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Experimental Evidence for a Partially Dissociated Water Bilayer on Ru{0001}

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Core-level photoelectron spectra, in excellent agreement with *ab initio* calculations, confirm that the stable wetting layer of water on Ru{0001} contains O-H and H₂O in roughly 3:5 proportion, for OH_x coverages between 0.25 and 0.7 ML, and $T < 170$ K. Proton disorder explains why the wetting structure looks to low energy electron diffraction (LEED) to be an ordered $p(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer, even though $\approx \frac{3}{8}$ of its molecules are dissociated. Complete dissociation to atomic oxygen starts near 190 K. Low photon flux in the synchrotron experiments ensured that the diagnosis of the nature of the wetting structure quantified by LEED is free of beam-induced damage.

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Because its structure is known quantitatively, the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ water (D₂O) adlayer on ruthenium is a key system for the study of wetting at the molecular level. Conventional wisdom has it that the close match in lattice parameters between Ru{0001} and the basal plane of ice I_h means the wetting superstructure is a chemisorbed, icelike bilayer of intact water molecules, with “dangling” O-H bonds pointing away from the surface on every second molecule. This “intact water bilayer” model [IWB (H-up) model, Fig. 1(a)] has often been used to explain the adsorption of water on late transition metals [1–4] pictorially, but Feibelman has recently concluded that this structure is thermodynamically unstable. Specifically, he found it to be less stable than three-dimensional ice clusters, and proposed instead that the wetting layer on Ru{0001} is a 1:1 mixture of water and hydroxyl molecules [“partially dissociated bilayer” (PDB) model, Fig. 1(b)], which is better bound by 0.2 eV/molecule [5]. In a follow-up study Michaelides *et al.* computed an activation barrier of 0.5 eV for partial dissociation of water molecules incorporated in a hydrogen bonded network, significantly lower than their result for monomers [6], but large enough to engender skepticism that a PDB would form below 170 K. In its favor, the PDB model is consistent with the O and Ru atom positions determined in a low energy electron diffraction (LEED)-IV structure analysis by Held and Menzel [7] for D₂O on Ru{0001}. The IWB model is not, whether conventionally H-up or, as has been discussed and rejected in Refs. [5,6], constructed with H-down, i.e., with the dangling hydrogen bonds pointing towards the substrate. A determination of the hydrogen positions

could help resolve the issue. Unfortunately, electron scattering by H (or D) atoms is too weak to determine their positions unambiguously by LEED [8]. The “IWB (H-down)” model, has recently been invoked by Denzler *et al.* [9] to explain their vibrational spectroscopy data acquired by sum frequency generation for D₂O on Ru{0001} (and earlier by Ogasawara *et al.* for water on Pt{111} [10]). Reference [9] does not explain, however, how an H-down structure can be consistent with the Held-Menzel result that the wetting layer O atoms lie nearly coplanar, nor why no stretch vibration is seen in the wetting layer associated with the D-down dangling bond. Attempts to discriminate between intact and partially dissociated water layers, based on vibrational spectroscopy, generally face the problem that the signal from the relevant O-H bonds is very weak because they are essentially parallel to the surface [3,9,11,12]. Also, O-H stretch frequencies in hydrogen bonded networks are almost wholly determined by the O-O distance and not by

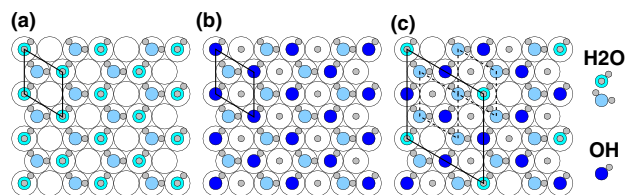


FIG. 1 (color online). Geometry models for the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ water bilayer: (a) intact water [IWB (H-up)], (b) partially dissociated (PDB), and (c) modified PDB consisting of $(\text{OH})_3(\text{H}_2\text{O})_5$ units in an arbitrary $p(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ arrangement.

the chemical nature of the molecule [13]. High resolution x-ray photoelectron spectroscopy (HRXPS) can provide the quantitative chemical information needed without these problems. Owing to the lack of resolution and possible x-ray-induced damage in an early XPS study of chemisorbed water on Ru{0001} by Pirug *et al.* [14], a clear distinction between the two proposed models is not possible on the basis of these data. Recent synchrotron-based HRXPS studies of water on Pt{111} [10] and on Cu{110} [15] have demonstrated, however, that this method is now capable of quantifying the degree of water dissociation with high accuracy.

The HRXPS experiments were carried out at beamline I311 of MAX-II in Lund (Sweden) using a Scienta 200 mm hemispherical analyzer at a detection angle close to the surface normal. For the O 1s (Ru 3d) spectra photon energies of 625 (400) eV were used with an overall energy resolution of $\Delta E = 0.23$ (0.12) eV. The photon current, $(5-10) \times 10^{10}$ ph s⁻¹, measured with a calibrated GaAsP photodiode, illuminated a 0.3×1.0 mm² spot on the surface. Unaware of any published total electron yield (TEY) data for Ru, we conservatively estimate the total electron flux through the adlayer to be $<5 \times 10^{12} e s^{-1} cm^{-2}$, based on the highest reported TEY, 0.15e/ph, for Au{111} [16]. Since this is about 100 times less than the electron flux in the LEED experiments of Ref. [7], we can conclude that our XPS diagnosis of the nature of the wetting structure quantified by LEED is free of beam-induced artifacts. Indeed, for chemisorbed water, no significant changes in the XP spectra were detected for irradiation up to 1 h. The total electron dose in our fastest spectra (28 s) was equivalent to less than 0.7 ph or 0.1e per water molecule. Beam-induced changes on a time scale much shorter than 28 s would imply that a single electron affects many water molecules, triggering the transition from a highly unstable state to the thermally preferred configuration. To draw conclusions concerning this scenario is outside the scope of the present experiments. We do note, however, that changes in the water multilayers were observable after a few minutes' irradiation, implying that they are less stable than the chemisorbed wetting layer [17].

The W/Re thermocouple attached to the sample was calibrated relative to the lowest temperature for which no water multilayers are formed under UHV conditions (145 K) [2]. After using standard cleaning procedures, no surface impurities were detectable by XPS (detection limit ≈ 0.01 ML). Purified water (H₂O or D₂O) was adsorbed by backfilling the chamber up to pressures of 10^{-8} mbar (base pressure: 5×10^{-11} mbar). All spectra were normalized with respect to the background intensity. The normalized O 1s signal intensity was used to determine the O atom coverage with the $p(2 \times 1)$ -O layer as reference (0.5 ML). We estimate the error margin for the coverages determined in this way around 10%.

Figure 2(a) shows a series of O 1s spectra recorded during H₂O adsorption at 145 K. Each curve represents an

average over five fast spectra with a total data acquisition time of 140 s. At 145 K no multilayers are formed. Therefore the adsorbate layer saturates at a coverage of oxygen atoms, Θ_O , around 0.61 ML, in good agreement with the value of 0.66 ML expected for a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer containing two OH_x species per unit cell. A faint $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern with satellite spots around the integral order spots was observed after saturating the surface at this temperature. In all spectra of Fig. 2(a) two peaks can clearly be resolved at binding energies (BE) 531.0–530.8 eV (FWHM 1.1 eV) and BE 532.7–532.3 eV (FWHM 2.0 eV). Both shift downward in BE with increasing coverage. Based on comparison with earlier XPS studies [4,10,15], we assign these peaks to hydroxyl and intact water molecules, respectively. Density-functional theory (DFT) calculations [19] predict an O 1s BE difference of 1.6 eV between the two inequivalent O atoms in the PDB model, in almost perfect agreement with the experimental value near saturation coverage. In contrast, the IWB (H-up) and (H-down) models lead to BE differences of only 0.37 and 0.26 eV, respectively. Figure 2(b) shows the hydroxyl and water coverages derived from the experimental data

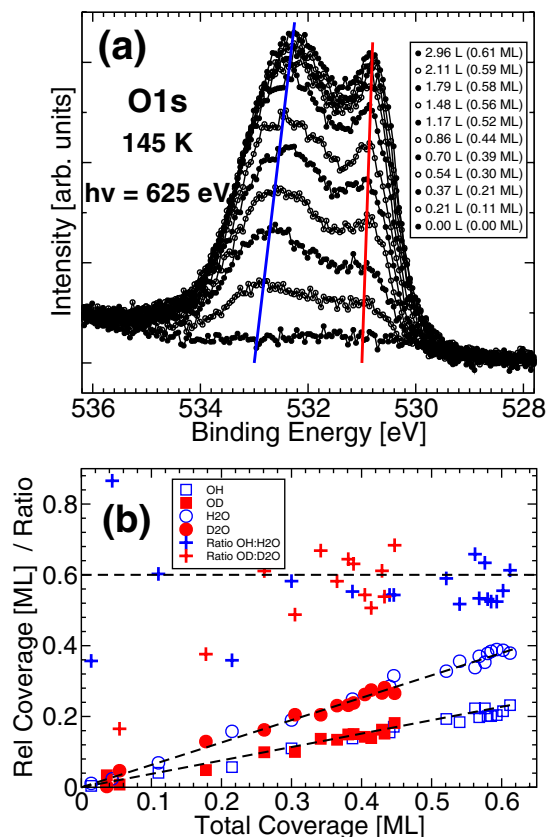


FIG. 2 (color online). (a) Series of O 1s spectra, recorded during H₂O adsorption at 145 K (1.6×10^{-9} mbar), total data collection time 140 s per spectrum, the exposure values (1 L = 10^{-6} Torr s) refer to the end of data acquisition; (b) development of O-H (OD) and H₂O (D₂O) peak intensities during adsorption at 145 K (squares and circles) and their ratios (crosses).

in Fig. 2(a) vs Θ_{O} . Also included are data from an uptake experiment with D_2O under the same conditions, which show identical behavior. In both cases the hydroxyl-to-water ratio, as indicated in the diagram, is constant at 0.60 ± 0.08 above $\Theta_{\text{O}} = 0.25$ ML, consistent with a stoichiometry of $(\text{OH})_{3 \pm 0.25}(\text{H}_2\text{O})_{5 \mp 0.25}$. From the PDB model one would expect a ratio of 1:1. Thus a modified structure is needed to account for the observed intensity ratio. As shown in Fig. 1(c), however, the required modification is minimal. Replacing one of every four O-H by an intact water molecule, i.e., moving just one of 16 hydrogen atoms, provides a wetting structure compatible with the data and also explains the upright O-H stretch mode found in Ref. [12] for this layer. Since considerable proton disorder will be superimposed on such a structure, the modified PDB remains compatible with the observation of a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. Spectra very similar to those in Fig. 2(a) were recorded for H_2O and D_2O after dosing at 105 K. This suggests an activation barrier for dissociation significantly lower than the theoretically estimated value of 0.5 eV [6].

Further information about the adsorption geometry is gained from the surface core-level shifts (SCLS) in the Ru $3d_{5/2}$ signal. Figure 3 shows spectra of the clean surface and the surface saturated with water at 145 K ($\Theta_{\text{O}} = 0.61$ ML). The clean surface shows a characteristic SCLS of -0.38 eV ($S1$, BE 279.66 eV) with respect to the bulk signal (B , BE 280.04 eV) owing to the low coordination of the first layer Ru atoms. According to Lizzit *et al.* [28] the signal from the second layer ($S2$) is shifted by $+0.12$ eV with respect to B , which is in good agreement with our calculations but not resolved in the experimental data. Upon water adsorption the surface signal shifts towards higher BE and broadens significantly. Our DFT calculations for the PDB [19] predict SCLS's relative to B of -0.24 ($W1$), -0.12 ($W2$), -0.02 eV ($W3$, overlapping with B) for the first layer Ru atoms underneath H, H_2O , and O-H, respectively. The position of $S2$ remains essentially unchanged. A fit to the spectrum shows very good agreement within ± 0.05 eV

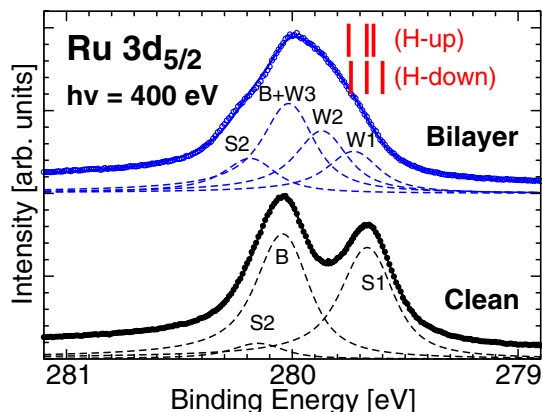


FIG. 3 (color online). Ru $3d_{5/2}$ spectrum of a saturated H_2O bilayer on Ru{0001} (top) and the clean surface (bottom).

of the predicted BE values (see Fig. 3). The intensity differences between the different peaks are within the range normally caused by diffraction. The predicted SCLS's for the two IWB models, between -0.29 and -0.44 eV (labeled “H-up” and “H-down” in Fig. 3), are incompatible with the experimental data. For Ru{0001} it has been shown that SCLS's probe essentially only the emitter atom's involvement in a chemical bond [28]. Thus, the nearly complete absence of the $S1$ peak indicates that most surface Ru atoms are in direct contact with an adsorbate, just as postulated by the PDB model.

Figure 4 shows O $1s$ spectra recorded during the step-wise desorption of a H_2O bilayer prepared at 145 K. Before recording a spectrum, the sample was annealed with a heating rate of 3 K/s, then cooled to 100 K after the specified temperature was reached. Distinct changes were observed only above 178 K: in a first step (190–203 K) the water and the hydroxyl peak were reduced in intensity by about the same factor and a shoulder appeared at BE 530.0 eV; in the second step, the H_2O and O-H peaks disappeared completely, leaving behind a narrow peak at 530.0 eV, which we assigned to atomic O by comparison with the spectra from a chemisorbed oxygen layer. The remaining small peak at 532 eV is due to residual CO adsorption of less than 0.08 ML, which does not interact with the water bilayer; it can be removed by annealing to 500 K. The annealing temperatures prior to recording the spectra cannot be related directly to the temperature scale of temperature programmed desorption data because the heating rate was not constant throughout in our experiments. Nevertheless, it appears justified to correlate the changes in the XP spectra with the two desorption peaks A_2 (around 170 K) and A_1 (around 210 K) reported for water layers prepared under similar conditions [1,2]. After the first desorption peak, A_2 , the adsorbate layer has still a similar stoichiometry as the saturated bilayer $[(\text{OH})_3(\text{H}_2\text{O})_5]$, with an additional small amount of atomic oxygen, owing to complete dissociation of water (up to 0.07 ML or 18% of the total O $1s$ intensity in the 203 K spectrum). After the second desorption peak, A_1 , no more water or hydroxyl is found. From further complete dissociation, however, 0.16 ML of O is left behind on the surface. The following mechanism plausibly explains these results: After the first desorption step, islands form, consisting of $(\text{OH})_3(\text{H}_2\text{O})_5$ units like those which make up the PDB. Single hydrogen atoms can now move into the space between these islands and find more favorable adsorption sites [5]. Once the hydrogen atoms have disappeared from the vicinity of the O-H- H_2O units complete dissociation is possible, which takes place concurrently with the second desorption peak. We always found an O coverage of ≈ 0.16 ML remaining after complete desorption of the saturated bilayer, which is higher than the values around 0.10 ML reported earlier [2,14]. This could reflect differences in the annealing process or might indicate that the step density plays an important role in this final dissociation step.

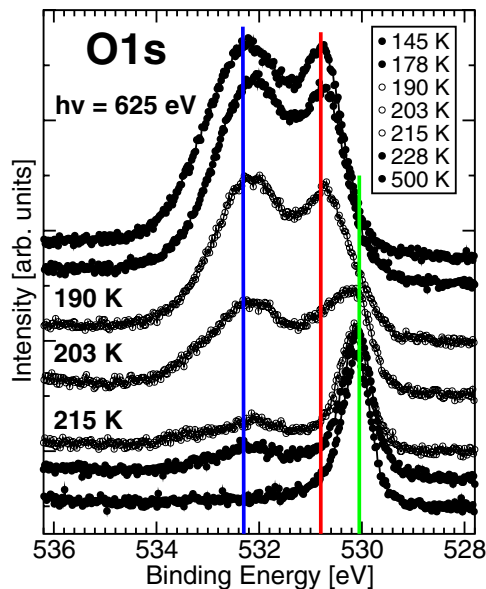


FIG. 4 (color online). O 1s spectra taken after annealing of the bilayer to the specified temperatures with a heating rate of 3 K/s and cooling down immediately afterwards.

In summary, we have confirmed via HRXPS and DFT that a partially dissociated water bilayer forms on Ru{0001}. Both the formation and desorption of this structure are mediated by supramolecular units consisting of intact water and hydroxyl molecules in a ratio near 5:3. They form at temperatures as low as 105 K, indicating a low activation barrier for partial dissociation of water, and exist independent of long-range order. After a first desorption step the $\text{H}_2\text{O} + \text{OH}$ units form islands, allowing the hydrogen atoms to find more favorable adsorption sites outside the PDB structure.

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