Ionization and Solvation of CsCl Interacting with Solid Water

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The interaction of CsCl with solid water, deposited on tungsten at 130 K, was investigated. Metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy [UPS(He I)] were applied to study the emission from the ionization of Cl(3p) and Cs(5p) and $1b_1$, $3a_1$, and $1b_2$ of molecular water. Below a critical stoichiometry of about CsCl·6H$_2$O the UPS spectra are quite similar to those for co-deposition of water and CsCl on tungsten, also studied here, and from chlorides solvated in liquid water inasmuch as the relative positions and intensities of the water and salt features are concerned. Very little emission from Cl(3p) and Cs(5p) is observed with MIES. We propose that CsCl dissociates, and the resulting ions become solvated in solid water. For supercritical stoichiometries Cs and Cl appear at the solid water surface and become accessible by MIES. CsCl-induced destruction of the water network takes place at the surface, and water molecules interact mainly with Cs and Cl, rather than with other water molecules. When subcritical films are heated above 135 K, the water-induced part of the spectrum changes its shape and becomes more gas phase like. Beyond 160 K no water can be detected with MIES. Above this temperature only Cs and Cl are found on the surface and desorb around 450 K. We have also studied water adsorption at 130 K on CsCl films. CsCl becomes solvated and migrates into the water overlayer.

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). Recently, sophisticated surface-analytical techniques were applied to study the interaction of atoms and molecules with solid water films. Explicitly, we mention the application of TPD,[6] FTIR,[7] low-energy reactive ion scattering,[8] and NEXAFS[9] to the interaction of HCl with solid water, of the electron-stimulated desorption to the ion release from solid argon, partially covered by NaCl,[10] and of the low-energy reactive ion scattering to the hydration of Cs$^+$ ions scattered from ice films[11] and to ionic dissociation of NaCl on solid water.[12]

In the past, electron spectroscopic techniques have been demonstrated to be a powerful tool to study the physics and chemistry on surfaces.[1,13] For insulating substrates the problem of the surface charge-up could be circumvented by performing the experiments on sufficiently thin films deposited on conducting substrates. We study the surface chemistry on water films under ultrahigh vacuum conditions with metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron

spectroscopy [UPS(He I)]. The films are grown "in situ" via deposition onto a tungsten substrate at 130 K. As was pointed out previously, this approach has several advantages: (1) it is a relatively simple matter to investigate both surface and bulk phenomena for films when using the particular technique combination of MIES and UPS,[5] (2) surface charging is eliminated when using sufficiently thin films,[5] and (3) condensation of water molecules below about 135 K results in the formation of an amorphous form of solid water (SW).[6,14] To a large extent, the properties of SW are believed to be comparable to those of liquid water, in particular with regard to its molecular orientation; SW can therefore be considered as a liquid water substitute, although with a significantly lower water pressure. This makes a comparison of the results with those obtained by UPS on liquid water surfaces and aqueous solutions meaningful.[15−18] Previous studies carried out under similar conditions were on the interaction of SW with Na atoms and CH$_3$OH.[5]

We report here combined MIES/UPS studies for CsCl molecules interacting with ultrathin SW films prepared as indicated above. Among the electron spectroscopic tools MIES is characterized by its extremely high surface sensitivity because the He* probe atoms interact with the edge of the surface when still 3−5 au away from the surface.[18,19] Consequently, only the species adsorbed on top of the film will be seen with MIES, in contrast to UPS which will detect both the surface-adsorbed species and those within about three layers below the top of the film. Thus, the combination of MIES and UPS appears well-suited to study the adsorption and dissociation of salt molecules at and the penetration of the resulting ions into solid water surfaces. As compared to other chlorides, CsCl offers the advantage that cation and anion are both accessible to ionization with the techniques employed in this study. We present evidence for ionic dissociation of CsCl during its interaction with water

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at 130 K, followed by migration of solvated species into the layer. The stoichiometry up to which the film surface still closely resembles condensed water is approximately $CsCl \cdot 6H_2O$. Beyond that, interaction of water is mainly with solvated ions, rather than among themselves. A preliminary account of some of the results can be found in ref 20.

2. Experimental Remarks

Experimental details were given previously.[21-25] Briefly, the apparatus is equipped with a cold-cathode gas discharge source for the production of metastable He*(^{3}S/^{1}S) ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy and He I photons ($E^* = 21.2$ eV) as a source for ultraviolet photoelectron spectroscopy (UPS). The intensity ratio ^{3}S/^{1}S is found to be 7:1. In MIES metastable He*1s2s atoms are utilized to eject electrons from the surface. Since the metastables approach the surface with near-thermal kinetic energy (60–100 meV), this technique is nondestructive and highly surface sensitive (see refs 18 and 19 for more detailed introductions into MIES and its various applications in molecular and surface spectroscopy). A discharge serves both as a source for an intense beam of He*1s2s atoms for MIES and as a He I photon source for UPS (He I with 21.2 eV). The spectral contributions from metastables and photons are separated by means of a time-of-flight technique. 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. The measurements were performed using a hemispherical analyzer (Leybold EA10/100). To minimize charge-up phenomena, we worked with low beam current densities, and thus an energy resolution of 600 meV was employed for MIES/UPS. The spectra showed no basic changes at 250 meV resolution.

By applying suitable biasing, electrons emitted from the Fermi level, E_F, are registered at 19.8 eV (the potential energy of He*-(2^3S)). Consequently, the onset of the spectra at low kinetic (high binding) energies 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 liquid N_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. The water was cleaned by several freeze–pump–thaw cycles. The cleanliness of the water was checked with a quadrupole mass spectrometer. The amount of surface-adsorbed water is estimated on the basis of our previous results concerned with the water–titania interaction:[25] essentially, we make use of the fact that (a) water adsorption leads to an initial work function decrease up to half coverage of the surface, and (b) the MIES signal from water saturates for full coverage of the surface. From this we conclude that at 2 langmuirs (L) exposure the surface is covered by 1 bilayer (BL) of water. At 5 L emission from the tungsten substrate has essentially disappeared in the UPS(He I) spectra.

The CsCl exposure is given in units of monolayer equivalents (MLE); at 1 MLE the surface would be covered by one CsCl layer if not for penetration effects. Our previous results for salt adsorption on tungsten indicate that the observed work function minimum occurs at 0.5 MLE.[26-29]

Annealing of the prepared films is done stepwise; during the collection of the MIES/UPS spectra the substrate temperature is kept constant.

3. Results

This section starts with the discussion of the spectral features expected from the ionization of CsCl and water, and a comparison with the information available in the literature on these and similar species. All results are presented as a function of the binding energy, E_B, of the emitted electrons. Electrons from the Fermi level would appear at zero energy in the MIES and UPS spectra. The change of the work function (WF) with exposure is determined from the cutoff of the MIES spectra at large binding energies.

In the present paper we confine ourselves to a qualitative analysis of the MIES spectra: the comparison of the MIES and UPS spectra indicates that the spectral features seen in MIES are due to Auger deexcitation of He*.[18,19] In this case the position of the spectral feature gives the binding energy of the electron emitted from the considered species, and the intensity of the feature is a direct image of the density of states related to the species. Quantitative methods are available to either synthesize MIES spectra[30,31] (see ref 32 for an example) or to deconvolute them.[18]

3.1. Signature of CsCl and Water Species on W(110). The spectra for a CsCl-exposed tungsten surface will be presented below when discussing the adsorption of water on CsCl films. Peaks are seen from the Cs(5p) (11.5 and 13 eV for Cs($5p_{3/2}$) and Cs($5p_{1/2}$), respectively) and Cl(3p) (5 eV) ionization. Although the relative intensities of the Cs(5p) fine structure components are different in MIES and UPS, the overall similarity of the spectra suggests that the MIES spectra are due to the Auger deexcitation process. Combined MIES/UPS results for other alkali metal halides on tungsten are available for NaCl,[26] CsI,[27] and LiF,[28,29] and the energetic positions of Cl-(3p) and Cs(5p) reported here and in refs 26 and 27 agree well.

Water exposure at 130 K produces the three features $1b_1$, $3a_1$, and $1b_2$ seen both with MIES and UPS (see spectra presented below). Combined MIES/UPS results were published for the water adsorption on MgO[5] and TiO$_2$;[25] the spectra from water multilayers are rather similar in all cases studied so far with MIES/UPS. It should also be noticed that our UPS date for SW films are rather similar to those for liquid water.[15]

First principles calculations carried out on ice[33] suggest that the $1b_2$ peak represents an intramolecular bonding combination between O(2p) and H(1s) orbitals. The $1b_1$ peak can be assigned to lone-pair electrons on oxygen atoms; the hydrogen contribution is much smaller than in $1b_2$. The $3a_1$ feature (which appears considerably more diffuse in the spectra than $1b_1$ and $1b_2$) corresponds to delocalized states with intermolecular contributions from different water molecules interacting via hydrogen bonds. Thus, the broad $3a_1$ feature is characteristic for condensed water, in either the liquid or solid phase, and signals the presence of a water network, formed by hydrogen bonds.

3.2. Water–CsCl Interaction. In the following we present three sets of MIES/UPS results that give information on the CsCl–water interaction at 130 K: (1) co-deposition of water and CsCl on tungsten (Figure 1), (2) CsCl deposition on solid water films (Figure 3), and (3) water deposition on CsCl films (Figure 4). Also shown are results obtained during the annealing of the films produced in (1)–(3) (Figure 2).

For a comparison with UPS data for aqueous liquid salt solutions, we have studied the co-deposition of water and CsCl (see Figure 1 for MIES (a) and UPS (b)). We have deliberately chosen a CsCl exposure rate at which little emission from Cs and Cl appears in the MIES spectra. Nevertheless, Cl(3p) and Cs(5p) emission is clearly seen in the UPS spectra. Since we still see weak Cl(3p) emission in MIES (as suggested by the
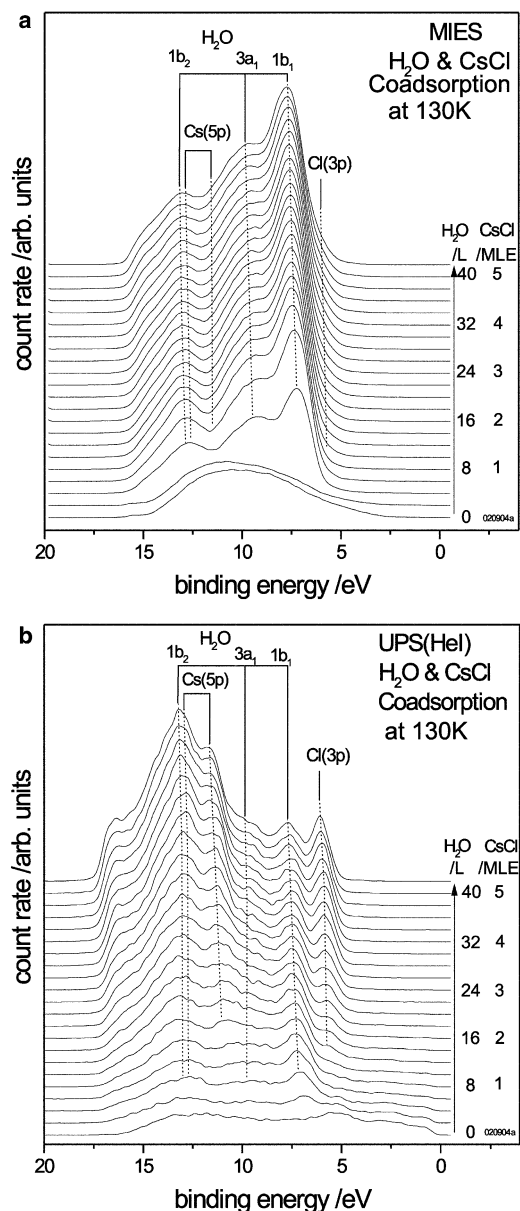
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Figure 1. (a) MIES spectra obtained during the co-deposition of CsCl and water onto W(110) held at 130 K. Exposure is given in langmuirs (L) (1 langmuir = 10^{-6} Torr·s).
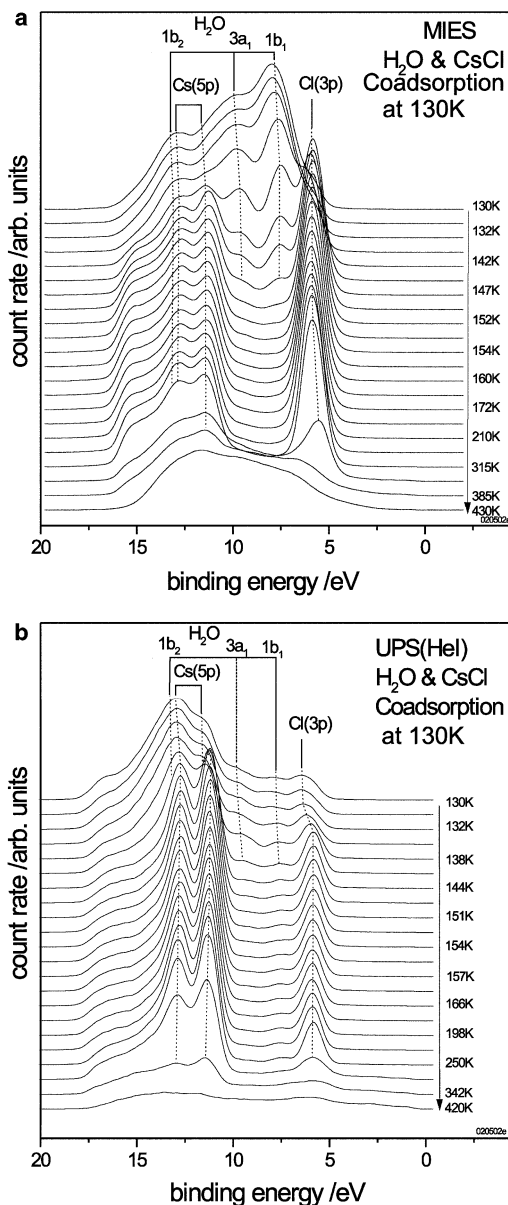

Figure 2. (a) Spectral changes observed with MIES when annealing the top spectrum of Figure 1a. (b) Spectral changes observed with UPS-(He I) when annealing the top spectrum of Figure 1b.

onset of the $1b_1$ water peak, which is softer than for pure water), we conclude that the Cl(3p) species, covered by not more than one water layer, exist near the film surface. The estimated stoichiometry is $CsCl·6H_2O$. To arrive at this estimate, we have taken into account the different surface density of the molecules in water and CsCl layers, and assumed a homogeneous depth distribution of the salt species. Alternatively, we can compare the peak areas in the UPS spectra: when assuming equal cross sections for photoionization of Cl(3p) and the three water states $1b_1$ to $1b_2$, we arrive at the same stoichiometry.

We can compare our UPS(He I) results with those for a CsF· $2.6H_2O$ solution, which is close to the salt saturation concentration.[16] As far as the Cs- and water-induced spectral features are concerned, the spectra compare well with ours. It should, however, be noted that in ref 16 a different interpretation is given to that part of the spectra where the $1b_2$ and Cs($5p_{1/2}$) features overlap. It was already questioned in ref 15 whether the small feature seen at 12.5 eV kinetic energy is due to F(2p) ionization. Indeed, we find that for CsF adsorption on SW the spectral features F(2p) and $1b_1$ almost coincide, and that their

intensity ratio is comparable to that of Cl(3p) and $1b_1$ in the present work.[34]

Concerning the Cl(3p) emission, we can compare with the He I spectra of a 3 M KCl aqueous solution[15] (stoichiometry about $KCl·18H_2O$). The Cl-induced part is rather similar to CsCl, as far as both the energetic positions and the shape of the Cl- and water-induced features are concerned. The Cl/water intensity ratio is about 3 times smaller than in the present case. The similarity of the present UPS results suggests that, as in liquid aqueous salt solutions, ionic dissociation takes place for co-deposition of CsCl and water at 130 K, and Cs^+ and Cl^- are present as solvated species.

Figure 2 presents MIES and UPS results obtained when heating the film, characterized by the top spectra in Figure 1, from 130 to 430 K. Before heating, the signature of the Cs and Cl species can barely be seen in MIES. However, above 140 K the signature of Cs and Cl can clearly be noticed also in MIES, indicating that these species are now accessible to interaction with the He* probe atoms. The $3a_1$ structure (which is diffuse for pure water; see Figure 3) becomes rather well-defined. In
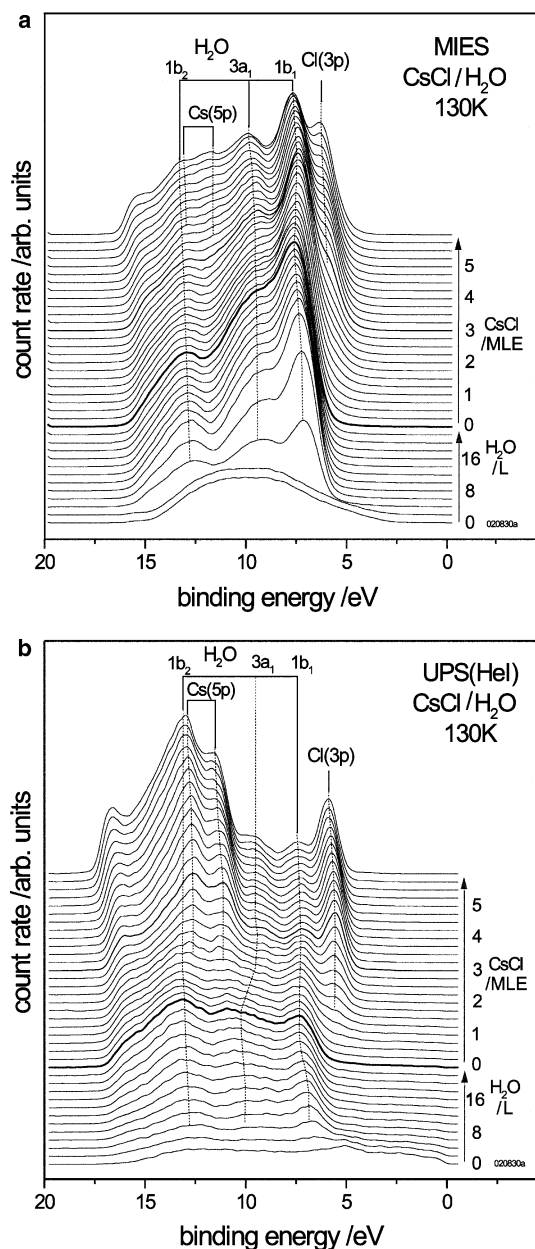
Figure 3. (a) MIES spectra during growth of water films (approximately 12 bilayers thick) on W(110) at 130 K, followed by exposure to CsCl. (b) UPS(He I) spectra during growth of water films (approximately 12 bilayers thick) on W(110) at 130 K, followed by exposure to CsCl.

Figure 4. (a) MIES spectra obtained for condensation of water onto CsCl film deposited on W(110) at 130 K. (b) UPS(He I) spectra obtained for condensation of water onto CsCl film deposited on W(110) at 130 K.

fact, the water part in MIES is reminiscent of gas-phase-like water spectra.[1,3] This indicates that direct interaction of water with Cs and/or Cl species dominates over water–water interactions and no hydrogen-bonded network exists at these temperatures. The shift in the onset of Cl(3p) with increasing temperature seen in Figure 2b could reflect the fact that the binding energy of solvated Cl species is larger by 0.6 eV than that in isolated CsCl molecules. In Born's model this situation is modeled by embedding the Cl species in a cage formed by the surrounding dielectric medium.[15] However, small changes in the onset of the spectra at large binding energies and of the Cl(3p) energetic position could also be caused by charge-up phenomena. They would shift the spectral features Cl(3p) and $1b_1$ to $1b_2$ from water simultaneously, which is not the case, neither in Figure 2 nor in Figure 4. Thus, we tend to believe that the observed shift may indeed reflect the change in binding energy of the Cl(3p) electron upon solvation. According to
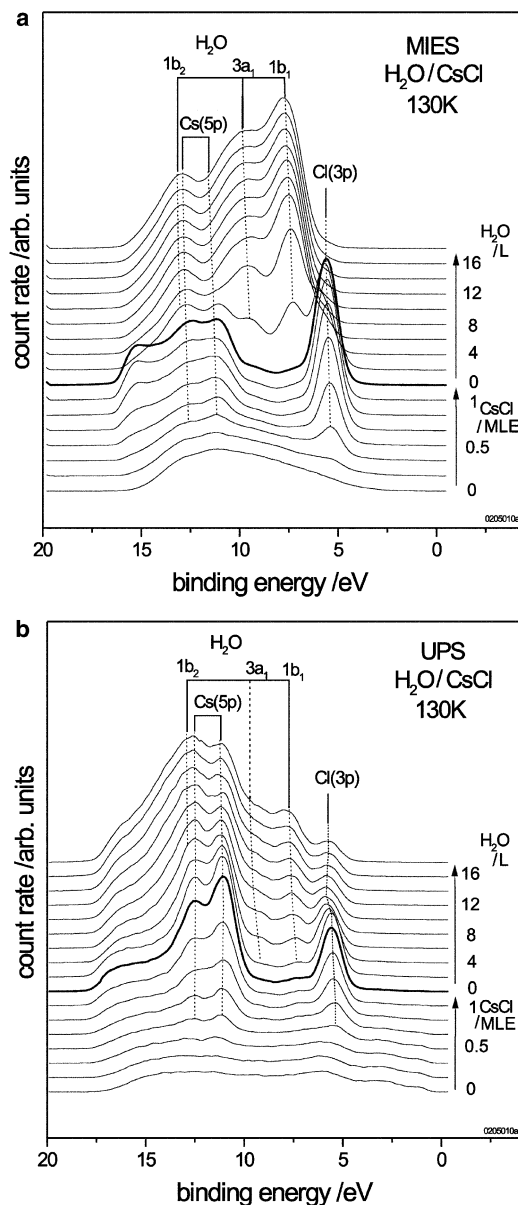
MIES, most of the water has desorbed around 155 K (the small feature seen in UPS near the position of $1b_1$ is due to incomplete separation of the MIES and UPS contribution to the spectra). Above 160 K only Cs and Cl species can be detected by MIES and UPS and desorb around 350 K. We do not detect any OH fragments which could, as in the case of solid water on MgO, be produced at the water/tungsten interface.[5]

Figure 3 displays the results obtained during the deposition of CsCl onto SW (12 bilayers). Already during the early stage of exposure pronounced Cl(3p) emission develops in the UPS spectra at $E_B = 5.8$ eV (Figure 3b) while it remains rather weak in the MIES spectra up to 3 MLE (7% of the total emission), and merely produces the small shoulder on the rise of the strong $1b_1$ peak from water (Figure 3a). Moreover, while the Cs(5p) emission is the dominant spectral contribution to UPS, it cannot be detected unambiguously with MIES at this stage. Up to 3 MLE the SW spectral features change little in MIES as far as their energetic position and shape is concerned. This, together with the weak Cl(3p) emission and the absence of Cs(5p)

emission in the MIES spectra at this stage, indicates that the top layer must consist of water molecules mainly; they shield the Cl and Cs species efficiently from their interaction with the He* probe atoms. According to MIES, water−water interaction dominates in the top layer. This implies migration of the adsorbed species into the water film after deposition. At this stage both the MIES and UPS spectra resemble closely those obtained by co-deposition of CsCl and water (Figure 1). For co-deposition we have evidence that ionic dissociation of CsCl may take place. Therefore, the stated similarity is indication that for small exposures solvation and dissociation of the adsorbed CsCl take place prior to the migration of Cs and Cl into the film.

For exposures beyond 3 MLE the $3a_1$ feature seen with MIES narrows considerably and becomes a well-defined peak, very similar to what is seen in Figure 2 when heating films produced by co-deposition. Clearly, CsCl-induced destruction of the water network takes place at the surface. At 3 MLE the nominal stoichiometry corresponds to that chosen in Figure 1 for coadsorption, namely CsCl·6H_2O; in the following it will be called the critical stoichiometry. Nevertheless, Cl(3p) is twice as large as in Figure 1b. This indicates that under the conditions of Figure 3 the depth distribution of the salt molecules is not homogeneous. When the film represented by the top spectrum of Figure 3 (supercritical stoichiometry) is heated, the MIES and UPS spectra become similar to those in Figure 2, in particular above 140 K.

Figure 4 shows MIES (a) and UPS (b) results for the condensation of water on a CsCl film (1 monolayer) on tungsten held at 130 K. Below about 4 L the water-induced features $1b_1$, $3a_1$, and $1b_2$ remain well-defined peaks in MIES; for larger exposures, however, the spectrum typical for condensed water develops, displaying, in particular, the rather diffuse $3a_1$ feature. Beyond about 6 L both Cl(3p) and Cs(5p) have disappeared in MIES almost completely. In contrast, their signature is still clearly seen in UPS, and the respective UPS intensities show only a weak exposure dependence at least up to 18 L, i.e., up to exposures where 9 water bilayers would have built up on tungsten. We notice the water-induced shift of Cl(3p) of 0.6 eV at 3 L already seen in Figure 2b.

Taking into account the combined LEED and UPS results,[36] and the ion scattering data for water condensation on NaCl,[12] we are led to the following interpretation: initially, two-dimensional (2D) water condensation takes place whereby the interaction is predominantly with Cs and Cl species. At this stage the existence of gas-phase-like water features, in particular the well-defined $3a_1$ peak, excludes water clusters. In the case of NaCl the LEED reflexes from, in particular, the water superstructure disappear at this stage, indicating that a transition from 2D to 3D (three-dimensional) condensation takes place around 3 L. For CsCl the $3a_1$ feature becomes diffuse in MIES around 6 L, indicating that now water−water interaction begins to dominate in the top layer, and a transition from 2D to 3D condensation has taken place. Since the Cs- and Cl-induced emission has almost completely disappeared in MIES at 6 L, but persists in UPS up to at least 18 L, we conclude that CsCl becomes solvated into the deposited water film. This view is supported by the observed water-induced shift of the Cl(3p) peak. For a NaCl surface at 273 K, covered by more than about 2 BL of water, it was demonstrated by IR spectroscopy that ions from the substrate are indeed incorporated into the film.[37]

4. Solvation and Dissociation of CsCl on Solid Water

We concentrate now on the fate of CsCl adsorbed on SW at 130 K. MIES reveals that the CsCl species tend to become

covered by molecules of the water film. From our results alone we cannot exclude that molecular hydration, followed by the migration of the hydrated molecular CsCl into the film, takes place. However, when our data are combined with previous work, mainly on NaCl, it appears more likely that at 130 K, as for NaCl,[11,12] ionic dissociation of CsCl takes place at subcritical stoichiometries; the Cl and Cs species form complexes with water molecules, penetrate the surface, and become embedded into the film.

The dissociation is suggested by the close similarity of the UPS results of Figure 3 with those for co-deposition (Figure 1) and liquid salt solutions.[15,16] This view is supported by the following facts: (1) at least for NaCl no hydrated molecular species exist,[12,35] (2) at 15 K Na^+·$(H_2O)_n$ complexes are formed when NaCl and H_2O molecules are co-deposited on solid Ar,[10] and (3) low-energy reactive ion scattering experiments show that NaCl dissociates almost completely on SW surfaces, even at 110 K, forming solvated ions.[12]

$Cs(H_2O)_n$ complex formation, as a precursor for solvation, even on the time scale of 10^{-13} s, was demonstrated very directly by scattering Cs^+ ions from SW.[11]

The surface penetration follows from the fact that, as verified by MIES, water forms the top layer (except for supercritical stoichiometries). Inspection of theoretical results for the penetration of pollutants into SW films suggests that the ions may mostly be located within the first two water bilayers.[38] On the other hand, for NaCl on SW of 110 K the diffusion of Na^+ into the water film is insignificant, although efficient dissociation of NaCl still takes place.[12]

The solvation is suggested by the fact that our results for salt and water co-deposition (Figure 1) and for CsCl adsorption on solid water (Figure 3) are rather similar. Also the water-induced shift of Cl(3p) seen in Figures 2 and 4 supports this view. Solvation may be accompanied by the transport of water molecules from inside the film to the surface as suggested in ref 7, thus restoring the composition and topology of the surface, and, consequently, allowing additional water molecules to become accommodated at the surface. New data taken by us between 80 and 150 K show that the probability for hydration and penetration of CsCl is greatly reduced below 115 K.

A molecular dynamics simulation is available for a concentrated aqueous CsF solution.[17] The surface of the system was found to consist of nearly pure water; this region extended about 0.2 nm below the surface. It was concluded that the F^- and Cs^+ ions are solvated, and keep their solvation shell intact at the surface. A tendency was found that the Cs ions are located somewhat closer to the surface than the F ions. In the present case a similar tendency cannot be substantiated.

The annealing experiments (Figure 2) suggest that water is present in two different environments: (i) hydrogen bonded, without direct interaction with the salt components, and (ii) involved into the solvation of the ions.

The results for water deposition on CsCl films (see Figure 4) are consistent with the scenario proposed above: CsCl dissociation takes place at the (H_2O−CsCl) interface. The resulting solvated Cs and Cl ions migrate into the water adlayer. MIES will not be able to detect these species because they retain their solvation shells. On the other hand, UPS will register those solvated ions that become located within the information depth of UPS underneath the top of the water layer.

A scenario similar to that discussed above appears to describe the HCl interaction with SW: at 130 K HCl is dissociated as suggested by the occurrence of broad IR bands characteristic for hydronium ion (H_3O^+) formation[7] as well as from the

reactive ion scattering spectra which display hydronium ions.[8] Above about 125 K rapid migration into the water film takes place, which leads to the formation of a trihydrate phase HCl·3H$_2$O.[7]

5. Summary

We have shown that MIES, in combination with UPS(He I), can be employed successfully to investigate processes between salt molecules, CsCl in the present case, and solid water. We have studied the adsorption of CsCl on water and the co-deposition of CsCl and water on tungsten, both 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. With MIES we establish that up to a critical stoichiometry of CsCl·6H$_2$O very little Cl and Cs are located at the surface and, thus, the ions become solvated in the water film. The water top layer is formed by the Cl and Cs ion solvation shells which remain intact at the surface. Above the critical stoichiometry, besides water, Cl and Cs species are found in the top layer, indicating that the migration of CsCl species is largely suppressed. In this range the water contribution to the spectra becomes more gas phase like; the 3a$_1$ structure, in particular, develops into a well-defined peak, indicating that above the critical stoichiometry ion-induced destruction of the hydrogen-bonded water network takes place at the surface, and ion−water, rather than water−water, interactions dominate. When the film is heated, MIES provides information on the solvation shells: it is found that they consist of water molecules which bond among each other via hydrogen bonds, on one hand, and water molecules that interact directly with the ions, on the other hand.

We have also studied the water adsorption on CsCl films at 130 K. Initially, 2D condensation takes place whereby the water interaction is mainly with the ions of the CsCl film. According to UPS, solvated Cs and Cl species are formed at larger water exposures and migrate into the water film.

References and Notes

(1) Henrich, V. E.; Cox, P. A. *The surface science of metal oxides*; Cambridge University Press: Cambridge, 1994.

(2) Brown, G. E., Jr.; et al. *Chem. Rev.* **1999**, *99*, 77.

(3) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211.

(4) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *285*, 1−308.

(5) Günster, J.; Krischok, S.; Kempter, V.; Stultz, J.; Goodman, D. W. *Surf. Rev. Lett.* **2002**, *9*, 1511.

(6) Graham, J. D.; Roberts, J. T. *J. Phys. Chem.* **1994**, *98*, 5974.

(7) Haq, S.; Harnett, J.; Hodgson, A. *Phys. Chem. B* **2002**, *106*, 3950.

(8) Kang, H.; Shin, T.-H.; Park, S.-C.; Kim, I. K.; Han, S.-J. *J. Am. Chem. Soc.* **2000**, *122*, 9842.

(9) Bournel, F.; Mangeney, C.; Tronc, M.; Laffon, C.; Parent, P. *Phys. Rev. B* **2002**, *65*, 201404.

(10) Souda, R. *Phys. Rev. B* **2002**, *65*, 245419.

(11) Shin, T.-H.; Han, S.-J.; Kang, H. *Nucl. Instrum. Methods B* **1999**, *157*, 191.

(12) Park, S.-C.; Pradeep, T.; Kang, H. *J. Chem. Phys.* **2000**, *113*, 9373.

(13) Ertl, G.; Küppers, J. *Low Energy Electrons and Surface Chemistry*; VCH Publishers: New York, 1985.

(14) Devlin, J. P. *Int. Rev. Phys. Chem.* **1990**, *9*, 29.

(15) Faubel, M. In *Photoionization and Photodetachment, Part I*; Ng, C. Y., Ed.; World Scientific: Singapore, 2000; p 634.

(16) Böhm, R.; Morgner, H.; Overbrodhage, J.; Wulf, M. *Surf. Sci.* **1994**, *317*, 407.

(17) Dietter, J.; Morgner, H. *Chem. Phys.* **1997**, *220*, 261.

(18) Morgner, H. *Adv. At. Mol. Opt. Phys.* **2000**, *42*, 387.

(19) Harada, Y.; Masuda, S.; Osaki, H. *Chem. Rev.* **1997**, *97*, 1897.

(20) Borodin, A.; Höfft, O.; Krischok, S.; Kempter, V. *Nucl. Instrum. Methods Phys. Res. B* **2003**, *203*, 205.

(21) Maus-Friedrichs, W.; Wehrhahn, M.; Dieckhoff, S.; Kempter, V. *Surf. Sci.* **1991**, *249*, 149.

(22) Ochs, D.; et al. *Surf. Sci.* **1996**, *365*, 557.

(23) Ochs, D.; Brause, M.; Braun, B.; Maus-Friedrichs, W.; Kempter, V. *Surf. Sci.* **1998**, *397*, 101.

(24) Ochs, D.; Braun, B.; Maus-Friedrichs, W.; Kempter, V. *Surf. Sci.* **1998**, *417*, 390.

(25) Krischok, S.; Höfft, O.; Günster, J.; Stultz, J.; Goodman, D. W.; Kempter, V. *Surf. Sci.* **2001**, *495*, 8.

(26) Dieckhoff, S.; Müller, H.; Brenten, H.; Maus-Friedrichs, W.; Kempter, V. *Surf. Sci.* **1992**, *279*, 233.

(27) Hitzke, A.; Pülm, S.; Müller, H.; Hausmann, R.; Günster, J.; Dieckhoff, S.; Maus-Friedrichs, W.; Kempter, V. *Surf. Sci.* **1993**, *291*, 67.

(28) Pülm, S.; Hitzke, A.; Günster, J.; Müller, H.; Kempter, V. *Radiat. Eff. Defects Solids* **1994**, *128*, 151.

(29) Ochs, D.; Brause, M.; Stracke, P.; Krischok, S.; Wiegershaus, F.; Maus-Friedrichs, W.; Kempter, V.; Puchin, V. E.; Shluger, A. L. *Surf. Sci.* **1997**, *383*, 162.

(30) Eeken, P.; Fluit, J. M.; Niehaus, A.; Urazgil'din, I. *Surf. Sci.* **1992**, *273*, 160.

(31) Kantorovich, L. N.; Shluger, A. L.; Sushko, P. V.; Günster, J.; Stracke, P.; Goodman, D. W.; Kempter, V. *Faraday Discuss.* **1999**, *114*, 173.

(32) Brause, M.; Skordas, S.; Kempter, V. *Surf. Sci.* **2000**, *445*, 224.

(33) Casassa, S.; Ugliengo, P.; Pisani, C. *J. Chem. Phys.* **1997**, *106*, 8030.

(34) Borodin, A.; Höfft, O.; Kempter, V. *J. Phys. Chem.*, in preparation.

(35) Cziczo, D. J.; Abbatt, J. P. D. *J. Phys. Chem. A* **2000**, *104*, 2038.

(36) Fölsch, S.; Stock, A.; Henzler, M. *Surf. Sci.* **1992**, *264*, 65.

(37) Foster, M.; Ewing, G. E. *Surf. Sci.* **1999**, *427−428*, 102.

(38) Girardet, C.; Toubin, C. *Surf. Sci. Rep.* **2001**, *44*, 159.