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Insight into H_2O-ice adsorption and dissociation on metal surfaces from first-principles simulations

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Density-functional theory has been used to perform a systematic study of (intact) H_2O bilayer and (dissociated) H_2O-OH-H overlayer adsorption on hexagonal $3d$, $4d$, and $5d$ transition- and noble-metal surfaces. Through careful decompositions of the H_2O adsorption energies, we find that variations in the relative stability of intact bilayers and dissociated overlayers depend mainly on variations in adsorbate-substrate bonding, and not on variations in H bonding as previously assumed. Further, we show that the H_2O dissociation energy in the bilayers is controlled by the OH-metal bond strength in the dissociated overlayers.

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The interaction between H_2O and metal surfaces is of considerable importance to numerous areas of scientific endeavor as well as to many aspects of daily life.[1] Despite this, there remain major gaps in our understanding of H_2O-metal interfaces. For example, the structures assumed by ordered water-ice overlayers on single-crystal metal surfaces are still not known; and this apparently simple issue is currently the focus of an intense debate.[2–9]

On the late transition-metal surfaces, in particular those with hexagonal symmetry, H_2O adsorption is traditionally thought to proceed through bilayer formation.[1] The lower set of H_2O molecules in the bilayer lies nearly parallel to the surface, with each molecule involved in three H bonds. The higher-lying set has its molecular axes in the plane of the surface normal. Only one OH bond from each H_2O of this type is implicated in the H bond network. The other OH bonds are ‘‘free,’’ and practically since the advent of surface science, it had been assumed that these free OH bonds point away from the surface [‘‘H-up’’ model, Fig. 1(a)].[1] Recently, however, on Pt{111} it was shown that these OH bonds are instead directed at the surface [‘‘H-down’’ model, Fig. 1(b)], resulting in a rather compressed H_2O bilayer.[5] And on Ru{0001}, Feibelman has argued, based on density-functional theory (DFT) calculations, that the free OH bonds are *broken* and that H_2O wets Ru{0001} as a H_2O-OH-H ‘‘partially dissociated’’ adlayer [Fig. 1(c)].[2] Clearly the picture that is emerging for H_2O adsorption on metal surfaces is more complicated than had been anticipated. Our current understanding requires a systematic study with a rigorous theoretical framework aimed at understanding when and why a particular overlayer model may be favored.

We have used DFT to examine intact H_2O bilayer and dissociated H_2O-OH-H overlayer adsorption on a range of transition- and noble-metal surfaces. Specifically we have looked at adsorption on the {111} facets of Ni, Cu, Rh, Pd, Pt, and Ag, and on the {0001} facet of Ru. Our primary aim is to elucidate the interplay between adsorbate-substrate and H bonding interactions in dictating the stability of H_2O-ice and dissociated overlayers. By analyzing the H_2O adsorption energies, we find that variations in the stability of both types of overlayer depend mainly on variations in adsorbate-substrate bonding, and *not* on variations in H bonding as previously assumed. In addition, we reveal that the tendency for H_2O dissociation in the bilayers depends mainly on the OH-metal bond strength in the final state.

Total-energy calculations were performed with the CASTEP (Ref. 10) code with a setup similar to that described previously[7,11] (see also Ref. 12). Metal surfaces were modeled by periodic arrays of four-layer-thick slabs separated by vacuum regions equivalent to a further six metal layers. $\sqrt{3}\times\sqrt{3}$-$R30°$ unit cells (henceforth termed $\sqrt{3}$) with $4\times4\times1$ Monkhorst-Pack **k**-point meshes were used. $\sqrt{3}$ periodicity is the most common periodicity for an adsorbed bilayer and the one we use throughout.[13] Admittedly, on some surfaces, assuming $\sqrt{3}$ periodicity is an oversimplification of the observed state. For example, on Pt a $\sqrt{39}\times\sqrt{39}$-$R16.1°$ overlayer forms.[14] Calculations with a unit cell of this size are beyond our reach computationally. However, we believe that the $\sqrt{3}$ structures are good, albeit not perfect, representations and serve as useful models to discuss the basic question of molecular versus dissociative adsorption. One should bear in mind, however, that bilayers in larger unit cells have been shown to be approximately 70 meV/H_2O more stable.[9]

Table I lists the ‘‘total H_2O adsorption energy’’ per H_2O molecule, $E^{(1)}_{\text{ADS-TOT}}$, in the various overlayers. We define $E^{(1)}_{\text{ADS-TOT}}$ as

$$E^{(1)}_{\text{ADS-TOT}}=(E_{\text{2H2O/M}}-2E_{\text{H2O}}-E_{\text{M}})/2, \qquad (1)$$

where $E_{\text{2H2O/M}}$ is the energy of the adsorbed H_2O bilayer or H_2O-OH-H overlayer; E_{H2O} is the energy of a single H_2O molecule in vacuum; E_{M} is the energy of the bare metal slab; and 2 is the number of H_2O molecules (H_2O molecule equivalents) in the adsorbed bilayers (H_2O-OH-H overlayers) per $\sqrt{3}$ cell. $E^{(1)}_{\text{ADS-TOT}}$ for the H-up and H-down bilayers are listed in Table I as well as for two H_2O-OH-H overlayers: One H_2O-OH-H overlayer is displayed in Fig. 1(c) and has the chemisorbed H located at an atop site in the center of the H_2O-OH network. In the other (referred to as H_2O-OH +H/M) the H atom has been removed to a separate $\sqrt{3}$ cell and allowed to adsorb at its favored site on each surface (threefold sites). This H_2O-OH+H/M state therefore models the scenario in which H atoms ‘‘escape’’ from the H_2O-OH overlayer and adsorb on patches of clean surface.

A consideration of $E^{(1)}_{\text{ADS-TOT}}$ for the intact bilayers reveals that on all substrates the total adsorption energies are reasonably similar;[15] ranging from -0.37 eV on Ni (H-down) to -0.56 eV on Pd (H-down). In addition, the stability of the

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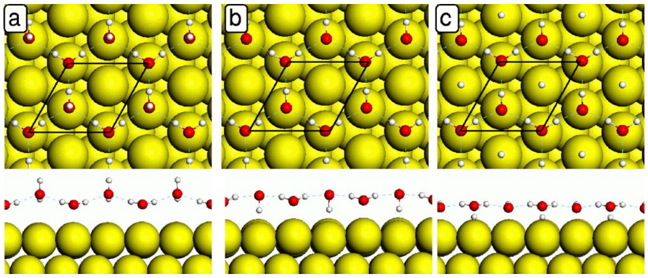

FIG. 1. (Color online) Structures of (a) H-up bilayer; (b) H-down bilayer; and (c) H_2O-OH-H overlayer on a hexagonal metal surface. The parallelogram indicates the surface, $\sqrt{3}\times\sqrt{3}$-$R30°$, unit cell.

H-up and H-down bilayers is comparable (within $0.05\ \mathrm{eV}/H_2O$). In contrast, the stability of the dissociated overlayers varies considerably; ranging from -1.00 eV on Ru to $+0.26$ eV on Ag. Moreover, the dissociated overlayers with the chemisorbed H atoms, once removed to separate $\sqrt{3}$ cells, are always more stable.[16] However, the most important information contained within Table I is that we can identify the overlayer that is most stable on each substrate: Intact bilayers are favored over dissociated overlayers on Ag (H-down), Pt (H-down), and Cu (H- up) by 0.43, 0.11, and 0.05 (Ref. 17) eV, respectively. On Ru, Rh, and Ni, dissociated overlayers are preferred over intact bilayers by 0.46, 0.23, and 0.20 eV, respectively. And on Pd the H-down and H_2O-OH+H/M overlayers are, to within the accuracy of the calculations, equally stable.[17] However, this picture is quite sensitive to the final location of the chemisorbed H atom. If we assume that in the dissociated overlayers the chemisorbed H atoms remain at the atop sites[3] [Fig. 1(c)], then it is only on Ru that the H_2O-OH-H overlayer is predicted to be more stable than either type of intact bilayer.

Many H_2O bilayer adsorption studies have speculated about the balance between H bonding and H_2O-metal bonding. Here, we decompose $E^{(1)}_{\text{ADS-TOT}}$ into these two contributions and quantitatively investigate their interplay. For intact bilayers we employ two complimentary approaches. In the first, we estimate the amount of H bonding per H_2O molecule, $E^{(1)}_{\text{H-BOND}}$, from

$$E^{(1)}_{\text{H-BOND}}=(E_{\text{BILAYER}}-2E_{\text{H2O}})/2, \tag{2}$$

where E_{BILAYER} is the total energy of a bilayer in vacuum fixed in the structure it assumes when adsorbed.[18] The bonding between the bilayer and the substrate, $E^{(1)}_{\text{ADS-BILAYER}}$, is then estimated per H_2O molecule from

$$E^{(1)}_{\text{ADS-BILAYER}}=(E_{\text{2H2O/M}}-E_{\text{BILAYER}}-E_{\text{M}})/2. \tag{3}$$

TABLE I. Adsorption energies for $\sqrt{3}\times\sqrt{3}$-$R30°$ intact and partially dissociated overlayers. The most stable overlayer(s) on each surface is (are) indicated in bold.

	$E_{\text{ADS-TOT}}{}^{(1)}$ (eV/H_2O)			
	H-up	H-down	H_2O-OH-H	H_2O-OH+H/M
Ni	−0.42	−0.37	−0.12	**−0.62**
Cu	**−0.45**	−0.43	−0.07	−0.40
Ru	−0.54	−0.50	−0.77	**−1.00**
Rh	−0.53	−0.55	−0.51	**−0.78**
Pd	−0.52	**−0.56**	−0.16	**−0.56**
Pt	−0.46	**−0.49**	−0.31	−0.38
Ag	−0.46	**−0.48**	+0.26	−0.05

In the second approach we make the approximation that the total bilayer-substrate bonding is equivalent to the chemisorption energy of a single H_2O monomer[7] $E_{\text{ADS-MONO}}$. Thus the bilayer-substrate adsorption energy per H_2O molecule, $E^{(2)}_{\text{ADS-BILAYER}}$, is

$$E^{(2)}_{\text{ADS-BILAYER}}\equiv(E_{\text{ADS-MONO}})/2=(E_{\text{H2O/M}}-E_{\text{H2O}}-E_{\text{M}})/2, \tag{4}$$

where $E_{\text{H2O/M}}$ is the energy of a single adsorbed H_2O monomer. Here, we divide by 2 to take an average of the two H_2O molecules in the $\sqrt{3}$ unit cells. The H bonding per H_2O molecule within this scheme, $E^{(2)}_{\text{H-BOND}}$, is taken as the difference between the total H_2O adsorption energy and $E^{(2)}_{\text{ADS-BILAYER}}$:

$$E^{(2)}_{\text{H-BOND}}=E^{(1)}_{\text{ADS-TOT}}-E^{(2)}_{\text{ADS-BILAYER}}. \tag{5}$$

In any energy partitioning scheme, a unique decomposition of the total adsorption energy will not be arrived at, and, inevitably, there are limitations upon the schemes employed here. The first does not take account of H-bond changes during adsorption of the bilayers, and the second assumes that the H_2O-metal bonding in the system remains constant upon adsorption of the second layer of H_2O molecules on top of the first.[19] However, these standard approximations for adsorption energy decompositions are justified here by the finding that both approaches predict the same general trends and yield H-bond estimates that differ by $\leqslant 0.04$ eV/H bond (which can be taken as an error margin on the decomposition estimates).

Figure 2(a) plots the total H_2O adsorption energy, the H-bond energies, and the H_2O-metal bond energies for the H-up bilayer on each surface, shown as a function of the next-nearest-neighbor (NNN: $\sqrt{3}$) metal lattice constant. The decompositions reveal the interplay between H_2O metal and H bonding in adsorbed bilayers. We highlight three important features. First, the largest proportion of $E^{(1)}_{\text{ADS-TOT}}$ is always H bonding; H bonding accounts for $\geqslant 68\%$ ($E^{(2)}_{\text{HBOND}}$) or $\geqslant 80\%$ ($E^{(1)}_{\text{HBOND}}$) of the total H_2O adsorption energies. Second, *H bonding is nearly always the same, regardless of the substrate*; the $E^{(1)}_{\text{HBOND}}$ estimates are $-0.43\pm0.01\ \mathrm{eV}/H_2O$ and the $E^{(2)}_{\text{HBOND}}$ estimates are $-0.37\pm0.02\ \mathrm{eV}/H_2O$. Expressed per individual H bond, the H-bond strengths in the adsorbed bilayers are therefore ~ -0.29 eV/H bond ($E^{(1)}_{\text{HBOND}}$) or ~ -0.25 eV/H bond ($E^{(2)}_{\text{HBOND}}$). The third noteworthy feature in Fig. 2(a) is that *the observed variations in* $E^{(1)}_{\text{ADS-TOT}}$ *are almost exclusively a result of differences in bilayer-metal bond energies* ($E^{(1)}_{\text{ADS-BILAYER}}$ and $E^{(2)}_{\text{ADS-BILAYER}}$) and not due to variations in H bonding. This finding is important since generally the contrary is assumed to be true.[1]

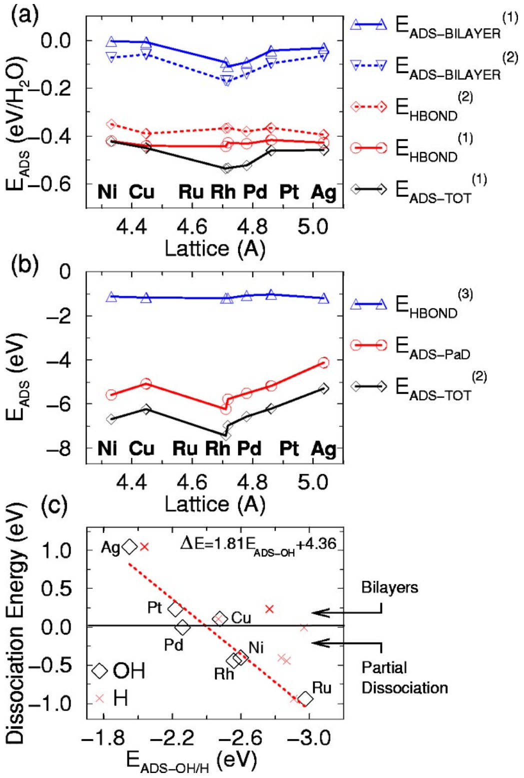

FIG. 2. (Color online) Total H_2O adsorption energy and its decomposition into adsorbate-substrate and H bonding contributions for (a) H-up bilayers and (b) H_2O-OH+H/M overlayers, shown as a function of the calculated substrate lattice constant. Each quantity is defined in the text. (c) Bilayer dissociation energy against OH adsorption at atop sites and H adsorption at threefold fcc sites on metal surfaces. The dotted line is a least-squares fit to the OH points, which are labeled (diamonds).

It has been argued that as the mismatch between the substrate lattice constant—specifically the NNN lattice distance—and the NNN O-O distance in ice I_h increases, the H bonding strength in the adsorbed bilayer decreases. Figure 2(a) shows that for a range of NNN lattice distances (4.33 Å for Ni to 5.04 Å for Ag) straddling the equilibrium value of ice I_h (4.50 Å^1) this is not the case. When we examine in detail the structure of each overlayer it becomes clear that the two-dimensional (2D) bilayers possess a flexibility that is not present in bulk ice. The 3D H-bonding network in bulk ice constrains the O-O interlayer buckling to a given value (0.92 Å). In a 2D bilayer, however, because the H_2O molecules are not H bonded to molecules in other layers, there are no such constraints and any lateral strain induced by a mismatch with the underlying substrate is alleviated through vertical relaxations of H_2O molecules in the bilayer. These displacements alter the O-O interlayer buckling and maintain close to optimal O-O bond lengths. A further implication of Fig. 2(a) that should not be overlooked is that the weak interaction of the bilayers with certain substrates (e.g., Cu or Pt) means that on these surfaces there is no strong desire for the H_2O overlayers to be in registry with the underlying substrate. This explains, in part, why on, for example, Cu or Pt $\sqrt{3}$ overlayers are in practice not observed.[13] Decompositions of $E^{(1)}_{\text{ADS-TOT}}$ have also been performed for the H-down bilayers on each surface (not shown): Similar behavior, albeit more complex, is observed.

The relative importance of adsorbate-substrate and H-bonding interactions has also been explored in the H_2O-OH+H/M overlayers. To aid the following discussion, we reference the total adsorption energy to a new gas phase reference state of H_2O, OH, and H as opposed to one consisting of intact H_2O molecules [$E^{(1)}_{\text{ADS-TOT}}$; Eq. (1)]. The new total adsorption energy $E^{(2)}_{\text{ADS-TOT}}$ is

$$E^{(2)}_{\text{ADS-TOT}}=E_{\text{PaD}}-E_{\text{H2O}}-E_{\text{OH}}-E_{\text{M}}+E_{\text{ADS-H}}, \tag{6}$$

where E_{PaD} is the energy of the partially dissociated H_2O-OH overlayer; E_{H2O} and E_{OH} are the energies of isolated H_2O and OH molecules in vacuum; and $E_{\text{ADS-H}}$ is the adsorption energy of H in a separate $\sqrt{3}$ cell. This new reference state simply calculates the chemisorption of the partially dissociated overlayers, which we then decompose into adsorbate- substrate and H-bonding interactions. To estimate the amount of adsorbate-substrate bonding in each OH-H_2O+H/M partially dissociated overlayer, $E_{\text{ADS-PaD}}$, we sum the adsorption energies of separate H_2O, OH, and H species:

$$E_{\text{ADS-PaD}}=E_{\text{ADS-MONO}}+E_{\text{ADS-OH}}+E_{\text{ADS-H}}, \tag{7}$$

where $E_{\text{ADS-MONO}}$ is the adsorption energy of a H_2O monomer [Eq. (4)] and similarly $E_{\text{ADS-OH}}$ and $E_{\text{ADS-H}}$ are the adsorption energies of OH and H. For consistency with the H_2O-OH overlayer, isolated H_2O and OH adsorption is considered at atop sites. The H-bond energies $E^{(3)}_{\text{HBOND}}$ are defined to be equal to the adsorbate-adsorbate interaction energies and are taken as the difference between $E^{(2)}_{\text{ADS-TOT}}$ and $E_{\text{ADS-PaD}}$:

$$E^{(3)}_{\text{HBOND}}\equiv E_{\text{INT}}=E^{(2)}_{\text{ADS-TOT}}-E_{\text{ADS-PaD}}. \tag{8}$$

Figure 2(b) plots $E^{(2)}_{\text{ADS-TOT}}$, $E_{\text{ADS-PaD}}$, and $E^{(3)}_{\text{HBOND}}$ on the various substrates. Since we are now dealing with OH and H (radical) adsorption as opposed to pure H_2O (closed shell) adsorption the total adsorption energies are much larger; ranging from -5 to -7 eV, of which adsorbate-substrate bonding $E_{\text{ADS-PaD}}$ constitutes the largest proportion. The intact bilayers, as we have seen, on the contrary, are mainly composed of H bonding. Further, Fig. 2(b) reveals that the large variations in the stability of the partially dissociated overlayers result from changes in adsorbate-substrate bonding and not from H bonding. The H-bond contribution $E^{(3)}_{\text{HBOND}}$ varies much less and is essentially overwhelmed by adsorbate-substrate bonding. According to Eq. (8) the total interaction energy in the dissociated overlayers averages at -1.14 eV. This is equivalent to -0.38 eV/H bond, larger than the H-bond energies in the intact bilayers (-0.25–-0.29 eV). This implies that in the mixed overlayers, the total interaction energy consists not only of H-bonding interactions but also there are significant contributions from other adsorbate- adsorbate attractive interactions.

Finally, the specific roles played by the H_2O, OH, and H moieties in determining the overall stability of the H_2O-OH

+H/M overlayers have been examined. We already know that the H_2O monomer adsorption energy $E_{\text{ADS-MONO}}$ changes little on the substrates considered here [Fig. 1(a), $E_{\text{ADS-MONO}}=2[E^{(2)}_{\text{ADS-BILAYER}}]$]. Therefore the large variations in the stability of the partially dissociated overlayers must be related to H and OH adsorption. Figure 2(c) plots the bilayer dissociation energy (ΔE) (Ref. 20) as a function of $E_{\text{ADS-H}}$ and $E_{\text{ADS-OH}}$ for every surface. We find that a clear relationship exists between ΔE and $E_{\text{ADS-OH}}$, in that the relative stabilities of the intact and partially dissociated overlayers correlate with the OH adsorption energy. This correlation is not a coincidence, for example the correlation between ΔE and $E_{\text{ADS-H}}$ is considerably less pronounced. Although the precise value of ΔE on a given surface obviously depends on many factors, the significance of a simple relationship between ΔE and $E_{\text{ADS-OH}}$ is clear. It provides a simple predictive rule as to when dissociated overlayers will be thermodynamically favored over intact bilayers on other substrates. At the present level of theory Fig. 2(c) indicates that when OH is more strongly bound to atop sites than approximately -2.4 eV, the partially dissociated overlayers become stable.

To recap, systematic DFT studies have shown that the stability of H_2O-OH-H overlayers varies considerably between substrates whereas the stability of the intact bilayers does not. Further, variations in the stability of both types of overlayer are primarily determined by variations in adsorbate-substrate bonding and not by variations in H bonding. In particular, the large variations in the stability of H_2O-OH-H overlayers can be traced back to the OH adsorption energy on each surface. Indeed it has been shown that the strength of the OH bond with the substrate is a useful guide to predict if wetting will take place in the form of intact H_2O bilayers or mixed H_2O-OH-H overlayers.

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

[2] P. J. Feibelman, Science **295**, 99 (2002).

[3] D. Menzel, Science **295**, 58 (2002).

[4] P. J. Feibelman, Phys. Rev. B **67**, 035420 (2003).

[5] H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L. G. M. Petterson, and A. Nilsson, Phys. Rev. Lett. **89**, 276102 (2002).

[6] S. Meng, L. F. Xu, E. G. Wang, and S. Gao, Phys. Rev. Lett. **89**, 176104 (2002).

[7] A. Michaelides, A. Alavi, and D. A. King, J. Am. Chem. Soc. **125**, 2746 (2003).

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

[9] P. J. Feibelman, Phys. Rev. Lett. **90**, 186103 (2003).

[10] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[11] A. Michaelides, V. A. Ranea, P. L. de Andres, and D. A. King, Phys. Rev. Lett. **90**, 216102 (2003).

[12] The Perdew-Wang '91 GGA was used: J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992). In all structure optimizations the bottom three metal layers were fixed and the remaining atoms were allowed to relax.

[13] On Ni{111}, Ru{0001}, Rh{111}, and Pd{111} $\sqrt{3}$ LEED patterns are observed and on Cu{111} and Ag{111} periodic overlayers have not been identified (see Ref. 1 for details).

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

[15] Thermodynamically 3D ice formation will be favored over 2D wetting when the sublimation energy of ice (E_{SUB}) is greater than the H_2O adsorption energy in the adsorbed overlayers. With the same level of theory we calculate, for a proton ordered system, a value of -0.75 eV/H_2O for E_{SUB}. Table I shows that the calculated value of E_{SUB} is $\geqslant 0.13$ eV/H_2O more stable than $E^{(1)}_{\text{ADS-TOT}}$ on all metals investigated here, except for the H_2O-OH+H/M overlayers on Ru and Rh and the H_2O-OH-H overlayer on Ru. Bearing in mind that calculations of bilayers in larger cells may be more stable by approximately 70 meV (Ref. 9) the implication remains that H_2O should not wet the other substrates considered here; rather, 3D ice particles should form. This apparent finding contradicts experimental evidence. However, we caution that this discrepancy should not be overinterpreted. The success of DFT in comparing *relative* energies is often due to cancellation of errors in the exchange-correlation functionals. When the physical systems are very different, as in bulk ice and adsorbed bilayers, this cancellation is not expected to work as well. This issue, however, has little bearing on the present study, which focuses on comparing total energies in similar systems and on understanding *trends* in the behavior of adsorbed water overlayers.

[16] This mainly reflects the greater stability of H atoms at threefold over atop sites.

[17] Zero-point energies (ZPE's) are not included in the calculations. On Ru{0001} it was shown that an H_2O-OH overlayer has a lower ZPE than an intact bilayer by 53 meV/H_2O (Ref. 4). If similar ZPE differences exist on Cu{111} and Pd{111} then this would make the H-down and H_2O-OH+H/M overlayers degenerate on Cu and tip the balance on Pd slightly in favor of the H_2O-OH+H/M overlayer.

[18] Allowing for local relaxation in the bilayers does not appreciably change the energetics.

[19] This is partly justified through a cancellation of errors: any new H_2O bond formed between the upper H_2O molecules and the substrate will be offset by weakening of the bond between the low-lying H_2O molecules and the surface.

[20] The bilayer dissociation energy is the total-energy difference between the most stable intact bilayer and the H_2O-OH+H/M overlayer on each surface.