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The chemistry of alkali atoms on solid water: a study with MIES and UPS

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Abstract

The chemistry of Na atoms in a multilayer aqueous environment was studied with metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS) under UHV conditions. Films of solid water were grown at 130 K on a rutile, 1×1 reconstructed, $\text{TiO}_2(110)$ single crystal, and exposed to Na. The Na–water interaction was studied between 10 and 130 K.

At small exposures, Na-induced water dissociation takes place whereby the Na gets ionized. Initially the outermost water layer remains intact. The number of OH species seen at the surface increases with exposure; finally, no molecular water, but only OH species can be detected with MIES and UPS. At sufficiently large exposures Na atoms are detected at the surface. We find that efficient water dissociation and Na solvation take place only above about 100 K.

Under annealing, the mixed film is destroyed around 200 K; the titania surface is then covered by Na^+ and hydroxyl groups which desorb around 400 K.

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1. Introduction

The demand for investigating the chemistry at oxide–aqueous solution interfaces was stressed in [1,2]; the importance of such studies for the cor-

rosion of surfaces in contact with contaminated air/water and for the atmosphere, where water is present in various forms (gas phase and condensed in clouds), is evident. 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 is in the focus of [3], while [1] concentrates on the interaction of atoms, Na and Mg, with multilayers of solid water (SW).

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In the present study we use SW films produced at 130 K on TiO₂ and Pt substrates as a model for liquid water. In this way problems connected with the high vapour pressure of water at elevated temperatures are circumvented, and electron spectroscopy can be applied. However, the adsorbed alkali atoms are still very mobile in an aqueous multilayer system as long as the temperature is above 100 K as shown in previous studies [1]. 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) (providing information on the top layer only) with UPS (providing information on several layers) is essential to get information of the reactions in such a system.

2. Experimental remarks

The experiments were carried out in ultra-high vacuum (UHV) systems (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 are described in detail elsewhere [4–6]. 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 [7,8].

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 alkalated titania [9]. 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 (WF), irrespective of the actual interaction process which produces the electrons.

Na atoms were dosed employing carefully out-gassed commercial dispenser sources (SAES Getters). They operate at a rate of 0.05 monolayers (ML)/min, typically. The procedure for the cali-

bration of the alkali coverage is described elsewhere [9]. The exposure is given in units of monolayer equivalents (MLE); at 1 MLE the surface would be covered by a Na monolayer if it would not be for penetration effects.

The surface temperature can be varied between 10 and 2000 K [5,6]. The surface was exposed to water by backfilling the chamber at a substrate temperature between 110 and 130 K. This ensures the formation of a closed, non-porous and amorphous SW film [10]. The formation of an ordered film would require a certain degree of mobility of the water molecules; below 140 K this mobility does not exist anymore. The relative amount of surface-adsorbed water can be estimated on the basis of earlier work with TPD and MIES [5,11]. Prior to Na exposure the surface prepared in the way as described above was cooled to the desired temperature.

3. Results and discussion

The following spectral features are expected when Na and water interact with surfaces:

The 2pNa-orbital, due to its high ionization energy, is not accessible by the chosen techniques. If the Na coverage becomes of the order of 0.5 ML, surface-adsorbed Na is partially neutral. With UPS (HeI) the partially occupied 3s orbital is practically not seen due to its low photoionization cross-section [12]. However, in MIES it causes the dominating feature Na(3s), close to E_F . This underlines the power of MIES for investigating the chemistry between Na and water, which can be expected to be driven by the 3s-valence electron.

Molecularly adsorbed water produces three peaks identified as emission from the three uppermost occupied water orbitals 1b₁, 3a₁ and 1b₂ [13,14] (binding energies 7.8, 10.0 and 13.2 eV, respectively). In contrast, the adsorption of water onto partially alkalated titania leads to water dissociation provided the precoverage is larger than about 0.5 ML [5]. The ionization of the OH 1 π and the 3 σ orbitals yields peaks at $E_B = 7.0$ and 11.2 eV, respectively [13,14].

We will confine ourselves to a qualitative analysis of the MIES spectra, based on the assumption

Under exposure to Na the spectra remain virtually unchanged apart from the change of the peak positions simultaneously with the Na-induced WF change. Above 1 MLE the MIES spectra are governed by OH emission. The exposure required to see appreciable OH emission with MIES is increasing with the SW film thickness (not shown here). At still larger exposure the OH structure fades away gradually; instead, peaks (1), (2) and (3) from the ionization of Na 3s appear at $E_B = 1.2$, 2.2 and 4 eV, respectively. For exposures >4 MLE (1) dominates, and the spectra resemble those for Na adsorption on metals where (1) dominates. The origin of (1)–(3) will be discussed below.

The intensity of feature (2) of the Na(3s) structure, $1b_1$ (from molecular water), and 1π (from OH) are presented in Fig. 2 versus the Na exposure for 130, 110 and 10 K (graphs (a)–(c), respectively). Results for the other alkali atoms (not shown here, see [16]) are qualitatively rather similar. At 130 K (Fig. 2(a)), the peculiar exposure dependence of the 1π and $1b_1$ emission suggests that the intensity decrease of $1b_1$ is to a large extent caused by the appearance of OH species at the surface, suggesting that the water molecules in the surface become replaced by OH species from the reaction with Na.

When annealing the film characterized by the bottom spectrum in Fig. 1(a) between 130 and 500 K, the intensity of the hydroxyl-related features grows initially with increasing temperature. Around 200 K Na(3s) disappears, the hydroxyl peaks gain in intensity and shift to lower binding energy by about 1 eV. Under further annealing the hydroxyl peaks disappear; at 500 K the MIES spectrum is already similar to that for clean titania. UPS spectra show similar changes in the same temperature range.

The same spectral features are seen for Na adsorption on SW at 110 and 10 K (Fig. 1(b) and (c)). However, their dependence on exposure is different (Fig. 2(b) and (c)). At 10 K, appreciable Na(3s) emission (signaling partially neutral Na species) is seen already at 0.25 MLE, and the OH peaks remain comparatively small for all studied exposures. H_2O is not converted into OH at the surface, but the intensity of the molecular peak $1b_1$ is simply attenuated by the shielding of the water by the Na atoms. At 110 K the situation is inter-

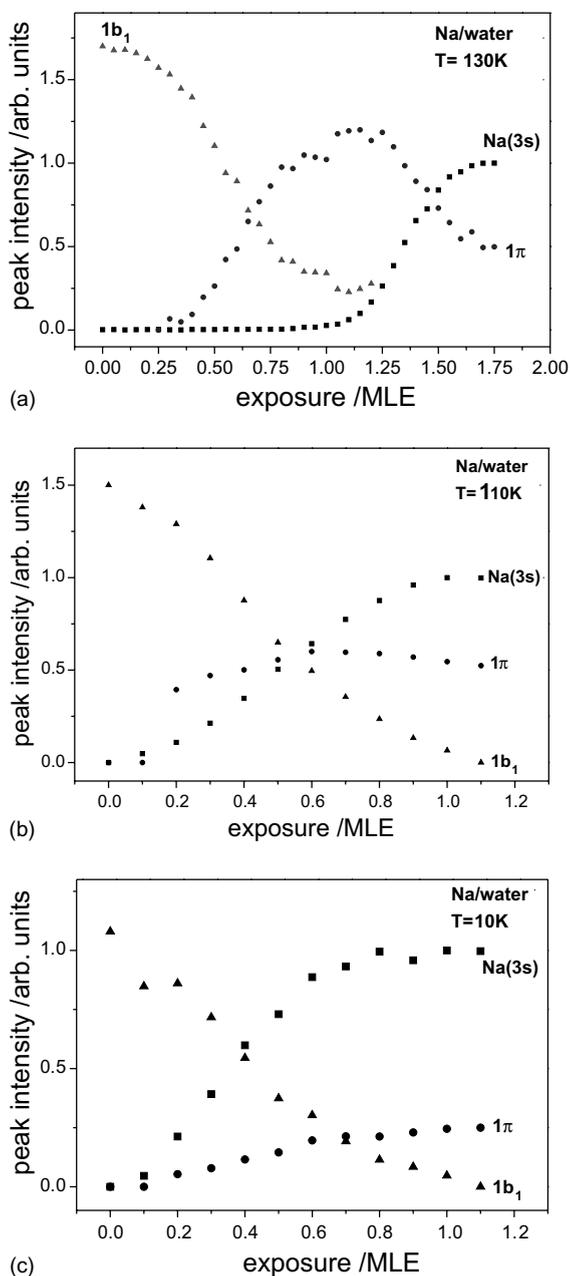


Fig. 2. Intensities of molecular water ($1b_1$), OH (1π) and Na (Na(3s); peak (2)) (data from Fig. 1) for Na exposure to SW films held at (a) 130, (b) 110, (c) 10 K.

mediate between 10 and 130 K. Clearly, the reaction between Na and water does not take place anymore efficiently at 10 K; from additional data

for SW films on MgO [1] we estimate that the threshold is around 100 K.

Our earlier results for the adsorption of water molecules on titania, precovered by alkali atoms, and those for codeposition of alkali and water on titania [5,17,18] underline the importance of the alkali s-valence electron for the water dissociation: only when the alkali-induced structure, Na(3s) in the present case, is seen, i.e. when the Na is partially neutral, OH features occur in the spectra, and dissociation takes place. With this in mind we invoke the following scenario in order to explain our results for the Na interaction with the film held at 130 K: exposure leads to the formation of Na⁺ and OH⁻ species. Although details of the underlying reaction are not clear at present, the above-mentioned results suggest that the 3s Na-electron plays a key role in the process. At least two possibilities come to mind that could lead to Na⁺ formation:

- (1) A direct transfer of the 3s electron between the Na adsorbate and the substrate via resonant tunneling could take place through the relatively thin SW film. In fact, the dependence of the Na(3s) signal, observed as a function of the SW film thickness [6], points to the possible relevance of this mechanism.
- (2) A transition could occur between different states of a Na–water–surface complex, as from Na_m·(H₂O)_n to Na_m⁺·(H₂O)_n⁻ [19].

Proton mobility may be responsible for the removal of the OH⁻ species from the surface and its solvation in the SW film; a mechanism leading to OH-solvation in ice is discussed in [20].

At least at 130 K, the Na species are also removed efficiently from the surface and become solvated. Consequently, at low exposures an intact water surface, as seen with MIES for <0.5 MLE, is preserved. This implies that the water molecules possess enough mobility to hydrate the alkali species efficiently. The formation of alkali ion–water clusters was also seen in low-energy reactive scattering from SW [21]; multi-hydrated cluster Cs(H₂O)_n⁺ ions are produced with substantial intensities in low-energy Cs⁺ collisions with SW. It is concluded that these clusters are created through condensed-phase reactions in the SW top layer.

Unfortunately, no information on the fate of the H-species from the water dissociation can be obtained from our techniques.

The process sequence invoked above takes place as long as Na finds an intact molecular water surface. As consequence of the formation of an OH⁻ surface layer at large exposures, the transfer of the 3s electron to the film is inhibited, and neutral Na species appear at the surface as manifested by the structure Na(3s). However, initially Na(3s) is shifted against the position observed for the alkali adsorption on metallic surfaces, and gives rise to peak (2). We believe that this shift is caused by the influence of the aqueous environment [22]. Only when Na multilayers are being formed, the peak Na(3s) adopts the energetic position (peak (1)) found for metals. The small peak (3), at about 2 eV larger binding energies, possibly originates from a surface plasmon loss involving small Na clusters with a narrow size distribution [1,6].

There is no need to invoke additional processes in order to explain the data obtained at the lower temperatures $T = 110$ and 10 K of the SW film. Apparently, all processes, the hydration of Na⁺ and OH⁻ in particular, proceed considerably slower because of the reduced water mobility. Consequently, the surface sites required to accommodate and eventually ionize newly arriving Na atoms may become blocked. This will explain the much faster build-up of regions consisting of neutral Na.

4. Conclusions

The present study gives insight into the chemistry between Na and an aqueous multilayer environment. At 130 K the supply of Na to a film of SW induces efficient dissociation of water molecules, whereby OH⁻ and Na⁺ ions are formed. At low exposures these reaction products are removed from the surface and become solvated in the film. This process sequence takes place as long as newly arriving Na atoms find an intact molecular water surface. As soon as this is not anymore the case, Na supply leads to the adsorption of neutral Na species at the surface. At temperatures below

about 110 K the OH production becomes less efficient and Na atoms appear already at much smaller exposures. It is our interpretation that the surface sites active in water dissociation become blocked because the solvation of Na–water complexes formed at the surface does not take place efficiently anymore.

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