



# Electron spectroscopy (UPS(HeI and II) and metastable impact electron spectroscopy (MIES)) applied to molecular surfaces: the interaction of atoms and molecules with solid water

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## Abstract

We report studies of the interaction of atoms and molecules with solid molecular surfaces, water in particular, by combining photoelectron spectroscopy, UPS with HeI and II, and metastable impact electron spectroscopy (MIES). In MIES charge exchange processes of the Auger-type taking place between metastable He atoms and the surface under study are utilized to gain information on their electronic structure. The MIES spectra give a rather direct image of the surface DOS. We concentrate on the following processes taking place on water films produced at 80 K:

(1) Interaction of Na Atoms with Amorphous Solid H<sub>2</sub>O Films: emphasis was on the role of the 3sNa electrons in the water dissociation process. In order to make a detailed comparison with density functional theory (DFT), DOS (density of states) information is compared with the MIES spectra. Our results are consistent with the theoretical prediction that the 3s-electron is delocalized from the Na-core and trapped (solvated) between the Na-core and water molecules of the surrounding water shell.

(2) Ionization and Solvation of NaCl Interacting with Amorphous Solid Water: at 90 K there is no interpenetration of H<sub>2</sub>O and NaCl. However, ionic dissociation of NaCl takes place when H<sub>2</sub>O and NaCl are in direct contact. At 105 K the solvation of the ionic species Cl<sup>−</sup> and Na<sup>+</sup> becomes significant. The desorption of H<sub>2</sub>O from the mixed film takes place between 145 and 170 K; those species bound ionically to Na<sup>+</sup> and Cl<sup>−</sup> are removed last.

(3) The Interaction of PBTs (persistent, bio-accumulative, and toxic substances), chlorobenzene and chlorophenyl, with amorphous solid water: the organic layers produced at 80 K were annealed up to 200 K under in situ control of MIES and UPS. The different behaviour of the interfaces for the three studied cases is traced back to the different

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mobilities of the molecules with respect to that of water. The interaction between  $\text{H}_2\text{O}$  and the benzene derivatives is discussed on the basis of qualitative free energy profiles.

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## 1. Introduction

So far, the study of molecular surfaces, with water as an important example, has found comparatively little attention [1–5]. On the other hand, such systems are of considerable interest for our atmosphere: the processes taking place at the surface and in the near-surface region of icy particles can catalyze processes that are suspected to be responsible for the ozone “hole” formation over the polar regions. Under atmospheric conditions (180–250 K, relevant partial pressures) it has proved difficult to separate and study each of the elementary reaction steps which might be involved in surface-induced transformations (adsorption, solvation, reaction and desorption processes).

At low temperatures water tends to condense in the form of crystalline films. However, their formation requires a certain mobility of the molecules which, below 140 K, is not anymore available. At these temperatures the condensation takes place in form of amorphous solid water. It can, to a certain extent, be considered as a substitute for liquid water, having however a much lower vapor pressure. This makes amorphous solid water (and the study of reactions with it) accessible to the application of sophisticated surface analytical techniques. Hence, such studies supplement those on liquid water which is barely accessible for this approach [6].

In this contribution we report studies of the interaction of atoms and molecules with solid water by combining photoelectron spectroscopy, UPS with HeI/II, and metastable impact electron spectroscopy (MIES). In MIES charge exchange processes, of the Auger-type in particular, between metastable He atoms and the surface under study are utilized to gain information on its electronic structure. Other than in UPS, in MIES the

probability for electron ejection depends only on the density of states (DOS) of the initial states at the surface [7]. Thus, the MIES spectra are a rather direct image of the surface DOS. Since the metastables approach the surface with near-thermal kinetic energy (60–100 meV), this technique is non-destructive and highly surface sensitive (see Refs. [8,9] for more detailed introductions into MIES and its various applications in molecular and surface spectroscopy). A detailed description of the apparatus can be found elsewhere [10]. The present report concentrates on processes at water films on tungsten substrates. Emission from the support material is seen neither with MIES nor UPS. Consequently, the chemical properties of the surface are those of the water film; the tungsten substrate merely provides a reliable support for the growth of the water multilayers. In the following, three topics will be discussed in some detail.

## 2. Results and discussion

### 2.1. Interaction of Na Atoms with amorphous solid water (SW) films: the role of solvated $\text{Na}^+\text{e}^-$ electrons in the water dissociation process

Although the exothermic reaction of Na atoms with liquid water, yielding NaOH and  $\text{H}_2$ , is well-known, the underlying mechanism for this simple-looking process is not well understood. One particular reason is that it is not easy to obtain direct detailed information on the 3sNa electron which plays an active role in this process. As compared to UPS, MIES possesses a rather large sensitivity for the detection of the 3sNa electron, and its pronounced surface sensitivity allows, in combination with UPS, to distinguish between species adsorbed atop and underneath the surface

under study. Previous work concerned with the interaction of alkali atoms with multilayers of water can be found in Refs. [5,11,12].

Theory has studied the Na–water interaction by applying first principles and/or molecular dynamics methods to Na–water clusters [13–16]; it was shown that the 3s-electron becomes delocalized from its respective core and is trapped between Na and the protons of the shell of hydrating water molecules pointing towards the Na. The electron distribution is unique in the sense that the electron becomes trapped by the surrounding (O–H) bonds, and is not centered at the  $\text{Na}^+$  core. It was demonstrated that the solvated 3s-electron plays an important role for the dissociation of the water [16]. The results presented below were collected with the purpose to make a detailed comparison with Ref. [16].

Fig. 1 (upper set of spectra) presents the MIES results obtained during Na deposition on a water film (3 bilayers of water) held at 90 K. The exposure is given in units of monolayer equivalents (MLE); at 1 MLE the surface would be covered by one Na monolayer if penetration of the Na into the molecular films could be neglected. For pure water we see the structures  $1b_1$ ,  $3a_1$ , and  $1b_2$  from the ionization of the three highest occupied water MOs (top spectrum). Up to 0.5 MLE Na exposure the spectra remain unchanged except for a change of the peak positions simultaneously with the observed Na-induced work function (WF) decrease (1 eV), and a smearing-out of the water features  $1b_1$ ,  $3a_1$ , and  $1b_2$ . Although no Na signature is seen in the early stage of exposure, Na species must become adsorbed/incorporated into the water film as suggested by the decrease of WF and the concomitant shift of the water spectra. Since no 3s-emission is seen, we conclude that no 3s electrons are present at the film surface. Above 0.5 MLE a shoulder, denoted by  $1\pi$ , emerges at the position where emission from  $1\pi$  of OH is expected [3,4]; the contribution expected from the ionization of  $3\sigma$  of OH at a binding energy larger by 3.7 eV [3,4] is obscured by the emission from  $3a_1$ . In the same exposure range emission, labeled Na(3s), appears. It resembles closely to the Na-induced emission seen with metals and semiconductors for coverages larger than about 0.5 ML. In these cases,

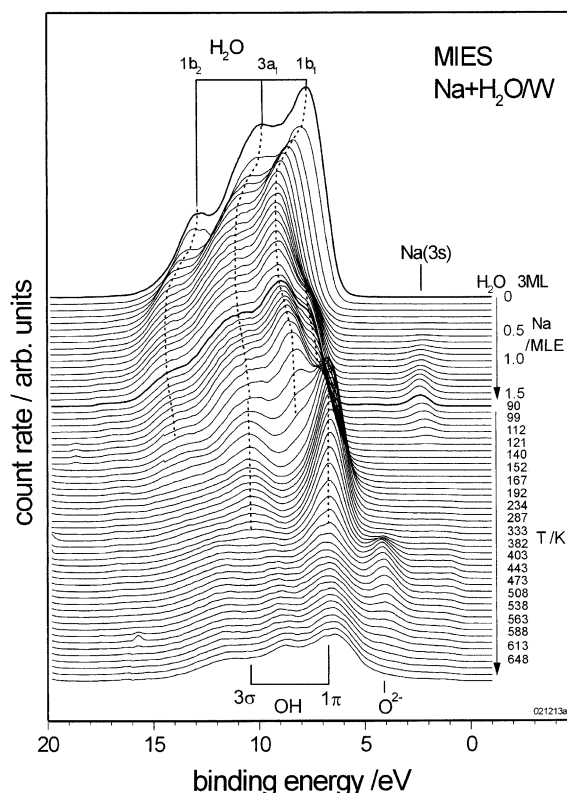


Fig. 1. MIES spectra for the adsorption of Na on solid water (three layers) prepared on tungsten (90 K) (upper set of spectra), and the spectral changes resulting from annealing the Na/H<sub>2</sub>O system over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

the emission is due to the presence of s-charge density at the alkali core, i.e. the Na adsorbate is not fully ionized anymore. We assume that Na(3s) has the same origin. However, the emission is peaked at  $E_B = 2.3$  eV which is about 1 eV larger than on solid surfaces. The WF is 2 eV, i.e.  $E_F$  is located 2 eV below the vacuum level. Thus, under the present conditions the 3s-ionization energy is  $(E_B + \text{WF}) \text{ eV} = 4.3$  eV.

The surface prepared by Na exposure was heated stepwise between 90 and 650 K. The results (lower set of spectra in Fig. 1) support the interpretation given to the feature  $1\pi$ : the molecular water desorbs at 155 K while OH-species can be detected on the surface up to 390 K as suggested by the presence of the two peaks  $1\pi$  and  $3\sigma$  at a

distance of 3.7 eV [3,4]. The  $1\pi$  shoulder develops smoothly into the peak labeled  $1\pi$ , and is caused by OH species from the Na–water reaction. When annealing further, the OH features disappear at 390 K. Apart from the tungsten substrate emission, seen between about 5 and 13 eV, a prominent peak,  $O^{2-}$ , appears at 4 eV; it persists up to 600 K. Its energetic position is characteristic for  $O^{2-}$  species, stabilized by Na ions, suggesting that  $OH^-$  decomposition has taken place.

Na(3s) disappears when heating to 115 K, presumably because the mobility of the water molecules increases leading to Na solvation.

The interaction of Na with water ice will now be discussed on the basis of the theory results for sodium hydroxyl formation in water clusters [16]. The key point was to consider the consequences of the hydrolysis of Na species, Na atoms as well as of  $Na_2$  dimers. We demonstrate that the MIES spectra and the DFT results for the DOS of two sodium atoms trapped in a  $(H_2O)_{10}$  cluster before and after  $Na_2$  hydrolysis [16] are consistent (Fig. 2). We suppose in the following that unreacted, but solvated Na species (prior to the

reaction) and OH species from the Na-induced hydrolysis are both present at the surface. The DFT-DOS before Na ionization shows four peaks labeled A, B, C and D as in Ref. [16]. Peak A corresponds to the solvated electron (denoted by Na(3s) in the MIES spectra). Peaks B and C correspond mainly to the  $\pi$  and  $\sigma$  water lone pairs of electrons involved in OH bonds (denoted  $1b_1$  and  $3a_1$  in MIES). Peak D (labeled  $1b_2$  in MIES) is the antisymmetric OH contribution. B is well reflected in the experimental spectrum. C is also seen in the MIES spectrum, but overlaps with the contribution of the “ionized” system, consisting of  $Na^+$ , the solvated electron and the water cluster.

After hydrolysis, the solvated electron signal disappears from the DFT-DOS. Two shoulders appear in the DFT-DOS corresponding to the shift of the two water lone pairs connected with the two hydroxyl groups issued from  $Na_2$  ionization; a larger cluster would have produced a broad band analogous to the shoulder in the MIES pattern in the same energy region. The former peaks B, C and D are shifted towards the Fermi level, and the overall combination is well reflected in the experimental curve. The  $\sigma$  hydroxyl OH, located around 25 eV, is not displayed in this figure.

From the present experiment it is not possible to determine unambiguously whether the active Na species are single atoms, dimers (as assumed in the present work) or, as proposed in Ref. [14], as trimers. Nevertheless, the comparison between theory and experiment appears to be meaningful enough to support the reaction pathway involving Na dimers: in the first step, after film adsorption, Na is trapped inside the cluster. This perturbs strongly the original water DOS in mixing more intimately the lone pair and antisymmetric water OH wave functions. Therefore, the proton tunneling from one water molecule to a neighbouring one is greatly facilitated. The acceptor molecule releases one of its own protons to another neighbour. This process continues from site to site until the end of the H-bonded chain is reached. This happens at the protons pointing toward the solvated electrons. Such a proton is therefore able to capture one of these electrons producing, in the first step, an H radical atom, and then a  $H_2$  molecule.

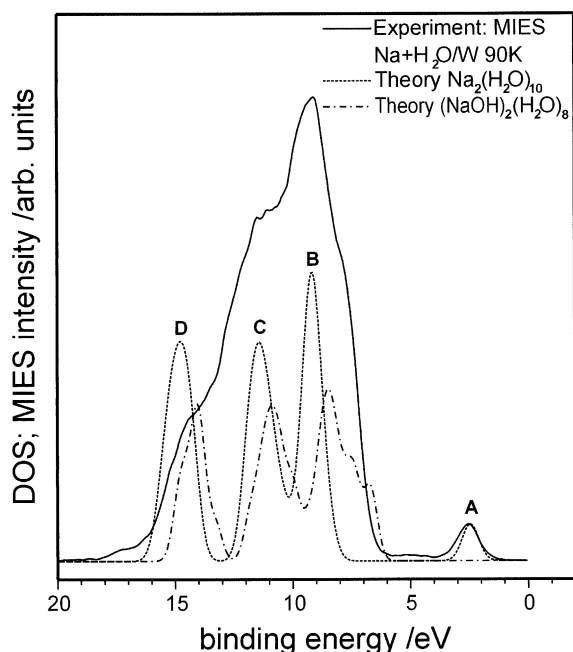


Fig. 2. DOS of the  $Na_2(H_2O)_{10}$ -cluster defined in the text and comparison with the results of Fig. 1 (heavy spectrum).

When heating beyond 115 K, Na species disappear from the surface, and become solvated in the water film. Therefore, a comparison of MIES results and theory is limited to temperatures below 115 K. At present, we study Na solvation and Na-induced processes for Na interacting with solid films of  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ .

## 2.2. Ionization and solvation of NaCl interacting with amorphous solid water

The understanding of the interaction of salt molecules with water and vice versa, of water molecules with NaCl surfaces, is of interest in various fields, ranging from biological systems to catalysis and environmental sciences. Hydrated NaCl particles extracted from the ocean may become part of the atmosphere or deposited on the ocean shore. In both situations they play an important role as providers for chloride species and/or catalysts for pollution reactions as f.i. those involving (N–O) compounds [17,18]. Low-energy reactive ion scattering (RIS) has proven to be a sensitive tool for monitoring surface species [19]. In RIS a low-energy  $\text{Cs}^+$  ion beam (3–100 eV) is surface scattered, and the scattered ions are mass analyzed. Among the scattered ions association products of  $\text{Cs}^+$  with neutrals adsorbed at the surface and, in addition, pre-existing ions from the surface are ejected. For NaCl exposed to solid water at 100 K RIS showed that NaCl dissociates almost completely, forming  $\text{Na}^+$ –water complexes [19].

So far, information is available on the initial step of the interaction: ionic dissociation of NaCl takes place even at temperatures as low as 100 K [19]. It is the aim of the present work to study details of the solvation process for NaCl interacting with solid water by combining MIES and UPS. Emphasis is laid on the determination of the temperature at which migration of the ionic species, strongly interacting with the surface water molecules, takes place into the film. Water films held at 80 K (denoted by SW) were exposed to NaCl, and the change of the electronic structure with the temperature of the NaCl-exposed film was monitored under in situ control of MIES and

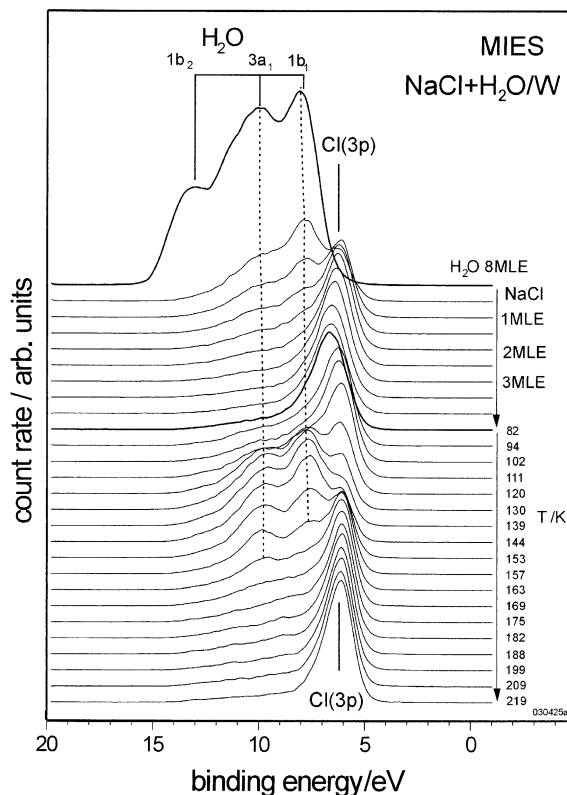


Fig. 3. MIES spectra for solid  $\text{H}_2\text{O}$  (8 BL) on tungsten kept at 80 K (top spectrum), and for NaCl exposure of the  $\text{H}_2\text{O}$  film. Lower part: spectra obtained during annealing of the NaCl-exposed film (80–219 K). (BL: bilayer).

UPS. Related work for  $\text{CsCl}/\text{H}_2\text{O}$  can be found in Refs. [20,21].

Fig. 3 summarizes the MIES results obtained for a film of SW, held at 80 K (abbreviated by NaCl/ $\text{H}_2\text{O}$ ), during its exposure to NaCl, followed by film heating to 300 K. The top spectrum is for SW(8BL). The following nine spectra display the changes occurring during the exposure of 4 MLE NaCl. A shoulder develops at the right side of  $1b_1$  and turns into the peak denoted by Cl(3p), identified as emission from the  $3p_{\text{Cl}}$  orbital [20,21]. Apparently, a closed NaCl layer can be produced on SW at this temperature (10th spectrum from top). When heating (see lower set of spectra), the spectral features of water reappear beyond 105 K, and become the dominant structures in the spectra between 120 and 140 K; clearly,



water species have become part of the toplayer. Around 145 K water desorption becomes significant as signaled by the reappearance of Cl(3p) and the decrease of the water features. Around 165 K, according to MIES, all water has desorbed, and Cl(3p) is seen only. Additional information on the first step of the NaCl interaction with SW comes from our UPS(HeI) results (not shown here): as long as the chloride species are in contact with water, the Cl(3p) feature is seen as a single, sharp peak at  $E_B = 5.6$  eV. After the water has desorbed, Cl(3p) develops the double-peak structure typical for the NaCl bulk, here for NaCl film formation on the W substrate. We suggest that the sharp Cl(3p) peak found in aqueous environment should be considered as evidence for ionic dissociation during NaCl adsorption. Apparently, the resulting species  $\text{Cl}^-$  and  $\text{Na}^+$  adsorb independently without much mutual lateral interaction. This is in full accord with the findings of RIS where dissociative adsorption of NaCl on SW, followed by the formation of  $\text{Na}^+$ -water clusters, was found at 100 K [19]. Support for cluster formation comes also from the study of the ion emission during ESD from NaCl and water coadsorbed on a condensed Ar substrate (35 K) [22]. It was demonstrated that solvated  $\text{Na}^+$  ions,  $\text{Na}^+(\text{H}_2\text{O})_n$  ( $n=1-4$ ), desorbed more intensively than bare  $\text{Na}^+$  ions.

We have also collected MIES and UPS data for  $\text{H}_2\text{O}/\text{NaCl}$ , i.e. for the adsorption of water on a NaCl film held at 80 K, followed by the heating of the film prepared in this way. These data (not shown here) will be included in the following discussion: Fig. 4 displays the MIES intensities of  $\text{H}_2\text{O}(1b_1)$  and  $\text{Cl}(3p)$ , extracted from our MIES data for NaCl/ $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{NaCl}$  versus the annealing temperature. In the case of NaCl/ $\text{H}_2\text{O}$ , when starting with a water film fully covered by NaCl, the feature  $1b_1$  becomes clearly visible for  $T > 115$  K. The rise of  $1b_1$  is correlated with a decrease of Cl(3p). Above 137 K the temperature dependence of the signals is the same for both NaCl/ $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{NaCl}$ . This suggests that the composition of the toplayer is the same: in both situations only  $\text{Na}^+$  and  $\text{Cl}^-$  together with their solvation shells are present; water molecules not involved in bonds with ions have already

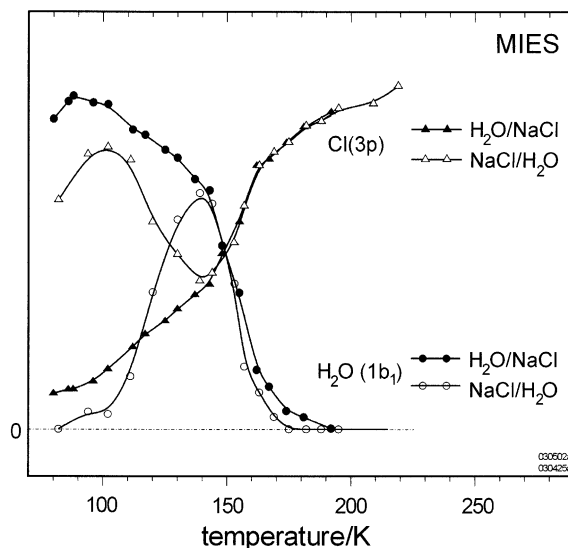


Fig. 4. Intensities of  $1b_1$   $\text{H}_2\text{O}$  and  $3p\text{Cl}^-$  as a function of the annealing (80–210 K) for (a) NaCl (1 MLE)/ $\text{H}_2\text{O}$ (3 BL) and (b)  $\text{H}_2\text{O}$ (1 BL)/NaCl(3 MLE).

desorbed. Support comes from the fact that the MIES spectra of water in this range are gas phase like, featuring well-defined peaks from the ionization of  $1b_1$  and  $3a_1$ . This holds in particular for the  $3a_1$  emission which is unstructured and diffuse for condensed water [23]. This indicates that, at this stage, the emission originates from water species that are not anymore involved in a H-bonded network, but are stabilized by their electrostatic interaction with the salt ions.

Our results appear to be compatible with following scenario for the interaction at interfaces between NaCl and water: no significant intermixing of the species takes place at the interface as long as the temperature stays below about 105 K. Indeed, no penetration effects could be seen when depositing NaCl on solid water films or vice versa below this temperature. However, already at 90 K there is strong interaction between NaCl and water species at the interface: the NaCl species become dissociated ionically, as already concluded from RIS results obtained at 100 K [19]. In our work the dissociation is suggested by the peculiar shape of the Cl(3p) emission in UPS under conditions where NaCl is in close contact with water. As

demonstrated by RIS, ( $\text{Na}^+$ –water) complexes are formed at the interface.

We discuss now the solvation effects seen above 105 K: the free energy profiles for the  $\text{Na}^+$  and  $\text{Cl}^-$  interaction with liquid water have two minima, one for adsorption at a “surface” site and another for adsorption at a “solvent-separated” site; it was shown that the ions are more stably adsorbed under “solvent-separated” conditions, i.e. as fully solvated species [24]. For  $\text{NaCl}/\text{H}_2\text{O}$  a decrease of  $\text{Cl}(3p)$ , accompanied by an increase of  $1b_1$ , is observed above 105 K, and indicates that water molecules have become embedded into the  $\text{NaCl}$  toplayer. Following [24],  $\text{Cl}^-$  species have moved from a surface site (“direct” adsorption) to an, energetically more favored, “water-separated” site in which the  $\text{Cl}^-$  species are less accessible to MIES due to solvation by water molecules. In turn, the solvating water molecules, initially forming the underlayer, become accessible to MIES.

### 2.3. The interaction of the PBT's (persistent, bio-accumulative, and toxic substances) chlorobenzene and chlorophenol, with amorphous solid water

PBTs are of global and local concern: photochemical reactions involving PBT's play a major role in the atmosphere, in natural water, on soil, and in living organisms [25]. Snow and ice are important components of cold ecosystems and influence the fate and the reactions of PBT's. The process of uptake of these chemicals into nascent water crystals can take place either by adsorption onto the surface of ice particles in stratospheric clouds or through co-deposition with water into growing crystals or films. However, our present understanding of how PBT's interact with frozen water is relatively limited, and the study of the interaction has only recently become a subject of detailed investigations. A quantitative model to assess and evaluate the environmental fate and behaviour of PBT's in cold ecosystems is not available, and would include to know about (i) the efficiency and the mechanism of snow scavenging from the atmosphere by the chemicals, (ii) the behaviour (migration, solvation, etc.) of the chemicals into snow are ice particles, and (iii) the

release, i.e. the desorption of chemicals, products from photochemical reactions in particular, into the ecosystem. In order to shed more light into the origin of the different photochemistry of PBT's in solid and liquid water, we have applied MIES, in combination with photoelectron spectroscopy (UPS with HeI and HeII), to the study of processes at interfaces between benzene  $\text{C}_6\text{H}_6$ , the substituted benzenes  $\text{C}_6\text{H}_5\text{Cl}$  and ortho- $\text{C}_6\text{H}_4\text{OHCl}$ , and solid water at 80 K.

Fig. 5(a)–(c) compare MIES and UPS(HeI/II) spectra for benzene (B) (a), chlorobenzene (CB) (b), and *o*-chlorophenol (CPH) (c) adsorbed on a solid water film (3 bilayers (BL) thick, deposited on tungsten held at 80 K). Also shown are MIES spectra for water adsorbed on a tungsten substrate

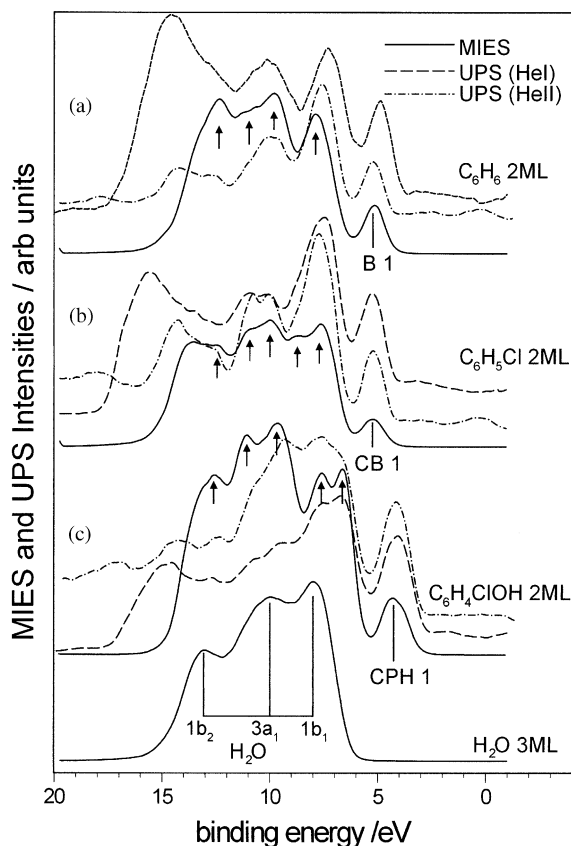


Fig. 5. MIES spectra for the adsorption of water on tungsten (80 K), and MIES and UPS(HeI and II) spectra for (a) benzene (2ML), (b) chlorobenzene, and (c) *o*-chlorophenol on water films (80 K; 3 BL).

at 80 K. The identification of the spectral features marked by arrows is possible on the basis of MIES/UPS results obtained on single molecules of the benzenes [26,27] and by consulting molecular structure calculations [26,28]. It is of considerable importance for data evaluation that no contribution from the ionization of water interfere with B1, CB1, and CPH1. These peaks arise from the ionization of the MO's  $\pi_2$  and  $\pi_3$  of the benzene rings.

Fig. 6(a) shows the temperature dependence of  $1b_1$  and B1 for a benzene (B) layer (1 ML thick) deposited on a water film (80 K; 3 BL) (denoted by B/H<sub>2</sub>O) as a function of the annealing temperature. At 80 K B is adsorbed atop. The simultaneous decrease of B1 in MIES and UPS seen above

95 K suggests that B starts to desorb from the water film, and has practically disappeared at 130 K. If B would penetrate into the water film, B1 should disappear in MIES, but would still be present in the UPS spectra which is not the case. Water desorption takes place around 140 K, and is complete around 150 K.

Fig. 6(b) presents the corresponding results for chlorobenzene (CB) (1 ML) deposited on solid water (denoted by CB/H<sub>2</sub>O). The simultaneous decrease of CB1 in MIES and UPS and the rise of  $1b_1$  seen between 115 and 140 K indicate that the desorption of CB species becomes sizeable above 115 K. However, although CB1 has become rather small around 135 K in MIES, desorption is not complete at that point because CB reappears both in MIES and UPS at  $T=145$  K when water has desorbed. The small CB1 signal between 128 and 140 K suggests that CB is shielded from the interaction with He\*, and, consequently, implies that in this temperature range the toplayer consists of water mainly. CB species are seen up to 165 K; they are bound to the tungsten substrate because only 0.25 ML of CB is left after water desorption.

Fig. 6(c) displays the corresponding results for an *o*-chlorophenol (CPH) film (3 ML) deposited on water (80 K; 3 BL) (denoted by CPH/H<sub>2</sub>O). No significant change of the CPH1 intensity has yet occurred at 145 K where water is expected to desorb. Instead, CPH desorption becomes significant above 170 K. No water-induced emission is seen in the entire studied range of temperatures. From above's results we estimate the temperatures at which half of the initially deposited material has desorbed. We obtain  $T_D = 105, 130, 170$  K for B, CB, CPH, respectively.

The interaction at the (H<sub>2</sub>O–benzenes)-interface will be discussed with the help of free energy (FE) profiles (Fig. 7) [29]: for B/H<sub>2</sub>O  $T_D(B)$  is considerably lower than for water. Therefore, in the FE profile of Fig. 7(a) water is considered as the solvent and B as the solute. The observed temperature dependence of B1 and  $1b_1$  simply implies that  $V_{SB} \gg V_{SG}$ ; this is expected because the large B species are unable to enter the rather dense water lattice at temperatures well below  $T_D$  of water. As soon as  $T > T_D(B)$ , the probability for B desorption from well (I) into the vacuum becomes

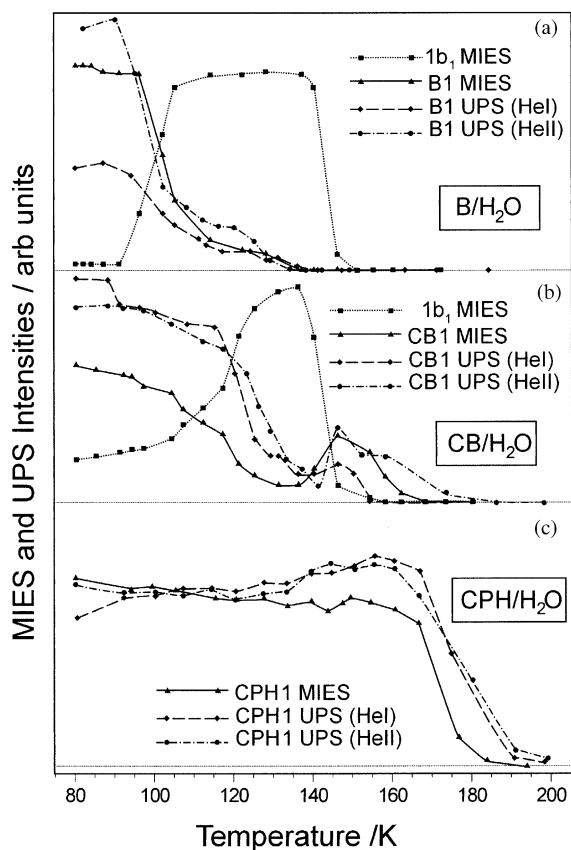


Fig. 6. Intensity changes of various spectral features (H<sub>2</sub>O( $1b_1$ ) in MIES; B1 (CB1; CPH1) in MIES, HeI and II) during the annealing of a film of benzene (a), chlorobenzene (b), and chlorophenol (c) deposited on a water film (80 K; 3 BL).



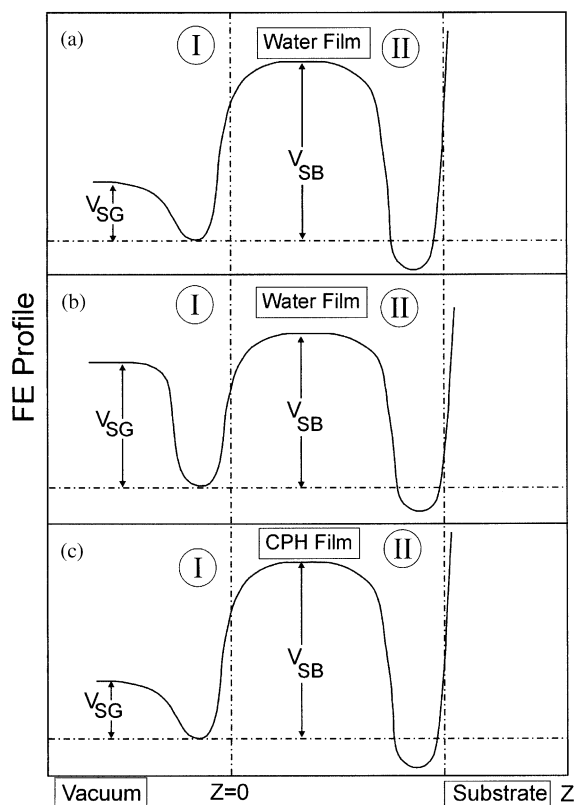


Fig. 7. Free energy profiles (qualitatively) for the interaction at interfaces between water and the benzenes (a)  $C_6H_6$ , (b)  $C_6H_5Cl$ , and (c)  $C_6H_4OHCl$ .  $V_{SG}$  and  $V_{SB}$  are the barriers for desorption into the vacuum and migration into the solvent film, respectively;  $z=0$  at the interface between film and vacuum.

rather high while that for migration into the film and to the tungsten substrate remains low.

For the discussion of the interaction at the  $(H_2O-CPH)$ -interface we interchange the roles of solvent and solute, and consider CPH as solvent. We arrive at the FE profile displayed in Fig. 7(c). Other than for  $B/H_2O$ , the barrier  $V_{SB}$  is now low because the water molecules can move relatively freely through the comparatively open CPH lattice. As soon as water becomes mobile, molecules will migrate from II to I through the CPH lattice. Because  $V_{SG}$  is also low, the residence time of water species that have migrated through the CPH film to the surface is short (between  $10^{-12}$  and  $10^{-9}$  s [29]), and accounts for the absence of water-induced features in the spectra.

For the  $(CB-H_2O)$  system the  $T_{DS}$  of the two components are rather similar. Consequently, it appears reasonable to assume that interpenetration of the two components takes place before desorption is complete. Indeed, above 145 K, when all water has desorbed, CB species, originally deposited atop of the water film, are found on the tungsten substrate. Thus, CB species must have migrated through the water film to the substrate. On the other hand, the simultaneous decrease of CBI in MIES and UPS, seen for  $T > 110$  K demonstrates that CB desorption starts already at 110 K. In the FE profile for  $(CB-H_2O)$  (Fig. 7(b)) the choice  $V_{SG} \approx V_{SB}$  allows for the simultaneous occurrence of desorption and penetration. It was claimed that the formation of cages of coadsorbates under water takes place on metallic surfaces [30]. There are no indications that caging may take place for the large organic molecules under study.

### 3. Conclusions

The present study, employing the MIES in combination with UPS, gives insight into the interaction of atoms and molecules with water ice films at temperatures between 80 and 120 K. For Na/ice we concentrated on the role played by the Na3s electron for the reaction between Na and the ice film. The MIES spectra are in good agreement with the density of the states of Na- $H_2O$  clusters as obtained from first principles DFT calculations. Theory predicts that the 3s electron is delocalized from its  $Na^+$  core and trapped between the core and surrounding solvent molecules, i.e. the 3sNa electrons become solvated by the surrounding molecules. Calculations and experiment both underline that the delocalized 3s electron triggers the Na-water dissociation.

For NaCl/ $H_2O$  the solvation of the  $Na^+$  and  $Cl^-$  species resulting from the dissociative adsorption at 80 K was studied. It is found that the solvation is complete around 120 K.

For  $C_6H_6/H_2O$  desorption starts around 105 K; no benzene penetration into the water film could be detected. For  $C_6H_5Cl/H_2O$  ( $CB/H_2O$ ), both species become mobile around 120 K; not all CB

molecules have desorbed before the water film desorbs near 140 K. Some of them interact with the metallic substrate, and finally desorb at 170 K. For *o*-C<sub>6</sub>H<sub>4</sub>OHCl/H<sub>2</sub>O (CPH/H<sub>2</sub>O), all water has desorbed before CPH desorption sets in (*T*=170 K). We suggest that water can migrate through the comparatively open CPH lattice, as soon as the H<sub>2</sub>O molecules of the underlayer become sufficiently mobile, e.g. above 120 K. Qualitative free energy profiles are proposed that can account for the experimental results.

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