

Scanning tunneling microscopy study of the molecular arrangement of *meta*- and *para*-xylene on Pd(111)

D. N. Futaba, J. P. Landry, A. Loui,^{a)} and S. Chiang^{b)}
Department of Physics, University of California, Davis, California 95616

(Received 9 October 2000; accepted 26 February 2001)

We have performed an experimental study of *meta*- and *para*-xylene isomers, C₆H₄(CH₃)₂, adsorbed on Pd(111). Using scanning tunneling microscopy we imaged the characteristic surface structures and investigated the molecular ordering for *meta*- and *para*-xylene. A triangular shape characterized the *meta*-xylene, and the *para*-xylene showed a distinctive diamond shape. Both isomers showed some propensity to order and a correlation between azimuthal orientation and the close-packed directions of the metal. © 2001 American Vacuum Society.
[DOI: 10.1116/1.1366698]

I. INTRODUCTION

The adsorption of aromatic hydrocarbons on transition metal surfaces is an interesting problem in surface science. By determining the adsorbate structure of hydrocarbons, we can gain a better understanding of the molecule–substrate interaction, which is the microscopic foundation for adhesion and lubrication. Benzene is a model aromatic hydrocarbon and has been widely studied in adsorption.^{1,2} However, the adsorption of dimethyl-substituted benzene molecules on metal surfaces has not been as well investigated.^{3–5}

We used scanning tunneling microscopy (STM) to obtain the highly detailed molecular structure of xylene isomers on a Pd(111) surface. Figure 1 is a schematic diagram of the two xylene isomers in this study.

II. EXPERIMENT

We performed room temperature STM studies of the adsorption properties of xylene isomers on Pd(111) using an Oxford Instruments ultrahigh vacuum (UHV) variable temperature STM. The Pd(111) single crystal was cleaned under UHV conditions by repeated argon ion sputtering and annealing cycles. After verifying the cleanliness of the sample using x-ray photoelectron spectroscopy and STM, the chamber was backfilled using a variable leak valve with 99+% purity *meta*- and *para*-xylene. The xylene was purified by direct pumping for 5–10 min and its purity verified using a residual gas analyzer. Because of the difference in vapor pressure at room temperature between xylene and benzene, an observed principal contaminant, freezing was not necessary.

III. RESULTS AND DISCUSSION

A. *Meta*-xylene

STM images of *meta*-xylene exhibited a distinctive three-fold symmetric shape. Intensity profiles on highly resolved images revealed that two corners were approximately 0.15 Å higher than the third. In addition, a slight indentation was observed separating the two similar taller corner features.

These two features suggest the locations of the methyl groups [Fig. 2(b)]. Peak-to-peak dimensions between the methyl groups were measured for a variety of images and averaged ~4.5 Å.

At full coverage, a weak 3×3 pattern was observed by low energy electron diffraction (LEED). STM images revealed isolated ordered domains consisting of approximately 30 molecules. As seen in Fig. 2(a), the *meta*-xylene molecules appear to be not only disordered but randomly oriented as well. Upon closer inspection, however, we are able to determine the directionality of the molecules by resolving the subtle indentation on one side of the molecules [Fig. 2(b)]. Though height profiles were limited by the resolution, we suspect this indentation to be the node between the two methyl groups. We found that the molecules oriented in one of three distinct directions, which are approximately 120° with respect to each other.

We suspect that the observed weak LEED pattern is a product of small ordered domains. We rule out the possibility that the apparent disorder is a result of the random orientations of the molecules from the following examination. Given the locations of the indentations and the assumption that the xylene chemisorbs through the phenyl group, we generated a pattern by marking the suspected locations of each phenyl group. The ensuing pattern showed no periodicity.

Molecules which adsorbed along step edges parallel to the close-packed directions were found to align with one side parallel to the step [Fig. 3(a)]. Since the resolution was not sufficient to detect the indentation on the molecule, we could not make a complete determination of the relationship be-

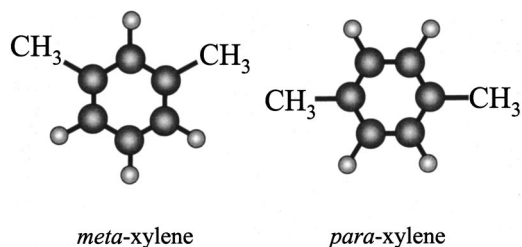


Fig. 1. Schematic diagrams of *meta*- and *para*-xylene.

^{a)}Electronic mail: aloui@landau.ucdavis.edu

^{b)}Corresponding author; electronic mail: chiang@physics.ucdavis.edu

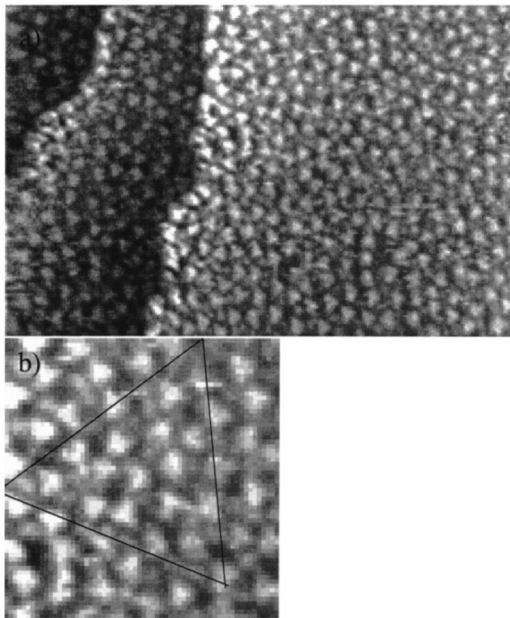


FIG. 2. $270 \times 160 \text{ \AA}$ unoccupied states STM image of *meta*-xylene molecules. An overlay is drawn to indicate molecular orientations. (inset) Enlargement showing the indentation on one side of the molecule which provides directionality information. Tunneling conditions: $I_{\text{tun}} = 1.0 \text{ nA}$ and $V_{\text{bias}} = 100 \text{ mV}$.

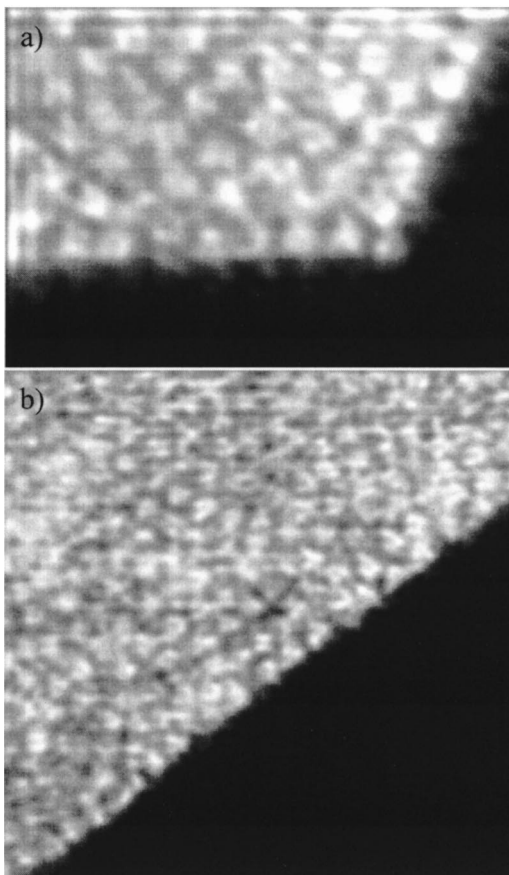


FIG. 3. (a) $170 \times 140 \text{ \AA}$ STM image showing preferential ordering at the upper terrace of close-packed step edges. (b) $210 \times 210 \text{ \AA}$ STM image also showing preferential ordering at the upper terrace of close-packed step edges. Gray scale was chosen to enhance the contrast of the molecules on the upper step. Tunneling conditions: $I_{\text{tun}} = 1.0 \text{ nA}$ and $V_{\text{bias}} = 100 \text{ mV}$.

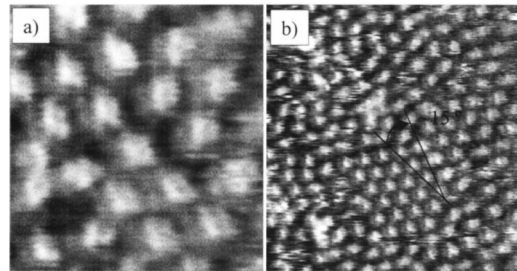


FIG. 4. (a) $42 \times 42 \text{ \AA}$ STM image showing the ordering and molecular shape of *para*-xylene. (b) $120 \times 120 \text{ \AA}$ STM image showing the ordering and the molecular alignment of *para*-xylene. The 15° offset angle between the direction of the molecules and the close-packed direction of the overlayer structure is indicated in the image. Tunneling conditions: $I_{\text{tun}} = 0.1 \text{ nA}$ and $V_{\text{bias}} = 100 \text{ mV}$.

tween the molecule orientation and the direction of the steps in the close-packed direction. Measurements showed a uniform spacing of about 8.2 \AA , which corresponds to three nearest-neighbor lattice spacings of the metal substrate. Moreover, a hexagonal 3×3 ordering propagated from the closed-packed steps onto the terrace, which continued laterally for about 3–5 molecules before growing increasingly disordered [Fig. 3(b)]. A small fraction of the *meta*-xylene molecules adsorbed onto close-packed steps were oriented with a corner protruding from the step edge. These molecules extended slightly further out from the step edge than the other orientation [Fig. 3(b)].

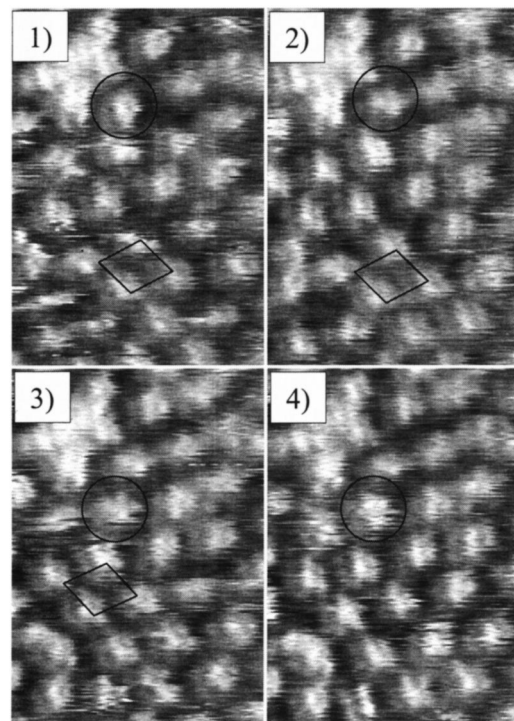


FIG. 5. Sequence of $42 \times 60 \text{ \AA}$ images showing molecular movement of *para*-xylene. Acquisition time for each image scan was 13 s. Both a rotation (circle) and a rotation and translation (diamond) are illustrated as indicated in the figure. Tunneling conditions: $I_{\text{tun}} = 0.1 \text{ nA}$ and $V_{\text{bias}} = 100 \text{ mV}$.

B. *Para*-xylene

Para-xylene exhibited a distinctive diamond shape [Fig. 4(a)]. Higher resolution images of the *para*-xylene molecules showed some intramolecular structure of the adsorbed phenyl group on the Pd(111) surface (Fig. 4). The methyl groups appeared as single lobe protrusions from the phenyl group.

The symmetry of the molecule allowed for easy visual identification of an overlayer pattern. STM images showed that *para*-xylene ordering was much more prevalent than that for *meta*-xylene [Fig. 4(b)]. The hexagonal overlayer unit cell measured 9.35 ± 0.38 Å, which suggests a $2\sqrt{3} \times 2\sqrt{3}$ R30° structure. This agreed with previously observed ordering of *para*-xylene on Rh(111).⁴ Peak-to-peak dimensions between methyl groups were measured to be ~ 5.2 Å. Three domains, each separated by 60°, were observed. In the ordered domains, the molecules were aligned parallel to each other and at 15° with respect to the overlayer close-packed direction. Cernota *et al.*⁴ observed *para*-xylene molecules that formed angles of 30° with respect to the close-packed directions on Rh(111), but unfortunately, no observations of close-packed steps were observed.

Furthermore, as indicated in Fig. 5, *para*-xylene molecules were observed to be mobile both in ordered and disordered regions. This motion occurred on a time scale of less than 13 s, which was the time required to acquire a single image. Translation and rotation of the molecular orientations to directions 60° apart were observed.

IV. CONCLUSIONS

We used STM to image *meta*- and *para*-xylene isomers, $C_6H_4(CH_3)_2$, adsorbed on Pd(111). *Meta*- and *para*-xylene each exhibited a characteristic surface structure. A triangular shape best described the molecular shape of the *meta*-xylene molecule. The *para*-xylene showed a distinctive diamond shape. Both isomers showed some propensity to order, with correlations between their azimuthal orientation and the close-packed directions of the metal.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-95-20366 and by the Campus Laboratory Collaborations Program of the University of California. An acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society for partial support of this research.

¹P. Sautet and M.-L. Bocquet, Phys. Rev. B **53**, 4910 (1996).

²P. S. Weiss and D. M. Eigler, Phys. Rev. Lett. **71**, 3139 (1993).

³D. E. Wilk, C. D. Stanners, Y. R. Shen, and G. A. Somorjai, Surf. Sci. **280**, 298 (1993).

⁴P. D. Cernota, H. A. Yoon, M. Salmeron, and G. A. Somorjai, Surf. Sci. **415**, 351 (1998).

⁵D. N. Futaba and S. Chiang, Surf. Sci. **448**, L175 (1999).