Structure and Bonding of Water on Pt(111)

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We address the adsorption of water on Pt(111) using x-ray absorption, x-ray emission, and x-ray photoelectron spectroscopy along with calculations in the framework of density functional theory. Using the direct relationship between the electronic structure and adsorbate geometry, we show that in the first layer all the molecules bind directly to the surface and to each other through the in-layer H bonds without dissociation, creating a nearly flat overlayer. The water molecules are adsorbed through alternating metal-oxygen (*M*-O) and metal-hydrogen (*M*-HO) bonds.

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Water is the most abundant compound in the biosphere and covers most real solid surfaces. Consequently, the water-metal interaction has been one of the most studied adsorption cases since the establishment of modern surface science some 25 years ago [1,2]. The structure of water on metal surfaces has traditionally been considered a buckled bilayer where only every second water binds to the metal [Fig. 1(a) [1]]. In view of its importance it is surprising that the structure of this contact layer is still a matter of argument. Here we find that water is adsorbed on Pt(111) in a flat layer [Fig. 1(b)] with both metal-oxygen (*M*-O) and metal-hydrogen (*M*-HO) bonding species.

In the bilayer structure model [Fig. 1(a)], proposed by Doering and Madey [3], water is thought to bind to metal surfaces via an oxygen lone pair orbital; only half of the molecules bind directly to the metal substrate through the oxygen and the other half are displaced towards vacuum. In addition to this ice I_h-like structure, where the layer is buckled, water can form a two-dimensional hexagonal hydrogen bond network. However, a low energy electron diffraction (LEED) study of water on Ru(0001) by Held and Menzel [4] found only a small vertical displacement (0.15 Å) between the two different water molecules, contradicting the bilayer structure that estimates a much larger value of 0.96 Å. Feibelman, using density functional theory (DFT) calculations, interpreted this as a partial dissociation of water leading to a near-planar, hexagonal mixed network of water and hydroxyls [5]. It was argued that in order to achieve a favorable interaction the proton pointing towards the substrate needed to be removed. The suggested coexistence of water and hydroxyl is strongly supported by the appearance of two different O 1*s* photoemission peaks at 531.3 and 533.3 eV for water on Ru(0001) [6]. However, on most hexagonally close-packed surfaces water does not dissociate. The compilation in Ref. [2] of O 1*s* photoemission data supports nondissociative adsorption of water on, e.g., Ni(111), Cu(111), Rh(111), and Pt(111) ([7], Fig. 2 left). A partially dissociated model can thus not be applied as a general model of water on metal surfaces. This leads to the question of what the structure of a nondissociated overlayer on a metal surface is.

In the case of Pt(111), the formation of an ordered 2D layer in a hexagonal arrangement has been demonstrated by LEED, helium atom diffraction, and scanning tunneling microscopy with 2/3 of monolayer saturation coverage [8–11]. In either case these measurements have not determined the positions of the O and H atoms, which are central to the understanding of the nature of the contact layer. Here we have used x-ray photoelectron spectroscopy (XPS) to address the coordination of atoms to the surface, x-ray absorption spectroscopy (XAS) to determine the orientation of the OH bonds in the water molecule with respect to the surface, and x-ray emission
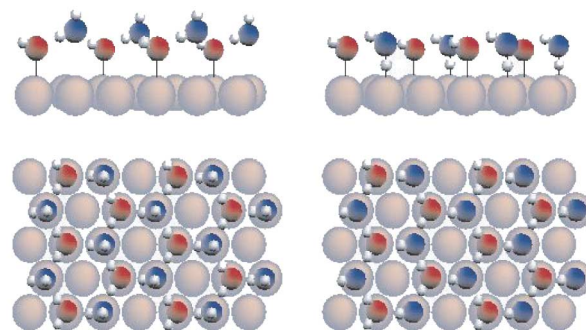

FIG. 1 (color online). (a) The bilayer ice structure on metal surfaces. Dark spheres represent O atoms. Half of the water molecules bind directly to the surface metal atoms. The other half are displaced toward the vacuum in the H-up configuration. (b) The flat ice structure on metal surfaces. Dark spheres represent O atoms in Pt-O and Pt-HO bonding water molecules, respectively. All water molecules bind to the surface metal atoms. The thickness of the layers is 0.96 Å (a) and 0.25 Å (b), respectively.
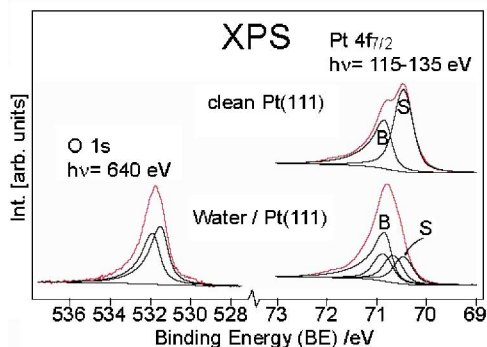

FIG. 2 (color online). XPS spectra for clean and water covered Pt(111). The components obtained from a curve fitting analysis, according to the structural model [Fig. 1(b)], are shown with solid lines. (Left) O $1s$ photoemission spectrum estimated with two separated peaks corresponding to the Pt-O and Pt-HO bonding water molecules. The relative intensities (53% for low and 47% for high BE peak) reflect the ideal 50% expected from the model in Fig. 1(b). (Right) Summed Pt $4f_{7/2}$ spectra taken at three excitation energies (115, 125, and 135 eV) to average out photoelectron diffraction effects. For clean Pt(111), the bulk (B) and surface (S) binding energies are split by 0.4 eV with relative intensities 41% (B) and 59% (S). (Right bottom) Water coordinating to the metal shifts contributions towards the bulk value. We estimate that the uncoordinated surface peak (S) is lowered in intensity by more than 60% independent of the used fitting parameters and constraints. The essential results showing nondissociated water and a low concentration of noncoordinated surface Pt atoms can be seen directly in the experimental spectra and are independent from the details in the fitting parameters.

spectroscopy (XES) together with DFT calculations to explain the detailed bonding mechanism.

XPS, XAS, and XES experiments were performed at the MAX-lab synchrotron radiation facility on beamline I511. The monolayer of water was obtained by annealing a water multilayer to 140 K, and was kept between 100 and 120 K during the measurements. D_2O was utilized in order to minimize beam damage. XPS and XAS spectra were obtained using total energy resolution better than 0.1 and 0.3 eV, respectively. XES spectra were taken at an energy resolution of 0.7 eV. The structures were optimized using the plane-waves based DaCapo program [12] using periodic boundary conditions. XAS spectra were calculated for cluster models with four water molecules and seven Pt atoms using the deMon StoBe program [13]. Gradient-corrected exchange and correlation functionals were used throughout. The computed oscillator strengths were convoluted using Gaussians of increasing full width at half maximum to obtain the simulated spectra. The orbitals for the excitations were determined with a half-occupied core level on the excited molecule and expanded with a double basis set technique [14].

XPS provides information about the chemical state of adsorbate and substrate atoms [15]. O $1s$ XPS measurements for water on Pt(111) show one broad peak, indicating an upper limit of 0.8 eV for the chemical shift between the two water O $1s$ components, consistent with the nondissociated model. We have determined the amount of water molecules coordinated to surface Pt atoms through the surface core-level shift [16]. For clean metals, the lower coordination of atoms at the surface leads to a different core-level binding energy compared to the bulk. On Pt(111) this splitting is 0.4 eV for the Pt $4f$ XPS peak (Fig. 2, right). The introduction of water on Pt(111) shifts the Pt $4f$ surface state towards the bulk value for the atoms that now coordinate to water. From the change in intensity, we estimate that 2/3 ($\pm$ 10%) of the surface Pt atoms are coordinated to water molecules. This value corresponds to the saturation coverage of the water layer on Pt(111), and all water molecules are thus coordinated to surface metal atoms. It is clear that the "bilayer structure" cannot give such a high surface coordination. Furthermore, computed O $1s$ binding energies of the two waters in the "bilayer ice" model gives a chemical shift of 1.9 eV that is inconsistent with our experimental data (Fig. 2). Such a large shift appears if the two layers of water will have different screening channels upon core ionization [15] as is the case for the bilayer model.

A theoretical geometry optimization also leads to a flat ice layer on the Pt surface [Fig. 1(b)] [17]. In this case, each water molecule in the flat ice layer has three hydrogen bonds that are involved in the hydrogen bond network. Every second water will thus have a H atom that is not coordinated to another water molecule. The question is now whether these uncoordinated water OH bonds will point away from the metal (H-up) or down towards the surface (H-down).

Uncoordinated OH bonds can, however, be detected through the effect on the molecular orbitals. XAS, also denoted near edge x-ray absorption fine structure (NEXAFS), is used to selectively probe the local unoccupied orbital structure in different orientations in the contact layer [18]. It was recently demonstrated that the electronic structure of liquid water strongly depends on the H-bonding environment and that this can be probed by XAS [19–21]. Specific strong spectral features in the low energy part of the spectrum (535 eV) are related to uncoordinated OH groups due to broken H bonds on the H-donating site. Similar spectral features have also been seen for uncoordinated OH groups at the ice surface (free OH) and should be present also in the H-up case [21]. To theoretically distinguish between the H-up and H-down cases we have first optimized the structures using energy gradients; in both cases the resulting structure is a rather flat, nondissociated ice layer, but the energy difference between the two cases is rather small. In Fig. 3(a) we compare the computed O K-edge spectra for the resulting H-up and H-down structure models with experiment; the polarization shown is with the E vector perpendicular to
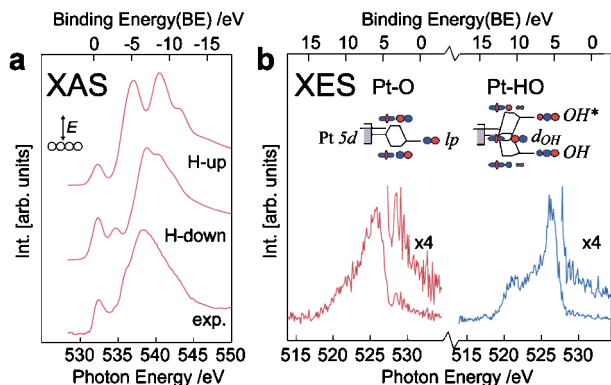
FIG. 3 (color online). (a) XAS spectra of water on Pt(111) corresponding to the p_z component. Computed XAS spectra of the flat ice on Pt(111) with uncoordinated OH toward the vacuum (H-up) and toward the substrate (H-down). The H-down spectrum is in agreement with the experimental XAS spectrum (bottom). (b) XES spectra (p_z components) from Pt-O (left) and Pt-HO (right) bonding species showing the occupied orbital structure. The insets represent schematic diagrams of the Pt-O and Pt-HO bonding interactions.

the surface (z direction), i.e., in the direction of the uncoordinated OH groups [22]. The computed H-up structure gives rise to a strong feature at 536.5 eV assignable to orbitals localized at the uncoordinated OH bond pointing toward the vacuum. In the H-down configuration, the peaks are broadened and lose intensity due to interactions with the Pt surface. Comparison with the experimental x-ray absorption spectrum immediately shows that this feature is missing except for a weakly discernible shoulder. Furthermore, the computed O 1s chemical shift is 0.75 eV for the H-down model, consistent with the upper limit of 0.8 eV estimated from the curve fitting in Fig. 2. The H-up model with a flat layer gives a chemical shift of 1.1 eV. We conclude that water adsorbs on Pt(111) in the overlayer shown in Fig. 1(b).

This result confirms the observations from vibrational spectroscopies [9,23–25]. In the reported vibrational spectra [9,23,24], the intensity of the uncoordinated OH group peak is extremely weak compared to that at the ice surface. The residual contribution of uncoordinated OH can be estimated to be 3%–5% of the intensity of that at the ice surface, indicating only a minor contribution of H-up species. This is explained by the weakening and elongation of the internal OH bonds through the interaction with the metal substrate. Indeed, we find a very shallow calculated potential for the stretching of this OH bond providing a redshift in the IR spectrum as experimentally observed [23]. Furthermore, we expect different adsorption bond strengths for the Pt-O and Pt-HO species. In fact, substrate-adsorbate stretching vibration measurements show two peaks at 133 and 266 cm^{-1} [25].

In order to address the details of the mechanism by which water bonds with the OH group toward the surface, we use XES to consider the occupied electronic states of the overlayer in an atom-specific way [26]. By carefully tuning the excitation photon energy [27], we selectively observe the occupied electronic states projected on the oxygen atom of, respectively, the Pt-O and Pt-HO bonding species [Fig. 3(b)]. We compare the XES spectra for the waters binding through oxygen and hydrogen and focus on the p components projected along the (vertical) z direction, which corresponds to the direction of the surface bond.

The interaction of the O lone pair (lp) orbital of the Pt-O bonding species with the substrate d band will result in bonding and antibonding combinations. We can find the bonding combination as the strong asymmetric peak between 6–15 eV. We can recognize a weak feature between 4 eV and the Fermi level that has an antibonding character in the molecular orbital analysis of the computed XES spectrum. This band is not fully occupied, and we can observe the unoccupied contribution of this band in the XAS spectrum as the peak at 532 eV [Fig. 3(a)]. We can see the repulsive character of the Pt-O bonding in the charge density difference plot (Fig. 4, top). The charge density is decreased along the bond indicating charge polarization to the surroundings in order to minimize the Pauli repulsion between the lone pair orbital and the Pt d orbital.

For the Pt-HO bonding species the two OH groups in the water molecule have different surroundings, either coordination to the surface or involvement in donating a H bond to another water in the overlayer. This results in a substantial rehybridization of the molecular orbital structure into localized OH orbitals. If we consider only the OH orbital directed to the surface and one Pt atom, a simple molecular orbital picture for the Pt-HO interaction can be derived. The bonding involves three atoms in the interaction and results in three molecular orbitals that are different in the number of nodes [Fig. 3(b), right]. The lowest orbital is bonding and the highest antibonding between hydrogen and Pt. The middle orbital will have a node between the O and the Pt causing a nonbonding
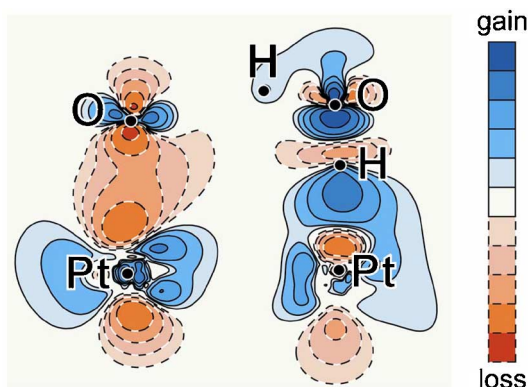

FIG. 4 (color online). Charge density difference plots for Pt-O (left) and Pt-HO (right) bonding species.

interaction and essentially pure oxygen p character, seen in the XES spectrum at 5 eV. The other two orbitals will reside above and below this state and will not have a prominent intensity in the XES spectrum since they involve mainly hydrogen character. The antibonding orbital is composed of mainly Pt character and forms a broad band with contributions above the Fermi level, seen in the XAS spectrum [Fig. 3(a)] around 535 eV. The rearrangement of charge due to net bonding contributions can be seen in the charge density difference plot (Fig. 4). We observe an increase of density between the H and Pt atoms (electron pairing) from the bonding combination and a decrease on the H atom along the OH bond from the nonbonding combination. We can thus say that the Pt-HO bonding results in the formation of a Pt-H bond together with the weakening of the water internal O-H bond.

Adsorption of water on metal surfaces is generally found to lead to a decrease in the work function [1]. Because of the small chemisorption energy the orientation of the water dipoles in the layer has been considered as the main influence on the work function. However, the charge transfer interactions with the substrate in opposite directions for the Pt-O and Pt-HO species, charge rearrangements in the Pt substrate, as well as H bonding within the overlayer, make such a simple picture of work function changes questionable.

Our studies thus show that (i) water is adsorbed intact on Pt(111) and forms flat ice, (ii) free, uncoordinated OH groups are not present, and (iii) the water layer has both oxygen bonding and hydrogen bonding to the surface. The unique nontetrahedral arrangement of flat ice to allow both M-O and the unusual M-HO bonding is the key to understanding the reactions of water on surfaces. The M-HO bonding results from the balance between M-H bond formation and O-H bond weakening. On a metal surface that has a sufficiently high hydrogen affinity O-H bond cleavage may occur, which is why water forms the partially dissociated layer on Ru(0001) [5].

[1] P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987).

[2] M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).

[3] D. L. Doering and T. E. Madey, Surf. Sci. **123**, 305 (1982).

[4] G. Held and D. Menzel, Surf. Sci. **316**, 92 (1994).

[5] P. J. Feibelmann, Science **295**, 99 (2002).

[6] G. Pirug, C. Ritke, and H. P. Bonzel, Surf. Sci. **241**, 289 (1991).

[7] W. Ranke, Surf. Sci. **209**, 57 (1989).

[8] A. Glebov, A. P. Graham, A. Menzel, and J. P. Toennies, J. Chem. Phys. **106**, 9382 (1997).

[9] S. Haq, J. Harnett, and A. Hodgson, Surf. Sci. **505**, 171 (2002).

[10] M. Morgenstern, T. Michely, and G. Comsa, Phys. Rev. Lett. **77**, 703 (1996).

[11] M. Morgenstern, J. Müller, T. Michely, and G. Comsa, Z. Phys. Chem. **198**, 43 (1997).

[12] DaCapo is a free software developed at the Center for Atomic-scale Materials Physics (CAMP) funded by the Danish research council.

[13] M. E. Casida *et al.*, deMon Software, 2001.

[14] L. Triguero, L. G. M. Pettersson, and H. Ågren, Phys. Rev. B **58**, 8097 (1998).

[15] N. Mårtensson and A. Nilsson, in *Application of Synchroton Radiation; High Resolution Studies of Molecules and Molecular Adsorbates*, edited by W. Eberhardt (Springer, Berlin, Heidelberg, 1995), Vol. 35.

[16] O. Björneholm *et al.*, Surf. Sci. **315**, L983 (1994).

[17] The weak bonding to the surface generates a potential that is rather flat, indicating large error bars in the total energy-based estimated layer distance. In this case computed spectra and O $1s$ binding energies provide more sensitive measures. A geometry optimization provides a layer distance to the substrate of 2.8 Å. When the layer distance has been shortened to 2.3–2.4 Å, we can see an overall agreement between experiment and theory in both the XAS and XPS results.

[18] J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, Heidelberg, 1992).

[19] S. Myneni *et al.*, J. Phys. Condens. Matter **14**, L213 (2001).

[20] K. R. Wilson *et al.*, J. Phys. Condens. Matter **14**, L221 (2001).

[21] M. Cavalleri, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson, Chem. Phys. Lett. **364**, 363 (2002).

[22] D. Coulman *et al.*, J. Chem. Phys. **93**, 58 (1990).

[23] H. Ogasawara, J. Yoshinobu, and M. Kawai, Chem. Phys. Lett. **231**, 188 (1994).

[24] M. Nakamura, Y. Shingaya, and M. Ito, Chem. Phys. Lett. **309**, 123 (1999).

[25] K. Jacobi, K. Bedürftig, Y. Wang, and G. Ertl, Surf. Sci. **472**, 9 (2001).

[26] A. Nilsson *et al.*, J. Electron Spectrosc. Relat. Phenom. **110-111**, 15 (2000).

[27] The oxygen bonding species has XAS threshold at lower energy than that for the hydrogen bonding species. This allows separated XES spectra for the Pt-O and Pt-HO bonding species to be obtained by using two excitation energies (532 and 538 eV) and a subtraction procedure.