

# Supporting Information

## Cationic and Anionic Impact on the Electronic Structure of Liquid Water

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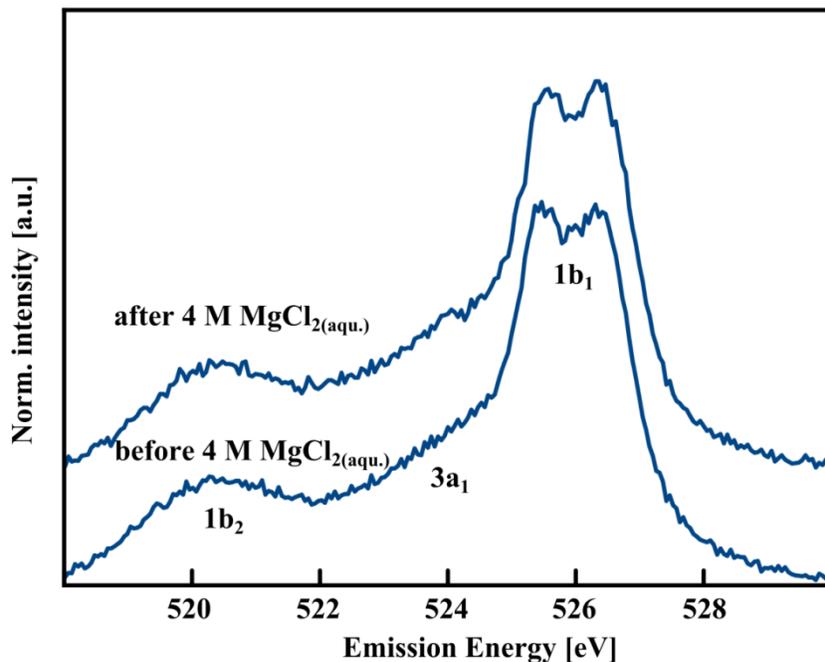
### **Supplementary discussion of the experiment:**

#### **XES before and after salt solution**

In this supporting information we compare the pure water spectrum before and after the measurement of the 4M MgCl<sub>2</sub> solution. The comparison in Fig. S1 validates that there are no experimental artifacts due to perturbation in the experimental setup.

The reproduction of the non-resonant water spectrum rules out any significant changes during the measurement. Both measured pure water spectra agree with previous studies<sup>S1</sup>.

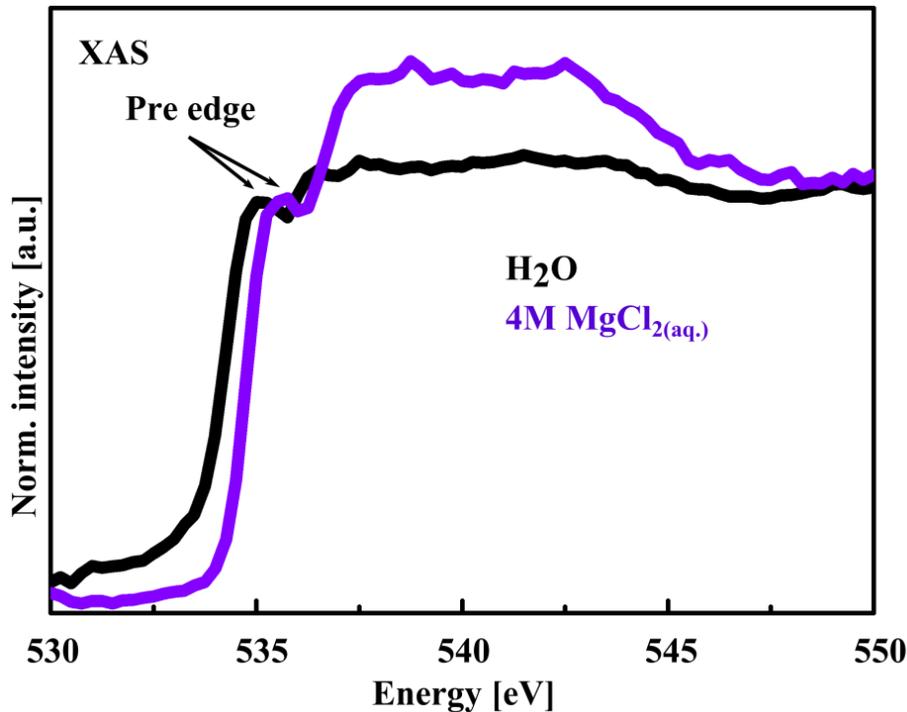
S2



**Fig. S1:** The water spectrum before and after the measurement of 4 M MgCl<sub>2</sub>

### XAS of water and 4M MgCl<sub>2</sub> solution

The X-ray absorption spectra of pure water and 4 M MgCl<sub>2</sub> solution on the oxygen K-edge are shown in Fig. S2 recorded in total fluorescence yield (TFY). For the salt solution, the spectrum has been normalised to the pre edge peak. As can be seen, the XA characteristics for liquid water consist of three different features: pre edge (~ 535 eV), main edge (~ 538eV) and post edge (~ 540 eV).<sup>S3</sup> Compared to the pure water spectrum, the pre edge feature of the salt solution is shifted towards higher energy, which is in



**Figure S2:** X-ray absorption spectrum of liquid water and 4M MgCl<sub>2</sub> salt solution.

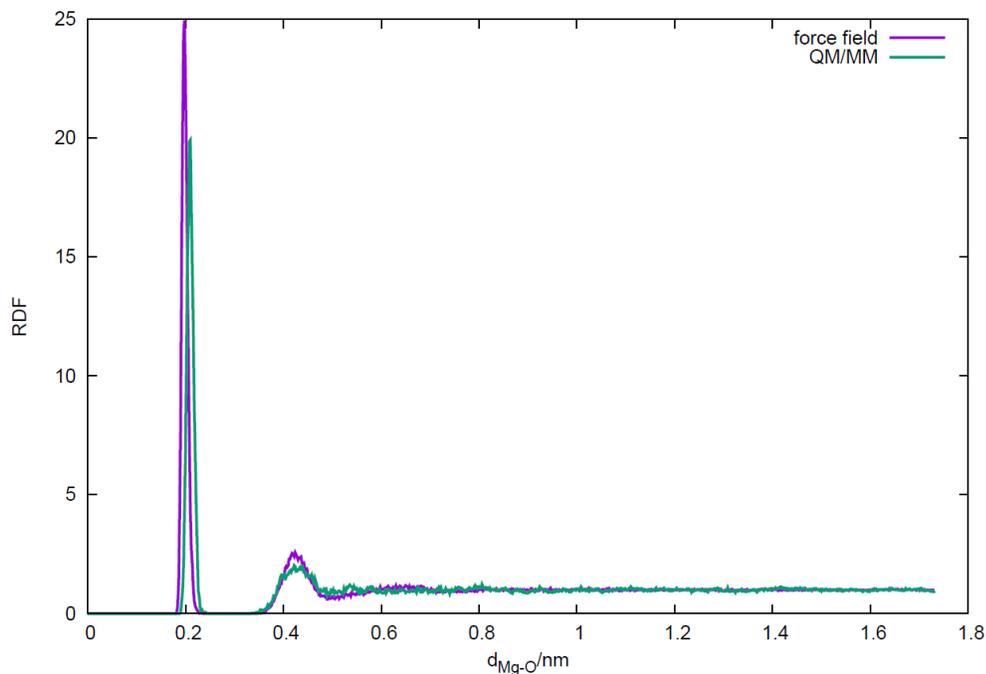
agreement with previous XAS results.<sup>S4, S5</sup> Further differences in the spectrum are higher intensity in the main and post area. We consider the higher intensity in the main and post edge area to be artefacts due to the measurements in TFY mode. In TFY mode, all photons from secondary processes after core hole creation are recorded. In a bulk material the emitted photons can be absorbed again by the sample before detection (self-absorption) leading to deviations from the true absorption cross section and false peak ratios. Because of this, TFY is very sensitive to the actual experimental setup, changing the liquid sample from pure water to salt solution leads to slightly different experimental conditions. As shown above, these slight changes do not affect the results of the XES measurements. The energy shift of the pre edge feature is a consequence of interactions of water molecules with the ions though. The XA spectra indicate that the probing sample

is in the liquid phase, since the energy of the pre-edge of pure water and 4M MgCl<sub>2</sub> solution is characteristic for the liquid phase.<sup>S3-S5</sup>

## **Supplementary discussion of the calculations:**

### **Force field validation**

In the MD simulation the interaction of the water molecules with the dication was modeled with the gromos45a3 force field.<sup>S6</sup> To confirm the validity of this approach, we performed a QM/MM simulation where the 1<sup>st</sup> solvation layer around the Mg<sup>2+</sup> ion and the ion is included in the QM region. We use the same parameters as specified in the main text for the force field simulation but only simulated for 10ps. The QM region was embedded via the ONIOM<sup>S7</sup> scheme and the electronic structure calculation were conducted with an interface to gamess-us<sup>S8</sup> employing restricted Hartree-Fock with a 6-31G(d) basis set. Figure S3 shows the radial distribution function obtained with the QM/MM and the pure force field simulation. As can be seen, the Mg<sup>2+</sup>-oxygen distance distribution is very similar. Both simulations indicate a first solvation shell at Mg<sup>2+</sup>-Oxygen distance of ~0.2 nm. This first solvation shell is slightly tighter in the force field simulation. Another shallow maximum is seen around 0.41 nm indicating the distance for the second solvation shell. In the force field simulation both of these distribution maxima are slightly more peaked compared to the QM/MM simulation. Altogether, the differences are only minor; therefore, we consider that the force field approach correctly samples the characteristic geometries of the hydration shells around the Mg<sup>2+</sup> cation.

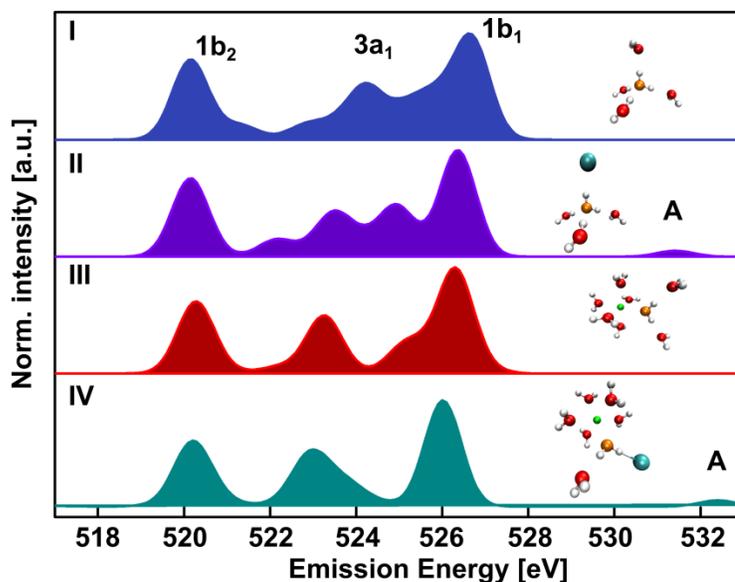


**Figure S3:** The distribution function of the  $\text{Mg}^{2+}$ -O distance from the force field calculation compared to the one from the QM/MM simulation.

### **X-ray emission spectrum for water molecule neighbouring both ions**

In the main text we speculate about the additive character of the ions impact on the electronic properties of water molecules. Figure S4 shows the calculated XE spectrum of water molecules in different geometry configuration in vacuum with and without ions. The different geometrical arrangements have been obtained by geometry optimization employing electronic structure calculations as described above but in vacuum. The ionized water molecule is labelled by orange colour. Panel I shows the XE spectrum of a water molecule in a tetrahedral configuration with full hydrogen bonds. In panel II the water molecule is neighbouring a  $\text{Cl}^-$  anion with two hydrogen bond acceptor molecules and one donor molecule. Panel III displays the ionized water molecules in the first

hydration shell of an  $\text{Mg}^{2+}$  ion with two hydrogen bond donors. Panel IV illustrates the XE spectrum for a geometrical configuration where the ionized water molecule is neighbouring both ions and an additional hydrogen bond donor. The calculated spectra show some changes in the  $1b_2$  and  $3a_1$  contributions. These changes appear since the calculations are performed in vacuum and with single geometrical configurations. Apart from that the discussed ion specific features in the calculated spectra follow the discussed systematics: In panel II an additional contribution above the lone pair signal is seen (labelled A) stemming from the  $\text{Cl}^-$  contributions. In panel III the red shift of the lone pair contribution is seen due to the impact of the  $\text{Mg}^{2+}$  dication. In panel IV, both of the cation and anion characteristic features are seen. This supports our speculation of the additive nature of the ion induced impact on the electronic properties of water.



**Figure S4:** The calculated XE spectra of water in different configurations and vacuum with and without ions. The ionized water molecule is orange coded. The different geometrical structures are displayed in the inset.

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