Site Dependence of the Apparent Shape of a Molecule in Scanning Tunneling Microscope Images: Benzene on Pt{111}

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We present scanning tunneling microscope images of benzene adsorbed on the Pt{111} surface. We find three distinct types of images for isolated benzene molecules, depending upon the benzene adsorption site. This site dependence is in agreement with recent theoretical calculations, and may limit the usefulness of the scanning tunneling microscope in elucidating the structures of adsorbed molecules.

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Scanning tunneling microscope (STM) images display aspects of the structure of molecules adsorbed on surfaces. Motivations to interpret these images unambiguously include the desire to identify unknown molecules on surfaces according to their appearance, and to determine the structure and composition of molecules and of molecular complexes. The unambiguous interpretation of these images is complicated by the fact that the STM does not record the location of atomic nuclei. What it does record is the local variation in the electronic structure of the surface at the adsorbed molecule. Here we report on the imaging of isolated benzene molecules on Pt{111} at 4 K and demonstrate that the appearance of a molecule, as imaged with the STM, can vary dramatically according to the binding site of the molecule. On one hand, this places constraints on the use of the STM as an analytical tool; on the other, it demonstrates the STM's sensitivity to variations in the chemical environment of adsorbed molecules.

Benzene was the first adsorbate imaged with the STM which appeared to show internal structure [1]. Ohtani *et al.* coadsorbed benzene with CO in order to form an ordered overlayer on the Rh{111} surface [1,2]. Benzene appeared as a feature with three lobes at the vertices of an equilateral triangle with spacings close to the *meta* carbon separations. All of these triangles were oriented in the same direction, but within each molecule the lobes were not all the same height. Ohtani *et al.* [1,2] inferred from their data and the previous low energy electron diffraction (LEED) results [3] that these images were due to benzene molecules adsorbed parallel to the surface at hcp-type threefold hollow sites. Theoretical calculations by Sautet *et al.* of these STM images are consistent with the experimental positions and orientations of the lobes, but show lobes of equal height [4].

Further calculations of adsorbed benzene have predicted varying STM images depending upon the surface, adsorption site, metal Fermi level, and tunneling conditions [4–7]. Sautet and Bocquet have recently performed calculations of isolated benzene molecules adsorbed on Pt{111} directly related to the experimental data presented here, and find that the images vary based upon adsorption site [5]. They find that the benzene in hcp and fcc hollow sites and in bridge sites have essentially the same chemisorption energy, ~30 kcal/mole. Benzene adsorbed at atop sites was less stable, with substantially lower chemisorption energy, ~20 kcal/mole. Site dependent STM images at low bias voltages have also been predicted in theoretical studies by Fisher and Blöchl for adsorbed benzene on MoS_2 and graphite [6]. Wander *et al.* have recorded diffuse LEED data for disordered benzene at high coverage and surface temperatures of $170 < T < 300$ K on Pt{111}, and found benzene adsorbed at bridge sites and somewhat distorted [8]. The images and sites calculated by Sautet and Bocquet correspond closely to those found here, and are discussed below.

In Fig. 1 we present an STM image of the Pt crystal recorded after dosing to a coverage of approximately 0.001 monolayer (ML) of benzene. The benzene molecules appear as protrusions from the otherwise flat terraces of the Pt{111} surface. When these features are examined at higher resolution, as shown in Figs. 2(a)–2(c), we find three characteristic types of protrusions. It is this variety among image types that is the main focus of this

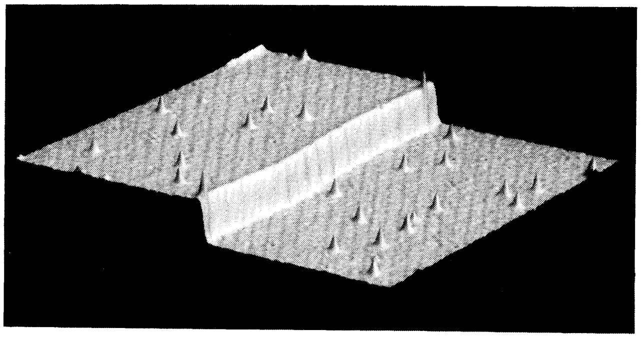

FIG. 1. STM image of a 500 Å×500 Å region of Pt{111} which has been covered with 0.001 monolayer of benzene. One monatomic height step is shown in the image which was recorded with the tip at $V_{\text{bias}} = -0.010$ V and with $I_{\text{tunnel}} = 100$ pA. The vertical scale is expanded so as to fill the image, and the minimum to maximum height difference in the image is 3.95 Å.

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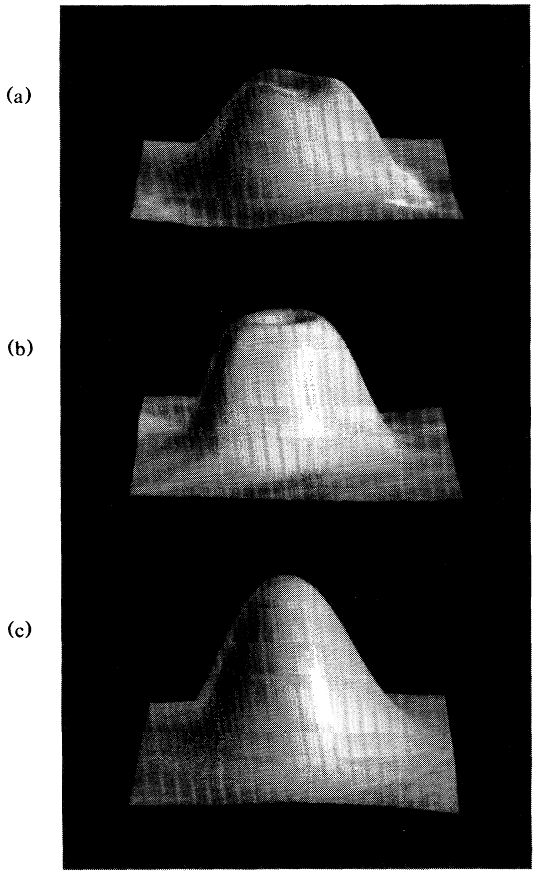

FIG. 2. STM images of three different 15 Å×15 Å regions of Pt{111} each showing a single adsorbed benzene molecule. The images were recorded with (a) $V_{\text{bias}} = -0.050$ V, $I_{\text{tunnel}} = 100$ pA; (b) $V_{\text{bias}} = -0.010$ V, $I_{\text{tunnel}} = 1$ nA; and (c) $V_{\text{bias}} = -0.010$ V, $I_{\text{tunnel}} = 100$ pA, respectively. The minimum to maximum height differences in the images are (a) 0.58 Å, (b) 0.72 Å, and (c) 0.91 Å, respectively. The observed images of individual molecules did not change qualitatively for a wide range of tunneling parameters.

paper. In the hundreds of images that we have recorded of isolated benzene molecules, we found for each molecule only one of these three types of images. For bias voltages of $0.01 \leq |V_{\text{bias}}| \leq 0.3$ V, and tunneling currents up to 1 nA, we have found no qualitative changes in the images for any single benzene molecule. Let us consider the possible explanations for these multiple characteristic image types.

The Pt crystal was essentially free of protrusions prior to dosing. We may thus eliminate the possibility that the protrusions are due to the process used to prepare the Pt surface. The purity of the benzene was checked *in situ* by mass spectroscopy prior to dosing. This would have revealed any significant contamination of the source benzene or the presence of undesired chemical reactions between benzene and species adsorbed on the walls of the UHV system. Auger spectra of the "as prepared" Pt crystal indicated (0.2–2)% carbon impurity in the near-surface region [9].

The images of Figs. 2(a)–2(c) are *characteristic* in that no simpler or higher resolution images of these protrusions could be obtained despite many deliberate rearrangements of the atoms on the end of the STM tip. In addition, we have recorded images in which all possible pairs of the image types appear, and the STM tip did not change during multiple, identical sequential images. We thus eliminate tip effects as a possible explanation for the distinct image types.

Despite our occasional ability to image the Pt{111} lattice corrugation, we are unable to determine the benzene adsorption sites directly from our images. This is partly because the mechanism by which the fcc{111} lattice is resolved remains unclear [10], and it is thus uncertain whether the observed peaks of the lattice corrugation correspond to the metal atom positions.

The type of image found in Fig. 2(a) matches the appearance of benzene coadsorbed with CO on Rh{111} in Refs. [1] and [2] and is thus unlikely to be associated with a surface defect. While Ohtani *et al.* found only one orientation of the three lobes on the surface [1,2], we have found two possible orientations, rotated 60° with respect to one another. Ohtani *et al.* attributed their observation of a single orientation to occupation of only hcp-type sites for the ordered overlayers, consistent with the structures determined from LEED. Because we observe two orientations, we infer that we have imaged benzene at both hcp-type and fcc-type adsorption sites. Calculations by Sautet indicate that these sites have nearly identical chemisorption energies, are stable in that no lower energy sites exist on the perfect crystalline surface, and give STM images with three symmetric lobes [5]. With the exception of the symmetry of the lobes, these predictions match our experimental data.

We have only found the image type shown in Fig. 2(b) near other adsorbates or defects on the surface. We do not know the role of the surface environment in determining the image type shown in Fig. 2(b). Sautet and Bocquet have calculated that benzene adsorbed at atop sites should give ringlike images with six lobes weakly resolved for their atomically sharp theoretical tip, but should be unstable relative to translation to energetically more favorable sites [5]. We have not resolved lobes within the ringlike structures. We conclude (as do Sautet and Bocquet) that the chemical environment, i.e., the nearby adsorbates and defects, may play a role in stabilizing adsorption at the atop site, and tentatively assign the image type shown in Fig. 2(b) to these sites.

We have eliminated the possibility that the image type displayed in Fig. 2(c) associated with a defect on the surface by picking up such a molecule with the STM tip, moving it elsewhere on the surface, and then reexamining the original adsorption site [11]. For high coverages of disordered benzene, Wander *et al.* found that benzene adsorbed at bridge sites, rotated 30° from the orientation found for the threefold hollow sites of coadsorbed benzene and CO on both Pt{111} and Rh{111} [8]. Our images of the type shown in Fig. 2(c) often appear to have C_{2v} symmetry; however, it is difficult to distinguish this from tip effects. We thus cannot differentiate between C_{2v} and higher symmetries for the images of the type shown in Fig. 2(c). Sautet and Bocquet have calculated that bridge-bonded benzene on Pt{111} is stable if properly oriented, with chemisorption energies essentially identical to those for threefold hollow sites [5]. Their calculated images closely resemble the single bump structure shown in Fig. 2(c), but are elongated perpendicular to the "bridge" giving features with C_{2v} symmetry [12]. We therefore assign the bump structures such as those shown in Fig. 2(c) to be bridge-bonded benzene.

We conclude that the variations between the characteristic image types are due to adsorption of benzene at different sites on the surface for three reasons. First, experiments and calculations have shown that when benzene is adsorbed on the Pt{111} surface it adsorbs at multiple sites [5,8,13]. Second, there are many examples where the overlap of the conduction electrons with molecular orbitals at the Fermi level depend upon the binding site of the molecule [14]. Since at low bias voltages the STM images the extent to which the Fermi-level conduction electrons extend beyond the surface, variations in appearance according to binding site are to be expected. As detailed above and in Ref. [5], STM images of benzene on Pt{111} have been calculated to be strongly dependent upon adsorption site [15], in agreement with our data. Third, when we dose the Pt{111} surface at different temperatures and then record STM images at 4 K, we get different distributions of these three types of images. Dosing at room temperature, then cooling the crystal to 4 K before imaging, leads to ratios of ca. 2:1:3 for the image types displayed in Figs. 2(a), 2(b), and 2(c), respectively. Dosing the crystal at 4 K with benzene let into the room temperature chambers as for Xe in Ref. [17], then imaging without warming the crystal, we find predominantly the image type shown in Fig. 2(c), with small percentages of the other two types. For room temperature adsorption, the benzene molecules are able to diffuse across the surface to find energetically favorable sites (i.e., some of the small number of surface defect sites). Upon cooling, as the crystal is moved to the 4 K STM, the molecules freeze into specific sites (at some temperature). The ability of the molecules adsorbed at room temperature to sample the surface leads to many more molecules at and near defects [e.g., molecules such as the one shown in Fig. 2(b)] than are found for adsorption at 4 K. For low temperature adsorption there is no thermally activated diffusion and the only means by which benzene molecules sample the surface is via transient mobility upon adsorption before losing their momentum parallel to the surface [17,18]. From the distribution of the isolated benzene molecules we can place an upper limit of a few lattice sites on the accommodation lengths for this parallel momentum. We thus understand the larger fraction of molecules adsorbed at and near defects in the case of room temperature adsorption to be due to these molecules sampling a larger area of the surface and having the opportunity to find defect sizes, whereas the molecules adsorbed at 4 K do not [19]. We conclude that the different image types correspond to different benzene adsorption sites.

In the images of benzene having three "lobes" such as

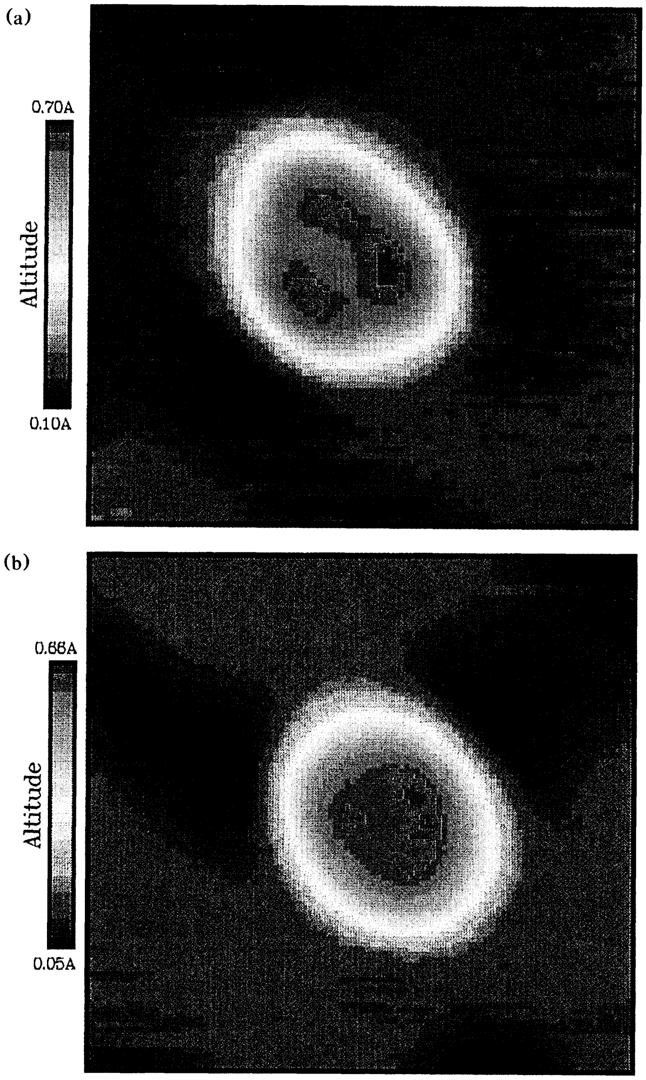

FIG. 3. Topographic displays of STM images of two 20 Å×20 Å regions of Pt{111} showing isolated benzene molecules which appear as three lobed features. The lobes of the two molecules appear rotated 60° from each other. The images were recorded with (a) $V_{\text{bias}} = -0.050$ V, $I_{\text{tunnel}} = 100$ pA and (b) $V_{\text{bias}} = +0.010$ V, $I_{\text{tunnel}} = 100$ pA, respectively. Note the depressions in the images of the surrounding metal along the direction of the lobes from the center of each molecule.

in Fig. 2(a), there appear three depressions in the images of the surrounding metal substrate. As shown in Fig. 3, both the depressions and lobes due to the benzene occur in only two possible orientations, rotated 60° about the surface normal with respect to each other. These are the structures attributed to the fcc-type and hcp-type threefold hollow sites. The surrounding depressions appear to be 6–10 Å from the center of the molecules nominally along the direction of the lobes [20]. We interpret these depressions within the framework of the Tersoff-Hamann approximation [21] to indicate a long-range electronic perturbation of the local density of states induced by the adsorbed benzene. Such effects were not seen for the other two types of benzene images. We speculate that these effects depend upon the specific adsorption site, and thus the specific electronic interactions of the adsorbate with its underlying surface atoms [22]. Such long-range electronic effects may have dramatic consequences in directing the approach of electrophilic versus electrophobic species to adsorbates. This may allow directed chemical synthesis with mediation (or modulation) of the adsorbate-adsorbate interaction by the charge redistribution that one or both adsorbates induce in the substrate.

We have shown how the appearance of adsorbates in STM images can vary according to binding site. While providing useful information on how electronic structure varies with chemical environment, it also places constraints on using the STM to identify molecules on surfaces.

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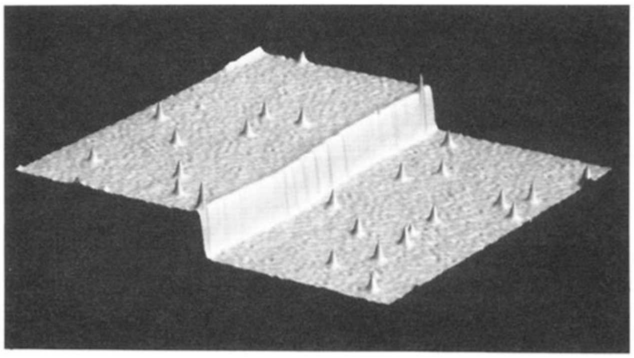

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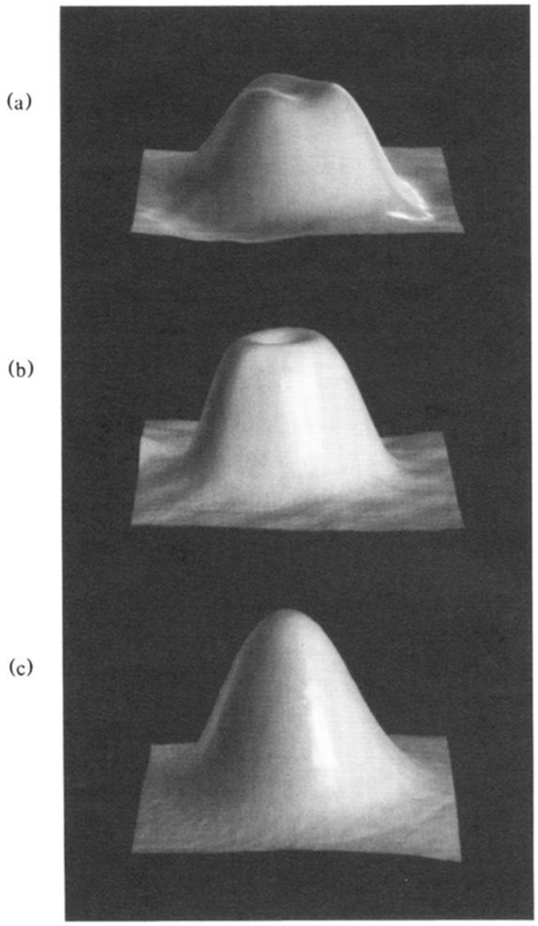

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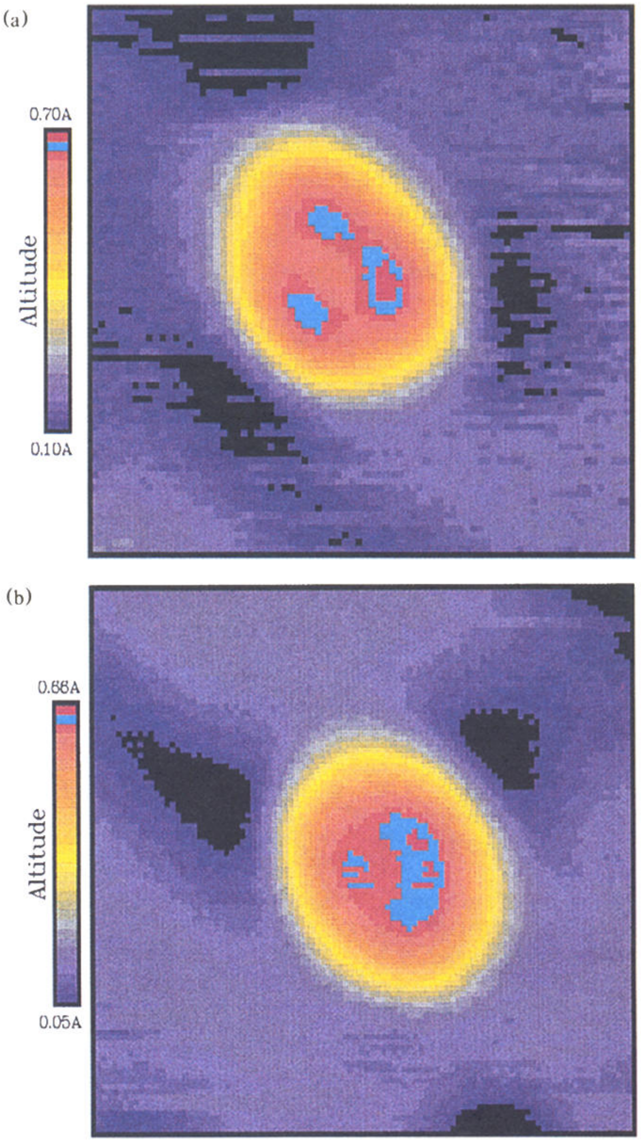

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