

# Sodium Halide Adsorption and Water Structure at the $\alpha$ -Alumina(0001)/Water Interface

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## **SUPPORTING INFORMATION**

### **Comparison of solid relaxation**

The interaction between solid and water not only makes the properties of interfacial water different from those of bulk water but affects the solid structure near the interface as well. However, such phenomenon cannot be observed if the solid atoms are kept frozen during the simulations. Since in this work, all solid atoms are free to move, solid relaxation can be investigated by comparing the position of the oxygen atoms of the solid surface and the distance

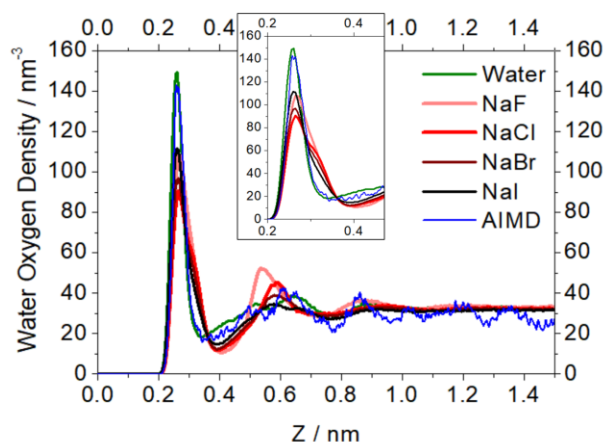
of the second layer oxygen is higher than other layers, which is in agreement with X-ray reflectivity spectra<sup>1</sup> and AIMD simulation by SCAN<sup>2</sup>.

**Table S1.** Solid oxygen positions from classical MD simulation and X-ray spectra. Column “Distance” is the distance from oxygen position from last layer.

	Classical Simulation		XRR <sup>1</sup>	
	Position(Å)	Distance(Å)	Position(Å)	Distance(Å)
Surface O(H)	0	0	0.044	0
1st O	-2.224	2.224	-2.111	2.155
2nd O	-4.464	2.240	-4.33	2.219
3rd O	-6.687	2.223	-6.48	2.15

### **Perturbation of water density profile by ion adsorption**

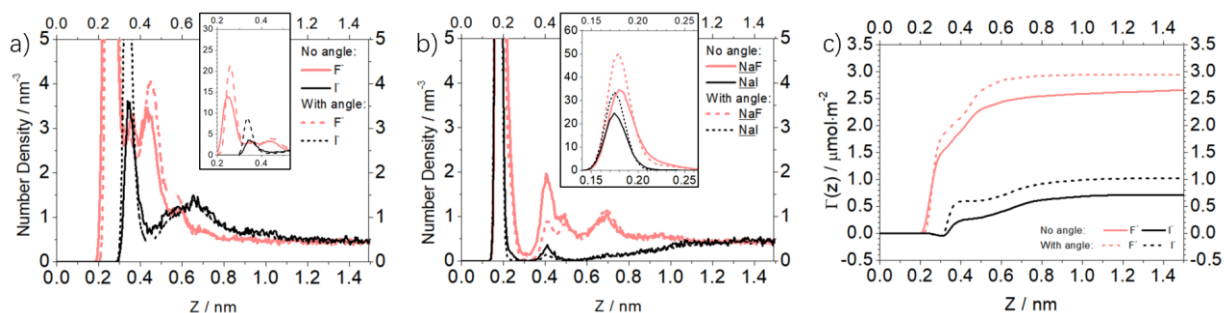
As described in the main text, ion adsorption also affects the water density distribution at the interface. An interesting phenomenon is that the height of the first peak (0.26 nm) in water density profile shows the sequence of NaI > NaBr > NaCl, indicating that higher ion adsorption can substitute more interfacial water. The shoulder peak at about 0.32 nm shows an inverse sequence of that at the first peak, we assume that those are water molecules from the first peak that are pushed to 0.32 nm region due to ion adsorption. An exception is NaF, which has the strongest ion adsorption but its first peak of water density is still rather high. Our hypothesis for this phenomenon is that first, F<sup>-</sup> is small, which saves the space for water; second, the interaction between F<sup>-</sup> and water is very strong, so the adsorbed F<sup>-</sup> can keep water in the first-peak region.



**Figure S1.** Comparison of water density profile from each simulation. Simulations details are described in the main text.

### Impact of the Al-O-H angle bending potential on ion adsorption

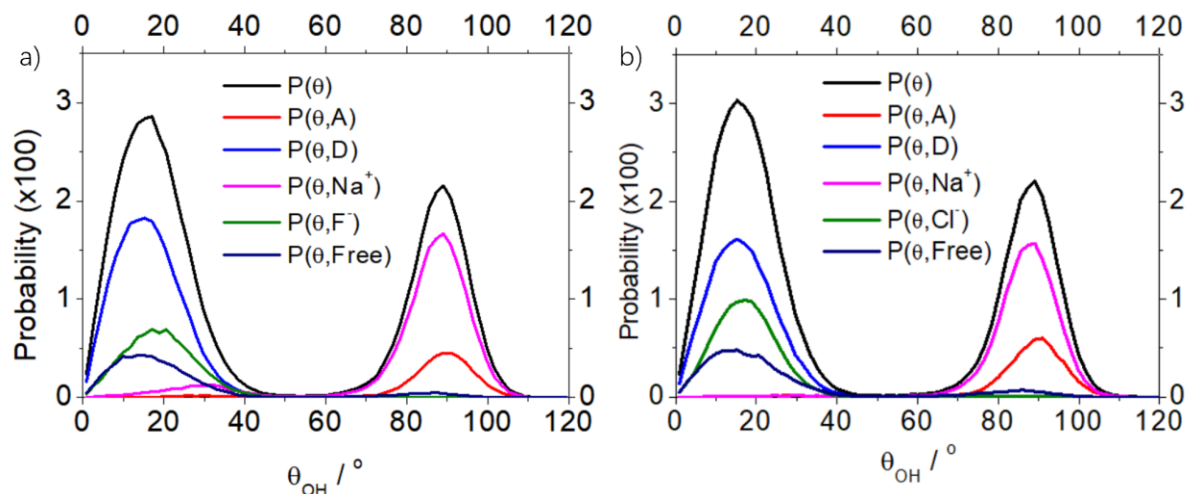
Simulations of the water/alumina interface with NaF or NaI without the surface Al-O-H bending potential are also carried out to determine its impact on ion adsorption; all other simulation details are the same as in the main text. Ion adsorption is reduced due to a more disordered surface OH orientational structure (Figure S2). For both sets of ions, turning off this potential decreases the ion density at the interface and reduces the adsorption,  $\Gamma(\infty)$ , by about  $0.3 \mu\text{mol}/\text{m}^2$  for  $\text{F}^-$  and  $\text{I}^-$ , as shown in Figure S2c. The model with the Al-O-H angle potential slightly underestimates the  $\text{F}^-$  adsorption with respect to experimental estimates, and neglecting this bending potential further decreases the accuracy of the model, underscoring the importance of accurately modeling the structure of the surface.<sup>3</sup>



**Figure S2.** (a) Density profile for  $F^-$  and  $I^-$ , all solid lines come from simulations without the Al-O-H bending potential, and all dashed lines are with such a potential, as discussed in the main text. The inset only shows the first peak for clarity. The position of each peak is generally the same but the height is lower. (b) Density profile for  $Na^+$ . (c) Thermodynamic adsorption  $\Gamma(Z)$  profile. Comparing to results with the bending potential, simulations without it underestimate ion adsorption.

### Comparison of the surface OH orientation distribution of different halides

Figure S3 shows the comparison of the surface OH orientation distribution between NaF and NaCl. The results for the “in-plane” mode surface OH of the two simulations are similar, most surface OH either accept a hydrogen bond from interfacial water or coordinate with  $Na^+$ . However, since most  $Cl^-$  can accept three hydrogen bonds from surface OH groups, this leads to a decrease in the surface OH population that donates hydrogen bonds to water and a transfer to the population that donate hydrogen bonds to  $Cl^-$ .

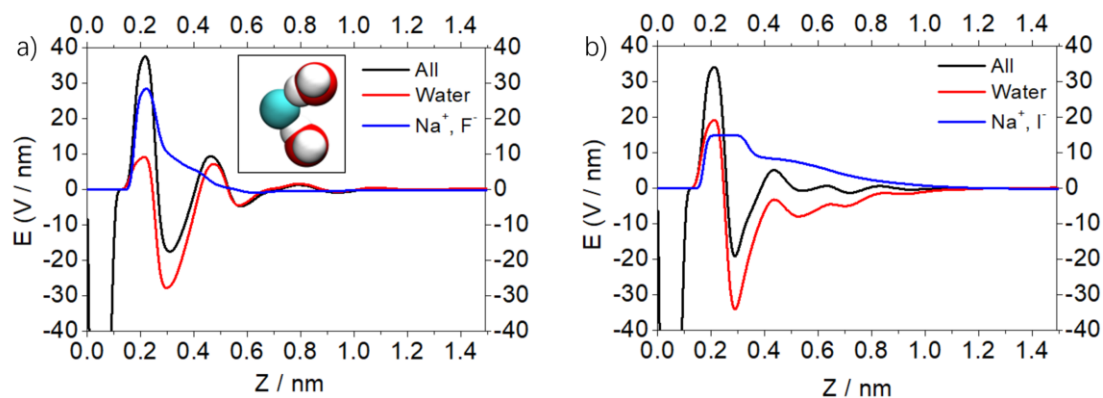


**Figure S3.** Comparison of the surface OH orientation distribution decompositions. (a) Decomposition of the  $P(\theta_{OH})$  in the simulation in the presence of NaF with respect to different

bonding modes. (b) Decomposition of the  $P(\theta_{OH})$  in the simulation in the presence of NaCl. “A” stands for the surface OH group that accepts hydrogen bonds from water; “D” stands for the surface OH group that donates hydrogen bonds to water, “A+D” stands for the surface OH group that donates and accepts hydrogen bonds to water at the same time and “Free” stands for the surface OH group does not have hydrogen bonds with water. “Na<sup>+</sup>”, “F<sup>-</sup>” and “Cl<sup>-</sup>” stand for the surface OH group coordinates with Na<sup>+</sup> or donates hydrogen bond to F<sup>-</sup> or Cl<sup>-</sup>, respectively.

### **Electric field profile**

The electric field profiles near the surface in the presence of NaF and NaI (Figure S4) illustrate the driving forces for water orientation. Excess Na<sup>+</sup> near the surface can create a positive electric field, helping order water and making water oxygen atoms point to the solid surface. In both simulations of NaI and NaF, ions always provide a positive electric field near solid surface, indicating that there are always more positive Na<sup>+</sup> than negative halides, which is already discussed in the main text. At the same time, water molecules always try to screen this electric field. However, the electric field of the NaF solution is more complicated as there is an abnormal positive peak of water at 0.5 nm from the solid surface. One assumption is that this is due to the strong interaction between F<sup>-</sup> and the water hydrogen atoms. Besides the first peak, F<sup>-</sup> also accumulates and forms a second peak at about 0.4 nm from solid surface. The hydration shell of the F<sup>-</sup> distorts the local water orientation and causes the oscillation of the water electric field. However, the electric field still shows a negative value further away before reaching 0 at 1.2 nm.



**Figure S4.** Electric field profiles of simulations in the presence of (a) NaF and (b) NaI. The blue and red curves reflect the contribution of the electric field due to ions and water, respectively. The black curve is the total electric field of all the atoms in the simulation box.  $Z = 0$  corresponds to the position of the surface oxygen atoms of alumina. The inset snapshot illustrates the hydration shell of  $F^-$ , which inverses the local water orientation at  $Z = 0.5$  nm.

## REFERENCES

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