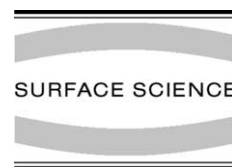




ELSEVIER

Surface Science 495 (2001) 8–18



www.elsevier.com/locate/susc

H₂O interaction with bare and Li-precovered TiO₂: studies with electron spectroscopies (MIES and UPS(HeI and II))

S. Krischok^{a,*}, O. Höfft^a, J. Günster^b, J. Stultz^c, D.W. Goodman^c, V. Kempter^a

^a Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Leibniz-Strasse 4, D-38678 Clausthal-Zellerfeld, Germany

^b Institut für Nichtmetallische Werkstoffe, Technische Universität Clausthal, Zehntner Strasse 2a, D-38678 Clausthal-Zellerfeld, Germany

^c Department of Chemistry, Texas A&M University, College Station, TX 77843–3255, USA

Received 17 May 2001; accepted for publication 22 August 2001

Abstract

TiO₂(1 1 0) single crystals and titania thin films on Mo(1 1 0), bare and precovered by Li atoms, were exposed to water at 120 K. During the adsorption process metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS)(HeI and II) spectra were collected in situ. Spectroscopic and temperature-programmed desorption data were obtained during the annealing of water multilayers grown at 120 K.

For the adsorption on the bare TiO₂ surface we conclude that an initial dissociative adsorption at defect sites is followed by molecular adsorption up to multilayer formation. From the exposure dependence of the MIES and UPS signals we conclude that, even before the completion of the first adlayer, no isolated water molecules are sampled, and strong lateral interaction between adjacent adsorbates stabilizes molecular water.

On TiO₂(1 1 0), precovered by about 1 ML of Li atoms, water is adsorbed dissociatively both at 120 K and at room temperature until the first, mixed layer consisting of Li and OH species, is completed. On top of the first layer additional water is adsorbed molecularly. Annealing experiments show that the first layer remains intact when the second layer forms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metastable induced electron spectroscopy (MIES); Photoelectron spectroscopy; Water; Alkali metals; Titanium oxide

1. Introduction

Ion sorption and chemical reactions at interfaces between metal oxides and water are central features in many natural and industrial processes.

Examples include transportation of ground water contaminants, electrode phenomena, corrosion, and dissolution. For geochemistry and atmospheric chemistry, surfaces of metal oxides are of particular interest as these compounds are major components of rocks, soils, and airborne dust particles. For many oxides it has been found that water molecules dissociate upon contact with the surface, forming various types of surface hydroxyl

* Corresponding author. Fax: +49-5323-72-3600.

E-mail address: stefan.krischok@tu-clausthal.de (S. Krischok).

groups. It is also well established that these hydroxyl groups play a decisive role in many chemical properties of oxide surfaces, including ion sorption, dissolution, and catalytic activity [1,2]. Despite a great deal of investigation, the adsorption of water on oxide surfaces is still poorly understood.

Titania (TiO_2) has attracted particular attention. Initially this derived from the observation of the photoelectrolysis of water on rutile TiO_2 surfaces [3], but it rapidly became apparent that a wealth of scientific challenges is present in the study of TiO_2 surface chemistry. Now TiO_2 is widely used as support for metal catalysts, as a sensor material, and in powder form as a catalyst, pigment and opacifier.

For a long time theoreticians were unanimous in predicting dissociation at all coverages [4–6]. Very recently molecular adsorption [7], or mixed molecular and dissociative adsorption [8,9] have been proposed, and the obvious discrepancy with experimental results (see below) could be partly remedied. Lindan et al. [8,9] predict that isolated water molecules adsorb dissociatively, but with increasing coverage intermolecular hydrogen bonding stabilizes a mixed (molecular and dissociated) configuration with respect to complete dissociation. Stefanovich and Truong [7] claim that isolated molecular species adsorb with the molecule oriented perpendicularly to the surface and the O atom pointing towards 5-fold coordinated Ti cations. In their opinion, previous calculations lead to dissociation because of the use of periodic boundary conditions with high adsorbate coverages which might result in distorted adsorbate geometries and several kcal/mol errors in the adsorption energy.

The experimental situation is also far from being clear. Studies of microcrystalline powders [10] indicate that water dissociation occurs on TiO_2 surfaces and that the (1 1 0) surface is the most active. Single crystal UHV studies have been performed with a wide variety of experimental techniques including temperature-programmed desorption (TPD), ultraviolet and X-ray photoemission spectroscopies (UPS and XPS), high-resolution electron-energy loss spectroscopy (HREELS) and work function measurements (WF). Several schemes of water adsorption have been proposed: on the

(1 1 0) surface water adsorbs molecularly and only dissociates at defect sites [11], dissociatively at low coverages and thereafter molecularly [12], either dissociatively or molecularly depending on temperature [13], or that the surface is inert [1].

In the present study we investigate the adsorption of water on rutile $\text{TiO}_2(1 1 0)$ single crystals with metastable impact electron spectroscopy (MIES), UPS(HeI and II) and TPD. Besides giving information about the desorbing species, the TPD data allow us to correlate the various MIES and UPS results with the water coverage. The UPS data enable us to compare our data with previous studies on this system. MIES, due to its high surface sensitivity, is a powerful tool to investigate the early stage of water adsorption, as already demonstrated for water adsorption on MgO [14,15]. In that case, water forms hydrogen-bonded clusters, far before the completion of the first adlayer.

In order to establish criteria for the conditions under which water adsorption takes place in form of hydroxyl species, we have also studied water adsorption on $\text{TiO}_2(1 1 0)$ precovered by Li atoms.

2. Apparatus

The apparatus (1), employed for the studies on $\text{TiO}_2(1 1 0)$, has been described previously [16–18]. Briefly, it is equipped with a cold-cathode gas discharge source for the production of metastable $\text{He}^*(^3\text{S}/^1\text{S})$ ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy and HeI photons ($E^* = 21.2$ eV) as a source for UPS. The intensity ratio $^3\text{S}/^1\text{S}$ is found to be 7:1. Additionally, the apparatus is equipped with XPS, Auger electron spectroscopy (AES) and a UPS(HeI and II) source (type HIS 13, Omicron).

Metastable and photon contributions within the beam were separated by means of a time-of-flight method using a mechanical chopper. MIES and UPS spectra were acquired with incident photon/metastable beams 45° with respect to the surface normal; electrons emitted in the direction normal to the surface are analyzed. Collection of a set of MIES/UPS spectra requires approximately 100 s. The measurements were performed using a hemispherical analyzer (Leybold EA10/100) with an

energy resolution of 250 meV for MIES/UPS. Since the metallic crystal support and the analyzer are in electrical contact, the Fermi energy appears at a constant energy and permits the WF change of the surface to be measured directly from the low energy cut-off of the electron spectra.

The apparatus (2) was employed by us previously for the study of water interaction with MgO using TPD and electron spectroscopy, and has also been described previously [19]. Briefly, it is equipped with a MIES/UPS source of the same type as in (1). The availability of MIES in (1) and (2) enables us to crosslink the data obtained in the two experiments. Additionally, the sample preparation could be controlled by XPS, AES and LEED. TPD is available for the absolute calibration of the water coverage.

In both (1) and (2) the sample could be cooled with LN₂ to 120 and 100 K, respectively. The temperature was measured with a thermocouple in direct contact with the front of the TiO₂ single crystal (or the Mo(110) substrate employed in (2)). The MIES and TPD studies with (2) were carried out on thin titania films grown on Mo(110). Titania layers with a thickness of a few nanometers were prepared by coadsorption of Ti and oxygen (O₂ pressure in the UHV chamber: 9×10^{-7} Torr) on a Mo(110) substrate held at 700 K. The Ti was evaporated from a Ti wire (purity: 99.999%) wrapped around a tungsten wire. The as-prepared film was annealed at 1000 K for about 60 s. Thin films prepared in the way described above were investigated by Oh et al. [20] and Guo et al. [21]. LEED revealed that ultrathin films are oriented in the (001) direction. However, no LEED pattern was obtained from our thick films. From the fact that the (110) surface is the most stable one and from the comparison with previous TPD data [22], we do not expect that our films are well ordered and preferentially oriented in the (110) direction. No chemical impurities of our films could be detected with AES.

The polished TiO₂(110) single crystals were introduced into the UHV chamber and annealed at approximately 800 K for several hours. This procedure was successfully used in Ref. [21]. The single crystal showed an (1 × 1) LEED pattern; a small contamination of carbon was indicated by AES.

However, we decided to prepare the crystal without sputtering to avoid the introduction of defects [21].

The sample could be exposed to Li atoms evaporated from a commercial dispenser source (SAES Getters). The relation between evaporation time and alkali coverage can be established via the relation between WF and coverage (for details see Ref. [23]).

The surface was exposed to water by backfilling the chamber. The water was cleaned by several freeze–pump–thaw cycles. The cleanliness of the water was checked with a quadrupole mass spectrometer. With (1) H₂O was used for the experiments on the TiO₂ single crystals, whereas with (2) D₂O (CIL, 99.9%) was used. The relative amount of surface-adsorbed water can be estimated on the basis of the TPD spectra obtained with (2). This relationship was employed to correlate the spectra collected with (1) and (2). All exposures given in the following refer to apparatus (1).

3. Experimental results

This section starts with the identification of spectral features caused by OH and H₂O species on titania as obtained by MIES and UPS and their comparison with the corresponding spectral features available from literature. Then, a presentation of our MIES, UPS and TPD results for the water adsorption on TiO₂ single crystals and films follows. In general, the MIES and UPS spectra of the as-prepared TiO₂ films are very similar to those for TiO₂ single crystals. Therefore, we do not present the corresponding film spectra which are documented elsewhere [24].

All results are presented as function of the binding energy, E_B , of the emitted electrons. Electrons from the Fermi level would appear at $E_B = 0$ eV in the MIES and UPS(HeI and II) spectra. The change of the WF with exposure is determined from the cut-off of the MIES and HeI spectra at high-binding energies.

3.1. Signature of water species on titania

In Table 1 we have collected the information obtained so far with MIES and UPS(HeI and II)

Table 1

Water-induced features for $\text{H}_2\text{O}/\text{TiO}_2$ and MgO as observed with MIES and UPS. If not otherwise stated, data are from the present work. Energies are in eV with respect to the Fermi level

Surface	Technique	$1b_1$	$3a_1$	$1b_2$	1π	3σ
$\text{Li}/\text{TiO}_2(110) + \text{H}_2\text{O}$	MIES	9.3	11.5	15		
$\text{H}_2\text{O}/\text{TiO}_2(110)$	MIES	7.8	10.0	13.2		
$\text{H}_2\text{O}/\text{TiO}_2(110)$	UPS(HeI)	7.9	11.2	13.5		
$\text{H}_2\text{O}/\text{TiO}_2(110)$	UPS(HeII)	7.8	9.8	13.2		
$\text{H}_2\text{O}/\text{TiO}_2(\text{film})$	MIES	8.0	10.2	14.1		
$\text{H}_2\text{O}/\text{Ni}(221)$ [33]	UPS(HeI)	6.7	8.9	11.7	5.1	8.2
$\text{H}_2\text{O}/\text{Ni}(775)$ [33]	UPS(HeI)	6.3	8.2	12.7		
$\text{H}_2\text{O}/\text{MgO}(\text{film})$ [34]	MIES	7.2	9.2	13.6		
$\text{Na}/\text{MgO}(\text{film}) + \text{H}_2\text{O}$ 100 K [34]	MIES				8.0	11.7
$\text{Li}/\text{TiO}_2(110) + \text{H}_2\text{O}$ 300 K	MIES				7.2	11.2
$\text{H}_2\text{O}/\text{TiO}_2(110) + \text{Li}$ 100 K	MIES				6.9	11.1
0.1 ML $\text{Li}/\text{Ni}(775) + \text{H}_2\text{O}$ [33]	UPS(HeI)				4.9	9
H_2O Li coad. $\text{Ni}(775)$ [33]	UPS(HeI)				5.9	9.2
$\text{K}/\text{Ni}(775) + \text{H}_2\text{O}$ [33]	UPS(HeI)				4.7	8.3

for water interacting with oxide surfaces, MgO and TiO_2 in particular. Typically, molecular water produces the features, $1b_1$, $3a_1$, and $1b_2$. In general, these spectra and those for water multilayers, i.e. for amorphous solid water (ASW), look rather similar. When compared to gaseous water, they appear considerably broadened showing relatively flat structures with three local maxima (Ref. [25] and references cited therein). It should be noticed that the photoelectron spectra for liquid water and ASW are rather similar [26]. OH species produce two features 3σ and 1π whose separation is between 3.7 and 5.4 eV depending on the chemical environment of the OH species. For comparison we have also included some results for water interacting with metals.

The results obtained when exposing water to an alkali-precovered titania surface are particularly illuminating because OH (H_2O) features dominate at low (high) exposures, respectively (see below). This fact allows us to establish their relative energetic positions.

3.2. Water adsorption at 120 K

3.2.1. Electron spectroscopic results for bare TiO_2

Fig. 1(a) presents MIES spectra of the bare $\text{TiO}_2(110)$ surface at 120 K exposed to water. Up to 2 L the surface was exposed to 0.135 Langmuir per spectrum, thereafter an exposure of 0.5

Langmuir per spectrum was chosen. The difference spectra for 0 to 2 L, obtained by subtracting the spectrum for the bare surface without additional scaling (bottom in Fig. 1b), are shown in Fig. 1(b). They show clearly that the main pathway is molecular adsorption at all exposures. However, from the behavior of the WF during the cycle of flashing and cooling to 120 K, dosing water and heating the surface, we conclude that during the cooling procedure some contaminants must have adsorbed on the surface.

The structure seen initially (up to 0.5 L) in the difference spectra can be interpreted as a superposition of molecular and hydroxyl features. The arrows indicate where the hydroxyl peaks 1π and 3σ should occur with respect to the molecular features according to our results for OH formation on Li precovered titania (see below and Table 1). In particular, 1π may account for the asymmetry of $1b_1$, and 3σ could contribute to $3a_1$. A rough estimate for an eventual OH coverage of the surface can be derived as follows: the molecular contribution is removed from the difference spectrum with the presumably largest OH contribution (spectrum 4 from the bottom) by subtracting the top spectrum of Fig. 1(b), normalized at 8 eV. This yields an OH coverage of at most 5% at this point.

The WF drops by about 0.5 eV from 4.9 eV within 1.5 L and stays roughly constant thereafter (see Fig. 3). For exposure > 2 L only rather weak

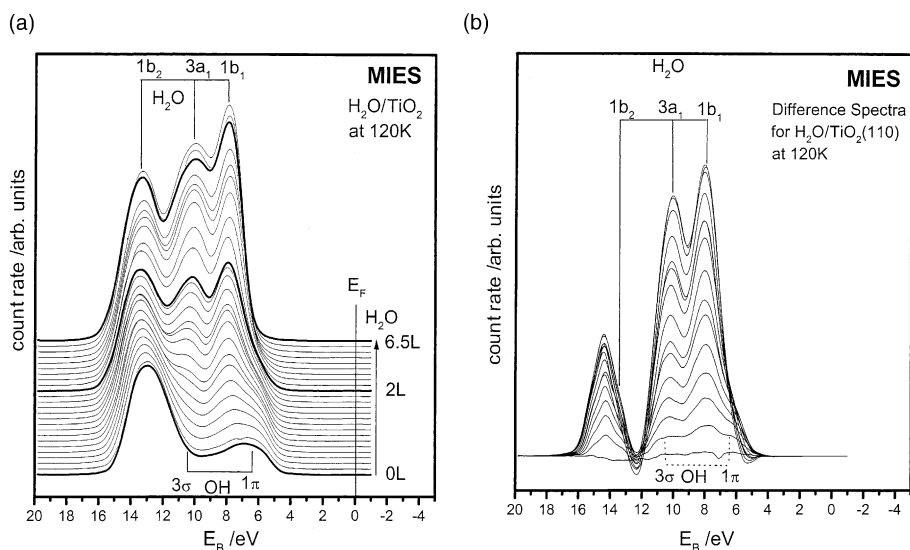


Fig. 1. (a) MIES spectra for $\text{TiO}_2(110)$ exposed to water at 120 K (see text for the acronyms). (b) MIES-difference spectra for the first 2 L of Fig. 1(a). Contributions to the spectra from the bare titania surface are removed.

substrate emission can be detected, indicating that surface oxygen is largely shielded from the interaction with the He^* probe atoms. Above 4 L surface oxygen is apparently no longer accessible to He^* .

HeI and II UPS spectra for bare titania (see Fig. 2(a) and (b)) were collected under the same conditions. HeI spectra could be obtained in two

ways, namely (a) quasi-simultaneously with the MIES spectra because the MIES source can also serve as a source for HeI photons, and (b) by using the commercial UV lamp as source for both HeI and II. The HeI data obtained with the two sources agree well with each other and with literature spectra. Weak band gap emission seen with HeI around $E_B = 1.2$ eV, denoted by Ti(3d), can

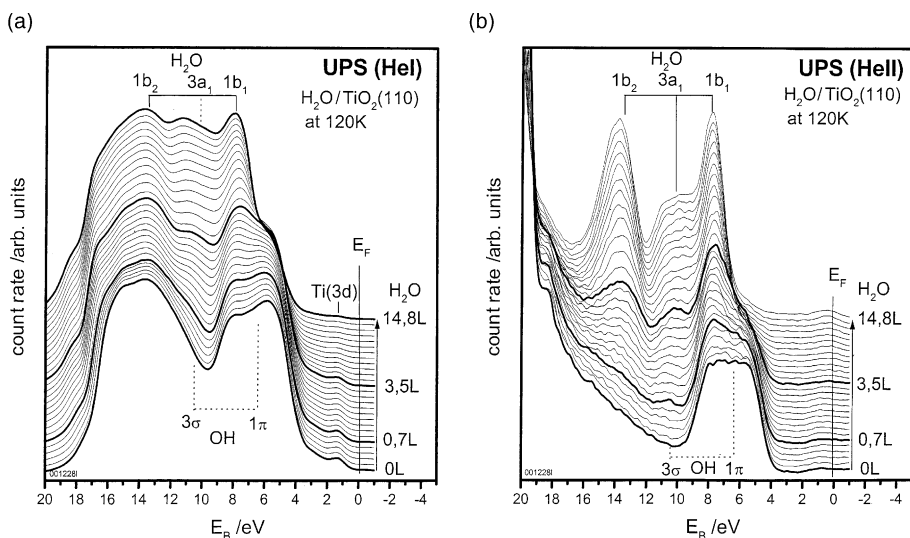


Fig. 2. (a) UPS(HeI) spectra for $\text{TiO}_2(110)$ exposed to water at 120 K. (b) UPS(HeII) spectra for $\text{TiO}_2(110)$ exposed to water at 120 K.

be attributed to reduced $Ti^{3+}(3d)$ cations, probably related to oxygen vacancies in the bridging oxygen rows, and was discussed previously when studying alkali adsorption on titania [23].

Emission from molecular water dominates the spectra. At low exposures, between 1 and 2.5 L in particular, some contribution of OH species cannot be excluded, though. The main differences between the UPS and MIES spectra are the relative intensities and the shape of the three water induced peaks, and that the substrate emission can be seen for larger exposures (beyond 4 L in HeII and up to at least 14 L in HeI) than for MIES reflecting the finite escape depth of the photo-emitted electrons.

The exposure dependence of the substrate emission, O(2p), the water-induced (molecular) features (H_2O), and the WF is shown in Fig. 3. A correlation is observed between the initial drop of WF, the increase of the water-induced signals, and the decrease of O(2p): H_2O roughly levels off at 12 L whereas the WF saturates around 2 L. The saturation of the WF, the 240 K TPD peak, and

the growth of the 165 K peak in the TPD spectra coincide. At this coverage the intensity of the water-induced features is about 50% of its final value. Therefore, we correlate 2 L on apparatus (1) to 0.5 ML. In UPS, however, the substrate O(2p) emission is still rather strong. The exposure dependence of H_2O , as seen with MIES, is linear up to around 0.5 ML and grows nonlinearly at higher coverages. The nonlinear rise of the MIES signal beyond 0.5 ML is inconsistent with layer-by-layer growth. Unlike the MIES results, the exposure dependence of the water-induced signals in UPS remains linear over a wide exposure range.

3.2.2. Electron spectroscopy results for TiO_2 pre-covered by Li atoms

The MIES spectra for $TiO_2(110)$ precovered by about 1 ML Li and exposed to water at 120 K are shown in Fig. 4. The presence of Li on the surface manifests itself in the structure denoted by Li(2s). It is due to the Auger deexcitation (involving the Li 2s electrons) of He^* probe atoms. The two

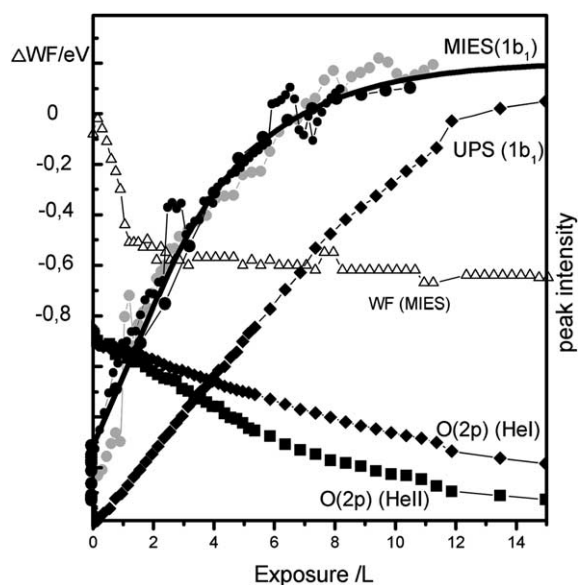


Fig. 3. Exposure dependence of the WF and various spectral features in the MIES and UPS spectra for H_2O/TiO_2 . WF: work function with respect to bare TiO_2 ; O(2p): valence band emission; $1b_1$: molecular water as seen with MIES or UPS; Solid line: simulation of the MIES $1b_1$ signal.

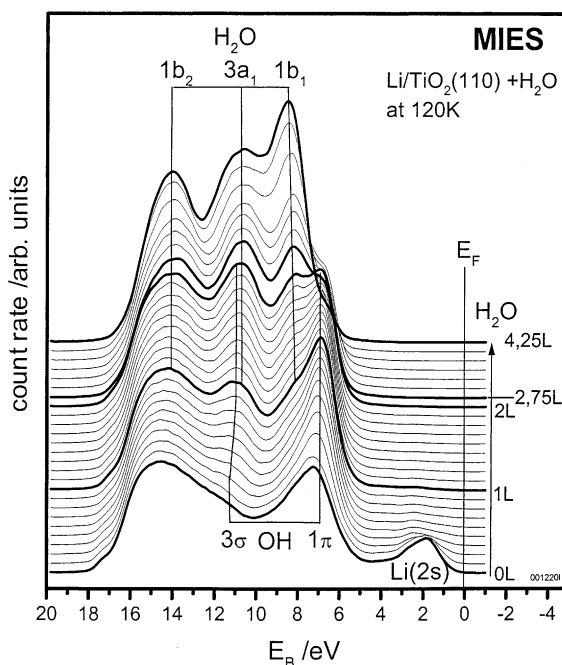


Fig. 4. MIES spectra for a Li-precovered $TiO_2(110)$ surface exposed to water at 120 K (see text for the symbols and acronyms).

features 1π and 3σ develop during water exposure. An inspection of Table 1 shows that they are due to OH species resulting from dissociative water adsorption. Interestingly, molecular adsorption has been reported for water adsorption on a Li film at room temperature [25]. Above 1.5 L the spectrum changes: apparently, 1π and 3σ become attenuated gradually, and beyond 2.5 L the spectra are dominated by the three molecular features $1b_1$, $3a_1$, and $1b_2$ already familiar from the water exposed bare $\text{TiO}_2(110)$ (see Fig. 1).

Provided that the position of the OH features is only weakly dependent on the chemical environment of the hydroxyl species, the results for the Li/ TiO_2 system are helpful for the interpretation of the spectra of Fig. 1: they allow us to position the OH features relative to those for molecular water. Accordingly, 1π and 3σ can be expected in Fig. 1 at the positions indicated by arrows. This makes it understandable that, for exposures below 0.5 L, small amounts of OH species are hard to identify on the bare titania substrate for the reasons that 1π overlaps with the, still present, O(2p) emission from the titania valence band, and 3σ overlaps with the $3a_1$ feature of H_2O .

UPS(HeI and II) and MIES spectra for Li/ $\text{TiO}_2(110)$ (for details see Ref. [24]) show the same behavior: OH formation occurs during the initial stage of water exposure as indicated by the growth of 1π and 3σ . At exposures beyond 2 L these OH features become, to a large extent, replaced by the three peaks $1b_1$, $3a_1$, and $1b_2$, similar to those from Fig. 1. However, both HeI and II indicate that the mixed layer grown initially, in contact with the substrate, remains intact at large exposures and is apparently topped by a water film: during the formation of the second layer the spectra still show emission from 1π ionization around 5.5 eV. For the 3 L exposure the HeII spectrum is characteristic for ASW [25], and for 12 L there is no structure different from ASW at all.

3.3. Water desorption by annealing to 600 K: electron spectroscopy and TPD results

TPD spectra were collected from titania films with different coverages of water in the temperature range between 100 and 600 K (for details see

Ref. [24]). For the mass 20 signal (D_2O) three different structures are visible. At low coverages a state around 240 K becomes populated. Then, an additional peak appears at 165 K, and finally the 155 K peak related to water multilayer formation starts to grow. Generally, our TPD results are in good agreement with those of Henderson [11]. TPD will be helpful for the following interpretation of our spectroscopic results.

Fig. 5(a) shows the MIES spectra of an ASW film (film thickness approx. 8 L) during annealing; the corresponding difference spectra obtained in the same way as those of Fig. 1(b) are shown in Fig. 5(b). Around 155 K multilayer water desorbs, and the intensities of $1b_1$, $3a_1$, and $1b_2$ decrease sharply. In the difference spectra the molecular features can be identified up to 220 K. Between 150 and 160 K the $3a_1$ feature appears best resolved which may be indication for structural changes in the water film occurring during the multilayer desorption. During multilayer desorption $1b_1$ develops a shoulder in the difference spectra. We attribute it to the presence of hydroxyl groups. They are responsible for the shoulder (1π), and contribute to the $3a_1$ peak around 10.5 eV (3σ). Above 220 K no clear features attributable to OH or molecular water can be identified.

As expected, the ASW film on Li/ TiO_2 desorbs around 155 K. The first mixed layer consisting of Li and OH, however, remains stable up to 400 K. This proves that the mixed layer, containing the OH species, remained intact when the second and the following layers of molecular species formed.

4. Discussion

Lindan et al. [9] reported first principle calculations for water adsorption on rutile(110) in which the consequences of interactions between adsorbed water molecules were taken into account explicitly. They predict that, because of hydrogen bonding, a monolayer of water contains both molecular and dissociated species. Our interpretation of the MIES and UPS spectra is guided by their results. In particular, the shape and exposure dependence of the water-induced spectral features can be explained best when assuming a strong

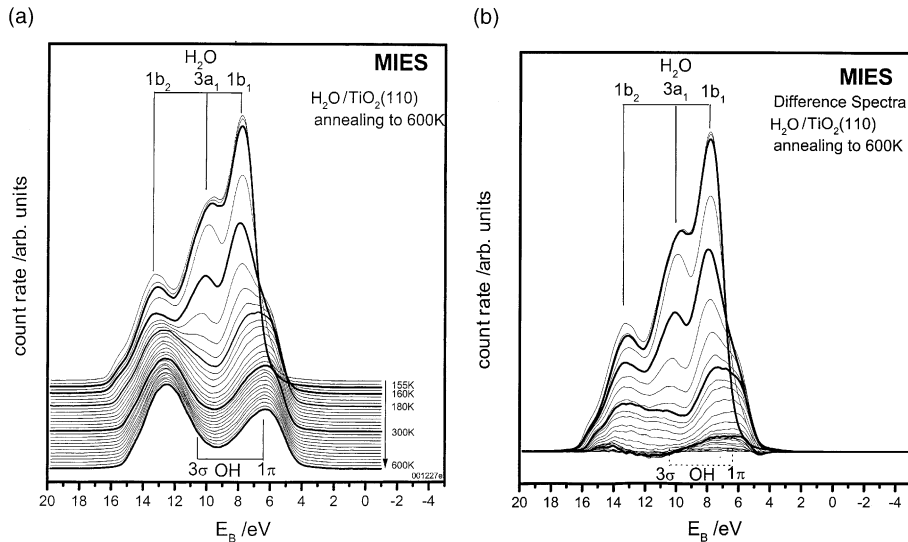


Fig. 5. (a) MIES spectra recorded during the annealing of an ASW film grown on TiO_2 at 120 K. (b) MIES-difference spectra from the results of Fig. 5(a). Contributions to the spectra from the bare titania surface are removed.

lateral interaction between the adsorbed molecules.

We have already stated that for exposures < 0.5 L the difference spectra suggest that molecular water and OH groups are present simultaneously. In the following we confine ourselves to the regime where molecular adsorption dominates.

The initial WF drop is caused by water nucleation at Ti sites [12]. Consequently, water nucleation at Ti sites is complete around 2 L where the WF saturates at about 4.3 eV. At larger exposures, additional sites will become populated. This picture is consistent with the decrease in the O2p intensity in UPS.

TPD has shown that the sticking probability of water at 120 K is constant [11]. Consequently, the coverage, both in MIES and UPS, initially increases linearly. The linear exposure dependence seen with MIES up to 2 L is compatible with a preferential adsorption at Ti^{4+} sites in good agreement with TPD (see Ref. [11], Fig. 4). The nonlinear exposure dependence of the water features beyond 2 L is inconsistent with layer-by-layer growth. This suggests the formation of 3D water clusters for exposures of 2 L. According to TPD the beginning of multilayer formation starts before the 170 K peak is saturated, in good agreement

with 3D water cluster formation above 2 L as determined from MIES. The small difference in the desorption temperatures of the 155 and 170 K states supports the possible formation of clusters. However, it is noteworthy that the amount of multilayer water with respect to that adsorbed in the 170 K state is much higher as seen in MIES than in TPD. This discrepancy can be explained in the following manner: in MIES the state is observed after adsorption. In TPD the situation is somewhat different because desorption of the molecules is observed for rising temperatures. Therefore, it is possible that part of the multilayer water is converted into the slightly thermodynamically favored 170 K state.

Another important finding is that no systematic variation is seen in the shape of the water-induced features over the range of submonolayer coverages to ASW. Moreover, the discrepancy with theory still exists that first principle calculations (except Ref. [7]) predict that isolated water species would be adsorbed as hydroxyl species on titania surfaces. Both facts can be explained conveniently if we assume that lateral interaction between adjacent water molecules is also important during the 2D growth (below 2 L), and is required to stabilize the molecular water species. Consequently, even at

low exposures, the adsorbed species find a local environment similar to that of ASW.

Our finding of a strong lateral interaction between adjacent water species on titania will remove the discrepancy between the theoretical and experimental results because so far, except for Ref. [9], theory has only studied the interaction of *isolated* water species with titania. In this case, hydroxyls are found to be the most stable adsorbed species. However, this is obviously not the situation studied experimentally: here, the lateral interaction between the adsorbed species is quite important, and may, even for low exposures, be responsible for the stabilization of molecular water. Recently, first principle calculations have been carried out for a (1×1) water overlayer on $\text{TiO}_2(110)$ [27] where the lateral interaction between the water molecules in the water rows is taken into account. Indeed, molecular adsorption is found to be energetically favored in this situation.

Fig. 3 displays a simulation (solid line) of the $(1b_1)$ signal, as seen with MIES, made as follows: 2D growth for <2.5 L would imply that the MIES signal rises linearly because the number of adsorbed molecules increases linearly with exposure, as long as the sticking coefficient is constant. Above 2.5 L it is supposed that the sticking probability for water on top of the bridging oxygen is equal to that on top of an already adsorbed one. This picture is supported by the fact that the desorption temperature of these two species is almost identical. Under these assumptions an exponential decrease of the number of substrate sites available for water adsorption with exposure is predicted.

The water interaction with MgO was studied with LEED and HAS [28] and with MIES, UPS, and TPD [14,19]. The following conclusions important for the interpretation of the present data come from that work: water exposure to MgO at 100 K leads to molecular adsorption, lateral interaction is already important during the 2D growth phase, and water is adsorbed, even before the first adlayer is complete, in form of 3D molecular clusters held together by the strong hydrogen bonding between the water species. The valence band spectra, including their exposure

dependence, are rather similar to the present results adding support for strong lateral interaction between water species on titania in the sub-monolayer regime.

MIES spectra for multilayer water formation on a CCl_4 film were reported in Ref. [29]. Clearly, because CCl_4 is highly hydrophobic, film formation in that case must be caused by lateral hydrogen bonding. Again the spectra are rather similar to those observed in the present work. The rather similar results obtained for TiO_2 , MgO, and CCl_4 strongly suggest that in all three cases the growth mode of the water film is rather similar.

Further evidence for the suggested importance of lateral interactions at sub-monolayer coverages comes from the HeII results for water on $\text{Ag}(111)$ [30]. As in the present case very similar spectra were reported for ASW and monolayers; moreover, the reported spectra are similar to ours for water/titania. In that case it is well known that hydrogen-bonded water species exist in the first adlayer [25]. Caused by these lateral interactions, $3a_1$, in particular, appears reduced in intensity and severely broadened. This adds support to our suggestion that the close similarity of ASW and sub-monolayer spectra for TiO_2 is also caused by lateral interactions between the adsorbed species.

The inspection of the difference spectra in Figs. 1(b) and 5(b) reveals that the intensity of hydroxyl features seen after the ASW desorption is larger than that found during the initial stage of the water exposure of the surface. Consistent with theory it was found for MgO [15] that dissociative adsorption of water at the MgO–ASW interface is energetically more favorable than molecular adsorption [15]. The stabilization of charged hydroxyl species was found to be due to the polarization of the surrounding solvent. The observation of OH intensity in Fig. 5 after the multilayer desorption suggests that some hydroxyl formation takes place at the ASW– TiO_2 interface.

The results for $\text{Li/TiO}_2 + \text{H}_2\text{O}$ furnish additional information on the water–surface interaction. On the basis of the available experimental and theoretical information on the adsorption site of potassium atoms on $\text{TiO}_2(110)$ and (100) surfaces (see Refs. [31,32]), we expect that the Li species occupy specific surface sites close to or on

top of the bridging oxygen rows. Upon water exposure the intensity of Li(2s) in the MIES spectra disappears quickly indicating that the Li2s electron is involved in the bonding of water to the Li precovered titania surface. Soon after Li(2s) has disappeared in the MIES spectra no further hydroxyl formation is observed. Most likely this is caused by a blocking of the reaction pathway because no 2sLi electrons are available anymore. The transfer of the 2s electron to the OH species suggests the formation of a (Li–OH)-hydroxide species. The finding that Li dissociates water efficiently is not surprising because alkali metals are well known in chemistry as electron donors; liquid water reacts instantly with alkali metals leading to the formation of hydroxides and the evolution of H₂.

Once the mixed adlayer consisting of Li and hydroxyl species is completed, additional water is adsorbed molecularly on top of this layer. The MIES and UPS spectra for multilayer water on Li/TiO₂ resemble those for ASW closely. Therefore, it appears likely that strong hydrogen bonding between the water species is responsible for molecular adsorption in the second and following layers.

We find [24] that Li deposition on ASW gives rise to a destabilization of molecularly adsorbed water: deposition of more than about 0.3 ML of Li leads to the formation of hydroxyl groups, at least in the proximity of Li. This finding again underlines the strong influence of Li on the dissociation of water: molecular water decays when proximate to coadsorbed Li species, because the stabilizing action of the hydrogen bonding with adjacent water molecules is reduced or even completely absent under these conditions.

5. Summary

We report electron spectroscopy (MIES and UPS(HeI and II)) and TPD results for water adsorption on bare and Li-precovered TiO₂, rutile(1 1 0) and films grown on Mo(1 1 0) at 120 K. For the adsorption on the bare TiO₂ surface we conclude that, apart from an eventual dissociative adsorption at defect sites which accounts for less than about 5% surface coverage, the adsorption is

molecular up to multilayer formation. Combining the information from the exposure dependence of the MIES and UPS signals and the TPD results we conclude that, even before the completion of the first adlayer, strong lateral interaction between adjacent species exists and stabilizes molecular water.

On TiO₂(1 1 0), precovered by about 1 ML of Li atoms, water is adsorbed dissociatively until the first mixed layer consisting of Li and OH species, is completed. A direct transfer of the Li2s electron to the hydroxyl species, compatible with hydroxide formation, takes place during the dissociation process. On top of the first layer, additional water is adsorbed molecularly.

Acknowledgements

Stimulating discussions with T. Bredow, E. Stefanovich, and D. Vogtenhuber are gratefully acknowledged. The authors would like to acknowledge the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for gracious financial support of this work.

References

- [1] V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, 1994.
- [2] H.-P. Boehm, H. Knözinger, in: *Catalysis: Science and Technology*, vol. 2, Springer, Berlin, 1983.
- [3] A. Fujishima, K. Honda, *Nature (London)* 238 (1972) 37.
- [4] A. Fahmi, C. Minot, *Surf. Sci.* 304 (1994) 343.
- [5] J. Goniakowski, M.J. Gillan, *Surf. Sci.* 350 (1996) 145.
- [6] T. Bredow, K. Jug, *Surf. Sci.* 327 (1995) 398.
- [7] E.V. Stefanovich, T.N. Truong, *Chem. Phys. Lett.* 299 (1999) 623.
- [8] P.J. Lindan, N.M. Harrison, J.M. Holender, M.J. Gillan, *Chem. Phys. Lett.* 261 (1996) 246.
- [9] P.J. Lindan, N.M. Harrison, M.J. Gillan, *Phys. Rev. Lett.* 80 (4) (1998) 762.
- [10] P. Jones, J.A. Hockey, *Trans. Farad. Soc.* 2669 (1971) 2679.
- [11] M.A. Henderson, *Surf. Sci.* 355 (1996) 151.
- [12] M.B. Hugenschmidt, L. Gamble, C.T. Campbell, *Surf. Sci.* 302 (1994) 329.
- [13] R.L. Kurtz, R. Stockbauer, T.E. Madey, E. Roman, J.L. de Segovia, *Surf. Sci.* 218 (1989) 178.

- [14] J. Günster, G. Liu, J. Stultz, S. Krischok, D.W. Goodman, *J. Phys. Chem. B* 104 (2000) 5738.
- [15] M.A. Johnson, E.V. Stefanovich, T.N. Truong, J. Günster, D.W. Goodman, *J. Phys. Chem. B* 103 (17) (1999) 3391.
- [16] W. Maus-Friedrichs, M. Wehrhahn, S. Dieckhoff, V. Kempter, *Surf. Sci.* 237 (1990) 257.
- [17] W. Maus-Friedrichs, S. Dieckhoff, V. Kempter, *Surf. Sci.* 249 (1991) 149.
- [18] D. Ochs, W. Maus-Friedrichs, M. Brause, J. Günster, V. Kempter, V. Puchin, A.L. Shluger, L.N. Kantorovich, *Surf. Sci.* 365 (1996) 557.
- [19] J. Günster, G. Liu, V. Kempter, D.W. Goodman, *J. Vac. Sci. Technol. A* 16 (1998) 996.
- [20] W.S. Oh, C. Xu, D.Y. Kim, D.W. Goodman, *J. Vac. Sci. Technol. A* 15 (1997) 1710.
- [21] Q. Guo, W.S. Oh, D.W. Goodman, *Surf. Sci.* 437 (1999) 49.
- [22] M.A. Henderson, *Langmuir* 12 (1996) 5093.
- [23] M. Brause, S. Skordas, V. Kempter, *Surf. Sci.* 445 (2000) 224.
- [24] S. Krischok, Ph.D. thesis, TU Clausthal (2001).
- [25] P.A. Thiel, T.E. Madey, *Surf. Sci. Rep.* 7 (1987) 211.
- [26] M. Faubel, in: C.Y. Ng (Ed.), *Photoionization and Photodetachment*, part I, *Adv. Ser. Phys. Chem.*, vol. 10A, World Scientific, Singapore, 2000, pp. 635–690 (Chapter 12).
- [27] D. Vogtenhuber, R. Podloucky, *Phys. Rev.* in press.
- [28] D. Ferry, A. Gebrov, V. Senz, J. Suzanne, J.P. Toennies, H. Weiss, *Surf. Sci.* 377–379 (1997) 634.
- [29] J. Günster, D.W. Goodman, S. Krischok, V. Kempter, *Surf. Sci. Rep.* in press.
- [30] P.M. Blass, X.-L. Zhou, J.M. White, *J. Phys. Chem.* 94 (1990) 3054.
- [31] T. Bredow, E. Apra, M. Catti, G. Pacchioni, *Surf. Sci.* 418 (1998) 150.
- [32] J. Muscat, N.M. Harrison, G. Thornton, *Phys. Rev. B* 59 (1999) 15457.
- [33] C. Mundt, C. Benndorf, *Surf. Sci.* 405 (1998) 121.
- [34] J. Günster, S. Krischok, J. Stultz, D.W. Goodman, *J. Phys. Chem. B* 104 (2000) 7977.