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

Jonas Weissenrieder
MAX-lab, Lund University, S-22100 Lund, Sweden

Anders Mikkelsen and Jesper N. Andersen
Synchrotron Radiation Research, Institute of Physics, Lund University, S-22100 Lund, Sweden

Peter J. Feibelman
Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, USA

Georg Held∗
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
(Received 5 May 2004; published 3 November 2004)

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 OHx 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(√3 × √3)R30° adlayer, even though ≈ 2/3 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.

Because its structure is known quantitatively, the p(√3 × √3)R30° 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 Ih 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(√3 × √3)R30° water bilayer: (a) intact water [IWB (H-up)], (b) partially dissociated (PDB), and (c) modified PDB consisting of (OH)x(H2O)y units in an arbitrary p(2√3 × 2√3)R30° 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 $0.5 \times 1.0$ mm$^2$ 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 (H$_2$O or D$_2$O) was adsorbed by backfilling the chamber up to pressures of $10^{-8}$ mbar (base pressure: $5 \times 10^{-11}$ 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 H$_2$O 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, $\Theta_{\Delta \Theta}$, 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.
in Fig. 2(a) vs $\Theta_0$. Also included are data from an uptake experiment with D$_2$O under the same conditions, which show identical behavior. In both cases the hydroxyl-to-water ratio, as indicated in the diagram, is constant at $0.60 \pm 0.08$ above $\Theta_0 = 0.25$ ML, consistent with a stoichiometry of $(\text{OH})_{3.25.25}(\text{H}_2\text{O})_{0.25}$. 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 modified PDB remains compatible with the observation of disorder will be superimposed on such a structure, the found in Ref. [12] for this layer. Since considerable proton atoms, provides a wetting structure compatible with the minimal. Replacing one of every four O-H by an intact shown in Fig. 1(c), however, the required modification is bilayer on Ru{0001} (top) and the clean surface (bottom).
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 H$_2$O + OH units form islands, allowing the hydrogen atoms to find more favorable adsorption sites outside the PDB structure.

We thank the Swedish Research Council and EPSRC (U.K.) for financial support. The support by the MAX-lab staff is also gratefully acknowledged. P.J.F.’s work was supported in part by the DOE Office of Basic Energy Sciences, Division of Material Sciences and Engineering. Sandia is a multiprogram laboratory operated by the Lockheed-Martin Company for the U.S. DOE under Contract No. DE-AC04-94AL85000.

![Figure 4](image-url)

**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 conclusion, 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 H$_2$O + OH units form islands, allowing the hydrogen atoms to find more favorable adsorption sites outside the PDB structure.

We thank the Swedish Research Council and EPSRC (U.K.) for financial support. The support by the MAX-lab staff is also gratefully acknowledged. P.J.F.’s work was supported in part by the DOE Office of Basic Energy Sciences, Division of Material Sciences and Engineering. Sandia is a multiprogram laboratory operated by the Lockheed-Martin Company for the U.S. DOE under Contract No. DE-AC04-94AL85000.

---

*Electronic address: gh10009@cam.ac.uk*

[17] An independent XPS study, by Andersson et al. [18], recently came to our attention. Its conclusion, that the water layer on Ru{0001} is essentially undissociated at 150 K, disagrees with ours. However, there is no disagreement that the thermodynamically favored wetting layer is dissociated.
[19] Core-level BE differences were calculated by using the fully screened core-hole approximation, in which the total energy of the system plus core hole is computed by setting the core potential of the ionized atom to that of the same atom with the appropriate core electron missing. The Perdew-Wang 1991 generalized gradient approximation [20,21] was used in the projector augmented wave implementation of VASP [22–26]. A 700 eV plane-wave basis cutoff ensured high accuracy. Methfessel-Paxton Fermi-level smearing [27], with width 0.2 eV, was employed to accelerate electronic relaxation. The Ru substrate was represented by a seven-layer Ru{0001} slab with a $p(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ surface supercell. The upper three layers were allowed to relax and the lower four were held in DFT-optimal positions ($a = 2.72 \AA$, $c = 8.60 \AA$). The relatively large surface supercell kept atoms containing core holes isolated from their periodic images. The surface Brillouin zone was sampled with a $6 \times 6$ grid of equally spaced $k$ vectors. Convergence tests suggest that the computed BE shifts are numerically accurate to 0.03 eV.