

# Simulation of scanning tunneling microscope image of benzene chemisorbed on a Pd(111) electrode surface by density functional theory

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**Abstract:** A computational method based on density functional theory was used to simulate the scanning tunneling microscopy (STM) images of benzene chemisorbed on a Pd(111) electrode in order to confirm the adsorption site of the aromatic molecule on the metal surface held at a certain applied potential. The simulated STM images on various adsorption sites were obtained and compared with the experimental electrochemical STM images. The simulation results indicate that when the potential of the Pd electrode is held at 0.3 V, benzene is chemisorbed on a threefold hollow site; at 0.55 V, the molecule is adsorbed on a position between a threefold and a twofold bridge site. These findings corroborate previously published experimental electrochemical STM results.

**Keywords:** STM simulation, benzene chemisorption, Pd(111) surface, potential-dependent adsorbate reconstruction, electrochemical compact layer

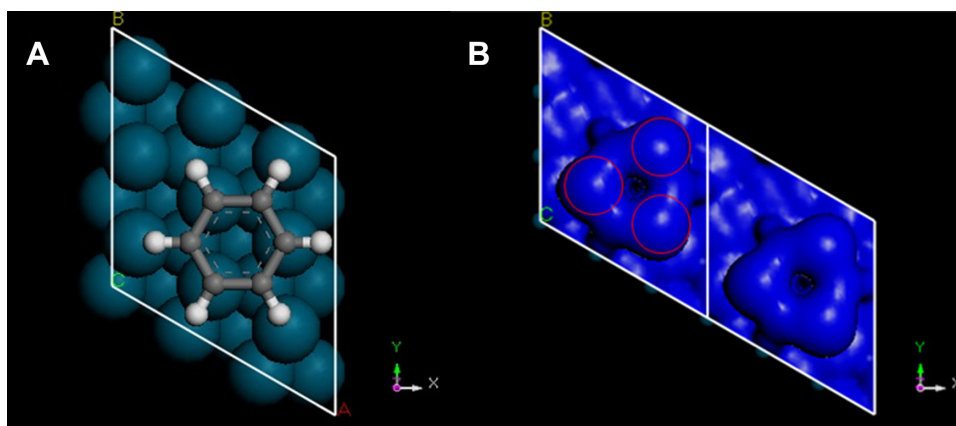
## Introduction

In the field of electrochemical surface science, it is of fundamental importance to determine the structure of molecular species chemisorbed on electrocatalyst surfaces. A surface-sensitive technique that can be used for this purpose is electrochemical scanning tunneling microscopy (EC-STM). However, interpretation of molecular STM images is not straightforward, since they do not always unambiguously reveal the actual positions of the atoms; instead, the electronic states of the interface near the substrate Fermi energy level are shown.<sup>1</sup> Fortunately, STM profiles can be simulated by computational methods such as those based on density functional theory (DFT). By comparison of experimental and theoretical STM results, elucidation and confirmation of certain structural features such as adsorbate orientations and adsorption sites can be achieved.

The chemisorption of aromatic molecules such as benzene on Pt(111) surfaces has been studied by STM. It has been observed that the STM images of benzene molecules on metal surfaces are dependent on the molecular adsorption site.<sup>2</sup> With the aid of STM images simulated based on the electron scattering quantum chemical (ESQC) method, the following results were obtained: (1) when benzene is chemisorbed parallel to the surface at a threefold hollow site, the molecule appears triangular with three lobes at each vertex of the triangle; (2) if the molecule is on a twofold bridge site, the molecular images appears to be a single elongated bump; and (3) a ring-like structure with six lobes is observed only when the molecule is on a top site.<sup>1,3,4</sup>

Simulation of STM images of benzene adsorbed on Pd(111) surfaces has also been carried out.<sup>5</sup> In that theoretical investigation, extended Hückel molecular orbital

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**Figure 1** (A) Adsorption geometry of benzene adsorbed on a threefold hollow site on a Pd(111) surface. (B) Simulated scanning tunneling microscope images of the surface in (A).

theory (EHT) was employed in the computations. The results were similar to those obtained with Pt(111).<sup>1,3,4</sup>

In an earlier report, several EC-STM images were described of benzene adsorbed, at certain potentials, on Pd(111) electrode surfaces.<sup>6</sup> The images suggested that when the potential of the Pd electrode is held at 0.3 V, benzene is chemisorbed on a threefold site in a Pd(111)–( $3 \times 3$ )–C<sub>6</sub>H<sub>6</sub> adlattice. However, at 0.55 V, the molecule is located on a spot between a threefold and a twofold site as a Pd(111)– $c(2\sqrt{3} \times 3)$ –*rect*–C<sub>6</sub>H<sub>6</sub> adlayer. To validate those scenarios, DFT-based simulated STM profiles of benzene are presented here at various adsorption sites on a Pd(111) surface; the computed results are then compared with the experimental images.<sup>6</sup>

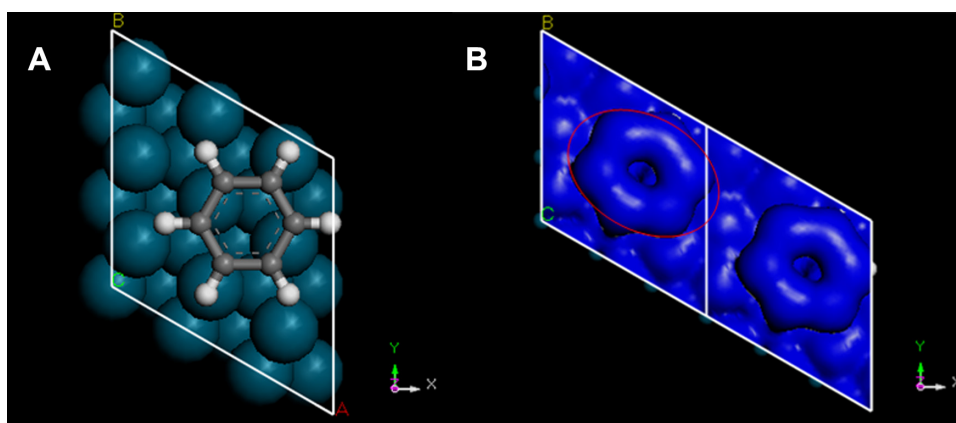
## Computational details

The Cambridge Sequential Total Energy Package (CASTEP) code was used in the calculations.<sup>7</sup> This DFT-based module

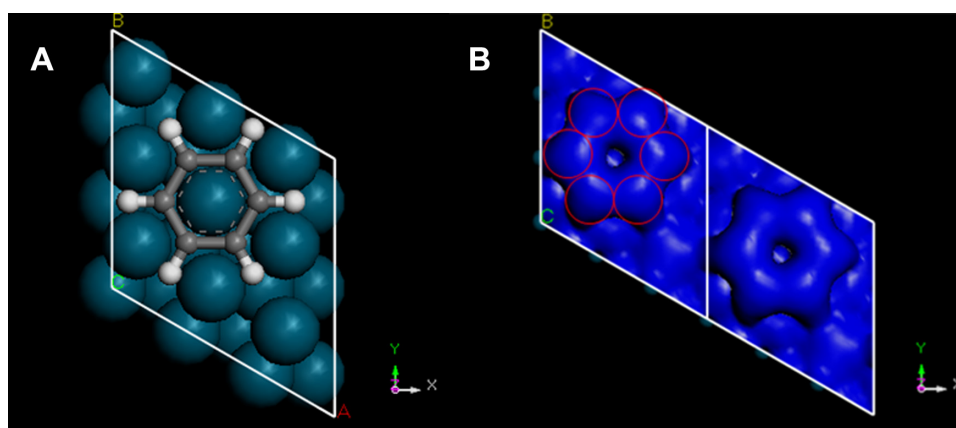
is incorporated in Material Studio 5.0 of Accelrys Inc, employs Vanderbilt-type ultrasoft pseudopotentials that allow calculations to be performed at a lower cutoff energy, and solves the Kohn–Sham equations using a plane-wave basis set.

Geometry optimization and energy calculations were performed utilizing a  $3 \times 3 \times 1$  Monkhorst–Pack grid, a cutoff energy of 300 eV, and a Fermi smearing of 0.1 eV. Earlier studies showed that these conditions are adequate enough in obtaining acceptable energy values.<sup>8,9</sup> The generalized gradient approximation<sup>10</sup> and the Perdew–Wang exchange–correlation functional (PW91)<sup>11</sup> were used to address exchange and correlation effects.

The calculations employed a  $3 \times 3$  supercell to minimize lateral interactions between the molecule and its neighboring periodic images,<sup>8,12</sup> and to simulate low adsorbate coverage conditions as seen in the actual EC-STM experiments performed before.<sup>6</sup> In this structure, the surface was created as a



**Figure 2** (A) Adsorption geometry and (B) Simulated scanning tunneling microscope images of benzene chemisorbed on a twofold bridge site on a Pd(111) surface.



**Figure 3** (A) Adsorption configuration of benzene adsorbed on a top site on a Pd(111) surface. (B) Simulated scanning tunneling microscope images of the Pd(111) surface with benzene on a top site.

metal slab containing four layers of Pd atoms, with the upper two layers allowed to relax. The cell was also built in such a way that the slab was separated from its periodic images with a vertical vacuum space of  $\sim 15$  Å.<sup>8,9,12</sup>

The STM profiles were obtained using DFT to determine the energy levels of the Pd-benzene system and the Tersoff–Hamann method<sup>13</sup> to display a two-dimensional plot of the surface local density of states or the electron density isosurface produced by electronic states at a certain energy away from the Fermi energy level. In actual STM experiments, the precise energy difference from the Fermi level is determined by the applied bias on the STM tip. With CASTEP, and in this simulation, a hypothetical tip potential can be set to view the surface local density of states and thus simulate the STM image. A theoretical tip voltage of 0.100 V was used in this study to emulate the conditions used in the previous EC-STM experiments.<sup>6</sup>

Geometry optimization was performed on the structures before simulated STM images were obtained. This implies that the molecule's most favorable adsorption structure and distance to the surface were computationally predetermined, and the resulting geometry was used for STM image simulation. Optimizing the structure using this DFT method takes into account all possible interactions within the aromatic compound, on the surface, and between the molecule and the surface. It is also important to note that this method of simulating STM images was also used in studying the adsorption of sulfate anions on Pd(111) surfaces.<sup>14</sup>

## Results and discussion

Unlike the ESQC method, which calculates the actual tunneling current obtained from the scattering matrix for the electrons

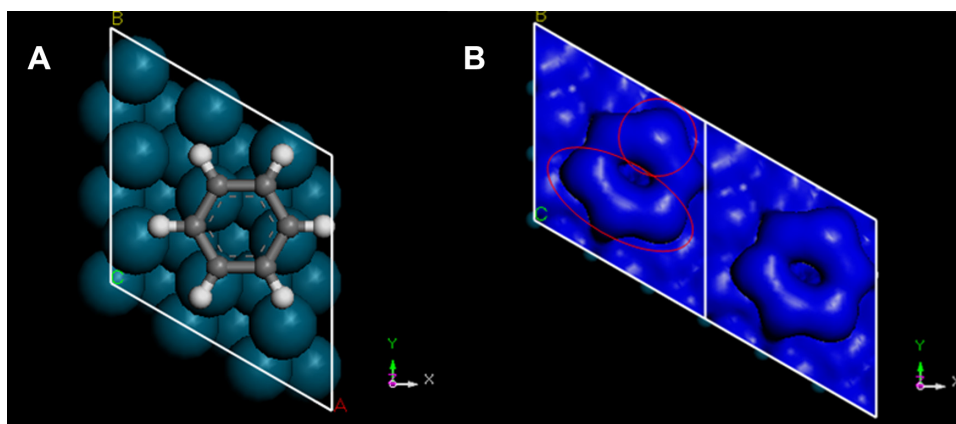
on the tunnel gap,<sup>3</sup> or the EHT-based approach, which uses the semi-empirical Hückel method in calculating the energy levels,<sup>5</sup> the STM-simulation method adopted in this research relies on DFT to calculate and determine the energy levels of various electronic states, and the Tersoff–Hamann<sup>13</sup> method to display the electron density isosurface as the STM profile.

Figure 1A shows the adsorption geometry of benzene chemisorbed on a threefold hollow site on a Pd(111) surface. The corresponding simulated STM image is displayed in Figure 1B. Based from the simulated profile, it is apparent that benzene in this adsorption site adopts a triangular shape with three humps at each vertex of the triangle. These humps are believed to correspond to the three bright spots observed in the ESQC-based and EHT-based simulated STM images of benzene adsorbed on the hollow sites of Pt(111)<sup>1</sup> and Pd(111)<sup>5</sup> surfaces, respectively.

Figure 2A displays a Pd(111) surface with benzene on a twofold bridge site, and its simulated STM profile is presented in Figure 2B. In this image and in this adsorption site, benzene conforms to an oval-shaped figure, which is quite similar to the form observed in the ESQC-based<sup>1</sup> and EHT-based<sup>5</sup> STM simulations.

The adsorption configuration of benzene chemisorbed on a top site on a Pd(111) surface is shown in Figure 3A. Based on its DFT-based STM profile as presented in Figure 3B, six humps or protrusions can be observed on the ring. This corresponds perfectly well with the six bright spots or lobes observed in the simulation on the Pt(111) surface using a similar adsorption structure.<sup>3</sup>

The dependence of the molecular STM image on the adsorption site originates from the specific interactions between the electronic states of the adsorbed molecule and



**Figure 4** (A) Adsorption geometry and (B) Simulated scanning tunneling microscope images of benzene chemisorbed on a site between a threefold hollow and a twofold bridge site on a Pd(111) surface.

those of the surface metal atoms directly below it. Individual adsorbate molecular orbitals will have varying contributions to the perturbation of the surface electronic structure at different adsorption sites since the symmetries of the orbitals and of the sites are different.<sup>3</sup>

The difference in the simulated STM profiles of benzene on various adsorption sites on a Pd(111) surface may be utilized to identify the molecule's site of adsorption on several experimental EC-STM images of Pd(111) single-crystal electrodes immersed in dilute solutions of benzene. The EC-STM image of benzene on a Pd(111) electrode surface at an applied potential of 0.3 V has been described previously. It is apparent that the molecule is composed of three spots since the fourth and faintest spot is considered to be due to a co-adsorbed water molecule.<sup>6,15</sup> Upon comparison of this STM image with those in Figures 1–3, it is clear that at 0.3 V, benzene is chemisorbed on a threefold hollow site as shown in Figure 1A. This confirms the previous findings obtained earlier.<sup>6</sup>

The EC-STM image of benzene on a Pd(111) surface held at 0.55 V has been shown elsewhere. It is significant to note that in this STM image, the benzene molecule can be perceived as comprising two spots, with one spot larger than the other to form a semi-triangular shape. Obviously, this does not correspond to any of the STM images in Figures 1–3. However, when benzene is on a position between a threefold hollow and a twofold bridge site as shown in Figure 4A, an STM profile that shows a wide and a narrow hill or lobe is obtained (Figure 4B). This simulated STM profile clearly resembles the adsorbate images published earlier. This validates the results proposed earlier.<sup>6</sup>

## Conclusion

DFT was employed to simulate the STM images of benzene chemisorbed on various adsorption sites on a Pd(111)

surface. The simulated profiles were compared with the experimental EC-STM images in order to verify the adsorption site of the aromatic molecule on the Pd(111) electrode surface at a certain applied potential. Theoretical results suggest that at 0.3 V applied potential, benzene is chemisorbed on a threefold hollow site. At 0.55 V, the center of the ring lies on a location between a threefold hollow and a twofold bridge site. Results from this theoretical study confirm the interpretations made in an earlier published study.

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## Disclosure

The authors report no conflicts of interest in this work.

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