Two-Dimensional Wetting of a Stepped Copper Surface

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Highly corrugated, stepped surfaces present regular 1D arrays of binding sites, creating a complex, heterogeneous environment to water. Rather than decorating the hydrophilic step sites to form 1D chains, water on stepped Cu(511) forms an extended 2D network that binds strongly to the steps but bridges across the intervening hydrophobic Cu(100) terraces. The hydrogen-bonded network contains pentamer, hexamer, and octomer water rings that leave a third of the stable Cu step sites unoccupied in order to bind water H down close to the step dipole and complete three hydrogen bonds per molecule.

The interaction of water with surfaces plays a key role at many interfaces of technological importance, either as the active species or by modifying the stability of other adsorbates. Water-surface bonds typically have a similar strength to that of the water-water hydrogen bond, with the result that water bound in confined environments may have quite unique [1] and potentially useful properties. Examples include frictionless transport of 1D chains in carbon nanotubes [2–4] and molecular sieves of graphene oxide with the potential for cheap desalination [5], while the ability of certain surfaces to nucleate ice efficiently plays an important role in areas as diverse as atmospheric precipitation [6] and ice formation (or inhibition) at biological interfaces [7]. Many of these surfaces are complex, and their behavior poorly understood. For example, ice forming proteins typically display regular linear arrays of hydrophilic and hydrophobic binding sites, but exactly why their structure has such a unique ability to nucleate ice remains unclear.

Water at a solid interface must simultaneously optimize both the water-water and water-surface interaction, causing small variations in the strength of the water-surface bond, or the symmetry of the surface, to generate quite different structures, with theory predicting many unusual phases [8,9]. Plane surfaces provide a key test ground to understand how water behaves and a range of different structures have been observed [10,11], including nonhexagonal 2D networks on close packed metal surfaces [12–14], chains of water pentagons on a rectangular metal surface [15], and a network of interlinked water tetramers on sodium chloride [16]. Wetting of oxide surfaces is characterized by adsorption or hydroxylation at specific surface sites and chain formation [17], but less is known about formation of extended hydrogen-bond networks [18] where the heterogeneity of the surface becomes important [19]. Although hexagonal water networks can be engineered by templating a suitable surface [20], none of the plane surfaces studied so far produces a true

"icelike" layer that might be considered an ideal template for 3D ice nucleation [21], while the analogy to ice forming proteins [7] suggests ice nucleation might instead be enhanced by a different symmetry, such as the periodic arrays of binding sites found on a stepped surface.

In this study we investigate water adsorption on a stepped Cu(511) surface, consisting of (111) steps separated by narrow (100) terraces, as shown in Fig. 1(a). Unlike hydrophobic Cu(100) [22], water binds strongly at low coordination step sites [23], resulting in a regular array of hydrophilic and hydrophobic binding sites, separated by the step spacing of 6.6 Å. Water chains have been observed decorating steps on various metal surfaces [24–26], even when the surface is otherwise nonwetting [27–30]. Steps on Pt stabilize significantly more water than can be associated with a simple linear chain [26,31–34], with electronic structure calculations indicating interlinked rings grow along the step [26,35], but the transition to crystalline ice growth is
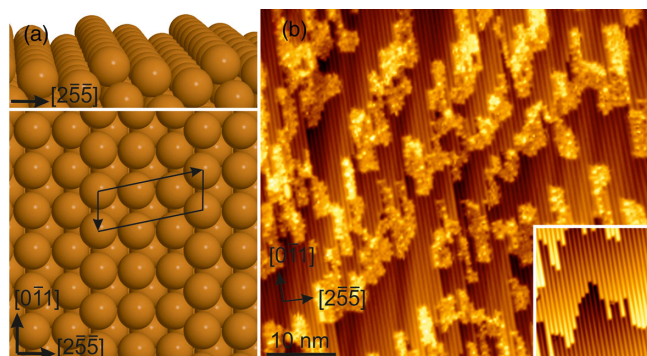

FIG. 1. (a) Representation of the Cu(511) surface. The $[2\bar{5}\bar{5}]$ direction points "up" the Cu steps. (b) STM image showing 0.3 ML water adsorbed at 77 K. The inset shows the surface before water adsorption with the Cu steps appearing as bright lines along $[0\bar{1}1]$ (−208 meV and 41 pA).

not well understood [31]. Here we show that water on Cu(511) creates an extended 2D hydrogen-bonded network, rather than forming 1D chains along the step. The 2D network consists of interlinked octomer, hexamer, and pentamer units, containing short zigzag chains of water along the Cu step. Density functional theory (DFT) structure calculations find water is tightly bound flat on the step, the network being completed by H-bonded water that bridges across the hydrophobic (100) terraces. Based on the DFT calculations, we examine the factors that stabilize the 2D network and discuss the balance between chain formation and 2D wetting on such corrugated surfaces.

A Cu(511) crystal, polished to 0.05 μm and aligned <0.1° (Surface Preparation Lab), was cleaned by repeated sputter anneal (773 K) cycles. STM images were recorded at 77 K using a Createc UHV STM. Helium atom scattering (HAS), low energy electron diffraction (LEED), and temperature programed desorption were recorded as described earlier [20,36]. STM images shown in Fig. 1 reveal close packed Cu rows running along the [0$\bar{1}$1] direction. The orientation of the Cu steps was determined directly from images of added rows of Cu at the edge of (511) terraces [see Supplemental Material (SM) for details [37]]. At 77 K water aggregates preferentially on the top edge of steps between the Cu(511) terraces, forming chains and disordered clusters that are elongated along the [0$\bar{1}$1] step direction. Although a few steps are decorated by linear clusters, all the structures observed are at least 13 Å wide, bridging across three or more Cu steps. It is apparent that water adopts a 2D hydrogen-bonded structure in preference to forming 1D chains, even though this requires some water molecules to adsorb above the (100) terrace.

Annealing the water covered surface to 135 K, or depositing water at temperatures where it is mobile, orders water into an extended 2D network. LEED measurements [Fig. 2(a)] and HAS (see SM [37]) show a sharp (31, −31) diffraction pattern, becoming intense as the coverage is increased towards completion of the first layer. The LEED pattern has symmetric diffraction beams, with no evidence
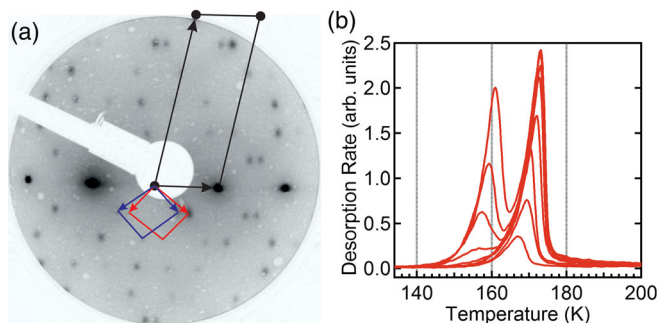
of 1D growth or limited order in any particular direction. Diffraction disappears rapidly with electron exposure, most likely due to electron induced dissociation [38]. Heating the surface causes water to desorb intact near 174 K [Fig. 2(b)], stabilized 12 K above the multilayer peak that appears at higher coverage. Water desorption is zero order, consistent with water forming dense 2D islands and desorbing via a precursor mediated mechanism, but HAS measurements suggest dissociation can occur slowly at temperatures above 140 K, similar to the behavior on Cu(110) [39].

STM images of the (31, −31) structure reveal highly ordered islands that extend across the Cu(511) terraces, eventually covering the entire surface. Figure 3(a) shows one domain of this structure, revealing a highly ordered water network built from rings of three different sizes. To aid discussion of this structure, Fig. 3(a) also shows the network formed by overlaying a STM image by vertexes ca. 2.7 Å long, the O─O separation in ice. On this basis the structure can be assigned to a mixture of octomer, hexamer, and pentamer rings. The octomer rings are separated from each other by two face sharing pentamers in one direction and by a row of distorted hexamers in the other. This network tessellates the surface, with each O site having three hydrogen bonds. STM images showing the registry between water islands and the Cu(511) terrace (Fig. S3 of SM [37]) find that the center of the large ring is aligned directly above the Cu(511) step, as shown in Fig. 3(b). This arrangement creates a short zigzag chain of four water molecules along the top of each Cu step, marked in bold in Fig. 3(b), separated from the next chain by the octagonal ring. STM images displayed little sensitivity to the bias voltage, with filled states images showing the same pattern of octomer, hexamer, and pentamer rings (see Fig. S4 of SM [37]).

The STM images provide two other clues to the nature of the water structure. Although the underlying (31, −31) network shows excellent long-range order, extending unbroken across entire Cu terraces, the highest contrast feature appears at different sites within the unit cell, marked
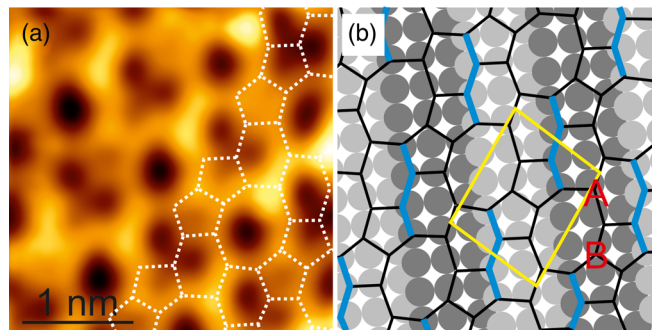

FIG. 2. (a) LEED image (50 eV) of 0.6 layers of water adsorbed at 135 K showing the metal reciprocal unit cell (black lines) and the two (31, −31) domains. (b) Temperature programed desorption of water (1 K s^{-1}) as a function of coverage from 0.2 to 1.8 times saturation of the first layer.

FIG. 3. (a) STM image showing one domain of the (31, −31) structure (−110 meV, 100 pA). (b) Registry of the rings perpendicular to the Cu steps, with H bonds above the Cu steps indicated in bold (blue).

either A or B in Fig. 3(b). This variation in contrast was characteristic of all STM images (see Fig. S4 of SM [37]), suggesting that more than one possible H-bonding arrangement exists within the same topographical H-bond network. The second observation is that water above the Cu step site appears faint in STM images. Analogy with other surfaces, where water adsorbed flat shows low contrast in STM [12,15,40], suggests that water at the step is likely bonded flat to Cu via the O, consistent with the stable monomer binding site found by DFT [23].

In order to explore the driving force to form this unusual 2D network, we performed DFT calculations on trial structures using VASP [41,42] with the optB86b-vdW exchange-correlation functional [43,44]. This functional includes van der Waals interactions, which are known to be important in stabilizing surface adsorption relative to 3D ice formation [45,46], and has a similar performance to other vdW functionals for systems where physisorption is important [47]. Further details of the supporting DFT calculations and structures obtained are given in the SM [37], which includes Refs. [48,49]. As expected [23], an isolated water monomer prefers to adsorb at the Cu step, with O atop Cu, one H atom pointing down towards Cu in the lower terrace, and a binding energy of 0.549 eV. The binding energy increases to 0.678 eV/water when a continuous zigzag chain is formed with water bound to the step via O; see Fig. 4(a). Breaking the chain to form tetramers [Fig. 4(b)] reduces the binding energy only marginally to 0.667 eV/water, despite reducing the average H-bond coordination by 25%, implying there is no overriding energetic drive to form extended water chains along the step. As a consequence, 2D structures that contain short chains may be stable if the increased water H-bond coordination is sufficient to compensate for having vacant step sites.

Calculations for 2D water structure were based on the network found by STM, Fig. 3, with two examples shown in Figs. 4(c) and 4(d). All the low energy arrangements we found have 4 out of 10 water molecules per unit cell lying flat along the Cu step (blue vertices in Figs. 3 and 4), bonded directly to Cu via O in an arrangement similar to the water chains shown in Fig 4(a). In order to complete the H-bonding network, the remaining six water molecules include one double donor species [circled in Figs. 4(c) and 4(d)] and five single donors per unit cell, each with one uncoordinated H pointing either towards the surface (H down) or towards the vacuum (H up). These additional water molecules do not bind directly to Cu but complete the H-bond network. The choice of the final double donor site, the location of H between O, and the orientation of uncoordinated H atoms create a large number of possible arrangements for the same topographical H-bond network. All the structures we calculated that have water arranged H down towards Cu are >0.1 eV/water more stable than the 1D water chain, having a binding energy of 0.774–0.762 eV/water (see Figs. S5
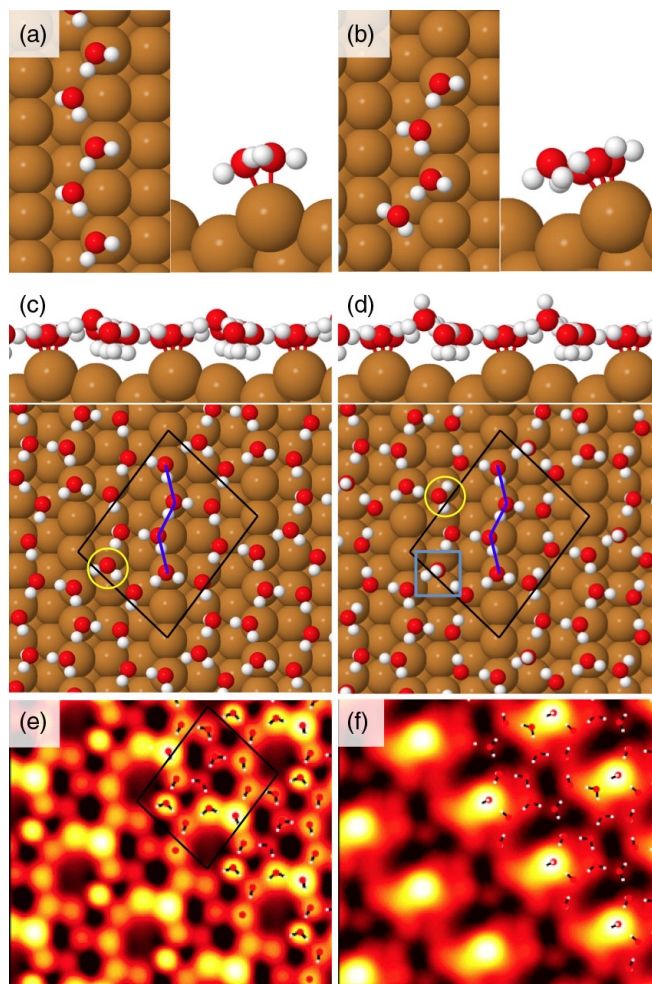

FIG. 4. Calculated structures for (a) a continuous 1D water chain and (b) a tetramer at the Cu step (binding energy 0.678 and 0.667 eV/water, respectively). (c) 2D structure (Fig. S4A of SM [37], 0.770 eV/water), showing the four flat water molecules at the step (indicated by the blue lines) and the location of the final double donor water (yellow circle). (d) 2D structure containing an H-up water (blue square). (e),(f) STM simulations of the structures above (bias voltage −100 meV).

and S6 in SM for more details [37]). DFT calculations were also carried out to test the assumption that water is adsorbed flat at the Cu step site and the effect of rotating uncoordinated H atoms to point away from the Cu surface. Disrupting the flat water tetramer above the Cu step was extremely unfavorable, decreasing the interaction with the Cu surface and reducing the binding energy by more than 0.29 eV (see Fig. S8 of SM [37]). Rotating H to point H up away from the Cu surface has a less dramatic effect, but even the best H-up arrangement [shown in Fig 4(d)] was 0.11 eV less stable than the equivalent H-down arrangement. Tersoff-Hamann STM simulations for H-down arrangements [Fig. 4(e)] reproduce well the interlocking network of octomer, hexamer, and pentamer rings seen in the experimental images, whereas H-up simulations [Fig 4(f)] find the image dominated by the

upright H, inconsistent with the experimental images and confirming the H-down arrangement found by DFT.

The difference in binding energy between H-down arrangements that have water flat on the step sites is very small, with five structures having a binding energy $0.772 \pm .002$ eV/water. These energy differences are small compared to the intrinsic accuracy of the calculations, implying the H location within the overall H-down structure cannot be distinguished on the basis of their calculated binding energy. As discussed above, STM images for the $(31, -31)$ structure showed variation in the contrast of particular features within the overall H-bond network, indicating changes in the local H arrangement between different regions within a $(31, -31)$ water domain. We conclude that the $(31, -31)$ network is made up of water oriented flat along the step sites and H down above the (100) terraces, with some variation in H orientation and location of the final double donor species.

Having understood the structure of the $(31, -31)$ water network on Cu(511), we can now investigate the factors that favor its formation in preference to 1D chains or small clusters. One obvious driving force to form the 2D network [Fig. 4(c)] is the increased H-bond coordination, with three H bonds/water instead of two for the infinite 1D chain [Fig. 4(a)]. Comparing the binding energy of different structures in the gas phase and on the surface provides a measure of the intermolecular hydrogen bonding intrinsic to the different arrangements in the gas phase and the energy released by their interaction with the surface. The 2D network is stabilized by 0.359 eV/water in vacuum and the linear 1D chain by 0.320 eV/water. Bearing in mind the 50% increase in H-bond coordination of the 2D network, the 12% increase in H bonding in the gas phase is small and implies the stability of the 2D structure cannot be understood simply on the basis of the increased H-bond coordination. The 2D structure on Cu(511) is stabilized by a further 0.415 eV/water when in contact with the surface, rather greater than the 0.353 eV/water of the 1D chains, despite the fact that every water in the chain structure forms a Cu—O bond, whereas only 40% do so in the 2D network. Ru(0001) binds particularly tightly to water, yet the water-Cu(511) interaction is only 10% weaker than that calculated for the hexagonal chain network on Ru(0001) (0.322 and 0.462 eV/water for water-water and water-surface interactions, respectively, compared to 0.771 eV/water for bulk ice [45]), even though half the water forms Ru—O bonds. It is clear that the strong interaction between Cu(511) and water is due to more than just the number of direct O—Cu(step) bonds formed in the 2D network.

In order to understand why this 2D network is so stable on the stepped surface, we compare its structure to that of short 1D chains. Although the dimer (see Fig. S9 of SM [37]) has a similar geometry to water in the 1D chain [Fig. 4(a)], with both molecules bonded to Cu, longer chains show a distinct change in structure. The terminal water moves away from the Cu step,

breaking the Cu—O bond and rotating H down towards the lower Cu terrace, so that H sits close to the metal on the lower Cu terrace with O above the step; see Fig. 4(b). This arrangement aligns the water dipole in opposition to the Cu step dipole, stabilizing the water dipole and enhancing H bonding, making this water a particularly good proton acceptor with a very short H bond (1.65 Å). The result is that short water chains have a binding energy similar to that of the complete 1D chain, despite breaking a Cu—O bond and having fewer H bonds. The 2D structure formed on Cu(511) has 3/10 water molecules aligned H down immediately next to the step dipole, in a similar geometry to the 1D chain, stabilizing charge separation in the 2D network and enhancing the H bonding. Formation of the 2D network is also accompanied by a reduction in the Cu—O separation at the step from 2.40 Å for the 1D chain to 2.15 Å in the $(31, -31)$ structure, consistent with a strengthened Cu-water interaction.

Based on our picture of water on Cu(511), we can ask how this system compares to other stepped surfaces and what drives formation of the 2D network in preference to 1D water chains. The 3 atom wide (100) terrace on Cu(511) is sufficiently narrow for water to complete the 2D structure by bridging between stable adsorption sites (4/10 water flat above the step and 3/10 H down immediately below the step dipole) with just 3/10 water molecules adsorbed above the terrace itself. Although we can expect similar arrangements of water to be stable at steps on other surfaces, increasing the step separation (either by changing the face exposed or increasing the metal lattice parameter) would require additional water molecules to be present on the terrace to link water at the steps into a 2D network, disfavoring a 2D network over 1D structures. This picture is consistent with a transition occurring between formation of an extended 2D phase on surfaces that have narrow terraces, to formation of clusters along the steps, followed by 2D growth across the terraces, on surfaces where the steps are widely spaced. Vibrational spectroscopy of water on the (511) surfaces of Ag and Au [28,29] (which have a 13% larger spacing than Cu) finds that some uncoordinated H atoms point away from the metal, unlike on Cu(511). The network formed is not known from experiment, but calculations on Au suggest water orients H down on the (100) terrace below the step in a 2D network [30]. On Pt, calculations again suggest water in small clusters will bind flat atop the step and H down beside it [26,35]. Desorption measurements [31,32] find a transition occurs between surfaces with narrow terraces and those with wider step spacing. Whereas Pt surfaces with wide terraces have one desorption component that is weakly bound, similar to that from a flat surface, and another that is stabilized by the step, surfaces with narrow terraces show only a stabilized desorption peak, although no ordered 2D phase was found. The behavior found here on Cu(511) suggests that formation of a single desorption peak can be specifically associated with formation of a 2D network rather than clusters along the steps.

The Cu(511) $(31, -31)$ water structure represents the first system where a well-defined 2D water network has been reported on a stepped surface, offering insight into how water responds to a highly corrugated surface with hydrophilic and hydrophobic stripes. The unusual 2D network, containing pentamer, hexamer, and octomer rings, maximizes the number of water molecules bound in stable sites at the step, while minimizing the number of additional molecules that are needed to complete the 2D hydrogen-bonding network. Formation of this 2D structure relies on the particular step spacing found on Cu, indicating that this parameter will be critical in predicting the behavior on other corrugated surfaces. A linear defect similar to the 2D network formed here was seen bridging hexagonal domains on Ru(0001) [40], suggesting this unusual motif may recur in other systems to relieve lateral strain.

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