Reactive Wetting: $H_2O/Rh(111)$

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First-principles calculations imply that neither H_2O bilayers nor half-dissociated, $H_2O + OH + H$ monolayers are thermodynamically stable on clean Rh(111). Thus, the experimental observation that Rh(111) supports a periodic 2D water adlayer needs an explanation. Chemistry involving common surface impurities, notably C atoms, may be the answer. Calculations show they provide favorable binding sites for H atoms detached from H_2O. The resulting OH fragments can anchor a 2D water layer to the surface.

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Understanding water-solid interactions at the atomic level may have broad implications regarding both the natural environment (inducing rainfall, confining buried pollutants, etc.) and technology (e.g., nanofluidics, microelectromechanical systems, corrosion). Contact-angle measurements make it possible to characterize surfaces as "hydrophilic" or "hydrophobic." But macroscopic categorization is only the beginning if one is interested in the flow in narrow channels, the approach of dissolved reactants to a solid, or the nucleation of ice crystals.

Surfaces that support a periodic water adlayer are optimal for studying the forces that cause wetting. On them [1], water molecules adsorb in just a few bonding environments and diffraction experiments probe only the periodic regions of what might be a heterogeneous adlayer. Though this simplifies the job of extracting structural parameters, an experimental adlayer geometry has been determined for just one wetting system, $(\sqrt{3}\times\sqrt{3})R30^\circ$ $D_2O/Ru(0001)$ [2].

Reference [2]'s surprising inference that the O atoms of the D_2O adlayer are nearly coplanar, instead of forming an icelike "bilayer," was the key clue in the discovery [3] that water wets Ru(0001) by forming a half-dissociated H-bonding network. To understand the periodic wetting of other precious metal surfaces, such as $(\sqrt{3}\times\sqrt{3})R30^\circ$ $H_2O/Rh(111)$ [4] and $(\sqrt{39}\times\sqrt{39})R16.1^\circ$ $H_2O/Pt(111)$ [5,6], similar clues would be welcome. Water dissociation is not favored on either metal's close-packed face [7], since Rh and Pt are relatively unreactive. However, calculated heats of adsorption on these surfaces (see Table I) *also* disfavor intact-molecule wetting layers relative to the formation of 3-dimensional ice mounds.

In the absence of telling clues, I have used *ab initio* total energy calculations to search for thermodynamically favorable wetting structures [8] and here present results for H_2O on Rh(111). The search was organized around two ideas: (1) Formation of OH fragments promotes wetting, since OH binds more strongly to a metal than H_2O, a closed-shell molecule. (2) OH formation is favored by availability of strong binding sites for H atoms.

These thoughts suggest that wetting of Rh(111) might be "reactive," i.e., that OH wetting-layer "anchors" might be formed by surface impurity atoms that strip H off H_2O. Among candidate impurity species, C is particularly interesting. C is a common contaminant in Rh, and the hypothetical reaction, $C_{ad} + 4H_2O \rightarrow CH_4(gas) + 4OH_{ad}$, would produce four anchors per adsorbed C atom (ad-C). Density functional theory (DFT) [9,10] results make this speculation plausible. They show reactive wetting to be thermodynamically favored, if the C impurity concentration on Rh(111) exceeds ~3% monolayer (ML).

To compute heats of adsorption, I used VASP [11–14], a plane-wave DFT code, and the PW'91 generalized gradient approximation (GGA) [15,16], which gives a reasonable account of the binding and elastic properties of bulk ice I*h* and of water on Ru, Rh's neighbor in the periodic table [3,17]. Plane-wave calculations involving Rh, H, or D and especially O atoms can require large basis sets. This requirement is mitigated in VASP by the use of ultrasoft pseudopotentials [18–21] (USP's) or, for greater accuracy, the projector augmented wave (PAW), all-electron description of the electron-ion-core interaction [22,23]. Most of the results reported here are for USP's and a 29.1 Ry cutoff. I used PAW potentials and a 51 Ry cutoff to spot-check the numerical accuracy of computed energy differences.

Though Gibson, Viste, and Sibener (GVS) report a $(\sqrt{3}\times\sqrt{3})R30^\circ$ He-atom diffraction pattern for $H_2O/Rh(111)$ [4], to take this result literally is to assume that perfectly proton-ordered water layers were produced in their experiments. This is the only possibility in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ unit cell (see Fig. 1). Formation of such layers is clearly opposed by entropy, but might be favored energetically, as proton-ordered ice XI is favored relative to ice I*h* [24]. To check this possibility, I supplemented calculations for a $(\sqrt{3}\times\sqrt{3})R30^\circ$ $H_2O/Rh(111)$ [4] cell with an optimization of a $(4\sqrt{3}\times 3\sqrt{3})R30^\circ$ $H_2O/Rh(111)$ [4] adlayer containing a locally proton-disordered arrangement of 24 H_2O admolecules [25].

TABLE I. Calculated binding energies per H_2O in intact water molecule structures on Rh(111) (not including zero-point energy). The large unit cell calculations were for 3-layer slabs; the small cell results are for 5-layer slabs. All are based on the use of ultrasoft pseudopotentials to represent the electron-core interaction and a 400 eV plane-wave-basis cutoff. Note that these hypothetical adlayers all have significantly lower binding energies than 0.72 eV, the lattice energy of ice I*h* at the same level of DFT convergence.

Supercell	Free-H orientation	Proton order in unit cell?	Binding energy/H_2O (eV)
$(\sqrt{3} \times \sqrt{3})R30°$	Free H-down	Yes	0.55
$(\sqrt{3} \times \sqrt{3})R30°$	Free H-up	Yes	0.51
$(4\sqrt{3} \times 3\sqrt{3})R30°$	Free H-down	No, "random"	0.62

In all the calculations, I modeled semi-infinite Rh(111) as a thin slab of five metal atom layers in the $(\sqrt{3} \times \sqrt{3})R30°$ case and of three for the $(4\sqrt{3} \times 3\sqrt{3})R30°$ adlayer. To find geometries corresponding to GGA relative energy minima, I relaxed the positions of the adspecies and of the Rh atoms of the upper two slab layers till forces on them were <0.03 eV/Å, fixing the remaining Rh atoms at *ab initio*, bulk Rh relative positions ($R_{nn} =$ 2.722 Å). I used a 4 × 4 set of equally spaced k vectors to sample the surface Brillouin zone of the $(\sqrt{3} \times \sqrt{3})R30°$ cell and the $\overline{\Gamma}$ point only for the $(4\sqrt{3} \times 3\sqrt{3})R30°$ calculations. I accelerated electronic relaxation with Methfessel and Paxton's Fermi-level smearing method (width = 0.2 eV) [26], and corrected for the contact potential difference associated with placing an adlayer on only one side of an Rh slab using Kresse's adaptation [27] of Neugebauer and Scheffler's method [28].

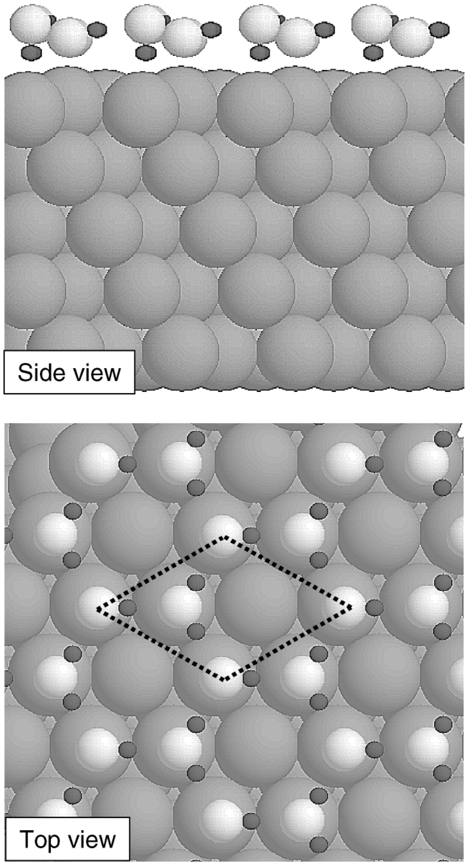

FIG. 1. Top and side views of a $(\sqrt{3} \times \sqrt{3})R30°$ "H-down" water adlayer on Rh(111). The dotted parallelogram indicates the surface unit cell. Rh, O, and H atoms are represented by gray, white, and black spheres. Because of the small cell, the adlayer is necessarily perfectly proton ordered. The O atoms with H's below them lie 3.12 Å above the underlying Rh's. The O atoms which have two H-bonding H atoms are 2.54 Å above the Rh's to which they are bound.

The GGA binding energy results presented in Table I make clear that dissociative wetting of some sort must be considered. The reason is that water molecules bind 0.17 eV more strongly in ice I*h* than in perfectly proton-ordered $(\sqrt{3} \times \sqrt{3})R30°$ water bilayers. Somewhat surprisingly, in the locally disordered molecular arrangement of the $(4\sqrt{3} \times 3\sqrt{3})R30°$ adlayer, the molecular binding *strengthens by 0.07 eV.* But this is still not enough to make the hypothetical 2-dimensional structure thermodynamically stable against ice formation. Zero-point energy (ZPE) is not included in these comparisons. But as estimated below, it adds just a few tens of meV to the binding energies of the 2D adlayers, leaving the basic conclusion unaltered.

The same problem arose in analyzing the wetting of Ru(0001) [3]. However, Ru, binds H and OH strongly enough to make partial dissociation of adsorbed water molecules energetically favorable. On Rh(111), a less reactive surface, half-dissociated arrangements of water molecules such as those proposed [3] for Ru(0001) are less well bound than the intact-molecule adlayers, unless the dissociated H atoms can diffuse away from water islands to patches of bare Rh(111) metal (see Table II). Since the existence of bare patches was excluded by GVS's He-atom scattering data [29], a new idea is needed to explain why water wets Rh(111).

GVS provide a hint: "Our experiments indicate that the better-ordered overlayers are due to a small amount of some coadsorbate, quite possibly oxygen; they occurred with a slower cooldown after cleaning the crystal, allowing a longer time for the adsorption of background gases" [4]. They also say, "Small amounts of (deliberately) preadsorbed oxygen resulted in a vast improvement in the long-range order of the H_2O overlayer." Indeed, surface O atoms, as well as other species such as C and B, which commonly migrate from hot, bulk Rh to its surfaces,

TABLE II. Calculated binding energies per H_2O in "reactive wetting" structures on Rh(111), for comparison to 0.72 eV, the similarly calculated GGA lattice energy of ice I*h*. In all cases, free H's are oriented downward. Values quoted exclude zero-point energy. The $(\sqrt{3}\times\sqrt{3})R30°$ structures are all half-dissociated, $OH + H_2O$ hydrogen-bonded networks, and are necessarily perfectly proton ordered. In the first two rows the dissociated H atoms are at atop and fcc sites within the network. In the third row, they are in a 1 × 1 island on a bare patch of metal, and in the fourth, they have been evolved as H_2 gas. The $(4\sqrt{3}\times 3\sqrt{3})R30°$ structures, proton disordered within the unit cell, involve H transfer onto preadsorbed impurities. In the first, there are 22 H_2O's and 2 OH's in the unit cell, presuming an initial isolated O. In the second, there are 23 H_2O's, 2 OH's, and a BH_2, presuming an initial B atom. In the last, there are 20 H_2O's and 4 OH's plus a gas-phase methane molecule, presuming an initially adsorbed C atom.

Supercell	Location of dissociated H	Reference surface	E_b/H_2O
$(\sqrt{3}\times\sqrt{3})R30°$	Atop site	Clean Rh(111)	0.43 eV
$(\sqrt{3}\times\sqrt{3})R30°$	fcc hollow	Clean Rh(111)	0.46 eV
$(\sqrt{3}\times\sqrt{3})R30°$	fcc on bare metal	Clean Rh(111)	0.71 eV
$(\sqrt{3}\times\sqrt{3})R30°$	Gas phase H_2	Clean Rh(111)	0.45 eV
$(4\sqrt{3}\times 3\sqrt{3})R30°$	Two OH's per preadsorbed O	Isolated O adatom	0.65 eV
$(4\sqrt{3}\times 3\sqrt{3})R30°$	One ad-BH_2 from one preadsorbed B	Isolated B adatom	0.59 eV
$(4\sqrt{3}\times 3\sqrt{3})R30°$	One CH_4 from one preadsorbed C	Isolated C adatom	0.67 eV

could provide sites where H is bound sufficiently well that stripping of deposited H_2O molecules is favorable. If this happens, the resulting OH fragments might anchor a 2-dimensional wetting layer to the surface.

With O atoms preadsorbed, the likely product of water deposition, via disproportionation (i.e., H_2O + ad-O → 2 ad-OH) is an adlayer containing two OH anchors per initial O atoms. For B impurities, BH_3 or B_2H_6 molecules might evolve leaving three OH anchors per ad-B, or ad-BH_2 might form on the metal together with two OH's per initial B. One can imagine analogous possibilities for an ad-C, with the energetically most favorable outcome, likely, the formation of a CH_4 molecule and four ad-OH's. Calculated energy balances for some of the possible reactions are reported in Table II.

To compute reaction energies I used isolated impurity atoms on Rh(111), rather than islands of their favored structure, as reference configurations. Because the impurity concentrations must be small, according to GVS, I performed the reactive wetting calculations in the $(4\sqrt{3}\times 3\sqrt{3})R30°$ unit cell, containing 36 Rh atoms per layer, and at most 24 H_2O's. In this cell, one impurity atom represents 1/36 or 2.8% ML. Disproportionation onto a single ad-O thus produces a unit cell containing 2 OH's and 22 H_2O's, per incident 23 H_2O's. Onto a single ad-B, it can produce an ad-BH_2, 2 OH's, and 21 H_2O's per incident 23 H_2O, or perhaps a gas phase BH_3, 3 ad-OH's, and 21 H_2O's per incident 24 H_2O's. A reaction with an ad-C can yield, e.g., one gas phase CH_4, 4 OH's, and 20 H_2O's per incident 24 H_2O's (see Fig. 2).

C appears the most likely impurity to promote wetting of Rh(111), in Table II, with O a close second. Excluding ZPE, the reaction 24 H_2O + ad-C → 4 ad-OH + 20 ad-H_2O + CH_4 (gas) is predicted to be exothermic by 0.67 eV per H_2O. This is only 50 meV shy of the lattice energy gained by water molecules in forming ice I*h* (computed at the same level of approximation) [3]. I now show that ZPE eliminates even this energy deficit.

A GGA-based estimate of the ZPE of H_2O ice I*h*, relative to gas-phase water, is roughly 124 meV per molecule [30] (close to Whalley's experimental value of 120 meV [31]). Subtracting this from the calculated ice lattice energy, 0.72 eV, I obtain an ice formation energy of ~0.60 eV per water molecule [32].

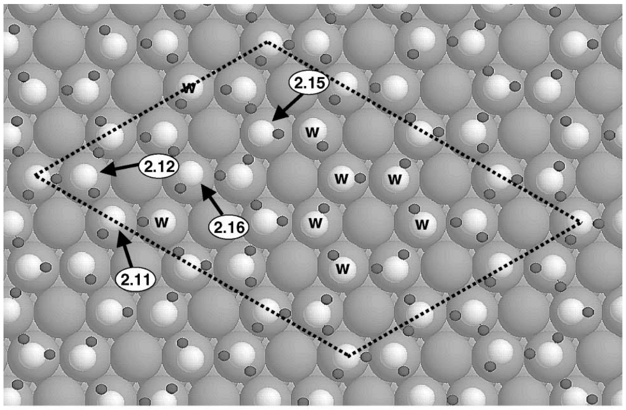

FIG. 2. Top view of a $(4\sqrt{3}\times 3\sqrt{3})R30°$ OH-tethered water adlayer on Rh(111), containing 20 H_2O molecules and 4 OH fragments per surface unit cell, in a locally proton-disordered, H-bonded network. The dotted parallelogram indicates the unit cell. Rh, O, and H atoms are represented by gray, white, and black spheres. Arrows point to the OH fragments. The adjacent numbers are distances in Å of their O atoms from the underlying Rh's. Intact, H-down water molecules are labeled "w." Each has an H atom between its O atom and the underlying Rh, with the result that their O-to nearest-Rh distances are 3.08 to 3.48 Å, i.e., rather large. The O atoms of the remaining water molecules (which have two H atoms in H bonds) lie 2.21 to 2.48 Å above the Rh's to which they are bound.

To estimate the ZPE contribution of the contents of the $(4\sqrt{3} \times 3\sqrt{3})R30°$ cell I average vibration frequency results for adlayers with smaller unit cells. Specifically, I assume that the ZPE of the $(4\sqrt{3} \times 3\sqrt{3})R30°$ cell containing 20 H_2O molecules and 4 OH fragments roughly equals the ZPE of eight $(\sqrt{3} \times \sqrt{3})R30°$ cells of a bilayer with two intact H_2O molecules per cell, plus that of four $(\sqrt{3} \times \sqrt{3})R30°$ cells of an $H_2O + OH$ adlayer.

I compute the small-cell ZPE's, using numerical differentiation to obtain dynamical matrices followed by the solution of Newton's equations to evaluate harmonic vibration frequencies [33]. Again referencing to the ZPE of gas phase H_2O [34], the results are that the intact-molecule cells contribute 91 $\mathrm{meV/H_2O}$ to the ZPE, while the $H_2O + OH$ cells, largely by virtue of their missing O-H bonds, contribute -55 $\mathrm{meV/H_2O}$. The average, $(16 \times 91 - 8 \times 55)/24$, amounts to 42 $\mathrm{meV/H_2O}$. To this I add the ZPE of the CH_4 molecule produced (per 24 incident waters), 32 $\mathrm{meV/H_2O}$, and subtract the ZPE associated with the initial ad-C, 4 $\mathrm{meV/H_2O}$. Reactive wetting of the C-contaminated surface should accordingly be about 70 meV less exothermic per incident water molecule because of ZPE, with an overall wetting energy of 0.60 $\mathrm{eV/H_2O}$.

Reactive wetting of a Rh(111) surface contaminated with 2.8% ML isolated C adatoms thus releases virtually the same energy as adding the same water molecules to an ice I*h* crystal. For higher impurity concentrations, the balance shifts in favor of wetting.

That reactive wetting might underlie GVS's periodic water layer is admittedly a speculation. It is an interesting one, though, because it is falsifiable, i.e., demonstrably not true if CH_4 is not evolved as wetting occurs, and because reactive wetting is a novel, general concept. If C is not the wetting agent on Rh(111), perhaps something else strips H atoms from deposited water molecules. The results presented here imply that more preadsorbed O or B adatoms are necessary, compared to C's, to make wetting occur. Nonetheless, they could have been involved.

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