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Site Dependence of the Apparent Shape of a Molecule in STM Images: Benzene on Pt(111)

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SITE DEPENDENCE OF THE APPARENT SHAPE OF A MOLECULE IN STM IMAGES: BENZENE ON Pt{111}

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Abstract

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 of Fisher and Blöchl, 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 the desire 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 4K 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]. In the work of Ohtani *et al.* the benzene, which was coadsorbed with CO in order to form an ordered overlayer on the Rh{111} surface, appeared as a feature with three lobes [1]. These lobes appeared at the vertices of an equilateral triangle with spacings close to the *meta* carbon separation in benzene. Theoretical calculations of these STM images are consistent with the experimental results [2].

In Fig. 1 we present an STM image of the Pt crystal recorded after dosing to a coverage of approximately 0.001 monolayers (ML) of benzene. The benzene molecules appear as protrusions from the otherwise flat terraces of the Pt{111} surface. When examined closely (Figs. 2 a-c) we find three characteristic types of protrusions. For bias voltages of $0.01\text{V} \leq |V_{\text{bias}}| \leq 0.3\text{V}$, and tunneling currents up to 1 nA, we have found no qualitative changes in the images found for any single benzene molecule. Let us consider the possible explanations for 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 to the walls of the UHV system.

We have found that the images of Fig. 2 are *characteristic* in that no simpler nor 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 of the possible combinations of two of the image types appear, and the STM tip did not change during multiple, identical sequential images. We may thus eliminate tip effects as a possible explanation for the distinct image types.

Auger spectra of the "as prepared" Pt crystal indicated 0.2-2% carbon impurity in the near-surface region. We observe nominal 0.1 Å deep point defects which we tentatively identify as carbon impurity atoms (this assignment agrees with calculated images of C adatoms [3]). We have eliminated the possibility that the image type displayed in Fig. 2c is associated with a point defect on the surface by picking up such a molecule with the STM tip, and carefully reexamining the surface where the molecule was originally adsorbed. The type found in Fig. 2a matches the appearance of benzene coadsorbed with CO on Rh{111} as observed by Ohtani *et al.* [1] and is thus unlikely to be associated with a defect on the surface. We have only found the image type shown in Fig. 2b near another adsorbate or near a defect on the surface. We do not know the role of the surface environment in determining the image type shown in Fig. 2b.

Finally, the variation in appearance between the characteristic image types can be due to adsorption of the benzene at different sites on the surface. We favor this explanation not for the lack of an alternative explanation but because *it is expected* for the following two reasons. First, when benzene is adsorbed on the Pt{111} surface it adsorbs at multiple sites and does not order [4,9]. Second, there are many examples where the overlap of the conduction electron wavefunctions with molecular orbitals at the Fermi level has been shown to depend upon the binding site of the molecule. For example, both theory [10] and experiment [11] agree that the back-donation of conduction

electrons to the $2\pi^*$ antibonding orbital of CO depends upon adsorption site. When low bias voltages are used the STM images the extent to which the Fermi-level conduction electrons extend beyond the surface. Recent theoretical calculations of STM images of benzene adsorbed on graphite and MoS_2 surfaces predict that at low bias voltage, $|V_{\text{bias}}| \leq 2\text{V}$, the benzene merely modifies the image of the conduction electrons of the substrate, and thus the image depends strongly on adsorption site [12]. This result is in agreement with our observations.

In the images of benzene that appear to have three "lobes" such as the image in Fig. 2a, there appear three depressions in the images of the surrounding metal substrate. As shown in Fig. 3, both these depressions and the three lobes apparently due to the benzene occur in only two possible orientations. These two orientations are rotated 60° about the surface normal with respect to each other. The depressions appear to be $6\text{--}10\text{\AA}$ from the center of the molecules and in all cases are nominally along the direction of the lobes (from the center of the molecule). Such depressions could not be seen by Ohtani *et al.* [1], because at room temperature full ordered overlayers were required to keep the molecules from diffusing faster than the time scale of the measurements. The lateral spatial extent of the electronic perturbation of the adsorbate molecules in each case is of the order of $200\text{\AA}^2$, and is consistent with the scattering cross section measured for isolated adsorbates using Helium scattering [5]. We interpret these depressions within the framework of the Tersoff-Hamann approximation [6] 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 of the benzene molecules, and thus the specific electronic interactions of the adsorbate with its underlying surface atoms. On semiconductor surfaces, effects such as these have been found -- for oxygen on $\text{GaAs}(110)$ and for alkali atoms on $\text{Si}(100)$ [7,8]. We find the semiconductor results less surprising than the results here because of the directional covalent bonding of the semiconductors as opposed to the delocalized metallic bonds of the Pt. Such long-range electronic effects may have dramatic consequences in directing the approach of electrophilic vs. 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 an adsorbate in an STM image can vary according to binding site. While this provides useful information on how electronic structure varies according to chemical environment, it also places constraints on the use of the STM in identifying molecules on surfaces.

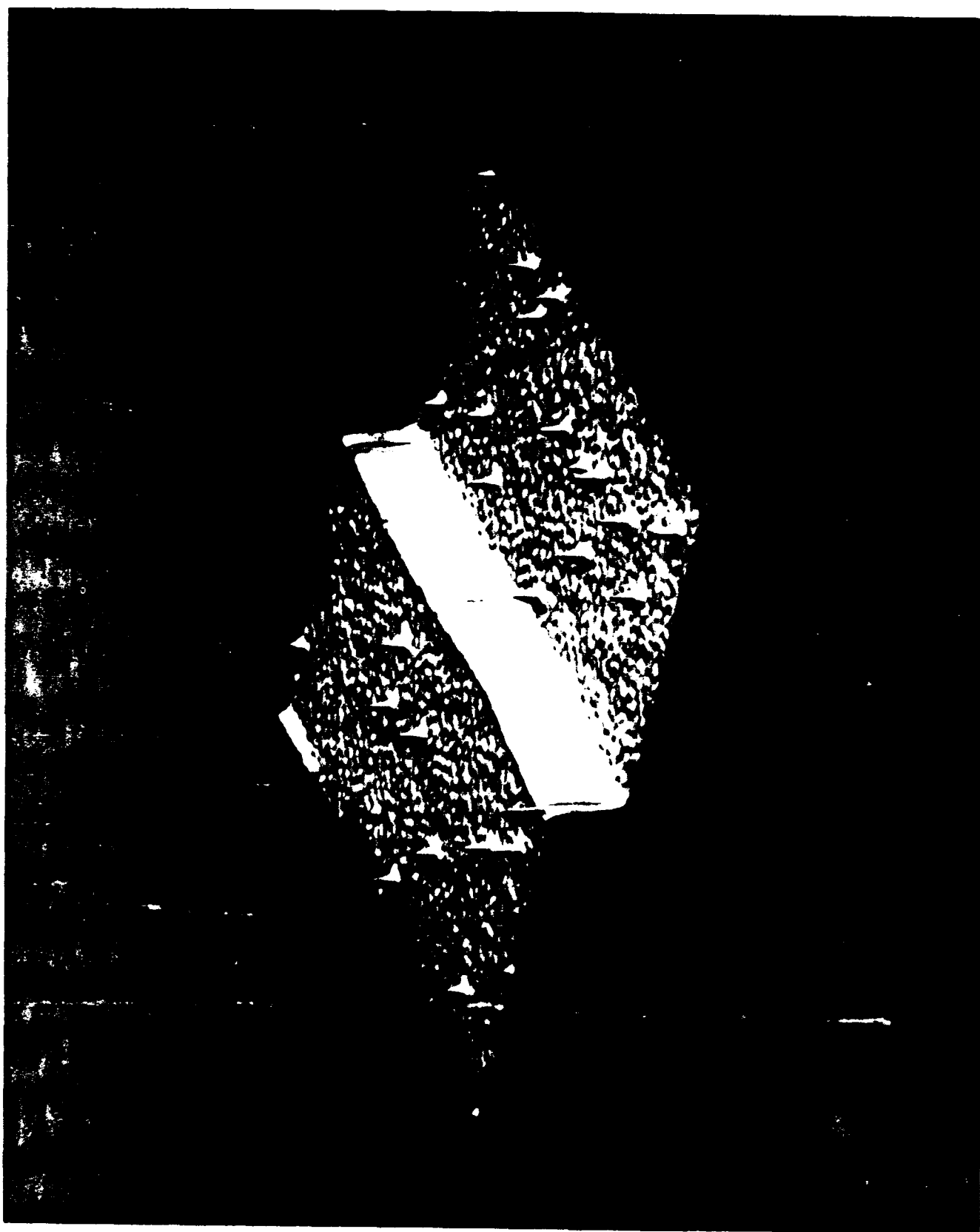
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FIGURE CAPTIONS

1. STM image of a $500\text{\AA} \times 500\text{\AA}$ region of Pt{111} which has been covered with 0.001 monolayers of benzene. One monatomic height step is shown in the image which was recorded with the tip at $V_{\text{bias}} = -0.01\text{V}$ and with $I_{\text{tunnel}} = 100\text{ pA}$. The vertical scale is expanded so as to fill the image, and the minimum to maximum height difference in the image is $3.95\text{\AA}$.
2. STM images of three different $15\text{\AA} \times 15\text{\AA}$ regions of Pt{111} each showing a single adsorbed benzene molecule. The images were recorded with: a) $V_{\text{bias}} = -0.050\text{V}$, $I_{\text{tunnel}} = 100\text{ pA}$, b) $V_{\text{bias}} = -0.010\text{V}$, $I_{\text{tunnel}} = 1\text{ nA}$, and c) $V_{\text{bias}} = -0.010\text{V}$, $I_{\text{tunnel}} = 100\text{ pA}$, respectively. The minimum to maximum height differences in the images are: a) $0.58\text{\AA}$, b) $0.72\text{\AA}$, c) $0.91\text{\AA}$, respectively. As discussed in the text, for a wide range of tunneling parameters, the observed images of an individual molecule did not change qualitatively.
3. Topographic displays of STM images of two $20\text{\AA} \times 20\text{\AA}$ 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. Note that as one looks from the center of each molecule along the direction of the lobes onto the surrounding metal, there are depressions in the image of this part of the metal surface. The images were recorded with: a) $V_{\text{bias}} = -0.050\text{V}$, $I_{\text{tunnel}} = 100\text{ pA}$, and b) $V_{\text{bias}} = +0.010\text{V}$, $I_{\text{tunnel}} = 100\text{ pA}$, respectively.





Altitude
0.70A



Altitude
0.66A
0.05A

