

Analysis of Adsorption Sites of Benzene Molecules on the Pd(110) Surface Through Calculations of STM Images

Gabin Treboux^{*,†,‡} and Masakazu Aono^{†,‡}

Department of Precision Science and Technology, Osaka University, Suita, Osaka 565, Japan, and The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351, Japan

Received: November 8, 1996; In Final Form: February 19, 1997[⊗]

Use of scanning tunneling microscopy (STM) to determine the adsorption sites of molecules on a metallic surface with accuracy has become a powerful technique. As an example, we demonstrate, using elastic scattering quantum chemistry calculations, that STM images of benzene molecules adsorbed on a palladium-(110) surface exhibit strong internal structures. We demonstrate that each possible high-symmetry adsorption site as well as the molecular orientation with respect to the surface plane can be resolved using STM imaging.

1. Introduction

The interaction of molecules with surfaces is relevant in many different fields, most notably in catalysis where the overall reaction rate is strongly dependent on the adsorption, diffusion, and dissociation properties of molecules. Knowledge of the detailed atomic geometry of the molecule on the surface is a necessary prerequisite. Scanning tunneling microscopy (STM) has been proven to be a very powerful tool for atomic resolution imaging of surfaces. Recently, there has been special interest in the capability of STM to provide images of molecules adsorbed on a conducting surface. Benzene was the first adsorbate imaged using STM which appeared to show an internal structure.¹ More recently, it was demonstrated that the appearance of a benzene molecule, as imaged using STM, can vary dramatically according to the binding site of the molecule.² However, interpretation of the experimental STM images is complicated because these data are governed by local variation in the electronic structure of the surface interacting with the adsorbed molecule instead of being a direct map of a location of atomic nuclei. Nonetheless, some groups developed advanced algorithms,^{3,4} which reproduce the experimental STM images with high accuracy. These algorithms are powerful tools for translating the experimental data in terms of atomic nuclei positions. Moreover, they permit elucidation of the electronic processes involved in STM imaging.^{5,6} In the special case of the benzene molecule adsorbed on various substrates, it was clearly shown that the elastic scattering quantum chemistry (ESQC) algorithm is able to differentiate between specific adsorption sites as well as to elucidate the molecular patterns.^{7,8}

Theoretical prediction of the adsorption site of benzene on various surfaces through potential energy surfaces (PES) calculations remains dubious due to drastic approximations used in the current models. Even if careful studies are performed,⁹ neglect of electron correlation in such models cannot permit us to be confident of the accuracy of the results. It seems then that, instead of a direct calculation of the PES, the theoretical calculation of STM images may be a promising method for predicting, by comparing experimental and theoretical images, the binding sites of molecules on surfaces. Nonetheless, the surface orientation is a key parameter which governs the appearance of the STM images. Instead of the symmetry of the molecule, the STM pattern follows the symmetry of the

substrate, so that for instance the benzene on the (111) surface is resolved as a 3-fold pattern. In this paper, we studied the case of the (110) orientation of a fcc transition metal. As a benchmark, we investigated the case of a benzene molecule on a Pd(110) surface from ESQC package calculations and demonstrated that the STM experiment can be used as a method to determine the adsorption site as well as the orientation of the molecule.

2. Atomic Model Presentation

In all the calculations presented here, the Pd(110) surface is described by two layers each containing 16 atoms with its known crystal geometry. This surface has a C_{2v} symmetry with the two substrate mirror planes in the [001] and $[1\bar{1}0]$ directions. The bulk of the palladium substrate is described by a periodic continuation of these two layers. For the tip wire, the same two-layer unit cell as used for the substrate has been selected. The tip apex is represented by four palladium atoms arranged in a pyramidal way. The base of the pyramid is then constituted by three atoms instead of one for the end of tip. The orbital description of each palladium atom is a set of (4d, 5s, 5p) where the d orbitals are of the double-zeta description. At the end of the tip apex, a diffuse d orbital is added in order to fit the experimental corrugation obtained on the palladium(110) clean surface. The whole model for the clean surface gives an $I = f(z)$ characterized by a slope of one order of magnitude per Angstrom. The different parameters needed for extended Hückel molecular orbitals calculations were taken from ref 10 for the palladium atom and from ref 11 for the benzene molecule.

The palladium parameters given in ref 10 were optimized for molecular species and lead to an unphysical gap for the palladium crystal. Then energetic atomic level parameters were changed by shifting the d and s levels in order to reproduce the overall shape of the density of states (DOS) of palladium calculated under local density approximation (LDA) formalism reported in ref 12. We can compare this overall shape with that shown in Figure 1, where we plotted the number of channels in the scattering matrix calculation included in the ESQC algorithm as a function of their corresponding energy. In the calculated DOS reported in ref 12, the Fermi level is 0.06 eV above a dominant peak in the DOS and is followed by a characteristic small peak at 0.26 eV above the Fermi level, followed by a very low and flat area. These features are apparent in Figure 1 and permit us to define the position of the

[†] Osaka University.

[‡] The Institute of Physical and Chemical Research (RIKEN).

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

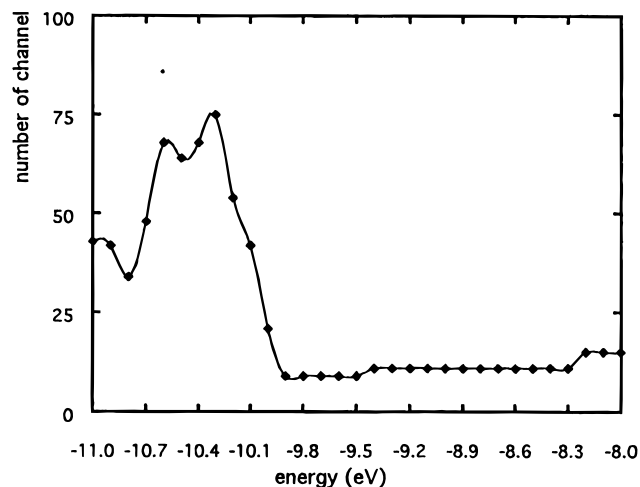


Figure 1. Number of channels which contribute to the tunneling current as a function of the energy band level.

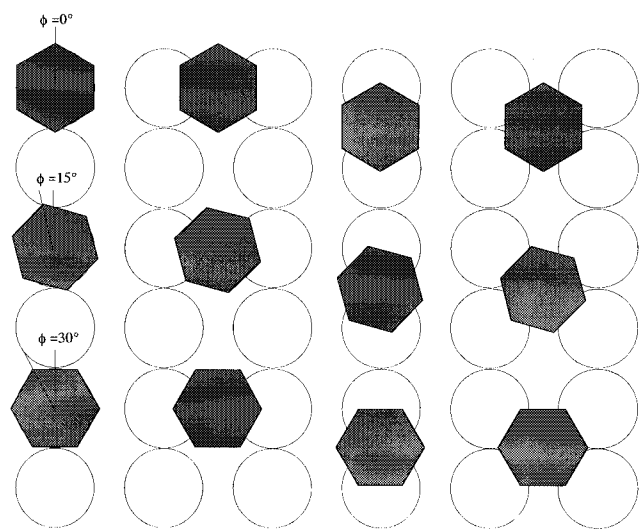


Figure 2. Different possible adsorption sites of a benzene molecule on a Pd(110) surface. The positions are labeled in the text following a matrix arrangement (1a ... 1d/ 2a ... 2d/ 3a ... 3d) from the left upper position. The polar angle θ is fixed at 0° for all the positions while the azimuthal angle ϕ is set to 0° (top), 15° (middle), and 30° (bottom), respectively.

Fermi level in the ESQC calculation. Nonetheless, we do not expect more than a qualitative description of the palladium surface in this study because it is clear that relativistic effects, for instance, which are known to be important for palladium, cannot be taken into consideration in the present model. Throughout the calculations we selected $I = 1$ nA for the tunneling current and $V = -10$ mV for the sample voltage parameters, which correspond to typical experimental conditions.

3. Adsorption Sites

For this system, four adsorption sites can be defined: top (Figure 2, column a), long bridge (Figure 2, column b), short bridge (Figure 2, column c), and hollow 4 (Figure 2, column d) sites. Several parameters must be added to accurately define the adsorption site such as the distance d between the center of mass of the molecule and the surface plane and the tilt angle θ and the rotation angle ϕ of the benzene plane from the surface plane. For a given adsorption site, each of these geometrical parameters may change the STM image. For instance, we calculated for each site a series of images by fixing d at 2.1 Å and θ at 0° while changing the rotation angle ϕ to 0, 15, and

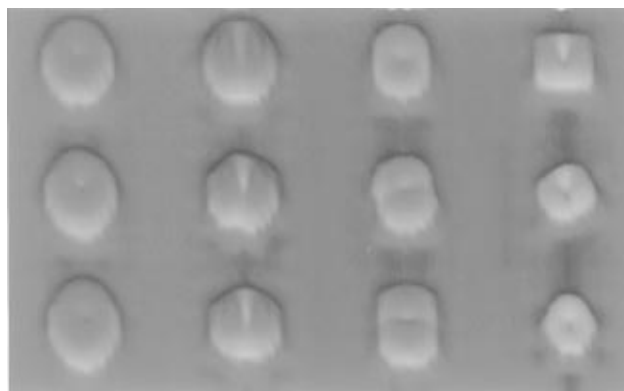


Figure 3. $19.45 \text{ Å} \times 13.75 \text{ Å}$ calculated topographic STM images (bias, 10 mV; current, 1 nA) of benzene molecules at different possible adsorption sites on a Pd (110) surface. The corresponding 12 orientations are classified according to the order defined in Figure 2. The z range is $[5.3-6.6] \text{ Å}$ from red to dark green. The average z value on the bare surface region (from the tip apex to the Pd surface) is 5.45 Å .

30° , respectively. The 12 possibilities are defined in Figure 2, and the corresponding calculated STM images are reported in the same order in Figure 3.

3.1. Low Coverage Case. A limited number of studies exist on the adsorption geometry of benzene on fcc transition metal surfaces with a (110) orientation. An analysis of the angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) experiments for the low coverage of benzene on Ni(110)¹³ was reported in which the authors concluded that the benzene molecules are adsorbed with their molecular planes parallel to the surface and the corners oriented along the [001] direction ($\theta = 0^\circ$, $\phi = 30^\circ$). The mirror planes of the molecule coincide with the [110] and [001] directions of the substrate. The symmetry of the adsorption complex is therefore C_{2v} . Nonetheless, it must be recalled that no conclusions regarding the adsorption site can be derived so that all the positions, 3a–d in Figure 2, are compatible with this result. The same value for $\phi = 30^\circ$ was obtained from time-of-flight scattering and recoiling spectroscopy measurements¹⁴ as well as from semiempirical calculations.⁹ If the same trend is obtained for benzene on Pd(110), then our calculations predict that an STM study will be able to distinguish between the four sites. The images of molecules at the top site are predicted to be volcano shaped (see Figure 3, position 3a), the long bridge site appears as a two-lobed structure with a depression in the [110] direction (see Figure 3, position 3b), as opposed to a two-lobed structure with a depression in the [100] direction for the short bridge site (see Figure 3, position 3c). The hollow 4 site can undoubtedly be characterized by the trough ($\sim 0.15 \text{ Å}$ deep) in the [110] direction, induced on the surface state (see Figure 3, position 3d, where the depression appears in red), as well as by its rather small size. This last characteristic is not particular to such a surface and has already been found for benzene on the Pt(111) surface.⁸ This was rationalized through the interference between the through space coupling between the tip and surface metal atoms and the through molecule coupling. This interference is constructive in the center of the molecule, while it is destructive in the outer region.⁸

Depending on the orientation of the benzene, the overlap between the benzene orbital of E symmetry and the atomic orbital of the palladium atoms varies. This overlapping leads to a preponderance of one of the E levels in the corresponding image. This phenomenon governs the node properties depicted for each site. It must be noted that changing the Fermi level to deeper energy modifies the appearance of all the images in the same way, i.e., by increasing the tunneling current in the middle

of the benzene ring. Such a phenomenon is due to the increasing role of the A_1 orbital of the benzene. In summary, we can predict that an STM image will be able to determine without doubt the adsorption site of the benzene on the Pd(110) surface.

3.2. Full Coverage Case. In the case of full coverage adsorption of benzene on palladium and on nickel(110) surfaces, it was reported that the molecules are arranged in a densely packed $c(4 \times 2)$ structure.^{15,13} On the basis of ARUPS measurement results, it was proposed that the benzene on the palladium-(110) surface is azimuthally oriented with corners along the $[1\bar{1}0]$ direction and tilted to the $[001]$ direction with an inclination angle of the order $10\text{--}20^\circ$.¹⁵ The proposed interpretation is that this tilt is induced by the lateral interaction in this densely packed layer. It is possible to test such a hypothesis by shrinking the substrate mesh by 10% in moving from palladium to nickel in order to increase the molecular strain to see whether this would produce a significantly tilted molecule in the monolayer. Using near-edge X-ray adsorption fine structure measurements, the same authors showed that it is not induced by the lateral interaction.¹⁶ In ref 13, where the full coverage benzene case in Ni(110) was studied, it was reported that the molecules are adsorbed with their molecular planes parallel to the surface. This strong lateral interaction is reported to induce instead an azimuthal rotation of the molecule so that the substrate mirror planes do not coincide with the mirror planes of the molecule.

From a densely packed $c(4 \times 2)$ monolayer of benzene on Pd(110), the STM image appears as a two-lobed pattern separated by a depression, each lobe of the pattern being similar. This depression direction does not coincide with the $[001]$ direction or the $[1\bar{1}0]$ direction.¹⁷

A tilting distortion (variation of θ) cannot explain the existence of the two equivalent lobes. On the other hand, we report here that azimuthal rotation from the highest symmetry positions (variation of ϕ) leads, for the short bridge site (see Figure 3, position 2c) as well as the hollow 4 site (see Figure 3, position 2d), to a two-lobed pattern where the depression does not correspond to the $[001]$ or the $[1\bar{1}0]$ direction. This pattern is not obtained from the top (see Figure 3, position 2a) and long bridge sites (see Figure 3, position 2b).

4. Conclusion

It was reported that the adsorption site of a benzene molecule on a (111)-oriented platinum surface can be determined from

its STM image.^{2,8} In this article we propose that such a technique can be used to determine adsorption sites for other orientations. As a benchmark, we investigate, at low coverage, the case of benzene molecules on a Pd(110) surface from ESQC package calculations which show specific patterns according to the bending site of the molecule.

Concerning the full coverage case, the calculation shows that only the hollow 4 and short bridge adsorption sites are compatible with the experimental STM images. Moreover, it is proposed, by comparing the experimental result and the theoretical STM images, that in the densely packed $c(4 \times 2)$ monolayer of benzene on Pd(110) the molecules are still adsorbed with their molecular planes parallel to the surface and that azimuthal rotation from the highest symmetry positions occurs.

Acknowledgment. We thank Dr. J. Yoshinobu and Dr. M. Kawai for the communication of results prior to publication and Dr. C. Joachim for providing the program used in the present study as well as for fruitful discussions. We are grateful to the Computational Center at RIKEN, where the calculations were performed.

References and Notes

- (1) Ohtani, H.; Wilson, R. J.; Chiang, S.; Mate, C. M. *Phys. Rev. Lett.* **1988**, *60*, 2398.
- (2) Weiss, P. S.; Eigler, D. M. *Phys. Rev. Lett.* **1993**, *71*, 3139.
- (3) Sautet, P.; Joachim, C. *Chem. Phys. Lett.* **1988**, *153*, 511; *Chem. Phys.* **1989**, *135*, 99.
- (4) Tsukada, M.; Shima, N. *J. Phys. Soc. Jpn.* **1987**, *56*, 2875.
- (5) Sautet, P.; Joachim, C. *Surf. Sci.* **1992**, *271*, 387.
- (6) Sautet, P.; Dunphy, J.; Ogletree, D. F.; Salmeron, M. *Surf. Sci.* **1993**, *295*, 347.
- (7) Sautet, P.; Joachim, C. *Chem. Phys. Lett.* **1991**, *185*, 23.
- (8) Sautet, P.; Bocquet, M. L. *Surf. Sci. Lett.* **1994**, *304*, L445.
- (9) Grimm, F. A.; Huntley, D. R. *J. Phys. Chem.* **1993**, *97*, 3800.
- (10) Basch, H.; Viste, A.; Gray, H. B. *Theor. Chim. Acta* **1965**, *3*, 458.
- (11) Hoffmann, R. J. *Chem. Phys.* **1963**, *39*, 1397.
- (12) Chen, H.; Brenner, N. E.; Callaway, J. *Phys. Rev. B* **1989**, *40*, 1443.
- (13) Huber, W.; Weinelt, M.; Zebisch, P.; Steinruck, H.-P. *Surf. Sci.* **1991**, *253*, 72.
- (14) Bu, H.; Bertrand, P.; Rabalais, J. W. *J. Chem. Phys.* **1993**, *98*, 5855.
- (15) Netzer, F. P.; Rangelov, G.; Rosina, G.; Saalfeld, H. B.; Neumann, M.; Lloyd, D. R. *Phys. Rev. B* **1988**, *37*, 10399.
- (16) Ramsey, M. G.; Steinmuller, D.; Netzer, F. P.; Schedel, T.; Santaniello, A.; Lloyd, D. R. *Surf. Sci.* **1991**, *251/252*, 979.
- (17) Yoshinobu, J.; Kawai, M. Personal communication.