

Unveiling the Mechanism of Water Partial Dissociation on Ru(0001)

Sabine Maier,^{1,2} Ingeborg Stass,^{1,3} Jorge I. Cerdá,⁴ and Miquel Salmeron^{1,5,*}

¹*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

²*Department of Physics, University of Erlangen-Nürnberg, Erwin-Rommel-Strasse 1, 91058 Erlangen, Germany*

³*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*

⁴*Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Cantoblanco, 28049 Madrid, Spain*

⁵*Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA*

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We have studied the mechanism of the partial dissociation of water on Ru(0001) by high resolution scanning tunneling microscopy (STM). The thermal evolution of water at submonolayer coverage has been tracked in the 110–145 K temperature range to identify the precursor structures for the partial dissociation. These were found to consist of hexagons arranged in thin stripes aligned along the close packed Ru $[2\bar{1}\bar{1}0]$ directions. The partially dissociated phase, on the other hand, contains a mixture of H₂O and OH hexagons arranged into wider stripes and rotated by 30° with respect to the intact water stripes. The atomic structure of both types of stripes is determined with the aid of density functional theory and STM simulations, providing insights into the partial dissociation reaction path. The reaction is found to be exothermic by around 0.4 eV and initiating at the edges of the intact water stripes. Hydrogen atoms, from water dissociation or already present at the surface, are found to play an important role in the kinetics of the reactions.

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Water and its dissociation products play an important role in electrochemistry, corrosion, environmental chemistry, or heterogeneous catalysis either in the form of reactants, products, or intermediates. Numerous experimental and theoretical studies have been performed with the aim to understand the adsorption structures of water on hexagonal metal surfaces [1–5]. Ru(0001) has acted as a model substrate, as it allows for the growth of mixed H₂O-OH phases due to thermal and electron stimulated dissociation [6–10]. The understanding of the water dissociation mechanism is a crucial step in the development of efficient catalysts for splitting of water for hydrogen production, a major goal of renewable energy research. In spite of the fact that the structures of both intact [11–15] and partially dissociated water [6–10,16,17] on ruthenium are now reasonably well understood, the mechanism for the dissociation of water on ruthenium (i.e., the reaction path) remains unknown.

At low temperature water adsorbs forming metastable phases of intact molecules consisting of narrow stripes or small clusters [11,14,15]. These structures were rationalized by proposing two-dimensional (2D) rules for H₂O adsorption on metals [11,14]. According to these water forms a network of H bonds (HBs) connecting hexamer rings of nearly flat molecules where each donates two hydrogen bonds and accepts one, while bonding to the metal substrate through the O-lone pair. Since an extensive network of flat-lying water molecules is not possible topologically, molecules at the edges change from planar to tilted orientations with the non-H bonded hydrogen atoms out of the surface plane. Partially dissociated water structures on Ru(0001) consist of water-hydroxyl mixtures

forming elongated stripes, 2.5 to 6 ruthenium lattice distances wide, with a honeycomb internal structure in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ epitaxial relationship with the Ru lattice [9]. Previous theoretical works on water dissociation have been based on extended HB network models [18–20] which are clearly different from the cluster structures experimentally found.

In this Letter we present a combined STM and density functional theory (DFT) study that offers new insights into the dissociation process of water on Ru(0001). First, we report on the structural changes of the water clusters occurring during the transition from intact to partially dissociated water. Next, we discuss the precursor and mixed water-hydroxyl phases with special attention to the role played by hydrogen atoms. We finish with a discussion on the energetics involved in the process and propose a reaction path for the dissociation process.

The experiments were performed using a homebuilt low temperature STM operated in an ultrahigh vacuum chamber at 6 K [21]. While dosing water, the sample was kept at temperatures between 50 and 145 K followed by annealing. All theoretical calculations [22] have been performed with the GREEN code [23]. Those involving total energy optimizations were carried out using the DFT based SIESTA package [24] via a suitable interface implemented in the GREEN code. STM image simulations were performed following the procedure described in Ref. [25].

Figure 1 shows a series of STM images of intact and partially dissociated water structures formed after different annealing temperatures and times. Figure 1(a), obtained after annealing at 110 K for 7 min, shows islands with irregular shapes a few nm in size separated by dark contrast

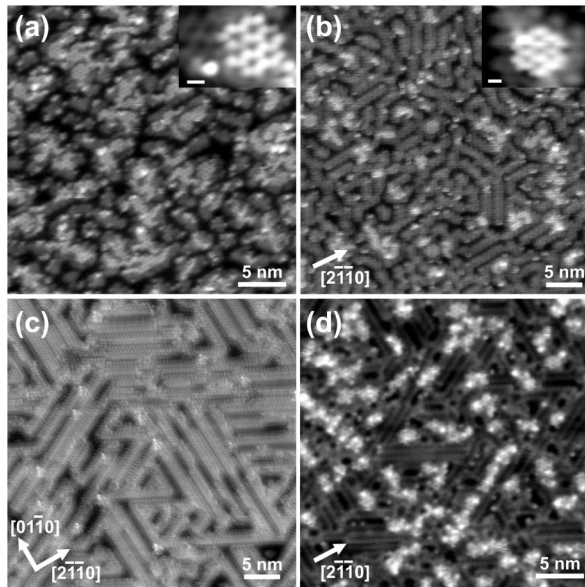


FIG. 1. Thermal evolution of water structures on Ru(0001): (a) Islands of intact water formed after annealing for 7 min at 110 K. The islands contain high-lying (bright) and low-lying molecules (gray) surrounded by the bare metal substrate (dark). The inset shows the high-lying rotated hexagonal structures (scale bar 5 Å). (b) Stripelike clusters of intact water after deposition at 145 K. The hexagonal clusters of high-lying molecules are resolved, as shown in the inset (scale bar 5 Å). (c) Transformation of (b) to mixed H₂O-OH structures after an additional annealing at 145 K for 30 min. (d) Mixture of intact and partially dissociated water structures formed after annealing for 50 min at 138 K. STM parameters: (a) 27 pA, -108 mV, (b) 37 pA, -93 mV, (c) 25 pA, -144 mV, and (d) 22 pA, -51 mV.

areas that correspond to the uncovered substrate. In each island we can observe low- and high-lying regions of intact water with apparent heights differing by 30–50 pm. The latter are the bright regions in the images near the center of the islands. The molecules in this region are slightly lifted from the metal owing to their weaker interaction with the surface and form hexagons rotated by 30° which are connected by pentagons and heptagons to the surrounding ones in contact with the Ru [15].

As shown in Fig. 1(b), increasing the deposition temperature to 145 K induces significant rearrangements of the water molecules into long stripes, 2 hexagons wide, along the $[2\bar{1}\bar{1}0]$ -type directions, as determined from atomically resolved images of the Ru substrate. In addition, the density of high-lying structures (bright areas) decreased substantially. Further annealing at 145 K for 30 min produces new one-dimensional structures shown in Fig. 1(c). They are up to 30 nm in length and oriented along the $[01\bar{1}0]$ -type directions, i.e., rotated by 30° relative to those in (b), indicating that the water molecules have diffused and rearranged on the surface. The structures have the same internal features as those reported in previous work [9] for mixed H₂O-OH stripes, indicating

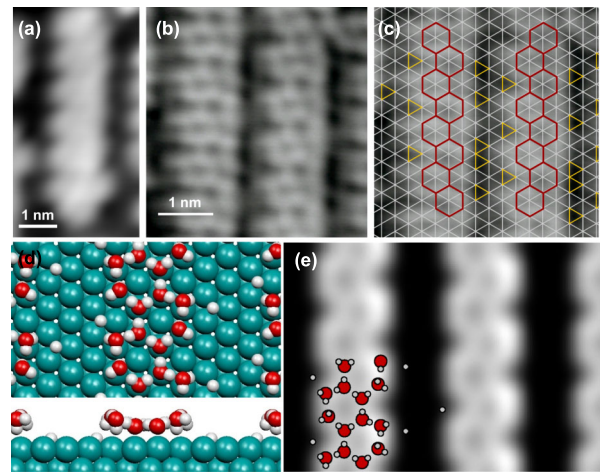


FIG. 2 (color online). (a),(b) High resolution STM images of one-dimensional intact water structures imaged with (a) a metal tip and (b) a functionalized tip. In (c) a Ru lattice is superimposed to outline the asymmetry in the position of the hollow sites relative to the stripe (red hexagons), where on one side the hexagon edge is close to an hcp site (right), and on the other it is closer to an fcc site (left). At the fcc sites marked by yellow triangles, H is adsorbed. (d) DFT optimized structures and (e) STM simulated image corresponding to this asymmetric phase. STM parameters: (a) 0.9 nA, 7 mV, (b) 14 pA, -64 mV.

that the partial dissociation process has been completed. The image in Fig. 1(d), obtained after annealing to 138 K for 50 min, shows again mixed H₂O-OH stripes but this time the reaction is incomplete and small bright structures corresponding to high lying intact water molecules remain on the surface. This is a new and important observation that indicates that the partial dissociation starts at the low lying domains of intact water.

We now examine the structure of the intact water stripes along the compact $[2\bar{1}\bar{1}0]$ -type directions, which we identify as the precursor phase for the partial dissociation of water. Figures 2(a) and 2(b) present high resolution STM images of such stripes showing a zigzag arrangement of hexagons exposing armchair edges, as sketched in Fig. 2(c), where the Ru-lattice and the water hexagons have been superimposed on the image. The appearance of the stripe edges is markedly asymmetric, smoother on the right side and rougher on the left. This asymmetry was found to alternate among neighboring terraces (left side rougher on one terrace, right side on the other and vice versa), as expected from the hcp stacking of Ru(0001) (see Fig. S3 [26]). Close inspection of the troughs between stripes reveals dark spots which we ascribe to preadsorbed residual H [21]. As indicated by the triangles in Fig. 2(c), and discussed in detail in Ref. [26], the hydrogen atoms are all located at fcc sites, which are more stable than the hcp sites by 30 meV [21,27]. These H atoms are at the origin of the stripe asymmetry as they are arranged differently along each edge.

Figure 2(d) shows the DFT optimized structure obtained for this intact water precursor phase. Water molecules arrange into zigzag hexagons satisfying the 2D-water rules inside the stripes while at the edges they tilt and pair establishing H bonds among them in a configuration reminiscent of that found for the lace and rosette structures on Pd(111). [11] The edge molecules lie 0.7–0.9 Å higher than the inner ones and are thus less tightly bound to the metal. They present a H atom pointing towards a threefold hollow site (i.e., pseudo-H-down configuration). The STM simulation for this model, shown in Fig. 2(e), is in reasonable agreement with the experimental one. The inclusion of H atoms at fcc sites close to the stripe edges, as Fig. 2(c) shows, leads to an asymmetry in the simulated image in accordance with the experiment.

We next focus on the 30° rotated stripes of mixed H₂O-OH. Figure 3(a) shows an image of a partially dissociated water layer consisting of stripes with widths ranging from 2.5 to 4 Ru lattice constants, a , with the narrower ones, $2.5a$ wide, containing no hydroxyl groups. Figure 3(b) shows in more detail the structure of a $4a$ -wide stripe separated by two lattice constants from adjacent stripes. DFT indicates that the configuration in Fig. 3(c), with the OH deeper inside the stripe, is more stable than alternative structures with OH located closer to the edges [9]. In this model, the edges consist of single water molecules accepting just one H bond and having two

unsaturated hydrogen atoms. As a result, the molecule buckles with the hydrogen coming closer to the surface and the oxygen lifted by 0.8 Å with respect to the inner ones, which lie 2.1–2.3 Å above the surface. The OH presents a marked asymmetry in the HB lengths, with values of 1.5 and 1.9–2.0 Å when the OH accepts and donates a HB, respectively (the HB length among intact water molecules is typically 1.7–1.8 Å).

The space between stripes appears densely occupied by depressions about 10 pm deep in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement which we assign to H atoms [28,29]. The presence of hydrogen is a direct evidence that partial dissociation has occurred and allows us to estimate the H₂O:OH ratio on the surface after dissociation. From Fig. 3(b) six oxygen atoms (corresponding to H₂O and/or OH maxima) and two hydrogen atoms next to the stripe (dark spots) per unit cell can be resolved, leading to a ratio of $4:2 = 2$ if all the hydrogen is assumed to come from dissociated molecules. Taking into account that some preadsorbed hydrogen is already present on the surface due to background adsorption (about 1% of all fcc sites), this value represents a lower limit. When compared against the partially dissociated stripe model in Fig. 3(c), with a larger 5:1 ratio, we may conclude that the partial dissociation in Fig. 3(a) is not complete. This can also be inferred from the presence of bright spots in the images, associated with intact water structures. Stripes with larger widths, $5a - 6a$, require more OH groups per unit cell and this hinders their growth, probably as a result of the denser H coverage in the troughs separating the stripes, which leaves no space to accommodate further hydrogen. Figure 3(b) also shows two clear depressions located at the center of the inner hexagons (on top of a Ru atom), which for size reasons can only be hydrogen. Such unusual on-top hydrogen adsorption geometry was considered theoretically initially by Feibelman in extended H-bonding networks after partial dissociation of a water bilayer [18–20]. The structure was found to be metastable by about 0.4 eV relative to H on an empty fcc site [19]. Our DFT optimized model for the $4a$ wide stripes [Fig. 3(c)] supports also the possibility of hydrogen adsorption at a top site. The STM simulated image in Fig. 3(d) is in good agreement with the experimental one in Fig. 3(b) and shows a depression at the location of the hydrogen atoms at top sites thus confirming that the partially dissociated hexagons may act as a cage for the hydrogen which is trapped at the center on a top site.

So far we have identified the precursor phase for the partial dissociation of water and addressed the role played by hydrogen in the kinetics of the reaction. Still, relevant questions related to the reaction path lack an answer: which molecules dissociate first? Or why do the stripes' directions rotate by 30° upon dissociation? Based on previous theoretical studies where the H-down molecules were found to have a smaller barrier for dissociation than the

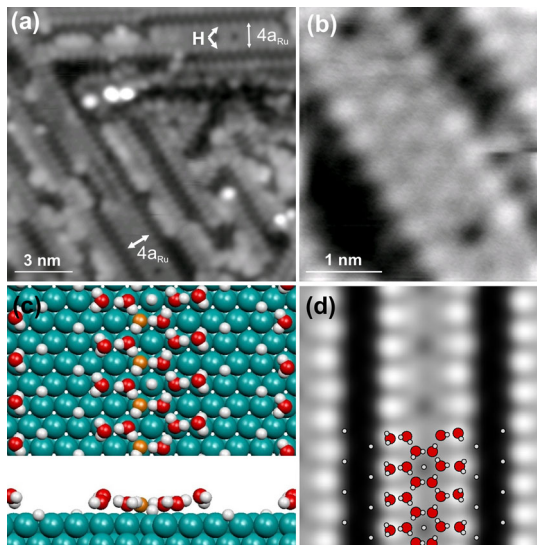


FIG. 3 (color online). (a),(b) STM images of mixed H₂O-OH clusters formed by the partial dissociation of water. (Heated to 132 K, 103 pA, -6.1 mV.) (b) The center of the hexagonal unit cells in the partially dissociated water stripes shows different contrast. We suggest that the deep depressions correspond to hydrogen atoms adsorbed in the center of the unit cell. (c) DFT optimized geometry for the $4a$ mixed H₂O-OH stripes. H atoms are placed in the troughs at fcc sites while one additional H has been placed at a top site in the center of the inner hexagon every two unit cells. (d) The associated STM simulated image.

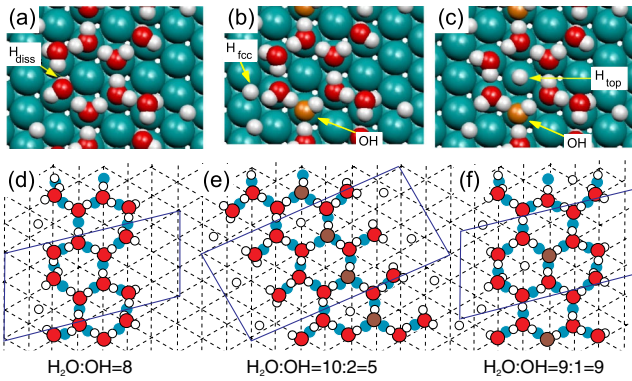


FIG. 4 (color online). (a) Top view of the precursor intact water stripe with the arrow pointing to the H atom which is assumed to dissociate, (b),(c) relaxed structures after placing H_{diss} at an fcc site (H_{fcc}) and at a top site at the center of the hexagon (H_{top}), respectively. Top views of (d). Intact water stripes, (e) $4a$ wide mixed H_2O -OH stripes, (f) an alternative partially dissociated stripe which has not rotated with respect to (d). Dashed lines refer to the Ru lattice.

flat lying ones [19], we propose that the pseudo-H-down molecules at the edges of the precursor stripes are the first to dissociate.

An estimate of the energy gained upon their partial dissociation can be obtained by removing a H atom from the precursor phase, H_{diss} in Fig. 4(a), and placing it at a nearby fcc site in the trough, H_{fcc} in Fig. 4(b), or at the center of the hexagon, H_{top} in Fig. 4(c). In both cases we find a substantial energy gain of 0.42 and 0.35 eV, respectively, relative to the intact water stripe [30]. In Fig. 4(b) this difference becomes even larger (by 0.16 eV) if the liberated H_{fcc} atom is allowed to migrate to a nearby fcc site farther from the stripe. As expected [9], in the relaxed geometries of Figs. (b) and (c) the hydroxyl group ends up located inside the stripe after transferring a proton to the edge, which now consists of two H-bonded H_2O molecules each with one dangling H. If the dissociation continues at the other edge following a similar mechanism, an $\text{H}_2\text{O}:\text{OH}$ ratio of $6:2 = 3$ would be obtained for this transient phase, which is consistent with the lower limit of 2 discussed above; i.e., it suffices to dissociate just one molecule at each of the armchair edges for the partial dissociation reaction.

In order to explain the 30° stripe rotation, we sketch in Figs. 4(d) and 4(e) the intact and partially dissociated water stripes, respectively. Because of the unsaturated hydrogen atoms at the edges in Fig. 4(e), the density of HBs is smaller than in Fig. 4(d), with average values of 1.17 and 1.25 HBs per oxygen atom, respectively. Furthermore, one may consider the alternative partially dissociated model shown in Fig. 4(f), which is not rotated and presents an even larger HB density of 1.3. On the other hand, the $\text{H}_2\text{O}:\text{OH}$ ratio for this latter model is as large as 9:1, almost twice as that in Fig. 4(b). Therefore, one may conclude that the driving force for the stripe rotation upon partial dissociation is to

minimize the $\text{H}_2\text{O}:\text{OH}$ ratio rather than maximizing the number of HBs. This picture is corroborated by simple energy arguments, as the estimated energy gain upon the formation of a HB on Ru, 0.13 eV [22], is substantially smaller than the 0.3–0.4 eV gain upon dissociation.

In summary, we have characterized the structural evolution of water adsorbed on Ru(0001) in the temperature range between 110 and 145 K using low temperature STM. Below 130 K water is intact and tends to form stripes of hexagons connected in a zigzag geometry with the armchair edges along the compact $[2\bar{1}10]$ -type directions. These structures are the precursors for the partial dissociation, the extent of which increases either by increasing the temperature or annealing time. The dissociation occurs in the tilted pseudo H-down molecules at the edge of the stripes. After a substantial molecular rearrangement, mixed water-hydroxyl stripes, preferentially 4 Ru lattice constants wide, are formed which are rotated by 30° with respect to the intact water stripes in order to maximize the number of dissociated molecules. The hydrogen liberated by the dissociation adsorbs mostly in the Ru fcc sites located between the H_2O -OH stripes although occasionally H atoms can be trapped at the center of water hexagons, as proposed in previous theoretical models of the partial dissociation of a complete water bilayer [18–20]. Our work highlights the necessity of an accurate structural characterization, at the molecular level, in order to track the reaction path in the partial dissociation of water on Ru(0001).

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* mbsalmeron@lbl.gov

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