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# Calculations of scanning tunneling microscope images of xylene on Rh(111)

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# Abstract

We performed a comparative study of scanning tunneling microscope (STM) images of three different isomers of xylene  $[(CH_3)_2C_6H_4]$  adsorbed on Rh(111) using a computational method based on extended Hückel molecular orbital theory (EHT). We calculated images for both the isolated molecules and for molecules chemisorbed on a rhodium cluster. The intramolecular structure of calculated images agreed well with previous experimental results. The calculated images exhibit a dependence on neither the binding site nor the molecular orientation on the surface. No difference was observed between the calculated images of occupied and unoccupied states. © 2000 Elsevier Science B.V. All rights reserved.

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# 1. Introduction

The ability to identify molecular species on surfaces greatly enhances the understanding of surface chemistry. The scanning tunneling microscope (STM) provides the ability to obtain the highly detailed molecular structure of reactants, intermediates and products on a metal surface. A relatively simple and crude computational method, based on extended Hückel molecular orbital theory (EHT), furnishes the ability to predict the distinguishing surface features of specific organic adsorbates and their preferred binding sites and orientations on metal clusters [1-4].

We performed these calculations for the three isomers of xylene in *para*, *meta* and *ortho* configurations. We generated images both for the isolated molecules and for molecules chemisorbed on single-layer Rh(111) clusters consisting of 20-25atoms. Hückel parameters for rhodium are taken from the literature [5] and are listed in Table 1.

# 2. Method

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The EHT calculation can be simply summarized by the following two steps: (1) calculate the preferred molecule–cluster separation for each con-

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Table 1 EHT parameters of rhodium

Orbital	Valence orbital ionization potential (eV)	Slater exponent
4d	-12.50	4.290 (0.5807) 1.970 (0.5685)
5s	-8.09	2.135
5p	-4.57	2.10

figuration by plotting the binding energy as a function of molecule–cluster separation; and (2) compute and plot  $15 \text{ Å} \times 15 \text{ Å}$  images for both occupied and unoccupied states, which correspond experimentally to negative and positive sample bias settings. A more detailed explanation of the EHT method for predicting STM images is given in Ref. [2].

Calculations were performed for the three xylene isomers, each on the three high-symmetry binding sites (on-top, bridge and three-fold hollow) and for two molecular azimuthal orientations on each site. Binding energy calculations were performed to find preferences in orientation and molecule–cluster separation. In addition, because of some uncertainty regarding the tilt angle of the methyl groups with respect to the plane of the carbon ring after adsorption on the metal surface, the calculations were also performed for tilt angles ranging from 20 to  $40^{\circ}$ .

## 3. Results and discussion

Fig. 1 shows a schematic diagram of the three isomers of xylene. Although the binding energy showed a dependence on the molecule–cluster separation, the binding energy calculations for all



Fig. 1. Schematic diagram of the three isomers of xylene.

isomers provided no information regarding preferences of the molecular binding site, the molecular orientation on the surface. or the molecule-cluster separation distance. We suspect that this site and orientation independence is a result of the substituted methyl groups (CH<sub>3</sub>), as compared with previous studies of benzene on Pt(111) in which benzene exhibited a definite site dependence [6,7]. 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  $40^{\circ}$ . 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 platinum and palladium [4].

# 3.1. para-Xylene

We first calculated images for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the isolated molecule of *para*-xylene (*p*-xylene). The HOMO consists of two lobed features from the methyl groups and a feature that resembles one of the two degenerate HOMOs of the benzene molecule (Fig. 2a). The LUMO showed no molecular features corresponding to the methyl groups and looked qualitatively identical to a LUMO of benzene (Fig. 2b).

When adsorbed on Rh(111), the hybridization of the molecular orbitals of *p*-xylene with the atomic orbitals of the rhodium cluster accentuated the features seen in the HOMO. In addition, images of both the occupied (Fig. 2c) and unoccupied (Fig. 2d) states have qualitatively identical features: a central ring-like 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.

The calculated images agreed very well with the STM images of Cernota et al. [8] (Fig. 3a). They

D.N. Futaba, S. Chiang / Surface Science 448 (2000) L175-L178



Fig. 2. Calculated images of all three isomers for the isolated molecule and for the adsorbed molecule. (a) HOMO of p-xylene; (b) LUMO of p-xylene; (c) occupied-states image of adsorbed p-xylene on Rh(111) cluster; (d) unoccupied-states image of p-xylene on Rh(111) cluster; (e) HOMO of m-xylene; (f) LUMO of m-xylene; (g) occupied-states image of adsorbed m-xylene on Rh(111) cluster; (h) unoccupied-states image of m-xylene on Rh(111) cluster; (i) HOMO of o-xylene; (j) LUMO of o-xylene; (k) occupied-states image of adsorbed o-xylene on Rh(111) cluster; and (1) unoccupied-states image of o-xylene on Rh(111) cluster.

observed a length A from peak to peak along the long axis of the *p*-xylene molecule as approximately 4.05 Å, while the width *B* along the short axis was about 1.87 Å. These corresponding dimensions on the calculated images are 5.78 Å and 3.02 Å, respectively. We suspect that the apparent variance



Fig. 3. (a) Experimental STM image of *p*-xylene on Rh(111). *A* and *B* are the length and width dimensions as discussed in the text. (b) Experimental STM image of *m*-xylene on Rh(111). (From Ref. [8].)

in the dimensions is a direct result of the tilting of the methyl groups, due either to the adsorption to the metal surface or to the proximity of neighboring molecules on the rhodium surface, or both. For the calculated images shown here, only a single molecule was considered, and no tilt angle was included due to the inconclusive results of the energy calculations discussed earlier. The inclusion of a tilt angle in other calculated images for this molecule (not shown) gave an unmistakable reduction in the length and a corresponding reduction in the width of the adsorbed molecule, but displayed the same general symmetry as for the calculated images shown here.

# 3.2. meta-Xylene

The calculated image of the HOMO for isolated *meta*-xylene (*m*-xylene) showed a distinct triangu-

L177

lar shape with the carbon ring showing features of a benzene HOMO (Fig. 2e and f), just as with *p*xylene. Similarly, the image for the LUMO showed triangular symmetry with the character of the LUMO of benzene.

The calculated images of adsorbed *m*-xylene on rhodium are also distinguished by a triangular geometry (Fig. 2g and h). 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-states images. Again, given the locations of these brighter features, they correspond to the electronic structure of the two methyl groups.

These calculated surface features agree well with the experimental STM data of Cernota et al. [8] (Fig. 3b). While they were able to resolve the triangular shape and the higher corrugation of the two corners in the STM images, the depression in the middle of the ring was not observed.

## 3.3. ortho-Xylene

The calculated image of the HOMO for *ortho*xylene (*o*-xylene) showed the same characteristic bright lobe features resulting from the methyl groups and a benzene-like HOMO (Fig. 2i). The calculated image for the *o*-xylene LUMO was also characterized by two lobes and a benzene-like LUMO (Fig. 2j).

The predicted images of *o*-xylene adsorbed on a rhodium cluster are characterized by a ring with a definite centered indentation and two bright adjacent lobes slightly separated from the central ring (Figs. 2k and 1). Again, 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 *p*-xylene, images calculated with the inclusion of tilted methyl groups showed the same general shape as the ones without. Thus, we do not expect much difference in experimental images as a result of the tilt. Currently we have no experimental data with which to compare, but

experimental STM measurements of low coverages of o-xylene on Pd(111) are currently in progress in our laboratory.

# 4. Summary

We calculated STM images using extended Hückel molecular orbital theory for the three isomers of xylene to compare with experimental STM data. In all three cases the molecules showed neither site nor orientation dependence, but in the cases of *p*-xylene and *m*-xylene, calculated images agreed well with previous experimental data [8]. No experimental *o*-xylene images exist yet with which to compare, but given the success of the calculations for the other two isomers, we expect to have very good agreement with future experiments.

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