Water Dissociation on Ru(001): An Activated Process

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It is shown using x-ray photoelectron spectroscopy that water is adsorbed either nondissociatively or partially dissociatively on Ru(001) under ultrahigh vacuum conditions. We found an activated dissociation process with a barrier slightly larger than that of desorption. A difference in dissociation barriers is found between H_2O and D_2O that explains the anomalous isotope effects in the thermal desorption. Previous theoretical and experimental disagreements can be rationalized based on electron or x-ray beam-induced dissociation of the water overlayer and an earlier underestimation of the dissociation barrier.

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The compilation of studies of water on metal surfaces [1,2] shows that Ru(001) is on the border between active and inactive metal surfaces with respect to dissociation of water. No dissociation is observed on the surfaces of neighboring elements to the right in the periodic table, e.g., Ni(111), Cu(111), Rh(111), and Pt(111), whereas water dissociates on surfaces of Fe, the element located directly above Ru in the periodic table. There are only very small differences in the adsorption energy for the water monolayer between these substrates. What then determines the dissociative or nondissociative adsorption of water?

Feibelman recently reported a novel structure for water on Ru(001) [3]. He found a partially dissociated layer to be energetically more favorable than the archetypical model of a molecularly intact hexagonal icelike bilayer [1,2]. The partially dissociated phase was proposed as the only plausible model to explain wetting on Ru(001). The work used total energy based geometry optimizations in the framework of density functional theory and the partially dissociated structure agreed very well with structural parameters extracted from a low energy electron diffraction (LEED) study of water on Ru(001) [4]. A feature assignable to adsorbed hydroxyl groups in an x-ray photoelectron spectroscopy (XPS) study [5] was taken as evidence for partial dissociation of water. However, no evidence for dissociated water was found in a recent vibrational spectroscopy study [6], and there remain difficulties whether partial dissociation is compatible with other experimental findings as well [7]. Adding to the results for wetting structures on metal surfaces, an only slightly corrugated nondissociated overlayer where all water molecules in the first layer bind directly to the surface through alternating metal-oxygen (M-O) and metal-hydrogen (M-HO) bonds was recently revealed for the water/Pt(111) system [8].

In the present work we have undertaken an XPS study of the water/Ru(001) system to address whether water dissociatively wets the surface or not. By studying O 1*s* XPS we can find direct evidence for the presence or the absence of dissociated species, while Ru 3*d* core level shifts provide direct information on wetting. We find, in contradiction to the previous reports [3,5], that water wets the surface nondissociatively at 150 K. Furthermore, we show that the energy pathway leading to thermal dissociation of adsorbed water lies above the energetic barrier for thermal desorption. The water layer sensitivity to x-ray irradiation was also quantified.

The experiments were performed at the undulator beamline 11.0.2 at the Advanced Light Source with energy resolution better than 20 and 100 meV for Ru 3*d* and O 1*s* spectra, respectively. O 1*s* spectra were recorded at a photon energy of 785 eV and for Ru 3*d* photoelectron diffraction effects were averaged out by the summation of spectra recorded at 380, 390, and 400 eV. The water monolayer on Ru(001) was prepared by careful control of dosage using a capillary array doser. Multilayers show the XPS peak at higher binding energy than that of the monolayer and were removed by annealing at 150 K, ensuring the same initial water phase as in the works of Refs. [4,6]. In order to minimize beam damage to the water layer, the sample was scanned in front of the spectrometer while recording the photoemission spectra [9]. Surface contaminants such as C and O were below detection limits of XPS ($<0.1\%$) in our experiments. We estimate an upper limit of 1% of surface H contamination from residual hydrogen in our vacuum chamber based on the base pressure of our vacuum chamber of 7×10^{-11} Torr and the 10–15 min duration of the experiments. The surface core level shift in XPS is sensitive to adsorbed H. This was exploited by the use of Ru 3*d* XPS to check the amount of adsorbed H; the results were consistent with the above mentioned upper limit on H contamination.

The O 1*s* XPS for the monolayer of D_2O in Fig. 1(a) consists simply of a broad peak with a maximum at 533.0 eV and offers no evidence of dissociation. The conclusion of no dissociation for the spectra in Fig. 1(a) is

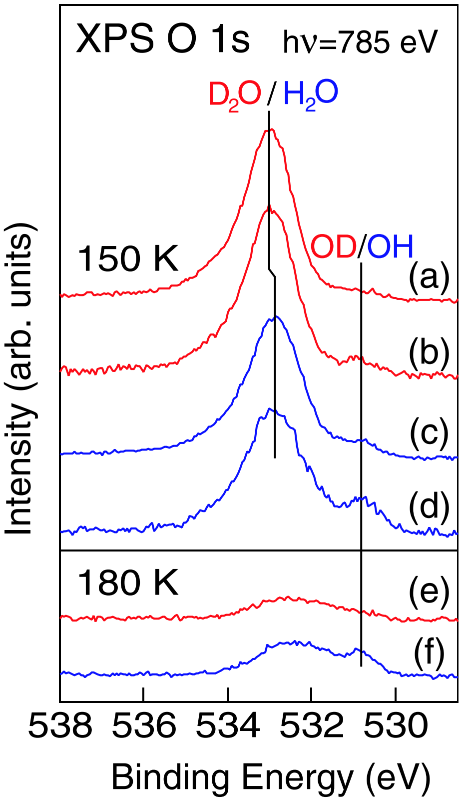

FIG. 1 (color online). O 1*s* XPS for water on Ru(001): all spectra are normalized to the same background. (a) D_2O monolayer, (b) the same preparation after x-ray irradiation for 3 min at about 0.1–1 photons and 1.8 electrons per water molecule (0.3 mC cm^{-2}). Total photon and electron dosage is approximately 60 times higher than that in (a) [9]. A peak at 530.8 eV is assigned to hydroxyl species formed as a result of x-ray beam-induced dissociation. (c) H_2O monolayer under the same conditions as in (a). (d) The same preparation after x-ray irradiation for 3 min. (e) D_2O exposure with 2×10^{13} molecules cm^{-2} s^{-1} at 180 K, and (f) H_2O exposure under the same conditions as in (e). The peak for hydroxyl species is observed in (f) but not in (e).

further substantiated by our experiments to quantify beam damage. When the sample was not scanned during the XPS measurement, severe beam damage was observed in a matter of minutes, as in Fig. 1(b) showing the XPS after 3 min of irradiation. A new peak at 530.8 eV, assigned to hydroxyl species, increased in intensity with irradiation dose. We also confirmed nondissociative adsorption at low coverages down to a few percent of a monolayer. Nondissociative adsorption of the H_2O monolayer was also confirmed by the spectrum shown in Fig. 1(c). The H_2O monolayer is more sensitive to irradiation than the D_2O monolayer. Figure 1(d) shows the XPS for the H_2O monolayer obtained after 3 min of irradiation, i.e., the same conditions as in Fig. 1(b). Comparing Figs. 1(b) and 1(d), we can see a larger amount of hydroxyl in the H_2O monolayer than in the D_2O monolayer. The tiny amount of hydroxyl species in Fig. 1(c) could be explained by radiation induced dissociation in spite of the precautions taken. We also observed a broadening of peak width and a 0.15 eV shift of the O 1*s* peak maximum toward lower binding energy; these effects originate from the vibrational fine structure.

It is well known that water can dissociate upon thermal or nonthermal activation. Nonthermal pathways include excitations induced by, e.g., visible, UV, and x-ray wavelength photons and low energy electrons (0–600 eV). For *in vacuo* thin water films these probes induce processes such as dissociation, desorption, and ice crystallization ([2] and references therein). The main agent for these processes is inelastically scattered electrons. When a photon is used as a probe, these electrons are created in photoionization and subsequent inelastic scattering events. The previous XPS study [5] most likely suffered from effects of beam damage to the water at the surface. Ultraviolet photoemission spectroscopy (UPS) data in the same study did not display any well-resolved O-H-related peaks in the valence band electronic structure that would correspond to the O-H-related peak in XPS, but UPS also inflicts less damage to the water layer as compared to XPS.

Careful attention should furthermore be given to induced damage when an electron beam is used as a probe. Electron-induced damage has been discussed in LEED studies of molecularly thin water films [10,11]. Starke *et al.* found that to circumvent beam damage, incident beam currents had to be reduced to about 1 pA [10]. Harnett *et al.* reported that total electron doses even as low as $0.02e^-$ per water molecule (4 μC cm^{-2}) induced cluster formation of multilayer ice [11]. In the structural LEED study by Held and Menzel [4], electron beam currents in the 100–300 nA range were used, adding up to a total electron dose of $(3–9)e^-$ per water molecule (0.5–1.5 mC cm^{-2}) at each spot used on their sample. Beam-damage effects inducing the same symmetry LEED pattern as observed in the structural study were later briefly discussed in another paper by the same authors [12]. We observe significant beam damage around an estimated total dose of $1.8e^-$ per water molecule (0.3 mC cm^{-2}); see Figs. 1(b) and 1(d). The $(3–9)e^-$ dose per water molecule used in the structural LEED study [4] falls within the range where we find significant electron-induced damage. Therefore we suggest that the flat layer found in the LEED study corresponds to the damaged layer with water and hydroxyl species.

By minimizing beam damage we have ensured that the adsorbed water layer on Ru(001) is not affected by the measurements, and we find it to be molecularly intact. Now we wish to determine the coordination of water to the substrate. The Ru 3*d* surface core level shift is a direct probe of the coordination number of the surface Ru atoms. In Fig. 2(a), a spectrum for clean Ru(001) is shown

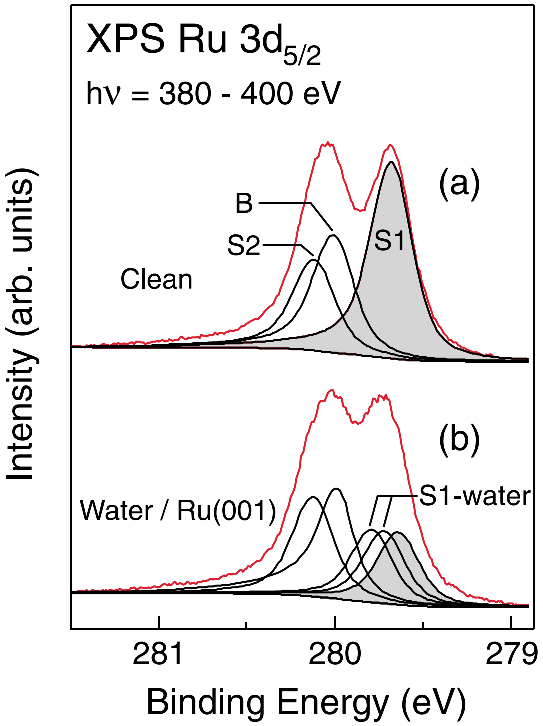

FIG. 2 (color online). Ru 3*d* XPS spectra for clean and water covered Ru(001). Spectra from photon energies 380, 390, and 400 eV were summed to average out photoelectron diffraction effects. (a) Clean Ru(001). Components obtained from a curve fitting are labeled as surface peak (S1), bulk peak (B), and second layer peak (S2). (b) D_2O monolayer on Ru(001). Intensity of the surface peak (S1) drops by more than 60% compared to (a). The adsorbed water related components are denoted as S1-water.

and is fitted in a similar manner to that used in Ref. [8]. Three components obtained from the fitting analysis are denoted as a surface peak (S1), a bulk peak (B), and a second layer peak (S2) [13]. Water adsorption causes a drop in the intensity of the surface peak (S1). Here the fraction of water molecules coordinating with the surface, i.e., influencing the peak (S1), is the parameter used to define wetting. For the monolayer [see Fig. 2(b)] the decrease in intensity of S1 was found to be more than 60% irrespective of fitting constraints [14]. Intensity related to Ru surface atoms coordinated to water (S1-water) appears on the high binding energy side of S1. Taking into account the interfacial D_2O/Ru ratio of 0.66 for the monolayer, the more than 60% reduced intensity of S1 is evidence that water fully wets the surface, i.e., that all water molecules bind directly to Ru(001).

Based on Ru 3*d* and O 1*s* XPS results we therefore conclude nondissociative wetting on Ru(001) at 150 K. The essential results showing nondissociated water and a low fraction of noncoordinated surface Ru atoms can be seen directly in the experimental spectra and are independent of the details in the fitting parameters. Wetting by water without dissociation has also been concluded for Pt(111) where the water molecules are adsorbed through alternating M-O and M-HO bonds [8]. We find the results for water on Ru(001) to be very similar to those obtained for water on Pt(111). From Ru 3*d* XPS we find the number of Ru surface atoms coordinated to water to be the same as the saturation coverage of water, which was also found for water on Pt(111) from analysis of Pt 4*f* XPS data. In the O 1*s* XPS, the observed broad peak can be decomposed into two components assignable to M-O and M-HO bonding species. Assuming these two species, an upper limit on the separation of the two peaks used to fit the O 1*s* spectrum is found to be 0.6 eV for water on Ru(001) similar to the value (0.8 eV) found for water on Pt(111). The similarities in results for the two systems suggests a water layer on Ru(001) where all water molecules in the first layer bind directly to the surface through alternating M-O and M-HO bonds with a slight corrugation similar to water on Pt(111) [8].

In our study we have thus not found the partially dissociated layer even though it was found to be of lowest total energy in the theoretical study [3]. How can we then account for the fact that the partially dissociated phase is not generated in our experiment? An essential point is that the kinetics of a possible dissociation process must be considered. Perhaps the barrier for desorption of the nondissociated layer is smaller than the barrier to form a partially dissociated phase?

In order to test this hypothesis, we exposed Ru(001) to a H_2O molecular beam, 2×10^{13} molecules $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, with the sample held at 180 K, i.e., above the desorption threshold. The results are shown in Fig. 1(f) where we see an O 1*s* peak at 530.8 eV corresponding to dissociated water on the surface. We therefore conclude that a partially dissociated phase forms for H_2O in the presence of a sufficient flux of water and high enough substrate temperature to overcome a kinetic barrier. These results experimentally confirm a slightly larger activation barrier for dissociation than for desorption. A recent theoretical study of the water/Ru(001) system [15] arrived at similar results with a barrier for dissociation very close to the adsorption energy for a nondissociated water layer.

H_2O on Ru(001) displays desorption peaks at 185 and 220 K [1,2]. A temperature dependent XPS study allowed us to directly assign the 220 K peak in the thermal desorption spectra to the partially dissociated phase, whereas the desorption peak at 185 K was assigned to the nondissociated phase. Since the partially dissociated phase is stable at higher temperatures than the nondissociated phase, we conclude that the partially dissociated phase is energetically more favorable than the nondissociated phase. This agrees with reported total energy calculations of the two phases [3,15].

An anomalous isotope effect and kinetics in the thermal desorption spectra of water on Ru(001) has previously been discussed [12,16,17]. In the thermal desorption of H_2O the desorption related to the nondissociated phase became dominant with an increased heating rate. We interpret that this is related to the H_2O dissociation process at the surface upon heating; a faster heating rate kinetically quenches the pathway to dissociation. In contrast to the case of H_2O, no desorption from a partially dissociated phase for D_2O was found: an observed extremely weak peak was attributed to the isotope impurity in D_2O (HDO or H_2O) [12,17]. We performed an experiment for D_2O under the same conditions as in Fig. 1(f); see Fig. 1(e). We found that D_2O remains intact, consistent with the thermal desorption results. We consider the isotope effect to arise from differences in reaction rates toward dissociation between H_2O and D_2O. The dissociation pathway is considered to involve elongation of an O-H or O-D bond. H_2O has a 0.1 eV higher zero-point vibrational energy compared to D_2O in the dissociative pathway. Assuming that the barrier for dissociation without considering the zero-point vibrational effect is 0.1 eV higher than the adsorption energy of the nondissociated layer, the barrier for dissociation thus becomes comparable to desorption in the case of H_2O.

The chemistry of adsorbed water strongly depends on the metal surfaces [1,2]. We can, however, find only very small differences in the desorption temperatures for the nondissociated monolayer between different surfaces. It is not the adsorption energy of water but the activation barrier of dissociation that governs the chemistry of water on metal surfaces. On metals where water adsorbs molecularly intact, a larger activation barrier is predicted. As discussed above, dissociation is kinetically hindered due to the competition with desorption, but partial dissociation may still occur under higher pressure or/and higher temperature. In the case of the Ru(001) surface a delicate energetic difference results in qualitative differences in the chemistry of the water isotopes.

Our studies thus show that (i) water wets Ru(001) either nondissociatively or dissociatively, (ii) a partially dissociated overlayer is energetically favored, but (iii) the dissociation is kinetically hindered due to the competition with desorption. Since the activation barrier for desorption is very similar between substrates, the activation barrier for dissociation determines nondissociative or dissociative adsorption on metal surfaces [18].

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