

Interaction of CsF with Multilayered Water

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Received: April 25, 2005; In Final Form: June 20, 2005

The interaction of CsF with multilayered water has been investigated with metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy with HeI (UPS(HeI)). We have studied the emission from the ionization of H₂O states 1b₁, 3a₁, and 1b₂; of Cs5p and of F2p. We have prepared CsF–H₂O interfaces, namely, CsF layers on thin films of multilayered water and vice versa; they were annealed between 80 and about 280 K. Up to about 100 K, a closed CsF layer can be deposited on H₂O and vice versa; no interpenetration of the two components H₂O and CsF could be observed. Above 110 K, CsF (H₂O) layers deposited on thin H₂O (CsF) films (stoichiometry CsF·1.5H₂O) gradually transform into a mixed layer containing F, Cs, and H₂O species. When annealing, H₂O molecules can be detected up to 200 K from the mixed F–Cs–H₂O layer (while for pure H₂O desorption is essentially complete at 165 K); a water network is not formed under these conditions, and all H₂O molecules are involved in bonding with Cs⁺ and F[−] ions. When CsF is deposited at 120 K on sufficiently thick water multilayers, full solvation of both F and Cs takes place, even for the species closest to the surface, as long as the stoichiometry remains CsF·(H₂O)_n with $n > 3$.

1. Introduction

The understanding of the interaction of halide salt molecules with water and vice versa is of interest in various fields, ranging from biological systems to catalysis and environmental sciences. Hydrated salt 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 halide species and/or catalysts for pollution reactions.^{1,2}

Molecular dynamics (MD) calculations have been performed on a number of alkali halides (in molar concentration as opposed to single ions) at the air–water interface.^{3,4} It was concluded that the distribution of the halide ions becomes structured as the anion size increases and that a spatial separation of cations and anions occurs in the interfacial region.⁴

A number of surface-analytical techniques have proven to be capable of providing detailed information on saltwater at low temperatures (below 140 K, typically): low-energy sputtering (LES)⁵ and reactive ion scattering (RIS)⁶ have proven to be sensitive tools for monitoring surface-near species in saltwater systems. Vibrational sum-frequency spectroscopy has, so far, only been applied to the surfaces of aqueous solutions of Na halides, including NaF;⁷ the results suggest a significantly diminished population of the anions at the interface. In metastable impact electron spectroscopy (MIES),^{8,9} metastable He atoms of thermal energy interact via Auger processes exclusively with the species at the surface of the saltwater system. The ejected electrons bear information on the electronic structure of the surface top layer. Thus, MIES appears to be well-suited to study solvation processes, as those occurring in the salt interaction with multilayered water. In the past, we have

applied the combination of metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy with HeI (UPS(HeI)) to the study of the interaction of CsCl with amorphous solid water at 130 K.^{10,11} For NaCl–water, the focus was on the solvation process which became noticeable for $T > 115$ K;¹² the spectroscopy results were backed up by first-principles density functional theory (DFT) calculations, concentrating on the electronic structure of solvated Cl[−] ions.

In the present work, we apply the combination of MIES and UPS(HeI) to the study of the CsF interaction with multilayered water. The F[−] anion, isoelectronic with water, is believed to be able to replace H₂O on all lattice sites without disturbing the lattice structure; that is, it is considered to be a “structure building” ion.¹³ Cs⁺, in turn, is a “structure breaking” ion and does not compete with water for lattice sites. The choice of a Cs salt allows the release of the uppermost p-electron of the cation, 5pCs, by MIES and UPS(HeI) which would not be possible for all other alkali cations. Emphasis is put on the details of the solvation process, that is, its onset with temperature and the structure of the solution. For this purpose, water films held at 80 K were exposed to CsF, and the change of the surface electronic structure with the temperature was monitored under the in situ control of MIES and UPS. Additional information on the solvation process was obtained by studying the interaction of H₂O molecules with CsF films.

The use of films, in the present case grown in situ on a tungsten substrate, 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 MIES and UPS,¹⁴ (2) surface charging is minimized when using sufficiently thin films,¹⁴ and (3) condensation of H₂O below about 135 K results in the formation of an amorphous form of solid water.^{15,16} To some extent, amorphous solid water can be considered as a “liquid water substitute”, possessing however a significantly lower vapor pressure. This allows a comparison

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of the present UPS results with those for liquid water surfaces and for aqueous salt solutions.^{3,8,17–19}

2. Experimental Section

The apparatus has been applied to the study of saltwater systems previously, and experimental details can be found in refs 10–12. Briefly, the apparatus is equipped with a cold-cathode gas discharge source for the production of metastable $\text{He}^*(^3\text{S}/^1\text{S})$ ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy and HeI photons ($E^* = 21.2$ eV) as a source for ultraviolet photoelectron spectroscopy (UPS(HeI)). The intensity ratio $^3\text{S}/^1\text{S}$ is found to be 7:1. Metastables of thermal kinetic energy (60–100 meV) approach the surface; therefore, this technique is nondestructive and highly surface sensitive (see refs 8 and 9 for more detailed introductions into MIES and its various applications in molecular and surface spectroscopy). The spectral contributions from metastables and photons are separated by means of a time-of-flight technique. MIES and UPS spectra were acquired with photon/metastable beams incident under 45° with respect to the surface normal; electrons emitted in the direction normal to the surface are analyzed using a hemispherical analyzer. 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 a suitable bias, electrons emitted from the Fermi level, E_F , are registered at 19.8 eV (the potential energy of $\text{He}^*(^2^3\text{S})$). 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 LN_2 to 80 K, as 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 amount of surface-adsorbed water is estimated on the basis of our previous results concerned with the water–titania interaction:²⁰ 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 L exposure the surface is covered by one bilayer (BL) of water. At 5 L, emission from the tungsten substrate has essentially disappeared in the UPS(HeI) spectra. Annealing of the prepared films is done in a stepwise manner; during the collection of the MIES/UPS spectra, the substrate temperature is kept constant.

The CsF exposure is given in units of monolayer equivalents (MLEs); at 1 MLE, the saturation coverage of the surface would be reached if it were not for penetration effects. Our previous results for salt adsorption on tungsten indicate that the observed work function minimum occurs at 0.5 MLE.^{21–24}

3. Results

This section starts with the identification of the spectral features expected from H_2O and CsF. In the present paper, we confine ourselves to a qualitative analysis of the MIES spectra: the comparison of the MIES and UPS spectra shows that the features induced by F, Cs, and H_2O in MIES occur at the same energies. This implies that the He^* –surface interaction is via Auger de-excitation (AD) of He^* .^{8,9} In this case, the position of the spectral features gives the binding energy of the electron emitted from the considered species.^{25,26} The Auger neutralization (AN) process takes place only at the bare W substrate. All

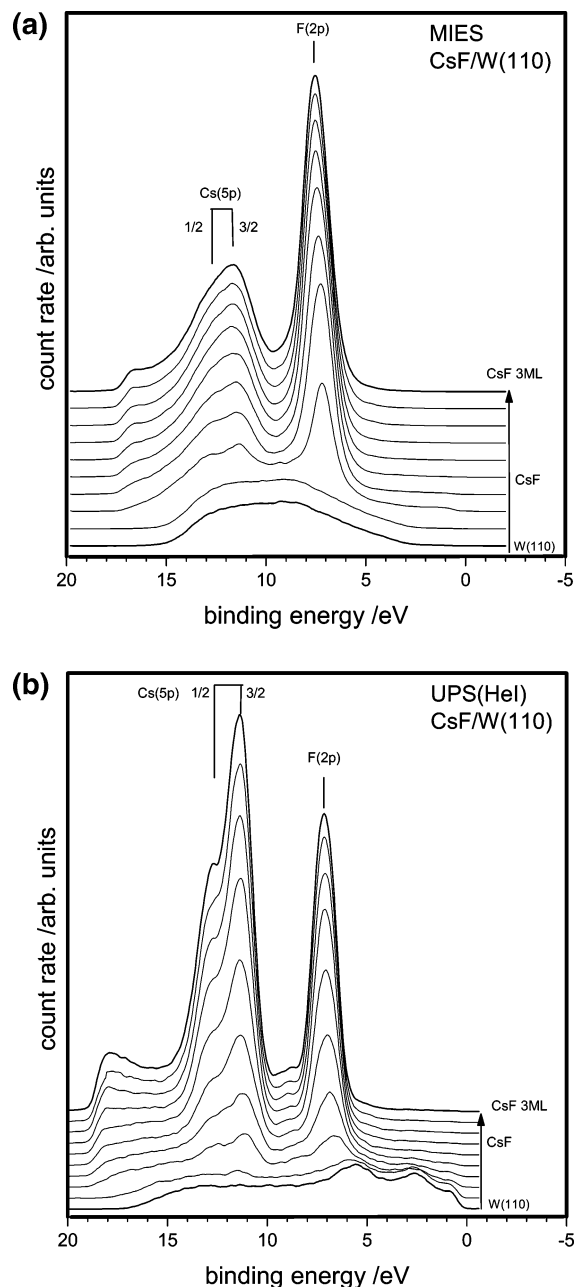


Figure 1. MIES (a) and UPS(HeI) (b) spectra recorded during the deposition of CsF onto W(110) at room temperature. The acronyms are explained in the text.

results are presented as a function of the binding energy, E_B , of the emitted electrons with respect to the Fermi level. As in ref 12, we suppose that the intensity of the spectral features from the AD process reflects directly the density of states initially populated. For quantitative methods for either synthesizing (see refs 25, 26, 27) or deconvoluting them (ref 8). By adding the work function to the reported E_B 's, the vertical ionization energies (VIEs) of the states involved in the ionization process are obtained.

3.1. Signature of Cs Halide and Water Species in MIES and UPS. Combined MIES/UPS results for CsX films are available for X=I on tungsten²² and for X=Cl on solid water.^{10,11} Peaks are seen from the ionization of $5p\text{Cs}$ (11.5 and 13 eV for $5p_{3/2}\text{Cs}$ and $5p_{1/2}\text{Cs}$, respectively) and the $np\text{X}$ orbital (5.5 and 4.7 eV for Cl and I, respectively). Figure 1 displays the MIES and UPS(HeI) spectra recorded during the deposition of CsF onto tungsten at room temperature; spectra for deposition

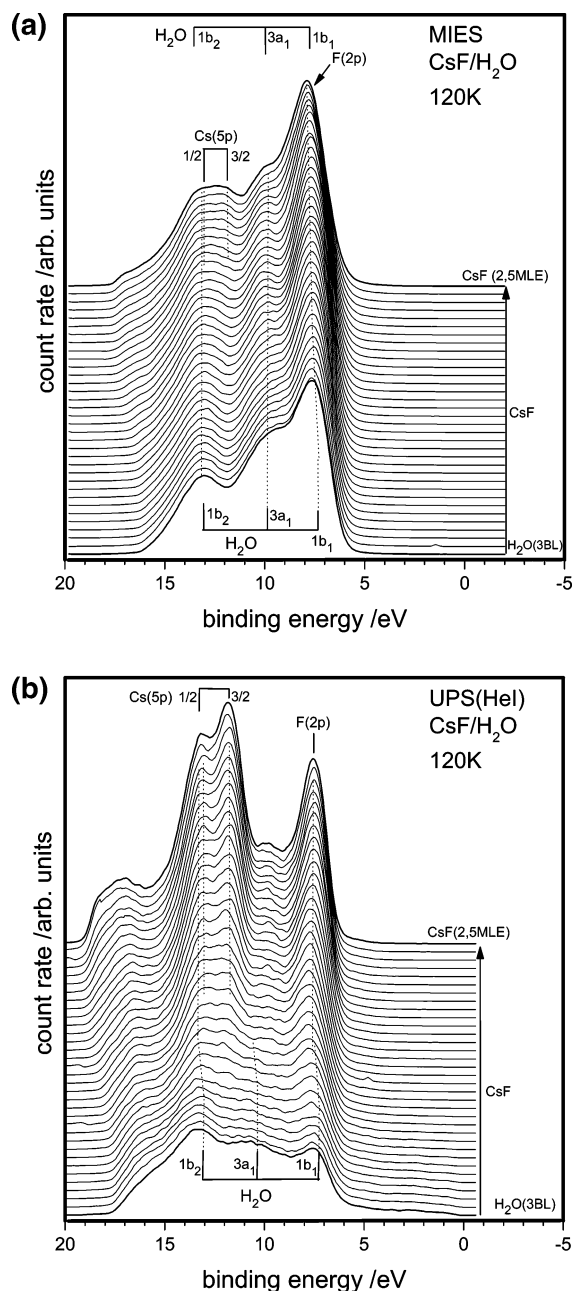


Figure 2. MIES (a) and UPS(HeI) (b) spectra recorded during the exposure of CsF onto multilayered water (3 BLs) at 120 K.

at 80 and 120 K are virtually identical. The CsF film is thermally stable up to about 450 K. 2pF ionization produces the peak at 7.2 eV, denoted as F(2p), at a binding energy which is about 1.7 eV larger than that of 3pCl. It was claimed that the 2pF ionization energy is about 2.5 eV smaller than that of 1b₁ which would imply that a peak from 2pF ionization should be seen near 5.0 eV (with respect to E_F).¹⁹ The expected feature was however not seen in the UPS results on water jets seeded with KF molecules.¹⁷ The emission from the ionization of 5p_{3/2}Cs and 5p_{1/2}Cs, denoted as Cs(5p), is seen at 11.1 and 12.3 eV, respectively.

Water exposure between 80 and 130 K produces the three H₂O-induced features 1b₁, 3a₁, and 1b₂^{14,20} seen both with MIES and with UPS (7.5, 9.8, and 12.9 eV with respect to E_F , Figure 2, bottom); hereby, the UPS data are rather similar to those for liquid water.¹⁷ First-principles calculations carried out on ice^{12,28} suggest that 1b₂ represents an intramolecular bonding combination between O2p and H1s orbitals. 1b₁ can be assigned to lone-

pair electrons on oxygen atoms; the hydrogen contribution is much smaller than that in 1b₂. Under conditions where the signatures of both H₂O and F occur in the spectra, the features 2pF and 1b₁, being separated by 0.3 eV only, will overlap and cannot be separated easily. 3a₁ (considerably more diffuse than either 1b₁ or 1b₂) corresponds to delocalized states with intermolecular contributions from different water molecules interacting via hydrogen bonds. Thus, the broad 3a₁ feature is characteristic of condensed water, in either the liquid or solid phase, and signals the presence of a water network, formed by hydrogen bonds.

3.2. Interaction of CsF with Water. In Figure 2, the stoichiometry CsF/H₂O is varied, starting from pure water, while the temperature is kept constant: the spectra, recorded during the exposure of CsF onto multilayered water (3 BLs) at 120 K, are presented. Neither F(2p) nor Cs(5p) can be seen in MIES up to an exposure of 1 MLE. On the other hand, the UPS spectra show Cs- and F-induced features, namely, emission from 5p_{3/2}Cs (11.1 eV) and a change of the shape and intensity of 1b₁, caused by the contribution of F(2p). Only above a CsF exposure of 2 MLEs (8th spectrum from top), Cs(5p) emerges in MIES and an increase of the emission around 7.5 eV due to a contribution of F(2p) becomes evident. As evidenced by the complete absence of both Cs and F features in the MIES spectra during the early stage of exposure, the salt species become fully solvated. This holds true also for the F and Cs species next to the surface (which keep their solvation shells). This is also found for aqueous NaF solutions at room temperature which suggest a significantly reduced population of anions at the surface.⁷ This is further supported by CsF supply onto thicker water films (15 BLs)²⁹ where Cs and F features are even absent in MIES up to about 3 MLEs of CsF. Moreover, codeposition of CsF and H₂O (stoichiometry CsF·8H₂O) at 120 K produced a mixed film where neither Cs nor F features were evident in MIES; nevertheless, Cs(5p) could be identified clearly in HeI.²⁹ We can compare the UPS(HeI) results of Figure 2 with those for a CsF·4.2H₂O solution;¹⁹ these spectra compare well with ours. It should, however, be noted that a different interpretation is given in ref 19 to that part of the spectra where the 1b₂ and Cs5p_{1/2} features overlap. Moreover, it was already questioned in ref 17 that the small feature seen about 2 eV above 1b₁ can be attributed to 2pF ionization. Indeed, Figure 1 proves that the spectral features F(2p) and 1b₁ almost coincide and under the conditions of ref 19 cannot be separated. At any rate, we can state that at 120 K the UPS spectra resemble those from aqueous CsF solutions at room temperature closely. Moreover, the similarity of the present spectra and those from aqueous CsF solutions suggests that already at 120 K solvation takes place in the form of the hydration of the ions F⁻ and Cs⁺, just as at room temperature. The MIES results support the conclusion of the MD calculations of ref 3 (although performed at room temperature) that both F⁻ and Cs⁺ have the tendency to keep their hydration shells intact, even near the surface. A small, but significant decrease of E_B of the 5p_{1/2,3/2}Cs peaks is seen when going from full to at most partial solvation (see top spectra in MIES). When annealing the film prepared in Figure 2 (stoichiometry CsF·2H₂O), F(2p) and Cs(5p) appear very clearly above 140 K (similar to what is seen in Figure 3 after preparation at 80 K (see below)), and above 190 K, the spectrum is typical for multilayers of CsF on tungsten (see Figure 1).

In the following, we present the results obtained for the case that the stoichiometry is kept constant while varying the temperature of the film. To get as much information as possible from the use of the available techniques, we have chosen a

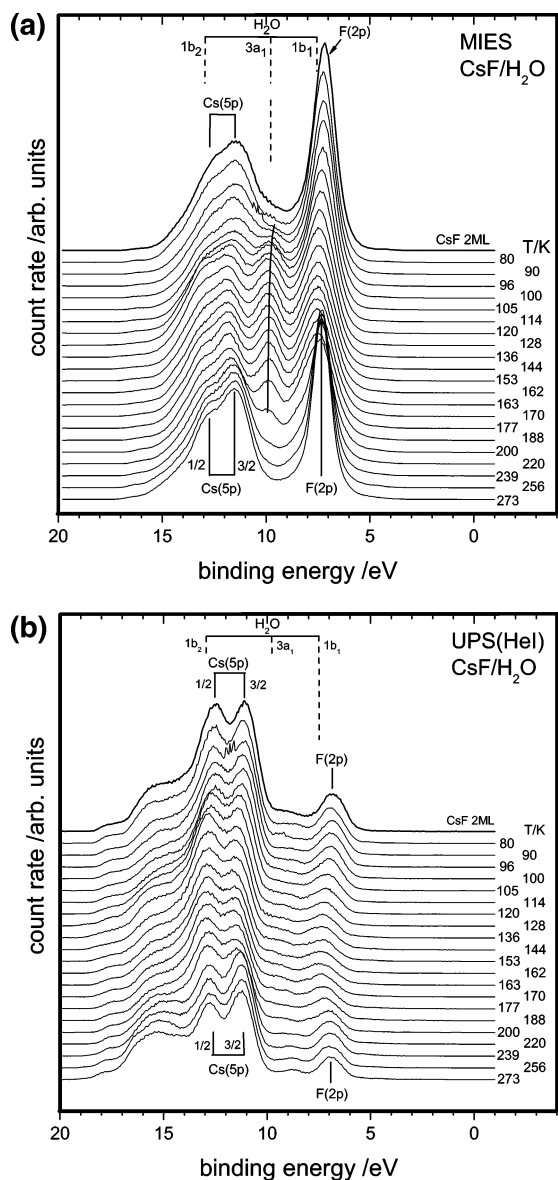


Figure 3. MIES (a) and UPS(HeI) (b) spectra of a CsF film (3 MLEs) deposited on multilayered water at 80 K (top spectrum) and spectral changes recorded during annealing (80–273 K).

stoichiometry that cannot produce full solvation: Parts a and b of Figure 3 (top) respectively present the MIES and UPS results obtained for a CsF film, about 2 MLs thick, deposited at 80 K on multilayered water (about 2 BLs thick). After preparation, the film is annealed between 80 and 270 K. The properties of the system may be compared with those of the highly concentrated CsF solution studied in refs 3 and 19. Following preparation at 80 K, only F(2p) and Cs(5p) are seen; no contribution to the spectra is seen from the water underlayer. The spectra resemble those from CsF on tungsten closely. Upon annealing the CsF–H₂O system beyond 105 K, molecules from the water film become embedded into the CsF toplayer. This is obvious from the appearance of the 3a₁ feature ($E_B = 9.8$ eV), seen very clearly in MIES but only faintly in UPS. The other two expected structures, 1b₂ and 1b₁ of H₂O, overlap with the 5p_{1/2}Cs and 2pF features, respectively. Thus, between about 110 and 220 K, the structures seen around $E_B = 7$ and 13 eV represent a superposition of salt and water features. In contrast to condensed water (see Figure 2a, bottom), 3a₁ appears as a well-defined peak in MIES. As pointed out above, a diffuse 3a₁ structure would be characteristic for a H-bonded water

network, which is obviously not formed under the chosen conditions. Other than in Figure 2, no pure water toplayer exists in the entire range of studied temperatures. Instead, under the conditions of Figure 3a, the toplayer contains Cs, F, and H₂O species which display gas-phase-like water spectra, in particular, a well-defined 3a₁ peak. The stoichiometry established at 120 K experiences little change up to about 170 K. Interestingly, complete desorption of the H₂O molecules in the mixed toplayer requires more than 220 K, while pure water multilayers would have desorbed at 165 K.³⁰ This suggests that a rather stable structure, consisting of F, Cs, and H₂O, is formed at the surface. A separation of the mixed spectrum into water and CsF contributions can be achieved by subtracting a suitably normalized spectrum for pure CsF (see Figure 1); a stoichiometry of about CsF·3H₂O follows for the toplayer. The MIES and UPS spectra obtained after heating to 120 K are not the same as those in Figure 2, although the stoichiometry is comparable (with that of the spectra at the top of Figure 2). Apparently, the solvation process is different in both cases: under the conditions of Figure 3, one starts with a CsF toplayer on a water film; hereby, the CsF layer is stable up to about 450 K. Consequently, the solvation of the Cs and F species would require their penetration into the CsF lattice which is rather rigid at 120 K. On the other hand, under the conditions of Figure 2, single CsF molecules are deposited onto the water film whose molecules are already comparatively mobile at 120 K.

As soon as H₂O species become embedded into the toplayer (above 105 K), a shift (0.4 eV) of Cs(5p) toward larger binding energies can be noticed, both in MIES and UPS. Upon annealing, it disappears together with the 3a₁ peak, that is, after all water has desorbed from the surface. An analogous shift of F(2p) can be noticed in the UPS spectra.

In Figure 4, the order of exposure is reversed as compared to Figure 3. The MIES and UPS results after the deposition of a water film, about 3 BLs thick, at 80 K on a CsF film (about 3 MLs thick) are presented. In MIES, the top spectra are for the “as prepared film” and are typical for multilayered water,^{17,30} no indications of F(2p) and Cs(5p) can be noticed. However, during film annealing, Cs(5p_{3/2}) appears above 127 K where, at the same time, 3a₁ narrows considerably; this is evidence that, for the chosen stoichiometry, the destruction of the H-bonded water network has started. Peak 3a₁ remains visible up to 200 K. In UPS, the Cs(5p_{1/2,3/2}) peaks appear clearly around 120 K; weak 5p_{3/2}Cs emission is noticeable even at 80 K due to the finite sampling depth of UPS(HeI). We note that above about 140 K the MIES spectra of Figures 3 and 4 resemble each other closely. We suppose that in this range the films prepared in the different ways become identical: a new structure, consisting of F, Cs, and H₂O, forms in either situation by those species that originally constitute the H₂O–CsF interface; those water molecules that were not involved in bonds with the ionic species have desorbed. After water desorption (complete around 200 K), Cs(5p) and F(2p) remain visible up to 450 K.

4. Discussion

The results provide evidence that solvation of the Cs and F species sets in above about 110 K:

(1) For CsF on multilayered H₂O, water-induced emission appears in MIES at about 110 K when starting with a CsF film that displays no water-induced emission at 80 K; in the same temperature range, the emission due to 5pCs and 2pF starts to decrease, indicating that H₂O species become part of the toplayer (consisting of Cs and F species only after preparation). The work

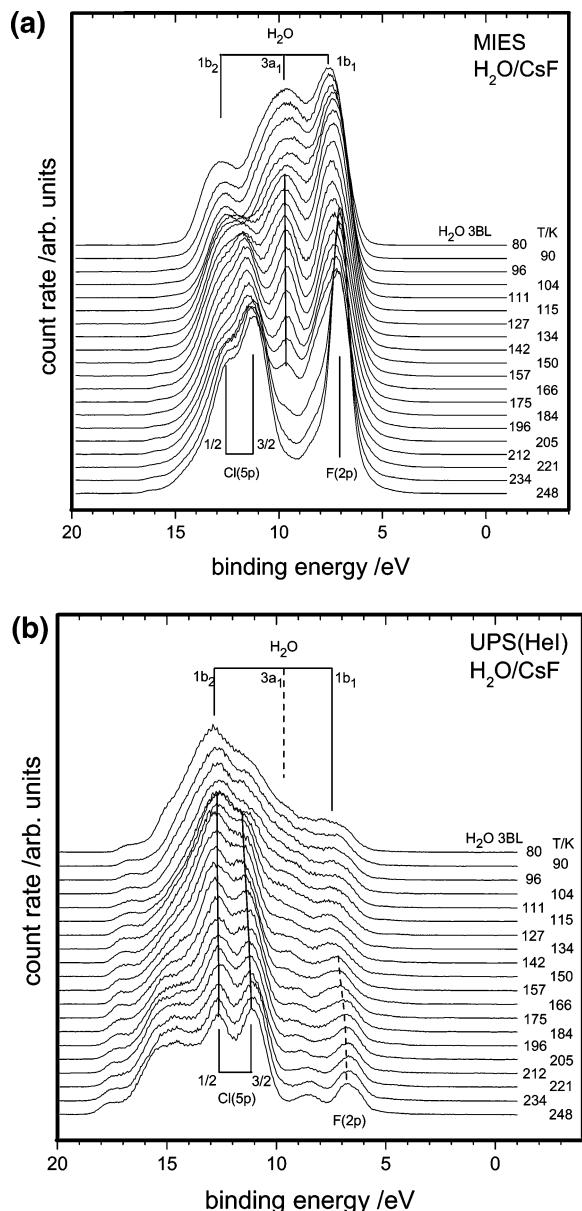


Figure 4. MIES (a) and UPS(HeI) spectra of a H₂O film (2 MLEs) deposited on CsF film at 80 K (top spectrum) and spectral changes recorded during annealing (80–248 K).

of ref 31 shows that the vertical migration of H₂O between the first and the underlying layer takes place on a time scale of 10 s at 140 K. The activation energy was measured to be close to the interstitial migration energy and much lower than the diffusion activation energy in bulk ice (15 as compared to 52 kJ mol⁻¹). Thus, water molecules near the water surface are comparatively mobile and experience self-diffusion which facilitates the observed intermixing of the F and Cs ions.

(2) A shift of Cs(5p) and F(2p) by about 0.4 eV takes place, suggesting a change in the molecular environment of the salt species.

(3) A narrow, gas-phase-like 3a₁ peak appears that is characteristic of H₂O species that are not part of a water network, as is found in condensed water, being either isolated or attached individually to salt ions.

(4) The vertical ionization energy (VIE), that is, the energy required for the transition of F⁻(np⁶) → F⁰(2p⁵) (10.3 eV), is rather close to that estimated for F species in aqueous CsF solution (10.7 eV¹⁷).

(5) Convincing evidence for hydration is provided by the results of Figure 2 (see ref 11 for corresponding results on CsCl), indicating that at 120 K no closed CsF overlayers on water can be obtained anymore.

The 2pF level of free, isolated F⁻ ions experiences a solvation shift when the ions are embedded into a polarizable medium, as during hydration. This has been shown very directly by measuring the npX (X =: halogen) binding energy as a function of the number of H₂O molecules surrounding the X⁻ ion.³² In other words, the electron affinity of free X, EA(X) (3.4, 3.62, and 3.06 eV for F, Cl, and I, respectively³³), increases by several electronvolts. In the present situation, most of the increase of EA(F⁰) takes place during the Cs–F formation and during the CsF deposition onto the water film, probably due to the formation of CsF islands.

A minor increase of the 2pF binding energy by about 0.4 eV occurs after CsF dissociation during the hydration. From the comparison of our results at 120 K with those for aqueous CsF solutions, we concluded (see point 2, above) that solvation takes place in the form of the hydration of the ionic species F⁻ and Cs⁺. The small value is indeed expected, as the comparison of the Coulomb energy, W_C , experienced by F⁻ due to its interaction with the CsF lattice, on one hand, and the interaction energy, W_B , of F⁻ with a shell of surrounding H₂O molecules, estimated with Born's cavity model, on the other hand, shows.

For X⁻ in the CsX crystal, the increase of EA(X⁰), W_C , can be approximated by

$$W_C = -e^2A/4\pi\epsilon_0r_0$$

where A is the Madelung constant (A is about 1.75 for the studied cases) and r_0 is the sum of the ionic radii of Cs⁺ and X⁻ (6.0, 6.7, and 7.5 au) for CsF, CsCl, and CsI, respectively. This yields $W_C = 7.9, 7.1,$ and 6.3 eV for F, Cl, and I, respectively, to be compared with the measured VIEs of 10.3 eV for X:=F (present work), 9.3 eV for Cl (ref 12), and 7.5 and 8.6 eV for I 5p_{3/2} and 5p_{1/2}, respectively (ref 34), as calculated from the sum of the binding energies of the X⁻(np) peaks and the work functions of the CsX–H₂O films (see section 3). Agreement would become almost quantitative when taking into account the repulsion between the lattice and the final state X⁰(2p⁶) after the ionization process; it can be expected to be between 1 and 2 eV.

When the increase of EA(X⁰) is due to the interaction of X⁻ with the surrounding polarizable H₂O molecules, it can be estimated by applying Born's cavity model¹⁷ in which the X⁻ is thought to be located in a cavity formed by the surrounding polarized medium water, characterized by its dielectricity constant, ϵ_r (=78 for water). This model gives

$$W_B = (1 - 1/\epsilon_r)1/(4\pi\epsilon_02r_X) + EA(X^0)$$

r_X is the cavity radius which we choose to approximate by the ionic radii of X⁻ (2.66, 3.62, and 4.4 au for F⁻, Cl⁻, and I⁻, respectively). This yields 8.4, 7.4, and 6.2 eV for the VIEs of F⁻, Cl⁻, and I⁻, respectively, in an aqueous environment, slightly (0.4 eV) larger than those for X⁻ in the CsF bulk. Again, the agreement would become more quantitative when taking into account the repulsion between the hydration shell and the X species in its final state X⁰(np⁶) after the ionization process (see above). A more systematic estimate of the VIEs for X⁻ in an aqueous environment has been obtained very recently by combining MD calculations with a fractional charge representation of the water solvent.¹⁸ The predicted VIEs for Cl and I are within 0.5 eV with those of the present work; for F, the

calculated value is too large by about 1 eV. It should also be noticed that the present VIEs of the X^- interacting with solid water are rather close to those found in an aqueous environment.^{17,18} To conclude, 15.5 eV was estimated for the VIE for $Cs^+5p_{3/2}$, in good agreement with the value of 15.2 eV estimated from the present spectra.¹⁸ The absence of a stabilization shift below about 110 K suggests that at lower temperatures the ionic dissociation is still incomplete; that is, a complete separation of F^-Cs^+ contact ion pairs may not yet have taken place, requiring a sufficiently high water mobility, only available above about 120 K.

MD calculations were performed on aqueous $CsF \cdot 2.6H_2O$ solutions at room temperature.³ Density profiles across the surface of the solution were presented for the F^- , Cs^+ , and H_2O species. It was predicted that the F^- species are completely shielded by a water toplayer of 3.75 Å thickness, that is, should be hardly accessed by MIES. On the other hand, the Cs^+ species were found to be somewhat closer to the surface and, thus, were predicted to be somewhat less efficiently shielded than F^- . According to MIES (see Figure 2), neither Cs nor F features can be seen at 120 K, and thus, both Cs and F appear to be fully solvated. MD calculations were performed for all Na halides (1.2 M concentration); both the Na^+ and F^- ions are repelled from the surface region, leaving an ion-free layer of about 3.5 Å thickness.⁴

For CsF/H_2O , prepared at 80 K with the stoichiometry $CsF \cdot 2H_2O$, full solvation cannot take place; that is, a water top layer cannot form in the studied temperature range. Under these conditions, it needs to be considered that well-defined (F^-H_2O) complexes form when annealing the film beyond about 120 K; these structures may create a network that is more stable than that of pure water. The structure, spectra, and electronic properties of F^- -water clusters, $F^-(H_2O)_n$, with small n values have found much interest. The H-bond in F^-H_2O is the strongest for $F^-(H_2O)_n$ with $n = 1$ (bond length 1.4 Å); with increasing n , the H-bond length increases (1.53 Å for $n = 2$); that is, the increase of the number of water molecules in the F^- hydration shell weakens the H-bond in (F^-H_2O).³⁵ Up to $n = 3$, the ($n + 0$) structures (without H-bonds between the H_2O molecules) are the most stable ones. DFT-based MD calculations dealing with the solvation of F^- are available.¹³ A well-defined first solvation shell is formed whereby the five surrounding H_2O molecules form a square pyramidal structure. Strong H-bonds are formed with a well-defined distribution of H-bond lengths, centered around 1.66 Å; the water molecules remain bonded for a relatively long time of about 17 ps. The solvation shell of F^- appears to integrate well into the water network because all first shell water molecules have about the same number of donating and accepting H-bonds as in the water network, explaining the structure building properties of F^- .

So far, the formation of a mixed network at high CsF concentration, comprising H_2O and F^- species in a well-defined stoichiometry (into which Cs species are embedded), has apparently not been considered. Candidates as building blocks for the network could be the $F_2-(H_2O)_2$ clusters found in concentrated aqueous CsF solutions at room temperature (see Figure 8 of ref 3). We speculate that the very strong H-bonds in these clusters may be responsible for the stability of the mixed network.

The Cs^+ ions are less tightly bound to H_2O than the F^- ions, as is also reflected by the mean bonding time of water to these ions.³ Therefore, the strong H-bonds in F^-H_2O clusters (bond length of 1.66 Å as compared to 2.19 Å in Cl^- clusters¹³) are apparently responsible for the high water desorption temperature

(about 40 K higher than that for multilayered water) from CsF /water; no similar increase of the desorption temperature of water is seen for $CsCl/H_2O$ ¹¹ or for $NaCl/H_2O$ (155 K).¹² The structure building properties of F^- may also be reflected in the fact that no distortions can be recognized in the water part of the MIES spectra after full solvation (see Figure 2). Moreover, the formation of a mixed (H_2O-F^-) network under the conditions of Figure 4 is suggested by the peculiar shape of $3a_1$, namely, a well-defined gas-phase-like peak, indicating that no water network is formed. Apparently, for the chosen stoichiometry of $CsF \cdot 2H_2O$, all water species bond to ions, without forming H-bonds among themselves. Thus, $3a_1$ contains much less intermolecular contributions from neighboring water molecules, and consequently, $3a_1$ is less diffuse than in pure multilayered water.

5. Summary

The interaction of CsF with multilayered water was investigated with metastable impact electron spectroscopy (MIES) and UPS(HeI). $CsF-H_2O$ interfaces were prepared on tungsten substrates at 80 and 120 K, namely, CsF layers on multilayered water and H_2O adlayers on thin CsF films. These films were annealed up to about 280 K. The emission from the ionization of the H_2O states $1b_1$, $3a_1$, and $1b_2$ of $5pCs$ and of $2pF$ was monitored by MIES and UPS(HeI), both during the film preparation and the annealing procedure.

At 80 K, closed CsF layers were obtained on H_2O and vice versa; no intermixing of the two components water and salt could be observed during preparation. Above 110 K, intermixing of H_2O and CsF layers becomes significant and manifests itself in a solvation shift of the F^- and Cs^+ -induced features. Hereby, salt solvation takes place in the form of the hydration of F^- and Cs^+ ions. At lower temperatures, no solvation shift is seen; the direct contact between H_2O and CsF alone does not apparently lead to complete ionic dissociation of CsF .

For water-rich stoichiometries (above $CsF \cdot 3H_2O$), full solvation of hydrated F and Cs species takes place above about 120 K; according to MIES, the toplayer consists then of H_2O molecules exclusively. For stoichiometries with less water, H_2O (CsF) overlayers, prepared at 80 K on CsF (H_2O) films, gradually transform into a mixed layer containing both water and salt ion species. This mixed structure exists between about 120 and 180 K. Cs and F species remain on the tungsten substrate during water desorption and finally desorb around 450 K.

In a forthcoming publication, we will present results concerning the interaction of CsI with multilayered solid water where we find an enhanced iodide concentration (as compared to that of Cs) at the water-vacuum interface.³⁴

Acknowledgment. Discussions of various aspects of this work with H. Kang (Seoul National University) are acknowledged.

References and Notes

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