

How Does Water Wet a Surface?

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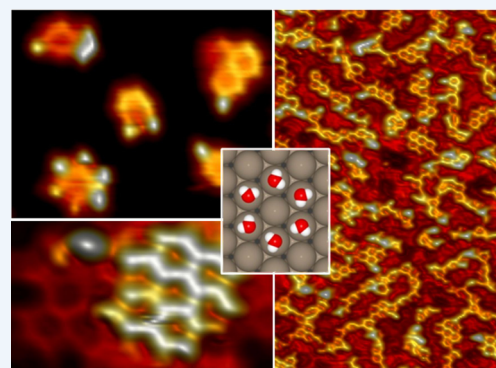
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CONSPECTUS: The adsorption and reactions of water on surfaces has attracted great interest, as water is involved in many physical and chemical processes at interfaces. On metal surfaces, the adsorption energy of water is comparable to the hydrogen bond strength in water. Therefore, the delicate balance between the water–water and the water–metal interaction strength determines the stability of water structures. In such systems, kinetic effects play an important role and many metastable states can form with long lifetimes, such that the most stable state may not be reached. This has led to difficulties in the theoretical prediction of water structures as well as to some controversial results. The direct imaging using scanning tunneling microscopy (STM) in ultrahigh vacuum at low temperatures offers a reliable means of understanding the local structure and reaction of water molecules, in particular when interpreted in conjunction with density functional theory calculations.

In this Account, a selection of recent STM results on the water adsorption and dissociation on close-packed metal surfaces is reviewed, with a particular focus on Ru(0001). The Ru(0001) surface is one where water adsorbs intact in a metastable state at low temperatures and where partially dissociated layers are formed at temperatures above ~ 150 K. First, we will describe the structure of intact water clusters starting with the monomer up to the monolayer. We show that icelike wetting layers do not occur on close-packed metal surfaces but instead hydrogen bonded layers in the form of a mixture of pentagonal, hexagonal, and heptagonal molecular rings are observed. Second, we will discuss the dissociation mechanism of water on Ru(0001). We demonstrate that water adsorption changes from dissociative to molecular as a function of the oxygen preadsorbed on Ru. Finally, we briefly review recent STM experiments on bulk ice (I_h and I_c) and water adsorption on insulating thin films. We conclude with an outlook illustrating the manipulation capabilities of STM in respect to probe the proton and hydrogen dynamics in water clusters.



■ INTRODUCTION

Most of the surfaces exposed to atmospheric conditions are covered with a thin layer of water. Water is also involved in many physical and chemical processes at interfaces, including electrochemical and photochemical processes, surface reactions in heterogeneous catalysis, corrosion, and environmental science. An accurate atomic-scale understanding of the water structures at surfaces is an indispensable prerequisite to comprehend the mechanism of such processes. Consequently, numerous studies have been devoted to the adsorption and reaction of water at low temperatures in the past decade using nearly all traditional surface science techniques.^{8–10}

Hexagonal close-packed metal surfaces have been extensively used as model substrates for water adsorption and ice growth owing to a long-standing idea that a good crystallographic match between the (0001) planes of hexagonal ice I_h and the underlying substrate would stabilize an icelike water layer.^{10,12,13} In such icelike layers, the molecules form a honeycomb network

adopting a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (see Figure 1a). Half of the molecules bind to the surface via the O atom, and alternate with the other half where the molecules point their H either toward (H-down) or away from the surface (H-up) to complete the hydrogen bonding network. In bulklike ice layers, the oxygen atoms form a buckled bilayer with a vertical displacement of 0.96 Å between adjacent atoms to preserve the tetrahedral bonding motif.¹⁵

The arrangement of water molecules in wetting layers have until recently mainly been studied by interpreting indirect evidence from vibration and thermal desorption spectra (TDS), and by k -space measurements such as helium atom scattering (HAS) and low energy electron diffraction (LEED) experiments. Scanning probe microscopies (SPM), in particular STM in combination with density functional theory (DFT), have

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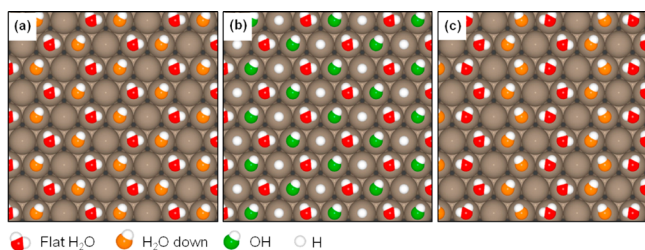


Figure 1. Schematics showing (a) an idealized (proton ordered) icelike water layer in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement on a close-packed metal surface, (b) a partially dissociated water layer, half water (red) and half OH (green) with H adsorbed at the top site, and (c) a chain structure composed of H-down (orange) and flat water (red) arranged in a complete hexagonal layer.

provided detailed information into the local structures of water on the nanoscale only in recent years.¹⁶ The structural information on local bonding motifs has helped to unravel the delicate balance between water–water and water–metal surface interactions. STM experiments have also proven powerful in deciphering the dynamics of individual water molecules, for example, the diffusion^{17–20} and dissociation,^{7,21} as well as the intramolecular and intermolecular proton dynamics^{22,23} by tip manipulation through electronic and vibrational excitation.

This Account elaborates on recent findings in regard to the adsorption and reaction of water on metal surfaces from a molecular view gained by STM and DFT, based on the particular example of Ru(0001). We conclude with a discussion and outlook on recent scanning probe experiments on water adsorption and manipulation on nonmetallic surfaces.

■ WATER ON RU(0001): A MODEL SYSTEM

The adsorption of water on the Ru(0001) surface was one of the first systems studied and has become a model one, owing to having one of the smallest lattice mismatch with bulk ice (3.7%) among the hexagonal close-packed metal surfaces.⁸ However, Ru is special in that it is the only platinum group metal where thermal dissociation of water is observed.^{25,26} This led initially to some controversy in the interpretation of

experiments aimed at determining the structure of the wetting layer.

HAS and LEED experiments implied that wetting layers adopt an *icelike* water structure with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity on Ru(0001) at low temperatures.^{12,13,27} DFT calculations by Feibelman²⁶ revealed however that the adsorption energy of intact water layers with coplanar O as observed in LEED-IV²⁸ is far too low. Instead the wetting layer is composed of water molecules and hydroxyl groups hydrogen bonded in a hexagonal structure. The extra hydrogen atoms in this model are bound directly to the metal in the center of the rings (see Figure 1b).²⁶ The dissociation process is an activated process on Ru(0001) with an activation barrier of around 0.5 eV,²⁹ which can be overcome by heating (above ~ 140 K)^{30,31} or by electron exposure.^{32,33}

The indirect evidence from ensemble-averaged measurements of water on Ru(0001) led to inconclusive models of the intact wetting layer structure. LEED, which is largely insensitive to H atom positions indicates O atom ordering,²⁸ whereas broad RAIRS bands,³⁴ low reflectivity and broad peaks in HAS implied a disordered phase.³⁵ In addition, the absence of a free OH stretch in SFG³⁶ and RAIRS³⁴ pointed to a structure assembled from H-down and nearly flat molecules, with the molecular plane nearly parallel to the surface. Based on these experimental observations, a chain structure was proposed composed of flat lying water molecules linked by H-down chains into a hexagonal hydrogen bonded network (see Figure 1c).^{34,35} The chain structure is 20% more stable than the conventional ice bilayer structure presumably owing to the ability of half the water to adsorb close to Ru in its preferred flat atop adsorption geometry. The example of intact water on Ru(0001) clearly shows that ensemble-averaging techniques reach their limit to unravel the local structures of water on surfaces.

■ FROM H₂O CLUSTERS TO THE WETTING LAYER: A MICROSCOPIC VIEW

The equilibrium adsorption site of water monomers on all metal surfaces is the atop site with an adsorption energy of around 0.4 eV/H₂O on Ru(0001).^{26,29,37} Thereby the

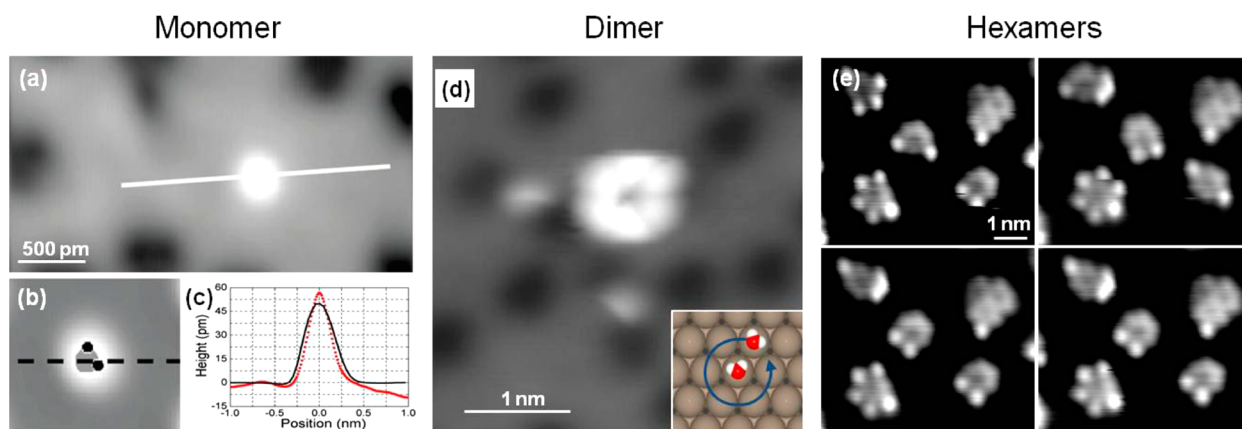


Figure 2. (a–c) Low temperature (4 K) STM image of an isolated water monomer on Ru(0001) with (b) a calculated STM image and (c) experimental (red dotted curve) and theoretical (black solid curve) height profiles. Reprinted with permission from ref 2. Copyright 2008 American Chemical Society (ACS). (d) Water dimer imaged as a rosette of six maxima due to the rotation of the hydrogen bond acceptor molecule around the donor molecule located at the center ($V_{\text{sample}} = 50$ mV; $I = 400$ pA). The dark spots correspond to adsorbed carbon impurities. Reprinted from ref 7 with permission from Elsevier. (e) STM images showing four hexagonal water clusters and a trimer of side-sharing hexagons (top right) acquired at 50 K at 1 min intervals. Reprinted with permission from ref 14. Copyright 2009 American Chemical Society.

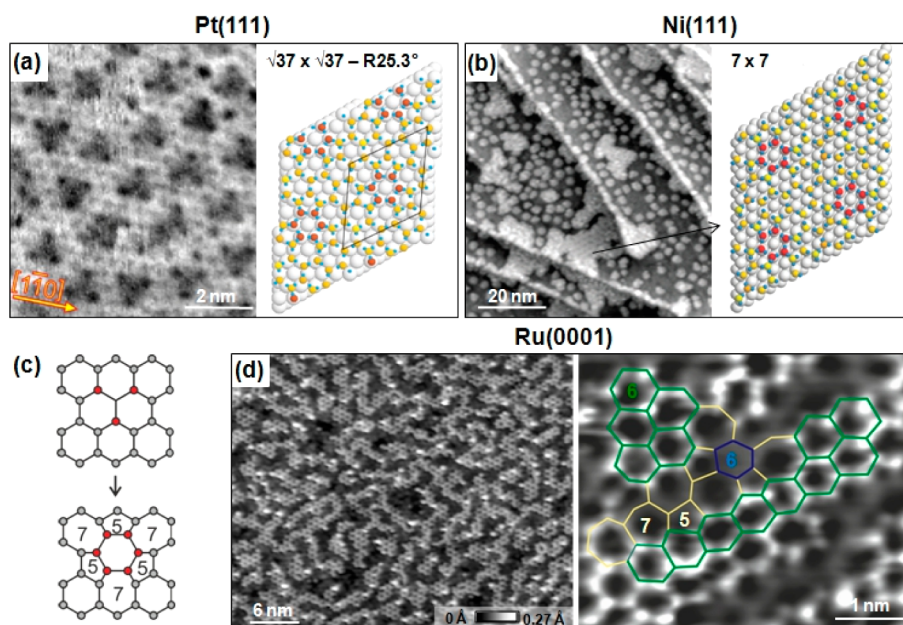


Figure 3. Nonhexagonal water layers on close-packed metal surfaces: (a) STM image of a water layer near completion deposited on Pt(111) at 140 K showing a disordered arrangement of triangular depressions along with a model of the $\sqrt{3} \times \sqrt{3} - R25.3^\circ$ phase of water. (b) STM image of an ~ 0.5 ML ice/Ni(111) film produced by first depositing 1.5 ML and subsequently evaporating some of the water by annealing at $T = 145\text{--}155$ K. Model of the observed 7×7 nonrotated water layer. (c) Schematic showing the formation of a “575757” di-interstitial defect in a hexagonal lattice. (d) H_2O wetting layer on Ru(0001) with high-lying (rotated, bright) and low-lying (in registry, dark) water domains. In the magnified image (right), the rotated hexagons (marked by green lines) are connected by pentagonal and heptagonal rings. Reprinted with permission from (a) ref 5, copyright 2010 APS; (b) ref 11, copyright 2014 AIP; and (d) ref 4, copyright 2014 APS.

molecular plane is nearly parallel to the surface and the main bonding occurs through the oxygen lone pair. A water monomer on a metal surface can only be imaged at low temperatures in STM due to its high mobility. It is generally imaged as a round shaped protrusion (see Figure 2a).^{2,38}

The first clusters that build on the surface are hydrogen bonded dimers.⁷ In a dimer, the donor H_2O molecule is bound to the surface via the O-lone pair orbital while the other is a H-acceptor molecule weakly interacting with the substrate. Water dimers can be distinguished by their higher mobility relative to the monomers as shown at the single-molecule level in STM experiments.^{18,19,39,40} This peculiar dynamics of the dimer was explained by an exchange of the roles of the two molecules from hydrogen donor and acceptor via hydrogen bond rearrangement, a process that was proposed to occur via quantum tunneling of the proton.^{39,40} In STM images, H_2O dimers are often imaged as a *rosette-like* object with a 6-fold symmetric contrast (see Figure 2b), as first observed on Pt(111).^{19,41} The *rosette-like* contrast can be explained as a result of “time-averaging” the position of the acceptor molecule as it rotates around the donor molecule fixed on the surface.

With additional water exposure, small aggregates of side-sharing, intact water hexamers are formed at temperatures below 140 K.¹⁴ The hexamers assemble initially to form a honeycomb network with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement in registry relative to the underlying metal lattice. On reactive surfaces such as Ru, where the H_2O molecules bind strongly to the surface, the hexamers are planar³⁴ in contrast to the noble metals Cu and Ag where buckled hexamers are observed.³⁸ The cluster growth occurs by attachment of molecules to edge vertices of the hexagons (bright spots in Figure 2(e)).¹⁴ These molecules incorporate and extend the hexagons but only to a limited size consisting of a few connected hexamers and with a density that increases with water exposure.

The peculiar size-limited cluster growth was rationalized by introducing a set of two-dimensional (2D) ice rules.^{14,42} According to these rules, water molecules preferentially bind to the metal via the O atom on atop sites in a nearly flat geometry; the molecules form a honeycomb network with the molecules inside the network donating two H-bonds to neighboring molecules and accepting one. In contrast to *icelike* layers, which can be indefinitely extended, the two-dimensional water network of flat molecules can only be continued for a limited number of hexamers owing to the imbalance of acceptor and donor sites. Larger islands require the presence of one or more nonflat double hydrogen acceptor molecules with H-up or H-down configuration. When a water molecule accepts more H-bonds than it donates, the extra H atom forms a weak bond with the metal, which results in a weaker interaction with the metal substrate. As a result this molecule is raised ~ 50 pm above the surface.^{14,39} On Ru these nonplanar molecules destabilize the structure by around 0.03 eV per molecule when located at the periphery of a cluster and even further when located inside.¹⁴ Energy optimization drives the formation of structures consisting of narrow stripes and rosettes no more than three hexagons wide, because these structures minimize the number of nonplanar molecules. The 2D water rules were initially observed by STM on Pd(111)^{14,18} and recently also on Rh(111).⁴³

At higher water coverage, islands of clustered hexagons are formed.⁴⁴ These islands show peculiar structures in molecularly resolved STM images: First, there are high-lying and low-lying domains of intact water with apparent heights differing by 30–50 pm. Second, the hexagons in the high-lying domains exhibit a weaker interaction with the substrate and are rotated by 30° with respect to those in the low-lying domains and with the hexagonal lattice of the metal surface. The transition between high-lying and low-lying domains is mediated by pentagonal

and heptagonal ring structures, as shown in Figure 3. This growth mode is observed not only for small clusters, but also in extended films. It is a consequence of optimizing the water–surface interaction that allows the low-lying rings of flat water molecules to be in atop sites without breaking the hydrogen bonded network.

DFT calculations of pentagon-hexagon-heptagon layers confirmed that compact clusters of flat-lying H₂O molecules strongly bound to the surface and of weakly bound rotated high-lying molecules, bridged by heptagonal and pentagonal rings, can form stable structures.^{5,44,45} Such pentagon–hexagon–heptagon layers have been observed by STM on Pt(111),^{5,45,46} Pd(111),⁴⁴ and Ni(111);¹¹ see Figure 3. This suggests that water structures on close-packed metal surfaces can be generated by constructing pentagon–hexagon–heptagon layers, drawing the curtain over the long-standing idea that water adopts an icelike structure. These nonhexagonal layers lead in general to large unit cells, for example, like the ($\sqrt{37} \times \sqrt{37}$)R25.3° and ($\sqrt{39} \times \sqrt{39}$)R16.1° supercells found on Pt(111)⁵ and the (7 × 7) found on Ni(111).¹¹ In contrast, on Ru(0001) and Pd(111) no long-range ordered layers have been observed by STM⁴⁴ consistent with HAS measurements^{35,47} that show a very low specular reflectivity, indicating a more disordered water layer.

From the observation of many nonhexagonal water arrangements, it has been suggested that a good match between the substrate and the nearest neighbor oxygen–oxygen distance is a better descriptor for the growth of icelike water overlayers than the good match to the bulk ice lattice constant originally assumed.^{48–50} A match of the O–O spacing allows water to adopt a flattened structure with the O nearly coplanar. This has been confirmed by DFT calculations^{48,49} and also experimentally demonstrated by LEED experiments on close-packed Sn substitutional alloy surfaces, whose lattice constants changed from 4% smaller to 7% greater than the bulk ice constant.⁵⁰ A good lattice match is certainly not a solid indicator of the propensity of a material to facilitate growth of bulk ice layers; also the binding energy and the mobility of the surface layer are important.

■ WATER DISSOCIATION

Water splitting is an important reaction, for example, in photosynthesis that sustains life on earth, and is a key to the management and production of future fuels. The efficiency of water splitting depends strongly on the catalyst: on oxide surfaces water dissociates at defect sites, and on metals fragmentation of water occurs only on active metals but not on noble metals.¹⁰

Ruthenium is one of those surfaces, where water readily dissociates into OH and H species after activation through heating or electron exposure.^{4,30–33} The activation barrier for water decomposition is comparable to the binding energy of the water molecules to the substrate or to other molecules as first evidenced by XPS³¹ and DFT.²⁹ The dissociation reaction shows a strong kinetic isotope effect on Ru, while D₂O stays intact upon heating up to the desorption temperature, H₂O undergoes partial dissociation.^{30,32} This is clearly observed in TDS, where D₂O shows a single desorption peak, rather than two peaks, one from intact molecules and another from OH and H recombination, for H₂O.³⁰

The dissociation process of water on Ru(0001) can be driven through excitations by electrons with energies above 1 eV, as shown in STM tip manipulation experiments.⁷ In contrast,

excitation of one quantum of the O–H stretch mode at 445 meV in single H₂O molecules resulted in the diffusion and desorption rather than dissociation of the molecule.

Figure 4 shows images of the thermal evolution of the water structure adsorbed at low temperatures on Ru(0001).⁴ First,

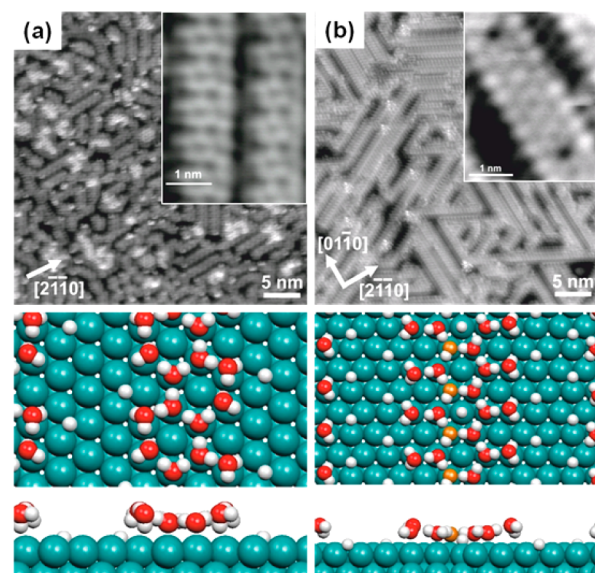


Figure 4. Partial dissociation of H₂O on Ru(0001): STM images of (a) intact water stripes after deposition at 145 K and its transformation to (b) partially dissociated H₂O–OH stripes after 30 min annealing at 145 K. Occasionally, dark spots are seen in the center of the hexagons (inset in (b)), corresponding to H atoms trapped inside, as in the original model of Figure 1b. In the DFT optimized structures shown, the OH group is highlighted by an orange O atom. Reprinted with permission from ref 4. Copyright 2014 APS.

narrow stripes form which are composed of intact water molecules following the 2D water rules. After further heating, the intact water stripes transform into mixed water-hydroxyl stripes, rotated by 30° with respect to intact ones. The reorientation can be explained by the maximization of the number of dissociated molecules that can be accommodated, as opposed to an optimization of the hydrogen-bond density.⁴ The partially dissociated water stripes are composed of hexagonal rings of molecular water and hydroxyl species,^{4,33} and have a width that varies from one to three or four hexamer units, corresponding to around 2.5–6 Ru lattice constants.³³ The narrow stripe structures differ drastically from the extended H-bonding network model put forward based on theoretical modeling of a completely covered surface (see Figure 1). The driving force for the stripe formation is the hydrogen liberated during the dissociation process, which prefers to adsorb on the Ru fcc sites located between the H₂O–OH stripes and outside the hexagonal rings. Occasionally, however, some H atoms can be trapped at the center of mixed water–hydroxyl hexagons as in the original model of Figure 1b.^{4,29} The hydroxyl groups were found to be located primarily inside the linear structures; see Figure 4b. A comparison of STM data and DFT calculations suggests ratios of H₂O:OH ranging from 3:1 to 4:0, with an average of roughly 5:3,^{4,33} which agrees with XPS data.^{25,51} The partially dissociated structures desorbed finally at around 230 K from the surface.²⁵

In contrast to the mostly intact water adsorption on flat close-packed Pt-group metal surfaces apart from Ru(0001),

water is more reactive at stepped surfaces. DFT predicted, for example, that on Pt(221) water molecules dissociate at steps, forming mixed hydroxyl/water structures, through an autocatalytic mechanism promoted by H-bonding.⁵²

■ WATER–OXYGEN INTERACTION: FROM COADSORBED OXYGEN TO OXIDES

The surface chemistry of small molecules is in general highly sensitive to relatively small surface modifications either by site blocking or by changing the binding and activation energies of the adsorbed molecules. Many coadsorption studies have been carried out with traditional surface science techniques, in particular water coadsorbed with alkalis, O, and CO.¹⁰ On Ru(0001), preadsorbed oxygen was found to result in a stronger binding of H₂O, owing to the formation of hydrogen bonds between the molecule and the chemisorbed oxygen.^{1,6,53,54} At the same time, the surface oxygen changes the chemical state of adsorbed water through strong H-bonding and can promote water dissociation.^{55,56}

STM and XPS experiments have shown that the presence of oxygen vacancies in the O(2 × 2)/Ru(0001) is necessary for H₂O dissociation to occur.^{54–56} Hence, only at low oxygen coverage, partial dissociation of H₂O occurs, as on the clean surface. In contrast, at oxygen coverages between 0.25 and 0.5 ML, dissociation is inhibited and the intact water molecules are bound to Ru top sites stabilized by H-bonds to two neighboring O; see Figure 5.^{1,6,54–56} At higher O coverage, when all top sites are blocked, water adsorption causes a shift of half of the oxygen atoms from hcp sites to fcc sites, creating a honeycomb structure where water molecules bind strongly to the exposed Ru atoms.⁶ The energy cost of reconstructing the oxygen overlayer is more than compensated by the larger adsorption energy of water on the newly exposed Ru atoms.

Finally, on RuO₂(110) thin films grown on Ru(0001), water splitting is readily observed.⁵⁷ The monomers adsorb molecularly at low temperatures (<230 K), with the O positioned above a 5-fold-coordinated Ru atom, see Figure 5c.²⁴ At higher temperatures, the monomers diffuse along Ru rows and dimerize. Water dimers deprotonate readily to form Ru-bound H₃O₂ and bridging hydroxyls.

■ BEYOND METAL SURFACES

Understanding water structures on oxides and alkali halide surfaces is more intriguing but more challenging than those on metal surfaces because of the complicated nature of the water interaction.⁵⁸ Oxides and alkali halide surfaces provide often inhomogeneous adsorption sites, such as vacancy defects. Local probe measurements on nonmetallic surfaces are thus particularly important and necessary to understand the influence of defects. Recent STM experiments of water on oxide and salt thin-films provided unique insights into the adsorption,^{3,24,58–61} diffusion,⁶² dissociation,²¹ and proton dynamics of water on nonmetal surfaces.^{22,61}

Owing to the electronic decoupling of water from the metal by thin NaCl layers on Au(111), Guo et al. visualized the frontier orbitals of water,³ making it possible to discriminate the orientation of the water monomer on the surface and the hydrogen bond directionality in the clusters, see Figure 6. Further, real space studies of the motion of single molecules revealed a squared diffusion pattern on NaCl consisting of a combined out-of cell motion and reorientation of the water.⁶²

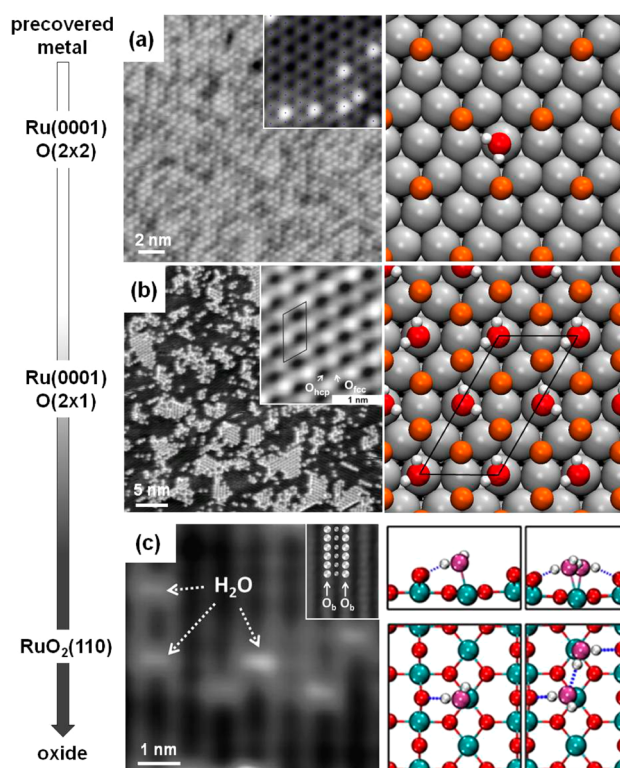


Figure 5. STM images (left) and calculated structures (right) of water adsorbed on the (a) O(2 × 2) and (b) O(2 × 1) Ru(0001) surface. Water molecules adsorb intact with the O bound to Ru top sites and the H atoms forming H-bonds to the neighboring O atoms in the lattice. (c) Water monomers adsorbed on Ru rows of RuO₂(110) along with the calculated adsorption geometry for the monomer and dimer. Adapted from (a) ref 1, copyright 2007 APS and (b) ref 6, copyright 2010 APS. Panel (c) reprinted with permission from ref 24. Copyright 2014 ACS.

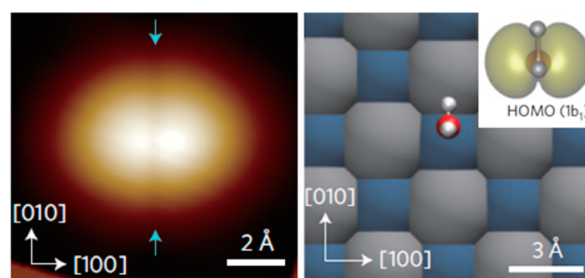


Figure 6. Orbital imaging of a water monomer. Left: High-resolution STM image of the HOMO orbitals of a water monomer on a NaCl(001) bilayer on Au(111). Right: Calculated adsorption configuration and molecular orbitals of the water monomer. Reprinted with permission from ref. [3], copyright 2014 Nature Publishing Group.

The electronic decoupling from the metal enhances also the lifetime of tunneling electrons in molecules. In this way new dissociation pathways of isolated single water molecules on MgO thin films were observed through vibrational and electronic excitation by means of injecting tunneling electrons as shown by Shin et al.²¹

■ PROBING HYDROGEN AND PROTON DYNAMICS

Hydrogen bonds are the path through which protons and hydrogen atoms can be transferred between molecules.

Recently, STM not only provided high-resolution images of the hydrogen bonded water networks, but it also proved to be the ideal tool to study intramolecular and intermolecular proton dynamics at the single molecule level in water clusters.^{22,23,40} On Cu(110), the transfer of H atoms along hydrogen bonded chains was controlled and triggered by excitation of molecular vibrations induced by inelastic tunneling electrons.²³ These results confirm that H atom transfer along hydrogen bonds is possible also on metal surfaces despite the strong binding of the water. On NaCl(001) films on Au(111), the concerted tunneling of four protons in an individual hydrogen bonded water tetramer was reported.²² This was achieved by monitoring the change in the hydrogen bond directionality using submolecular orbital-imaging.

MULTILAYER STRUCTURES

A microscopic view of the first water layer is just a first step toward understanding water–solid interfaces and wetting. While the interface layer is clearly influenced by the water–surface interaction, the water–water interaction should dominate the structure of thicker layers. LEED and RAIRS experiments showed that, at low temperatures (<140 K), where water mobility is limited, amorphous solid water films are formed.⁶³ These films are unstable and transform into multilayer ice crystallites upon annealing.

A microscopic view on ice multilayers by STM has been achieved on Pt(111),^{64–66} Ni(111),¹¹ and Cu(111).⁶⁷ Thürmer and co-workers used the ability to resolve molecular surface steps of ice in STM experiments to obtain insights into the growth mechanism of ice on Pt(111) and addressed the competing interaction between the two low pressure crystalline phases of ice I_h and ice I_c (cubic ice).^{64–66} Using noncontact atomic force microscopy (nc-AFM), they showed that on Pt(111) isolated 3D clusters grow in the form of ice I_h . Upon coalescence of the clusters, the I_c ice form is observed, and at thicknesses of 20 nm I_h becomes favorable again. The use of nc-AFM made possible the study of ice films of unlimited thickness with molecular scale resolution, which was not possible with STM due to the insulating nature of ice films thicker than a few layers.⁶⁶ In contrast, on Cu(111), three-dimensional clusters with a variety of complex structures were observed, but never with a simple I_h or I_c termination.⁶⁷

CONCLUSIONS AND OUTLOOK

Low temperature STM experiments have provided a detailed view of the local structure and bonding of water molecules in clusters. The variety of structures observed reflect the highly complex and metastable energy landscape which results from the delicate balance between hydrogen-bonding and metal–surface interaction. In recent years, it was clearly shown based on STM experiments and DFT that uniform two-dimensional ice bilayers do not form on close-packed metal surfaces. Instead hydrogen bonded layers consisting of a mixture of pentagonal, hexagonal, and heptagonal rings of water molecules were observed in extended layers. The structures are mainly driven by the preference of water to adsorb in a planar geometry, strongly binding through the oxygen to the metal atop site. STM in combination with DFT has provided a coherent picture of the structure of the wetting layer. In the future, SPM and, in particular, nc-AFM will play a crucial role in studies aimed at unraveling the molecular structure of multilayers as well as water structures on insulating substrates among others.

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The authors declare no competing financial interest.

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