Water bilayer on the Pd/Au(111) overlayer system: coadsorption and electric field effects

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Periodic density functional theory calculations within the generalized gradient approximation for the exchange-correlation functional have been performed in order to study a water layer on the bimetallic Pd/Au(111) overlayer system. It turns out that a water bilayer in the H-down ice-Ih configuration is the most stable structure. Hydrogen and CO adsorption energies are influenced by less than 10% by the presence of the water bilayer. If an external negative electric field is applied, the stability of the H-down and H-up bilayer is reversed when the field is sufficiently strong.

Keywords: Ab initio quantum chemical methods and calculations, metallic films, chemisorption, solid-gas interfaces, solid-liquid interfaces, hydrogen atom, palladium, water

I. INTRODUCTION

Bimetallic surfaces have been studied intensively in the field of heterogeneous catalysis [1–3], but they are also of strong interest in electrochemistry since the catalytically active material has to be placed on a conductive electrode. However, electrochemical reactions occur at the solid-liquid interface in the presence of an electrolyte and an external electric field. The realistic incorporation of any electrolyte and an additional external electric field in electronic structure calculations is not trivial but can be done nowadays. Using periodic density functional calculations in the supercell approach, water molecules can be explicitly included between the slabs representing the substrate [4] while the electrochemical potential can be influenced by changing the charge state of the substrate acting as the electrode.

Just recently, there has been a strong interest in the structure of water layers on metal surfaces [5–11]. Usually, if the surface is not too reactive, water molecules stay intact on metal surfaces and form an ice-like bilayer whose structure is similar to that of the densest layer of ice [12]. However, recently Feibelman has proposed that on the relative reactive Ru(0001) surface, the water molecules do not remain intact [6]. Instead, the water bilayer becomes partially dissociated forming a *half-dissociated* bilayer.

We focus here on the bimetallic overlayer system Pd/Au(111). This system has served as a model system of a transition metal deposited on an inert noble metal electrode in electrocatlysis [13–16]. It is catalytically active for the oxidation reactions of methanol, formic acid and carbon monoxide.

We have recently studied atomic hydrogen and CO adsorption on Pd/Au bimetallic surfaces by performing density functional theory (DFT) calculations [17, 18]. We have found that both the expansion of the Pd overlayer by 5% and the relatively weak coupling between the d bands of Pd and Au cause a stronger adsorbate bonding. In addition, we have evaluated hydrogen and CO adsorption energies on Pd_n nanoparticles with $n = 3, 7, 10$ deposited on Au(111) [19]. Interestingly enough, we find that the binding energies on these supported clusters are smaller than on the corresponding overlayer although the cluster atoms are less coordinated than the overlayer atoms. This is caused by the compression of the supported cluster together with the cluster-substrate interaction.

However, in these DFT studies [17–19] we had neglected the influence of the electrolyte on the binding energies of the adsorbate. Furthermore, we had not included any applied electrical field in the calculations. In this letter, we report a substantial extension of our previous calculations in order to contribute to the understanding of fundamental processes occuring at the liquid-solid interface on an Pd/Au(111) electrode. We have determined the most stable structure of a water layer on the surface and calculated the adsorption energy of atomic hydrogen and CO in the presence of the water adlayer. In addition, we have determined the influence of an external electric field on the structure of the adwater layer on Pd/Au(111). We note that a preliminary account of this work covering only the coadsorption of hydrogen and water will appear elsewhere [20].

II. COMPUTATIONAL METHODS

We have performed periodic DFT calculations using the Vienna *ab initio* simulation package (VASP) [21]. The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the Perdew-Wang (PW-91) functional [22]. This functional is known to give a reliable description of the hydrogen bonding in water networks [6]. We have mainly employed ultrasoft pseudopotentials [23, 24] in our calculations. In the case of the water adlayers, we have also used the projector augmented wave (PAW) method

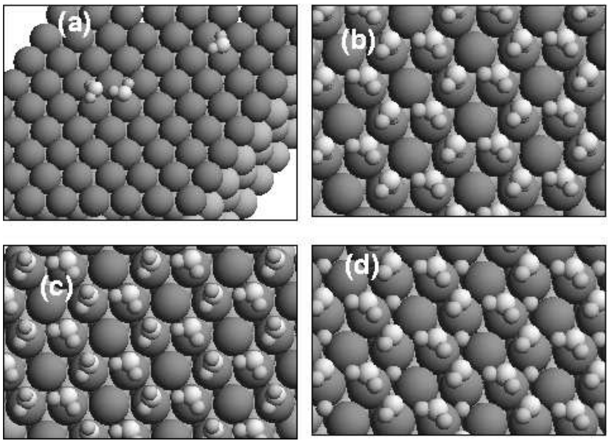

FIG. 1: Water structures on a Pd/Au(111) overlayer. a) equilibrium structure of the water monomer and dimer, b) H-down bilayer, c) H-up bilayer, d) half-dissociated water bilayer.

[25, 26] that corresponds to an all-electron method in order to check the reliability of our results.

The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with the size of the basis characterized by the maximum kinetic energy, the so-called cutoff energy. This necessary cutoff sensitively depends on the particular element. While for the description of hydrogen adsorption on the Pd/Au system a cutoff energies of 200 eV turned out to be sufficient, all systems containing oxygen required a cutoff energy of 400 eV. The PAW calculations for H_2O even made a cutoff of 700 eV necessary to obtain converged results.

The overlayer structure has been modeled by a slab of four layers of the Au(111) substrate on which one Pd overlayer has been deposited. The layer structures are separated by at least 10.5 Å of vacuum. The two bottom layers of the slabs have been kept fixed at their corresponding bulk positions, while all upper layers including the overlayers have been fully relaxed in all calculations.

All reported hydrogen adsorption energies are determined in a $(\sqrt(3) \times \sqrt(3))$ surface unit cell corresponding to a coverage of $\Theta = 0.33$. The surface Brillouin zone of the Pd/Au systems is sampled by a Monkhorst-Pack **k**-point set [27] of 9×9×1 for the $\sqrt(3) \times \sqrt(3)$ unit cell, corresponding to 25 **k**-points in the irreducible Brillouin zone. A Methfessel-Praxton smearing [28] of $\sigma = 0.2$ eV has been used in order to get a faster convergence of the electronic structure calculations. The external electric field is treated in the calculations by introducing a planar dipole layer in the middle of the vacuum region [29].

III. HYDROGEN AND CO ADSORPTION IN THE PRESENCE OF A WATER ADLAYER

As a first step, we have determined the adsorption energies of water in different structures on a Pd/Au(111) overlayer system with respect to a free water molecule in the gas phase. Some of the structures are shown in Fig. 1, and the water adsorption energies are listed in table I. It turns out that the water bilayer structure shown in Fig. 1b corresponds to the most stable structure.

We first focus, however, on the adsorption energies E_a of the water monomer and dimer which we have also determined in a (3×3) surface unit cell. For the monomer, this corresponds to a coverage of $\Theta = 1/9$. In Fig. 1a, the calculated equilibrium structures of the adsorbed water monomer and dimer are shown. The adsorption energies in the (3×3) surface unit cell are -0.316 eV and -0.854 eV, respectively.

In order to disentangle the different contribution to the adsorption energy of the water dimer, we determine the energy difference $\Delta E_{\mathrm{dimer}}$ between the adsorption energies of the water dimer and two isolated water monomers which corresponds to the energy gain upon the binding of a water dimer on the metal:

$$\begin{aligned} \Delta E_{\mathrm{dimer}} &= E_{\mathrm{a}}^{\mathrm{dimer}} - 2 \times E_{\mathrm{a}}^{\mathrm{monomer}} \\ &= -0.854\ \mathrm{eV} - 2 \times (-0.316\ \mathrm{eV}) = -0.222\ \mathrm{eV} \end{aligned} \quad (1)$$

We find that the dimer binding on the surface is weaker than the binding in the free dimer, $E_{\mathrm{H_2O-H_2O}} = -0.246$ eV. This could mean that the hydrogen bond between the water molecules becomes weaker by the adsorption on the Pd/Au(111) overlayer system. This is in contrast to H_2O adsorption on Pt(111) [8].

However, there is also another interpretation possible. The adsorption energy of the dimer $E_{\mathrm{a}}^{\mathrm{dimer}}$ can be divided into two parts: the interaction of the single water molecules with the metal $E'_{\mathrm{H_2O-M}}$ which is not necessarily the same as the interaction of a water monomer with metal $E_{\mathrm{H_2O-M}} = E_{\mathrm{a}}^{\mathrm{monomer}}$, and the water-water interaction energy $E'_{\mathrm{H_2O-H_2O}}$:

$$E_{\mathrm{a}}^{\mathrm{dimer}} = 2 \times E'_{\mathrm{H_2O-M}} + E'_{\mathrm{H_2O-H_2O}} \quad (2)$$

If we now consider the adsorption energy of the water dimer not with respect to free water molecules but with respect to the free water dimer, we obtain

$$E_{\mathrm{a}}^{\prime\,\mathrm{dimer}} = E_{\mathrm{a}}^{\mathrm{dimer}} - E_{\mathrm{H_2O-H_2O}} = -0.854\ \mathrm{eV} - (-0.246\ \mathrm{eV}) = -0 \quad (3)$$

This means that the binding energy per water molecule on the metal of $E'_{\mathrm{H_2O-M}} = 0.608/2$ eV $= 0.304$ eV is less than the binding energy of a single water molecule of 0.316 eV which suggests that the water-metal interaction becomes weaker by increasing the number of water molecules on the metal surface. We admit that the energy differences are almost too small to be meaningful considering the accuracy of the DFT calculations. However, our interpretation is supported by our results for the water bilayer structures for which the energy differences are much larger. If we evaluate the adsorption energy of a water bilayer with respect to a free water bilayer, we only obtain a binding energy of about 0.12 eV per water molecule on Pd/Au(111), i.e. most of the energy gain upon the formation of the water bilayer of the metal

TABLE I: H_2O adsorption energies in eV/H_2O for different coverages θ). The energies were obtained using ultrasoft pseudopotentials. The notation of the structures at a water coverage of $\theta_{H_2O} = 2/3$ refers to Fig. 1.

θ_{H_2O}	1/9	1/4	1/3	1/2	1	3/4	**2/3**(b)	2/3(c)	2/3(d)
$E_{ads}^{H_2O}$ (eV/H_2O)	-0.316	-0.308	-0.295	-0.419	+3.135	-0.465	**-0.528**	-0.499	-0.327

overlayer is due to the water-water interaction, and the water-metal interaction is reduced with respect to the adsorption of a single water molecule.

According to table I, the water bilayers in a $\sqrt{3} \times \sqrt{3}R30°$ structure with a water coverage of $\theta_{H_2O} = 2/3$ are the most stable ones. They correspond to a hexagonal ice(Ih) bilayer with an hydrogen atom of every second water molecule either pointing towards or away from the surface, respectively (see Figs. 1b,c). The H-down bilayer is slightly more stable than the H-up bilayer. The water molecules are located basically above the Pd atoms. We note, however, that there is no strong site preference for the water bilayer. If the water molecules are shifted to three-fold hollow positions, the adsorption energies are only reduced by 4% and 8% for the H-down bilayer and the H-up bilayer, respectively. This confirms that the interaction of the water molecules in the ice-like structure with the metal surface is weak. The half-dissociated water bilayer is less stable by about 0.2 eV per water molecule. Hence we can definitely rule out that the partial dissociation of water on Pd/Au(111) is stable.

It should be noted, however, that the calculated sublimation energy of water in a 32-molecule per cell model of ice-Ih, $E_{sub} = -0.712$ eV (ultrasoft pseudopotentials) and $E_{sub} = -0.666$ eV (PAW), is more negative than all calculated water adsorption energies on Pd/Au(111) in table I (see also Ref. [6]). As a consequence, the considered water adlayers would not be thermodynamically stable with respect to a three-dimensional ice cluster. The reason is that the lateral lattice constant of the pseudomorphic Pd/Au(111) overlayer is slightly larger compared to the water-water distance in ice. In order to find a stable water adlayer structure, larger surface unit cells have to be considered such as, e.g., $\sqrt{37} \times \sqrt{37}$ or $\sqrt{39} \times \sqrt{39}$, as in the case of water on Pt(111) [9, 10]. Since we are here mainly concerned with coadsorption and electric field effects that do not strongly depend on small changes of the water-water distance, we did not pursue this issue in more detail.

After determining the stable water structure on Pd/Au(111), we have calculated the adsorption energies of atomic hydrogen and CO in the presence of the H-down and H-up water bilayer on the threefold hollow fcc and hcp sites and on the top site. These energies are listed in Table II and compared to the corresponding results on the clean surface. The results show that the most favorable sites for hydrogen and CO are not changed by the presence of the water. The relaxed adsorption geometries are shown in Fig. 2. The CO adsorption induces a shift of the water bilayer structure from the on-top adsorption positions to three-fold hollow positions. This indicates that the CO-water repulsion is larger than the H-water repulsion. However, the most important issue is that the change of the hydrogen and CO adsorption energies at their most stable positions is below 35 meV (5%) and 200 mev (10%), respectively.

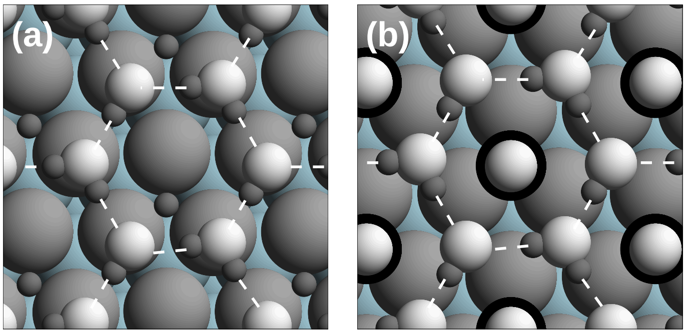

FIG. 2: The relaxed adsorption geometry of hydrogen (a) and CO (b) on the fcc hollow sites in the presence of the water. While a on-top site is more favorable for water molecules in (a) a shifted water bilayer is more favorable in (b).

The slight modification of the hydrogen and CO adsorption energies by the presence of a water adlayer suggests that theoretical studies of the energetics of hydrogen and CO adsorption on clean metal surfaces are also qualitatively and even semi-quantitatively meaningful for the specific hydrogen and CO adsorption in electrochemistry. The reason for this small change is the relatively weak binding of water to Pd/Au(111) which does not significantly perturb the electronic structure of the substrate and thus does also not affect the co-adsorbate-substrate bonds too much. It should be noted, however, that the adsorption kinetics will of course be strongly modified by the presence of the water.

The H-down and H-up water bilayers have a reversed dipole moment along the surface normal. Comparing the

TABLE II: Hydrogen and CO adsorption energies in eV at high symmetry sites in the presence of the water H-down and H-up bilayer and on the clean surface.

	H adsorption energies (eV)		
	H-down bilayer	H-up bilayer	clean
Fcc	-0.661	-0.660	-0.690
Hcp	-0.596	-0.595	-0.655
On-top	0.155	—	0.075
	CO adsorption energies (eV)		
Fcc	-1.831	-1.894	-2.023
Hcp	-1.866	-1.923	-2.043
On-top	-1.243	-1.317	-1.413

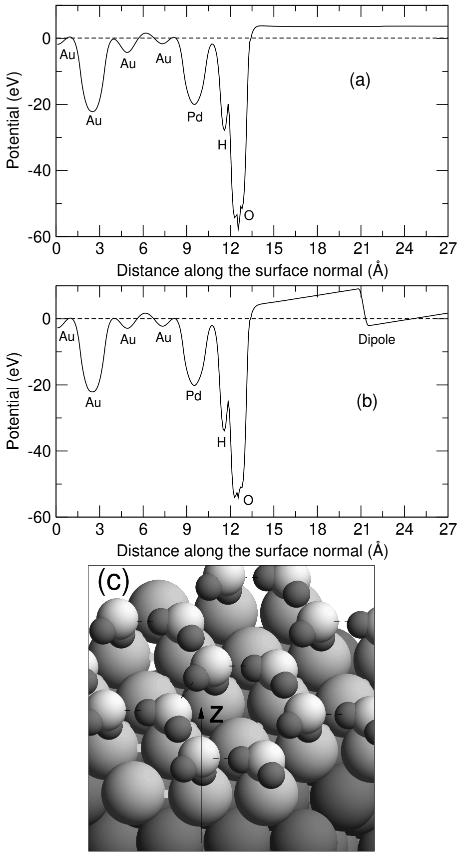

FIG. 3: Effective potential along the surface normal z which passes through the water molecule for (a) zero external field, (b) $E = -0.7$ V/Å, (c) illustrates the location of the z axis.

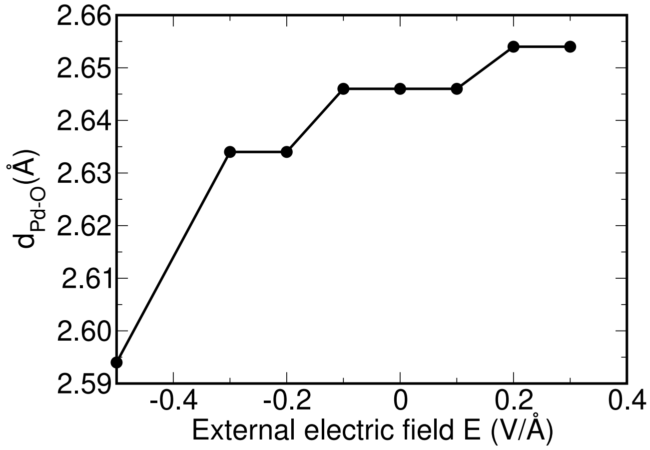

FIG. 4: Distance of the oxygen atom $d_{\mathrm{Pd-O}}$ of the water molecule from the surface in Å as a function of the external electric field.

hydrogen and CO adsorption energies for these two water structures allows to estimate the dipole-dipole interaction between the co-adsorbates. The comparison between the first and second column of Table II shows that the hydrogen adsorption energies are basically independent from the specific form of the water bilayer, and the CO adsorption energies are only changed by about 60 meV. This again confirms the weak interaction between water and hydrogen or CO.

IV. WATER ADSORPTION IN THE PRESENCE OF AN EXTERNAL ELECTRIC FIELD

In an recent experiment addressing the water adsorption on Ag(111) it was shown that the electric field induced by the tip of a scanning tunneling microscope (STM) may lead to the reorientation of adsorbed water molecules [30]. In an independent first-principles study on water adsorbed over a charged Ag(111) surface, Sanchez [31] showed that there is a gradual change in the angle between the water molecule plane and the surface plane by 180° for a surface charge density ranging from 15.7 to -15.7 μC/m^2. As the electric field induced by the tip is of the order of 0.1 V/Å, a charge density of this order of magnitude exists during STM imaging [30]. These findings are in agreement with the results of surface X-ray scattering experiments [32, 33] which also found a surprisingly large inward contraction of the water molecules for positive electrode potential.

The water-metal interface in the presence of an electric field has so far been studied theoretically mainly using empirical potentials [34, 35]. Here we study the water adsorption on Pd/Au(111) in the presence of an external electric field in a first-principles framework by introducing a planar dipole layer in the middle of the vacuum region [29].

The effective potential along the surface normal trough the water molecule in the H-down bilayer structure on Pd/Au(111) is shown in Fig. 3 in the absence of any additional external field and for a strong electrostatic field of $E = 0.7$ V/Å, respectively. The positions of the Au and Pd atoms, of the water molecule and the dipole layer are indicated in the figure and also illustrated in Fig. 3c. In the field-free case, the potential above the slab is larger than below the slab. This is a consequence of the fact that the slab is not symmetric which introduces a net dipole moment of the slab. If an external electric field is applied, the effective potential within the slab hardly changes, as a comparison of Fig. 3a and b indicates, since the field is very effectively screened by the metal. This means that the potential mainly falls off in the vacuum region. It also means that the exact external electric field at the position of the water layer is hard to specify.

In order to study a probable rotation of the water molecules on the metal surface from an H-down to an H-up configuration we first applied an external electric field ranging from $E = -0.7$ to $E = 0.7$ V/Å and relaxed the water structure. Because of the presence of the external field, the water molecules are attracted towards or repelled from the surface, depending on the sign of the electric field. The displacement of the water layer, however, is below 0.05 Å for electric field strengths up to

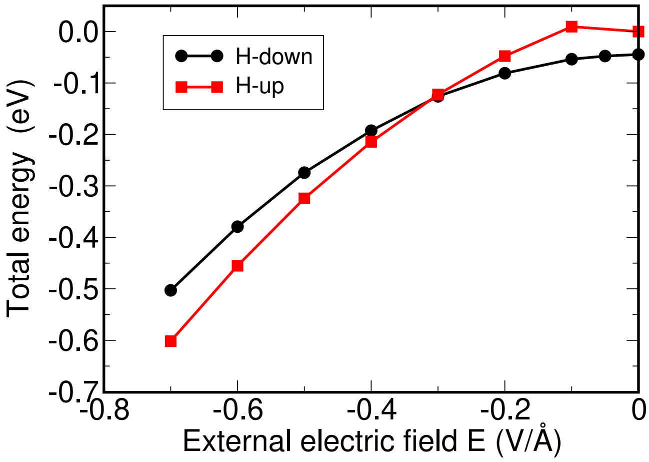

FIG. 5: Change of the total energy of the H-down and H-up water bilayers as a function of the external electric field. The energy zero corresponds to the H-up structure without any external electric field.

0.5 V/Å, as Fig. 4 demonstrates where the distance of the oxygen atom from the Pd layer is plotted as a function of the electric field. Thus we do not find any significant compression of the water layer in the presence of an external electric field, in contrast to the experiment [32, 33] but in agreement with previous theoretical studies [35]

Furthermore, we could not find any rotation of the H-down bilayer structure upon the relaxation of the water bilayer. This does not mean that the electric field does not induce a rotation, it just means that the rotation of the bilayer is hindered by an activation barrier. This is confirmed if we compare the stability of the H-down and the H-up bilayer as a function of the external electric field. We have calculated the total energy of both the H-down and the H-up bilayer water structure on the Pd/Au(111) surface as a function of the external electric field. The external field was varied from $E = -0.7$ V/Å to $E = 0.3$ V/Å.

The results for the negative electric field are shown in Fig. 5. For these fields, the total energy of both water bilayer structures decreases. The energy maximum for the H-up structure at $E = -0.1$ V/Å is not significant within the accuracy of the calculations; it is probably caused by the different numerical treatment with and without external electric field. The most important result is the change in the stability of the structures as a function of the electric field. While without any external electric field the H-down bilayer structure is stable, for external electric fields more negative than -0.3 V/Å the H-up bilayer becomes energetically favorable. Thus we obtain the same qualitative results as has already been found experimentally for water on Ag(111) [30, 33], namely that an external electric field can induce the rotation of adsorbed water molecules. This reorientation is obviously a consequence of the polar structure of the water molecules.

V. CONCLUSIONS

We have extended previous calculations for the properties of Pd/Au bimetallic surfaces in order to contribute to the understanding of fundamental processes occuring at the liquid-solid interface on a Pd/Au(111) electrode. We have determined the most stable structure of a water layer on the surface which is a water bilayer in the hexagonal ice(Ih) structure in the H-down configuration with one hydrogen atom of every second water molecule pointing towards the surface. In addition, we calculated the adsorption energy of atomic hydrogen and CO in the presence of the water bilayer. Since water is only weakly interacting with the substrate and the admolecules, their binding energies are lowered by less than 10% by the presence of the water bilayer. Because of this small perturbation of the adsorption energies by the presence of a water bilayer, calculated adsorption energies at the solid-gas interface might also be meaningful for the solid-liquid interface. If an external negative electric field is applied, the stability of the H-down and H-up bilayer is reversed when the field is sufficiently strong. However, we did not find any significant compression of the water bilayer due to the presence of the external electric field.

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