

# Interaction of alkali atoms with water multilayers adsorbed on $\text{TiO}_2(1\ 1\ 0)$ : a study with MIES and UPS

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## Abstract

The chemistry of alkali atoms (Li, Na, K, Cs) embedded in a multilayer aqueous environment was studied with metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS) (HeI and II) under ultra high vacuum (UHV) conditions. The water multilayers were grown at 130 K on a rutile,  $1 \times 1$  reconstructed,  $\text{TiO}_2(1\ 1\ 0)$  single crystal. The behavior of the multilayer system was investigated as a function of the temperature (130–500 K). Due to the relatively large escape depth of the emitted electrons UPS provides spectroscopic information about several layers in contrast to MIES which is only sensitive to the outermost layer. This allows us to discriminate between species adsorbed at the water multilayer and species, which are embedded in the solvent or at the substrate–solvent interface. Furthermore, MIES is, in contrast to UPS, very sensitive to the outermost s-states of adsorbed alkali atoms, which are considered to be responsible for the high reactivity of these metals.

The present study gives insight into the complicated chemistry of alkali atoms added to an aqueous multilayer system. The chosen combination of MIES and UPS allows us to distinguish clearly between various phases depending on the amount of offered alkali atoms. For low alkali concentrations the alkali atoms penetrate the water surface whereby they dissociate some water. With increasing exposure more and more water molecules become dissociated, whereby the outermost water layer remains intact. Finally, the chemistry between water and alkali atoms takes place at the outermost surface too, which is manifested by the formation of OH-groups at the surface. With further increasing alkali concentration the atoms start to adsorb as neutral atoms; whereby the spectrum of the alkali species is then strongly influenced by the underlying solvent system. For very high exposure the observed spectra are not influenced by the underlying aqueous system anymore; the formation of an alkali metal film is observed. Under annealing, the entire multilayer system desorbs around 200 K; a titania surface covered by hydroxyl groups and alkali ions is remaining. This adlayer desorbs under further annealing above room temperature (around 400 K, but dependent on the particular alkali atom) resulting in a titania surface.

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## 1. Introduction

At real surfaces (under natural conditions, far away from UHV) water is always present, either in form of hydroxyls or as molecular species [1]. The interaction between multilayers of water and

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molecular species at surfaces is also important for the corrosion of surfaces in contact with contaminated air/water. Another fascinating field, illustrating the importance of the chemistry of aqueous multilayer systems, is the atmosphere, where water is present in various forms (gas phase and condensed in clouds). This underlines that the chemistry of atoms and molecules at surfaces covered with multilayers of water constitutes a highly interesting field for surface science. The demand for investigating the chemistry at oxide-aqueous-solution interfaces was stressed in Refs. [1,2], and it was concluded that an understanding of the interfacial chemistry at the atomic level has not been achieved yet.

Recent reviews are available that deal with various aspects of the interaction of atoms and molecules with a multilayer solvent environment: the interaction of molecular (atmospheric) pollutants with ice [3], and atoms, as Na and Mg, with multilayers of solid water [2].

In heterogeneous catalysis the promoting role of alkalis is well known [4]. The coadsorption of alkali atoms and water has been studied at several occasions; the present knowledge is summarized in Ref. [5]. However, these studies deal with water coverages in the sub-monolayer regime mostly. The study of the chemistry on multilayers of water, liquid films in particular, is hampered by the high water vapor pressure which makes the application of standard surface-analytical techniques difficult. Recently, some studies on liquids with low vapor pressure were done [6]. Aqueous solutions of alkali halide salts were investigated with UPS(HeI) [7].

In the present study we use solid water films produced around 130 K as a model for liquid water. In this way the problems of the high vapor pressure of water at elevated temperatures are circumvented. However, the adsorbed alkali atoms are still very mobile in an aqueous multilayer system as long as the temperature is above 120 K as shown in previous studies [8].

The high mobility of the adsorbed atoms results in a rather complicated chemistry. Therefore, the combination of an extremely surface sensitive technique as the metastable impact electron spectroscopy (MIES) (which provides information on the top layer only) with UPS (which provides in-

formation about several layers) is essential to get information of the reactions in such a system including the reaction sites.

## 2. Experimental

The experiments were carried out in an ultra high vacuum (UHV) system (base pressure  $< 2 \times 10^{-10}$  Torr) equipped with low energy electron diffraction (LEED), X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS(HeI and II)), Auger electron spectroscopy (AES), and MIES, and is described in detail elsewhere [9,10]. In MIES metastable helium atoms ( $2^3S/2^1S$ ) are utilized to eject electrons from the substrate surface. A more detailed introduction in MIES and its various applications in molecular and surface spectroscopy can be found in recent reviews [6,11]. The energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level, denoted by  $E_F$ , i.e. electrons with the maximal kinetic energy, appear at the fixed energy  $E_B = 0$  eV. The position of  $E_F$  is determined from MIES spectra for alkaliated titania [12]. In the MIES spectra  $E_F$  is positioned at 19.8 eV by choosing a suitable bias potential; the low-energy cutoff in the spectra gives directly the surface work function, irrespective of the actual interaction process which produces the electrons. The UPS spectra presented in this work were collected with a separate UV-source (HIS 13, Omicron). This source allows the collection of HeII spectra, which is not possible with the combined MIES/UPS-source. The energy scale of the UPS spectra was adjusted in the same way as described above. Alkali atoms were dosed employing carefully out-gassed commercial dispenser sources (SAES Getters). They operate at a rate of 0.05 monolayers/min, typically. The procedure for the calibration of the alkali coverage is described elsewhere [12]. The surface was exposed to water by back-filling the chamber. The water was cleaned by several freeze-pump-thaw cycles. The relative amount of surface-adsorbed water can be estimated on the basis of earlier work with TPD and MIES [8,13]. The sample can be cooled with liquid nitrogen and heated by electron bombardment. A

temperature range between 130 and 2000 K is accessible.

### 3. Results and discussion

We begin the discussion with a summary of the spectral features observed during the growth of water films on titania and alkalated titania.

The adsorption of alkali atoms onto titania leads to a strong decrease of the surface work function (WF) due to an electron transfer from the adsorbate to the substrate [12]. As a consequence, the alkali atoms are adsorbed as  $M^{\delta+}$  ( $\delta$  close to 1). Therefore, the MIES and UPS(HeI) data exhibit a shift of the onset of the spectra to higher binding energy. In case of Cs a two peak structure arising from the ionization of the Cs(5p) orbital is visible at  $E_B \approx 12.5/13.8$  eV. For all other investigated alkali atoms (except for K in UPS(HeII)) the p-orbital is not visible in the spectra due to its high ionization energy. For K the emission from the 3p-orbital should be visible with UPS(HeII) and, indeed, is observed. However, a detailed discussion is difficult: in the same energy range emission originating from HeI ( $\beta$ - and  $\gamma$ -line) obscures the observed peaks. In addition, the O(2s) orbital is very close to the K(3p) orbital.

With increasing alkali coverage  $\delta$  decreases drastically. The resulting occupied outermost s-orbital is not seen for UPS, but, in contrast, is the dominating feature in the MIES spectra. The peak close to the Fermi edge ( $E_B \approx 1$  eV) clearly shows the power of MIES for investigating the chemistry between alkali metals and water, which is driven by the s-electron of the outermost orbital of the alkali (see for example [14]). The adsorption of water results in three peaks [5,15]. These peaks can be identified as emission from the three uppermost occupied water orbitals ( $1b_1$ ;  $3a_1$  and  $1b_2$ ). The corresponding binding energies in the MIES spectra are 7.8; 10.0 and 13.2 eV respectively. In addition, it is known for titania that water adsorption starts (beside possible adsorption at defect sites with eventual dissociation of water in the very low coverage regime) on the  $Ti^{4+}$  sites, followed by the growth of clusters [5]. The adsorption of water onto an alkalated titania surface (which

shows a partially filled s-orbital) leads to a strong dissociation of water. The resulting OH-species exhibits a two-peak structure ( $E_B = 7.0$  and 11.2 eV in case of Li) originating from the ionization of the  $1\pi$  and the  $3\sigma$  orbitals [5,15]. Furthermore, it was shown that MIES is able to distinguish between the coexisting water and hydroxyl-groups at the surface. The importance of the s-electron for the chemistry between alkali and water is underlined by coadsorption studies at room temperature, which clearly show that an alkali ion does not dissociate water molecules [16].

Here we will confine ourselves to a qualitative analysis of the MIES spectra, based on the assumption that the discrete features seen, are due to the AD process, and that the spectral feature represents the surface density of the states of the respective species. As was demonstrated in Refs. [6,9,12,17], a more quantitative analysis of the MIES spectra is possible.

#### 3.1. Adsorption of potassium onto solid water

Here we discuss our findings for the K-water system. The MIES results for an solid water film (3 ML thick) exposed to K ions are shown in Fig. 1. The bottom spectrum shows the typical structure already identified as molecular water. Under exposure to potassium the observed spectra remain virtually unchanged except for the change of the absolute position of the peaks parallel to the WF change. With increasing potassium coverage a doublet appears resulting finally in MIES spectra governed by two peaks at approximately 7 and 11 eV due to OH-species (see above). It is worth noting that the amount of alkali atoms needed to induce this two-peak structure is increasing with the water film thickness (not shown here). Under further potassium dosage the two-peak structure starts to disappear and a peak at  $E_B = 1.5$  eV starts to grow together with a satellite peak at 3 eV. For higher K exposures these peaks become smaller and a third peak at the Fermi level starts to grow.

The corresponding UPS (HeII) spectra (Fig. 2) show the following behavior. Initially (the uppermost spectrum) the fingerprint of the molecular water and to some extent of the O(2p) band of the



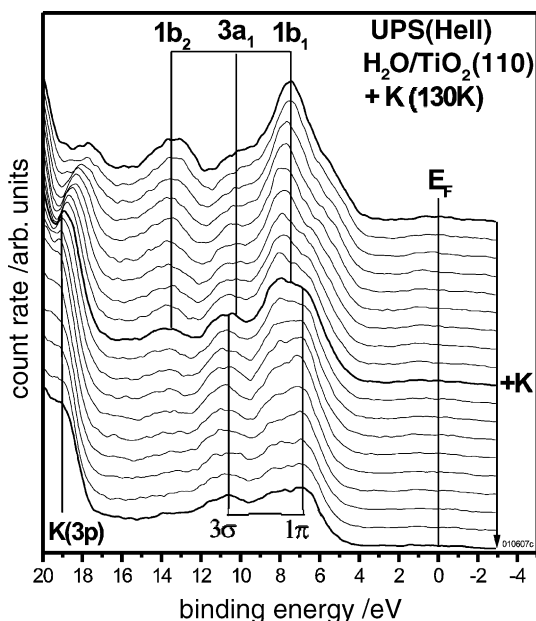


Fig. 2. UPS(HeII) spectra for the adsorption of potassium onto a solid water film (3 ML thick) at 130 K.

of the water surface. Most likely, the transport of the alkali<sup>+</sup> and OH<sup>-</sup> species, resulting from the water dissociation, is facilitated by their (partial) hydration.

For sufficiently large exposures this mechanism is not working anymore (due to the decreasing concentration of molecular water) and the accommodation of OH groups starts also at the surface: hydroxyl groups become visible with MIES.

The s-electron of the adsorbed alkali atoms is still not seen with MIES, which clearly shows the formation of alkali ions. Under further exposure the UPS spectra are virtually unchanged except for the loss in intensity of the OH related peaks. At large exposures the alkali atoms adsorb as a neutral species because a peak (at 2.1 eV with a satellite at 3.8 eV) related to the ionization of the outermost s-electron appears in the MIES spectra. However, it is shifted against the position observed for very high exposures, which is identical with that for the alkali adsorption on solid surfaces (including TiO<sub>2</sub>). The shift shows the influence of the aqueous environment and can be understood on the basis of the Born model [7].

No information on the fate of the H-species from the water dissociation can be obtained from our techniques. We cannot exclude the desorption of the formed H-species. However, in the light of the results available for the HCl–water interaction [3,18], it appears not unlikely that the hydrogen originally bonded to water moves to another water molecule, thereby forming H<sub>3</sub>O<sup>+</sup>.

### 3.2. Annealing of the alkali-exposed water multilayer

Figs. 3 and 4 show the change of the MIES and UPS(HeII) spectra respectively upon annealing films containing neutral alkali atoms and solvated alkali hydroxide between 130 and 500 K.

In MIES the intensity of the hydroxyl related features grows with increasing temperature. At approximately 200 K the spectra change drastically: the emission marked as K(4s) disappears suddenly and the hydroxyl peaks gain in intensity and shift to lower binding energy by approximately 1 eV. Under further annealing the hydroxyl peaks disappear; at 500 K the MIES spectrum is rather similar to that for clean titania.

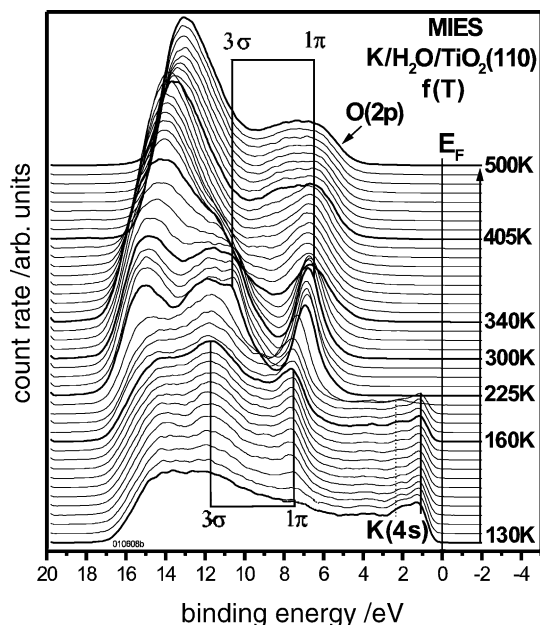


Fig. 3. MIES spectra during the annealing of the multilayer system produced in Fig. 1.

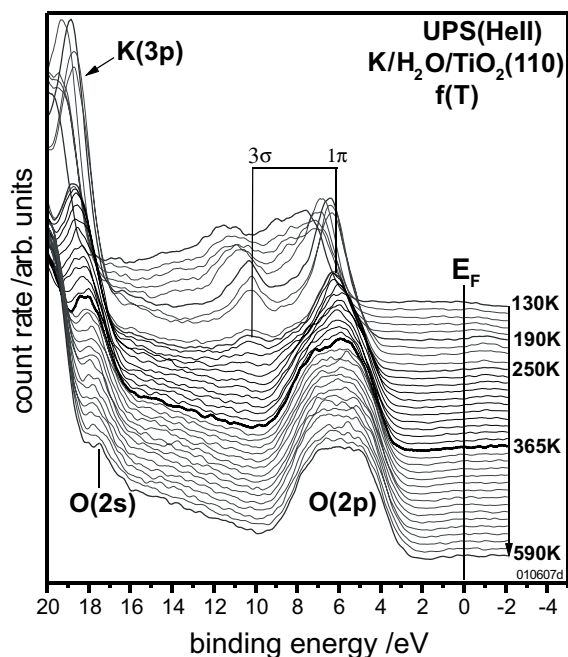


Fig. 4. UPS(HeII) spectra for annealing the multilayer system produced in Fig. 2.

In the UPS spectra drastic changes of the spectra are seen in the same temperature range. At 190 K a dramatic rise in the hydroxyl intensity is observed. Under further annealing the hydroxyl peaks disappear gradually and the O(2p) band of the underlying titania is gaining intensity until the spectrum for clean titania is observed.

We offer the following explanation for these results: with rising temperature the complete system becomes more and more mobile resulting in a slightly higher amount of hydroxyls at the surface as judged from the MIES spectra. At a certain temperature ( $\approx 200$  K for potassium) the neutral alkali atoms desorb. This leads to the disappearance of the peaks close to the Fermi edge which originate from the s-orbital of the alkali atoms in the MIES spectra and to the strong increase of the signal related to the remaining hydroxyl species both in MIES and UPS. This results in a  $\text{TiO}_2$  surface which is terminated with a layer consisting of  $\text{OH}^-$  (and probably alkali ions as suggested by the presence of Cs(5p) emission in corresponding measurements on the Cs-water-system in MIES

and UPS). Under further annealing this adlayer gradually desorbs as is suggested by the disappearance of features related to the adsorbed species and the continuous growth of the substrate induced structures. Finally, both in MIES/UPS, spectra of the clean  $\text{TiO}_2$  are seen.

#### 4. Conclusions

The present study gives insight into the chemistry between alkali atoms and an aqueous multilayer environment (here a multilayer of solid water). Besides the identification of the reaction site in various coverage regimes, the resulting adsorbed species are identified. The supply of alkali atoms induces, in contrast to alkali ions [13], a dissociation of adsorbed water molecules, whereby OH-species and alkali<sup>+</sup>-ions are formed. The reaction products are first accommodated below the surface and show up at the outermost surface for comparatively high exposures. Further alkali supply leads first to the adsorption of a neutral alkali species interacting with the hydroxyl top layer and finally to the formation of an alkali film with metallic properties. Annealing experiments show that the most stable species is a hydroxyl species, eventually stabilized by alkali ions, at the solid surface.

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