

Experimental and theoretical STM imaging of xylene isomers on Pd(111)

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We have performed a theoretical and experimental study of the three isomers of xylene, $C_6H_4(CH_3)_2$, adsorbed on Pd(111). Using scanning tunneling microscopy (STM), we imaged the characteristic surface structures and investigated the molecular ordering for *meta*-, *para*-, and *ortho*-xylene adsorbed on Pd(111). We used extended Hückel theory to predict the characteristic features of individual xylene molecules and to perform binding energy calculations for the preferred molecular orientations. STM observations of the surface features showed good agreement with the predictions, and the binding energy preferences correlated well with experiment.

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I. INTRODUCTION

Understanding the adsorption of hydrocarbons on transition-metal surfaces is an important and interesting problem in surface science. By determining the adsorbate structure of a hydrocarbon, we can gain a better understanding of the molecule-substrate interaction, which is the microscopic foundation for adhesion and lubrication.

Aromatic molecules represent an important class of hydrocarbons. Benzene has been widely studied in adsorption^{1,2} as a model aromatic hydrocarbon. However, the adsorption of dimethyl-substituted benzene molecules on metal surfaces has not been as well investigated.^{3–5}

The scanning tunneling microscope (STM) affords the ability to obtain a highly detailed molecular structure of molecular adsorbates on a metal surface. In conjunction with a relatively simple computational method, based on extended Hückel molecular orbital theory (EHT), comparisons are made with predicted images showing the distinguishing surface features of organic adsorbates. In addition, by examining the calculated binding energies and energetic preferences, speculation regarding the adsorption sites of the individual molecules is made.^{6–9}

We performed these calculations for the three isomers of xylene in *meta*-, *para*-, and *ortho*-configurations. We generated images both for isolated molecules and for molecules chemisorbed onto single-layer Pd(111) clusters consisting of 20–35 atoms. Figure 1 shows schematic diagrams of the three isomers of xylene.

II. EXPERIMENT

We performed room-temperature STM and low-energy electron diffraction (LEED) studies of xylene isomers adsorbed on Pd(111) using an Oxford Instruments Tops-3 ultrahigh-vacuum (UHV) variable-temperature STM. The Pd(111) single crystal was cleaned under UHV conditions by repeated argon-ion sputtering (1.2 kV, $\sim 2.5 \mu A$) and annealing cycles ($\sim 900^\circ C$ for 5 min). After verifying the cleanliness of the sample by x-ray photoelectron spectroscopy (XPS) and STM, the chamber was backfilled with 99+%-purity xylene using a variable-leak valve. The xylene was purified by direct pumping for 5–10 min and its purity veri-

fied using a quadrupole mass spectrometer. Because of the significant difference in the room-temperature vapor pressures of xylene and benzene, an observed principal contaminant, freezing was not necessary.

Exposure was incrementally increased from 0.3 to 3 Langmuir (L) where we observed full monolayer coverage.

A. *Meta*-xylene

Experimental images of the *meta*-xylene molecules showed a distinctive threefold symmetric shape [Fig. 2(a)]. Intensity profiles on more highly resolved images [Fig. 2(b)] revealed that two corners were approximately $0.15 \text{ \AA}$ higher than the third. In addition, an apparent minimum was observed separating the two apparently taller corner features, suggesting the locations of the methyl groups. Peak-to-peak dimensions between the methyl groups were taken for a variety of images and averaged approximately $4.5 \text{ \AA}$.

Though incremental increases in the exposure of *meta*-xylene were performed, individual molecules were too difficult to image at subsaturation coverages. We suspect this difficulty arose from the mobility of the molecule on the metal surface at room temperature.

Molecules adsorbed along step edges parallel to the substrate close-packed direction (110) were observed to align with one edge parallel to the step [Fig. 3(a)]. Measurements showed a uniform spacing of about $8.2 \text{ \AA}$, which corresponds to three nearest-neighbor lattice spacings of the metal substrate. Moreover, LEED revealed a weak 3×3 ordering. STM images revealed a hexagonal 3×3 ordering propagated from the close-packed steps into the terrace, which continued for about three to five rows inward from the step before growing increasingly disordered [Fig. 3(b)]. A small fraction of the *meta*-xylene molecules adsorbed onto close-packed

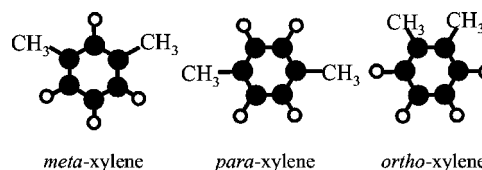


FIG. 1. Schematic drawings of the three xylene isomers. Large (small) circles indicate C(H) atoms.

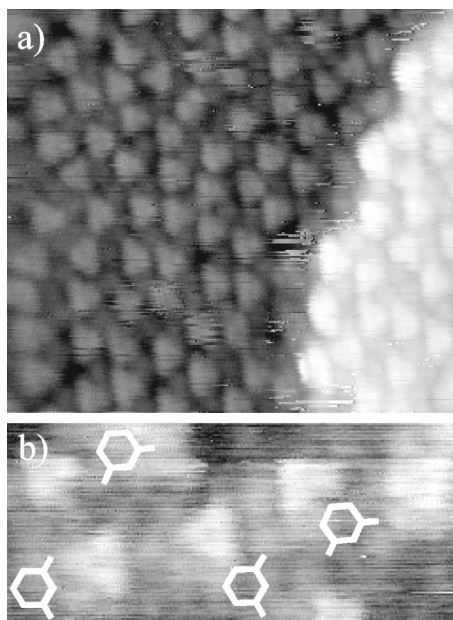


FIG. 2. (a) $100 \text{ Å} \times 100 \text{ Å}$ image showing the distinctive triangular surface features of *meta*-xylene. (b) A close-up image of individual *meta*-xylene molecules exhibiting the two lobes of the methyl groups. Included are suggestions of the molecule orientation based on height profiles.

steps were oriented with a corner protruding from the step edge and extended slightly further out than the other orientation [Fig. 3(b)]. Images with sufficiently high resolution to ascertain the directionality of the molecule were taken. In addition, isolated ordered domains were also observed away from the step edges [Fig. 3(c)].

The measured number density was found to be $0.0125 \text{ molecules/Å}^2$. Approximating the molecule using the van der Waals radii, the number density for a closed-packed configuration is $0.012 \text{ molecules/Å}^2$.

B. Para-xylene

Para-xylene showed a higher propensity for ordering than *meta*-xylene [Fig. 4(a)]. Ordered domains were approximately 50 Å wide on average. The hexagonal overlayer unit cell measured $9.35 \text{ Å} \pm 0.38 \text{ Å}$. With a Pd metal substrate nearest-neighbor spacing of $\sim 2.75 \text{ Å}$, the overlayer spacing suggested a $2\sqrt{3} \times 2\sqrt{3} R30^\circ$ structure, agreeing with the previously observed ordering of *para*-xylene on Rh(111).⁴ Three domains, each separated by 120° , were observed in our study. Closer observation showed a distinctive diamond shape [Fig. 4(b)]. Higher-resolution images of the *para*-xylene molecules show some intramolecular structure of the adsorbed phenyl group on the Pd(111) surface. The methyl groups appeared as single-lobe features while the phenyl group consisted of a pair of lobes with a definite node separating them along the axis of the molecule. In the ordered domains, the molecules were aligned parallel to each other and at $15^\circ \pm 5.2^\circ$ with respect to the overlayer close-packed direction (Fig. 5). Upon closer examination, the molecules were seen to exhibit a height asymmetry along their long

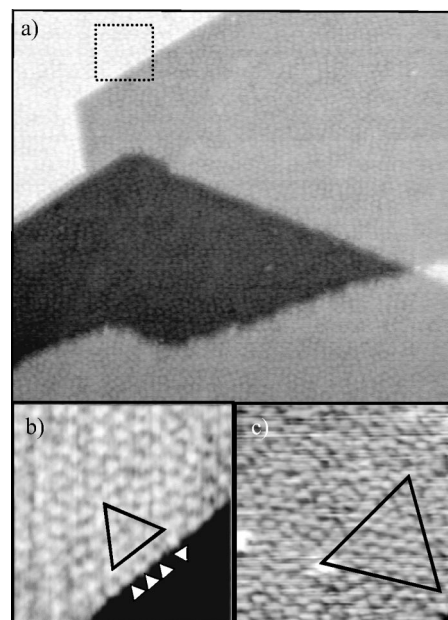


FIG. 3. (a) $500 \text{ Å} \times 500 \text{ Å}$ STM image showing preferential ordering at upper terrace of close-packed step edges. (b) $80 \text{ Å} \times 80 \text{ Å}$ close-up image showing the subsequent 3×3 ordering beginning from the step. Note the molecule oriented at 180° with respect to its neighbors, breaking the alignment along the step edge and thus into the terrace. Included are models to further clarify the orientations of the molecules. (c) $100 \text{ Å} \times 100 \text{ Å}$ image of an isolated 3×3 ordered domain found on the terrace.

axis, as shown in the line profile in Fig. 5 (inset). Peak-to-peak dimensions between methyl groups were measured to be $\sim 5.2 \text{ Å}$. Cernota *et al.*⁴ observed *para*-xylene molecules formed 30° angles with respect to the close-packed directions on Rh(111), but unfortunately, no observations of (110) steps were observed to make a definite correlation between molecular orientation and the structure of the Pd metal close-packed directions.

Furthermore, as shown in Fig. 6, *para*-xylene molecules were observed to be mobile in both ordered and disordered regions. This motion occurred on a time scale of less than 13 sec, which was the time required to acquire a single image. Translation and rotation of the molecular orientations between directions which are 60° apart was observed.

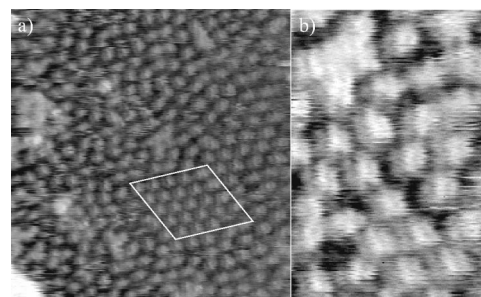


FIG. 4. (a) $170 \text{ Å} \times 170 \text{ Å}$ STM image showing the ordering of *para*-xylene molecules. (b) $66 \text{ Å} \times 47 \text{ Å}$ STM image showing the internal molecular detail of *para*-xylene.

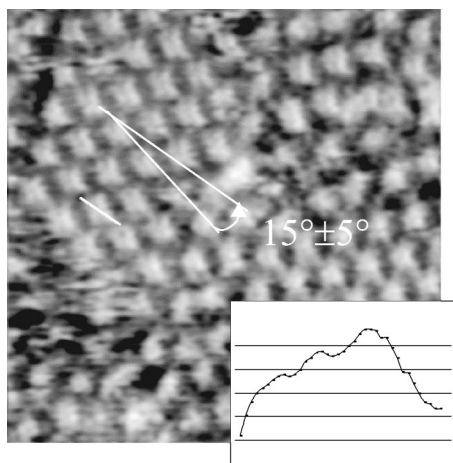


FIG. 5. $120 \text{ Å} \times 120 \text{ Å}$ high-resolution STM image demonstrating the asymmetry of the molecule as observed in ordered domains and the observed 15° offset angle. Inset: height profile of *para*-xylene along long axis showing asymmetry in methyl group height.

C. *Ortho*-xylene

When adsorbed on the palladium surface, *ortho*-xylene was relatively more difficult to image. The molecules exhibited no particularly unique surface features besides an overall ovoidal shape [Fig. 7(a)]. In addition, LEED observations showed no long-range ordering, but we did observe some short-range molecular arrangement. Groups of molecules on the order of 10 were observed to arrange in apparent hexagonal arrays with a spacing of $\sim 9.5 \text{ Å}$. Moreover, molecules appeared oriented parallel to one another.

We also observed domains of molecules arranged in periodic rhombuses [Fig. 7(b)]. The molecular spacing was measured to be $\sim 6.0 \text{ Å} \times 8.65 \text{ Å}$. Along both lateral directions, adjacent unit cells appear to be shifted by half of a unit cell and then repeated.

III. THEORETICAL METHOD

Though limited to aromatic molecules, a method for predicting STM images based on EHT has been successful in reproducing the detailed internal structures of such carbon-ring structures as naphthalene, azulene, monomethylazulene, dimethylazulene, and trimethylazulene on Pt(111).^{6,7} The EHT treatment of conjugated hydrocarbons is a semiempirical calculation, which combines linear combination of

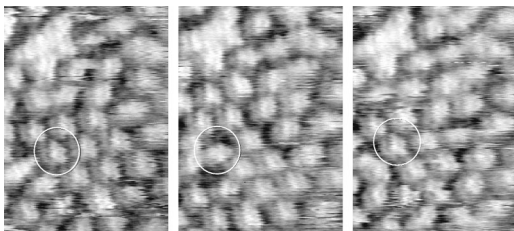


FIG. 6. A sequence of images showing molecular movement as indicated. Acquisition time for each image scan was 13 sec. Both a rotation and a rotation with translation are illustrated as indicated on the figure.

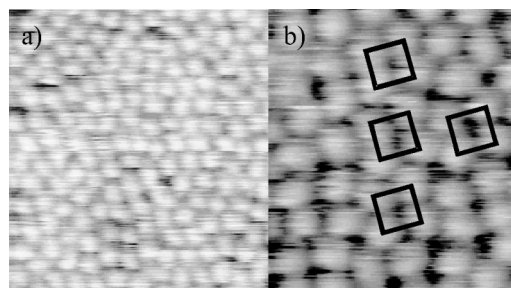


FIG. 7. (a) STM of *ortho*-xylene molecules showing 3×3 ordering. (b) Close-up STM image showing the short-range order of the apparent disordered regions.

atomic orbitals (LCAO), the variational method, and matrix mechanics. The total wave function is represented as a linear combination of Slater-type atomic orbitals of all the valence electrons in the system. By minimizing the total energy with respect to each coefficient, the contributions from the atomic orbitals to the complete molecular orbital(s) for an isolated molecule or for a molecule adsorbed onto a metal cluster are computed. No other energy minimization or molecular relaxation was performed. Hückel parameters for Pd are taken from the literature.^{10,11}

Binding energy calculations were performed for the three xylene isomers, each on the three high-symmetry binding sites (on-top, bridge, and threefold hollow) and for two molecular azimuthal orientations on each site. Although the binding energy showed dependence on the molecule-cluster separation, as for our calculations for xylene on Rh(111),⁵ the binding energy calculations for all isomers provided no information regarding preferences of molecule-cluster separation distance. We suspect that this site and orientation independence is a result of the substituted methyl groups (CH_3), as compared with previous studies of benzene on Pt(111) in which benzene exhibited a definite site dependence.^{1,2} We believe that the source of this problem may be the tendency for the methyl groups to tilt away from the molecular plane upon adsorption on a metal surface. This prompted us to perform the same type of calculations for all three binding sites for tilt angles of the methyl groups ranging from 20° to 40° . Unfortunately, these calculations were also inconclusive and failed to find energetic preferences of the molecule. We suspect that this effect on the binding energy calculation could be a direct result of assuming a rigid molecule and not including any relaxation of the molecule or substrate. Consequently, we used the molecule-cluster separation of 2 Å found in previous calculations for benzene on Pt and Pd (Ref. 9) and performed angle-dependent binding energy studies of the isomers for various binding sites.

Metal clusters were composed of a single layer of ~ 30 – 40 metal atoms. Calculations were performed using a three-layer metal cluster consisting of over 60 metal atoms, and while the absolute binding energy was different, the trends in the resultant binding energy curves were within several percent of those using a single layer. Therefore, all calculations for this study were performed using a single layer.

To test the accuracy of the binding energy calculations

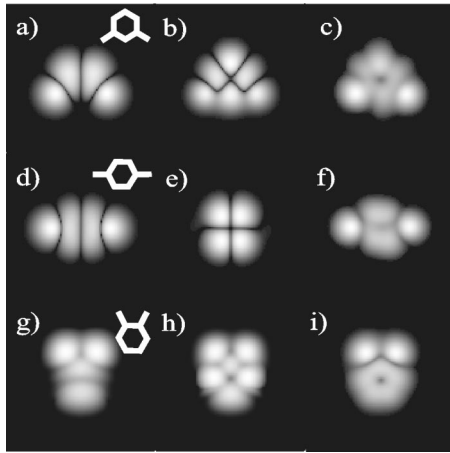


FIG. 8. Predicted images of each of the xylene isomers: (a) *meta*-xylene HOMO, (b) *meta*-xylene LUMO, (c) *meta*-xylene unoccupied states, (d) *para*-xylene HOMO, (e) *para*-xylene LUMO, (f) *para*-xylene unoccupied states, (g) *ortho*-xylene HOMO, (h) *ortho*-xylene LUMO, and (i) *ortho*-xylene unoccupied states.

using EHT, a similar calculation was made using the local density approximation of density functional theory with pseudopotentials.^{12,13} Using a plane-wave basis set cutoff of 12 Ry the self-consistent program was run until the energy was converged to within 10^{-6} Ry.¹⁴ We computed the binding energies for *para*-xylene on a hollow site¹⁵ and compared the result to the respective differences in the binding energies as calculated by EHT. Naturally, the absolute values of the binding energies for the individual orientations were different from each of the computational techniques, but the trends were found to be the same. We attribute the differences between the results to the application of EHT (tight-binding theory) to metal atoms. With the agreement with density functional theory, we are fairly confident in the numerical values calculated for this study by EHT.

A. *Meta*-xylene

The calculated image of the highest-occupied molecular orbital (HOMO) for isolated *meta*-xylene showed a distinct triangular shape with the carbon ring showing features of a benzene HOMO [Fig. 8(a)]. Similarly, the image for the lowest-unoccupied molecular orbital (LUMO) showed triangular symmetry with the character of the LUMO of benzene [Fig. 8(b)].

The calculated images of adsorbed *meta*-xylene on a Pd cluster were remarkably similar to the case on Rh.⁵ They are also distinguished by a triangular geometry [Fig. 8(c)]. More specifically, a depression is visible at the center of the carbon ring, and two of the corners have a higher intensity in the local density of states (LDOS), corresponding to taller features, than the third corner. These features are observed for both the occupied and unoccupied state images. Again, given the locations of these brighter features, they correspond to the electronic structure of the methyl groups.

Binding energy calculations for *meta*-xylene on terraces showed about a 1 eV preference for adsorption onto hollow or bridge sites over a top site. On hollow sites, calculations

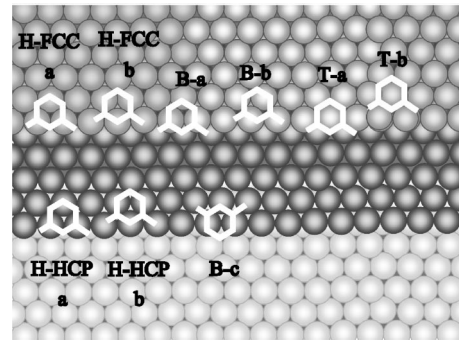


FIG. 9. Definitions of the various binding sites on upper step edges calculated for *meta*-xylene. H=hollow, T=top, and B=bridge.

showed that the molecule preferred to orient itself with its methyl groups parallel to the close-packed direction. On bridge sites, however, the calculations showed equal preferences for orienting the methyl groups both parallel and at 30° with respect to the close-packed direction. In both cases, the potential barriers were approximately 0.36 eV, and the minima sat within 0.25% of each other.

Calculations for sites on the (110) upper step edge were performed for four hollow sites (two fcc and two hcp), two top sites, and three bridge sites (Fig. 9). For the hollow and bridge site cases, the binding energies were found to be about 25% greater than those for the terrace sites. For top site *a*, the binding energy was about 55% smaller than its associated terrace value, while top site *b* was 16% smaller, suggesting that adsorption is not likely on top site *a*. In general, the greater binding energies associated with a binding site located near the step edges suggested that adsorption is preferred on the upper step edge on the other seven sites versus on the terrace.

Molecules on the hollow sites showed an energetic tendency to orient themselves with the methyl groups parallel to the step edge. Moreover, with a comparable binding energy and separated by a rotation barrier on the order of 10 eV, the molecules showed a preference between two orientations: methyl groups either move toward or away from the step edge. There was no significant difference between the fcc and hcp sites. Though the top-site-*a* adsorbed molecules showed a smaller binding energy than the top sites on the terrace, both top sites showed the same orientation preference for orienting the methyl groups parallel to the step edge in both orientations, as discussed with the hollow sites. The three bridge sites are described by Fig. 9. Calculations for bridge sites revealed a completely different trend than for the previous binding sites. The binding energy curve showed a preference for the molecule to sit oriented with the methyl groups parallel to all three close-packed directions. Though the binding energies are comparable to those found for the hollow site calculations, the rotation barriers of ~ 0.33 eV are significantly smaller.

B. *Para*-xylene

For *para*-xylene, the HOMO consisted of two lobed features from the methyl groups and a feature which resembles

one of the two degenerate HOMO's of the benzene molecule [Fig. 8(d)]. The LUMO showed no molecular features corresponding to the methyl groups and looked qualitatively identical to the LUMO of benzene [Fig. 8(e)].

With the addition of the palladium cluster, the hybridization of the molecular orbitals of *para*-xylene with the atomic orbitals of the Pd cluster accentuated the features seen in the HOMO [Fig. 8(f)]. In addition, images of both the occupied and unoccupied states have qualitatively identical features: a central ringlike feature and two distinct lobes located on opposite ends of the ring. From the location of these lobes, we conclude that they result from the methyl groups. Peak-to-peak distance between lobes was measured to be 6.2 Å in the calculated images.

Binding energy calculations for *para*-xylene on terraces showed about a 0.8 eV preference for adsorption onto hollow or bridge sites over top sites. Therefore, we do not expect significant adsorption on top sites. On hollow sites, the calculations showed preferences for the axis of the molecule to align itself approximately 22° from the palladium close-packed direction. Bridge sites showed a trend for the axis of the molecule to align either 90° or 30° from the close-packed direction [Fig. 10(b)].

C. *Ortho*-xylene

The calculated image of the HOMO for *ortho*-xylene showed the same characteristic bright lobe features resulting from the methyl groups and a benzenelike HOMO [Fig. 8(g)]. The calculated image for the *ortho*-xylene LUMO was also characterized by two lobes and a benzenelike LUMO [Fig. 8(h)].

The predicted images of *ortho*-xylene adsorbed onto a Pd cluster are characterized by a ring with a definite centered indentation and two bright adjacent lobes slightly separated from the central ring [Fig. 8(i)]. From the locations of these lobes, they result from the electronic structure of the methyl groups. Images of both the occupied and unoccupied states showed the same features.

As with *para*-xylene, calculated images including tilted methyl groups showed the same general shape as the ones without tilting. Thus we do not expect much difference in experimental images as a result of the tilt.

Binding energy calculations revealed a 0.8 eV preference for *ortho*-xylene adsorption on hollow and bridge sites over top sites. We therefore do not expect significant adsorption on top sites. On hollow sites, the *ortho*-xylene molecules showed a preference to not align the methyl groups within 15° of the close-packed direction of the metal surface. Though a rotation of $\pm 15^\circ$ about the (110) direction was allowed, we do not expect a greater rotation due to the presence of a 0.2 eV rotation barrier located midway between close-packed directions. For the bridge sites, the binding energy plots showed a definite preference for the molecules to align parallel to the close packed direction. These preferences are summarized in Fig. 10(c).

IV. DISCUSSION

Except for *ortho*-xylene, observed molecular features of the isomers agreed very well with predicted STM images

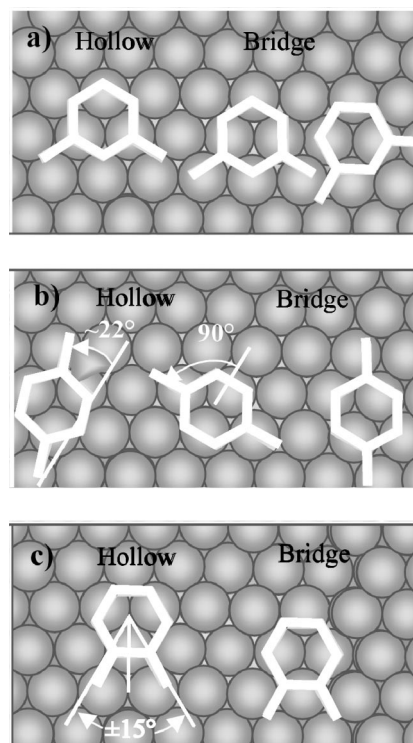


FIG. 10. Preferred orientations of xylene isomers on Pd(111) terraces from binding energy calculations. (a) On both the hollow and bridge sites, the *meta*-xylene molecules align with the methyl groups parallel to the close packed directions. On the bridge site it also prefers to sit at 30° with respect to the close-packed direction. (b) *Para*-xylene sits at 22° with respect to the Pd close-packed direction, while on bridge sites it prefers 90° and 30° from the metal close-packed direction. (c) *Ortho*-xylene molecules prefer to orient with the methyl groups parallel to the (110) direction. On hollow sites, however, the binding energy curves show that $\pm 15^\circ$ rotation about the preferred orientation is allowed.

based on Hückel calculations (Fig. 8). From the calculated images, the phenyl group displayed features similar to that of a benzene molecule adsorbed to Pt(111) or Pd(111).⁹

Calculations for *meta*-xylene on Pd(111) indicate that methyl groups as shown in Fig. 2(b) are located at the positions of the higher features with the observed node between them. The corresponding peak-to-peak distance between methyl groups on the calculated images was 6.0 Å. The difference from the observed 4.5 Å indicates that the *meta*-xylene exhibited significant tilting of the methyl groups upon adsorption onto the metal surface. Tilting is not unexpected because a methyl group is attached by only a C-C single bond.

On terraces, *meta*-xylene was observed to predominantly align with one side parallel to a close-packed direction. Although the STM images did not have sufficient resolution to distinguish the methyl groups, from the threefold symmetry of the molecules it can be deduced that if any one side is parallel to a close-packed direction, then the methyl groups will be as well. To a much lesser degree, *meta*-xylene was observed to be oriented 30° from the close-packed directions.

Although the specific binding site cannot be determined for molecules adsorbed along the upper step edge of close-packed oriented steps, we believe that the molecules are all

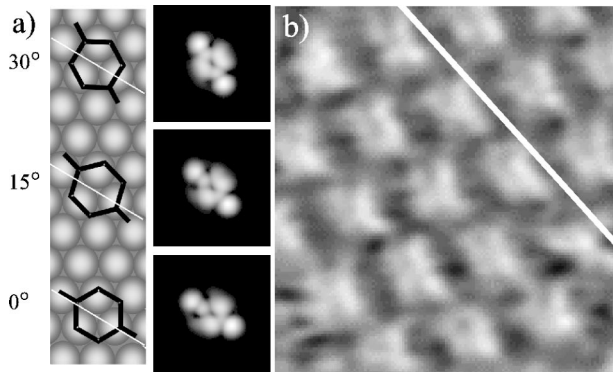


FIG. 11. (a) Schematic drawings illustrating the relative molecular orientation for *para*-xylene on the surface and associated calculated images, for decreasing angular difference between the molecular axis and the overlayer close-packed direction (denoted in white). As the angular difference decreases, the image displays an increasingly symmetric profile. (b) STM image of *para*-xylene molecules, with the overlayer close-packed direction denoted in white.

sitting in the same binding site because of the commensurate spacing along the step edge. Theoretically, preferences for each of the sites showed both an orientation toward and away from the step edge. This would explain the observation of “inverted” *meta*-xylene molecules at the step edge, but not the preponderance of the other orientation. For the hollow sites, we do not suspect that rotation is possible due to the large rotation barrier (~ 10 eV) calculated in the binding energy studies. Even for the bridge sites, the rotation barrier was calculated to be 0.33 eV, far larger than the thermal energy available at room temperature.

For *para*-xylene, energy calculations suggest that molecules adsorb on hollow sites at angles between 15° and 30° with respect to the substrate close-packed direction. An orientation of $\sim 22^\circ$ with respect to the metal close-packed direction is energetically favored, but the potential well is broad, allowing for free rotation between -22° and $+22^\circ$. However, no rotation of this sort was observed experimentally. The angular difference between the close-packed direction of the overlayer structure and the orientation of the *para*-xylene molecules was experimentally measured to be $15^\circ \pm 5.2^\circ$, which is consistent with the calculation.

As illustrated in Figure 11(a), images calculated for various orientations on the hollow site exhibit an increasing symmetric profile across the long axis of the molecule as the orientation decreases from 30° to 0° with respect to the close-packed direction of the overlayer (indicated by the white line). As observed with STM, intensity profiles showed an asymmetry along the axis of the molecule. This behavior agrees remarkably well with calculated images for the misaligned case on the hollow site. Therefore, this would suggest that *para*-xylene molecules arranged in ordered domains are located on hollow sites. This would also explain the difference in the measured peak-to-peak dimensions for the calculated image (6.2 Å) and the experimentally observed one (5.2 Å). Because of the symmetry difference between the binding site and molecule, one methyl group lies directly above a metal atom. Not only does this cause an increased electron density, but based on the reduced dimension, there

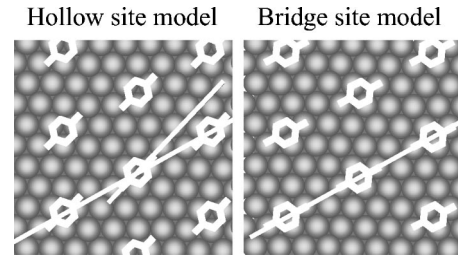


FIG. 12. Two possible models for *para*-xylene ordering on Pd(111). Based on binding energy calculations, the hollow site model exhibits a misalignment angle of $\sim 22^\circ$ with respect to the overlayer close-packed direction, while the bridge site model exhibits a misalignment angle of 0° . The latter case is not observed experimentally and therefore discounted.

must be significant tilting of that C-C bond.

From the binding energy calculations, both the hollow and bridge sites prefer a misalignment from the close-packed direction, but we discount the possibility for the ordered molecules being in bridge sites based on several points. First, from energy considerations for a single adsorbed molecule, both domains obtainable from bridge sites would have the molecules on bridge sites oriented parallel to the overlayer close-packed directions as shown in Fig. 12. This is contrary to experimental findings where an unmistakable misalignment between the molecule orientation and lattice vectors of the overlayer structure is observed. Moreover, calculated images for molecules on bridge sites show no apparent asymmetric profile along the molecule. This result is not surprising because only the hollow site breaks the twofold symmetry of the molecule. Certainly intermolecular interactions cannot be ignored, as the parallel alignment of the molecules is a result of it. But while the molecules face a rather small diffusion barrier between hollow and bridge sites, the barrier between the hollow and bridge sites was calculated to be 0.8 eV, which is nearly 4 times greater than the rotation barrier for any site (0.23 eV). A more rigorous relaxation study would be necessary to fully elucidate this fact.

STM images of *ortho*-xylene intramolecular surface features were uninteresting. At room temperature, we were unable to obtain the distinguishing features predicted by EHT [Figs. 8(g), 8(h), and 8(i)]. The node separating the methyl groups was only resolvable for the best images of the *meta*-xylene where the methyl groups are separated by 120° . Perhaps it is not surprising that for *ortho*-xylene, where the methyl groups are located on adjacent carbon atoms of the phenyl group, the methyl groups are not separately resolvable. In addition, the side of the molecule with the methyl groups was expected to show an apparent height difference, which was not observed. We exclude the possibility of tilting as *ortho*-xylene was found to adsorb with the phenyl group parallel to the surface on Pt(111).³

V. CONCLUSIONS

We obtained detailed STM images revealing structural and ordering information for the xylene isomers on Pd(111).

Experimental observation for the *meta*- and *para*-xylene isomers agreed well with predicted images using extended Hückel theory. *Meta*-xylene molecules align along upper close-packed step edges with one side parallel to the step, with small hexagonal domains appearing near steps. *Para*-xylene molecules arrange in hexagonal domains with the molecule axis oriented approximately $15^\circ \pm 5^\circ$ from the overlayer close-packed rows. The arrangement of *ortho*-xylene molecules shows no long-range order, but molecules assemble in small arrays of rectangles.

Images were calculated for both the isolated molecule and the molecule adsorbed on a single-layer Pd(111) cluster consisting of 20–35 atoms. Calculated intramolecular features agreed well with experimental ones for *meta*- and *para*-xylene. Binding energy calculations for all three isomers showed preferences for the hollow and bridge sites. Such calculations for *meta*-xylene on both steps and terraces showed a preference for the molecule to orient with the methyl groups parallel to the Pd close-packed directions. *Para*-xylene molecules showed a preference for orienting 22° with

respect to the metal close-packed directions. In addition, calculated images showed an asymmetric profile down the long axis of the molecule, which is consistent with the experiments. For *ortho*-xylene, the calculations predict intramolecular structure, binding site preferences, and molecular orientation, but these details have not yet been observed experimentally.

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