PERSPECTIVES: SURFACE SCIENCE

Water on a Metal Surface

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The interaction of water with solid surfaces plays a crucial role in catalysis and weathering. The structure and properties of the first water layers on well-defined metal surfaces have been widely investigated, but there are no clear and easy answers so far, and controversy still exists.

A new proposal is put forward by Feibelman on page 99 of this issue (*1*). On the basis of ab initio quantum chemical calculations, the author suggests that the existing discrepancies result from the assumption that intact water molecules form the first layers on a transition-metal surface. Instead, he proposes that half of them dissociate on a Ru(0001) surface. The study is exciting not only because Ru surfaces are important model catalysts but also because it signifies a special stage in the development of surface science.

Surface science is a well-established part of physics and chemistry, with a highly developed arsenal of experimental tools and methods. For a long time, it was difficult to adapt solid state or molecular theories for surfaces, which combine the difficulties of many particles and lowered symmetry—translational periodicity makes solids tractable despite the large number of atoms present, and molecules typically contain fewer atoms. The development of density functional theory (DFT) methods has helped to bring theory to a state of reliability similar to that of experiments. Discrepancies now point to a gap in our physical understanding or to a basic problem with the theoretical or experimental methods used.

There are now cases of excellent agreement between theory and experiment for the structure, binding, and interactions of atomic and molecular adsorption layers, where the discontinuity of the solid prepares special conditions for the bonding of molecules and their reactivity. In some cases, theory even gave an important hint to experimenters what to look for. However, some points of distinct disagreement remain. A particularly interesting disagreement concerns the geometry of the first layers of water on a metal surface.

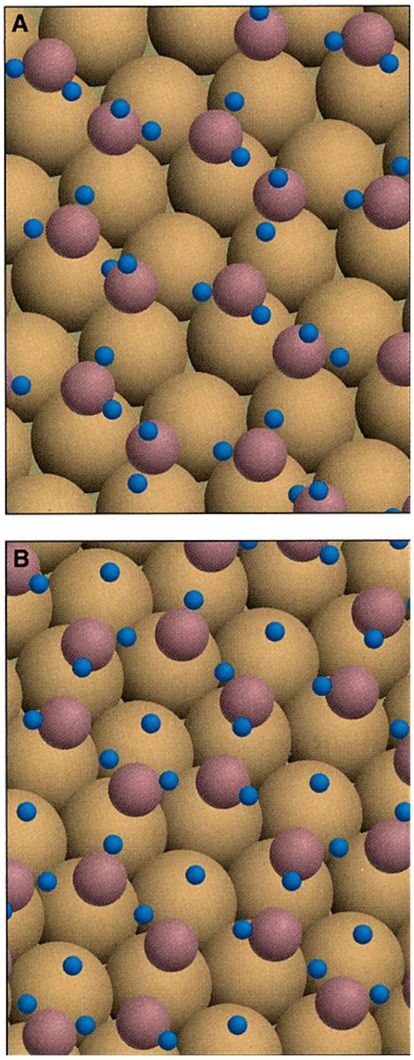
For a long time the accepted picture has been that, except for very reactive surfaces, the first water layers on a metal surface consist of intact molecules, and that their structure is best described as a "bilayer," that is, two layers of water molecules whose arrangement is similar to that of molecules in the densest layers of ice (*2*). In the bilayers, six water molecules each are connected by hydrogen bonds to form a puckered ring, and each connects to one of the next rings. Half the oxygen atoms of the water molecules then lie in a plane about 0.1 nm above that of the other half. The corresponding structure fits rather well onto many hexagonally close-packed transition-metal surfaces, such as Ru, Rh, or Pt. From all these metals, water desorbs mostly intact upon heating.

Only one well-ordered water bilayer has been characterized in high structural detail: that of D_2O adsorbed on the hexagonally close-packed Ru(0001) surface and annealed for perfect order. The layer desorbs essentially intact upon heating; a small amount of dissociation likely occurs at defects. Its geometry has been determined by quantitative low-energy electron diffraction (LEED) (*3*, *4*). The lack of structural data is partly due to the high radiation sensitivity of water adsorption layers. Low-damage methods had to be developed to enable the measurement (*5*).

The experiments show that the lateral arrangement of the oxygen atoms is that of a (slightly) buckled ring, with all oxygens above Ru atoms, and half of them at somewhat smaller distance, as expected for a bilayer structure; the other half are in a second, higher plane, as if connected by hydrogen bonds (see panel A in the figure). However, the distance between the two planes was only 0.01 nm, 10 times less than in the corresponding ice layers. This compression compared with ice was explained by charge rearrangement in the adsorbed water molecules and polarization interactions with the metal surface. A structural isotope effect was also found: Only D_2O forms the fully commensurate layer, whereas H_2O leads to striped domains that can be explained by a misfit due to a slightly different hydrogen bond length.

Since the publication of this structure, intense attempts have been directed at calculating its geometry from first principles, in particular by D. R. Jennison at Sandia National Laboratories. But the results did not agree with experiment: The compression of the bilayer was not found; rather, the bilayer geometry was closer to that of the ice structure. Reanalysis of the experimental data corroborated the initial interpretation, clearly pointing to a discrepancy of experiment and calculation.

Feibelman first repeated the earlier calculations with the best presently available methods, and concluded that a molecular bilayer of intact water molecules should not even be bound to the metal surface, no matter what its geometry. It would not wet the metal surface but should cluster three-dimensionally. Next, Feibelman investigated the possibility that wetting could be accomplished by partial dissociation. A layer consisting of half H_2O and half OH, interconnected in rings of six molecules by hydrogen bonds, turned out to be stable and thus wet the surface (see panel B) if the split-off H atom was also



Out with the old? **(A)** The traditional model of water bilayers adsorbed on ice. **(B)** Feibelman's alternative structure, in which half the water molecules are dissociated.

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adsorbed on the Ru surface. He proposes that this partial dissociation is a necessary prerequisite for wetting, at least on Ru(0001).

If this is correct, then theory and experiment are reconciled. H or D scatter electrons very weakly and contribute very little to the LEED determination, which mainly yields the locations of the O atoms. And for these, the Feibelman structure agrees with the LEED data. But other findings are difficult to reconcile with partial dissociation. For example, thermal desorption spectra do not show any evidence of two species and of recombination (*6*). The calculations also do not explain why water should partially dissociate below 150 K but fully associate back to the desorbing molecule above 170 K.

A similar layer on Pt(111) (*7*), which vibrational spectroscopy suggests to consist of intact water molecules, has LEED curves identical to that of a layer supposed to consist of OH (*8*). Hence, either the "intact" layer is mixed, or the structures of intact and partially dissociated layers are indistinguishable. Mixed H_2O + OH layers certainly can exist (*9*); the question is whether they are the only stable layers.

A definitive experiment to resolve this question is difficult to devise because the only difference between the structures in panels A and B is that in panel B, one H atom has been moved from being bound to O to being bound to Ru. Neutron scattering cannot be used to study surface species, and other structural tools do not respond sufficiently to H; most spectroscopic techniques cannot distinguish between adsorbed H_2O and OH. On the theory side, all is not so well either. Even the best available DFT procedures cannot model van der Waals interactions reliably; their absence might have tipped the energy balance in the present case. Also, the adequacy of DFT to model hydrogen bonds might be debatable because the calculations do not treat the atoms quantum mechanically (the hydrogen atoms are given infinite mass; their zero point energy is taken care of by rescaling the energy scale).

Two focal points of surface science—the comparison of theory and experiment, and the understanding of an extremely interesting particular system—coincide to make water on metal surfaces an interesting and challenging issue. Feibelman's study points toward an interesting possible solution and will trigger further experimental and theoretical work. Clearing up the issue of how the first water layer binds to a transition surface will require—and lead to—improvements in both theory and experiment of surface interactions.

References

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PERSPECTIVES: PLANT BIOLOGY

Prime Time for Cellulose

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Every year, plants make more than 10^{11} metric tons of cellulose, the chain of glucose residues that is the principal component of the plant cell wall. However, biochemical dissection of the three steps of cellulose synthesis—initiation of the sugar chain, elongation, and termination—is still in its infancy. A notable advance has been the recent identification of the *CesA* genes that encode protein subunits of cellulose synthase, the rosette-shaped enzyme complex in the plant cell plasma membrane that synthesizes cellulose (*1–3*). Despite this advance, it has still proved difficult to coax plant extracts to make cellulose in the test tube—instead they make callose, a wound-response polysaccharide. It is possible that cellulose synthase is particularly fragile, or requires an intact membrane environment for activity. A big leap forward comes on page 147 of this issue with the identification by Peng *et al.* (*4*) of the lipid sitosterol-β-glucoside (SG) as the primer for cellulose synthesis in plants.

The structural backbone of plant cell walls comprises crystalline microfibrils of cellulose, each composed of 36 β-(1,4)–linked glucan chains. Noncrystalline (soluble) cellulose accumulates in response to the herbicide CGA 325′615 or plant mutations that block cellulose synthesis or activity of the Korrigan cellulase enzyme (*5*, *6*). In the new work, Peng *et al.* show that digesting noncrystalline cellulose with cellulase releases not only CesA proteins but also small amounts of a sitosterol lipid linked to glucose (*4*, *5*). Further metabolic studies led the authors to propose a biosynthetic pathway for cellulose that starts with transfer of a glucose residue from the soluble cytoplasmic substrate uridine 5′-diphosphate (UDP)–glucose onto sitosterol to form SG on the inner face of the plasma membrane (see the figure). SG then acts as a primer, initiating the polymerization of glucan chains catalyzed by CesA proteins of the cellulose synthase complex. The result is formation of lipid-linked oligosaccharides called sitosterol cellodextrins (SCDs). Formation of SG and SCDs is blocked by the herbicide DCB (2,6-dichlorobenzonitrile), which targets cellulose synthesis. The cellodextrins may be cleaved from the sitosterol primer by Korrigan cellulase, the active site of which is predicted to be located on the outer face of the plasma membrane. This model defines the point at which the primer is transferred through the energy barrier of the membrane lipid bilayer, although how this happens is unknown. Further elongation of the cellodextrins, catalyzed by the same or different CesA proteins, produces the glucan chains of cellulose, which then coalesce into microfibrils.

Peng *et al.* (*4*) replicated part of the plant cellulose synthesis pathway in transgenic yeast, the perfect model organism because they do not make cellulose. Yeast containing a single *CesA* gene, in this case *GhCesA-1* from cotton, make SCDs, whereas control yeast do not. The investigators thus were able to identify SCDs as lipid intermediates in the initiation of cellulose synthesis. The transgenic yeast, however, do not make cellulose, so some other part of the synthetic machinery is clearly missing. It is still a mystery how cellulose chains containing several thousand β–(1,4)–linked glucose residues are extruded into the walls of plant cells and then are terminated.

Plants cannot survive without cellulose, which may account for why they possess an extended family of *CesA* genes. Members of this family are expressed at different times and do different things; some pairs of *CesA* genes are even switched on together (*7–9*). Thus, plants with mutations in a particular *CesA* gene show reduced cellulose synthesis only in certain cell types or at specific life-cycle stages, resulting in distinct phenotypes such as root swelling or an irregular xylem.

The new work raises the intriguing pos-

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