Effects of an electric field on a water bilayer on Ag(111)

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Based on first-principles calculations, we studied the effects of an electric field on the water bilayer at the water/Ag(111) interface. We find that the commonly accepted “H-down” configuration is not the ground state under an external field, but instead, the “H-down-flipped” configuration is most stable under a negative E field with the largest spacing between the water and Ag layers, while under a positive E field, the “H-up” configuration is most stable. This means that water molecules on Ag(111) are reoriented under an applied E field. The lowest-energy configurations are those that optimize the interaction between the water dipole and the external field, if the hydrogen bonding network of water layer is not disrupted.

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I. INTRODUCTION

There has been strong interest in characterizing the structure of the water layer and the spatial distribution of water molecules at solid-electrolyte interfaces due to the importance of this interface in physical chemistry, electrochemistry, and other branches of science.1,2 Based on their x-ray scattering experiments, which demonstrated different properties of water on Ag(111) under an E field, Toney et al. found that as an imposed bias changed from negative to positive, the average molecular orientation in the first water layer changed from oxygen-up to oxygen-down, leading to a decrease in the spacing between O and Ag, and they concluded that water on Ag(111) was reoriented at a charged substrate.3 Since x-ray scattering experiments cannot provide information about hydrogen atoms, an interesting question is whether the water molecules are really reoriented at an electrode-electrolyte interface or whether it is a simple lifting of the water layer. Morganstern and Niemine compared the calculated scanning tunnel microscope (STM) images of a water adlayer on Ag(111) with those of STM experiments and concluded that the interference between different tunneling channels led to the reorientation of adsorbed molecules.4 Roudgar and Groß studied a water bilayer on Pd/Au(111) under an E field. They did not find any rotation of the H-down bilayer structure and any significant compression between water and substrate induced by an external E field.5 By introducing an extra charge profile to modify the potential at an interface, a recent work by Taylor et al. simulated the charged interface between water in an icelike structure and Cu layers. They found that in a negative charged interface, the distance between water and Cu was 0.26 Å larger than that in a positive charged interface.6 In addition, most of the published studies related to the observation of Toney et al.3,7 are mainly concerned with the dipole orientation, and up to now, there is no clear-cut confirmation of the change of oxygen-up and oxygen-down under electric field. As the structure of the water layer and the field effect would be very sensitive on the substrate, we will focus on the specific system of water on silver.

With the context of electrostatic considerations, the reorientation of water molecules under an E field seems to be reasonable due to the existence of an intrinsic dipole of water. However, the actual situation is much more complicated since the reorientation may be hindered by the hydrogen bonding network in the water layer, and we also need to consider the bonding between the water molecule and the substrate. In addition, none of the existing models for water adsorption on close-packed metal surfaces, including the H-up (Ref. 1) and H-down (Ref. 8) models, can easily explain experimental results of Toney et al. at a negative E field (by negative field, we mean that the surface is negatively charged). How an external electric field affects the structure of the water bilayer as well as the interaction between the water bilayer and the substrate remains an issue to be clarified.

We are going to address the problem by proposing a model for a water bilayer on Ag(111), for which both the orientation and the distribution of water on Ag(111) under a negative E field is qualitatively consistent with the x-ray scattering experiments of Toney et al.3

II. METHODS

Our results were obtained under the framework of density-functional theory as implemented in a slightly modified VASP package.9 Electron-ion interactions were described by ultrasoft pseudopotentials,10 and the wave functions were expanded in a plane-wave basis set with an energy cutoff of 300 eV. The exchange-correlation potentials were described by the generalized gradient approximation in the Perdew-Wang form.11 The lattice constant of the fcc silver was found to be 4.16 Å, in good agreement with the experimental value of 4.09 Å.12 The Ag(111) surface was modeled by the standard repeated slab geometry, separated by a vacuum space of about 15 Å. The slab was five layers thick. A ($\sqrt{3} \times \sqrt{3}$)R30° supercell was selected for the water bilayer that was adsorbed onto one side of the slab. The k points were sampled on a 4 × 4 mesh in the surface Brillouin zone. All of these ensure that the total energy difference between two configurations is convergent to 0.01 eV per two water molecules in the unit cell. We kept the atoms in the bottom three layers fixed, and all other atoms were relaxed until forces on atoms were less than 0.03 eV/Å. To include the effect of an
The structure of the water layer on metal surfaces was traditionally considered to be a buckled bilayer network connected by H bonds, where only half of the water molecules are directly bonded to the metal surface and the other half are buckled upward if the surface is not too reactive, allowing the water layer to stay intact on the metal surface forming an icerlike structure.\(^1\) We shall identify those half of the water molecules as the “horizontal” water molecules if their molecular planes are nearly parallel to the substrate, and the other half as the “vertical” water molecules if their molecular planes are perpendicular to the substrate. The corresponding oxygen atom of the water is also referred to as the horizontal or vertical oxygen for the sake of discussion in the following.

Three geometric configurations of the water bilayer on Ag(111) are considered in this work, which are shown in Fig. 1. The H-up [Fig. 1(a)] and H-down [Fig. 1(b)] bilayer models on Ag(111) \((\sqrt{3} \times \sqrt{3})R30^\circ\) have been adopted by previously studies.\(^20\) Based on x-ray scattering experiment, Toney et al. deduced that the orientation for the water layer on Ag(111) depends on the imposed \(E\) field.\(^3\) We thus consider another H-down-flipped configuration [Fig. 1(c)], which also satisfies the Bernal-Fowler-Pauling rules for water adsorbed on a metal substrate.\(^5,16\) This model has the advantage that all the water dipoles are pointing down toward the metal surface and can be favored under a negative field, and, in addition, the bilayer buckling is almost twice as large as that of the H-down configuration. These features can explain the x-ray experiments of Toney et al.\(^3\)

It is well known that a single water molecule favors the top site on Ag(111) (Refs. 17 and 18) due to the fact that the 1\(b\) orbital of water favors the interaction with the \(d_z^2\) orbital of the fcc substrate.\(^19\) For a water layer, we expect that the water-substrate interaction will be weakened due to the lateral water-water interaction, and thus the water layer will be less selective on the absorption site. However, there is no physical reason that the top site should not be favored, and we keep the water molecules anchored on the top sites in all the bilayer models we considered.

The structural parameters optimized for all three configurations of the water bilayer on Ag(111) are listed in Table I, in which the symbols \(\alpha\), \(Z_{OAg}\), and \(Z_{AgAg}\) indicate, respectively, the tilt angle between the water dipole moment and the direction parallel to the surface, the vertical distance between the two oxygen layers, the vertical distance between the O layer and the corresponding Ag layer, as well as the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\(\varepsilon\) (V/Å) & \(-0.3\) & 0.0 & 0.3 \\
\hline
H-up & \(\alpha_h\) (deg) & 7 & 7 & 10 \\
& \(\alpha_v\) (deg) & 37 & 37 & 38 \\
& \(Z_{OAg}\) (Å) & 0.44 & 0.51 & 0.53 \\
& \(Z_{AgAg}\) (Å) & 3.00 & 2.90 & 2.86 \\
& \(Z_{OAg}\) (Å) & 3.48 & 3.47 & 3.46 \\
& \(Z_{AgAg}\) (Å) & 0.03 & 0.06 & 0.07 \\
\hline
H-down & \(\alpha_h\) (deg) & 15 & 25 & 27 \\
& \(\alpha_v\) (deg) & 39 & 39 & 38 \\
& \(Z_{OAg}\) (Å) & 0.07 & 0.20 & 0.26 \\
& \(Z_{AgAg}\) (Å) & 3.07 & 2.91 & 2.83 \\
& \(Z_{OAg}\) (Å) & 3.30 & 3.30 & 3.33 \\
& \(Z_{AgAg}\) (Å) & 0.15 & 0.19 & 0.24 \\
\hline
H-down-flipped & \(\alpha_h\) (deg) & 5 & 3 & 16 \\
& \(\alpha_v\) (deg) & 39 & 38 & 38 \\
& \(Z_{OAg}\) (Å) & 0.50 & 0.41 & 0.06 \\
& \(Z_{AgAg}\) (Å) & 4.30 & 4.26 & 4.00 \\
& \(Z_{OAg}\) (Å) & 3.87 & 3.88 & 3.89 \\
& \(Z_{AgAg}\) (Å) & 0.03 & 0.03 & 0.05 \\
\hline
\end{tabular}
\caption{Calculated structures for the three configurations of the water bilayer on Ag(111) under different \(E\) fields. For symbols used, see text, and the subscripts \(h\) and \(v\) are used to distinguish the horizontal and vertical water molecules, respectively.}
\end{table}
vertical distance between the surface Ag layers.

As shown in Table I, for the H-up and H-down configurations, the horizontal water molecule has a lone pair pointing toward Ag with almost the same O-Ag vertical distance of 2.90 Å versus 2.91 Å, and the dipole directions of the horizontal water for the two configurations are also the same. The difference in structure between the H-up and H-down configurations lies mainly in the dipole directions of the vertical water molecule, which are 37° and −39°, respectively. The vertical water molecule provides a OH bond pointing upward (down) toward the substrate for the H-up (H-down) configuration, as shown in Figs. 1(a) and 1(b). For the H-down-flipped configuration, the dipole direction of the horizontal water molecule points downward (−3°), while that of the H-down configuration is at 25°. The equilibrium structure of the H-down-flipped configuration has a large buckling, as the vertical distance between the two oxygen layers is 0.41 Å, while for the H-down configuration, it is 0.20 Å. The closest vertical distance between the oxygen and the Ag for the H-down configuration is 3.88 Å, while that for the H-down configuration is only 2.91 Å, meaning that there is a significant interaction between the O and the substrate for the H-down configuration.

B. Energetics without E field

Among the three configurations considered in this work, the water bilayer on Ag(111) favors the H-down configuration at the zero E field, but the energy difference between the H-up and H-down configurations as well as that between the H-down-flipped and H-down configurations are only 0.02 and 0.01 eV per two water molecules in the unit cell, respectively. Such a small energy difference is within our calculational accuracy, consistent with the results of Michaelides et al.20 and other calculations for water adsorbed on other metal surfaces.8,21 We note that the H-down-flipped configuration was never considered, but it is, in fact, very competitive and apparently slightly lower in energy than the H-up configuration. We will see below that this model has the lowest energy under a negative field condition.

There are three factors that contribute to the energetics of this system at the zero electric field, and they are, namely, the bonding of the water lone pair with Ag, the water OH bonding with Ag, and the disruption of the H-bonding in the water layer (which can be characterized by the bending of the H bonds). The former two factors increase the chemical bonding and disruption of the H bonding in the water layer. The two oxygen atoms in the H-down configuration interact with Ag via the lone pair for the horizontal O or via the OH bond for the vertical O. The lone-pair bonding is stronger, so that the lone-pair bonding basically anchors the horizontal OH bond in the H-down configuration. The OH bond in the H-down configuration points toward the Ag substrate, so there is an additional advantage of OH bonding between water and Ag. We note that the OH-Ag bonding for a single water adsorbed on the top site of Ag is about 3.6 Å. So, if the vertical water is to attain the preferred OH-Ag bonding length of about 3.6 Å, it has to be uplifted significantly above the horizontal water, but that will severely strain the β2 angle. The H-down configuration is basically determined by the compromise between the OH-Ag bonding and the (β) angle bending. The outcome is a compressed bilayer, so that the vertical distance between the two oxygen layers is quite small. In fact, the small vertical distance between two O layers for water bilayer on metal surfaces has drawn attention for a long time.22,23 By using low-

### TABLE II. A summary of the qualitative information about the water molecule interaction.

<table>
<thead>
<tr>
<th></th>
<th>Lone-pair bonding with Ag</th>
<th>OH bonding with Ag</th>
<th>Bending of H bonds in water bilayer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Favorable</td>
<td>Favorable</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>H-up</td>
<td>Yes</td>
<td>No</td>
<td>Medium</td>
</tr>
<tr>
<td>H-down</td>
<td>Yes</td>
<td>Yes</td>
<td>Large</td>
</tr>
<tr>
<td>H-down-flipped</td>
<td>Weak</td>
<td>Yes</td>
<td>Small</td>
</tr>
</tbody>
</table>

FIG. 2. (Color online) Schematic description for the bending of the H bonds in the H-down configuration, given by cutting planes along the lines marked as “L” in Fig. 1(b) and projecting onto a plane.
energy electron diffraction, Held and Menzel found a small vertical displacement (0.15 Å) between the two inequivalent water molecules adsorbed on Ru(0001). Feibelman proposed a H dissociated model to explain this anomaly, while for the water bilayer adsorbed on other metal surfaces, most experimental and theoretical studies do not support his proposition. Our analysis above may provide a simple explanation for the small vertical distance between the oxygen layers. At the same time, the requirement of more spacing between the vertical O and the Ag beneath for the H-down configuration pushes the Ag atom beneath the vertical water molecule, leading to fairly large buckling (0.19 Å) of the Ag layer for the H-down configuration.

For the H-up model, we find that the vertical distance between the oxygen and the substrate is the same as that of the H-down model for the horizontal water. This is not surprising since both are governed by the lone-pair bonding between water and Ag. For the H-up model, the OH bond is flipped up, so there is no OH-Ag bonding. However, the corresponding bending of the H bonds is smaller than that of the H-down configuration, because there is no need for the vertical water molecule to get near the substrate. Geometrically, the buckling of the oxygen layer becomes larger. Energetically, this model loses out to the H-down model, but not very much since the loss in the OH-Ag bonding is compensated by smaller bending of the H-bonding network.

C. E-field effects on configurations

In the present work, we directly compare the total energy difference for systems under E field. Since the same unit cell is used for different configurations, the E-field energy in the vacuum will be canceled when we consider the energy differences. In other words, our results are independent of the vacuum thickness as long as the vacuum is thick enough.

The optimized structural parameters in response to an external E field are listed in Table I. Toney et al. found that the distances of Ag-O are 3.7 and 2.7 Å for negative and positive charged surfaces, respectively, separated by about 1 Å.7 Our calculations show that the average distance between Ag and the two O layers is 4.09 Å for the most stable model (H-down-flipped) under −0.3 V/Å E field, larger than the 3.16 Å found for the most stable model (H-up) under 0.3 V/Å E field. The separation of 0.93 Å is in reasonably good agreement with the experiment of Toney et al. We note that the ±0.3 V/Å E field corresponds to surface charge density of about ±2.65 μC/cm², which is considerably smaller than that of the experiment of Toney et al. (~10 and 25 μC/cm²). Our formulation does not allow us to consider a very large negative surface charge density. However, the results already show that the O-up and O-down configurations will be inverted under an external E field, supporting the observation of Toney et al. For the E field of ±0.3 V/Å, the induced energy differences are several tens of meV. The dominant interaction is a dipole-field interaction, which is linear in field. If we extrapolate to the experimental value by Toney et al., the induced energy difference could be as large as 0.1 eV between H-down-flipped and H-down and 0.5 eV between H-down-flipped and H-up for a −10 μC/cm² charged surface, as well as 0.5 eV between H-down and H-up and 0.7 eV between H-down-flipped and H-up for a 25 μC/cm² charged surface.

Then, we address the effect of an external E field on the dipole orientation. We know that the E field strength that can be applied usually is not strong enough to break chemical bonds, and thus the E field mainly reorients the dipole moments while doing minimum disruption to the H-bonding network.

We note that the α of all three configurations are about ±38°, implying that one OH bond of the vertical water molecule is just pointing up or down perpendicular to the substrate. This feature is unchanged under an external E field, which we can see from Table I. However, a different case exists for the α of; that is, the dipole orientation of the horizontal water molecule responds actively to the external E field. The different responses to the E field for the α of and the α can be attributed to two reasons. The first one is that in a water molecule, the angle between the two OH bonds is very rigid due to the repulsion of the same polarity, so it is almost impossible to adjust the dipole direction by changing the H-O-H angle to respond to an E field. The alternative way is to rotate the water molecular plane. Rotating the water molecular plane will cause a change of β or β, which enhances the bending of the H bonds making energy unfavorable, but it can be compensated by the dipole-field interaction. However, due to the fact that the H bond contributed by the vertical water molecule is stronger than that contributed by the horizontal,24 rotating the plane of the vertical water molecule is much more difficult than rotating that of the horizontal, so the α of is insensitive to the E field, in contrast to the α. That is the second reason.

Based on the x-ray scattering experiments, Toney et al. found that the spacing between the electrode and first water layer can be interpreted by an oxygen-up (oxygen-down) average orientation for negative (positive) charge.3 To see whether this is the case, we considered the energetics of our configurations upon the imposition of an external electric field. Using that of the H-down model as reference, the total energy differences for the H-up (open circles) and H-down-flipped (solid circles) models are plotted as a function of E-field strength in Fig. 3. From the figure, we see that the ground-state configuration is field dependent. For a positive electric field (0.3 V/Å), the most stable configuration is the H-up model (more favorable in energy than the H-down model with 0.06 eV per two water molecules in the unit cell), while for a negative electric field (−0.3 V/Å), the most stable configuration is the H-down-flipped model (more favorable in energy than the H-up model with 0.12 eV per two water molecules in the unit cell). This is quite reasonable considering the dipole orientations of the water layer in the three configurations. Among the three models, the H-down-flipped model is actually the configuration that has the maximum magnitude of the downward pointing dipole, while the H-up model has the maximum magnitude of the upward pointing dipole. This feature will play an important role when an external electric field exists.

Thus, we can estimate the energy gained by the water dipole under an E field for these different configurations, which can be expressed as \( U \approx \mathbf{p} \cdot \mathbf{E} \), where \( \mathbf{p} \) and \( \mathbf{E} \) are dipole
the difference of total energy and gained energy of dipole under field, respectively. Open and solid symbols represent the values for H-up–H-down and H-down-flipped–H-down, respectively.

and $E$ field, respectively. Given the optimal geometries of the three configurations, we can estimate the $\mathbf{p} \cdot \mathbf{e}$ term contribution to the energy of our systems. For the sake of an estimate, let us take the calculated value $|\mathbf{p}| = 1.86$ D as the dipole moment in the water layer, and we can then calculate the energy difference due to the field-dipole interaction between the H-up and H-down configurations and that between the H-down-flipped and H-down configurations. These results are displayed by star symbols in Fig. 3. From the figure, we find that the energy difference between the three configurations estimated by the dipole-field interaction energy (stars) agrees reasonably well with the total energy difference obtained by full-fledged self-consistent calculations (circles). Of course, we do not know the dipole directions without a self-consistent calculation, but once the geometry is known, we see that the total energy difference under the external $E$ field is mainly contributed by the energy difference of dipole under the $E$ field. Thus, we can conclude that the reorientation of water layer on Ag(111) under the $E$ field is largely due to the $E$-field effect on the dipole of water. For the case of H-up under a positive field, the estimation due to the field-dipole interaction is not as good as other cases. The discrepancy may be attributed to the $E$-field effect on the OH bond, which is perpendicularly pointing toward the vacuum and exposed directly under the $E$ field due to the field induced charge transfer; see our previous work for details.\(^{25}\)

IV. CONCLUSIONS

In conclusion, we considered three geometric configurations of the water bilayer on Ag(111) and found that an external field of the order of 0.1 V/Å can switch the energy between them. The H-down-flipped configuration we proposed for the water bilayer on Ag(111) becomes the most stable configuration under a negative $E$ field and has a vertical distance of 3.88 Å between the water and Ag layers, about 0.6 Å larger than that of the H-down configuration. It has a large buckling of the bilayer, in contrast to the small buckling in the H-down configuration that is favored at the zero field. Together with the H-up configuration of water bilayer on Ag(111), which is most favorable under a positive $E$ field with the smallest vertical distance between the water and Ag layers, we have now a picture that can explain the x-ray scattering experiment of Toney et al.\(^{3}\) We found that the energetics can be traced to the field-dipole interaction, although without a first-principles calculation, it would be difficult, if not impossible, to tell what would be the dipole directions that optimize the competing forces of field energy, water-substrate interaction, and the H bonding within the water layer.

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