

Interaction of Na with Multilayer Water on MgO(100)

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The reaction between Na and multilayer water on MgO(100)/Mo(100) has been studied by metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), and temperature-programmed desorption (TPD). A water multilayer was exposed to Na at 100 K. During exposure, an attenuation of the surface water concentration concomitant with the formation of surface hydroxyls and metallic Na clusters is observed. After an anneal to 155 K, the metallic Na clusters disappear and the surface hydroxyls are essentially removed from the outermost surface, leaving water as the dominant surface species. Further annealing to > 170 K leads to massive water and NaOH desorption, as indicated by TPD. After desorption of all multilayer components the species stabilized at the surface is primarily hydrated NaOH, which is stable up to 530 K.

1. Introduction

The chemistry between a solvent and a surface is a challenging field for surface science since it combines the complexities of a three-dimensional system, i.e., the solvent, with those of a two-dimensional system, i.e., the surface–adsorbate interface. The investigation of an isolated molecular species on surfaces is a common theme of many surface science studies, however little is known about the interfacial chemistry of multilayer systems, especially under well-defined conditions. In particular, the interaction of single water molecules with a model basic oxide, e.g., magnesium oxide, has attracted considerable recent attention.^{1–5} In general, those studies have addressed submonolayer–substrate interactions. However, in naturally occurring systems, surface–adsorbate reactions occur in the multilayer rather than the submonolayer coverage regime. Recently we have shown a marked contrast between the interaction between a MgO(100) surface with isolated water molecules compared to a water multilayer system.⁶ For example, the adsorption of submonolayer water on a MgO(100) crystal surface is found to be nondissociative,^{1,2,7,8} however, due to polarization of the solvent in a multilayer system, charged species formed at the solid–liquid interface can be stabilized and the dissociation of water can become energetically favorable.⁶ For chemistry at surfaces that occurs in an aqueous environment, the balance between solvation, chemical reaction, and stabilization of solvents and reaction products at the adsorbate substrate interface are important factors. Studying these processes can provide a more in-depth understanding of the chemistry of simple structured molecules with surfaces under conditions relevant to environmental chemistry. For that reason, we have examined in the present study the interaction between Na and multilayer water on MgO covered Mo(100).

The use of electron spectroscopic techniques to address the chemistry of small molecules on surfaces has been proved to be a very powerful approach. However, one general problem in the investigation of multilayer systems is the limited surface sensitivity of typical surface electron spectroscopies. The finite escape depth of the exiting electrons associated with a particular probe technique limits the sensitivity of the technique, often making it difficult to distinguish between a species adsorbed on and one solvated in a multilayer, adsorbate system. For that

reason we have applied in the present study metastable impact electron spectroscopy (MIES) as an electron spectroscopic technique which provides superior surface sensitivity.

2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) system (base pressure $< 2 \times 10^{-10}$ Torr). The UHV system consists out of two interconnected chambers, one for sample treatment, equipped with low energy electron diffraction (LEED) and temperature-programmed desorption (TPD) and the second, with facilities for X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), Auger electron spectroscopy (AES), and MIES. MIES and UPS spectra were measured simultaneously using a cold-cathode discharge source which provides both ultraviolet photons (HeI) and metastable He* $2^3S/2^1S$ ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy. The triplet-to-singlet ratio has been measured by He*–Ar impact as 7:1. 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 beam 45° with respect to the surface normal in a constant pass energy mode using a double pass cylindrical mirror analyzer (CMA), PHI model 15-255G. Collection of a MIES/UPS spectrum requires approximately 120 s. The energies denoted by E_F in the spectra correspond to electrons emitted from the Fermi level of the Mo(100) substrate. In the following spectra all binding energies are referenced to E_F . Since the metallic Mo substrate and the analyzer are in electrical contact, the Fermi energy appears, independent of the substrate work function, at a constant position in the spectra. An additional biasing of the sample (45 V, negative on the sample) permits the work function change of the surface to be measured directly from the high binding-energy cutoff of the spectra.

MgO films were grown by depositing Mg in 1×10^{-6} Torr of O₂ ambient on the Mo(100) surface at 550 K. The Mg source was constructed from a high-purity Mg ribbon wrapped around a tantalum filament. To ensure a stoichiometric MgO layer, the as-prepared surface was further annealed to 900 K in a 1×10^{-7} Torr of O₂ background for 20 min. As shown in previous investigations, MgO films prepared under these conditions grow

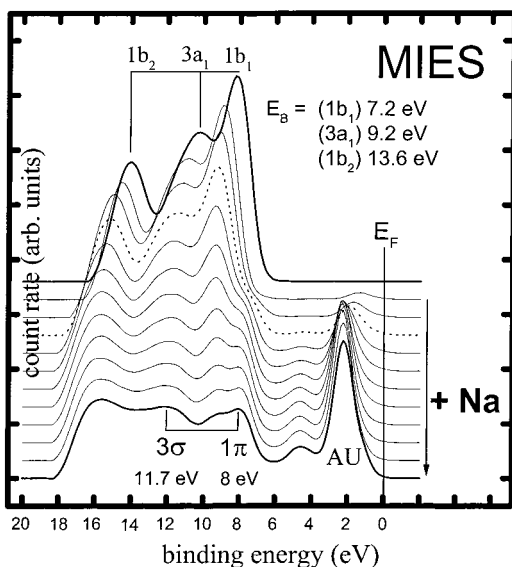


Figure 1. MIES spectra of the multilayer water covered MgO(100)/Mo(100) substrate as a function of the Na exposure. The uppermost spectrum shows the water-covered surface without Na. The direction of the data collection and the relative Na exposure are indicated by the arrow.

epitaxially on the Mo(100) substrate and their properties with respect to the adsorption of water are comparable to those of MgO single crystals.^{9,10} D₂O (CIL, 99.9%) was dosed to the surface by backfilling the vacuum system after purification via several freeze–pump–thaw cycles. Na was deposited onto the surface using a SAES Getters source.

3. Results

The sequence of MIES spectra in Figure 1 was acquired during Na exposure to a water precovered MgO(100)/Mo(100) substrate held at a temperature of 100 K. Since a similar experiment has been discussed in detail recently¹¹ we will introduce these data only briefly. Prior to the sodium exposure (uppermost spectrum), water (approximately 4 monolayers, ML) was dosed to the MgO covered Mo(100) substrate at 100 K. At this temperature, due to the limited mobility of the water molecules, the resulting water multilayer typically exhibits an amorphous structure designated as amorphous solid water (ASW). Binding energies for the three water bands 1b₂, 3a₁, and 1b₁^{12–14} are indicated in Figure 1. In the spectra of Figure 1 the sodium exposure increases linearly from top to bottom. In the initial stages of Na exposure, the high energy cutoff of the spectra shifts toward higher binding energies indicating a reduction of the substrate work function; the binding energies of the water bands show the same trend. With increasing sodium exposure, three additional modifications in the sequence of MIES spectra are noteworthy: (i) a lowering of the overall spectral intensity of the water bands; (ii) at 8.3 eV the appearance of a new feature, designated as 1π; and (iii) near E_F, the appearance of a prominent new feature (AU). The AU feature does not correlate with a change in the surface density of states (SDOS) but originates from resonant ionization of the He* projectile due to the overall lowering of the surface work function and the formation of sodium clusters with metallic character. The formation of this pronounced AU feature indicates that a significant portion of the impinging He* projectiles are resonantly ionized (He*⁻ formation) and ultimately decay via an auto-detachment (AU) process into the He ground state. In this context it is noteworthy that the AU process competes

directly with the Auger deexcitation process that is responsible for most of the intensity between 6 and 18 eV. Thus, the attenuation of the intensity between 6 and 18 eV with increasing Na coverage is partially due to an increasing probability for AU. However, AU becomes significant only at low work function surfaces with sufficient electron density near E_F.

From these observations the following picture for the adsorption of sodium on multilayer water at 100 K emerges. In the initial stages of sodium adsorption, the lowering of the substrate work function indicates the formation of a surface dipole layer likely induced by complete or partial electron transfer from the sodium adsorbate to the substrate. Since the water bands shift in concert with the substrate work function, the ionization energy of the water molecules remains essentially constant. Similar results have been reported by Blass et al.¹⁵ with UPS (HeII) while dosing water to a Ag(111) surface precovered by varying amounts of potassium. As a function of the potassium precoverage (up to 0.77 ML) the water bands shifted to higher binding energies. This shift was presumed to indicate the formation of a dipole layer at the water/potassium/Ag interface with a large fraction of the water located above the dipole layer.

In surface sensitive electron spectroscopies, spectral features following the substrate work function change are typically associated with species located within or on top of the dipole layer responsible for the work function change. In the present experiment, however, Na was added to a water multilayer. For that reason, a dipole layer formation below the outermost water layer is possible only if the Na penetrates into the ASW multilayer, presumably through the microporous structure previously proposed for ASW.¹⁶

The minimum work function of the surface is reached at the fourth MIES spectrum (dotted spectrum), in which the 1π and AU features are apparent. Increasing the Na exposure results in the enhancement and finally saturation of both structures. Blass et al., observed a feature similar to the 1π with UPS- (HeII), and interpreted it in terms of K⁺[(H₂O)⁻_n] complex formation. This, however, requires mobility to some extent of the water molecules. On the basis of the present data, an unambiguous interpretation of the 1π structure is not possible, since the formation of a hydroxide-like species (NaOH) at the outermost water surface is plausible. With this in mind, the anticipated position of the hydroxyl 3σ band at ~4.1 eV binding energy is indicated in the figure. The pronounced AU feature indicates that metallic sodium clusters are formed from the excess sodium at the vacuum–water interface. In this context the small AU-satellite at 2 eV higher binding energies, most likely originating from a surface plasmon loss from small Na clusters, lends additional support to the formation of clusters with metallic character. Since the surface plasmon energy depends strongly on the cluster size, a uniform cluster size distribution is apparent.

Figure 2 presents a sequence of MIES and UPS spectra obtained from the surface prepared in Figure 1, i.e., a sodium covered water multilayer, as a function of the substrate temperature. Spectral features assigned in the figure are the three water bands (1b₁, 3a₁, and 1b₂), the two hydroxyl bands (1π and 3σ), and the AU peak. Before discussing Figure 2 in detail, it is appropriate to define three temperature regions, each corresponding to a particular structure of multilayer water: (I) between 100 and 132 K, within which the adsorbed water molecules are randomly oriented and have a low mobility (ASW); (II) near 155 K, within which the mobility of the water molecules increases significantly, enabling the phase transition from ASW to thermodynamically favored crystalline ice;^{17,18}

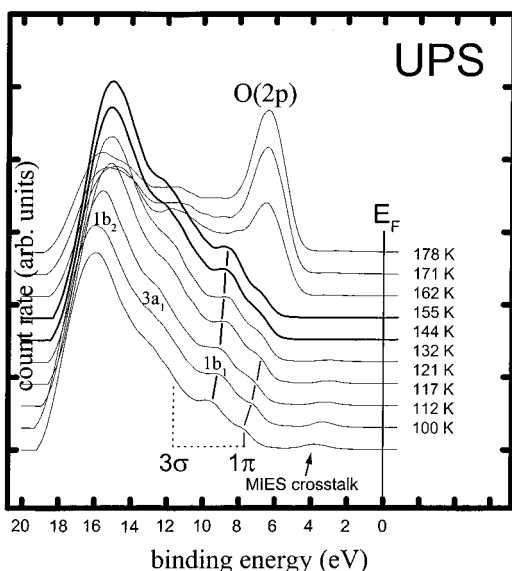
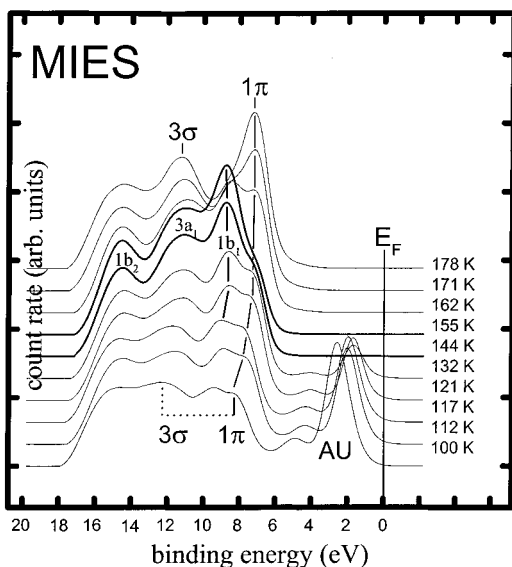


Figure 2. MIES and UPS spectra of the surface prepared in Figure 1, i.e., a Na covered water multilayer on MgO(100)/Mo(100), as a function of the anneal temperature.

and (III) over 170 K, within which multilayer water desorption becomes significant. Noting these three temperature regions, major changes are apparent in the sequence of MIES spectra in Figure 2. In region I, from 100 to 132 K, the attenuation of the AU peak indicates the disappearance of metallic sodium clusters formed at the outermost surface. The water and hydroxyl bands show no significant change in intensity, but shift ~ 1 eV toward lower binding energies, in direct contrast to the shift observed upon sodium exposure. The work function increases by about 1 eV. In region II, near 155 K, the 1π features is weakened whereas the water bands increase in intensity. Apparently, the increasing molecular mobility leads to reorganization such that the water concentration on the surface increases relative to the sodium. In this context formation and hydration of NaOH, as suggested in ref 15 for KOH, appears most likely. In region III, over 170 K, the hydroxyl bands become the overall dominant features. Because of its limited surface sensitivity UPS allows no clear discrimination between those three temperature regions (see Figure 2). On the other hand, UPS allows a relatively precise determination of the temperature at which multilayer

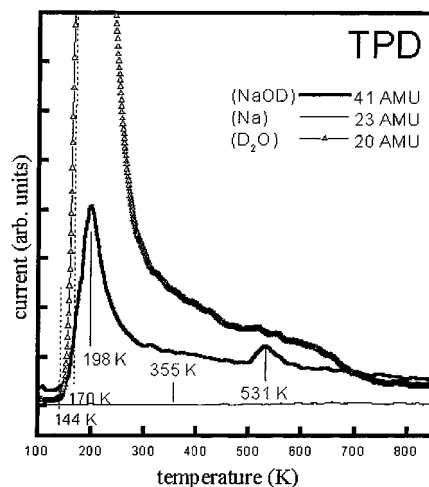


Figure 3. AMU 20, 23, and 40 TPD data taken from the surface prepared in Figure 1, i.e., a Na covered water multilayer on MgO(100)/Mo(100). The temperature ramp was 2 K/s.

desorption becomes significant (over 155 K) at which point a strong contribution from the MgO substrate is apparent.

We have performed TPD of Na dosed onto a multilayer water-covered MgO(100)/Mo(100), similar to the experiment shown in Figure 2. The TPD data for atomic mass units AMU 20, 23, and 40 are presented in Figure 3. The plot for AMU 23, corresponding to sodium, shows no desorption feature. On the other hand, the AMU 40 desorption trace (as well as the AMU 39 trace, not shown here) with desorption maxima at 198 and 531 K strongly implies a chemical reaction between water and sodium. In this context it is important to note that a mass spectrum (QMS) of pure NaOH (using an electron impact ionizer) showed significant intensity at AMU 23, Na, but no intensity at AMU 39, NaO, or AMU 40, NaOH, i.e., essentially all of the NaOH is fragmented during ionization. In the present experiment it is unclear as to what primary species gives rise to the AMU 39 and AMU 40 signals.

To clarify this point, an experiment was carried out in which solid NaOH, saturated with water, was annealed in UHV while detecting the decomposition products. Initially, a low-temperature anneal (~ 400 K) led to a QMS signal typical for water (AMU 16, 17, 18) with significant intensity at AMU 39 and 40. While maintaining a constant sample temperature, the intensities of AMU 16, 17, 18, 39, and 40 decrease gradually suggesting desiccation of the NaOH. Finally, annealing to higher temperatures (~ 700 K) led to a strong AMU 23, Na, signal indicative of NaOH sublimation. A plausible explanation for this behavior is that during the anneal, the water contaminated NaOH sample sublimates hydrated NaOH clusters, yielding fragments of water, NaOH, and NaO in the QMS ionizer. From the well-developed hydroxyl doublet in the MIES spectrum (> 170 K) in Figure 2 and Figure 4, we conclude that NaOH does indeed form on the MgO surface and is solvated by water. It is noteworthy that the temperature ramp rate of Figure 3 is significantly more rapid than that of Figures 2 and 4. The higher ramp rate of Figure 3 (2 K/s) compared with Figures 2 and 4 (~ 0.05 K/s) may result in a significantly higher local water partial pressure of water at the surface during the desorption process. This, in turn, could account for the stabilization of hydrated clusters of NaOH during the desorption process of Figure 3.

In addition, three temperatures are assigned in Figure 3: 144 and 170 K are the temperatures at which significant changes in

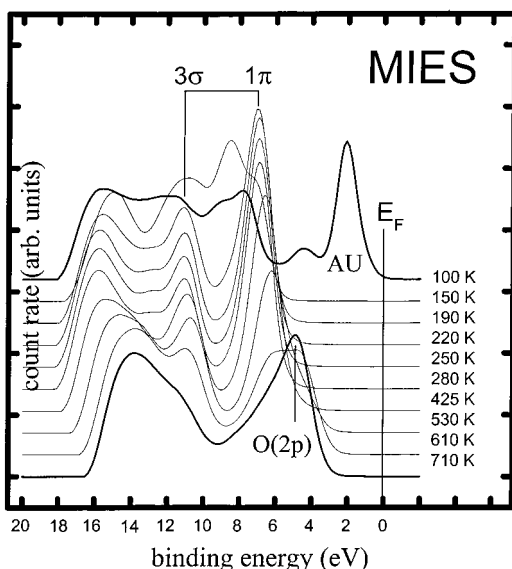


Figure 4. MIES spectra obtained from a surface similar to the one in Figure 2, i.e., a Na covered water multilayer on MgO(100)/Mo(100) as a function of the anneal temperature.

MIES are seen; 355 K is the expected desorption temperature for Na from MgO/Mo(100).

4. Discussion

The sequence of experiments can be divided into three distinct phases, each representing a single stage in the reaction of a multilayer water system on MgO(100) with a coadsorbate such as sodium: (i) the reaction between Na and water at the substrate surface; (ii) the solvation and further reaction of Na and its reaction products, and (iii) after multilayer desorption, the stabilization of reaction products at the substrate adsorbate interface. At low temperatures (100 K) the adsorption of Na on amorphous solid water (ASW) is expected to be a vacuum–water interface reaction. Because of the low mobility of the water molecules at 100 K, intermixing of the dosed Na with the ASW bulk can be excluded. This interpretation is supported by previous work¹⁸ in which long-range diffusion in multilayer water has been observed at temperatures close to the transition temperature of ASW to crystalline ice at about 160 K, but not below this temperature. In this picture, the effect of the Na condensation enthalpy is not considered, since the water condensation enthalpy apparently has no effect on water–water intermixing.¹⁸ As discussed above, the adsorption of Na leads to the formation of an hydroxyl-like species and metallic Na clusters, together with undissociated water, at the ASW surface. At elevated temperatures the mobility of the water molecules increases significantly. This is, in the case of a pure water phase, manifested in the irreversible phase transition from ASW to thermodynamically favored crystalline ice at ~ 160 K. Even at ~ 155 K, an increase of the surface water concentration relative to the hydroxyl indicates a change in the molecular arrangement at the surface (Figure 2). Since there are no significant AMU 23 and AMU 40 signals seen in TPD before 170 K (Figure 3), hydration, i.e., solvation of Na and hydroxyls in the multilayer water system, is presumed. The liquidlike transitional diffusion prior to the ASW crystalline ice transition at 155 K strongly supports this model.¹⁸ This picture is further supported by the

reappearance of the hydroxyl features in MIES at temperatures > 170 K. At 170 K, there is a desorption onset of multilayer water and solvated NaOH (see Figure 3), however, a fraction of the solvated hydroxyls appear to be stabilized at the MgO surface; metallic Na is not found on the MgO surface. As shown in Figure 4, the hydroxyl bands, 3σ and 1π , are the dominate features in MIES up to 530 K. At this temperature a prominent peak in the AMU 40 signal in TPD and a rapid attenuation of the hydroxyl bands in MIES indicate NaOH desorption. Finally, at 710 K water desorption from the MgO surface is complete (see Figure 3) and the MgO surface is adsorbate-free as seen by MIES (see Figure 4).

5. Conclusion

The electronic structure of multilayer water covered MgO/Mo(100) has been monitored as a function of the Na exposure by metastable impact electron spectroscopy (MIES) at 100 K. During Na exposure, the appearance of a new feature at 8 eV binding energy indicates a reaction between Na and water. In addition the formation of Na clusters with metallic character is observed. From MIES it is concluded that up to a temperature of 132 K the water concentration at the surface does not change significantly with respect to hydroxyls. However, the metallic Na clusters disappear from the surface. At ~ 155 K a significant increase in the water concentration at the surface suggests solvation of the surface hydroxyls in the multilayer water system. At temperatures > 170 K desorption of water and NaOH begins. After desorption of all multilayer components the species stabilized at the surface is NaOH, which is stable up to 530 K.

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