

Metastable adsorption of benzene on the Si(001) surface

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We have investigated the adsorption of benzene on the Si(001) surface using scanning tunneling microscopy. The central result is that benzene initially adsorbs in a metastable state and then converts to a lower-energy final state. The conversion to the final state occurs rather slowly at room temperature, with a time constant of 19 min, implying an activation energy barrier of about 1.0 eV. We study in detail the appearance of each state and its position relative to the underlying surface dimers in order to make a correspondence to existing proposed models for the structure of benzene adsorbed on Si(001). We measure a lower bound on the energy difference between the two states of 0.14 eV. [S0163-1829(98)50808-9]

The interaction of benzene with the (001) and (111) surfaces of silicon has proven to be an interesting model system for molecular adsorption on semiconductor surfaces. The earliest experiments revealed a strong chemisorption state for benzene on cleaved Si(111)-(2×1) at room temperature, whereas there was no evidence for adsorption on cleaved Ge or GaAs.^{1,2} Later experiments found that benzene is also chemisorbed on Si(111)-(7×7) at room temperature, although rather weakly, with an energy barrier for desorption of approximately 1.0 eV.^{3,4} In addition to this, a diffusion study of benzene on Si(111)-(7×7) found that surprisingly, the energy barrier to diffusion is comparable to that for desorption.⁵ This was found to lead to an unusual “frustrated motion” of benzene involving jumps to sites beyond nearest neighbors. Finally, in one of the first definitive demonstrations of crystal-face specificity in chemical bonding on Si, benzene was found to chemisorb on Si(001)-(2×1) through σ orbitals, in contrast to the π bonding observed on Si(111)-(7×7).^{4,6} In the present work, we use scanning tunneling microscopy (STM) to investigate the adsorption of benzene on Si(001).

The adsorption of benzene on the Si(001)-(2×1) surface has been studied in recent years by both surface science techniques and semiempirical methods.⁶⁻⁸ Based on a combined study using high-resolution electron-energy-loss spectroscopy, thermal-desorption spectroscopy, and Auger electron spectroscopy, Taguchi *et al.*⁶ showed that benzene is nondissociatively chemisorbed on the surface at 300 K with a fractional saturation coverage of 0.27 benzene molecules per surface Si atom. They found that most of the benzene desorbs at 460 K, but that approximately 17% of the coverage is more tightly bound to the surface and desorbs at 500 K. They attributed the 460-K desorption peak to benzene adsorbed on defect-free regions and the 500-K desorption peak to benzene adsorbed near defects. They proposed that benzene is *di- σ* bonded to two adjacent Si atoms. They presented two structural models of benzene chemisorbed on Si(001), in which the molecule is lying neither flat nor parallel to the surface. In each of these, the benzene molecule is on top of the dimer row and has two of its C atoms bonded to two Si atoms of a single surface dimer. They were unable to uniquely determine the best model, however, and did not exclude the possibility that the benzene molecule might be located between two dimers.

Subsequent theoretical calculations have employed semiempirical methods in attempting to identify the most energetically preferred structure for benzene on Si(001). These results do not completely agree with each other nor with the proposals of Taguchi *et al.*, especially regarding the number of C atoms and Si atoms involved in bonding benzene to the substrate.⁶⁻⁸ Craig used the SLAB-MINDO molecular orbital method in an energy minimization that yielded two preferred structures.⁷ One corresponds to benzene adsorbed on the defect-free terrace and is thus the dominant structure.⁹ In this arrangement, the molecule is located on top of a dimer row above one Si dimer and is tilted relative to the surface, with four adjacent C atoms of benzene bonded to two Si atoms of a dimer. A more recent calculation by Jeong *et al.*⁸ using an improved method yields results in contrast to Craig's. Jeong *et al.* concluded that the most stable structure on defect-free regions of the surface has four C atoms of benzene bonded to four Si atoms from two surface dimers. In this arrangement, the benzene molecule is located on top of a dimer row between two Si dimers and is lying nearly flat and parallel to the surface, as shown in Fig. 3(c). They also reported two other optimized structures, as shown in Figs. 3(b) and 3(a), which are higher in energy by 0.29 and 0.47 eV, respectively. These correspond to benzene bonded to one Si dimer.

We report that benzene initially adsorbs in a metastable state and subsequently converts to a lower-energy configuration. Using high-resolution images, we carefully investigate the appearance of each state and its location relative to the surface dimers in order to help resolve the confusion noted above regarding the structure of benzene adsorbed on Si(001). By making a close correspondence to existing theoretical models, we aim to stimulate further investigation of the unusual metastable adsorption of benzene on Si(001).

Our experiments are performed in a UHV chamber with a base pressure of 5×10^{-11} Torr housing a custom-built STM capable of imaging at elevated temperatures. Reagent grade benzene is purified using freeze-thaw cycles and introduced into the chamber through a precision leak valve. The exposure is monitored with a nude Bayard-Alpert type ion gauge calibrated with the sensitivity factor for benzene, 5.2 relative to N₂. Our Si(001) samples (*n*-type, *P*-doped, 0.01 Ω cm) are prepared by flashing briefly to 1250 °C, which yields a

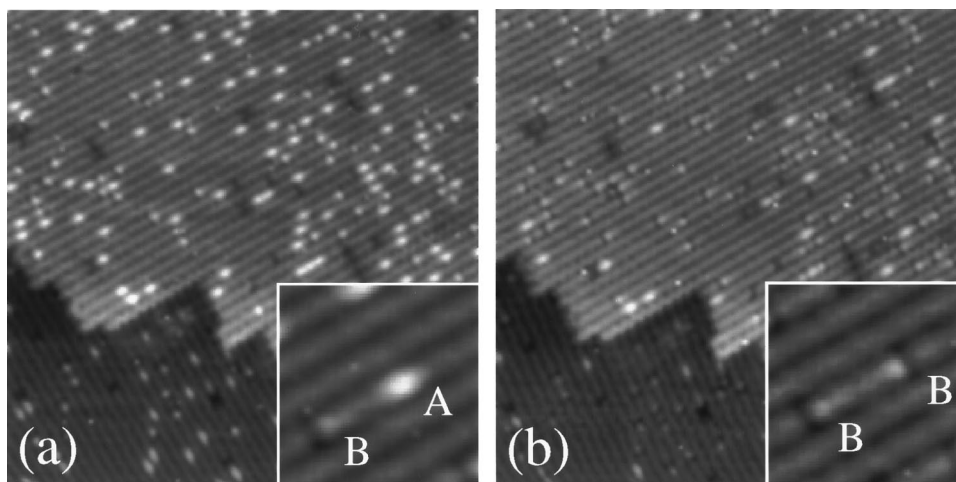


FIG. 1. A pair of $400 \times 400 \text{ \AA}^2$ STM images from a room-temperature experiment in which a clean Si(001) surface was exposed to 0.06 L of benzene. Part (a), about 8 min after the exposure, shows that benzene is initially adsorbed into a state (A) that appears bright and symmetric. Part (b), taken 28.6 min later, shows that nearly all of the benzene converts to a state (B) that is fainter in appearance. The insets show a $60 \times 60 \text{ \AA}^2$ area from two higher-resolution images, demonstrating a conversion event in greater detail. State B is asymmetric, appearing as a bright region adjacent to a dark region. These are filled-state images with sample bias -2.0 V .

clean sample displaying the (2×1) dimer row reconstruction. Imaging is carried out under the following tunneling conditions: the bias voltage is in the range -2 to $+2 \text{ V}$, and the tunneling current is 0.1 nA .

Upon exposing the clean Si(001) surface to benzene, we observe that benzene is always adsorbed on top of the dimer rows, is distributed randomly across the surface, and is immobile at room temperature. The closest spacing of benzene on top of the dimer rows is observed to be one benzene molecule per two surface dimers. This corresponds to a saturation coverage of 0.25 molecules per surface Si atom, in agreement with existing theoretical and experimental results.^{6–8} These observations are demonstrated in Fig. 1(a), which is a $400 \times 400 \text{ \AA}^2$ image from an experiment carried out at room temperature. This image was taken 8 min after an exposure of 0.06 L ($1 \text{ L} = 10^{-6} \text{ Torr s}$). This exposure results in a small coverage of benzene, ~ 0.04 molecules per Si atom.

Of central importance in Fig. 1(a) is the fact that nearly all of the benzene is in a bright, symmetric appearing state. This initial state (A) is observed to convert over time to a lower-energy state (B), which is fainter in appearance. This behavior is shown in Fig. 1(b), an image taken 28.6 min later. The images inset into Figs. 1(a) and 1(b) display the conversion of a benzene molecule in detail and show that state B is asymmetric in appearance, consisting of a bright region adjacent to a dark region. These observations reveal that surprisingly, benzene is initially adsorbed on the Si(001) surface in a state that is not the lowest-energy state, but is instead metastable.

The activation energy barrier to conversion from state A to B was measured by monitoring the region shown in Fig. 1 for a total time of 110 min. In a representative sample of 93 benzene molecules, 72 were initially in state A and 21 in state B. At the end of the experiment, 9 were in state A and 84 in state B. There were no conversions from B to A observed. The decay into state B over time of the 72 molecules initially in state A was fit by an exponential function with a time constant of $\tau = 1115 \pm 84 \text{ sec}$ (18.6 min). For thermally

activated conversion from A to B, the rate of decay is given by the Arrhenius relation: $R = 1/\tau = \nu e^{-E/kT}$. Here R is the rate, or the reciprocal of the time constant τ . The activation energy and prefactor for the process are E and ν , respectively. Assuming a typical value for the prefactor of 10^{13} Hz , we find an energy barrier of approximately 1.0 eV .

The energy difference between states A and B was estimated by measuring their relative population, which in equilibrium is given by the Boltzmann factor $e^{-\Delta E/kT}$, where ΔE is the energy difference. For this measurement, we heated the substrate to a temperature of 350 K in order to hasten the approach to equilibrium. Since the overwhelming majority of benzene molecules eventually convert to state B, this measurement has the difficulty of poor statistics for the number of molecules in state A. Upon exposing the surface to benzene at 350 K , waiting for equilibrium to be established, and imaging at temperature, we found that the population ratio of B to A is at least 100:1. With this ratio, we set a lower bound on the energy difference between states A and B of 0.14 eV .

A word about tip effects is necessary. In order to help assure that the measured rate of conversion from A to B is not dominated by tip-induced conversions, the large region shown in Fig. 1 was scanned infrequently. Typically, a short sequence of images of the region ($\sim 4 \text{ min}$ in length) was taken, followed by a pause of 20 min. During the pauses, a movie of higher resolution was taken of a small region outside the large region. Since the behavior of the small constantly scanned regions matched the behavior of the larger infrequently scanned region, we conclude that tip effects confined to the region of scanning do not seem to be present in this set of data. However, in other instances we found that under tunneling conditions identical to those of Fig. 1, the scanning tip would suddenly change its condition so that it began scraping benzene off of the region of scanning, patterning a square hole in the coverage of benzene. In one typical example, a $130 \times 130 \text{ \AA}^2$ area containing 25 benzene molecules was cleared of benzene after 40 sequential scans in a period of 20 min. At present, the cause of this sudden change in the effect of the tip on the scanned region is not

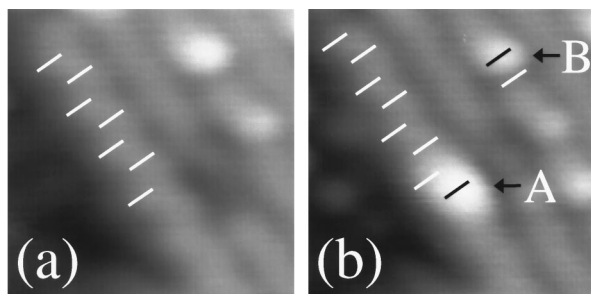


FIG. 2. A pair of $40 \times 40 \text{ \AA}^2$ STM images from an incremental deposition experiment at room temperature. Image (a) was taken following a 0.06-L exposure. Image (b) shows the same region following an additional exposure of 0.08 L. In image (b) a benzene molecule has adsorbed in state A directly over a single Si dimer, as evidenced by its position relative to the buckled dimers on which it rests. The buckling of these dimers is frozen in, allowing them to be distinguished and marked with line segments. (Note that the phase of the buckling has shifted by 180° between images.) In the upper right of image (b), a benzene molecule is in state B. The bright and dark regions of this state are marked with line segments, revealing that the two regions are spaced apart by exactly the same distance as the surface dimers (3.84 \AA). Based on the analysis of several STM movie sequences, we conclude that the bright and dark regions are situated above adjacent dimers. These are filled-state images with sample bias -2.0 V .

known. When this effect was not desired, pulsing the sample bias to 10 V with the tip in tunneling range usually changed the tip back to its normal state. This suggests that contamination on the end of the tip was responsible for scraping benzene off of the sample.

By imaging at high resolution and using the frozen-in buckling of dimers and missing dimer defects as reference points, we are able to locate the apparent position of the center of the benzene molecule in states A and B relative to the underlying surface dimers. An example of this technique is shown in Fig. 2 and the results were found to be consistently reproducible upon analysis of many such images. Figure 2(a) is an image at room temperature of a $40 \times 40 \text{ \AA}^2$ region after an exposure of 0.06 L. The positions of the dimers along a step edge are marked with white line segments. These dimers are distinguishable since the buckling of the dimer row to which they belong is frozen in, as is typical for dimer rows along a step edge. The next image, Fig. 2(b), is of the same region just after an additional exposure of 0.08 L. [Notice that the phase of the frozen-in buckling has shifted by 180° from the previous image, Fig. 2(a).] We see that a benzene molecule has adsorbed, in the symmetric appearing state A, on top of the dimer whose position is marked with a black line segment. We conclude that in state A, the center of the benzene molecule is located directly over a surface dimer.

In the upper right of Fig. 2 there is a benzene molecule in state B. In Fig. 2(b), line segments have been drawn over the bright and dark regions of this state, and we observe that their spacing is identical to that of the surface dimers (3.84 \AA). The apparent height difference between the two regions is about 1 \AA . Upon analyzing movie sequences showing conversions from state A to B, as in Fig. 1, we find that the bright region of state B is centered at the same location as the bright spot of state A, directly over a surface dimer.

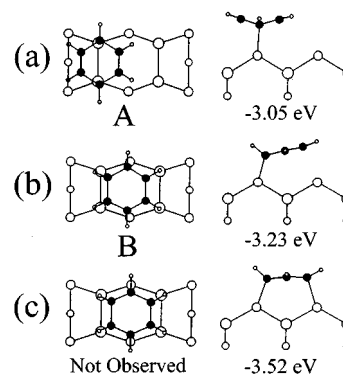


FIG. 3. The top and side views of structural models of benzene chemisorbed on Si(001) with their energies, as calculated by Jeong *et al.* (reproduced from Ref. 8 with permission). (a) depicts the model we assign to state A, and (b) depicts the model we assign to state B. These two structures are similar to those proposed by Taguchi *et al.* based on their experimental results (Ref. 6). (c) shows the lowest-energy state calculated by Jeong *et al.* (Ref. 8), which is not observed.

Since the spacing between the bright and dark regions of state B is identical to the Si dimer spacing, we conclude that the bright and dark regions are located above adjacent surface dimers. Assuming the center of the benzene molecule in state B is midway between the bright and dark regions, the benzene molecule must be located approximately between two surface dimers in state B. Therefore, in the conversion from state A to B, the benzene molecule apparently shifts over half a dimer spacing from a location centered above a dimer to a location in between two dimers.

We have in fact observed individual benzene molecules shifting to both the right and the left into state B from state A above a given dimer. These multiple conversions were induced by the scanning of the tip under the contaminated tip condition described above. This shifting in either direction from state A into state B further supports the conclusion that state A is symmetric relative to its underlying dimer.

These results may help resolve the confusion described earlier regarding the structure of benzene adsorbed on Si(001). First of all, we do not observe benzene adsorbed between the dimer rows, in contrast to the result of Craig's calculation that the lowest-energy structure is located between the dimer rows.^{7,9} Second, there is only one currently proposed structure that could correspond to state A. This structure is shown in Fig. 3(a), and it is one of the three optimized structures presented by Jeong *et al.* as a result of their recent theoretical calculations.⁸ It is also one of the two structures proposed originally in the experimental work of Taguchi *et al.*⁶ This structure is centered above a single dimer and has two C-Si bonds. It is oriented in such a way that it is very likely to appear as a symmetric bright spot in an STM image. Therefore, it is a good match to state A. Finally, our results strongly suggest that state B is tilted relative to the surface and is located between two dimers. In our view, the best candidate for the structure of state B is the other proposed structure common to the results of both Taguchi *et al.* and Jeong *et al.*^{6,8} This structure is shown in Fig. 3(b). It features two C atoms bonded to two Si atoms of a dimer, just as in the proposed structure for state A, and is tilted relative to the surface. Also, the placement of the mol-

ecule is such that it would seem to naturally produce the dark and bright regions over adjacent dimers observed in our STM images of state *B*. In fact, Jeong *et al.* calculate the energy of this structure to be lower than that of Fig. 3(a), consistent with the present results.⁸ The calculated energy difference is 0.18 eV, quite consistent with our lower bound of 0.14 eV.

If our assignments of the structures of Figs. 3(a) and 3(b) to states *A* and *B*, respectively, are correct, it is surprising that we do not observe the structure of Fig. 3(c), which is predicted by Jeong *et al.* to have the lowest energy.⁸ This optimized structure is quite symmetric in arrangement and lies flat and parallel to the surface. It therefore seems unlikely that it would produce the asymmetric image corresponding to state *B*. However, Jeong *et al.* point out that the position of this structure is not exactly symmetrical relative to its two underlying dimers.⁸ It would be useful to have more detailed knowledge of how this structure should appear in an STM image, as could be obtained from local density-of-states calculations, for example.¹⁰ Nevertheless, we note that Fig. 3(c) is the only structure that has four C atoms

bonded to four Si atoms. It could be that the calculation encountered some unforeseen difficulty in this situation. On the other hand, although it seems unlikely, perhaps there is a kinetic limitation that prevents the molecule from entering the structure of Fig. 3(c).

In summary, our STM experiments have revealed an intriguing behavior in the adsorption of benzene on the Si(001) surface. Benzene is initially adsorbed in a metastable state and proceeds to convert to a lower-energy final state. The activation energy barrier for this conversion process is measured to be 1.0 eV, assuming a prefactor of 10^{13} Hz. A lower bound on the energy difference between the two states is set at 0.14 eV. This unusual adsorption behavior poses an interesting question for further theoretical study: why does benzene initially adsorb in the metastable state *A*? As a first step, we have attempted to make a close correspondence between the two states we observe and the existing proposed structural models for benzene adsorption on Si(001).

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⁹The other structure is lower in energy by 0.35 eV. However, this state is located between the dimer rows of the surface, and Craig regarded it as benzene adsorbed at a defect site since the underlying surface dimers were not in their ideal (2×1) arrangement. This view is consistent with the conclusion of Taguchi *et al.* that the most tightly bound state is located at a defect site.

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