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New Chemical Manifestations of Hydrogen Bonding in Water Adlayers

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The interaction of water with metal and metal oxide surfaces is a topic that serves as a major meeting ground for several diverse disciplines, including electrochemistry, corrosion, and heterogeneous catalysis. In these fields and others, the surface chemistry of water is important for two reasons. First, water may influence a surface chemical reaction in which it does not play a direct role as reactant or product. Consider, for example, electrochemistry in aqueous media where the "double layer" of water dipoles is thought to control crucial aspects of electrochemical reactions such as transport and capacitance.¹ Consider also water's propensity for hydrogen bonding with other molecules; in this manner water may potentially influence adsorption site, adsorbate geometry, mobility, and aggregation of the reactive species. Because water can influence surface reactions, it is important to gain a fundamental understanding of the properties of water layers near solid surfaces and the ways in which this water interacts with other chemical species. Second, water may itself be consumed or produced via chemical reaction at a surface. Prominent examples of this in heterogeneous catalysis are the water-gas shift reaction and the related Fischer-Tropsch synthesis.² In corrosion, water is often the reactive agent that leads to metal oxidation.³ The direct participation of water in

important reactions makes it necessary to understand the catalytic chemistry of water at surfaces as well as the adsorption kinetics, surface mobility, and desorption kinetics of this molecule.

Over the past 15 years surface scientists have focused increasing attention on water as an adsorbate, particularly with "model systems" (i.e., with single-crystal substrates in ultrahigh-vacuum environments).⁴ The advantage of this approach is that it facilitates implementation of, and interpretation of data from, powerful surface-sensitive techniques.⁵ In this Account we describe recent results for one particular substrate, Ru(001). Our results demonstrate that unusual surface phenomena can result from water's propensity for hydrogen bonding, including an unexpected interaction with a coadsorbate, cyclohexane. The history of previous investigations on this system also sheds light on the way in which our understanding of more general aspects of water as an adsorbate has developed.

Review of Previous Investigations

The (001) face of ruthenium is the hexagonally close packed surface. The first investigation of water on this surface was reported by Madey and Yates in 1977,⁹ who concluded, on the basis of thermal desorption spectroscopy (TDS), that there is little dissociation of water

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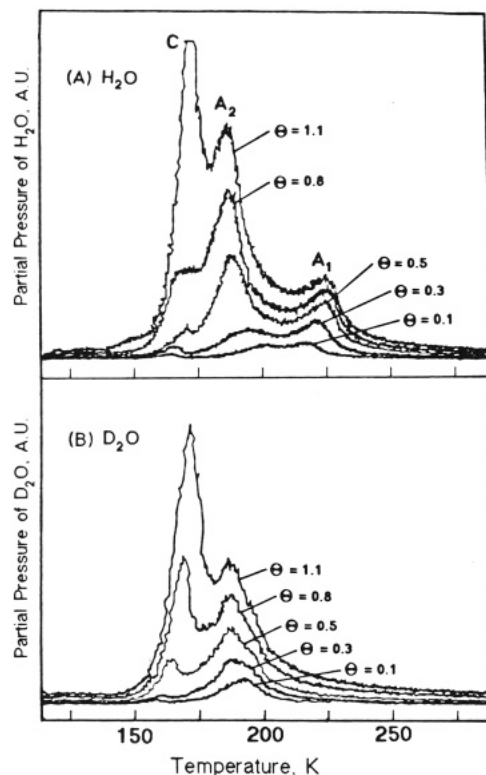


Figure 1. Thermal desorption traces for (A) H_2O and (B) D_2O . The curves are labeled with the water coverage in absolute monolayers (θ), assuming that the coverage that exists just before emergence of the ice multilayer is 0.67.^{9,14-16} Reprinted with permission from ref 19. Copyright 1987 Elsevier Science Publishers B.V.

on this surface (less than 0.05 monolayers) and that water sequentially fills discrete surface layers as coverage increases. These layers were proposed to account for the three different states in thermal desorption spectra, as shown in Figure 1. In this model, the high-temperature state, labeled A_1 , corresponded to the first layer, A_2 to the second layer, and C to the third and higher (ice) layers. The temperature of the A_1 -state desorption corresponded to a weak metal-water bond, which subsequent calculations have shown to involve electron donation from (primarily) the oxygen atom to the metal surface.⁶⁻⁸ Madey and Yates also reported H^+ ion angular distributions resulting from electron-stimulated desorption (ESDIAD), which showed patterns of 6-fold H^+ symmetry, reflecting the azimuthal and polar orientation of the parent O-H bonds.⁹ The patterns were interpreted to mean that the water maintains C_{2v} symmetry with respect to the surface normal and that the molecular planes stand parallel to one another in 3-fold-degenerate domains.

Subsequent studies substantiated the conclusion that there is little or no dissociation in this system, based upon data from ultraviolet photoemission spectroscopy¹⁰ and, more recently, X-ray photoelectron spectroscopy.¹¹ In fact, it has been found that most of the low-index faces of the group VIII B transition metals, including many catalytically useful metals (e.g., Pt, Pd, Ir, Ru, and Rh), do not catalyze water dissociation, at least not under the conditions of typical ultrahigh-vacuum experiments. This result can be rationalized

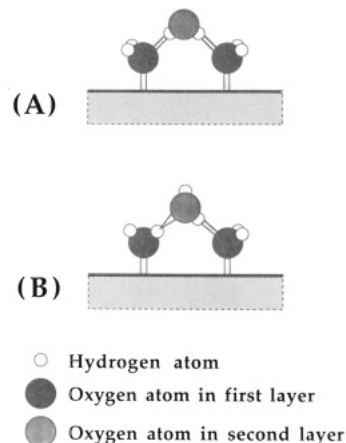


Figure 2. Schematic depiction of possible local arrangements of water in chemisorbed, hydrogen-bonded clusters viewed parallel to the surface plane.

in a thermodynamic sense by the relatively small enthalpy of formation of oxides of these materials.⁴

However, subsequent work did not support the original conclusions regarding adsorbate symmetry and sequential layer filling. Vibrational spectroscopy, particularly electron energy loss spectroscopy (EELS), revealed intense librational modes and also revealed that these modes are subject to the well-known dipole selection rule.⁹ Therefore, their large scattering cross section could only be explained by deviation from C_{2v} symmetry. Furthermore, the frequency and width of the O-H stretching vibration showed that hydrogen bonding is present even at very low coverages, before population of the "first" water layer.^{10,12} Hydrogen bonding had been relegated little importance in the previous report,⁹ perhaps because adsorbates studied until then had exhibited intermolecular interactions much weaker than the hydrogen bond. The new vibrational data, coupled with observation of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structure via low-energy electron diffraction (LEED), as well as the older ESDIAD and TDS data, led to a structural model in which water forms ice-like, hydrogen-bonded clusters even at low coverages with water's molecular plane in a variety of orientations with respect to the surface normal.¹⁰ It was proposed that such clusters are energetically feasible because the adsorption bond strength is weak—approximately 10 kcal/mol, based upon TDS—so that two intermolecular hydrogen bonds are energetically comparable. In bulk ice, for example, intermolecular hydrogen bond strengths are estimated to be 4–6 kcal/mol per bond.¹³ This propensity for clustering via hydrogen bonds was first explored thoroughly for $\text{H}_2\text{O}/\text{Ru}(001)$, but it has since become a common observation. Thus, water at metal surfaces tends to form three-dimensional, hydrogen-bonded networks in which some water molecules contact the metal directly and others attach only via hydrogen bonds to other molecules. Some local arrangements possible for water molecules constrained in such clusters are shown in Figure 2. Furthermore, it is generally thought that formation of such clusters is not kinetically limited: surface diffusion by single molecules is sufficiently rapid on the typical experi-

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mental time scale (ca. 1–60 min) that clusters such as those of Figure 3 form readily at adsorption temperatures of 80–100 K, and there is little evidence for isolated water monomers except at very low coverage (≤ 0.05 monolayers).^{10,14,15}

The structural model for the hydrogen-bonded clusters on Ru(001), and the assignment of the A_2 and A_1 desorption states, underwent further refinement when Doering and Madey correlated the ESDIAD patterns with TDS states.¹⁴ The structural models of Figure 3 resulted, wherein only the non-hydrogen-bonded O–H bonds were proposed to be ESDIAD-active. (Note that the perspective is different from that of Figure 2.) The O–H bonds at the edges of the clusters would then account for the pattern of 6-fold, nonnormal emission (three degenerate orientations of clusters), whereas the O–H bonds in the centers of the larger clusters and pointing away from the metal surface would give rise to normal emission. Doering and Madey proposed that desorption from the large clusters was the origin of the A_2 desorption state, whereas desorption from the small clusters was signaled by the A_1 state. This idea was supported by a later study of the temperature- and coverage-dependent splitting of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern, in which Williams and Doering showed that the average size of the hydrogen-bonded islands varied during adsorption and desorption in a consistent manner.¹⁶ Of course, further reinterpretation or refinement of the model for the $H_2O/Ru(001)$ system is always possible (as suggested, for example, in refs 11 and 15). However, the model described by Figure 3 enjoys the advantage of explaining data from a very wide variety of techniques, and our subsequent discussion is based upon it.

The fundamental difference between the two types of clusters (aside from size) is that the small cluster of Figure 3A contains only second-layer water molecules with *oxygen lone pair orbitals* perpendicular to the surface plane, whereas the larger clusters of Figure 3B contain some second-layer molecules with *free OH bonds* perpendicular to the surface. In other words, the small clusters (Figure 3A) comprise only the three-molecule units shown in Figure 2A, whereas the larger clusters (Figure 3B) also contain the units shown in Figure 2B. When the surface is covered by the large clusters, higher layers are thought to (ideally) adopt the extended structure shown in Figure 3C, which is simply the structure of ice.

The existence of the clusters shown in Figure 3 can be rationalized in terms of two sets of empirically derived rules, the well-known Bernal–Fowler–Pauling (BFP) rules, which describe the regular arrangements of water molecules in bulk ice,¹⁷ and the surface-modified BFP rules proposed by Doering and Madey.¹⁴ The latter rules, in effect, allow the hexagonal metal substrate to replace an extended ice lattice as a template for ice crystallization under the BFP rules. Because the oxygen nuclei of Figure 3 exist in two separate planes, both parallel to the metal surface, the adsorbed water

layer is often referred to as a “bilayer” with an ideal coverage, θ_{H_2O} , of 0.67 monolayers. Ru(001) is thought to be a particularly good substrate for formation of this bilayer because of the small lattice mismatch between the hexagonal metal substrate and crystalline ice. That is, the water molecules in direct contact with the metal can adopt specific, favorable adsorption sites yet can simultaneously participate in an ice-like network.

New Results

We have discovered two rather surprising properties of water adlayers on Ru(001), both of which appear to be related to the hydrogen-bonded water clusters that are stabilized by the metal substrate.

The first interesting phenomenon that we discovered is an isotope effect in the desorption of water.^{18,19} This effect is illustrated by Figure 1, where desorption traces of H_2O can be compared with those of D_2O . It is clear that the highest temperature state (A_1) is suppressed upon deuteration. However, this suppression is not always complete: if the heating rate is much slower than that used in Figure 1, the A_2 state becomes visible even for D_2O . In fact, slower heating rates enhance the population of the A_1 state relative to the A_2 state for *both* isotopes. This is illustrated by Figure 4, where the symbols show the increase in the ratio of A_2 to A_1 peak heights (A_1 -state suppression) both for H_2O and D_2O as the rate of temperature change increases. We interpret this to mean that the A_1 state must form by activated conversion from the A_2 state. Molecules can also leave the A_2 state by direct desorption into the gas phase, and these processes of conversion and desorption appear to be kinetically competitive under the conditions of our experiments. This naturally leads to the idea that conversion occurs more slowly for the heavier isotope, which reduces population of the A_1 state for D_2O .

The magnitude of the isotope effect can be estimated as follows. Define the isotope effect, k^* , as

$$k^* = \frac{k_c(H_2O)}{k_c(D_2O)} = \frac{k_c(H_2O)/k_{d,A_2}(H_2O)}{k_c(D_2O)/k_{d,A_2}(D_2O)} = \frac{k'(H_2O)}{k'(D_2O)}$$

Here we have assumed that the only isotope effect is on k_c , the rate constant for conversion from A_2 to A_1 , i.e., the rate constant for A_2 desorption, k_{d,A_2} , is the same for the two isotopes. This expression provides a connection with the experimental data because for each isotope the relative number of particles that desorb from the A_2 and A_1 states (measured roughly by the ordinate of Figure 4) is governed by the value of k' for that isotope. (We assume that desorption and conversion from the A_2 state are first-order processes, as well as desorption from the A_1 state.) Therefore, the numerator and denominator of the right-hand term can be extracted by modelling the relative A_2 and A_1 peak heights as a function of heating rate for each isotope. The solid lines in Figure 4 show that a qualitatively good fit can be obtained. The resultant value of k^* falls in a range of about 3–8 where the range is determined mainly by the uncertainty in fitting k' to the experimental data for each isotope. This corresponds to a difference in the activation barrier to conversion for the

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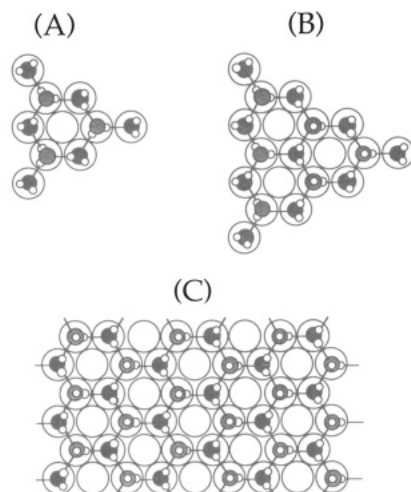


Figure 3. Schematic depictions of adsorbed water clusters viewed perpendicular to the Ru(001) surface plane. The key is the same as that in Figure 2, except that large open circles represent Ru atoms. (A) Small water clusters whose decomposition is associated with the A_1 state. (B) Large water clusters whose (partial) decomposition is associated with the A_2 desorption state. (C) Ice multilayer.

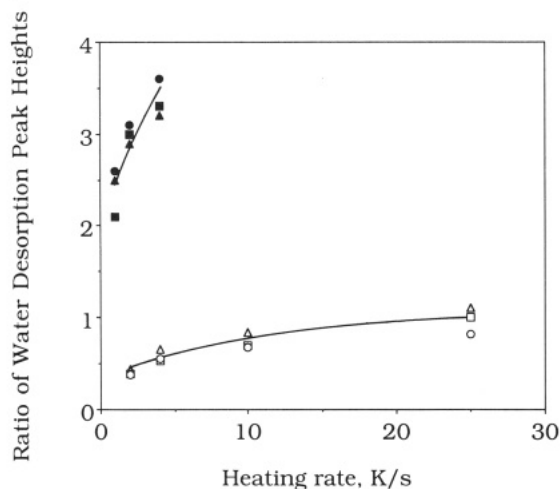


Figure 4. Relative A_2 and A_1 peak heights as a function of heating rate, both for H_2O and D_2O . The open symbols represent H_2O , the filled symbols D_2O ; data for three coverages (0.1, 0.2, and 0.3 monolayers) are represented by the squares, triangles, and circles, respectively. Reprinted with permission from ref 19. Copyright 1987 Elsevier Science Publishers B.V.

two isotopes of 0.5 kcal/mol.¹⁹

Returning to parts A and B of Figure 2 and associating these clusters with the A_1 and A_2 desorption states, respectively,¹⁴ it can be seen that conversion from the A_2 state to the A_1 state must involve not only a decrease in coverage but also a change in the orientation of molecules within the clusters. We propose that this change comes about when one or more water molecules rotate within the framework of the cluster, a rotation that is slower for D_2O than for H_2O .

The motion is illustrated by Figure 2, considering that the three-molecule units shown there are components of the extended two-layer clusters illustrated in parts A and B of Figure 3. Within the three-molecule unit of Figure 2B, the second-layer molecule rotates one OH bond away from the surface normal, down toward a first-layer molecule. This requires that one OH bond of the first-layer molecule rotate away from the second-layer molecule and may necessitate reorientation

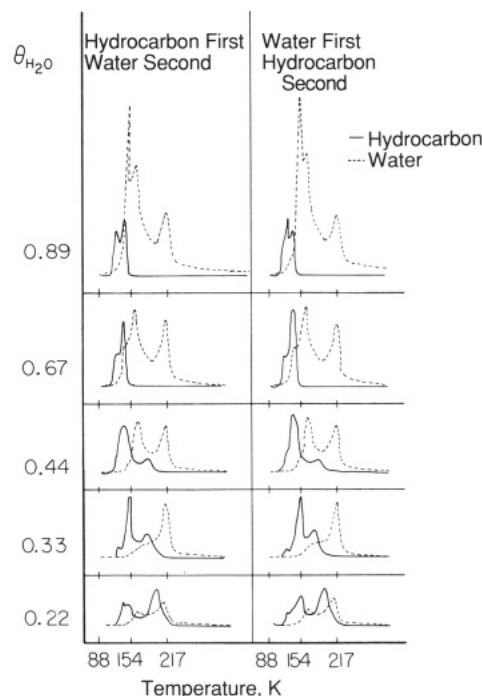


Figure 5. Thermal desorption traces of cyclohexane (solid lines) and water (dashed lines) following exposure of both adsorbates at 90 K. The curves are labeled with water coverage in absolute monolayers, as in Figure 1. Reprinted with permission from ref 22. Copyright 1986 Academic Press.

of other molecules even further in the extended cluster. The final orientation is that of Figure 2A. The clusters of Figure 3B cannot convert to those of Figure 3A during thermal desorption, unless this rotation occurs. We propose that the isotope effect is related to the fact that the zero-point energies for the crucial rotational motion depend upon the nature of the isotope, both in the ground state and in the transition state.

If this model is correct, then the isotope effect should be very sensitive to the nature of the hydrogen-bonded clusters which form at the surface. Specifically, the isotope effect should be absent on surfaces where the extended, well-ordered water clusters do not form because of lattice mismatch with the substrate or because of surface roughness. We have tested this hypothesis by comparing desorption of D_2O and H_2O from Ru(100), which is an atomically rough, row-and-trough surface.^{20,21} Even though this is the same metal, the desorption states of water are much different than for the (001) surface, and there is no measurable difference between the desorption traces of D_2O and H_2O . We take this to mean that the more atomically rough surface disrupts the extensive water clusters, and therefore no conversion from large clusters to small clusters can take place, consistent with the microscopic model proposed for the isotope effect on Ru(001).

We have discovered a second interesting and (we believe) related phenomenon on Ru(001). This is the fact that water acts very aggressively to displace a hydrocarbon, cyclohexane, from direct adsorption sites even though the adsorption bond strengths per molecule are comparable.²² The data that provide evidence for

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this displacement are illustrated by Figure 5. This figure shows thermal desorption traces after sequential exposure of the surface to the two gases at 80 K. The left-hand frames represent experiments wherein the sample is exposed to the hydrocarbon first and water second; the right-hand frames represent the opposite sequence of exposures. The dashed lines represent the water desorption traces, and the solid lines represent the cyclohexane desorption traces. A quick inspection shows that the left-hand side of the picture is virtually identical with the right-hand side, indicating that the results of the experiment are independent of the sequence of exposure. Therefore, the results discussed here are not limited by the kinetics of displacement or surface diffusion.

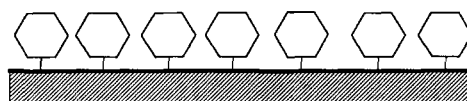
The exposure (and coverage) of cyclohexane is held constant from one experiment to the next, but the exposure (and coverage) of water increases upon going from the bottom frame to the top frame. With this in mind, first choose one side of Figure 5 (say, the left-hand side), and examine the H₂O desorption traces as water exposure increases from bottom to top. Comparison with Figure 1A reveals that the peak shapes and peak positions of H₂O are entirely unaffected by the presence of the hydrocarbon, even at very low water coverages (e.g., $\theta_{\text{H}_2\text{O}} = 0.22$) where the two molecules desorb simultaneously. This indicates that the hydrogen-bonded water bilayer remains intact in the presence of the hydrocarbon. However, the hydrocarbon is very strongly perturbed by water. As shown by Figure 5, it is pushed out of a high-temperature state at 200 K (which we, and other authors,²³ attribute to the chemisorbed layer of cyclohexane) and into lower temperature states at 136 and 150 K. The former is the signature of cyclohexane sublimation from a condensed state, whereas the latter is a new state, which we assign as cyclohexane atop water.

We interpret these data to mean that water displaces cyclohexane from the metal sites. Our model is illustrated in Figure 6. At low water coverages (e.g., $\theta_{\text{H}_2\text{O}} = 0.22$), water does not completely blanket the surface, as shown by Figure 6B. Instead, it clusters into hydrogen-bonded-bilayer islands and leaves patches of metal available for cyclohexane adsorption. As water coverage increases, however, a more contiguous layer forms until finally all the cyclohexane is forced into sites atop water, and/or atop cyclohexane.

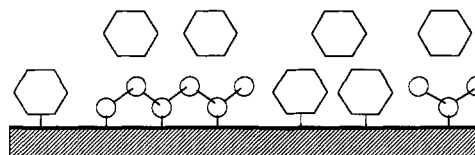
What drives this displacement reaction? The desorption data correspond to adsorption bond strengths of cyclohexane and water at 9 and 11 kcal/mol, respectively. However, these numbers should not be taken too literally; the value is particularly ambiguous for water, where aggregation may well invalidate the simple, first-order analysis of desorption peak shapes.²⁴ These numbers simply show that the adsorption bond strengths of the two molecules are roughly comparable, and so the efficient displacement reaction that we observe is surprising.

We believe that the explanation for this effect lies mainly in the relative packing densities of the two adsorbates. The hydrogen-bonded-bilayer arrangement allows water molecules to pack much more closely at the metal surface than cyclohexane. The ideal coverage

(A) Cyclohexane alone



(B) Cyclohexane plus water



(C) Cyclohexane plus more water

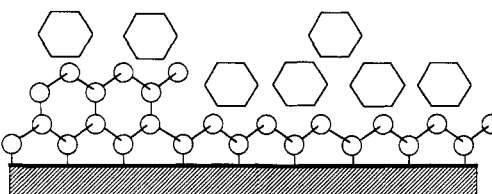


Figure 6. Model for displacement of cyclohexane by water on Ru(001). The open circles represent water molecules; the hexagons represent cyclohexane molecules.

of the water bilayer, 0.67 monolayers, far exceeds that of a filled cyclohexane layer, which we estimate to be 0.10–0.18 monolayers.²² Thus, about four to seven water molecules can fill the same two-dimensional area occupied by one cyclohexane molecule, and the only meaningful way to discuss the energetics of displacement is in terms of the energy change *per unit area*. In these terms, replacing cyclohexane with water achieves an enthalpy decrease of about 5–8 kcal/mol of surface Ru atoms. A rough estimate suggests that the entropy change which accompanies displacement (relative to the gas phase) is relatively small at 100 K. Therefore, it must be that the enthalpy change per unit area is the major energetic factor driving water to push cyclohexane away from surface sites. The enthalpy change per unit area is large because water forms the hydrogen-bonded bilayer, and cyclohexane does not. Thus, this is a second chemical phenomenon that can be traced to the unique properties of the water adlayer.

Conclusions

The importance of the hydrogen bond has long been recognized by the chemical community. In the field of surface science, the hydrogen bond continues to lead to surprising properties of water adlayers. In this Account we have discussed two such properties: an isotope effect in the desorption kinetics of water and a very efficient displacement of a hydrocarbon by water from surface sites. These properties probably depend strongly upon the atomic morphology of the metal substrate. The substrate that we have studied most extensively, Ru(001), serves as a particularly good template for the growth of an ice-like bilayer. Future studies that compare these properties at other metal surfaces will continue to be enlightening.

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