The interaction of CsCl with films of solid water

A. Borodin, O. Höfft, S. Krischok [1], V. Kempter [*]

*Institut für Physik und Physikalische Technologien der Technischen Universität Clausthal Leibnizstr. 4,
38678 Clausthal-Zellerfeld, Germany*

Abstract

The interaction of CsCl molecules with films of solid water (three layers thick, typically), deposited on a tungsten crystal at 130 K, was studied. Metastable impact electron spectroscopy (MIES) and UPS(HeI) were applied to study the emission from Cl3p and Cs5p and the highest occupied states $1b_1$, $3a_1$ and $1b_2$ of molecular water. Below a critical stoichiometry of about $CsCl \cdot nH_2O$ with $n = 6$ the UPS spectra are quite similar to those from chlorides solvated in liquid water in as much as the relative positions and intensities of the water and salt features are concerned; very little emission from the ionization of Cl3p and Cs5p is observed with MIES. We conclude that the CsCl molecules become solvated in the water film. As long as $n > 6$, the water spectrum remains characteristic for condensed water; at $n < 6$ it develops gas phase-like features. Moreover, the Cs and Cl ions located in the near-surface region are not entirely shielded anymore by their solvation shells and are accessed by MIES. When heating films with $n > 6$, water molecules not involved directly into the hydration of the salt molecules desorb around 140 K. Around 160 K all water has disappeared from the surface. Above this temperature only Cl and Cs (no OH-fragments) are detected on the surface up to about 400 K.
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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.

We study the interaction of CsCl with ultrathin water films under UHV conditions. The films are grown "in situ" via water deposition onto single crystal tungsten at 130 K. As was pointed out previously, this approach has several advantages [5,6]: (1) for films it is a relatively simple matter to investigate both surface and bulk phenomena when with the combination of metastable impact electron spectroscopy (MIES) and UPS(HeI), (2) surface charging is eliminated when using

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[*] Corresponding author. Tel.: +49-5323-72-2363; fax: +49-5323-72-3600.
E-mail address: volker.kempter@tu-clausthal.de (V. Kempter).
[1] Present address: Institut für Physik der TU Ilmenau, P.O.B. 100565, D-98684 Ilmenau, Germany.

sufficiently thin films, and (3) condensation of water molecules below about 135 K results in the formation of an amorphous form of solid water (SW) [7]. To a large extent its properties are believed to be comparable to those of liquid water, in particular with regard to its molecular orientation, and this form of SW can therefore be considered as a liquid water substitute, however with significantly lower water pressure. This makes a comparison of the results with those obtained with UPS on liquid water surfaces and aqueous solutions meaningful [8–11]. Previous studies carried out under similar conditions were on the interaction of SW with Na atoms [5], HCl [6,12] and CH_3OH [5].

Only the species adsorbed on top of the film will be seen with MIES, in contrast to UPS detecting both the surface-adsorbed species and those within about 3 layers below the top of the film [11,13]. Thus, the combination of MIES and UPS appears to be well suited to study adsorption, dissociation and migration of salt molecules at SW surfaces. CsCl offers the advantage that Cs and Cl are both accessible to ionization with the techniques employed in this study. We present strong evidence for CsCl migration into the water film upon adsorption at 130 K. Beyond a stoichiometry of approximately $CsCl \cdot 6H_2O$ the spectral features from water, as seen with MIES, are not characteristic anymore for condensed water, but develop gas phase-like features; the water molecules appear to be involved in bonds with Cs and/or Cl species mostly, rather than among themselves.

2. Experimental remarks

Experimental details were given previously [14–18] (see also [19], of this volume). 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 MIES/UPS spectrum requires approximately 100 s. By applying a suitable bias potential between sample and spectrometer, the electrons emitted from the Fermi level, E_F, are registered at 19.8 eV (the potential energy of $He^*(2^3S)$). The low-energy onset of the spectra occurs at the work function of the sample. The variation of the onset of the spectra at low kinetic energies with exposure gives then directly the exposure dependence of the surface work function.

The sample can be cooled with LN_2 to 130 K. The temperature was measured with a thermocouple in direct contact with the front of the tungsten single crystal. The surface was exposed to water by backfilling the chamber. This gives a closed, non-porous and amorphous film of SW [20] The amount of surface-adsorbed water is estimated on the basis of the water MIES and TPD spectra obtained previously [18].

3. Results

In the present paper we confine ourselves to a qualitative analysis of the MIES spectra: the comparison of the MIES and UPS spectra suggests that the spectral features seen in MIES are caused by the Auger Deexcitation process [11,13]. In this case the position of a particular spectral feature gives the binding energy of the emitted electron, and its intensity is a direct image of the density of states related with the species responsible for the electron emission. Quantitative methods are available to either synthesize MIES spectra [21,22] (see [23] for an example) or to deconvolute them [11].

In auxiliary experiments we have studied the spectra of a CsCl-exposed tungsten surface (see spectra for $T > 160$ K in Fig. 3). The peaks from $Cs5p_{3/2;1/2}$ and Cl3p ionization occur at 11.5 and 13 eV (Cs fine structure doublet) and 5.8 eV, respectively.

Water exposure at 130 K produces the three features $1b_1$, $3a_1$ and $1b_2$ seen both with MIES and UPS (see Fig. 1(a) and (b)). Combined MIES/UPS water spectra were published for the water adsorption on MgO [5] and TiO_2 [18], and the same overall spectral shape is seen in all cases studied so far with MIES/UPS. Based on these previous results we estimate that the water film thickness in the spectra of Fig. 1 is of about 3 layers. Results for layers of 12 layers thickness are qualitatively similar, but suffer from charge-up phenomena. It should also be noticed that our photoelectron spectra for SW films are rather similar to those for
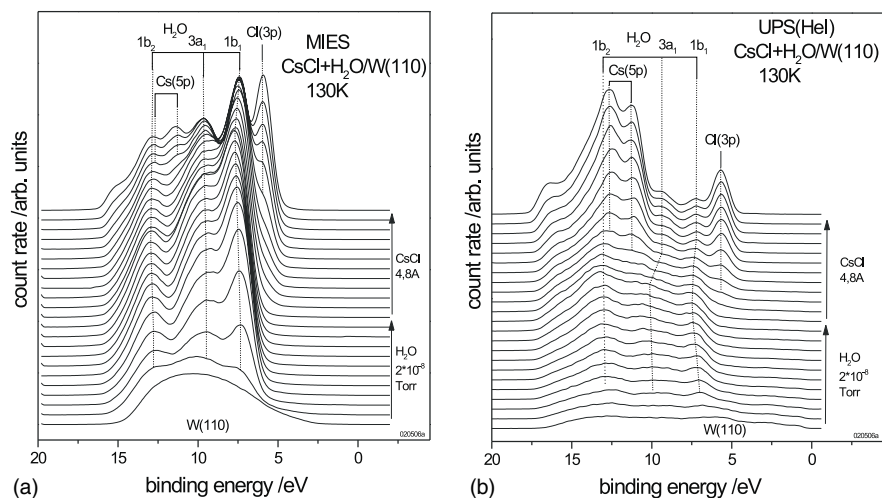
Fig. 1. MIES (a) and UPS(HeI) (b) spectra for the exposure of a solid film of water to CsCl. The water film ($\approx$3 monolayers (ML) thick) was grown on W(1 1 0) at 130 K. The CsCl exposure in the top spectrum would produce 1 ML CsCl if it would not be for penetration effects.

liquid water [8]. First principles calculations [24] suggest that the broad $3a_1$ feature is characteristic for condensed water, either in a liquid or in a solid film, and is thus indicative for the presence of a water network, formed by hydrogen bonds.

During the early stage of the CsCl exposure (lowest five spectra after starting the CsCl exposure) the spectral features of water show little change. Pronounced Cl3p emission develops in the UPS spectra ($E_B = 5.8$ eV) while it remains rather weak in the MIES spectra (7% of the total emission), and produces the small shoulder on the rise of the strong $1b_1$ peak from water. Moreover, while the Cs5p emission can clearly be seen in UPS, it cannot be detected unambiguously with MIES. The weak Cl3p emission and the absence of Cs5p emission in MIES at this stage indicate that the toplayer must consist of water molecules mainly which shield the Cl and Cs species efficiently from the interaction with the He* probe atoms. This implies migration of the salt molecules (or their constituents Cl and Cs) into the water film after deposition. At these exposures the water-induced part of the MIES spectra is essentially unchanged and remains characteristic for condensed water as judged, in particular, from the diffuse $3a_1$ feature.

For larger exposures the $3a_1$ feature seen with MIES narrows considerably and becomes a well-

defined peak. In fact, the spectra remind to gas phase-like water spectra both as far as the energetic positions and the shape of the water-induced peaks are concerned [1,3]. As judged from the ratio of the Cl3p peak area to the entire water emission in the UPS spectra, the change in shape of the $3a_1$ peak takes place at the stoichiometry $CsCl \cdot 6H_2O$ (which we call the critical stoichiometry). In order to arrive at this estimate, we have assumed that the photoionization cross sections of Cl3p and of the three water states $1b_1$ to $1b_2$ are of the same size. Although a considerable amount of water is still detected in the toplayer by MIES, the number of water molecules appears not large enough anymore to shield the salt components efficiently from the access of the He* atoms.

We can compare our UPS(HeI) results with those for a $CsF \cdot 2.6H_2O$ solution which is close to the salt saturation concentration [9]. As far as the Cs- and water-induced spectral features are concerned, these spectra compare well with ours for $CsCl \cdot 6H_2O$. It should however be noted that a different interpretation is given in [9] to that part of the spectra where the $1b_2$ and $Cs5p_{1/2}$ features overlap.

Concerning the Cl3p and water emission we can also compare with the HeI spectra of a 3 molar KCl aqueous solution [8] (stoichiometry about $KCl \cdot 18H_2O$). This part of the spectra is rather similar to

our results, both as far as the energetic positions and the shape of the Cl- and water-induced features are concerned. The Cl/water-intensity ratio is about three times smaller than in the present case.

Additional evidence for the migration of the salt molecules into the film of SW, suggested by the results of Fig. 1, comes from the codeposition results displayed in Fig. 2. Here, we have deliberately chosen a rather small CsCl exposure rate: the stoichiometry is well below the critical stoichiometry at which the $3a_1$ feature starts to narrow. Very little emission from Cs and Cl appears in the MIES spectra; on the other hand, Cl3p and Cs5p are very clearly seen in the UPS spectra. Since we still see, although extremely weakly, Cl3p emission in MIES (as suggested by the onset of the $1b_1$ water peak which is softer than for pure water), we conclude that the Cl3p species cannot be very far below the surface, and the Cl3p species definitely cannot be covered by more than one water layer.

Fig. 3 presents MIES (a) and UPS (b) results obtained when heating the mixed film (Fig. 2, top spectra) from 130 to 500 K. Similar results were obtained when annealing CsCl-exposed water films of less than the critical stoichiometry. Before heating, the signature of the Cs and Cl species can barely be seen in MIES. Around 140 K most of the water has desorbed as judged from the water-induced in-

tensity in UPS. The signature of Cs and Cl is now clearly seen also in MIES indicating that these species are only incompletely shielded by the residual water against interaction with the He* probe atoms. Sharp features $1b_1$ and, in particular, $3a_1$ (which is diffuse before heating) are now seen, similar to those seen for over-critical stoichiometries (see Fig. 2). From the fact that not all water desorbs at the same temperature we conclude that not all water molecules were involved into direct interaction with Cs and/or Cl species. On the other hand, those water molecules desorbing above 140 K obviously interact with Cs or Cl directly. According to MIES, all water molecules have desorbed around 152 K; above this temperature only Cl and Cs can be detected by MIES and UPS and disappear around 400 K. We do not detect any OH-fragments which could, as in the case of SW on MgO, be produced at the water/substrate interface [5]. The small feature seen at $E_B = 7.2$ eV at $T > 152$ K in UPS is an artefact due to the incomplete suppression of the MIES contribution in the UPS spectra.

4. Interpretation

Below the critical stoichiometry of $CsCl \cdot 6H_2O$ the close similarity of the present spectra for salt
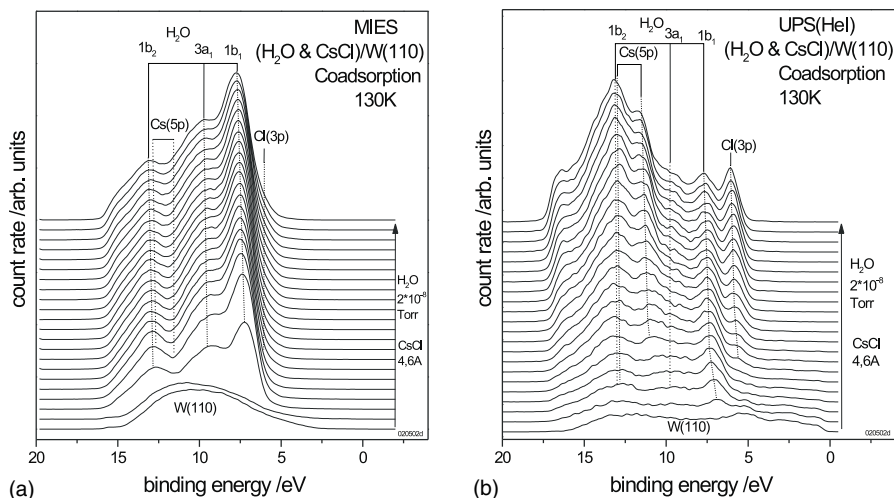

Fig. 2. MIES (a) and UPS(HeI) (b) spectra obtained during the coadsorption of CsCl and water onto W(110) held at 130 K. The film stoichiometry is about $CsCl \cdot 9H_2O$.
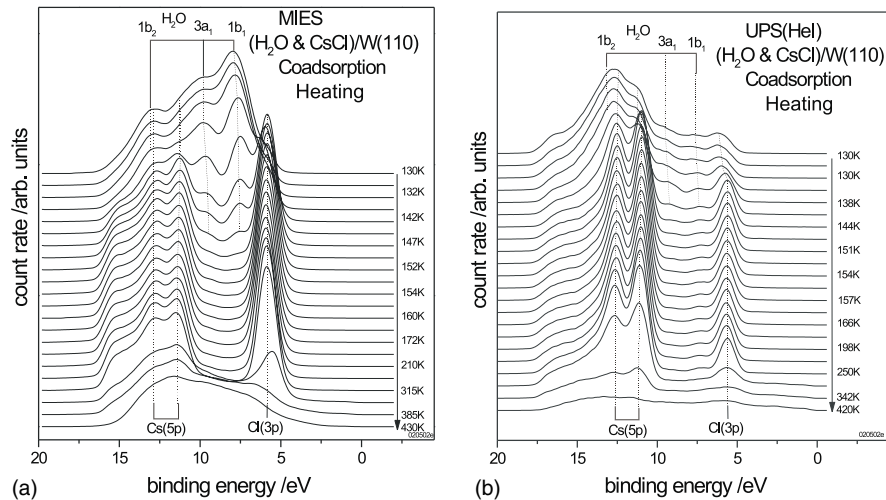
Fig. 3. MIES (a) and UPS(HeI) (b) spectra obtained during the heating (130–500 K) of the mixed CsCl/water film (top spectrum of Fig. 2; stoichiometry CsCl · 9H$_2$O).

deposition on SW and those for aqueous solutions of KCl [8] and CsF [9] suggests that CsCl dissociates when deposited onto SW of 130 K; hereby Cl$^-$ and Cs$^+$ ions are formed. Apparently, the water molecules possess enough mobility to create an interface site that allows for the dissociation of the salt species.

The comparison of MIES and UPS suggests the following scenario: the Cl and Cs species become hydrated, penetrate the surface and become solvated:

- The hydration and surface penetration follow from the fact that, as verified by MIES, water forms the toplayer (unless the amount of water is insufficient for hydration as for over-critical stoichiometries). Moreover, the annealing experiments suggest that water is present in two different environments, (i) hydrogen-bonded, without direct interaction with the salt components and (ii) involved into the hydration of the ions.
- The solvation is suggested by the fact that our results for CsCl deposition on SW (Fig. 1) and for salt and water codeposition (Fig. 2) are rather similar. The solvation of the species may be accompanied by the transport of water molecules from inside the film to the surface as

suggested in [12], thus restoring, to a large extent, the composition and topology of the surface, and, consequently, allowing additional water molecules to become accommodated at the surface.

The proposed scenario is similar to that for HCl reacting with SW films [12]: HCl is also initially dissociated; above about 125 K rapid migration into the water film takes place with the formation of a trihydrate phase HCl · 3H$_2$O.

Beyond the critical stoichiometry the solvation of the ions causes considerable changes in the water-induced part of the MIES spectra. The fact that this part of the spectrum develops gas phase-like features indicates that the behaviour of the water molecules is influenced by their interaction with the solvated ions mostly, rather than by interaction among themselves. The number of free water molecules is now not large enough anymore to create a dense solvation shell for newly arriving CsCl. This is concluded from the fact that Cl3p and Cs5p features appear in the MIES spectra and, at the same time, the 3a$_1$ feature develops into a well-defined peak.

A molecular dynamics simulation is available for a concentrated aqueous CsF solution [10]. The surface of the system was found to consist of

nearly pure water; this region extended about 0.2 nm below the surface. This was explained by the fact that the F^- and Cs^+ ions are hydrated, and keep their solvation shell intact at the surface, as is found for Cs^+ and Cl^- in the present case. A tendency was found that Cs^+ is located somewhat closer to the surface than F^-. In the present case a similar tendency cannot be substantiated.

5. Summary

We have shown that MIES, in combination with UPS(HeI), can be employed successfully to investigate the interaction of salt molecules, CsCl in the present case, and films of SW (three layers thick, held at 130 K). The UPS spectra are rather similar to the corresponding ones for liquid salt solutions. The following scenario describes our results consistently: the CsCl molecules dissociate into Cl^- and Cs^+ upon adsorption. The ions form complexes with water molecules and become solvated into the water film. With MIES we establish that up to a critical stoichiometry of $CsCl \cdot 6H_2O$ very little Cl and Cs is located at the surface. The MIES spectra are typical for condensed water where interactions between adjacent water molecules via hydrogen bonds dominate. It is concluded that both Cl^- and Cs^+ keep their solvation shells intact near the surface. Thus, a water top layer is formed by the solvation shells of the Cl and Cs ions.

Above the critical stoichiometry both Cl and Cs species can be detected with MIES; apparently, the solvation shells of near-surface ions become less dense. The water contribution to the spectra becomes more gas phase-like; in particular the $3a_1$ structure develops into a well-defined peak, indicating that beyond the critical stoichiometry the behaviour of the water molecules is increasingly governed by the interaction with the embedded ions. When heating the film, MIES provides information on the solvation shells: it is found that the shells consist of water molecules which bond among each other via hydrogen bonds, on the one hand, and others that interact directly with the ions, on the other hand.

Work at lower water film temperatures is in progress.

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