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STM and DFT Studies of Anion Adsorption at Well-defined Surfaces: Pd(111) in Sulfuric Acid Solution

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Density functional theory (DFT) has been employed to resolve compositional and structural issues related to the *in situ* (electrochemical) scanning tunneling microscopy (EC-STM) of a well-defined Pd(111) electrode surface in aqueous sulfuric acid solution. Fundamental concepts in inorganic chemistry had earlier been invoked to postulate that SO_4^{2-} anions, H_3O^+ counter-cations and H_2O were the most likely constituents in the compact layer. However, while the STM images distinctly revealed ordered rows of anions interspersed with hydronium ions and water molecules, details such as the orientations, spatial configurations and adsorption-site locations of the interfacial species could not be unambiguously ascertained. The present DFT-based geometry-optimization and total-energy calculations indicate that two layers of water molecules and hydronium ions are assembled, non-co-planar with one another, between the rows of surface-coordinated anions; the layer that is slightly elevated is comprised of counter cations.

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INTRODUCTION

The role of supporting-electrolyte anions in reactions that proceed at the electrode-solution interface is of fundamental importance in electrochemical surface science. The observation that the morphology of the current-potential curve of Pt(111) in perchloric-acid electrolyte is dramatically different than that in sulfuric acid is a well-known example (Kim et al. 2000).

The prevalent use of sulfuric acid as an "inert" supporting electrolyte has led to extensive studies on its interaction with the noble-metal electrodes (Kim et al. 2000, Magnusen et al. 1992, Sato et al. 2006, Funtikov et al. 1995, Funtikov et al. 1997, Wan et al. 1995, Wilms et al. 1996, Li and Nichols 1998, Arenz et al. 2001, Wan et al. 1999, Senna et al. 2001, Edens et al. 1994). A variety of experimental techniques that included electrochemical scanning tunneling microscopy (EC-STM), cyclic voltammetry, chronocoulometry, radiotracer measurements and optical spectroscopy has been employed; computational methods were also exploited. While results from various laboratories on interfacial coverages, structures and reactivities are in reasonable agreement with one another, the nature or identity of the adsorbed anion has not been unambiguously established. In an earlier investigation (Kim et al. 2000), we invoked

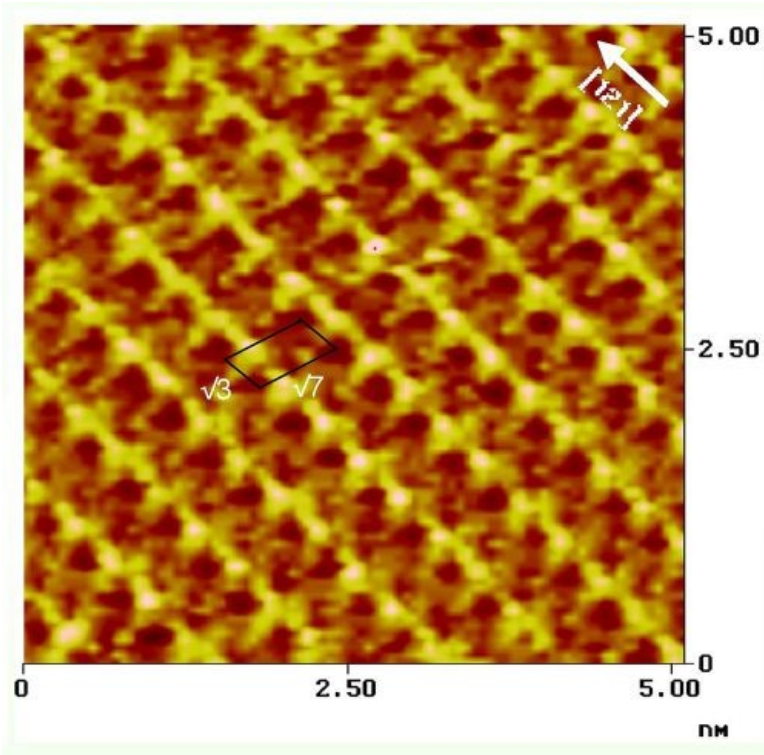

Figure 1. EC-STM image of a Pd(111) electrode surface in 0.05 *M* H_2SO_4 at 0.4 V that shows a (√3 × √7) adlattice structure. Tunneling current = 20 nA. Extracted from Kim et al. 2000.

fundamental concepts from inorganic chemistry to argue that only sulfate ions would be present on the electrode surface: If HSO_4^- were surface-coordinated via the oxygen lone-pairs, the inductive effect brought about by the pull of electron density away from the sulfur atom towards the more electronegative coordinated-oxygen atoms weakens the O-H bond since the decreased negative-charge density on sulfur would extract electron density from the O-H group. Consequently, when HSO_4^- binds to a transition-metal center, whether in homogeneous or heterogeneous complexes, the enhanced acidity of the O-H group will most likely yield SO_4^{2-} di-anions in the coordination sphere (compact layer).

We earlier reported results from EC-STM investigations on the interfacial structure of a Pd(111) electrode surface in 0.05 M H_2SO_4 (Kim et al. 2000). That study showed that, when a Pd(111) electrode is immersed in a dilute sulfuric acid solution, a well-ordered (√3 × √7) adlattice is formed on the Pd surface as shown in Figure 1. This structure is similar to those obtained from EC-STM studies on Au(111) (Magnusen et al. 1992, Sato et al. 2006), Pt(111) (Funtikov et al. 1995, Funtikov et al. 1997), Rh(111) (Wan et al. 1995), Cu(111) (Wilms et al. 1998, Li and Nichols 1998, Arenz et al. 2001), and Ir(111) (Wan et al. 1999, Senna et al. 2001) in dilute sulfuric acid solutions. The rows of bright spots are believed to represent the adsorbed anions, whereas the dim rows arise from the hydrogen-bonded chains of water molecules (Sato et al. 2006, Wan et al. 1995, Arenz et al. 2001, Wan et al. 1999) and hydronium cations (Kim et al. 2000, Funtikov et al. 1995, Funtikov et al. 1997, Senna et al. 2001, Eden et al. 1994).

Further examination of the three-dimensional and the zoomed-in images of the (√3 × √7) adlattice (Figures 2a and 2b) reveal important structural details: (i) the adsorbed sulfate is trigonally coordinated on the Pd(111) surface such that the ion is directly above a 3-fold hollow site, and (ii) two layers of water molecules and hydronium cations are formed between the anionic rows; the layers, however, are not co-planar with one another with the slightly elevated layer constituted by hydronium counter-cations. Two real-space structures, depicted in Figure 3, were proposed; the major differences in the two structures lie in the spatial orientations and the adsorption-site locations of the molecular and cationic species. EC-STM was not able to ascertain the actual structure. It is in this context that the EC-STM results have been revisited and computationally scrutinized.

The two issues targeted in the present study are: (i) the nature of the two co-adsorbed but non-co-planar layers of water molecules and hydronium cations, and (ii) the most favorable structure of the interfacial ensemble. The computational work was based on density functional theory (DFT). The dissection of structural nuances was accomplished by geometry-optimization calculations. The identification of the most favorable real-space structure was achieved by total-energy calculations in combination with STM-image simulations.

COMPUTATIONAL METHOD

The experimental details of the EC-STM measurements have already been published elsewhere (Kim et al. 2000) and will not be reproduced here; only the DFT-based computational algorithms will be described.

DFT states that all ground-state properties of a system are functionals of the charge density, ρ. Hence, the ground-state total energy, E_t, may be written as:

$$E_t[\rho] = T[\rho] + U[\rho] + E_{XC}[\rho] \qquad (1)$$

where $T[\rho]$ is the kinetic energy arising from non-interacting particles, $U[\rho]$ is the electrostatic energy attributable to coulombic interactions, and $E_{XC}[\rho]$ is the exchange and correlation energy from many-body contributions (Hohenberg and Kohn 1964, Levy 1979). The total energy is calculated by solving the Kohn-Sham equations and using a Self-Consistent Field (SCF) procedure. In this study, the Cambridge Sequential Total Energy Package (CASTEP), a first-principles DFT code integrated in Material Studio 5.0 of Accelrys Inc., was employed

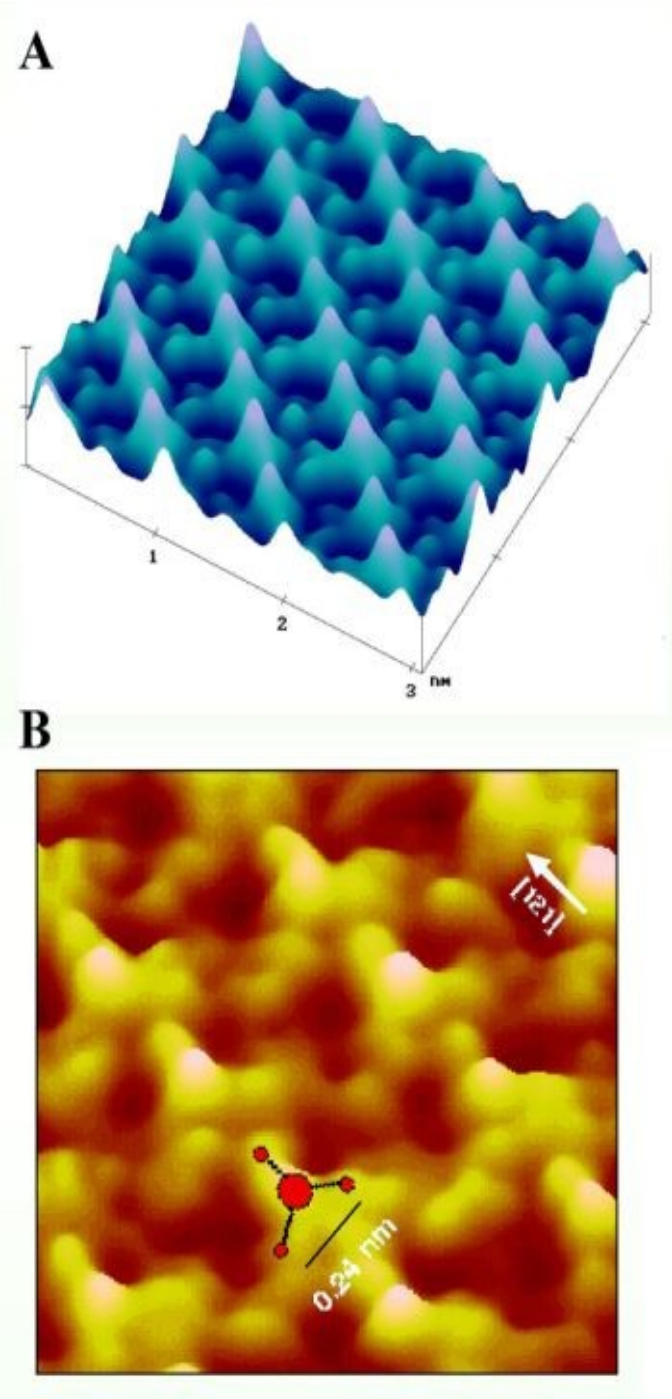

Figure 2. A: Three-dimensional plot of the (√3 × √7) adlattice on the Pd(111) surface in 0.05 *M* H_2SO_4 at 0.4 V. B: Zoomed-in high-quality EC-STM image of the same adlayer. Extracted from Kim et al. 2000.

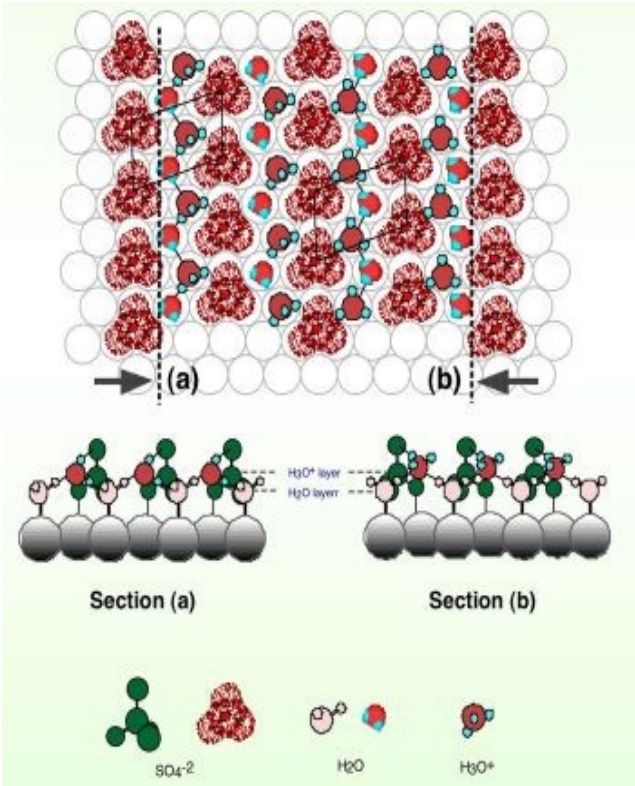

Figure 3. Two possible real-space structures of the Pd(111)-(√3 × √7)-SO_4^{2-}-H_3O^+-H_2O adlattice. Reproduced from Kim et al. 2000.

to perform the calculations (Clark et al. 2005). Vanderbilt-type ultrasoft pseudopotentials were used to allow computations to be done at lower cutoff energies and the generalized gradient approximation (GGA) (Perdew et al. 1996) and the Perdew-Wang exchange-correlation functional, PW91, (Perdew and Wang 1992) were utilized to treat exchange and correlation effects. The plane-wave basis set was employed in this method since a periodic system was used.

The ability of various computational methods to evaluate the derivative of the total energy, E_t, with respect to variations in geometry is a valuable tool since it permits the determination of the structure with the lowest energy and thus, allows the prediction of the true chemical structure during structural optimization calculations. In this work, geometry optimization was performed with a cutoff energy of 300 eV and the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method was employed as the energy minimization algorithm. A 3 × 3 × 1 k-point set was chosen for the Monkhorst-Pack grid and the Fermi smearing was set to 0.1 eV. As a criterion for convergence, the tolerance in energy, force, and displacement were 2.0 x 10^{-5} eV/atom, 0.05 eV/Å, and 0.002 Å, respectively. All of these

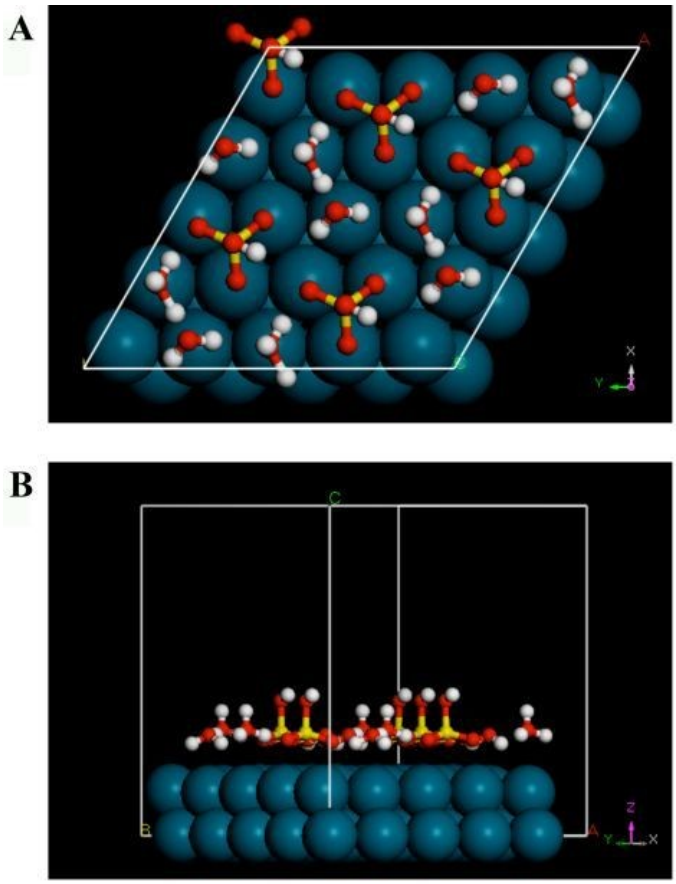

Figure 4. Top view (A) and side view (B) of the optimized geometry of Structure (a).

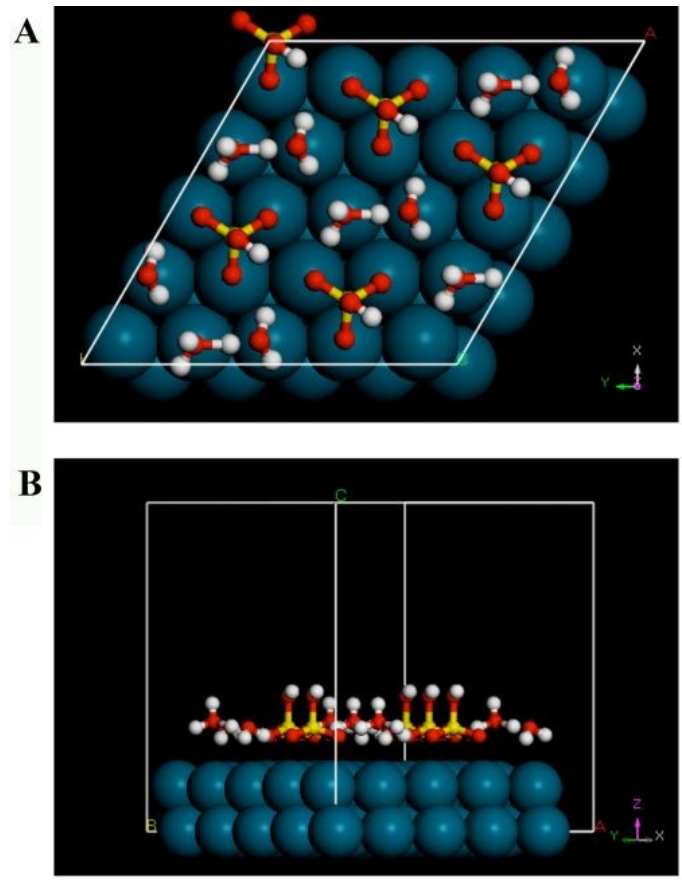

Figure 5. Top view (A) and side view (B) of the optimized geometry of Structure (b).

variables were sufficient in achieving a reasonable convergence in determining the optimized structure and the total energy of all the systems studied (Qian et al. 2010, Morin et al. 2003).

In an attempt to model the interface, a 5 × 5 supercell was used in order to accurately represent the Pd(111)-(√3 × √7)-SO_4^{2-}-H_3O^+-H_2O adlattice structures in Figure 3. The (111) metal surface was formed by using a metal slab consisting of two layers of Pd atoms; only the upper Pd layer was allowed to relax. A vertical vacuum space of *ca.* 15 Å separated the metal surface from its periodic images (Qian et al. 2010) and the adlattice consisting of sulfate anions, hydronium cations, and water molecules is placed in this vacuum space.

An actual STM image shows the surface local density of states (LDOS) or the electron density surface produced by electronic states with a certain energy difference relative to the Fermi energy level. The energy difference from the Fermi level is determined by the applied bias on the STM tip. Simulated STM images in this work are obtained in a similar manner. Density functional periodic calculations determine the electronic energy levels of the interfacial system. By specifying a hypothetical tip potential, CASTEP can display a two-dimensional plot of the surface LDOS from electronic states at a specific energy relative to the Fermi level using the Tersoff-Hamann method (Tersoff and Hamann 1985) and hence, simulate an STM image. A theoretical tip voltage of 0.200 V was used in this method to model the conditions used in obtaining the EC-STM images done in the previous experiment (Kim et al. 2000).

In this study, the two structural models [structure (a) and structure (b) in Figure 3] proposed for the (√3 × √7) adlattice are structurally optimized. The resulting geometries are evaluated as to whether or not (i) the two layers of water molecules and hydronium cations are present between rows of sulfate ions, and (ii) hydronium ions compose the upper layer. The more stable or favorable adsorption structure is determined by comparing the total energies, identifying the structure with the lesser total energy, and comparing the simulated STM images of the optimized structures with the experimental EC-STM images.

RESULTS AND DISCUSSION

The top and the side views of the optimized geometry of Structure (a) (Figure 3) are shown in Figures 4a and 4b, respectively. It can be observed that the original model in Figure 3 closely resembles the optimized structure except that the O–H bonds of water are pointing towards the metal surface for the latter.

Figures 5a and 5b display the top and the side views, respectively, of the optimized geometry of Structure (b) (Figure 3). The optimized structure differs from the model in Figure 3 mainly on the spatial orientation of the water molecules and the hydronium ions.

It is surprising to note that, on both structures, two layers of adsorbed species are formed between the sulfate rows wherein water molecules constitute the lower layer while the hydronium cations compose the upper layer. This substantiates the results acquired earlier from the EC-STM study (Kim et al. 2000).

Structures of various chemical systems have been identified based on total energy calculations (Qian et al. 2010, Morin et al. 2003, Morin et al. 2004, Lu et al. 2006). Likewise, in an attempt to determine the more favorable interfacial structure, the total energies of the two proposed structural models in Figure 3 were calculated. Structure (b) is found to be more stable than Structure (a) by 0.073 eV per sulfate anion. Due to this small difference, the more favorable structure cannot be identified with absolute certainty based on total energy calculations alone. However, comparison of the EC-STM images with the optimized structures can provide useful insights. Since the hydronium ions are situated above the water molecules, the regions in the STM image (Figure 2b) where these ions are located should show enhanced brightness. By comparing Figures 2b and 4b, it can be observed that regions where the hydronium ions are positioned in Figure 4b correspond to empty areas in Figure 2b. This indicates that Structure (a) is not likely to be the correct structure. On the contrary, the location of the hydronium ions in Figure 5b appears to be bright in Figure 2b, implying that Structure (b) is most certainly to be the true real-space structure.

To prove the argument cited above, simulated STM images of Structures (a) and (b) were obtained and are shown in Figures 6a and 6b, respectively. It is evident that Figure 2b closely resembles Figure 6b more than 6a since the bright spots between the sulfate rows in the actual EC-STM image (Figure 2b) coincide with the (rounded) protrusions in the simulated STM image in Figure 6b. This signifies that Structure (b) is most likely to be the prevalent structure.

It is important to note that, in CASTEP, the presence of the STM tip is properly accounted for in the simulation of the STM image. A theoretical tip-voltage is required for an accurate determination of the LDOS of the excited state at that voltage; the excited LDOS is just the simulated STM image. The latter, obtained from Structure (b) after geometry optimization, matches the actual EC-STM image in Figure 2b. It should also be mentioned that the molecules and ions directly above the Pd surface are not freely mobile as they are rather strongly adsorbed. For such system, the Tersoff-Hamann method is valid. Similar computational work has been undertaken for organic molecules chemisorbed on metal surfaces; examples are: benzene on Pt(111) (Sautet and Bocquet 1994), benzene on Pd(111) (Futaba and Chiang 1999), and thiophene on Pd(111) (Futaba and Chiang 1999).

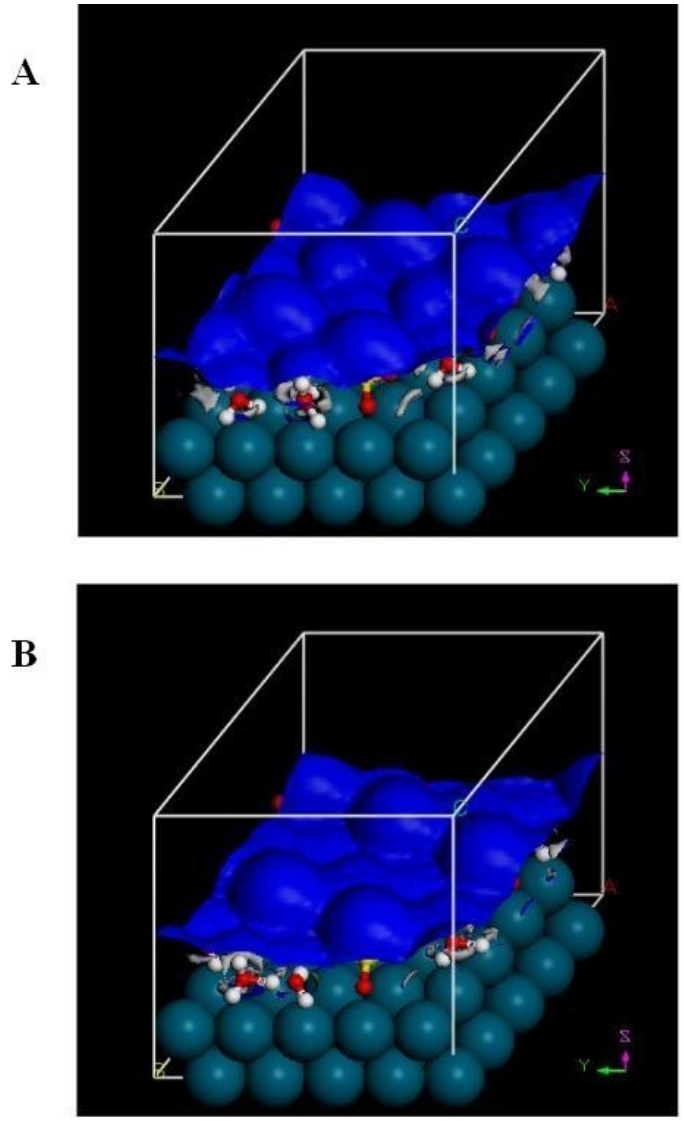

Figure 6. Simulated STM image of the optimized geometry of Structures (a) and (b).

CONCLUSIONS

Density functional theory was employed to resolve compositional and structural issues related to the electrochemical scanning tunneling microscopy of a well-defined Pd(111) electrode surface in aqueous sulfuric acid solution. Fundamental concepts in inorganic chemistry had earlier been invoked to postulate that SO_4^{2-} anions, H_3O^+ counter-cations and H_2O were the most likely constituents in the compact layer. The STM images clearly revealed ordered rows of anions interspersed with the hydronium ions and the water molecules; but other aspects such as the orientations, spatial configurations and adsorption-site locations of the interfacial species could not be unambiguously ascertained. The present DFT-based geometry-optimization and total-energy calculations indicate that two layers of water molecules and hydronium ions are assembled, non-co-planar with one another, between the rows of surface-coordinated anions; the layer that is slightly elevated is comprised of counter cations.

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NO CONFLICT OF INTEREST STATEMENT

No conflict of interest exists among the authors and their affiliated institutions whether in the implementation of the research described above or in the preparation and submission of the present manuscript.

CONTRIBUTIONS OF INDIVIDUAL AUTHORS

Mr. A. C. Javier carried out the density-functional computations. Dr. Y.-G. Kim and Dr. J. B. Soriaga performed the electrochemical scanning tunneling microscopy experiments. Professor P. B. Balbuena is the co-investigator and Professor M. P. Soriaga is the principal investigator; Soriaga is also the director of the Electrochemical Surface Science Laboratory and the Center for Electrochemical Systems and Hydrogen Research at Texas A&M University.

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