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Hydrogen adsorption energies on bimetallic overlayer systems at the solid–vacuum and the solid–liquid interface

Ata Roudgar [1], Axel Groß *

Physik-Department T30, Technische Universität München, James-Franck-Str. 1, D-85747 Garching, Germany

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Abstract

Atomic hydrogen adsorption energies on bimetallic overlayer systems have been determined by periodic density functional theory calculations within the generalized gradient approximation. On the pseudomorphic Pd/Cu(1 1 1) surface, both the substrate interaction and the lattice compression of the Pd overlayer lead to smaller hydrogen binding energies. For pseudomorphic Cu/Pd(1 1 1), on the other hand, the strong Cu–Pd interaction results in larger binding energies. Hence, both Pd/Cu(1 1 1) and Cu/Pd(1 1 1) exhibit an intermediate behavior between pure Cu(1 1 1) and pure Pd(1 1 1). In addition, we have determined the atomic hydrogen adsorption on Pd/Au(1 1 1) in the presence of a water overlayer. The hydrogen adsorption energies are changed by less than 60 meV by the most stable H_2O bilayer compared to the clean surface. This indicates that theoretical adsorption studies at the solid–vacuum interface might also be relevant for the solid–liquid interface.

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1. Introduction

The study of bimetallic surfaces has recently been of strong interest [1–4]. Bimetallic systems offer the possibility to prepare specific surface compositions and structures. This might be used to influence catalytic and other properties of the surface in a well-defined way [4]. Hence, an understanding of the electronic factors determining the reactivity of bimetallic surfaces could lead to the rational design of better catalysts. Bimetallic systems are also of particular interest in electrochemistry [5] since the catalytically active material has to be placed on a conductive electrode.

In the case of pseudomorphic overlayers, two effects influence the reactivity of the bimetallic

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* Corresponding author. Present address: Department of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany. Tel.: +49 731 50 22810; fax: +49 731 50 22819.

E-mail address: axel.gross@uni-ulm.de (A. Groß).

[1] Present address: Chemistry Department, Simon Fraser University, Burnaby, BC, Canada V5A 1S6.

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surfaces: the direct electronic interaction between substrate and overlayer, and geometric strain effects due to the lattice mismatch of substrate and overlayer. Both effects can be disentangled experimentally only if the pseudomorphic structure of the overlayers is preserved for a film thickness of several layers as for example in the system Pt/Ru(0001) [1].

However, often the strain of thick overlayers is relieved by the formation of dislocations making an analysis of the microscopic origins of a modified reactivity of the bimetallic system rather cumbersome. Therefore, electronic structure calculations are rather helpful since they allow to separate strain from substrate interaction effects by addressing model systems that cannot be realized experimentally.

In electrochemistry, Pd overlayers deposited on Au single crystal surfaces have served as a model system of a transition metal deposited on an inert noble metal electrode [6–10]. The electrocatalytic activity of the Pd/Au overlayers with respect to hydrogen adsorption/desorption [9,11] and to the electro-oxidation of small organic molecules such as formaldehyde [9] and formic acid [12] are very sensitive to the layer thickness of the deposited Pd films. Furthermore, significantly enhanced hydrogen evolution rates have been found on small Pd islands deposited on Au(111) in an electrochemical STM set-up [6].

We have recently studied atomic hydrogen and CO adsorption on Pd/Au bimetallic surfaces by performing density functional theory (DFT) calculations [13,14]. 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 an upshift of the d-band which in agreement with the predictions of the d-band model [15,16] leads to a stronger adsorbate bonding. Furthermore, we have determined H and CO adsorption energies on Pd_n clusters with $n \leqslant 10$ deposited on Au(111) [17]. Interestingly enough, we find that the adsorption 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 relatively strong cluster-substrate interaction.

We have now extended these studies into two directions. In order to establish chemical trends, we have replaced the Au(111) substrate by another noble metal substrate, Cu(111). Pd/Cu bimetallic surfaces are also interesting from a catalytic point of view as far as the CO oxidation and hydrogenation are concerned [18]. Besides, both H/Cu and H/Pd have served as model systems for the study of dissociative adsorption in surface science [19–22]. Usually the bimetallic PdCu system forms surface alloys [23,24]. Still we have studied the pseudomorphic overlayer systems in order to establish chemical trends. Cu has a much smaller lattice constant than Au; thus, pseudomorphic Pd overlayers on Cu(111) are compressed by 8%. We find that this compression does in fact lead to smaller adsorption energies. However, also the Pd/Cu interaction results in weaker binding in contrast to the Pd/Au system. As far as the hydrogen adsorption on the overlayer system with the opposite stacking sequence, a pseudomorphic Cu overlayer on Pd(111), is concerned, we find that the lattice expansion of Cu(111) has a negligible influence on the hydrogen adsorption energy, in agreement with a previous study [25]. However, for this stacking order the Cu–Pd interaction leads to a larger binding of hydrogen.

In all these calculations, the adsorption energies are determined at the solid–vacuum interface. The question arises whether these calculations are of relevance for the electrochemical situation of the solid–liquid interface. In order to address this question, we have calculated hydrogen adsorption energies in the presence of a water layer on Pd/Au(111). We find that the hydrogen adsorption energies are only slightly modified by the presence of water. Thus, calculated adsorption energies at the solid–vacuum interface can indeed be meaningful for an understanding of the binding at an electrochemical electrode.

This paper is structured as follows. First, we give an overview about the computational methods used. We will then briefly summarize the results for the Pd/Au overlayer system before we discuss in detail the hydrogen adsorption on bimetallic PdCu surfaces. Finally we address the hydrogen adsorption on Pd/Au(111) in the presence of a water adlayer and close the paper with some concluding remarks.

2. Computational method

We have performed periodic DFT calculations using the Vienna ab initio simulation package (VASP) [26]. The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the Perdew–Wang (PW-91) functional [27]. We have mainly employed ultrasoft pseudopotentials [28,29] in our calculations. In the case of the water adlayers, we have also used the projector augmented wave (PAW) method [30,31] 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 and the Pd/Cu systems cutoff energies of 200 eV and 235 eV, respectively, 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 structures have been modeled by a slab of four layers of the substrate on which up to three overlayers have been deposited. All layers structures are separated by at least 10.5 Å of vacuum. The three 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.

All reported hydrogen adsorption energies are determined in a (2×2) surface unit cell corresponding to a coverage of $\Theta = 0.25$. The surface Brillouin zone of the Pd/Au systems is sampled by a Monkhorst–Pack **k**-point set [32] of $7 \times 7 \times 1$ for the 2×2 unit cell, corresponding to 8 **k**-points in the irreducible Brillouin zone. Due to the low density of states of Cu close to the Fermi energy $23 \times 23 \times 1$ **k**-points corresponding to 56 **k**-points in the irreducible Brillouin zone have been used for the Pd/Cu systems. A Methfessel–Praxton smearing [33] of $\sigma = 0.2$ eV has been used in order to get a faster convergence of the electronic structure calculations.

The hydrogen adsorption energies are determined via

$$E_{\text{ads}} = E_{\text{slab+H}} - \left(E_{\text{slab}} + \tfrac{1}{2}E_{\text{H}_2}\right), \qquad (1)$$

where E_{slab} and $E_{\text{slab+H}}$ are the total energies of the slab without and with the adsorbed hydrogen. For the hydrogen binding energy E_{H_2} in the gas phase we have taken the calculated GGA value of 4.550 eV. Note that the energy gain upon adsorption corresponds to a negative adsorption energy. In the following, we will denote by binding energy the negative of the adsorption energy.

The calculated trends in the adsorption energies will be analyzed with respect to the underlying electronic structure using the d-band model [15]. In this model, the whole d-band is assumed to act as a single electronic level located at the center of the d-band ϵ_{d}. According to the d-band model [34,35], a shift in the position of the d-band center position $\delta\varepsilon_{\text{d}}$ is linearly related to changes in the chemisorption energies δE_{chem}

$$\delta E_{\text{chem}} = \frac{V^2}{\left|\varepsilon_{\text{d}} - \varepsilon_{\text{a}}\right|^2}\delta\varepsilon_{\text{d}}, \qquad (2)$$

where ε_{a} is the adsorbate level and V is the d-band coupling matrix element between adsorbate and the surface metal atom.

A reduced coordination or a smaller overlap between the metal orbitals leads to a smaller d-band width and to an upshift of the d-band due to charge conservation if the d-band is more than half-filled [36,37]. This model thus gives a natural explanation for the preferential adsorption on step edge atoms [35,38–40] or expanded surfaces [36].

3. Results

3.1. Pd/Au overlayers

In order to facilitate the discussion of the chemical trends in the adsorption on bimetallic surfaces, we will briefly summarize the results obtained for the Pd_n/Au(1 1 1) overlayers [13,14]. In Fig. 1, the hydrogen adsorption energies are plotted as a

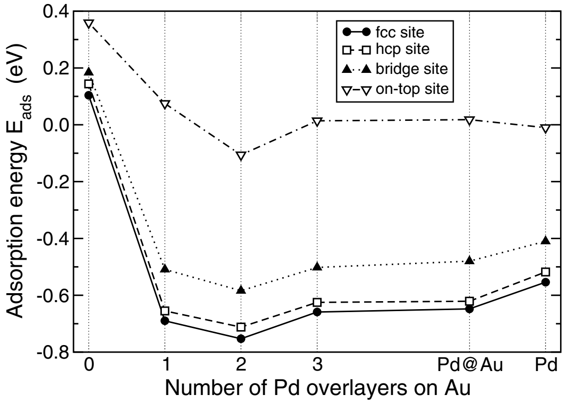

Fig. 1. Atomic hydrogen adsorption energies as a function of the number of Pd overlayers on Au(1 1 1) for different adsorption sites on the (1 1 1) at a coverage of $\theta = 0.25$. The pure Pd substrates with the lateral lattice constant of Au ($a = 4.18$ Å) and Pd ($a = 3.96$ Å) are labeled by Pd@Au and Pd, respectively.

function of the number of Pd overlayers on Au(1 1 1). The pure Pd substrates with the lateral lattice constant of Au ($a = 4.18$ Å) and Pd ($a = 3.96$ Å) are labeled by Pd@Au and Pd, respectively. Pseudomorphic Pd films deposited on Au(1 1 1) are expanded by 5%. Such an expansion leads to larger hydrogen binding energies at the higher-coordinated adsorption sites of the (1 1 1) surface in agreement with the predictions of the d-band model. However, reduced binding energies for expanded surfaces have also been found, for example at the top site of strained copper surfaces [25]. It is caused by the strong modification of the substrate density of states for H adsorption above the top site.

Furthermore, we see that the adsorption energies on three Pd overlayers on Au(1 1 1) are almost indistinguishable from the results for the expanded pure Pd(1 1 1) substrate denoted by Pd@Au in Fig. 1. This means that the electronic effect of the substrate is limited to the first two Pd overlayers. For Pd/Au(1 0 0), we have found that there is still some influence of the substrate up to the third layer which is caused by the fact that the more open (1 0 0) surface has a smaller layer spacing than the close-packed (1 1 1) surface.

The direct interaction of the substrate with the overlayers leads to a further increase of the hydrogen binding strength. As an analysis of the local density of states reveals, this increase is reflected by an upshift of the Pd d-band because of its relative weak interaction with the Au substrate [13]. Interestingly, the binding energies of hydrogen show a maximum for two Pd overlayers on Au. This maximum is not reflected by an extremum of the d-band center position. It is rather caused by the fact that on one Pd overlayer there is still some indirect unfavorable interaction between the adsorbate and the Au substrate which is no longer operative for two Pd overlayers on Au. It should be noted that all the trends in the adsorption of hydrogen on the Pd/Au overlayers have also been found in the case of CO adsorption.

3.2. Pseudomorphic Pd/Cu and Cu/Pd overlayers

In our study of the atomic and molecular binding on pseudomorphic Pd/Au overlayers we have found that both the lattice expansion of the Pd overlayers as well as the relatively small interaction of the Pd overlayer with the noble metal substrate lead to higher binding energies. In order to establish chemical trends in the adsorption strength on pseudomorphic overlayer systems, we decided to replace the Au substrate by another noble metal, namely Cu. While pseudomorphic Pd overlayers on Au are expanded by 5%, they are compressed by 8% on Cu. Due to this strong suppression, pseudomorphic Pd/Cu overlayers are not stable. They rather form an alloy [23,24], as Fig. 2 confirms. Here the surface alloy formation energy,

$$E_{\mathrm{surf}} = \frac{\left(E^{\mathrm{slab}}_{\mathrm{Pd}_x\mathrm{Cu}_y/\mathrm{Cu}} - E^{\mathrm{slab}}_{\mathrm{Cu}} - yE^{\mathrm{coh}}_{\mathrm{Cu}} - xE^{\mathrm{coh}}_{\mathrm{Pd}}\right)}{N_{\mathrm{sa}}}, \quad (3)$$

is plotted for an number of different $\mathrm{Pd}_x\mathrm{Cu}_y$ surface compositions. N_{sa} is the number of surface atoms per surface unit cell, i.e., $N_{\mathrm{sa}} = x + y$. $E^{\mathrm{coh}}_{\mathrm{Cu}}$ and $E^{\mathrm{coh}}_{\mathrm{Pd}}$ are the cohesive energies of Cu and Pd, respectively, which means that we have assumed that both Cu and Pd are in equilibrium with their corresponding bulk reservoirs. For a pure Cu surface, E_{surf} according to Eq. (3) is zero, i.e., the energies plotted in Fig. 2 are defined with respect to the pure Cu surface. The fact that the value for Cu in Fig. 2 is not exactly zero is due to the finite thickness of the Cu slab in the calculations.

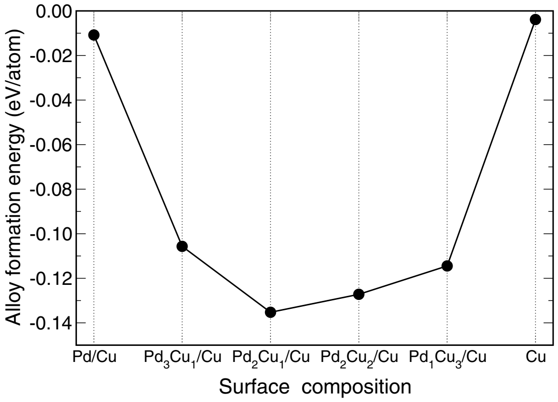

Fig. 2. Surface energy in eV/atom according to Eq. (3) for different surface compositions of PdCu alloys on Cu(1 1 1). The energy zero corresponds to a Cu layer on Cu(1 1 1), i.e., to a pure Cu(1 1 1) surface.

As Fig. 2 demonstrates, among the ordered surface alloys considered by us the Pd_2Cu_1 alloy is the most stable. The fact that Pd and Cu form alloys indicates that there is a strong attractive interaction between Pd and Cu. Interestingly enough, the pseudomorphic Pd overlayer on Cu(1 1 1) is even more stable than the pure Cu(1 1 1) surface, in spite of the strong compression of the Pd overlayer. We have also determined the adsorption energies per atom of a quarter monolayer of Pd and Cu atoms on Cu(1 1 1). We find that $E^{\mathrm{ads}}_{\mathrm{Pd/Cu(1\,1\,1)}} = -3.011$ eV/atom and $E^{\mathrm{ads}}_{\mathrm{Cu/Cu(1\,1\,1)}} = -2.704$ eV/atom. This shows that Pd atoms are in fact more strongly bound to Cu(1 1 1) than Cu atoms. Indeed, we have also found the same trend favoring alloying for the Pd(1 1 1) substrate. Cu atoms are more strongly bound to a Pd(1 1 1) surface than Pd atoms.

As far as the Cu–Pd bulk alloy system is concerned, the phase diagram at higher temperatures is dominated by a disordered solid solution in the fcc structure. Both theory and experiment give a maximum in the alloy formation energy at 1350 K for a Cu concentration of 60% [41]. At lower temperatures, three ordered phases exist based on the stoichiometric Cu_3Pd and CuPd phases. Although surface alloys can show unexpected properties compared to bulk alloys [41], the Cu–Pd bulk alloy phase diagram demonstrates the strong tendency of Cu and Pd for intermixing which is confirmed by our calculations for ordered surface alloys.

Although PdCu surface alloys are more stable than a pure Pd/Cu overlayer, we have still determined the hydrogen adsorption energies on the pseudomorphic overlayer system in order to compare the results with those for the Pd/Au overlayers. Furthermore, small domains of a Pd/Cu overlayer may exist in the submonolayer coverage regime [23]. In Fig. 3, we have summarized the calculated results for the atomic hydrogen adsorption energies on the different high-symmetry sites on pure Cu(1 1 1), on a pseudomorphic Pd overlayer on Cu(1 1 1) (Pd/Cu), on pure Pd(1 1 1) with the lateral Cu lattice constant (Pd@Cu) and on pure Pd(1 1 1).

We first note that the lateral compression of the Pd overlayer by 8% leads to a reduction of the hydrogen binding for the higher-coordinated adsorption sites. This can be well understood in terms of the d-band model. The lateral compression of the Pd overlayer causes a down-shift of the local Pd d-band center [36,37] which results in smaller binding energies. In Fig. 4, we have plotted the local d-band center for the different surface structures of Fig. 3. Indeed the d-band center of Pd shifts down by more than 0.5 eV upon 8%

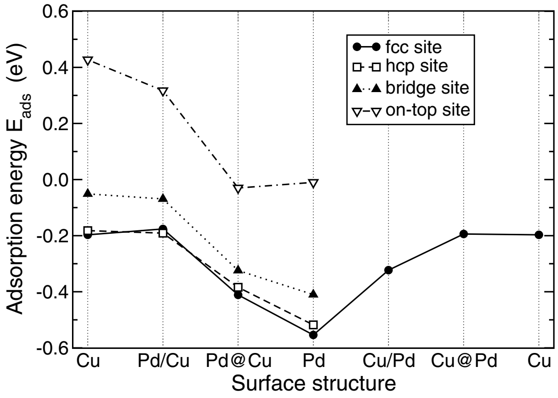

Fig. 3. Atomic hydrogen adsorption energy on bimetallic PdCu surfaces for a quarter monolayer hydrogen coverage, namely on pure Cu(1 1 1), on a pseudomorphic Pd overlayer on Cu(1 1 1) (Pd/Cu), on pure Pd(1 1 1) with the lateral Cu lattice constant (Pd@Cu), on pure Pd(1 1 1), on a pseudomorphic Cu overlayer on Pd(1 1 1) (Cu/Pd), and on pure Cu(1 1 1) with the lateral Pd lattice constant (Cu@Pd).

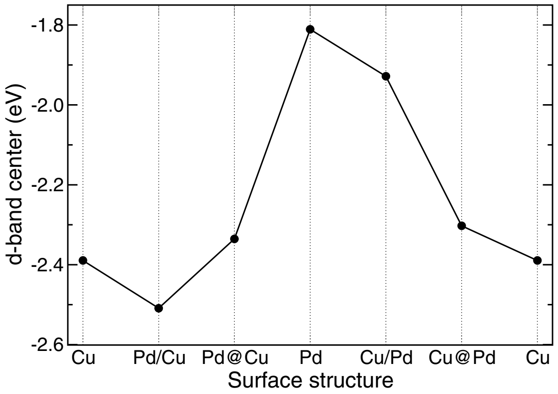

Fig. 4. Position of the local d-band center of the topmost layer on bimetallic PdCu surfaces. The considered structures are the same as in Fig. 3.

compression. Note that the hydrogen adsorption energy on the on-top site shows the opposite trend as the higher-coordinated sites. This trend has been obtained before for strained copper [25] and strained Pd surfaces [13,14]. At the on-top site, there is a strong electronic coupling between adsorbate and substrate, which makes the d-band model no longer fully applicable.

In contrast to the Pd/Au system, however, the interaction of Pd with the Cu substrate leads to a further down-shift of the Pd d-band center which is reflected in the lower hydrogen binding energies on the Pd/Cu(1 1 1) overlayer compared to the pure compressed Pd surface. In fact, the hydrogen adsorption energies on the Pd/Cu(1 1 1) overlayer are very similar to the hydrogen adsorption energies on the pure Cu(1 1 1) substrate. A corresponding result has also been found for CO adsorption on a Pd/Cu(1 1 1) overlayer in DFT-GGA calculations [42]. Although Au and Cu are both noble metals, it is important to realize that the coupling of their d-bands to Pd is quite different. While the Au d-band center is 1.6 eV below the d-band center of Pd, the Cu d-band center is lower by only 0.6 eV (see Fig. 4). Due to the large energetic overlap between the Pd and Cu d-bands, there is a strong hybridization between both bands, as an analysis of the local d-band density of states confirms. This hybridization is also reflected by the strong Pd–Cu interaction energies.

In order to round up the study of the CuPd overlayer system, we have also addressed the opposite stacking sequence, a pseudomorphic Cu overlayer on Pd(1 1 1). In contrast to the Pd/Cu(1 1 1) system, at room temperature Cu/Pd(1 1 1) has been found to grow in a layer-by-layer fashion for at least the first two layers [43]. Furthermore, underpotential deposition of Cu on Pd(1 1 1) in sulfuric acid solution has been observed [44,45]. Calculated atomic hydrogen adsorption energies at the fcc hollow site of a pseudomorphic Cu overlayer on Pd(1 1 1) and on a pure Cu substrate with the lateral lattice constant of Pd(1 1 1) are included in Fig. 3. We first note that the geometric expansion of the Cu substrate has no influence on the hydrogen adsorption energies although the d-band center has moved upwards (see Fig. 4), as we have already found in a previous study [25]. The strong coupling between Cu and Pd for the Cu/Pd(1 1 1) overlayer system, on the other hand, causes a significant upshift of the Cu d-band center and larger hydrogen binding energies.

Summarizing the section about the CuPd bimetallic surfaces, one might say that both Pd/Cu(1 1 1) and Cu/Pd(1 1 1) exhibit an intermediate behavior between pure Cu(1 1 1) and pure Pd(1 1 1) which is caused by the strong interaction between Pd and Cu. This is in contrast to the Pd/Au overlayer system where Pd/Au becomes more reactive than pure Pd. The Pd/Cu(1 1 1) overlayer shows adsorption properties similar to Cu(1 1 1) while the Cu/Pd(1 1 1) properties are closer to those of Cu(1 1 1) than Pd(1 1 1). This is mainly caused by the fact that the geometric strain hardly influences the adsorption energies on Cu while it has a large effect on Pd.

3.3. Hydrogen adsorption in the presence of a water adlayer

All results presented so far have been obtained at the solid–vacuum interface. Bimetallic surfaces have been studied intensively in the field of heterogeneous catalysis, 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. The realistic incorporation of any electrolyte in electronic structure calculations is not trivial. Recently, Desai et al. have investigated the effect of water molecules on the deprotonation of acetic acid over Pd(1 1 1) [46] using periodic density functional calculations. Here we follow a similar approach in order to study the influence of a water adlayer on the hydrogen adsorption energies on a bimetallic Pd/Au(1 1 1) surface.

Just recently, there has been a strong interest in the structure of water layers on metal surfaces [47–52]. 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 [53]. However, recently Feibelman has proposed that on the relative reactive Ru(0 0 0 1) surface, the water molecules do not remain intact [49]. Instead, the water bilayer becomes partially dissociated forming a *half-dissociated* bilayer.

Hence, as a first step we have determined the stable structure of water molecules adsorbed on a Pd/Au(1 1 1) overlayer system. The calculated water adsorption energies are listed in the second column of Table 1. In Fig. 5a, the calculated equilibrium structures of the adsorbed water monomer and dimer are shown. Their adsorption energies, determined in a (3×3) surface unit cell, are −0.316 eV and −0.427 eV, respectively. In contrast to H_2O adsorption on Pt(1 1 1) [47], we find that the H-bond energy in the adsorbed dimer $E_{\text{H-bond}} = (E_{\text{ads}}[\text{dimer}] - E_{\text{ads}}[\text{monomer}]) \times 2 = (-0.427-(-0.316)) \times 2 = -0.222$ eV is less than the hydrogen bond energy in the free dimer, $E_{\text{H-bond}} = -0.246$ eV (all energies in eV/H_2O molecule). This means that the hydrogen bond between the water molecules becomes weakened by the adsorption on the Pd/Au(1 1 1) overlayer system.

Table 1

H_2O adsorption energies in eV/H_2O and H adsorption energies ($\theta_H = 1/4$) in eV/atom on Pd/Au(1 1 1)

θ_{H_2O}	$E_{\text{ads}}^{H_2O}$ (eV/H_2O)	$E_{\text{ads}}^{\text{H fcc}}$ (eV/atom)	$E_{\text{ads}}^{\text{H hcp}}$ (eV/atom)
1/4	−0.308	−0.634	−0.592
1/3	−0.295	−0.606	−0.610
1/2	−0.419	−0.582	−0.602
1	+3.135	–	–
3/4	−0.465	−0.561	–
2/3(b)	**−0.528**	**−0.661**	**−0.596**
2/3(c)	−0.499	–	–
2/3(d)	−0.327	–	–
0	–	**−0.690**	**−0.655**

The energies were obtained using ultrasoft pseudopotentials. For the notation of the structures at a water coverage of $\theta_{H_2O} = 2/3$, see Fig. 5.

The considered $\sqrt{3} \times \sqrt{3}R30^\circ$ water structures are plotted in Fig. 5b–d. They correspond to the H-down bilayer, the H-up bilayer, and the half-dissociated water bilayer, respectively, with a water coverage of $\theta_{H_2O} = 2/3$ each. According to Table 1, the H-down bilayer structure is the most stable one while 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(1 1 1) is stable. However, it should be noted that the calculated sublimation energy of water in a 32-molecule per cell model of ice-Ih, $E_{\text{sub}} = -0.712$ eV (ultrasoft pseudopotentials) and $E_{\text{sub}} = -0.666$ eV (PAW), is more negative than all calculated water adsorption energies on Pd/Au(1 1 1) in Table 1 (see also Ref. [49]). This would mean that the considered water adlayers are not thermodynamically stable with respect to a three-dimensional ice cluster. The reason is that the lateral lattice constant of the pseudomorphic Pd/Au(1 1 1) overlayer is too large 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(1 1 1) [50,51]. Since we are here mainly concerned with the influence of water on the hydrogen adsorption energies, we did not pursue this issue in more detail.

In the third and fourth column of Table 1, the hydrogen adsorption energies at the threefold hollow sites of Pd/Au(1 1 1) in the presence of different water adlayer structures are compared to the case of the clean surface (last line). The most important issue is that the change of the hydrogen adsorption energies for most water structure is below 100 meV. For the most stable water structure, the H-down bilayer, the changes are even below 60 meV which is about 10% of the atomic hydrogen adsorption energy. The reason for this small change is the relatively weak binding of water to Pd/Au(1 1 1) which does not significantly perturb the electronic

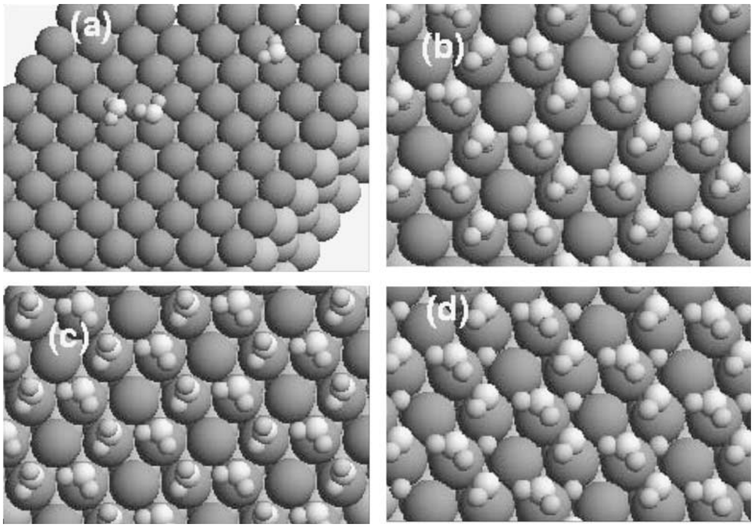

Fig. 5. Water structures on a Pd/Au(1 1 1) overlayer. (a) Equilibrium structure of the water monomer and dimer, (b) H-down bilayer, (c) H-up bilayer, (d) half-dissociated water bilayer.

structure of the substrate and thus does also not effect the hydrogen-substrate bond too much. Still, the polar water molecules induce an additional electric field at the surface. Apparently, these field effects only have a small influence on the hydrogen bonding. The slight modification of the hydrogen adsorption energies by the presence of a water adlayer suggests that theoretical studies of hydrogen adsorption on clean metal surfaces are also qualitatively and even semi-quantitatively meaningful for the specific hydrogen adsorption in electrochemistry.

4. Conclusions

Extending previous studies of the hydrogen and CO adsorption on Pd/Au overlayer systems, we have calculated atomic hydrogen adsorption energies on Pd/Cu(1 1 1) and Cu/Pd(1 1 1). Due to the strong interaction between Pd and Cu, both overlayer systems show intermediate properties between clean Pd(1 1 1) and Cu(1 1 1). Still, the modification of the Pd/Cu(1 1 1) overlayer with respect to pure Pd(1 1 1) is more pronounced since adsorption energies show a stronger strain dependence on Pd than on Cu.

Furthermore, we have studied the influence of the presence of a water adlayer on the hydrogen adsorption energy on Pd/Au(1 1 1). The binding energy of hydrogen is reduced by less than 100 meV because of the relatively weak interaction of water with the Pd/Au(1 1 1) substrate. This suggests that hydrogen adsorption studies at the solid–vacuum interface are also relevant for the interpretation of specific hydrogen adsorption at the solid–liquid interface.

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