Water Dissociation on Single Crystalline Anatase TiO_2(001) Studied by Photoelectron Spectroscopy

J. Blomquist,[†] L. E. Walle,[‡] P. Uvdal,[†] A. Borg,[‡] and A. Sandell*,[§]

Chemical Physics, Department of Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden, Department of Physics, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway, and Department of Physics and Materials Science, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden

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The adsorption of water on the anatase TiO_2(001)-(4 × 1) surface is studied using synchrotron radiation-excited core level photoelectron spectroscopy. The coverage-dependent adsorption of water at low temperature is monitored and compared to the sequence obtained after heating of a water multilayer. Two adsorption phases of submonolayer coverage can be defined: Phase 1 consists only of dissociated water, observed as OH-groups. This phase is found at low coverage at low temperature (190 K) and is the only state of adsorbed water above ∼230 K. The saturation coverage of phase 1 is consistent with dissociation on the 4-fold-coordinated Ti ridge atoms of the (4 × 1) surface reconstruction. Phase 2 is found at higher coverage, reached at lower temperature. It consists of a mixture of dissociated and molecular water with a ratio of 1:1 at 170 K. The molecular water is found to bond to the hydroxyl groups. The hydroxyl coverage of phase 2 is approximately 2 times that of phase 1. The results suggest that the OH and H_2O species of phase 2 are confined to the ridges of the surface.

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1. Introduction

Water interaction with solid surfaces is central for a wide range of fields, such as catalysis, photochemistry, electrochemistry, corrosion, and biocompatible materials.[1,2] Titanium dioxide (TiO_2) is a material used within a majority of the above applications because it is photoactive and chemically stable in a variety of environments.[3] Rutile TiO_2 of the (110) termination is the most stable surface of the most stable polymorph of titanium dioxide. Rutile TiO_2(110) single crystals are readily available, which is one reason why it is one of the most studied metal oxide surfaces in the world. Water adsorption on rutile TiO_2(110) can in turn be considered as the benchmark system for molecular adsorption on metal oxides. The observation of photoinduced splitting of water into hydrogen and oxygen on a rutile TiO_2 single crystal in 1972 is a discovery that has initiated many of these studies.[4]

The anatase polymorph of TiO_2 appears to be an even more potent photocatalyst than rutile.[5−7] Anatase is furthermore the preferred phase when TiO_2 nanoparticles are formed.[8] Nanoporous TiO_2 electrodes can be prepared by forming a network of sintered nanoparticles. These have been shown to be most useful for photoelectrochemical applications by virtue of the huge effective surface area.[9] Anatase nanoparticles typically expose (101) and (100)/(010) surfaces at about equal amounts together with small amounts of (001).[10] Consequently, comparative studies of water adsorption on well-defined anatase surfaces is a stepping stone toward an understanding of surface processes on nanocrystalline TiO_2 in aqueous environments. In addition, studies of water on anatase TiO_2 can further the understanding of the prototypical water/rutile TiO_2 system.

The structure and energetics of water adsorption on the anatase TiO_2(101) and (001) surfaces at various coverages have been studied by use of density functional theory (DFT) calculations.[10] It was shown that molecular water adsorption is favored on the (101) surface. The behavior on the (001) surface was found to be very different. At low coverages, water only adsorbs dissociatively, while at higher coverages water adsorption results in a dissociated layer onto which molecular water is hydrogen bonded. Dissociative adsorption on the (001) surface and molecular adsorption on the (101) surface have also been found in other theoretical studies.[11−13]

Experimental studies of water adsorption on single crystalline anatase TiO_2 are scarce. This can be attributed to the difficulty in obtaining high-quality single crystal samples. The adsorption of water on the anatase (101) surface under ultrahigh vacuum (UHV) conditions has been studied using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD).[14] The (101) surface was prepared by growing a homoepitaxial film on a (101) mineral sample to ensure purity. The results were found to confirm the theoretical prediction of molecular adsorption. Desorption states were found at 160, 190, and 250 K. These were assigned to multilayer water, water adsorbed on 2-fold-coordinated (bridge) O, and water adsorbed on 5-fold-coordinated Ti, respectively. In an earlier work, the photoactivities of the anatase (001) and (101) surfaces was compared.[15] The results were interpreted in terms of different water adsorption states on the two surfaces. However, no study of water adsorption on the (001) surface in UHV has been undertaken so far.

The clean (001) surface of anatase TiO_2 undergoes a (4 × 1) reconstruction in UHV.[16,17] A structure model of the (001)-(4 × 1) surface has been derived from scanning tunneling microscopy (STM) results in conjunction with DFT calculations.[18,19] The surface can be described as consisting of ridges separated by terraces. Recent calculations suggest that water dissociates also on the reconstructed (4 × 1) surface but only

* Corresponding author. Fax: +46 18 4713524. E-mail: anders.sandell@fysik.uu.se.
[†] Lund University.
[‡] Norwegian University of Science and Technology.
[§] Uppsala University.

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at the ridges.[20] The adsorption of formic acid on thin film anatase $TiO_2(001)$ has been studied by STM and noncontact atomic force microscopy.[19] The high reactivity of the ridges of the (001)-(4 × 1) surface was convincingly confirmed.

In this work, we study the coverage-dependent adsorption of water on the anatase $TiO_2(001)$-(4 × 1) surface by stepwise heating of a multilayer water film and by progressive water adsorption at low temperature. We find that water dissociates on the surface at low coverage. The dissociation is strongly connected to the highly reactive ridges forming the (4 × 1) reconstruction, thereby confirming the theoretical predictions. We also present evidence for a mixed phase consisting of dissociated and molecular water at higher coverages. This phase has not been addressed in the previous theoretical studies of water adsorption on the reconstructed surface.

2. Experimental Section

The O 1s core level photoemission spectra were recorded at beamline D1011 at the Swedish National Synchrotron Facility MAX II.[21] The end station comprises a 200 mm radius hemispherical electron energy analyzer of Scienta type. Binding energy (BE) calibration of the core level photoelectron (PES) spectra against the Fermi level was achieved by referencing to a Pt foil mounted on the sample holder.

Two types of anatase $TiO_2(001)$-(4 × 1) surfaces were prepared: one by metal organic chemical vapor deposition on a lattice matched substrate [$SrTiO_3(001)$] and one by cleaning of a natural single crystal. That single crystalline anatase $TiO_2(001)$ forms on $SrTiO_3(001)$ has been demonstrated previously.[16,17,22]

The Nb-doped (1.0 wt %) $SrTiO_3(001)$ crystals were purchased from MaTeck GmbH, Germany. Cleaning of the $SrTiO_3(001)$ substrate was accomplished by cycles of Ar^+ sputtering (1 keV) followed by annealing to 1000 K in O_2 atmosphere (5×10^{-7} mbar). Titanium tetra-isopropoxide (TTIP, 99.99% Aldrich) was dosed through a stainless steel dosing tube facing the sample. The TiO_2 film was grown at a TTIP background pressure of 5×10^{-8} mbar and a sample temperature of 850 K. The Sr 3d states were barely visible after TiO_2 film growth, suggesting a film at least 100 Å thick. The anatase $TiO_2(001)$ single crystal (provided by PI-KEM Ltd., UK) was cleaned by cycles of Ar-sputtering and subsequent annealing in oxygen to 920 K. For both surfaces, the formation of the (4 × 1) reconstruction characteristic for the anatase (001) surface was confirmed with low-energy electron diffraction (LEED). A representative LEED image is shown in Figure 1. The PES spectra of the Ti 2p core level and the valence region showed that the defect density of the pristine surfaces was very low. That is, the Ti 2p spectrum displayed only a Ti^{4+} state, and no discernible structures were found in the band gap region.

Radiation-induced effects have proved to be an important issue for adsorbed water, especially on metallic surfaces.[23,24] The insertion device used in the present case is a bending magnet, giving a spot size at the sample of about 2 mm^2. The photon flux is approximately 5×10^{10} photons mm^{-2}. Previous measurements on water on rutile $TiO_2(110)$ using a flux 1 order of magnitude greater were found to lead to minimal radiation damage after 1 h.[25] In our case, the only radiation-induced change was found for the mixed OH/H_2O layer where a very small decrease of the H_2O coverage was noted after about 1 h. Still, great care was taken to perform the measurement series as quickly as possible.

3. Results and Discussion

Figure 2a shows O 1s PES spectra recorded upon adsorption and subsequent stepwise annealing of a water multilayer on the single crystal surface. Figure 2b shows O 1s PES spectra after stepwise water adsorption on the anatase thin film surface at 190 ± 20 K. The spectra shown in Figure 2 are all normalized to the ring current and number of scans. They were measured at grazing emission angle (60°) and a photon energy of 610 eV to obtain a high surface sensitivity. The BE for the O 1s peak of the pristine TiO_2 surfaces is 530.60 eV for the film grown on $SrTiO_3(001)$ and 530.45 eV for the bulk single crystal sample. We attribute this effect to a higher defect density in the MOCVD grown film, which leads to shifts of this magnitude for defects at a percentage level.[26] Upon exposure to water, states at BE:s of 532 and 534 eV are observed, assigned to adsorbed OH and H_2O, respectively.[25,27]

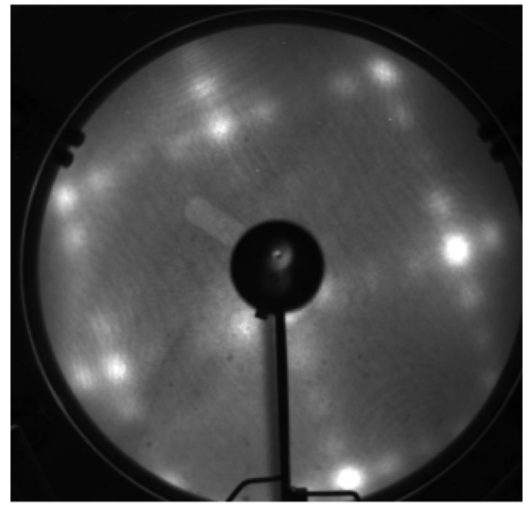

Figure 1. Low-energy electron diffraction (LEED) pattern of the pristine anatase $TiO_2(001)$ surface. The extra spots associated with the (4 × 1) surface reconstruction are clearly visible. The electron kinetic energy was 77 eV.

To derive quantitative information, the O 1s spectra have been delineated. This was accomplished by curve fitting in combination with subtraction procedures to establish binding energies and line widths. Spectra recorded in normal and grazing emission as well as spectra for the clean surface and after adsorption were used for the subtractions. The individual components are included in Figure 2. Noteworthy is that some additional intensity is found at the high BE side of the TiO_2 related peak for the pristine surface. Figure 3 shows that the change in the spectral shape when changing the emission angle is negligible. The weak high BE tail is therefore not likely to be due to an adsorbed species because its intensity relative to the main peak would then change significantly. We therefore propose that the high BE tail is an inherent property of the O 1s spectrum of pure anatase. To facilitate the analysis, a component with parameters similar to those of the hydroxyl component has been used to describe this structure. Noteworthy is that a structure of the same BE as adsorbed OH but associated with the oxide has been found for clean rutile $TiO_2(110)$, lending support for our interpretation.[25]

When comparing the intensities of the various components, it can be concluded that the OH and H_2O coverages above 170 K must be in the submonolayer regime. For this experimental setting, the major part of the O 1s intensity from the substrate and the water multilayer originates from ionization of the surface layer. The O 1s components assigned to OH groups and molecular H_2O have both a maximum intensity of about 20% of the clean substrate O 1s peak and about 14% of the O 1s peak for multilayer water. The low relative intensities together

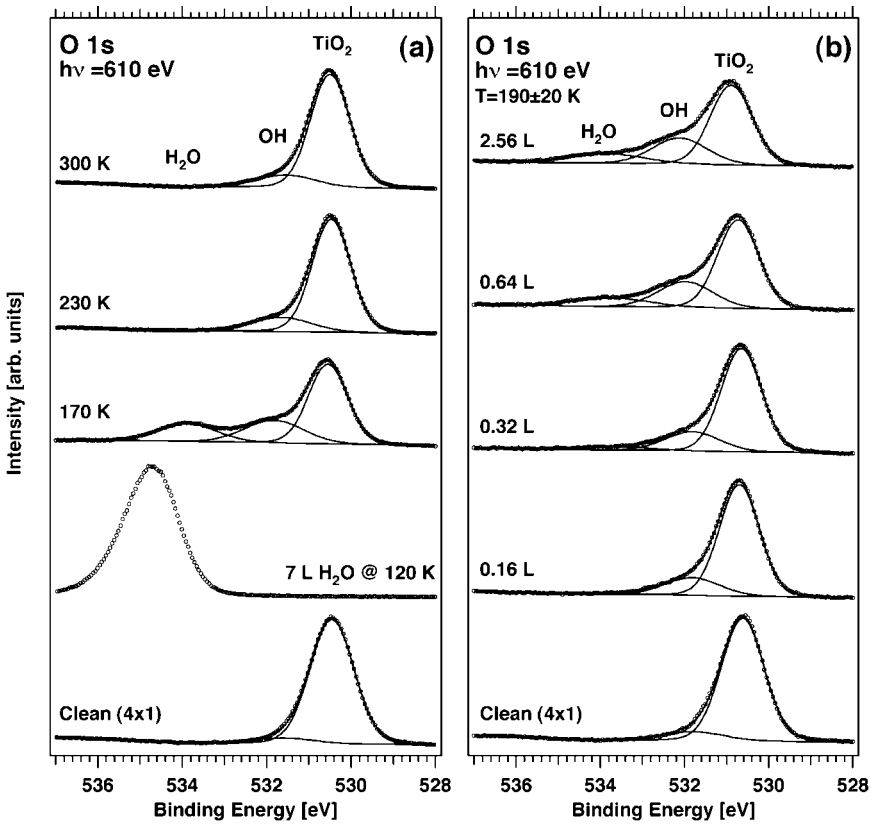

Figure 2. O 1s spectra for water adsorption on anatase TiO_2(001)-(4 × 1) recorded in grazing emission. The individual components associated with TiO_2 and adsorbed OH and H_2O obtained by curve fitting are included. (a) Heating series. (b) Growth series at a sample temperature of about 190 K.

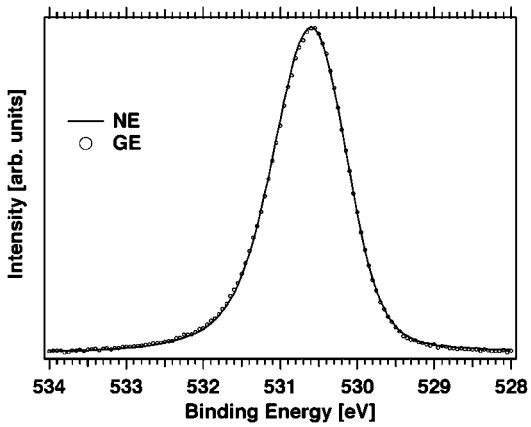

Figure 3. O 1s spectra for the pristine anatase TiO_2(001)-(4 × 1) surface recorded in normal (NE, —) and grazing (GE, ○) emission. A Shirley background has been subtracted in both spectra to facilitate the comparison.

with the fact that the substrate surface contains both O and Ti atoms show that the adsorbed OH and H_2O can only cover a fraction of the surface.

Better estimates of the adsorbate coverage can be derived from O 1s PES spectra recorded at two different angles, normal emission and 60° off normal emission. Two assumptions are needed: first, that the angle-dependent attenuation of the substrate signal follows the exponential expression and, second, that the angle dependence of the (OH):(total signal) ratio equals that of the (surface bridging O):(total signal) ratio. An advantage with this approach is that no estimate of an electron mean free path is needed. The intensities of the OH- and H_2O-peaks can in this way be translated into coverage relative to the surface bridging (2-fold-coordinated) O atoms of the clean (4 × 1) surface. The OH and H_2O coverages are summarized in Figure 4. The intensity of the OH-related component has been corrected by subtraction of the estimated contribution from the high BE tail associated with the pristine anatase surface.

The coverages derived from the temperature series start from the situation attained after desorption of the multilayer by heating to 170 K. At this point, the OH and H_2O coverages are very similar. The estimated coverage corresponds to about 0.4 per bridging surface O atom. Heating to 230 K results in nearly complete desorption of molecular water and a decrease in the hydroxyl coverage to about 0.2 OH groups per surface O atom. Subsequent heating to 300 K leads to a decrease in the OH coverage down to 0.17 OH groups per surface O atom.

Upon water dosing on the clean surface held at 190 ± 20 K, the OH-related peak increases rapidly after the first dose (0.08 L). The OH coverage is here estimated to 0.17 OH groups per surface O atom. After this point, the increase is slower, reaching a kink at 0.64 L, after which the coverage increases only very little. The OH coverage after 2.56 L amounts to 0.42 OH groups per surface O atom. A significant increase of the component assigned to adsorbed molecular water is not observed until after a dose of 0.32 L. The amount of adsorbed water increases further up to a dose of 0.64 L, after which the increase is very slow, just as for the amount of adsorbed OH. The OH/H_2O ratio after 2.56 L water at 190 ± 20 K is 1.6. When comparing to the temperature series, it is found that the OH/H_2O ratio at 190 K is indeed expected to be greater than that at 170 K.

The O 1s binding energy as a function of coverage for the different situations is shown in Figure 5. The binding energy of the OH-related O 1s component shows an increase by 0.25 ± 0.05 eV for increasing coverage. The binding energies for

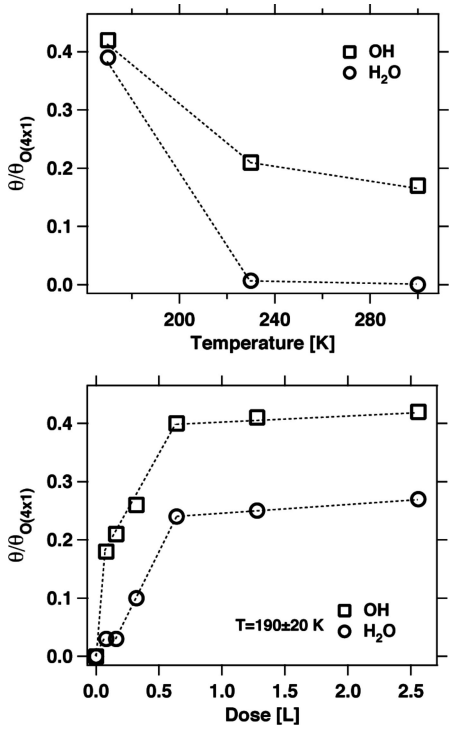

Figure 4. Summary of the quantitative results obtained from the O 1s spectra shown in Figure 1. The plots show the OH and H_2O coverages as a function of temperature (top) and water dose at 190 ± 20 K (bottom). The coverages are given relative to the number of bridging surface oxygen atoms within the (4 × 1) unit cell.

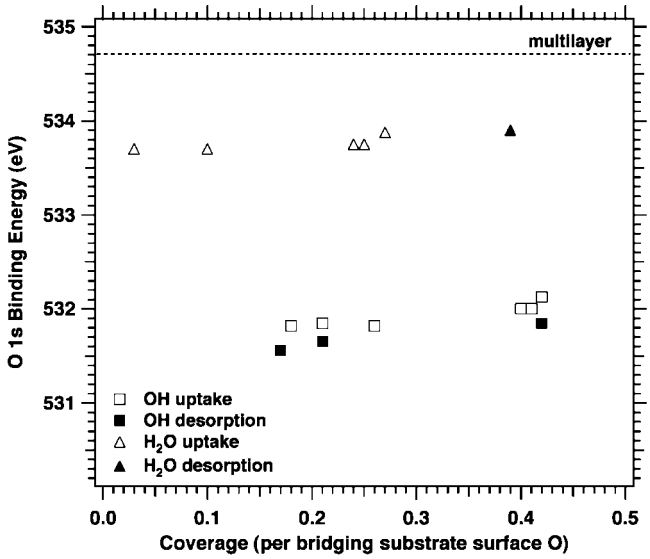

Figure 5. O 1s binding energies for the OH and H_2O components for the desorption series measured by successive heating steps and the growth series measured as the uptake at 190 K.

the uptake series are systematically greater by about 0.2 eV as compared to the desorption series. As noted above, this shift is also found when comparing the O 1s peaks of the clean surfaces and is most likely associated with slightly different defect densities in the two samples. The binding energy of the H_2O-related O 1s component increases by 0.20 ± 0.05 eV for increasing coverage. At the highest coverage (0.4 per substrate surface O), the O 1s binding energy for adsorbed water is found to be lower than that of multilayer water by about 0.8 eV.

To summarize, we can define two phases on the basis of the results presented in Figures 2 and 4, both of which are of

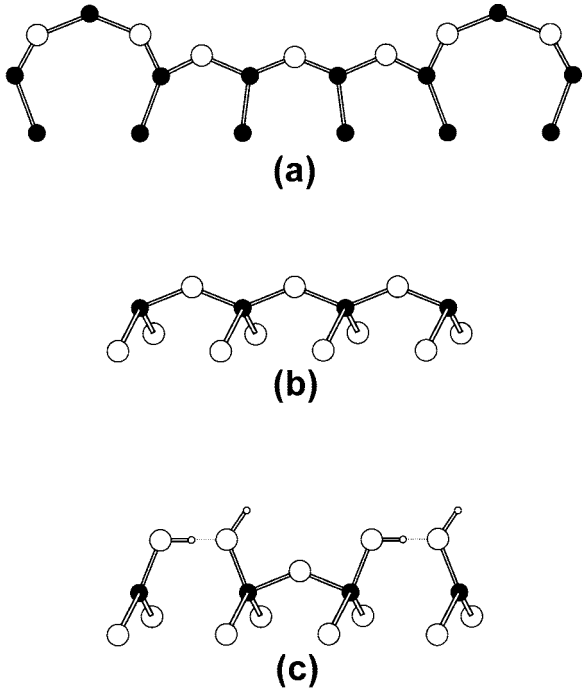

Figure 6. Schematic illustrations of the (4 × 1) reconstructed anatase TiO_2(001) surface before and after hydroxylation. The atomic structures are based on the ADM model.[18] (a) The clean reconstructed surface projected along the [100] direction. (b) Illustration of how the ridges extend along the [010] direction. (c) Hydroxylation of the ridge Ti sites as proposed in ref 20. This corresponds to phase 1 in the present study.

submonolayer coverage. The first phase consists only of dissociated water, observed as OH-groups. This phase is found at low coverage at low temperature and is the only state of adsorbed water above 230 K. We define phase 1 as the situation attained at 230 K, where the hydroxyl coverage is 0.2 OH per substrate surface O. This situation is also formed after dosing of 0.08−0.16 L water at 190 K. The second phase consists of a mixture of dissociated and molecular water, which is possible to form at higher coverage at low temperature. The maximum hydroxyl coverage for phase 2 is about 0.4 OH per substrate surface O, that is, approximately 2 times the hydroxyl coverage of phase 1. The water coverage associated with this hydroxyl coverage depends on the substrate temperature.

In the following, we will discuss plausible scenarios for the water adsorption and dissociation associated with the two different phases. The (4 × 1) surface structure is nonuniform, consisting of ridges separated by terraces. This has been verified by STM measurements.[19] Figure 6a and b illustrates schematically the ad-molecule (ADM) model, which is the atomic structural model that at present seems to be most compatible with available experimental data.[18] Within the ADM model, the (4 × 1) surface can be viewed as a transformation of the (1 × 1) surface by replacing bridging oxygen atoms by TiO_3 units.[18] The reconstruction is believed to occur to relieve the surface stress. The 4-fold-coordinated Ti atoms [Ti(4)] are located on the ridges, whereas 5-fold-coordinated [Ti(5)] atoms are located on the terraces. One (4 × 1) surface unit cell comprises six bridging O(2) atoms, four Ti(5) atoms, and one Ti(4) atom.[18]

The coverage estimate for phase 1 derived from the O 1 s spectra suggests the presence of dissociated water only on the Ti(4) atoms located on the ridges of the (4 × 1) structure. The OH amount of phase 1 is estimated to 0.20 ± 0.03 relative to the amount of bridging O atoms of the clean (4 × 1) surface,

which translates into 1.2 ± 0.2 OH groups per Ti(4) atom. This value can be regarded as an upper limit because minute traces of molecular water were observed after heating to 230 K, indicating that this temperature lies on or slightly below the border where mixed layer formation is allowed (water readsorption during the measurements is also possible). That the OH coverage is consistent with efficient water dissociation on the Ti(4) atoms is expected given the high reactivity of the ridges found in the study on formic acid adsorption.[19]

Our results provide the first experimental support of previous calculations for water adsorption on the (4 × 1) reconstructed surface. The theoretical work suggests that water dissociates effectively on the ridges while no dissociation occurs on the terraces.[20] The most favorable situation was found to be the one shown in Figure 6c. It is a structure in which one terminally bound hydroxyl group is found on all Ti(4) atoms on the ridge. This would correspond to phase 1. The calculations also present a feasible explanation to the low reactivity found for the terraces:[19,20] The (4 × 1) reconstruction causes the Ti(5) atoms to be pushed slightly away from the surface as compared to the (1 × 1) surface.[18]

Phase 2 is associated with additional water dissociation concomitant with the adsorption of molecular water. Within the temperature range 170−190 K, three different types of molecular water adsorption may be considered:[14,24,28] hydrogen bonded to hydroxyl groups, hydrogen bonded to O(2) atoms, and oxygen bonded to Ti(5) atoms. Bonding to O(2) and Ti(5) atoms is believed to occur on the anatase TiO_2(101) surface. However, when desorbing a water multilayer deposited on the TiO_2(101) surface, the O 1s BE is found to increase by 1 eV when reaching the submonolayer regime. The increased O 1s BE is associated with water adsorbed on the Ti(5) sites, while very similar O 1s binding energies are found for the water multilayer and water presumably adsorbed on the O(2) sites. The coverage dependence of the O 1s BE for water on the (101) surface is thus very different from the coverage dependence of the O 1s BE for water on the (001) surface. The 0.8 eV decrease in the O 1s BE for decreasing water coverage on the (001) surface is instead in very good agreement with the behavior found for water adsorption on a hydroxylated oxide surface.[28] From this follows that the molecular water observed on the (001) surface between 170−190 K is associated with hydrogen bonding to the hydroxyl groups formed by water dissociation.

When discussing extensive hydroxylation of the anatase TiO_2(001) surface, it is important to determine if the (4 × 1) reconstruction is affected. Calculations show that the unreconstructed (1 × 1) surface of anatase TiO_2(001) becomes stabilized by hydroxylation.[20,29] In a study of H_2O/O/Cu(110), it was furthermore found that the O p(2 × 1) reconstruction could be lifted upon water adsorption and dissociation below 220 K.[30] Thus, heating of the water multilayer on anatase TiO_2(001) could be complex and involve a (1 × 1) to (4 × 1) transition. In a preliminary study using a standard LEED, we find no sign of a lifting of the (4 × 1) structure upon water dosing at 160 K. This is not conclusive information because a partial lifting of the (4 × 1) structure can be difficult to observe and the LEED can also influence the adsorbate layer.[31]

Under the assumption of an unperturbed (4 × 1) surface, the additional water dissociation will most likely occur either on the already hydroxylated ridges or on the Ti(5) atoms located at the terraces. According to the proposed model of phase 1, the hydroxylated Ti sites on the ridges remain 4-fold-coordinated. Thus, these sites may still be reactive toward water dissociation but to a lesser extent due to the preceding hydroxylation step. A valuable comparison is the adsorption of formic acid on the (4 × 1) surface, which has been studied both experimentally and theoretically. Calculations suggest that a bidentate configuration on the Ti ridge atoms is energetically favored. The bidentate adsorption geometry leads to 5-fold-coordinated Ti. However, the bidentate geometry is not observed experimentally at room temperature.[19] Instead, formic acid appears to adsorb in a monodentate fashion.[19,20] Consequently, the results on formic acid suggest that doubly hydroxylated 5-fold-coordinated Ti atoms on the ridges may not be stable at room temperature, which is what we observe. Regarding dissociation on the terrace Ti(5) atoms, one OH group per Ti atom would result in an increased OH coverage by a factor of 5. This is not observed, making dissociation on the terraces less likely as was shown in the theoretical study.[20]

With respect to uncertainties in the results, we stress that the method of estimating the coverage is based on assumptions regarding the spectral intensities. The error within this approach is very difficult to estimate. One source of error is photoelectron diffraction effects, which can be significant for single crystal systems. In the case of water adsorbed on rutile TiO_2(110), modulations of about ±40% were observed in the kinetic energy regime used here.[25] Clearly, further studies are warranted. To estimate the diffraction effects, O 1s spectra for a range of photon energies are needed. Low-temperature STM and non-contact AFM studies can furthermore be important to shed light on the structure of the mixed layer. Regarding the adsorption mechanism, it is possible that the presence of molecular water can aid in the stabilization of the high hydroxyl coverage in the mixed layer. The interplay between the adsorbate−substrate bond and the hydrogen bonding within the mixed layer is something that could be worthwhile to address in future theoretical studies.

4. Conclusions

In summary, we have studied the adsorption of water on anatase TiO_2(001) with respect to temperature and coverage dependence. Above 230 K, only dissociated water is observed in the form of hydroxyl groups. The hydroxylation is suggested to occur on the 4-fold-coordinated Ti atoms located on the ridges of the (4 × 1) reconstructed surface. The high reactivity and the location of the hydroxyl groups confirm previous theoretical predictions. Below 230 K, it is possible to form a mixed layer consisting of hydroxyl groups and molecular water. The molecular water is found to bond to the hydroxyl groups. The OH coverage for the mixed layer can exceed that of the pure OH layer by a factor of 2. The relatively low increase in OH coverage suggests that also the additional water dissociation is associated with the ridges of the (4 × 1) surface structure.

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