$ nA), are imaged as small protrusions centered in depressions 0.4 Å deep. Similar to other $\{110\}$ oriented metal surfaces,¹⁶ molecules are adsorbed between the close-packed rows of the surface, as seen in the inset in Fig. 1(b). At this dilute coverage, groups of molecules at step edges are observed [Fig. 1(b)] to be in registry with the silver lattice below, keeping an intermolecular distance of 4.1 Å. This intermolecular distance is smaller than the distance found for solid benzene,¹⁷ as ob-

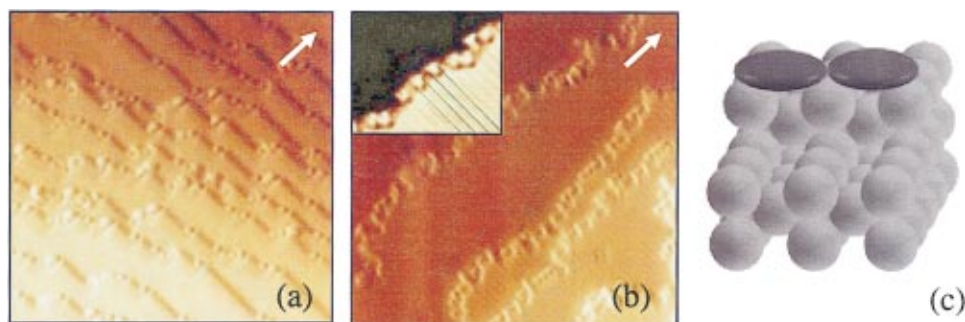


FIG. 1. (Color) STM images acquired at 4 K after the deposition of benzene molecules on Ag(110) at 66 K: (a) $V_s=50$ mV, $I=4.0$ nA, size=20 nm \times 20 nm and (b) $V_s=-500$ mV, $I=0.1$ nA, size=21 nm \times 21 nm. Arrows in both images point in the surface [100] direction. The benzene molecules only adsorb on the $[1\bar{1}0]$ step edges. The benzene molecules are positioned between the close-packed substrate rows as shown in the inset. (c) Schematic of benzene molecules adsorbed on the upper terrace of the $[1\bar{1}0]$ step edge.

served for adsorption at steps on other metal surfaces.³ We expect that the benzene molecules are still lying flat such that their π orbitals lie parallel to the surface on the Ag(110) in accord with previous studies.¹⁸

Steps, like other surface defects, often act as preferential sites for adsorption as they represent an interruption of the periodicity of a surface.¹⁹ At these defect sites, the two-dimensional electronic structure is disrupted and the atoms can be displaced from their bulk positions. This can lead to both positive and negative changes in the “local adsorption energy.” Often, the higher-coordination numbers of adsorbates at these defect sites can explain the higher adsorption energy. However, electronic effects such as the Smoluchowski effect²⁰ or the local density-of-states (LDOS) modulation at steps^{21–23} can also generate preferential adsorption at step edges in some aromatic systems.^{2,24} For the case of benzene on Cu(111), Weiss and co-workers explain that the increased interaction of the molecules at the step edges is due to a combination of the following in order of decreasing strength: the charge transfer at the step edge (Smoluchowski effect), the perturbations due to molecules already at the step, and the enhanced LDOS at the step edge caused by surface-state electron scattering.^{2,3,12} They also found molecules packed tightly into these most electronically favorable sites.

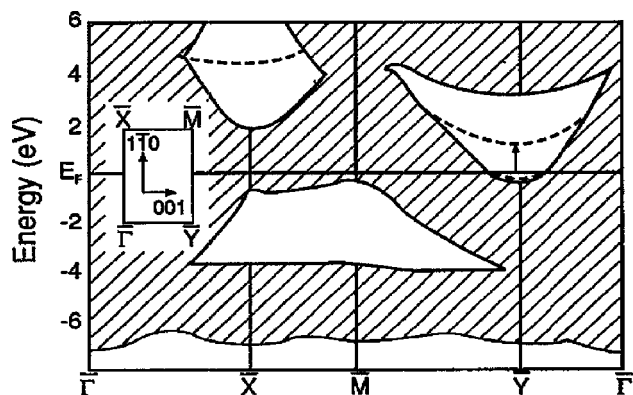


FIG. 2. Ag surface projected band structure reprinted with permission (Ref. 25). A band gap exists at the \bar{Y} point of the surface Brillouin zone. It is this gap that is believed to reduce the Smoluchowski effect and therefore inhibit adsorption on the $[001]$ step edge.

Our results show that benzene deposited at 66 K does *not* adsorb to the $[001]$ step edges. Chen *et al.* discovered that substituted thiophenes on Ag(111) adopt different orientations, but observed no adsorption preference at different step edges.²⁴ The electronic structure and adsorption energy will differ based on the geometrical arrangement of surface atoms at each step. In the case of Ag(110), anisotropy in the projected bulk density-of-states exists as shown in Fig. 2;^{25,26} a gap in the density-of-states at the Fermi level is found at the \bar{Y} point of the surface Brillouin cell. This gap causes charge

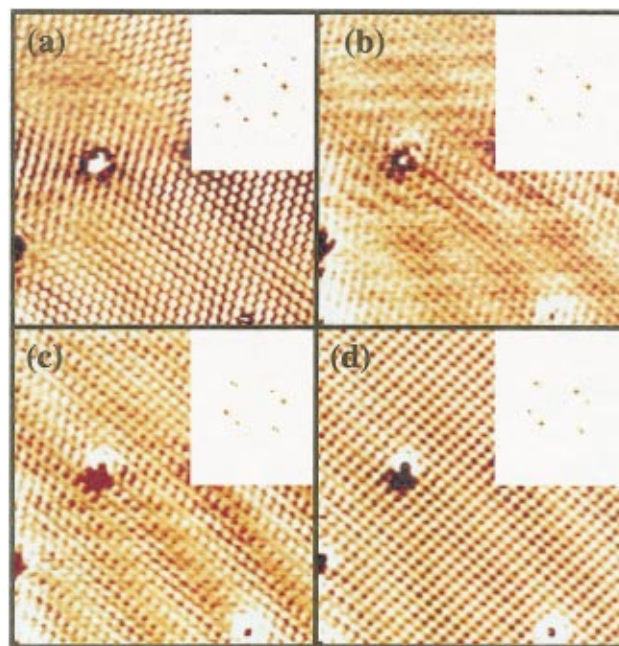


FIG. 3. (Color) Consecutive STM images of a complete monolayer of benzene adsorbed on Ag(110). These images were taken on the same area at the same bias voltage but at different tunneling currents. The sample states decay more quickly into vacuum compared to the overlayer states, so at large tip-sample distances, only the overlayer states are probed [(a) $V_s=-100$ mV, $I=0.1$ nA, size=8.4 nm \times 8.4 nm]. When the tip-sample distance is small [(d) $I=4.0$ nA], the sample electronic states are probed, and at intermediate distances [(b) $I=0.4$ nA, (c) $I=1.0$ nA] the image reflects an interference of both the surface and the molecule electronic states. Inset in each image is the corresponding Fourier transform.

transfer to be reduced for [001] steps, therefore reducing the ability of the step sites to accept charge from the benzene. In other words, the [001] step edges are less active adsorption sites because of their different electronic structure than the $[1\bar{1}0]$ step edges.

In contrast to these results, dosing larger quantities of benzene at 4 K results in saturation of the surface with a benzene monolayer. However, a different adsorption state is now populated, in which benzene molecules interact weakly with the substrate. As it is shown in Fig. 3(a), the weak surface-adsorbate interaction of these species allows the overlayer to form with a highly ordered hexagonal lattice. A surprising observation is the high density of the molecular packing. The value observed for the overlayer periodicity is approximately 3.7 Å, much smaller than the expected value from solid benzene.¹⁷ This value is also smaller than previously observed close-packing densities of benzene monolayers on other metal surfaces.⁷

An intriguing experimental observation is the dependence of the STM images on the tip-sample distance. As shown in the series of images in Fig. 3, the hexagonal periodicity of the benzene overlayer gradually becomes less apparent as we decrease the tip-sample distance to a point where we predominantly image the rectangular silver lattice. This is done by increasing the tunneling current, while maintaining a constant bias voltage. For intermediate current values, the superposition of both substrate and overlayer lattice creates a Moire pattern in our STM images. As observed in the images in Fig. 3, the interference creates long-wavelength periodicity, associated with the in-plane interference of both the Ag(110) and the overlayer lattices.

In the images in Fig. 3, we can additionally observe that the benzene monolayer is oriented along the substrate [001] direction. This orientation is found exclusively; we have never found domains oriented otherwise. We propose that the overlayer orientation is dictated by the step direction. While the Smoluchowski effect is dominant at the $[1\bar{1}0]$ step edge, this charge transfer is localized very close to the steps. This results in a single row of benzene molecules adsorbed at the step edge, as shown in the experimental images in Fig. 1. Additionally, the short-range nature of this effect has been calculated by Yang *et al.* for similar steps on the Cu(110) surface.²⁷ Therefore, the formation of the second and subsequent rows is dominated by molecule-molecule interactions and/or adsorbate-induced surface electronic perturbations. The latter was found to control the adsorption of benzene on Cu(111) steps.^{3,12} Either or both of these effects in combination with Smoluchowski pinning would account for the one-dimensional commensurate orientation of the

benzene monolayer.

The STM imaging transparency phenomenon has been previously discussed in the literature for the case of an aromatic molecular overlayer.^{28,29} In these studies, the STM images significantly depend on the applied bias voltage as a probe of different contributions from the overlayer states. Our measurements were performed with the sample bias held constant while only the tunneling current was modified to adjust the tip-sample distance. In this manner, we are probing only the decay and interference of the substrate and adsorbate wave functions without varying the probed electronic states.

We can extract a simple interpretation of these observations from the set of STM images in Fig. 3. The Fourier transformations (FT's) of the STM data, presented as insets in Fig. 3, give quantitative measurements of the corrugation amplitudes for the substrate and the overlayer. These can be extracted from the intensities of the FT peaks corresponding to each periodicity. The rapid decrease of the Ag wave functions can be explained by the dielectric screening of the benzene monolayer. This also explains why the benzene corrugation amplitude remains fairly constant as a function of tip-sample separation. The small corrugation amplitude of the benzene is due only to the tails of the benzene electronic wave functions that are sampled by the STM tip. Due to their weak interaction with the Ag surface, the highest-occupied and lowest-unoccupied molecular orbitals remain far from the Fermi energy, close to which we image.

By imaging benzene on Ag(110) using low-temperature STM, we have found that electronic effects at step edges strongly influence adsorption preferences of benzene at 66 K. Benzene molecules adsorb above $[1\bar{1}0]$ step edges due to the Smoluchowski effect, while the electronic structure of the [001] step edges inhibits electron transfer and thus adsorption at these sites. We have also investigated the apparent transparency of the molecules in STM images of full benzene monolayers deposited on Ag(110) at 4 K. This transparency is very dependent on the tip-sample distance and we attribute it to the dielectric screening of the Ag substrate electronic wave functions by the benzene monolayer.

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