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Ab initio studies of a water layer at transition metal surfaces

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This paper presents a detailed study of a water adlayer adsorbed on Pt(111) and Rh(111) surfaces using periodic density functional theory methods. The interaction between the metal surface and the water molecules is assessed from molecular dynamics simulation data and single point electronic structure calculations of selected configurations. It is argued that the electron bands around the Fermi level of the metal substrate extend over the water adlayer. As a consequence in the presence of the water layer the surface as a whole still maintains its metallic conductivity—a result of a crucial importance for understanding the process of electron transfer through the water/metal interface and electrochemical reactions in particular. Our results also indicate that there exists a weak bond between the hydrogen of the water and the Rh metal atoms as opposed to the widespread (classical) models based on purely repulsive interaction. This suggests that the commonly used classical interactions potentials adopted for large scale molecular dynamics simulations of water/metal interfaces may need revision. Two adsorption models of water on transition metals with the OH bonds pointing towards or away of the surface are also examined. It is shown that due to the very close values of their adsorption energies one should consider the real structure of water on the surface as a mixture of these simple “up” and “down” models. A model for the structure of the adsorbed water layer on Rh(111) is proposed in terms of statistical averages from molecular dynamics simulations. © 2005 American Institute of Physics. [DOI: 10.1063/1.1834489]

I. INTRODUCTION

In the last couple of decades advances in the electron density functional theory (DFT) have made it possible to model a variety of physical systems with an explicit treatment of the electronic structure of the matter.^{1–7} Perhaps one of the first subjects to be intensively studied after the introduction of the Car-Parrinello³ (CP) approach to DFT was liquid water.^{8–10} Quite recently another type of DFT-based molecular dynamics (MD) simulations, which differs from the CP method in the treatment of the electronic degrees of freedom, was also successfully applied to study bulk liquid water and the water-vapor interface.¹¹ The results of these so-called first-principles molecular dynamics simulations of liquid water were very promising and an increasing number of groups is now applying the same techniques to study water-metal interfaces in relation, for example, to heterogeneous reactions at transition metal surfaces, (electro)chemical processes, and the process of electron transfer through the interface.^{12–22}

Historically, one of the first and most successful theoretical models for electron transfer processes was proposed by Marcus in the second half of the 1950s.^{23–25} In this theory, the solvent is considered as a *homogeneous medium* with no microscopic (atomic) characteristics. However, recent studies have concluded that the atomic and electronic structures of the solvent may need to be included explicitly in the theoretical model, particularly in the case of the water/metal interfaces.^{26–30} Atomistic simulations, i.e., those accounting

for the atomic and molecular composition of the matter and possibly including the electronic structure, are therefore vital for modeling the interface.^{12,13,26}

Classical MD has been applied to study the microscopic arrangement of water molecules at a metal surface.^{31–33} At this level of theory the interactions between the oxygen and hydrogen atoms of the (often rigid) water molecules and the surface metal atoms are described through pair potentials which are fitted to experimental data or previous theoretical calculations. All atoms are treated as point masses. Most commonly it is assumed that the metal-oxygen interaction has an attractive and a repulsive component, while the metal-hydrogen interaction is *purely repulsive*.³² Recent electronic structure calculations by Feibelman of water adsorbed on Ru(0001) surface at different coverages and surface configurations suggests, however, that the water-metal interaction may be more complicated than previously thought and in certain conditions may lead to the dissociation of the molecule on the surface.^{18,20} A number of other studies considering electron transfer through the interface have also indicated that a water layer on a metal surface possesses an apparent conductivity due to a mixing of oxygen electronic states with the *d* band of the metal substrate.²⁸ This experimentally observed phenomenon, for which there is still only a limited theoretical description, can only be modeled using first-principles simulation techniques.

The present paper deals with self-consistent (i.e., Born-Oppenheimer) DFT-based electronic structure simulations of the water/transition metal surface interface. We investigate the structure and electronic properties of water molecules adsorbed at different coverages on Pt(111) and Rh(111) sur-

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FIG. 1. (a) Surface configuration of perfect water bilayer and the smallest surface unit cell $ABCD$. The substrate is represented through lines connecting the positions of the surface metal atoms. Full circles represent the oxygens of the first water layer (closest to the surface), shaded circles represent the oxygens of the second layer. Hydrogens are given with small circles. (b) Side view of a perfect water bilayer. For clarity only part of the unit cell is shown. (c) Side view of a configuration derived from the original water bilayer by flipping the configuration shown in (b) upside down. $M_{\parallel}$ and $M_{\perp}$ are the two surface atoms with adsorbed water molecules, M_* is the “free” surface atom.

faces, which are among the most commonly used transition metals for heterogeneous (electro)catalytic reactions. The high coverage systems can also be viewed as simplified models for the first water layer at the liquid water/metal interface. The goal of this work is to give a detailed description of the interactions between the water molecules and the metal surface and to provide a theoretical description of the observed conductivity of the water layer.

Both Rh and Pt have a metal-metal distance comparable to the oxygen-oxygen separation in the water dimer and liquid water and this close match presents excellent conditions for the formation of ordered interfacial structures with the water molecules arranged in a $(\sqrt{3} \times \sqrt{3}) R30^\circ$ surface configuration.^{12,13,28,34–42} No experimental evidence for dissociation of water on the clean metal surfaces has been found.⁴⁰

Based on experimental results a simple model for the water adlayer on a metal surface was proposed by Sass *et al.*⁴³ and Doering and Madey⁴⁴ already in the beginning of the 1980s [Figs. 1(a) and 1(b)]. This so-called “bilayer” model consists of two sublayers: (i) water molecules from the first sublayer are chemisorbed on top of the metal atoms [Fig. 1(a), oxygens denoted with black circles], while (ii) molecules from the second sublayer, though still on top, are further away from the surface with one of their hydrogens pointing away from the surface. The molecules from the two sublayers are bonded together through hydrogen bonds.

Recently, however, the validity of the simple model of Doering and Madey⁴⁴ was questioned based on DFT results considering structures in which the free OH bond also points towards the metal surface^{19–22} [Fig. 1(c)] as well as the so-called “reactive wetting” leading to a dissociation of the water molecules on the surface.²⁰ Meng *et al.*¹⁹ also showed that one can identify two types of hydrogen bonds between the water molecules within a bilayer (66% coverage) adsorbed on Pt(111). The simulations however could not distinguish between the two principal structures (OH bond pointing “up” or “down”) due to their close adsorption energies and similar properties.

In the current paper we present a theoretical study of these systems considering in detail the structural and electronic properties and the interactions between the water molecules and the surface. We will show that the unit cell used in the previous simulations by Meng *et al.*¹⁹ is not large enough for an accurate description of the system, a suggestion which was already made by Feibelman.²⁰ Considering the interactions with the surface, we will show that there is a weak attractive interaction between the Rh metal atoms and the hydrogen atoms from the water molecules, a component which is not included in the commonly used classical MD interaction potentials.

The electronic structure of the system will also be evaluated, relating the results to the scanning tunneling microscopy (STM) experimental data of Morgenstern *et al.*,²⁸ who observed that the H_2O bilayer adsorbed on a Pt(111) surface appears as an elevation to the STM. The authors assumed a metallic conductivity of the bilayer, i.e., it is capable of conducting electric current, and supported their experimental data with first-principles computational results. These calculations, however, were performed using a model consisting of a single water molecule adsorbed on a Pt_{10} cluster, which cannot account for the complete structure of the bilayer. In this work we present results for the electronic structure of a periodical surface model, particularly emphasizing the electronic states around the Fermi level (which are the ones capable of carrying current through the system). The spatial distribution of these states is of relevance to the process of charge transfer through the interface and is of importance in the development of theoretical models for electron tunneling and STM, in particular,^{45,46} as well as electrochemical reactions.^{26–29,47–49} Although in the Kohn-Sham (KS) approach,² employed also in this work, the exact wave function is not known, the KS wave functions can be used to describe the electronic properties of the molecules in a manner similar to the traditional molecular orbital approach.^{50–55}

II. COMPUTATIONAL DETAILS

The simulations were carried out using the DFT package VASP (Refs. 56 and 57) with ultrasoft Vanderbilt-type pseudopotentials⁵ provided by Kresse and Hafner.⁷ In contrast to the Carr-Parrinello MD, in this approach, which is also known as Born-Oppenheimer MD, the electronic ground state is calculated after a self-consistent iterative solution of the Kohn-Sham equations.^{2,56,57} We applied the PW91 exchange-correlation density functional proposed by Perdew and Wang,⁵⁸ which is commonly used in computational models of transition metals and heterogeneous reactions at the gas-metal interface. It has been shown¹¹ that the PW91 density functional provides a good description of liquid water which is comparable to the BLYP exchange-correlation density functional.^{9,59,60}

The employed models consisted of five metal layer slabs for the geometry optimization calculations and three metal layer slabs for the molecular dynamics. Accuracy tests of different computational settings and configurations of the bilayer on the surface showed that the three-layer model leads to a systematic error in the estimated values of the adsorption energy on the order of 5–6 kJ mol^{−1} lower than those ob-

tained with the five-layer model. However, the *relative* energies of the different configurations are affected by less than 2 kJ mol⁻¹. We therefore conclude that the use of a three-layer model will not have a strong influence on the statistical data collected during the molecular dynamics simulations.

The surface unit cells were constructed using the bulk fcc lattice parameters of 3.85 and 3.99 Å for Rh and Pt, respectively, as computed with VASP. For the Rh(111) slabs this corresponds to surface unit cell vectors of length 4.71 Å for the small unit cell ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ ($ABCD$ in Fig. 1; three surface metal atoms) and 9.43 Å for the large unit cell ($2\sqrt{3}\times 2\sqrt{3}$) $R30^\circ$ (12 surface metal atoms). For the Pt(111) slabs the surface unit cell vectors were 4.89 Å (only the small unit cell was considered).

For the geometry optimization calculations the sizes of the unit cells along the z axis perpendicular to the surface were 24.00 Å for the Rh(111) slabs (regardless of the size of the cell in the plane of the surface) and 24.90 Å for the Pt(111) slab. For the MD runs (three-layer Rh slab) the size of the unit cell was 19 Å. The geometry optimizations and molecular dynamics runs were performed using a cutoff for the plane wave basis set of 325 eV. For the integration of the band energies a $5\times 5\times 1$ Monkhorst-Pack-type mesh⁶¹ was used for the small surface unit cells and the Γ point for the large unit cells.

The electronic properties (work function, density of states) were evaluated using the optimized geometries, a cut-off of 400 eV, and $7\times 7\times 1$ and $3\times 3\times 1$ Monkhorst-Pack-type meshes for the small and the large unit cells, respectively. For the s -, p -, and d -local density of states, the bands were projected onto spherical harmonics-type projectors within spheres of radii of 1.50, 1.10, and 0.65 Å centered on the M ($M=\text{Rh,Pt}$), O, and H atoms, respectively, as implemented in VASP. The local (projected) density of states (LDOS) at a given site was calculated as the $|C_{ln}|^2$ -weighted total density of states (plus an augmentation part related to the pseudopotentials), where $C_{ln}=\langle Y_l|\phi_n\rangle$ is the projection of the wave function ϕ_n onto the projector Y_l with l being a composite index for the quantum number of the spherical harmonics used to construct the projector. In this scheme the total number of electrons is equal to the total density of states integrated up to the Fermi level and multiplied by a factor of 2. We also make use of a bonding-antibonding indicator of the interaction between two atoms A and B defined as the $(C_{l_A n}^* C_{l_B n} + C_{l_A n} C_{l_B n}^*)$ -weighted DOS. The two projectors $Y_{l,A}$ and $Y_{l,B}$ are centered on A and B , respectively. This bonding-antibonding indicator is (qualitatively) equivalent to the crystal orbital overlap population (COOP) as defined by Hoffmann,⁶² taking into account that the projections are complex numbers. The resulting curve will represent the phase coherency between the projections and is positive in the bonding, negative in the antibonding, and zero in the nonbonding regions. The computed density of states and band energies, including the Fermi energy, are given with respect to the total (ionic+electronic) electrostatic potential in the middle of the vacuum region. This corresponds to a distance of around 7.5 Å from the metal surface. The work function is then the negative of the Fermi energy.^{63,64}

The molecular dynamics simulations were performed us-

TABLE I. Selected properties of water molecule in vacuum W and water adsorbed on $M(111)$ surface ($M=\text{Pt,Rh}$) at different low coverages. E_F is the Fermi level with respect to the average total electrostatic potential in the middle of the vacuum region, $\Delta\phi$ is the change in the work function compared to the clean metal surfaces, $\alpha(\text{H}_2\text{O})$ is the tilt angle between the water axis and outward surface normal, and $\Delta z(M_\parallel)$ is the displacement along the z axis of the substrate atom $M_\parallel$ from the average plane of the other “free” surface atoms (positive value means displacement towards the vacuum). The KS eigenvalues are given relative to the lowest $2a_1$ MO.

	W	1/12 Rh	1/3 Rh	1/3 Pt
E_{ads} (kJ mol ⁻¹)	...	36.8	36.1	29.0
E_F (eV)	...	-4.39	-4.35	-4.91
$\Delta\phi$ (eV)	...	-1.30	-1.34	-0.32
$E_F - E_{2a_1}$ (eV)	...	22.2	21.9	21.3
$E_{1b_1} - E_{2a_1}$ (eV)	18.2	17.2	17.1	17.1
$E_{3a_1} - E_{2a_1}$ (eV)	16.2	15.7	15.8	15.8
$E_{1b_2} - E_{2a_1}$ (eV)	12.3	12.3	12.3	12.3
O-H (Å)	0.973	0.979	0.983	0.981
H-O-H (deg)	104.7	105.3	104.1	103.9
$M_\parallel$ -O (Å)	...	2.38	2.42	2.54
$\alpha(\text{H}_2\text{O})$ (deg)	...	79	94	98
$\Delta z(M_\parallel)$ (Å)	...	+0.13	+0.07	+0.05

ing a time step of 0.5 fs at a mean temperature of 300 K. No constraints on the positions of the metal atoms or the geometry of the water molecules were applied. *Two different* initial configurations corresponding the up and down structures were considered (for a description of these structures see Sec. III B). Equilibration runs were performed starting from either of the initial configurations for 1.8 ps followed by a statistical data collection for another 1.8 ps. Thus, accounting for the fact that two MD simulations were performed with water considered on both sides of the metal slab, the total length of statistical data is 7.2 ps and consists of four independent blocks. [The time evolution of the water layers on the two different surfaces of the slab were independent because the initial velocities of the atoms were assigned in a random way.]

III. RESULTS AND DISCUSSIONS

A. Low coverage adsorption on Pt(111) and Rh(111) surfaces

The low coverage adsorption case was studied using models containing isolated water molecules adsorbed on Rh(111) and Pt(111) at surface coverages of 1/3 (Rh and Pt) and 1/12 (only Rh). For the 1/3 coverage the ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ surface unit cell $ABCD$ was used with only the $M_\parallel$ adsorption site being occupied [full circles on Fig. 1(a)]. For the 1/12 surface coverage a four times larger ($2\sqrt{3}\times 2\sqrt{3}$) $R30^\circ$ unit cell was used, with one water molecule per surface per unit cell adsorbed on top of a Rh atom.

The results given in Table I show that the adsorption energies on the two metals are only slightly different and the adsorption energy is around 7 kJ mol⁻¹ more favorable in the case of Rh(111) compared to Pt(111) and are in very good agreement with previously established data.⁶⁵ The structural and electronic properties of water molecules adsorbed on Rh(111) and Pt(111) surfaces are similar, taking into account

FIG. 2. Water adsorption on a Rh(111) surface at a coverage of 1/3. (a) LDOS of the oxygen atom from the water molecule (solid line) and of the underlying Rh atom (dot-dashed line, for clarity shifted by a value of 2 to the right). The integrated density of states (IDOS) for the O atom is given with a dashed line and the OH *s-s* and *p-s* COOP curves are given on the right. The Fermi level is represented with a horizontal dotted line. (b) Electron density corresponding to all KS states with eigenvalues in the range of $[E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]$ mapped onto a plane along the vector *AC* (see Fig. 1) and perpendicular to the surface. The isolines are defined as $2^n \times 10^{-1} \text{ \AA}^{-3}$, $n = -7, -6, \dots, 2$, starting from the upper curve. The zero of the *z* axis, which is perpendicular to the surface, is in the middle of the five-layer metal slab.

the difference in the atomic radii of the two metals. The orientation of the water molecules is approximately parallel to the surface with an angle between the dipole moment of the molecule and the outward surface normal of 79° – 98° in all three cases. From earlier studies, it was found that at low coverages the molecular axis of the water molecule is tilted at an angle of 30° – 70° with the outward surface normal [see, for example, Refs. 12, 13, 15, and 16]. However, an orientation approximately parallel to the surface was also obtained recently by Sánchez,¹⁷ Meng *et al.*,¹⁹ and Michaelides *et al.*⁶⁵ for a variety of metal surfaces. The “flat” orientation is consistent with water-metal interaction through the $1b_1$ molecular orbital (MO) of water (for the definition of the symmetry-adapted MO orbital notation the reader is referred, for example, to Ref. 12). This MO is the oxygen lone electron pair and in this configuration of the molecule on the surface it is oriented along the surface normal. The interaction with the metal results in a broadening of the $1b_1$ MO [peak at ca. 9 eV in Fig. 2(a)], while the spacing between the eigenvalues of the occupied KS states does not vary with the type of the surface (Fig. 2; the projected DOS of water adsorbed on Pt is similar to Rh and is not shown).

At this point we also note the presence of a very small but nonzero local density of states at the site of the oxygen atoms around the Fermi level of the metal [Fig. 2(a)], which can be seen for both Rh and Pt. In this eigenenergy region the gas-phase water molecule does not possess electronic states. To verify that this is not a result of a fictitious overlap between the electron bands of the metal and the projector centered at the site of the oxygen, the spatial electron density which would correspond to all eigenfunctions within the energy interval of $[E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]$ was computed. As seen in Fig. 2(b), a *p*-type contribution to the electron charge density at the site of the oxygen center can be identified. The spatial distribution of the charge density corresponding to the electronic states around the Fermi level is relevant to the

process of electron transfer through the interface (see Sec. III C).

B. Bilayer of water on Pt(111) and Rh(111) surfaces, small unit cell

For the high coverage adsorption we employed two conformations of the bilayer on the surface. We used the original model of Doering and Madey,⁴⁴ which will be referred to as “hydrogen-up” model, and a “hydrogen-down” model, derived from the up configuration after flipping the bilayer upside down [see Figs. 1(b) and 1(c)].

As seen in Table II the up and down configurations of the bilayer adsorbed on either Pt(111) or Rh(111) surfaces appear very similar in their computed adsorption energies E_{ads} . Interestingly, the data indicate that the down configuration is energetically more favorable than the up configuration, although the differences are very small. This result was already reported by Meng *et al.*¹⁹ for Pt(111) and Michaelides *et al.*²¹ for Pt(111) and Rh(111). Another DFT study using similar computational setup by Meng *et al.*²² on Rh(111), however, indicates that the up configuration is more stable. In the latter simulations the authors reported different geometry parameters of the relaxed down structure with some of the metal-oxygen distances shorter than the ones found in the present study. Nevertheless the reported adsorption energies are comparable -52.2 kJ/mol by Meng *et al.*²² vs 56.4 kJ/mol in the present work. For comparison, the results for the adsorption energies of the up structures are 54.0 and 55.4 kJ/mol , respectively, from the previous and the current study, but these differences can be attributed to different computational parameters. A possible explanation for the difference in the Rh–O distances between our calculations and those reported by Meng *et al.*²² will be discussed below. The relative adsorption energies in the present work is in very good agreement with the results by Michaelides *et al.*,²¹ although no geometry parameters were reported there. One could then speculate, that the minimum-energy down structure found in the present work is the more stable conformation of the adsorbed water layer, although the difference in energies (but not geometry) are very small and are in fact very close to the energies of the up structures. This suggests that the actual structure of the water adlayer on the metal surface can be a “mixture” of the H-up and H-down configurations and should be described in terms of statistical averages obtained using finite temperature molecular dynamics simulations.

We also note, that one could consider that the energy gain during adsorption is due to the formation of hydrogen bonds between the H_2O in the layer and the interaction of this layer with the metal surface. To estimate the latter, we computed the energy of adsorption $E_{\text{ads}}^{\text{bilayer}}$ of an isolated water bilayer on the metal surface. The result shows that the interaction energy between the bilayer and the metal is in the order of 2 – 5 kJ mol^{-1} . [These values were estimated using as references an optimized structure of the bilayer in vacuum and “clean” optimized five-layer $M(111)$ slabs ($M = \text{Pt, Rh}$).] The results suggest that (at least in the framework of this model, i.e., small unit cell) the interaction between the metal and the H_2O layer as a whole is very weak, which is

TABLE II. Selected properties of water bilayer adsorbed on $M(111)$ surface, $M = \text{Rh, Pt}$, and a water bilayer in vacuum. E_F is the Fermi level with respect to the average total electrostatic potential in the middle of the vacuum region, $\Delta\phi$ is the change in the work function compared to the clean surfaces, $\alpha(\text{H}_2\text{O})$ is the tilt angle between the dipole moment of the molecule with oxygen center $\text{O}_\parallel$ and the outward surface normal, and $\Delta z(X)$ is the displacement along the z axis of the metal atom X ($X = M_\parallel, M_\perp, M_*$, see also Fig. 1) from the average plane of all three surface atoms (positive direction is towards the vacuum). The KS eigenvalues are given relative to the lowest $2a_1$ MO.

	“up”/Rh	“down”/Rh	“up”/Pt	“down”/Pt	Vacuum
E_{ads} (kJ mol ⁻¹)	55.4	56.4	52.7	56.5	...
$E_{\text{ads}}^{\text{bilayer}}$ (kJ mol ⁻¹)	2.4	3.4	1.5	5.3	...
E_F (eV)	-2.13	-6.14	-8.41	-6.01	...
$\Delta\phi$ (eV)	-3.56	0.45	-1.82	0.78	...
$E_F - \langle E_{2a_1} \rangle$ (eV)	22.0	19.6	20.9	19.6	...
$E_{1b_1} - \langle E_{2a_1} \rangle$ (eV)	17.5	17.6	17.5	17.6	17.7
$E_{3a_1} - \langle E_{2a_1} \rangle$ (eV)	16.0	16.1	16.2	16.1	16.2
	14.8	14.6	14.9	14.8	14.8
$E_{1b_2} - \langle E_{2a_1} \rangle$ (eV)	12.0	12.0	12.1	12.1	12.0
$\text{O}_\parallel - \text{H}$ (Å)	0.992	0.992	0.988	0.991	0.989
$\text{O}_\perp - \text{H}_p$ (Å)	1.011	1.017	1.005	1.002	1.021
$\text{O}_\perp - \text{H}_d$ (Å)	0.974	0.983	0.974	0.989	0.973
$\text{H} - \text{O}_\perp - \text{H}$ (deg)	104.9	103.4	104.2	102.3	104.3
$\text{H} - \text{O}_\parallel - \text{H}$ (deg)	107.9	108.4	107.9	107.1	108.4
$M_\parallel - \text{O}_\parallel$ (Å)	2.63	3.55	3.02	3.16	...
$M_\perp - \text{O}_\perp$ (Å)	3.42	3.49	3.45	3.34	...
$M_\perp - \text{H}_d$ (Å)	...	2.51	...	2.35	...
$\alpha(\text{H}_2\text{O})$	76	...	92	...	...
$\Delta z(M_\parallel)$ (Å)	+0.05	+0.02	+0.02	+0.04	...
$\Delta z(M_\perp)$ (Å)	-0.03	-0.02	-0.01	-0.03	...
$\Delta z(M_*)$ (Å)	-0.02	0.00	-0.01	-0.02	...

unexpected considering the relatively strong interaction of isolated H_2O with the surface (Sec. III A). In the case of a high coverage of water on the surface, formation of H bonds between the water molecules apparently dominates over the metal-water interaction. However, the periodic boundary conditions of the small unit cell containing only two water molecules may enhance this effect. In a larger unit cell one could expect that there might be configurations of the water layer, respectively, distance to the surface and orientations of the molecules, providing the necessary conditions for the formation of stronger water-surface bonds. We will further explore this issue in Sec. III D presenting molecular dynamics simulations of a model which is based on a larger unit cell.

The very weak interaction of the water bilayer “as a whole” was also reported by Meng *et al.*²² and may in fact explain why the binding energies in their and our studies are very similar, but the Rh–O distances differ significantly. Such a weak overall binding must be accompanied by a very shallow potential well for the Rh–O distances and may therefore lead to very different optimized Rh–O distances with very similar energies. This is an additional argument in favor of performing MD simulations generating distribution functions rather than producing a single optimized bond distance.

The alternation of the surface dipole between the up and down configurations has an effect on the Fermi level, respectively, the work function. As can be expected the work functions of the up configurations (Table II) are lower than the work functions of the clean five-layer slab models of Rh(111) and Pt(111) of 5.23 and 5.69 eV, respectively, as

computed with VASP. The opposite effect is observed for the down configurations. These large changes in the work function, i.e., the surface dipole moment, suggest that the orientation of the H_2O molecules at the metal surface may be controlled by the electric field on the electrode. This conclusion corroborates well with the potential dependence of the oxygen-surface separation, as determined experimentally using x-ray scattering (see, for example, the work of Toney *et al.*³⁵).

C. Electronic structure around the Fermi level—Conductivity of the water adlayer

The projections of the KS orbitals suggest that in spite of the elongated water-metal distances compared to the case of low coverage adsorption on the surface, the presence of a metal substrate still gives rise to a finite local density of states around the Fermi level at the site of the oxygen atoms (Fig. 3). From the electron density, corresponding to all electronic states with KS eigenvalues in the range of $[E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]$, a p_z -type contribution to the electron charge with the p -orbital oriented along the surface normal z can clearly be identified (Fig. 4). Note that the same p_z -type contribution to the charge density is present around the second water molecule which has its molecular plane *perpendicular* to the surface. In this configuration the lone electron pair of the central oxygen atom is parallel to the plane of the surface. Examining the spatial distribution of the electronic states around the Fermi level in artificially created configurations with the water molecules partially rotated (not

FIG. 3. Water adsorption on a Rh(111) surface at a coverage of $2/3$. LDOS of the two oxygen atoms $O_{||}$ and $O_{\perp}$ of the underlying $Rh_{||}$ and $Rh_{\perp}$ atoms and the set of OH s - s and p - s COOP curves. (a) Configuration "up" and (b) configuration "down." The definition of the lines corresponds to the one in Fig. 2(a).

shown) we were able to verify that regardless of the orientation of the water molecules, there is always a p -type contribution to the electron states with the p orbital centered on the O atom and oriented perpendicularly to the surface. This indicates that the finite density of states around the Fermi level of the metal and the corresponding spatial electron charge density distribution is to some degree independent of the orientation of the molecule and is (primarily) related to metal-oxygen interactions, rather than metal-water interactions. The extent of mixing between the atomic states from the oxygen and the metal substrate appears to be related to the distance to the surface and to the polarization of the surface (compare the spatial electron density of the up and the down configuration in Fig. 4; note that the water molecules in the down configuration are further away from the surface compared to the molecules in the up configuration).

Traditionally, the processes of interfacial electron transfer between molecules or ions in a solution and a metal electrode is modeled in the framework of the Marcus theory with the surrounding solvent (most commonly water) considered as a simple dielectric continuum.^{23–25} Recent publications dealing with the electron tunneling phenomena through wa-

FIG. 4. Water adsorption on $M(111)$ surface, $M = Rh, Pt$, at coverages of $2/3$. Electronic density corresponding to all KS states in the energy range of $[E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}]$ mapped onto a plane along the vector AC (see Fig. 1) and perpendicular to the surface. (a) Rh(111), configuration "up"; (b) Pt(111), configuration "up"; (c) Rh(111), configuration "down"; and (d) Pt(111), configuration "down." The definition of the isolines is the same as in Fig. 2(b).

ter layers have pointed out, however, that the full three-dimensional structure of the solvent and the quantum properties of the electron have to be taken into account when describing processes of nonadiabatic electron transfer through the water/metal interface.^{26–29} Although only a small amount of electron density of states around the Fermi level is present on the O atoms, the results illustrate that the water molecules from the adlayer closest to the metal surface can play an active role in electron transfer reactions and should not be considered as a simple dielectric but as a conductive medium. These results are also in agreement with the experimental observations of Morgenstern *et al.*,²⁸ who reported that water adsorbed on Pt(111) appears as an elevation to the STM and therefore must be capable of conducting electric current.

D. Structure of water layer adsorbed on Rh(111) surfaces

The geometry optimization calculations (Table II) showed that the difference in the adsorption energies of the up and down configurations using the small $(\sqrt{3} \times \sqrt{3}) R30^\circ$ unit cell is rather small and that they are practically indistinguishable from point of view of energetics. One can therefore expect that in reality the structure of the water layer on the metal surface will be a mix between the up and down

FIG. 5. Snapshot from the molecular dynamics simulation and the surface unit cell. (a) Top view and (b) side view. Rhodium, oxygen, and hydrogen atoms are given in gray, black, and white, respectively.

structures. At the same time the difference in the interaction energies of a single water molecule and a complete bilayer with the surface is quite large [for example, for Rh(111), 36 kJ mol⁻¹ for an isolated molecule to be compared with 2–3 kJ mol⁻¹ for a bilayer]. This suggests that due to the imposed translational symmetry of the small unit cell it is possible that in the case of high coverage adsorption the simulation may have not resulted in an energetically favorable structure of the adsorbed water layer.

In a search for a more stable conformation we performed molecular dynamics simulations of a water layer on the Rh(111) surface using a twice larger unit cell ($2\sqrt{3} \times 2\sqrt{3}$) $R30^\circ$. Two MD runs were performed using either the up or down configuration as determined in Sec. III B. During the equilibration starting from either the up or down structures, the original orientation of the molecules changed leading to a mixture of up and down OH bonds (see Fig. 5) and both simulations resulted in similar distribution functions. The results presented below were therefore evaluated using the MD data of the two simulations.

Adsorption Energy. Using a (random) configuration from the MD simulation a geometry optimization of the structure was performed in order to estimate the adsorption energy at 0

FIG. 6. (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal. The zero of the surface normal is in the middle of the three-layer metal slab. (b) Cross section of the oxygen number density and the angular distribution of the corresponding OH bonds. The isolines are defined as $2^n \times 10^{-1} \text{ \AA}^{-1}$, $n = -3, -2, \dots, 3$, starting from the outer curve. The density plots are normalized to the total number of atoms of the corresponding type.

K (which is the condition of the calculations in the previous sections). The adsorption energy of the resulting optimized structure is 64.7 kJ mol⁻¹. This is around 14 kJ mol⁻¹ higher (i.e., more favorable) than the values found for the perfect-bilayer structures using a three-layer model. Note, however, that the three-layer models incorporate a systematic error in the absolute adsorption energy on the order of 5–6 kJ mol⁻¹, as discussed in Sec. II. Assuming transferability of this result to the more accurate five-layer model, the estimated value for the adsorption energy of water adlayer on Rh(111) surface would be around 70 kJ mol⁻¹. It has to be mentioned that the calculated minimum-energy structure may not represent the global potential energy surface minimum, i.e., the above value should be interpreted as a lower boundary to the adsorption energy for this system at 0 K. We note however that using a larger unit cell, respectively introducing more degrees of freedom in the system, we were able to find a conformation of the layer which is significantly more stable than the “ideal” bilayer determined using the small unit cell.

Structure of the Layer. The oxygen distribution function along the surface normal z [Fig. 6(a)] reveals a bilayerlike arrangement of water molecules with two distinct maxima and a tail towards the vacuum region. The integrated value of the first peak, which will be referred to as sublayer L_1 , equals 2.5 oxygen atoms per unit cell, with the other 5.5 oxygen atoms per unit cell being in the second sublayer L_2 . This implies that the reconstruction of the initial conformations of the ideal bilayer results in a reduction of the number of close contacts between Rh and O atoms, which for the perfect bilayer is four.

It has to be noted that in order to speed up the simulation, the molecular dynamics was performed at an average temperature of 300 K, which is above the desorption temperature of around 180 K. However, desorption of water molecules from the surface does not occur in the course of the MD due to the short simulation time and the small size of the system. The minimum-energy structure, obtained in rela-

tion to the adsorption energy estimation, also corresponds to a conformation of the bilayer with less than four water molecules in close contact with the surface—the number of oxygens at distances in the range corresponding to the first peak $L1$ equals only three. An attempt to place a fourth water molecule closer to the metal surface resulted in a reconstruction of the adlayer during a geometry optimization with the “extra” water molecule being relocated back towards the vacuum region, i.e., away of the surface. We therefore conclude that for this particular system ($\text{H}_2\text{O}/\text{Rh}$) the specific structural and electronic characteristics of the metal substrate do not favor a formation of an ideal bilayer (four close contacts between oxygen and metal atoms).

Although the resulting structure still follows the $(\sqrt{3}\times\sqrt{3}) R30^\circ$ surface pattern, the arrangement of the molecules within the layer is more complicated and results on average to 2.5 close contacts with the surface. However, in the STM experiment, which relies on measuring the electric current through the interface, this fine structure of the layer will most probably be undetectable. The probability of a charge transfer and therefore of an electric current is related to the spatial distribution of the conducting electronic states in the immediate environment of the STM tip. The spatial distribution, however, is modified by the presence of the water molecules due to a mixing of the oxygen p orbital and the d band of the metal (see Sec. III C) as opposed to a simple screening of the metal by an (inactive) insulating adlayer. Comparing the corresponding charge densities (Fig. 4, especially evident in the case of Pt) we note that although the differences in orientation of the molecules and the distance to the surface, the charge density data for different configurations are practically indistinguishable. In other words regardless of the actual configuration on the surface the water adlayer will *appear* as a rather well ordered $(\sqrt{3}\times\sqrt{3}) R30^\circ$ surface pattern within the small periodic unit cell.

Considering the hydrogen distribution along the surface normal [Fig. 6(a)], note that there is a nonzero hydrogen number density at *shorter distances* to the metal surface compared to the oxygen. Looking at the cross section of the angular distribution of the OH bond with respect to the outward surface normal and the position of the corresponding oxygen center of the water molecules [Fig. 6(b)] we note that water molecules from sublayer $L1$ have their OH bonds tilted away of the surface with a maximum in the angular distribution function of around 70° [O_1H_{1x} in Fig. 6(c)]. These hydrogen atoms take part in hydrogen bonds with water molecules from $L2$. In turn, water molecules from $L2$ sublayer have one of their OH bonds approximately parallel to the surface (O_2H_{22} or O_3H_{31}), while the other points either towards the metal (O_2H_{21}) or towards the vacuum (O_3H_{32}). The shoulder observed in the hydrogen distribution function along the surface normal at short hydrogen-surface distances [Fig. 6(a)] therefore originates from the hydrogen atoms from water molecules in the second $L2$ sublayer. Note also that the peak corresponding to the hydrogen-down bond (O_2H_{21}) is sharper compared to the hydrogen-up bond (O_3H_{32}), indicating that the movement of the H_{21} -type hydrogen atoms is to some degree restricted due to the presence of the metal. This result will be further explored in the fol-

FIG. 7. (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along a line perpendicular to the surface. (b) Cross section of the oxygen and the underlying rhodium atom number densities. For comparison the cumulative rhodium number density is also given in left part of the subfigure, rotated on 90° . The isolines are defined as $2^n \times 10^{-1} \text{ \AA}^{-2}$, $n = -2, -1, \dots, 4$, starting from the outer curve. (c) Cross section of the hydrogen and the underlying rhodium atom number densities. The isolines are defined as $2^n \times 10^{-1} \text{ \AA}^{-2}$, $n = -3, -2, \dots, 4$, starting from the outer curve. The density plots are normalized to the total number of atoms of the corresponding type.

lowing section considering the Rh–H interaction.

The rhodium distribution function also appears broadened in the direction towards the water layer [Fig. 6(a)]. The origin of this broadening can be found in the cross section of the rhodium number density distribution along the surface normal with the oxygen and hydrogen number densities [Figs. 7(b) and 7(c)]. The distribution plot clearly shows that the relaxation of the surface in terms of the position of the Rh atoms in the direction perpendicular to the surface is caused by the interaction with oxygen atoms from the first sublayer $L1$ and leads to a displacement of the Rh atoms in close contact with water molecules towards the vacuum region on the order of $0.3 \text{ \AA}$. This results in a separation between the oxygen atoms from $L1$ and the underlying Rh atoms on the order of $2.3 \text{ \AA}$, which is shorter compared to the ideal bilayer (Sec. III B) and is in fact comparable to the low coverage results. Interestingly, the separation between the rhodium surface atoms and the H_{21} -type atoms is on the same order of magnitude while there is no relaxation of the surface (compare Fig. 7 in the areas of the O_1 and H_{21} atoms; the local configuration of a O_1 -type water molecule is characterized by the oxygen at a distance from the *middle of the three-layer metal slab* of around $4.7 \text{ \AA}$. The underlying Rh atom is at a distance of ca. $2.4 \text{ \AA}$. The corresponding heights of the H_{21} -type atom and the underlying Rh atom are 4.4 and $2.1 \text{ \AA}$).

In summary, molecular water adsorbed on Rh(111) surface forms a bilayerlike structure which can be regarded as a mixture of the simple up and down structures. An indication of what is the determining factor for the orientation of the individual molecules can be found in the computed cross

FIG. 8. (a) Number densities of rhodium (dashed line), oxygen (solid line), and hydrogen atoms (dot-dashed line) along the surface normal. (b) Cross section of the oxygen number density and the angular distribution function of the dipole moment of the molecule with respect to the outward surface normal. The isolines are defined as $2^n \times 10^{-1} \text{ \AA}^{-1}$, $n = -2, -1, \dots, 3$ starting from the outer curve. The density plots are normalized to the total number of atoms of the corresponding type.

section of the angular distribution of the water dipole moment with the position of the corresponding oxygen center [Fig. 8(b)]. As seen from the figure, the dipole moment of the water molecules from L1 is at an angle with the outward surface normal in the order of 55° – 60° . The orientation of the dipole moment of the molecules from L2 varies between pointing towards the vacuum and towards the surface, with a preferred orientation towards the surface. The maximum in the angular distribution function is around 130° . However, the average orientation of the dipole moment computed accounting for *all* water molecules (L1 and L2) is at an angle of 91° with the outward surface normal. This results in a very small contribution to the total surface dipole moment. This configuration is also the one which minimizes the long-range dipole-dipole repulsion. In conclusion, while the orientation of the molecules from L1, which are closer to the surface, is determined by the interaction with the metal substrate, the driving force for the orientation of the molecules from the second sublayer L2, i.e., those which are further away from the surface, is the electrostatic interaction with the L1 sublayer so as to minimize the total surface dipole moment.

E. Electronic structure and electron transfer through the interface

Using six configurations from the MD run equally spaced in time we estimated the *average* LDOS of all oxygen atoms and all surface Rh atoms [Fig. 9(a)]. The averaged oxygen LDOS consists of three principal peaks. The detailed structure of these peaks is revealed in Figs. 9(b) and 9(c), presenting the LDOS data evaluated for two selected oxygen atoms O₁ and O₂. These two oxygen centers belong to the different sublayers L1 and L2, respectively. The LDOS plots [Figs. 9(b) and 9(c)] indicate that the position and spacing between the energies of the local electronic states vary between the adsorption sites, which is to be expected and is due to differences in the local chemical environment and electro-

FIG. 9. Local density of states relative to the Fermi level of the metal ($E_F = 0$). (a) Averaged LDOS of all oxygen atoms (solid line) and the 12 surface rhodium atoms (dotted line) using six configurations from the MD simulation. (b) LDOS of the O₁ atom (solid line) and the underlying Rh₁ atom (dotted line). (c) LDOS of the O₂ atom (solid line) and the underlying Rh₂ atom (dotted line). All graphs are scaled independently (x axis).

static potential. The relatively broad peaks in the averaged LDOS plot are a “superposition” of otherwise well-defined electronic states of water. The peak closest to the Fermi level at -3 – -7 eV in the averaged LDOS is composed of both the $3a_1$ and $1b_1$ water MOs and this data is in good (qualitative) agreement with the experimental ultraviolet photoemission spectroscopy results from Wagner and Moylan.⁴⁰ Note also the finite local density of states around the Fermi level of the substrate at the site of the oxygen atoms. The current MD simulation data confirms the conclusion for an apparent small conductivity of a water layer adsorbed on a transition metal surface.

As it was shown above, the averaged orientation of the dipole moment of the water molecules is approximately in the plane of the surface. It must be pointed out that this does not necessarily mean that there is no change in the surface dipole compared to the clean surface. The change in the work function is $\Delta\phi = -1.1$ eV with fluctuations in the course of the MD simulation on the order of 0.5 eV (estimated using the 6 reference configurations). This means that the total surface dipole moment is altered upon adsorption of water molecules on the surface and this is due to a redistribution of the electron charge density. The electron charge transfer through the interface is illustrated in Fig. 10, presenting the so-called *electron charge transfer function*. The electron charge transfer function is defined as the electron density of the water-substrate system minus the sum of the electron densities of the isolated water layer and the clean metal substrate. In this case, the isolated water adlayer and the metal surface are in the same conformation as in the substrate-adsorbate system (no geometry optimizations). Based on this result we conclude that there is an electron charge transfer from the water adlayer to the metal surface, which leads to an increase in the electron density in the interfacial area (compare the electron charge transfer function in Fig. 10(c) at distances of 3–4 and 4.5–7 Å above the middle of the metal slab).

FIG. 10. Electron charge transfer through the interface of a selected configuration of water layer adsorbed on Rh(111) surface (side view of the unit cell). (a) Electron charge transfer function mapped onto a plane perpendicular to the surface and containing three selected surface rhodium atoms. (b) Three-dimensional plot of the electron charge transfer function showing also the plane used in (a). Positive electron charge transfer function, i.e., areas with an excess of electron density in the substrate-adsorbate system compared to the “clean” surface and the isolated water layer, is represented with white; black corresponds to negative electron charge transfer function. The positions of the O_2 and H_{21} atoms from sublayer $L2$ and an oxygen atom O_1 from sublayer $L1$ are also indicated. (c) Averaged electron charge transfer function along the surface normal. (d) Averaged electron density of the substrate-adsorbate system along the surface normal. The middle layer of the three-layer Rh(111) slab is at $z=0$ $\text{\AA}$ in (c) and (d).

F. Rhodium-hydrogen interaction

It is widely accepted that the metal-hydrogen interaction in the case of molecular water adsorbed on the metal surface is purely repulsive and this is also reflected in the analytical expressions for the commonly used classical MD interaction potentials. However, a detailed examination of the current *ab initio* simulation results can provide evidence for a possible attractive Rh–H interactions. For example the geometry optimizations of the perfect bilayer models revealed that the “dangling” $O_{\perp}-H_d$ bond is elongated in the down configuration compared to the up configuration. The down configuration is the configuration characterized with both $3a_1$ and $1b_1$ eigenenergies overlapping with the eigenenergies of the metal and thus the corresponding molecular orbitals are potential candidates for MO interactions with the substrate. Another example is the MD simulation data and particularly the OH angular distribution function (Fig. 6). As noted, the peak in the angular distribution function corresponding to OH pointing towards the surface is more narrow compared to the peak of the OH pointing towards the vacuum. This indicates that the motion of the hydrogen-down H atoms is restricted to some degree, although it does not provide any information on the nature of this interaction. In principle, restricted motion can be attributed to either space confinement (repulsion) or an attractive interaction with the substrate. In the present section it is argued that in the case of water chemisorbed on Rh(111) surface it is an attractive interaction between the rhodium and the hydrogen which is to be held responsible for these effects.

An indication for bonding between the molecule and the surface can be obtained through an analysis of the electronic properties of the O_{L2} water molecule (see Fig. 10) and the corresponding distribution of the electron charge. Comparing the clean surface with the substrate-adsorbate system, we note that there is an increase in the electron density in the region between the hydrogen atom H_{21} and the underlying

Rh_2 , indicating formation of a bond between the two atoms [Fig. 10(a)]. This also means that the interaction with the surface can potentially affect the stability of the molecule and the OH bonds in particular. Comparing the broadening of the MO peaks in the LDOS of selected atoms and configurations (not shown) we conclude that the Rh–H interaction is much weaker than the interaction through the oxygen atoms.

In view of this discussion, three different types of hydrogen atoms can be considered in the system: (a) “free” hydrogen atoms pointing towards the vacuum (H_{32}), (b) hydrogen atoms taking part in a hydrogen bond with a neighboring water molecule (H_{22} , H_{31} , H_{11} , and H_{12}), and (c) free hydrogen atoms pointing towards the surface (H_{21}). In search for a confirmation of the attractive interaction between the hydrogen and rhodium atoms, we examine the vibrational power spectrum of the three types of hydrogen atoms. As seen in Fig. 11, the H_{32} -type atoms pointing towards the vacuum are characterized with a well defined peak in the power spectrum at around 3750 cm^{-1} . This peak is identified as the OH stretch vibration. The corresponding peak for the H_{21} -type atoms is much broader and shifted towards lower frequencies. This indicates that the respective OH bond is weakened compared to the OH bond pointing towards the vacuum and this is due to the interaction with the metal. It is tempting to speculate that if the interaction with the metal was *stronger*, the water from the second layer $L2$ would spontaneously dissociate into adsorbed H and OH. Such a dissociation was recently reported by Feibelman¹⁸ for DFT calculations of a water bilayer on Ru(0001).

IV. SUMMARY AND CONCLUSIONS

The *ab initio* DFT structural optimizations of water adsorbed at low coverage on the (111) surfaces of Pt and Rh predict a “flat” orientation of the molecules with respect to

FIG. 11. Computed vibrational power spectrum of the hydrogen atoms: (a) “free” H atoms pointing towards the vacuum region (H_{31}), (b) H atoms taking part in hydrogen bonds with neighboring water molecules (H_{22} , H_{31} , H_{11} , and H_{12}), (c) “free” H atoms pointing towards the metals surface (H_{21}). The raw velocity autocorrelation data were filtered using a Blackman window in order to smooth the power spectrum. See also text.

the surface. The computed tilt angle between the water dipole moment and the outward surface normal is in the range of 79° – 98° . This orientation is consistent with an interaction with the metal substrate through the $1b_1$ lone electron pair of the oxygen atom. This results are in good agreement with previously published data.⁶⁵

At high coverages the water layer forms a bilayerlike structure with two distinct peaks in the oxygen distribution function along the surface normal. However, the structure of the bilayer is more complex than the original model proposed by Doering and Madey⁴⁴ with some of the free OH bonds point towards the metal surface. While the orientation of the molecules in close contact with the metal is determined by the interaction with the substrate, the determining factor for the orientation of the molecules which are further away are the electrostatic interactions. This leads to an average orientation of the dipole moment of *all* water molecules approximately in the plane of the surface (in the absence of an external field). The estimated value for the adsorption energy equals 70 kJ mol^{-1} .

The water molecules adsorbed on the surface possess a small metalliclike conductivity related to mixing of local states of the oxygen atom with the electron bands of the metal substrate. The extent of this mixing appears to some degree independent of the orientation of the molecules. The averaged local electronic density of states at the site of the oxygen atoms display three principal peaks, with the peak closest to the Fermi level being a superposition of the $3a_1$ and $1b_1$ molecular orbitals of water. This result is also in good (qualitative) agreement with experimental data. The analysis of the electronic structure indicates an electron charge transfer from the water molecules towards the surface, which results in the reduction of the work function of the system.

A rather interesting result is the existence of an attractive interaction between the surface rhodium atoms and the hydrogen atoms of the water molecules. Although the interaction is relatively weak, the computed power spectrum indicates that it is sufficient to alter the dynamics of the

hydrogen motion and therefore should not be disregarded in a proper description of the system.

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- ¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ²W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ³R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- ⁴M. C. Payne, M. P. Teter, D. C. Allen, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
- ⁵D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ⁶K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).
- ⁷G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
- ⁸K. Laasonen, M. Sprik, and M. Parrinello, J. Chem. Phys. **99**, 9080 (1993).
- ⁹M. Sprik, J. Hutter, and M. Parrinello, J. Chem. Phys. **105**, 1142 (1996).
- ¹⁰P. L. Silvestrelli, M. Bernasconi, and M. Parrinello, Chem. Phys. Lett. **277**, 478 (1997).
- ¹¹P. Vassilev, C. Hartnig, M. T. M. Koper, F. Frechard, and R. A. van Santen, J. Chem. Phys. **115**, 9815 (2001).
- ¹²P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987).
- ¹³M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).
- ¹⁴J. W. Halley, A. Mazzolo, Y. Zhou, and D. Price, J. Electroanal. Chem. **450**, 273 (1998).
- ¹⁵S. Izvekov, A. Mazzolo, K. VanOpdorp, and G. A. Voth, J. Chem. Phys. **114**, 3248 (2001).
- ¹⁶S. Izvekov and G. A. Voth, J. Chem. Phys. **115**, 7196 (2001).
- ¹⁷C. G. Sánchez, Surf. Sci. **527**, 1 (2003).
- ¹⁸P. J. Feibelman, Science **295**, 99 (2002).
- ¹⁹S. Meng, L. F. Xu, E. G. Wang, and S. Gao, Phys. Rev. Lett. **89**, 176104 (2002).
- ²⁰P. J. Feibelman, Phys. Rev. Lett. **90**, 186103 (2003).
- ²¹A. Michaelides, A. Alavi, and D. A. King, Phys. Rev. B **69**, 113404 (2004).
- ²²S. Meng, E. G. Wang, and S. Gao, Phys. Rev. B **69**, 195404 (2004).
- ²³R. A. Marcus, J. Chem. Phys. **24**, 966 (1956).
- ²⁴R. A. Marcus, J. Chem. Phys. **43**, 679 (1965).
- ²⁵R. A. Marcus, Angew. Chem. **32**, 1111 (1993).
- ²⁶I. Benjamin, Chem. Rev. (Washington, D.C.) **96**, 1449 (1996).
- ²⁷I. Benjamin, D. Evans, and A. Nitzan, J. Chem. Phys. **106**, 6647 (1997).
- ²⁸M. Morgenstern, J. Müller, T. Michely, and G. Comsa, Z. Phys. Chem. (Munich) **198**, 43 (1997).
- ²⁹J. R. Hahn, Y. A. Hong, and H. Kang, Appl. Phys. A: Mater. Sci. Process. **66**, S467 (1998).
- ³⁰C. Hartnig and M. T. M. Koper, J. Chem. Phys. **115**, 8540 (2001).
- ³¹C. Y. Lee, J. A. McCammon, and P. J. Rossky, J. Chem. Phys. **80**, 4448 (1984).
- ³²E. Spohr, J. Phys. Chem. **93**, 6171 (1989).
- ³³I.-C. Yeh and M. L. Berkowitz, J. Electroanal. Chem. **450**, 313 (1998).
- ³⁴A. E. Russell, A. S. Lin, and W. E. O'Grady, J. Chem. Soc., Faraday Trans. **89**, 195 (1993).
- ³⁵M. F. Toney, J. N. Howard, J. Richer *et al.*, Nature (London) **368**, 444 (1994).
- ³⁶M. F. Toney, J. N. Howard, J. Richer *et al.*, Surf. Sci. **335**, 326 (1995).
- ³⁷T. Iwasita and X. Xia, J. Electroanal. Chem. **411**, 95 (1996).
- ³⁸K. Ataka and M. Osawa, Langmuir **14**, 951 (1998).
- ³⁹J. J. Zinck and W. H. Winberg, J. Vac. Sci. Technol. **17**, 188 (1980).
- ⁴⁰F. T. Wagner and T. E. Moylan, Surf. Sci. **191**, 121 (1987).
- ⁴¹A. Glebov, A. P. Graham, A. Menzel, and J. P. Toennies, J. Chem. Phys. **106**, 9382 (1997).
- ⁴²K. D. Gibson, M. Viste, and S. J. Sibener, J. Chem. Phys. **112**, 9582 (2000).
- ⁴³J. K. Sass, K. Kretzschmar, and S. Holloway, Vacuum **31**, 483 (1981).
- ⁴⁴D. L. Doering and T. E. Madey, Surf. Sci. **123**, 305 (1982).
- ⁴⁵J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983).

- ⁴⁶J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
- ⁴⁷Y. A. Hong, J. R. Hahn, and H. Kang, J. Chem. Phys. **108**, 4367 (1998).
- ⁴⁸R. Naaman, A. Haran, A. Nitzan, D. Evans, and M. Galperin, J. Phys. Chem. B **102**, 3658 (1998).
- ⁴⁹A. Nitzan and I. Benjamin, Acc. Chem. Res. **32**, 854 (1999).
- ⁵⁰W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2000).
- ⁵¹E. J. Baerends and O. V. Gritsenko, J. Phys. Chem. A **101**, 5383 (1997).
- ⁵²P. Politzer and F. Abbu-Awwad, Theor. Chem. Acc. **99**, 83 (1998).
- ⁵³R. Stowasser and R. Hoffmann, J. Am. Chem. Soc. **121**, 3414 (1999).
- ⁵⁴T. Kar, J. G. Ángyán, and A. B. Sannigrahi, J. Phys. Chem. A **104**, 9953 (2000).
- ⁵⁵T. Kar, J. G. Ángyán, and A. B. Sannigrahi, J. Phys. Chem. A **105**, 660 (2001).
- ⁵⁶G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- ⁵⁷G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ⁵⁸J. P. Perdew, *Electronic Structure of Solids 91* (Akademie, Berlin, 1991).
- ⁵⁹A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
- ⁶⁰C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- ⁶¹H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ⁶²R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (VCH, New York, 1988).
- ⁶³N. D. Lang and W. Kohn, Phys. Rev. B **3**, 1215 (1971).
- ⁶⁴C. J. Fall, N. Binggeli, and A. Baldereschi, J. Phys.: Condens. Matter **11**, 2689 (1999).
- ⁶⁵A. Michaelides, V. A. Ranea, P. L. de Andres, and D. A. King, Phys. Rev. Lett. **90**, 216102 (2003).