

# X-ray Photoelectron Spectroscopy Study of Water Adsorption on BaF<sub>2</sub>(111) and CaF<sub>2</sub>(111) Surfaces

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The adsorption of water on BaF<sub>2</sub>(111) and CaF<sub>2</sub>(111) surfaces has been studied by X-ray photoelectron spectroscopy (XPS). Oxide and hydroxyl species are observed to form reactively on both surfaces with low sticking probability. XPS results imply an exchange of oxygen for fluorine at the surface. There is no evidence for molecularly adsorbed H<sub>2</sub>O species at 300 K with exposures up to 10<sup>7</sup> langmuirs in vacuum on either surface.

## 1. Introduction

The interaction of water with solid surfaces is of general interest from both fundamental and applied perspectives.<sup>1</sup> Water adsorption on non-oxide ionic substrates is not well understood, although some efforts have been focused on alkali halides. Recent results concerning the behavior of water on epitaxial NaCl films grown on a Ge(100) substrate<sup>2</sup> reveal that a three-dimensional ice layer forms at 130 K and completely desorbs at room temperature. It is also found that surface defects act as reactive sites which cause dissociation and OH production. Early work on polycrystalline alkaline-earth fluorides concentrated on the two-dimensional condensation of water under relatively high vapor pressure on high surface area powders.<sup>3-7</sup> Recently, Zink et al.<sup>8</sup> studied water adsorption on alkaline-earth fluorides by second harmonic generation (SHG) under ultrahigh vacuum (UHV) conditions at 300 K. Noticing the close match between the topmost F<sup>-</sup> sublattice and the oxygen lattice of ice-I, they suggested a possible pseudomorphic epitaxial growth of molecular water on BaF<sub>2</sub>(111).

In the present work we have used X-ray photoelectron spectroscopy to study the interaction between water and BaF<sub>2</sub>(111) and CaF<sub>2</sub>(111) surfaces under UHV conditions, as part of our efforts to understand more about the interaction of water with ionic substrates.<sup>9</sup> Our results suggest dissociative adsorption of water on these surfaces at 300 K. Interactions between the adsorbed species and the fluoride substrates result in the exchange of oxygen for fluorine at the surface. For the highest water exposure used in these experiments (~10<sup>7</sup> langmuirs), the largest coverages of adsorbed oxygen-containing species are approximately 1 monolayer.

## 2. Experimental Section

CaF<sub>2</sub> (~10 mm × ~7 mm × 0.5 mm, Commercial Crystal Laboratory) and BaF<sub>2</sub> (10 mm × 10 mm × 1 mm, Optovac) single

crystals with polished (111) surfaces are each mounted with ceramic adhesive (Aremco 516) on a piece of tantalum foil. The foil can be resistively heated to >800 K and the temperature is measured by a type E thermocouple mounted in the adhesive between the crystal and the Ta foil. The sample assembly can also be cooled down to ~130 K by liquid nitrogen.

All experiments are carried out in a stainless steel UHV chamber with a base pressure of 3 × 10<sup>-11</sup> Torr. The crystals are cleaned by Ar<sup>+</sup> sputtering and then annealed to >750 K to restore the surface order. The cleanliness of the surfaces is checked by XPS. After annealing, the CaF<sub>2</sub>(111) surfaces show sharp hexagonal LEED patterns characteristic of the expected 3-fold symmetry; the BaF<sub>2</sub>(111) surfaces also display hexagonal LEED patterns but they are weaker in intensity. Crystal surfaces can be moved to a position ~1 cm in front of a gas doser from which water vapor can be directed to the surfaces. During water dosing the partial pressure of water in front of the sample is much higher than the background pressure in the chamber as monitored by an ionization gauge. Based on other experiments in this chamber, we estimate the water exposure by assuming the direct H<sub>2</sub>O flux onto the sample surface to be 10 times greater than the random background flux. After water dosing, the chamber is evacuated and only water-related species which are stably adsorbed at the surface contribute to the XPS signals. Mg Kα (1253.6 eV) is used as the X-ray source, and a hemispherical analyzer, operated in the fixed analyzer transmission (FAT) mode with a pass energy of 25 eV, is used to energy analyze the photoelectrons emitted nearly normal to the surface. To compensate for static charging effects, all the binding energies are referenced to the F 1s peak for which the binding energy is set at 684.3 eV for BaF<sub>2</sub> and 684.8 eV for CaF<sub>2</sub>,<sup>10</sup> respectively.

## 3. Results

**3.1. Water Adsorption on BaF<sub>2</sub>(111).** No major changes in peak shape of F 1s and Ba 3d X-ray photoelectron spectra are detected during water adsorption at 300 K onto BaF<sub>2</sub>(111). Figure 1A shows the spectra of the O 1s region with increasing water exposure up to 10<sup>7</sup> langmuirs. An O 1s peak with a binding energy of 531.6 eV is observed to grow as the water exposure increases. We identify this feature as surface hydroxyl (OH) species; see section 4.2, below.

Water adsorption at low temperature (~130 K) is illustrated in spectra a, b, and c in Figure 1B. At an exposure of ~1 langmuir (spectrum a), the O 1s signal is dominated by a peak at 531.6 eV. When the exposure is increased to ~10 langmuirs (spectrum b), an intense peak

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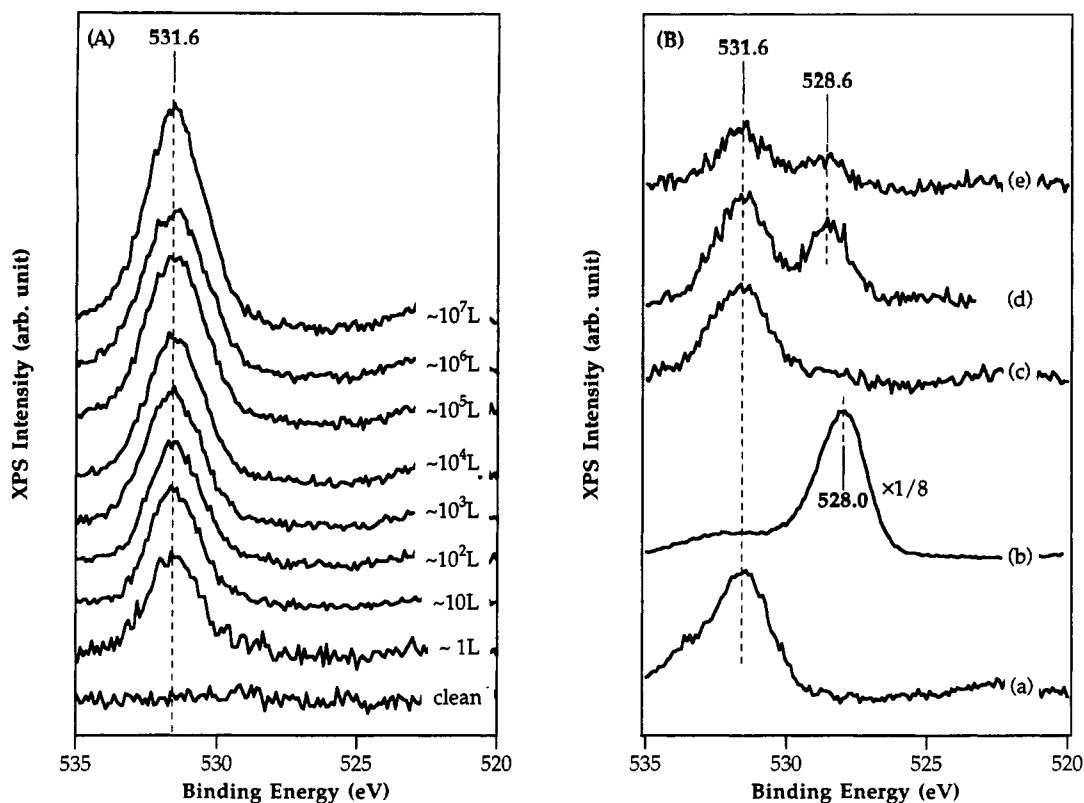
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**Figure 1.** (A) O 1s X-ray photoelectron spectra as a function of water exposure at 300 K on a BaF<sub>2</sub>(111) surface. (B) O 1s spectra from BaF<sub>2</sub>(111) surfaces under various conditions: (a) after  $\sim 1$  langmuir water exposure at  $\sim 130$  K; (b) after  $\sim 10$  langmuirs water exposure at  $\sim 130$  K with the formation of molecular multilayer; (c) after annealing to 300 K and the desorption of the multilayer; (d) after  $\sim 1$  langmuir exposure of O<sub>2</sub> on clean surface at 300 K; (e) after  $\sim 1$  langmuir water exposure and X-ray irradiation at 300 K. All binding energies are referenced to BE(F 1s) = 684.3 eV.

at 528.0 eV is observed. Concurrent with the O 1s peak growth, the F 1s and Ba 3d signals are strongly attenuated (spectra not shown). This peak is believed to be due to the formation of a molecular multilayer of water at low temperature, although it is surprising that the binding energy is so low. After annealing to 300 K and desorbing the water multilayer, the peak at 531.6 eV remains present while the 528.0-eV peak disappears (spectrum c). The peak at 531.6 eV is identical to that from water adsorbed on the BaF<sub>2</sub>(111) surface at 300 K.

For comparison with H<sub>2</sub>O adsorption, pure oxygen gas is also dosed onto a clean BaF<sub>2</sub> surface at 300 K (spectrum d). The O 1s curve contains two peaks after O<sub>2</sub> dosing, with binding energies of  $\sim 531.6$  and  $\sim 528.6$  eV, respectively. We also find two O 1s peaks related to an X-ray induced change on the BaF<sub>2</sub>(111) surface with  $\sim 1$  langmuir water exposure (the second spectrum from bottom in Figure 1A). After sufficiently long X-ray irradiation, a peak at  $\sim 528.6$  eV appears while the intensity of the original peak at 531.6 eV decreases (spectrum e in Figure 1B). As discussed below in section 4.2, we believe that the peak at  $\sim 528.6$  eV is due to adsorbed oxygen, and the peak at  $\sim 531.6$  eV is due to hydroxyl formed by the interaction of residual water with the oxygen-dosed surface.

According to the triple-layer model of (111) surfaces of the fluorite crystal structure,<sup>11</sup> the BaF<sub>2</sub>(111) surface is topped by fluorine ions with a surface density of  $5.9 \times 10^{14}$  atoms/cm<sup>2</sup>. Attenuation lengths for O 1s, Ba 3d, and F 1s photoelectrons in BaF<sub>2</sub> are estimated to be 10.1, 8.0, and 8.9 monolayers respectively by established meth-

ods.<sup>12,13</sup> Following a procedure similar to that proposed by Madey et al.<sup>14</sup> and using tabulated XPS sensitivity factors,<sup>12,15</sup> we can estimate the coverage of the oxygen-containing species on the surface. The oxygen coverage can be converted to monolayers assuming an equivalent surface atomic density as the substrate (i.e. 1 monolayer corresponds to  $5.9 \times 10^{14}$  atoms/cm<sup>2</sup>). Figure 2 shows the relation between the estimated coverage,  $\theta$ , and the total water exposure  $D$ . Saturation of the O 1s yield is not observed, even with exposures up to  $10^7$  langmuirs. Moreover, for a water exposure of  $10^7$  langmuirs, the coverage of oxygen-containing species is fairly low, only  $\sim 1.5$  monolayers. The coverage is approximately proportional to the logarithm of the exposure, so the sticking probability, which is proportional to  $d\theta/dD$ , can be estimated as inversely proportional to the dosage. This implies that the incremental sticking probability at high dosage becomes extremely low (on the order of  $10^{-7}$  after an exposure of  $10^6$  langmuirs). The dashed line in Figure 2 indicates the O 1s area after the multilayer is desorbed by annealing (spectrum c in Figure 1B), corresponding to an oxygen coverage of  $\sim 0.7$  monolayer. This value is reproducibly reached following desorption at 300 K, regardless of the initial multilayer water exposure (i.e.  $> 1$  langmuirs) at low temperature.

Normalized Ba 3d and F 1s peak areas are shown in Figure 3 as functions of water exposure at 300 K. A clear

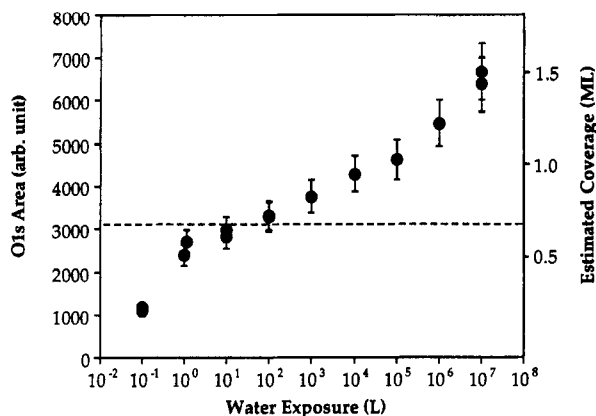
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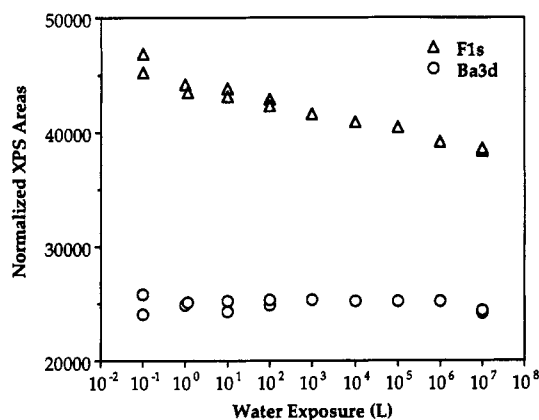
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**Figure 2.** Integrated O 1s area and estimated oxygen coverage from the BaF<sub>2</sub>(111) surface as function of the water exposure at 300 K. 1 monolayer corresponds to  $5.9 \times 10^{14}$  atoms/cm<sup>2</sup>. The coverage is roughly proportional to the logarithm of the exposure. The dashed line indicates the O 1s area and coverage after the desorption of the water multilayer by annealing to 300 K.



**Figure 3.** Dependency of the normalized XPS F 1s and Ba 3d area vs total water exposure, for water adsorption on BaF<sub>2</sub>(111) at 300 K.

decrease in the F 1s photoelectron intensity is observed as the water exposure increases, while the Ba 3d signal remains relatively unchanged. This result implies interesting chemical interactions between the adsorbed water and surface barium and fluorine ions (see below).

**3.2. Water Adsorption on CaF<sub>2</sub>(111).** Figure 4A presents the O 1s spectra for various water exposures at 300 K onto CaF<sub>2</sub>(111). Two features with binding energies of 531.4 and 528.8 eV, respectively, can be observed. The peak with the higher binding energy grows as the exposure increases and becomes dominant at high dosage. For comparison, Figure 4B presents O 1s spectra for the surface treated in several different ways. Annealing a clean CaF<sub>2</sub>(111) surface in  $1 \times 10^{-7}$  Torr of O<sub>2</sub> at  $\sim 750$  K for 2 h yields spectrum a with a peak at  $\sim 528.8$  eV. After the O<sub>2</sub>-annealed surface is exposed to  $\sim 50$  langmuirs water, an additional peak with a binding energy of  $\sim 531.3$  eV is observed. We assign these peaks as oxides ( $\sim 528.8$  eV) and hydroxyls ( $\sim 531.3$  eV), respectively (see section 4.2. below). Water multilayer formation at low temperature ( $\sim 125$  K) gives an intense O 1s peak with a binding energy of 531.8 eV (spectrum c), while F 1s and Ca 2p signals are greatly attenuated. Figure 4C is a summary of the observations in the Ca 2p region during our experiments. Comparing to the clean CaF<sub>2</sub>(111) surface (spectrum a), the Ca 2p curve shows a shoulder on the lower binding energy side of the doublet at high water dosage (spectrum b). This shoulder is much more clear after the sample is

annealed in oxygen (spectrum c). Water adsorption on CaF<sub>2</sub>(111) does not induce major changes in the F 1s peak shape.

The total O 1s area is plotted in Figure 5 as a function of water exposure at 300 K. The surface atomic density of fluorine on CaF<sub>2</sub>(111) is  $7.9 \times 10^{14}$  atoms/cm<sup>2</sup>. Attenuation lengths for O 1s, Ca 2p, and F 1s photoelectrons in CaF<sub>2</sub> are estimated to be 9.4, 10.5, and 8.3 monolayers, respectively, by the same method as the BaF<sub>2</sub> case. Analogously, the coverage of oxygen-containing species expressed in monolayers is estimated by assuming that 1 monolayer corresponds to  $7.9 \times 10^{14}$  atoms/cm<sup>2</sup>. Saturation of the O 1s signals is not observed on CaF<sub>2</sub>(111) with exposures up to  $10^7$  langmuirs; the largest oxygen coverage measured in this experiment is  $\sim 1.2$  monolayers. Similar to the BaF<sub>2</sub>(111) case, the sticking probability is also inversely proportional to the exposure and is very low at high water dosages. Figure 6 shows the decrease of total XPS F 1s intensity with increasing water adsorption, while the Ca 2p signal remains relatively constant. These results indicate that fluorine is exchanged with oxygen at the surface and that the water–CaF<sub>2</sub> interaction is analogous to the BaF<sub>2</sub>(111) case (Figure 3).

#### 4. Discussion

**4.1. Unusual Binding Energies of the Water Multilayer.** X-ray photoelectron spectroscopy can provide “fingerprints” of different adsorbed species generated by water adsorption on metal surfaces. For example, the formation of hydroxyl groups on Ni(210)<sup>16</sup> is characterized by the appearance of an O 1s feature at  $\sim 531$  eV binding energy, which is intermediate in energy between chemisorbed oxygen ( $\sim 530$  eV) and adsorbed molecular H<sub>2</sub>O ( $\sim 533$  eV). On clean magnesium surfaces the adsorbed atomic oxygen and hydroxyl groups yield O 1s XPS peaks at  $\sim 531$  and  $\sim 533$  eV respectively, while molecular water adsorbed at low temperature ( $< 150$  K) gives a feature at  $\sim 535$  eV.<sup>17</sup> For the three possible adsorbed species on metal surfaces the O 1s binding energies generally have the order of atomic oxygen < hydroxyl < molecular water, but the exact binding energy values vary for different metal surfaces. Moreover, multilayer water on metals generally has an O 1s binding energy slightly higher in value than the monolayer molecular water.<sup>18</sup>

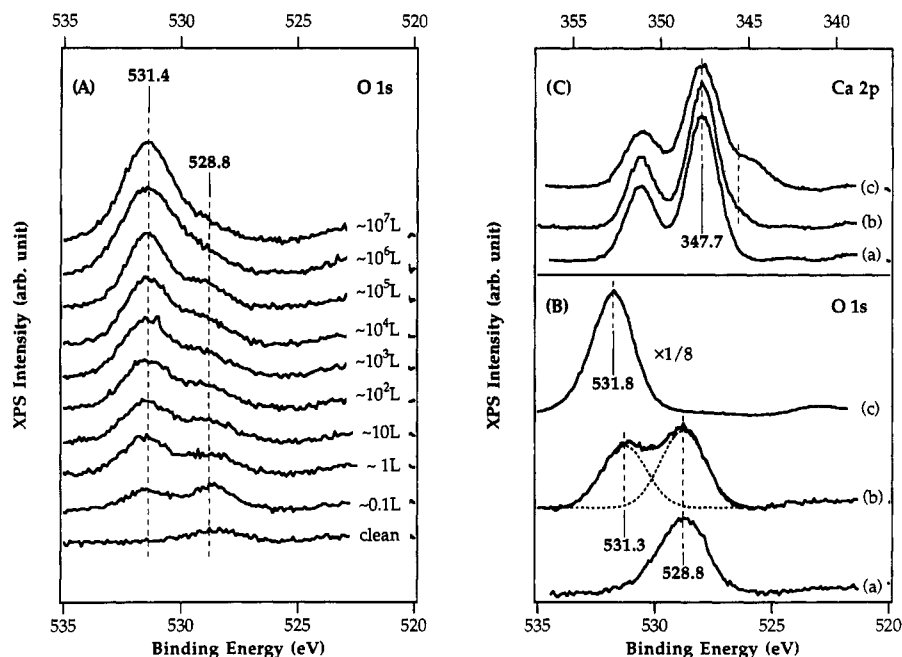
On the surfaces of insulators such as BaF<sub>2</sub> and CaF<sub>2</sub>, the interpretation of XPS spectra may be more complicated because of static charging developed under the X-ray irradiation and changes in final state screening. One unusual result observed in our experiment is the surprisingly low O 1s binding energy value (referenced to the substrate F 1s signals) for molecular water multilayers formed on BaF<sub>2</sub>(111) and CaF<sub>2</sub>(111) at low temperature. On BaF<sub>2</sub>(111) the O 1s peak of the water multilayer has an apparent binding energy of 528.0 eV (Figure 1B). This value is much lower than those on metal surfaces and  $\sim 3.6$  eV lower than the O 1s peak generated by water adsorption at 300 K (Figure 1A). On CaF<sub>2</sub>(111) the water multilayer has a higher O 1s binding energy than the adsorbed species at 300 K (Figure 4), but the binding energy value ( $\sim 531.8$  eV) is still significantly lower than the values expected from metal surfaces.

Prior to referencing the H<sub>2</sub>O O 1s spectra to the substrate F 1s peak position, the measured O 1s peak positions of the water multilayers are  $\sim 535.2$  eV on BaF<sub>2</sub>(111) and

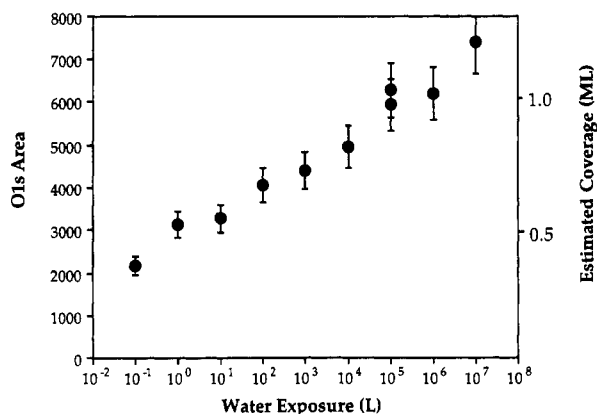
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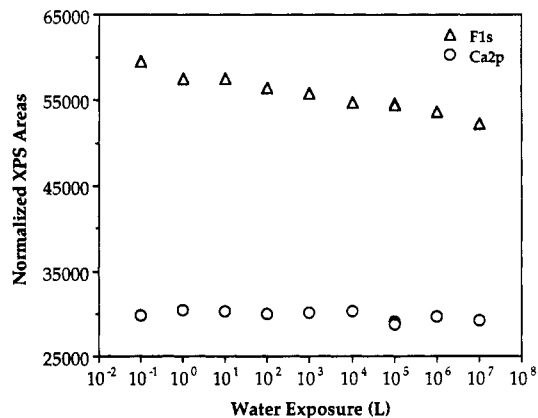


**Figure 4.** (A) O 1s X-ray photoelectron spectra as a function of water exposure at 300 K on a CaF<sub>2</sub>(111) surface. (B) O 1s spectra from CaF<sub>2</sub>(111) surfaces under various conditions: (a) after annealing in  $2 \times 10^7$  Torr O<sub>2</sub> for ~1 h; (b) after ~50 langmuirs water dosage to the O<sub>2</sub>-annealed surface, the dashed lines are the two Gaussian peaks used to fit the experimental data; (c) after ~10 langmuirs water exposure at ~125 K, corresponding to the formation of a water multilayer. (C) Ca 2p spectra from CaF<sub>2</sub>(111) surfaces: (a) the clean surface; (b) after ~10<sup>5</sup> langmuirs water exposure at 300 K; (c) after annealing in oxygen. Binding energies are referenced to BE(F 1s) = 684.8 eV.



**Figure 5.** Integrated O 1s area and estimated oxygen coverage from the CaF<sub>2</sub>(111) surface as functions of the water exposure at 300 K. 1 monolayer corresponds to  $7.9 \times 10^7$  atoms/cm<sup>2</sup>. The coverage is also roughly proportional to the logarithm of the exposure.

~535.8 eV on CaF<sub>2</sub>(111), close to the value of ~535 eV listed in ref 17. Before we make any charge compensation, the measured F 1s energies are ~691.5 eV for BaF<sub>2</sub>(111) and ~688.8 eV for CaF<sub>2</sub>(111), respectively. Nefedov et al. provide F 1s reference values, i.e. 684.3 eV for BaF<sub>2</sub> and 684.8 eV for CaF<sub>2</sub>, by referencing to the adventitious C 1s level of 285.0 eV.<sup>19,20</sup> Hence, relatively large static charging develops on the BaF<sub>2</sub> sample (~7.2 eV) and CaF<sub>2</sub> sample (~4.0 eV) during our XPS experiment. By referencing to the C 1s level at 284.6 eV, Wagner et al.<sup>21</sup> determine an O 1s binding energy of 532.9 eV for ice. This implies that an O 1s binding energy around ~533.3 eV is expected for a water multilayer, referenced to the C 1s level of 285.0



**Figure 6.** Dependency of the normalized XPS F 1s and Ca 2p area vs total water exposure, for water adsorption on CaF<sub>2</sub>(111) at 300 K.

**Table 1. F 1s and O 1s Binding Energies (eV) for Multilayers of H<sub>2</sub>O on Fluoride Samples**

XPS peak	binding energies as measured	expected values corrected for charging <sup>19,20 a</sup>	estimated shift due to charging	apparent binding energies after referencing to F 1s
BaF <sub>2</sub>				
F 1s	691.5	684.3	+7.2	
O 1s	535.2	533.3	+1.9	528.0
CaF <sub>2</sub>				
F 1s	688.8	684.8	+4.0	
O 1s	535.8	533.3	+2.5	531.8

<sup>a</sup> All the values are referenced to BE(C 1s) = 285.0 eV.

eV. On the basis, we can estimate the extent of positive charging for the water multilayers as ~1.9 eV on BaF<sub>2</sub> and ~2.5 eV on CaF<sub>2</sub> respectively. The relevant values of binding energy and static charging are summarized in Table 1. This comparison of charging in the adsorbed layers and substrates implies that water multilayers are

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charged to a less extent than the substrate fluorides under X-ray irradiation; we are not aware of similar observations for insulating layers on insulating substrates. The differences in electrical conductivity and/or secondary electron emission coefficients may be responsible for this phenomenon. The differences between the  $\text{CaF}_2$  and  $\text{BaF}_2$  may be attributed to the different conductivities, crystal thicknesses, and/or configurations of the sample holder.

**4.2. Dissociative Adsorption of Water at 300 K.** As indicated by Figures 2 and 5 for water adsorption at 300 K, the largest coverage of oxygen-containing species is only 1.2–1.5 monolayers on  $\text{CaF}_2(111)$  and  $\text{BaF}_2(111)$  for water exposures up to  $10^7$  langmuirs. Evidence that the oxygen-containing species are due to the dissociation of water on the fluorides surfaces is seen in several different ways: the displacement of strongly bound  $\text{F}^-$  by oxygen-containing species (Figures 3 and 6); the chemical shift in the surface cation (see curve b in Figure 4C); the chemical shift of O 1s.

Water adsorbed on the  $\text{BaF}_2(111)$  surface at 300 K yields a single O 1s peak with a binding energy of  $\sim 531.6$  eV (Figure 1A). The binding energy of this peak is much higher than the apparent value of a water multilayer ( $\sim 528.0$  eV) in our experiment but lower than the expected value ( $\sim 533.3$  eV, see section 4.1) for molecular water. The peak position implies that water adsorbed at 300 K is *not* in its molecular phase but in a dissociated form. This feature is identical to the main features of spectra a and c in Figure 1B. This is because even at low temperature ( $\sim 130$  K), dissociation of water occurs before multilayer formation; the dissociation products remain stable on the substrate after the multilayer is desorbed.

There is some ambiguity in the identification of the dissociation products.  $\text{O}_2$  exposure onto the clean  $\text{BaF}_2(111)$  surface gives two O 1s peaks with binding energies of  $\sim 531.6$  and  $\sim 528.6$  eV, respectively (spectrum d in Figure 1B). One of them should correspond to adsorbed oxygen species, and the other to hydroxyl groups formed by the interaction of the adsorbed oxygen with residual water in the vacuum chamber. Schulze et al.<sup>22</sup> reported a similar case in which  $\text{O}_2$  exposure to gadolinium also yields two XPS O 1s peaks with binding energies of 530.6 and 532 eV, corresponding to oxide and hydroxyls, respectively. On the  $\text{BaF}_2(111)$  surface with low water coverage ( $\sim 1$  langmuir) which is irradiated by X-rays for a sufficiently long time, a peak at  $\sim 528.6$  eV also appears in addition to the original  $\sim 531.6$ -eV peak (spectrum e in Figure 1B). The additional peak generated by X-ray irradiation disappears if the sample is exposed to water again. Taking all of these results together, the most consistent assignment of these peaks is the following. The peak with the binding energy of  $\sim 531.6$  eV can be assigned to the hydroxyl groups on the surface and the peak of  $\sim 528.6$  eV to signals from adsorbed oxygen species. At low water coverage the adsorbed oxygen can be generated by photon-induced decomposition of hydroxyl groups under X-ray irradiation and eliminated by additional water exposure through a mechanism similar to the following reaction:



$$\Delta G^\circ_{298} = -23.98 \text{ kcal/mol}$$

Mueller et al.<sup>23</sup> also reported that water reacts with high

efficiency on  $\text{BaO}$  films to form hydroxyl groups. This argument leads to the conclusion that the peak at  $\sim 531.6$  eV is due to hydroxyl groups that are the dominant species on the  $\text{BaF}_2(111)$  after water adsorption at 300 K.

On  $\text{CaF}_2(111)$ , water adsorbed at 300 K gives two peaks in the O 1s spectra (Figure 4A), and neither is at the expected position ( $\sim 533.3$  eV) for molecular water. The peak with the lower binding energy is identified as atomic oxygen, because it has virtually the same position,  $\sim 528.8$  eV, as the O 1s peak from the  $\text{O}_2$ -annealed sample (spectrum a in Figure 4B). Water adsorption on the  $\text{O}_2$ -annealed sample gives an additional peak with a binding energy of  $\sim 531.3$  eV (spectrum b in Figure 4B), which is believed to be due to the hydroxyl groups. Thermodynamically the reaction



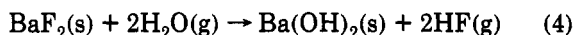
$$\Delta G^\circ_{298} = -15.82 \text{ kcal/mol}$$

is favored. The higher binding energy peak of the spectra in Figure 4A is at a similar position ( $\sim 531.4$  eV) and therefore is tentatively assigned to surface hydroxyl groups. Even though this is a reasonable interpretation, one unusual fact is that the peak at 528.8 eV is not observed to decrease in intensity with increasing water exposure, on either the clean or oxygen-annealed surfaces. This result is different from observations with the water/ $\text{BaF}_2(111)$  system. The thermodynamics favor reaction 1 for  $\text{BaF}_2$  more than reaction 2 for  $\text{CaF}_2$ , and the kinetics of this complex reactive adsorption may also be significantly different; however, further studies are needed for a decisive explanation.

**4.3. Interaction between Adsorbed Species and Substrates; Role of Defects in Dissociation.** The (111) surfaces of  $\text{BaF}_2$  and  $\text{CaF}_2$  are believed to be terminated by a layer of fluorine ions. An oxygen-containing layer directly on top of the fluorine layer will cause an attenuation of both anion (F 1s) and cation (Ca 2p or Ba 3d) photoemission. This is in contradiction to the results presented in Figures 3 and 6, where Ba and Ca cation signals are relatively constant with increasing water exposure. It is also unlikely from chemical bonding considerations that neutral or anionic O species would bond to anionic F species. Therefore it appears that the decrease of F 1s XPS intensity in Figures 3 and 6 is due to the depletion of fluorine from the surface. By comparison of their respective dependencies on the water exposure, it is clear that the decrease of the fluorine signals is roughly linear with respect to the estimated oxygen coverage. The loss of fluorine is estimated by the model which is used to calculate the coverage of oxygen-containing species. After the water exposure of  $10^7$  langmuirs, the top layer of fluorine of  $\text{BaF}_2(111)$  is completely lost; there is  $\sim 0.2$  monolayer of fluorine ions left on  $\text{CaF}_2(111)$  after the same water exposure. The ratio of the loss of fluorine to the gain of oxygen is about 1:1.5 on both surfaces. The appearance of a lower binding energy shoulder on the Ca 2p doublet is another strong suggestion of the formation of Ca–O bonds, inasmuch as the binding energy of Ca 2p<sub>3/2</sub> in  $\text{CaF}_2$  ( $\sim 347.8$  eV) is higher than that in  $\text{CaO}$  ( $\sim 346.1$  eV).<sup>10</sup> The dissociation of water will generate H species, and the loss of fluorine from these surfaces may be in the form of gas phase HF and  $\text{F}_2$  molecules. Thus, our results imply that the interaction between gas-phase water and the fluoride substrates is characterized by the reactive adsorption of water and the displacement of the surface fluorine by adsorbed hydroxyl groups and/or oxygen. The reactions

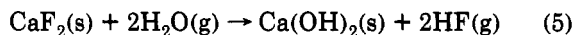
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$$\Delta G^\circ_{298} = +50.43 \text{ kcal/mol}$$

and



$$\Delta G^\circ_{298} = +43.60 \text{ kcal/mol}$$

are not thermodynamically favored. This fact may be the ultimate reason that the reactions between water and the fluorides are very slow and the total yield of the reactions is only 1.2–1.5 monolayers with water exposures up to  $\sim 10^7$  langmuirs. Several factors can make the reactions possible on the fluoride surfaces in spite of the unfavorable thermodynamics. First, during the experiments the partial pressure of H<sub>2</sub>O is much higher than that of HF, and this makes the reactions a little more favored. Second but more essential, the water/fluoride interfaces are not in the thermodynamic equilibrium described by eqs 4 and 5, which are the properties of bulk materials. This is suggested by the 1:1.5 ratio between the fluorine loss and oxygen gain. The "micro" structures of local chemical bonding can favor to a certain extent the displacement of fluorine by oxygen-containing species on these (111) surfaces, even though the reactions are prohibited by the "macro" thermodynamics.

Studies of water adsorption on alkali fluorides indicate that the cations are usually the preferred adsorption sites<sup>24</sup> and defects are responsible for the dissociation of water.<sup>2</sup> On the alkaline-earth fluoride surfaces discussed in this paper, defects which are not completely removed by annealing could also be responsible for the initial dissociation of the adsorbed water which then induces the displacement of surface fluorine. The occupation of these defect sites may be responsible for the relatively high sticking probability at low water exposure. On the other hand, the cations are believed to be partially buried under the layer of fluorine,<sup>8</sup> so further adsorption can only happen after the displacement of fluorine. The low sticking probability at high water exposures indicates that the depletion of fluorine is not fast or efficient under these

conditions. The lack of O 1s XPS intensity saturation with increasing water exposure is an additional indicator that the surface reaction is so slow that equilibrium is not reached in these experiments. The dashed line in Figure 2 corresponds to the adsorbed hydroxyl groups on BaF<sub>2</sub>-(111) after the desorption of the water by annealing the sample to  $\sim 150$  K. The coverage of  $\sim 0.7$  monolayer is an indication of the extent of the surface reaction at that low temperature. The uptake to  $\sim 1.5$  monolayers at 300 K indicates further reaction at higher temperatures.

Our results are in good agreement with the arguments by Kuroda et al.,<sup>4–6</sup> although their experiments concern water adsorption on CaF<sub>2</sub> powders and are carried out at much higher water pressures. These authors find that during adsorption isotherm measurements water is first dissociatively chemisorbed on CaF<sub>2</sub> powders as hydroxyls; well developed (111) facets are suggested by the crystallographic analysis to be the dominant exposed surface. The chemisorption is proposed as a slow process during which fluorine ions are replaced by hydroxyls. If these powders are treated at  $>500$  °C, sintering of CaF<sub>2</sub> may cause the loss of water adsorption sites, and it is difficult to regenerate the surface hydroxyl groups by further water exposure. This also supports the idea that defect sites are necessary for the dissociation of water.

### 5. Summary

(1) Water adsorption on BaF<sub>2</sub>(111) and CaF<sub>2</sub>(111) is studied by XPS. At 300 K, there is no sign of the formation of a molecular multilayer for exposures up to  $10^7$  langmuirs, contrary to a recent report.<sup>8</sup> Our results imply that water adsorbs dissociatively to a limited extent and is present on the surface as hydroxyl and/or oxygen species. For the highest water exposure used in these experiments ( $\sim 10^7$  langmuirs) the largest coverage of oxygen-containing species is of the order of 1 monolayer.

(2) The interactions between the adsorbed water and the substrate are sufficiently strong that surface fluorine ions are found to be displaced by oxygen-containing species.

(3) The lack of saturation of the surfaces by oxygen-containing species and the low sticking probabilities at very high water dosage imply that the reaction between water and the fluorides is very slow, as might expected from thermodynamic arguments.

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