

## General Model for Water Monomer Adsorption on Close-Packed Transition and Noble Metal Surfaces

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*Ab initio* density functional theory has been used to investigate the adsorption of H<sub>2</sub>O on several close-packed transition and noble metal surfaces. A remarkably common binding mechanism has been identified. On every surface H<sub>2</sub>O binds preferentially at an atop adsorption site with the molecular dipole plane nearly parallel to the surface. This binding mode favors interaction of the H<sub>2</sub>O *1b*<sub>1</sub> delocalized molecular orbital with surface wave functions.

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The interaction of H<sub>2</sub>O with metal surfaces is of fundamental importance. Particular relevance to heterogeneous catalysis and electrochemistry has motivated many studies [1,2]. However, our atomic level understanding of H<sub>2</sub>O adsorption systems remains unclear and basic questions on the binding site and orientation of H<sub>2</sub>O monomers on metal surfaces remain unanswered.

Experimental characterization of H<sub>2</sub>O monomer adsorption is difficult, complicated by facile H<sub>2</sub>O cluster formation. Cluster formation is problematic because it masks the true H<sub>2</sub>O-metal interaction, making it difficult to make any definitive statements about H<sub>2</sub>O-metal bonding [1]. In order to minimize cluster formation, it is necessary to work with low H<sub>2</sub>O coverages at low temperatures,  $\ll 100$  K. Several experiments have recently been performed under these conditions. Notable are a number of scanning tunneling microscopy (STM) studies on the {111} facets of Pt, Ag, Pd, and Cu [3–6]. However, to date, it has not been possible with STM to resolve the internal structure of adsorbed H<sub>2</sub>O molecules. Nor has it been possible to determine the orientation of the H<sub>2</sub>O molecule with respect to the surface normal.

The preferred orientation of H<sub>2</sub>O on a surface is important because it will affect how H<sub>2</sub>O responds to an applied electrochemical field, how H<sub>2</sub>O dissociates, and the stability and structure of H<sub>2</sub>O clusters that may form. Generally it has been assumed that H<sub>2</sub>O adsorbs “upright” with the O end down and the OH bonds pointing away from the surface, since this orientation maximizes the adsorbate-dipole substrate-image-dipole interactions [1,6–8]. Several spectroscopic techniques [9–11] and the electron stimulated desorption ion angular distributions (ESDIAD) [12,13] approach have been used to probe the orientation of H<sub>2</sub>O monomers on single crystal surfaces. However, results are conflicting and ambiguities have arisen, mainly because of difficulties in discriminating between H<sub>2</sub>O monomers and clusters.

Despite many theoretical studies in this area a clear consensus on the nature of H<sub>2</sub>O-metal bonding has not

been arrived at [14–21]. Some predict preferential adsorption at atop sites while others predict adsorption at higher coordination sites [16,17]. Further, it is often assumed that H<sub>2</sub>O sits upright in the plane of the surface normal [16,18,19]. When this has been explicitly investigated, however, a range of orientations from upright to nearly flat lying molecules have been predicted [19–23]. Clearly a systematic study with a consistent theoretical approach has the potential to shed new light in this area.

Here we present the results of a density functional theory (DFT) study of H<sub>2</sub>O monomer adsorption on a variety of metal substrates. Specifically, adsorption has been examined on Ru{0001}, Rh{111}, Pd{111}, Pt{111}, Cu{111}, Ag{111}, and unreconstructed Au{111}. From this database of adsorption systems a common binding mode is identified. H<sub>2</sub>O monomers bind preferentially at atop sites and lie nearly flat on the surface.

Total energy calculations within the DFT framework were performed with the CASTEP code [24]. Ultrasoft pseudopotentials were expanded within a plane wave basis set with a cutoff energy of 340 eV. Exchange and correlation effects were described by the Perdew-Wang 1991 [25] generalized gradient approximation. Metal surfaces were modeled by a periodic array of five or six layer slabs, separated by a vacuum region equivalent to at least six layers. A  $p(2 \times 2)$  unit cell was employed and a single H<sub>2</sub>O molecule was placed on one side of the slab [26]. Monkhorst-Pack meshes with at least  $3 \times 3 \times 1$   $\mathbf{k}$ -point sampling within the surface Brillouin zone were used.

Structure optimizations were performed for a variety of initial orientations of the H<sub>2</sub>O molecule on each surface. These included configurations in which H<sub>2</sub>O was initially placed in the surface normal with the H atoms either pointing away from the surface (upright H<sub>2</sub>O) or towards the surface [27] as well as structures in which H<sub>2</sub>O was initially parallel to the surface. Atop, bridge, and threefold sites were studied. From this extensive set of DFT calculations we find (i) on every surface the favored adsorption site for H<sub>2</sub>O is the atop site; (ii) at

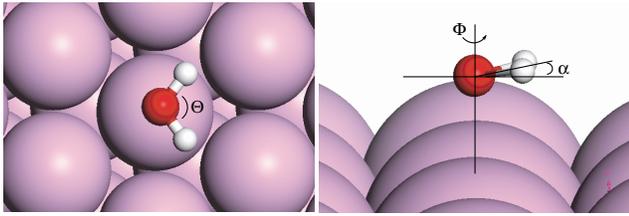


FIG. 1 (color online). Top and side views of the typical structure of a  $\text{H}_2\text{O}$  monomer adsorbed on a close-packed metal surface.

this site  $\text{H}_2\text{O}$  lies nearly parallel to the surface. The tilt angle ( $\alpha$ ) between the molecular dipole plane and the surface is, on average,  $10^\circ$ , with a minimum value of  $6^\circ$  on Ru and a maximum value of  $15^\circ$  on Cu. Such a common binding mode for  $\text{H}_2\text{O}$  on this large variety of metal surfaces was not anticipated [28].

Figure 1 illustrates this general binding mode for  $\text{H}_2\text{O}$  and structural parameters and adsorption energies are given in Table I. We notice from Table I that  $\text{H}_2\text{O}$  binds weakly to all surfaces investigated. The adsorption energies [29] range from 0.1 to 0.4 eV and are in the sequence:  $\text{Au} < \text{Ag} < \text{Cu} < \text{Pd} < \text{Pt} < \text{Ru} < \text{Rh}$ . Bond strengths in this energy regime place the  $\text{H}_2\text{O}$  metal bond in the weak chemisorption/physisorption limit. More importantly, this energy range straddles the energy of a typical H bond between  $\text{H}_2\text{O}$  molecules ( $\sim 0.25$  eV [1]). An implication for adsorbed  $\text{H}_2\text{O}$  clusters is that as one moves through the above series the relative importance of adsorbate-substrate and H bonding interactions is liable to be reversed. Also shown in Table I are the adsorption energies of  $\text{H}_2\text{O}$  at the next most stable site on each surface, which tends to be the bridge site.

From Table I several other interesting features of  $\text{H}_2\text{O}$  adsorption are revealed. First,  $\text{H}_2\text{O}$  deforms little upon adsorption: the O-H bonds are slightly elongated from a calculated gas phase value of  $0.97 \text{ \AA}$  to  $0.97\text{--}0.98 \text{ \AA}$ ; and the HOH angle ( $\Theta$ ) is expanded by no more than  $2^\circ$  from a calculated gas phase value of  $104^\circ$ . Secondly,  $\text{H}_2\text{O}$  is laterally displaced from the precise

atop site ( $\Delta O_{xy}$ ), by  $\approx 0.3 \text{ \AA}$  on Ru, Pt, and Ag. However the potential energy surfaces for diffusion in the vicinity of the atop sites are quite smooth. Typically it costs  $\sim 0.02$  eV to move  $\text{H}_2\text{O}$  from its equilibrium position back to the precise atop site. This is important as it explains the stability of small  $\text{H}_2\text{O}$  clusters that form on Ag [4], Pd [5], and Cu [6] despite apparent mismatches between the substrate lattice constants and the optimal O-O separation between H bonded  $\text{H}_2\text{O}$  molecules. The third feature is that the metal atom directly beneath  $\text{H}_2\text{O}$  is slightly displaced along the surface normal from the (three) other top layer metal atoms ( $\Delta_{metal}$ ). Finally, we notice that the largest variation between each adsorption system is the height of the  $\text{H}_2\text{O}$  molecule above the surface: the O-metal bond lengths vary from  $2.25 \text{ \AA}$  on Cu to  $3.02 \text{ \AA}$  on Au.

In discussing the preferred adsorption site for  $\text{H}_2\text{O}$ , previous studies have argued that  $\text{H}_2\text{O}$  acts as an electron donor and the substrate as an electron acceptor, favoring adsorption on atop sites [1,30]. Furthermore, approximate rules based on tight-binding arguments also predict atop adsorption for electron donors under appropriate conditions [31]. Although these ideas may prove to be simplistic, we find that they are indeed consistent with Mulliken population analyses, which indicate that typically  $\text{H}_2\text{O}$  donates  $0.1e$  to the metal. And, as we will show below, consistent with electron density difference plots, which reveal that  $\text{H}_2\text{O}$  mixes with the surface mainly through its occupied  $1b_1$  molecular orbitals.

We now examine more closely the orientation of  $\text{H}_2\text{O}$  at the atop site. First, rotation about the O-metal bond ( $\Phi$  in Fig. 1) has been examined on Ru, Pd, Pt, and Ag. In agreement with previous studies, this rotation is essentially unhindered. There tends not to be a clear azimuthal preference for  $\text{H}_2\text{O}$ , with different orientations within  $\sim 0.02$  eV of each other. This implies that adsorbed  $\text{H}_2\text{O}$  monomers will be randomly distributed about the surface normal. In addition, it becomes simple for two monomers adsorbed at adjacent atop sites to reorientate and form a dimer. With at most a small energy loss, the dimer profits from H bond formation. Rotation in a plane perpendicular

TABLE I. Adsorption energies ( $E_{\text{ads}}$ ) and optimized structural parameters for  $\text{H}_2\text{O}$  at its equilibrium (atop) site on several metal surfaces.  $\Delta_{metal}$  is the vertical displacement of the atop site metal atom from the other three surface layer metal atoms.  $\Delta O_{xy}$  is the lateral displacement of O from the precise atop site.  $\Theta$  is the HOH angle and  $\alpha$  is the  $\text{H}_2\text{O}$ -surface tilt angle as displayed in Fig. 1. Also given are the adsorption energies of  $\text{H}_2\text{O}$  at the nextmost stable site on each surface ( $E_{\text{ads}2}$ ).

Surface	$E_{\text{ads}}$ (eV)	O-metal ( $\text{\AA}$ )	O-H ( $\text{\AA}$ )	$\Delta_{metal}$ ( $\text{\AA}$ )	$\Delta O_{xy}$ ( $\text{\AA}$ )	$\Theta$ ( $^\circ$ )	$\alpha$ ( $^\circ$ )	$E_{\text{ads}2}$ (eV)
Ru{0001}	0.38	2.29	0.98	-0.01	0.30	106	6	0.12
Rh{111}	0.42	2.31	0.98	0.06	0.06	106	9	0.15
Pd{111}	0.33	2.28	0.98	0.03	0.18	105	7	0.17
Pt{111}	0.35	2.36	0.98	0.03	0.29	106	7	0.09
Cu{111}	0.24	2.25	0.98	0.07	0.03	106	15	0.19
Ag{111}	0.18	2.78	0.97	0.04	0.29	105	9	0.14
Au{111}	0.13	3.02	0.97	0.03	0.06	105	13	0.11

to the surface [ $\text{H}_2\text{O}$  tilting in the  $(\bar{1}\bar{1}2)$  direction,  $\alpha$  in Fig. 1] was investigated on Ru, Pd, Pt, and Ag. The total energy variation with the  $\text{H}_2\text{O}$  tilt angle is shown in Fig. 2. Two insights can be gleaned from this. First, the minima close to  $0^\circ$  confirm that  $\text{H}_2\text{O}$  lies almost parallel to each surface. Second, the maxima at  $90^\circ$  reveal that upright  $\text{H}_2\text{O}$  molecules are disfavored. Thus, despite assumptions that  $\text{H}_2\text{O}$  molecules sit upright when adsorbed, DFT calculations indicate that this is not the case.

Clearly it is desirable to understand this general tendency of  $\text{H}_2\text{O}$  to lie nearly parallel to the surface. To this end we first consider the two higher energy occupied molecular orbitals of  $\text{H}_2\text{O}$ , namely, the  $3a_1$  and  $1b_1$  orbitals, which are shown in Fig. 3. The  $3a_1$  orbital is in the  $C_{2v}$  symmetry plane of the molecule. The  $1b_1$  orbital is orthogonal to this, antisymmetric about a mirror plane in the molecule. It is plausible, therefore, that when  $\text{H}_2\text{O}$  approaches a metal surface an upright  $\text{H}_2\text{O}$  will favor interaction through the  $3a_1$  orbital, whereas a flat  $\text{H}_2\text{O}$  will favor interaction through the  $1b_1$  orbital. An examination of the electronic structure in these systems confirms these qualitative assumptions. Figure 3, for example, displays a partial density of states (PDOS) plot projected onto the O  $p$  orbitals for a relaxed  $\text{H}_2\text{O}$  ( $\alpha = 7^\circ$ ) and an upright  $\text{H}_2\text{O}$  ( $\alpha = 90^\circ$ ) on Pt. For each curve two peaks are visible. A careful examination of the real space distribution of the individual eigenstates within each peak reveals that states within the lower energy peak are mainly  $3a_1 - d$  states and states within the higher energy peak are mainly of  $1b_1 - d$  character. A representative example from each peak, for  $\text{H}_2\text{O}$  in its equilibrium structure, is displayed in Fig. 3. The approximate energies of the  $3a_1$  and  $1b_1$  orbitals in the gas phase are also shown in Fig. 3 [32]. By comparing the energy of the gas and adsorbed phase peaks and also by inspection of the individual eigenstates it is found that when  $\text{H}_2\text{O}$  is upright (dotted line) on Pt the  $3a_1$  derived orbitals mix most strongly with the surface and consequently experience the greatest stabilization. On the other hand when

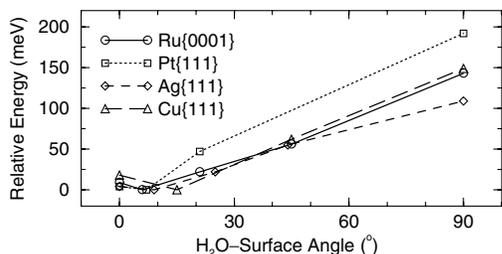


FIG. 2. Relative energy against  $\text{H}_2\text{O}$  tilt angle ( $\alpha$ ) for  $\text{H}_2\text{O}$  on several metal surfaces. A tilt angle of  $0^\circ$  corresponds to  $\text{H}_2\text{O}$  parallel to the surface, whereas a tilt angle of  $90^\circ$  corresponds to upright  $\text{H}_2\text{O}$  in the plane of the surface normal with the O end down. All points apart from equilibrium structures were obtained from single point energy optimizations with O at its equilibrium height above each surface

$\text{H}_2\text{O}$  lies flat (solid line) the  $1b_1$  derived orbitals undergo the largest mixing with the surface and experience the greatest stabilization. However, given that initially the  $1b_1$  orbital is closer to the Fermi level, orientations that maximize this interaction will be preferred. Indeed the crucial role played by the  $1b_1$  orbital for  $\text{H}_2\text{O}$  in its equilibrium structure is clearly seen in the density difference plot displayed in Fig. 3(b).

Competing with this covalent interaction is the interaction between the  $\text{H}_2\text{O}$  permanent dipole and its image beneath the surface. To understand the role played by the electrostatics we have estimated the interaction energies associated with parallel and perpendicular configurations of  $\text{H}_2\text{O}$ . A classical images picture, where the image plane lies  $1 \text{ \AA}$  outside the surface, has been employed [33,34]. For a set of three charges, using values from a Mulliken analysis that produce a dipole moment in agreement with the experimental value, the perpendicular configuration is favored over the parallel configuration by 0.05 and 0.02 eV on Pt and Ag, respectively. Thus from a purely electrostatic perspective there is a preference for  $\text{H}_2\text{O}$  to remain upright when adsorbed. However, it is apparent that this electrostatic desire is small and clearly it is not decisive. The dominant interaction, and the one that lies at the origin of the near-parallel configuration, is the covalent one. It is remarkable that this orientation persists on a wide variety of substrates: the adsorption only moderately deforms the molecule, yet the interaction is strong enough to impose a given orientation and even to slightly disturb the substrate.

Finally it is important to consider how comfortable this model for  $\text{H}_2\text{O}$  monomer adsorption sits with existing

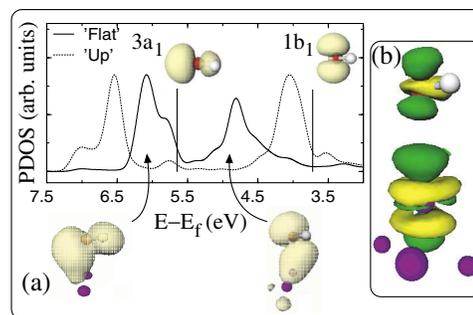


FIG. 3 (color online). (a) Partial density of states (PDOS) projected onto the  $p$  orbitals of O for  $\text{H}_2\text{O}$  adsorbed in its equilibrium (“Flat,”  $\alpha = 7^\circ$ ) and an upright configuration (“Up,”  $\alpha = 90^\circ$ ) on Pt{111}. The shape and approximate energies of the  $3a_1$  and  $1b_1$   $\text{H}_2\text{O}$  orbitals in the gas phase are displayed, as are two representative eigenstates from the  $3a_1$  and  $1b_1$  resonances for  $\text{H}_2\text{O}$  adsorbed in its equilibrium structure. (b) Isosurface of difference electron density for  $\text{H}_2\text{O}$  on Pt{111}. This was obtained by subtracting from the adsorption system the densities of a clean Pt slab and a  $\text{H}_2\text{O}$  molecule. Dark (light) regions correspond to a density decrease (increase) of  $3.6 \times 10^{-2} e\text{\AA}^{-3}$ .

experimental results. First, although often assumed to sit at atop sites the only actual characterizations of H<sub>2</sub>O monomer adsorption are the recent STM study on Pd{111} [5] and an x-ray absorption fine structure study on Ni{110} [35]. Satisfyingly, both conclude that H<sub>2</sub>O adsorbs at atop sites. Further, on Ni{110} it was shown that the molecular plane is significantly tilted ( $< 70^\circ$ ) from the surface normal [10,35]. A similar conclusion for the H<sub>2</sub>O tilt angle was reached from electron-energy-loss studies of H<sub>2</sub>O monomers at 10 K on Cu{100} and Pd{100} [9]. In apparent disagreement with this model, however, are the ESDIAD results for H<sub>2</sub>O on Ru{0001} from which it was concluded that H<sub>2</sub>O monomers sit upright [12,13]. However, these experiments were performed at 90 K at coverages of 0.2 monolayers. Subsequent infrared absorption spectroscopy (IRAS) experiments have shown that under these conditions on Ru{0001} the dominant surface species will be H<sub>2</sub>O clusters, probably tetramers, and not H<sub>2</sub>O monomers [11]. Monomeric H<sub>2</sub>O is only stable on Ru{0001} below 50 K and the IRAS results provide evidence that indeed it lies “nearly parallel” to the surface [11]. Thus it appears that the model for H<sub>2</sub>O adsorption identified here is not incompatible with experimental data, rather there are several results in apparent support of it.

In conclusion, a systematic DFT study has identified a general binding mode for H<sub>2</sub>O on close-packed metal surfaces. On all surfaces investigated, H<sub>2</sub>O adsorbs preferentially at atop sites and lies nearly parallel to the surface. This binding mode favors interaction of the H<sub>2</sub>O  $1b_1$  delocalized molecular orbital with the surface.

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