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Letter

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Cationic and Anionic Impact on the Electronic Structure of Liquid Water

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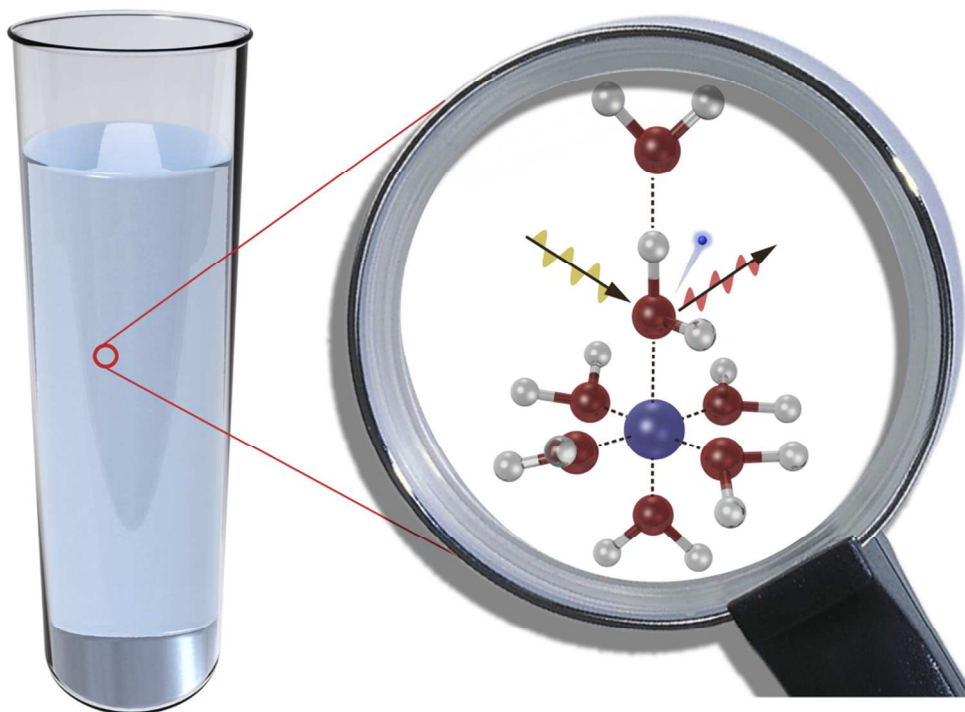
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ABSTRACT: Hydration shells around ions are crucial for many fundamental biological and chemical processes. Their local physico-chemical properties are quite different from bulk water, and hard to probe experimentally. We address this problem by combining soft X-ray spectroscopy using a liquid jet and molecular dynamics (MD) simulations together with *ab initio* electronic structure calculations to elucidate the water-ion interaction in an MgCl₂ solution at the molecular level. Our results reveal that salt ions mainly affect the electronic properties of water molecules in close vicinity and that the oxygen K-edge X-ray emission spectrum of water

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3 molecules in the first solvation shell differs significantly from bulk water. Ion specific effects are
4 identified by fingerprint features in the water X-ray emission spectra. While Mg^{2+} ions cause a
5 bathochromic shift of the water lone pair orbital, the 3p orbital of the Cl^- ions causes an
6 additional peak in the water emission spectrum around 528 eV.
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46 Aqueous solutions are ubiquitous in nature and play an important role for a wide range of
47 biological, environmental and chemical processes.¹⁻³ The solvation of water molecules around
48 ions is of particular interest since it determines the fundamental mechanisms and dynamics of
49 many chemical and biological systems.⁴⁻⁶ Ion induced changes include among others distortion
50 of the electronic properties as well as geometrical arrangements of water molecules. A
51 considerable number of experiments have been performed to elucidate the water-ion interaction
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3 and the interpretations of the data suggest sometimes a complex picture about the nature of the
4 ion solvation.⁷⁻²⁴ Studies from X-ray scattering,⁷ dielectric relaxations,^{8,9} infrared,¹⁰⁻¹³ NMR¹⁴
5
6 and terahertz spectroscopy¹⁵ showed that the impact on water molecules by solvated ions is
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8 mainly restricted to water molecules in close vicinity to the ion. Only for specific combinations
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10 of strongly hydrated salt ions it has been reported that the impact on the orientation of water
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12 molecules may extend beyond the first solvation shell.¹⁰ Nevertheless, neutron scattering studies
13
14 revealed that the oxygen-oxygen radial distribution function is altered by NaCl and KCl solutes
15
16 beyond the first solvation shell.¹⁶ The seemingly contradicting results may be due to the
17
18 sensitivity of the utilized methods to different properties of the aqueous solutions. While neutron
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20 scattering probes the average of the overall structure, IR spectroscopy for example is sensitive to
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22 the dynamical properties of water.
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30 Since the electronic properties of the water molecules are sensitive to their chemical
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32 environment, probing them may elucidate further information about the hydrogen bond (HB)
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34 structure. X-ray spectroscopy allows measuring directly the electronic properties of a system and
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36 provides direct information about the local electronic structure around a specific element in a
37
38 bulk chemical environment.²⁵⁻⁴⁰
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43 Previous soft X-ray absorption studies on aqueous solutions reported strong distortions of the
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45 pre-, main- and post edge of the X-ray absorption spectra on the oxygen K-edge in the vicinity of
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47 the ions.^{7,30,31,33} These changes have been assigned to weakening and strengthening of the
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49 hydrogen bonds in the solvation shell around the cations.^{7, 30-33}
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53 Complementary information to X-ray absorption spectroscopy is gained from X-ray emission
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55 spectroscopy (XES). XES probes the valence electrons, which are essential for the chemical
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3 bonding. The X-ray emission (XE) spectrum of water shows three prominent features ²⁷ which
4 attributes to the three outer valence orbitals of water, the lone pair orbital $1b_1$ at ~ 526 eV and the
5 internal bonding orbitals $3a_1$ at ~ 524 eV and $1b_2$ at ~ 521 eV. Experiments with higher energy
6 resolution revealed additionally a splitting of the lone pair orbital contribution into two parts and
7 further showed the sensitivity of this lone pair orbital fine structure to the hydrogen bond
8 environment based on temperature and isotope measurements.^{35, 36}

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10 Yet, the origin of the splitting has stirred a discussion about the nature of the fine structure.
11
12 Mainly two models have been suggested to explain this effect: The fine structure arises either (1)
13 from nuclear dynamics during the core hole lifetime^{35, 41} or (2) from two different structural
14 motifs.³⁶ In model (1) the higher energy peak arises from intact water molecules and the lower
15 energy peak from ultrafast proton transfer facilitated by intact hydrogen bonds.³⁴ In model (2)
16 the lower peak is from water molecules in a fully hydrogen bonded tetrahedral coordination
17 while the higher energy peak stems from water molecules in strongly distorted HB
18 configuration.³⁶ Despite this controversy, there is consensus that the XE spectrum of water on the
19 oxygen K-edge is a fingerprint of the hydrogen bond network.^{27, 35, 36}

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21 Recently, several soft XES experiments have reported that the electronic properties of water is
22 altered by the presence of salt ions only at high salt concentrations.^{28, 37-40} However, the
23 dominating change that is observed is an intensity decrease of the lower energy part of the split
24 lone pair orbital peak in dependence of the concentration and the type of salt ions, which
25 consisted mainly of Cl^- as anion and various cations (NH_4^+ , Li^+ , K^+ , Na^+ , Mg^{2+} & Ca^{2+}). These
26 changes were assigned to the distortion of the hydrogen bond network.^{28, 37-40} The modification
27 in the electronic properties were relatively small such that even at the highest concentration for
28 monovalent (7M) and divalent (4M for CaCl_2) salt ions the splitting was still observed.
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3 The changes were assigned to the impact of the cations by comparing changing cations with the
4 same Cl⁻ concentration^{28, 40}
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8 Jeyachandran *et al.*³⁷ introduced a three component fit based on water model (1) and assigned
9 one component to water molecules in the first solvation shell. Recently, the same authors also
10 studied KBr, KCl, MgCl₂ and CaCl₂ at various concentrations and observed in highly
11 concentrated (>3 M) solution a stronger increase of the extracted component for the Br⁻ anion
12 than the Cl⁻ anion.³⁹ Additionally, this component of MgCl₂ and CaCl₂ solutions was twice as
13 strong as for monovalent salt solutions. Therefore, they concluded that this component represents
14 the first hydration shell around anions. However, because of the higher charge of divalent cations
15 compared to the monovalent cations, it is also conceivable that the increase of the additional
16 component is due to the contribution by water molecules in the first solvation shell of the
17 divalent cations.
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33 The aim of the present study is therefore to elucidate the nature of ion-water interactions and its
34 effect on the electronic properties of water using a combined study of soft X-ray spectroscopy
35 with *ab initio* electronic structure calculation on aqueous solutions. We address the question how
36 salt ions change the electronic properties of liquid water and reveal the origin of the previously
37 observed additional peak at ~ 528 eV. To that end we investigate the impact of salt ions in
38 highly concentrated MgCl₂ solutions. Compared to monovalent cations like sodium or
39 potassium, magnesium is divalent and one expects a stronger interaction with the surrounding
40 water molecules. Also, because Mg²⁺ has a markedly shorter ion-water distance than Ca²⁺.⁴²
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Figure 1 shows the XE spectra of 4M MgCl_2 solution compared to pure water. The excitation energy was set at non-resonant energy above the post edge according to the XAS results, see SI. They have been area normalised for an accurate comparison of relative intensities.

For pure water (blue), three regions can be distinguished as described in the introduction. The lone pair peak shows a double peak structure in the pure water spectrum in agreement with previous results.^{35,36} For the 4M solution the intensity of the bonding orbitals $1b_2$ and $3a_1$ in MgCl_2 solution is more pronounced.

In contrast to the splitting in the lone pair region of pure water, for the 4M salt solution (red) only one peak is seen. Further, this $1b_1$ peak is shifted to lower energies and to a position between the peaks of the lone pair orbital for the pure water spectrum, while the position of the other contributions is rather similar.

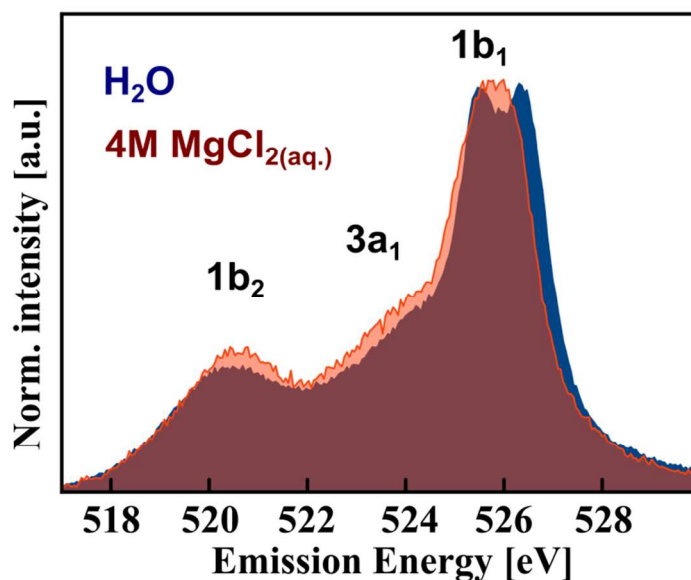


Figure 1: The X-ray emission spectra of pure water in comparison with 4M $\text{MgCl}_2(\text{aq})$ solutions on the oxygen K-edge are shown.

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3 In previous works no strong effects on the water's valence electronic configuration has been
4 observed for a 2M MgCl₂ and for a CaCl₂ solution with concentration up to 4M,³⁹ which
5 contains the same number of Cl⁻ anions as in our 4M MgCl₂ solution. The differences to these
6 previous studies are most likely due to the lower concentration (2M vs 4M) and the different
7 cation, since Mg²⁺ has a much tighter hydration shell than the Ca²⁺ cation.⁴²
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11 Given fact that former studies (experimental and theoretical) show a negligible effect of Cl⁻ ions
12 on the electronic structure of water, even for very high concentrations,^{7, 24, 28, 30, 32, 33, 40} we
13 assume the number of water molecules in direct contact with Mg²⁺ ions can explain most of the
14 salt-induced spectral changes in our 4M solution. Accordingly, we expect the major effects of
15 salt on the electronic properties can be understood to first approximation from the electronic
16 configuration of the water molecules in the first solvation shell around Mg²⁺ ion. Based on this
17 additional idea, we consider the solution spectrum of the valence electronic states of water $f(E)$
18 to be a linear combination of the spectra arising from water molecules in the first solvation shell
19 around Mg²⁺, $f_{Mg}(E)$, and those arising from water molecules not in direct contact with Mg²⁺,
20 contributing with the spectrum of bulk water, $f_{bulk}(E)$. Referring to the above arguments, we
21 assume that the XE spectrum of water molecules close to Cl⁻ anions is similar as the XE
22 spectrum of bulk water, such that the 4M MgCl₂ spectrum is given by $f(E) = \alpha f_{Mg}(E) + (1 -$
23 $\alpha) f_{bulk}(E)$.
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48 From the measured spectrum $f(E)$ we thus obtain a good approximation for the isolated spectrum
49 of water molecules in the first solvation shell of Mg²⁺, $f_{Mg}(E) = \frac{1}{\alpha} (f(E) - (1 -$
50 $\alpha) f_{bulk}(E))$, by taking the weighted difference of measured bulk water and solution spectra.
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56 The coefficient α is determined from the relative number of water molecules in the first solvation
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3 shell of Mg^{2+} . At 4 M concentration, there are ~ 13 water molecules per MgCl_2 salt moiety. Even
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5 at this high concentration direct ion pairing is unlikely⁴³, but there might be a relevant quantity
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7 of water molecules in direct contact with both ions. Since we ignore for the moment the impact
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9 of Cl^- ions altogether, we assume them to contribute to the spectrum like the water molecules in
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11 direct contact with an Mg^{2+} ion only. Considering the coordination number for Mg^{2+} , which is
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13 6,⁴⁴ results in $\alpha=6/13\approx 0.46$. Figure 2 shows the resulting spectrum, now dominated by the signal
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15 from water molecules in the first shell around Mg^{2+} . The difference spectrum shows two
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17 pronounced peaks $1b_1$ and $1b_2$ and a broad peak between them corresponding to the three outer
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19 valence orbital contributions. No clear splitting is observed in the lone pair region. Further, an
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21 additional shoulder appears at ~ 528 eV. This difference spectrum looks very similar to the new
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23 component extracted from the water model (1) reported in Ref [37].
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30 To explain the energy shifts and the additional shoulder ~ 528 eV, we compare these
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32 experimental results to *ab initio* electronic structure calculations on water clusters sampled from
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34 MD simulations with and without ions. To address the question to which distances the electronic
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36 properties of water are influenced by the ions, we calculate spectra for a very dilute solutions and
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38 inspect the spectra stemming from the different solvation shells around the ions. The comparison
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40 with the experimental difference spectrum at high salt concentration requires the additional
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42 assumption that the structure of the Mg^{2+} solvation shells is mainly unaffected by the MgCl_2
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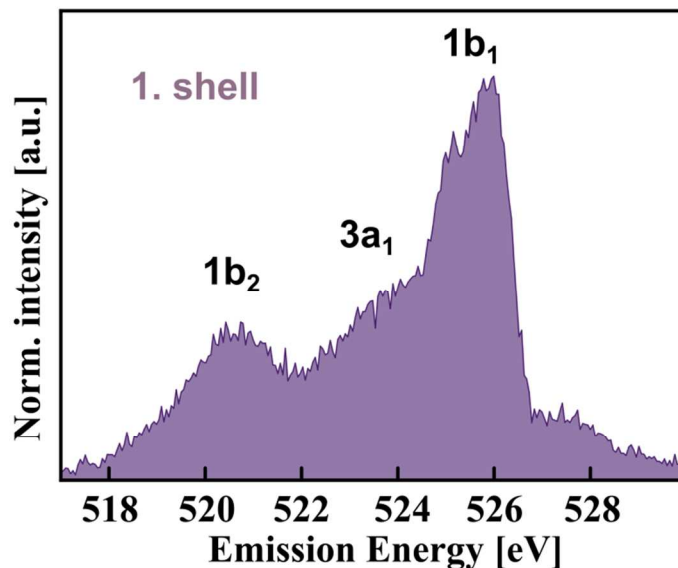


Figure 2: The difference spectrum between 4M MgCl_2 and pure water is displayed. The difference represents the first hydration shell of water molecules around Mg^{2+} .

In Figure 3 top tier (I & II) we compare the first solvation shell spectrum with pure water. A bathochromic shift (~ 0.4 eV) in the spectrum for the $1b_1$ orbital can be observed.

Figure 3 lower tier (III, IV, V & VI) shows the calculated fluorescence spectrum after core ionization for pure water (III) and for water in the first (VI) and second (V) solvation of Mg^{2+} and first (IV) shell of Cl^- . These are compared to the experimental results of pure water (I) and the measured difference spectrum corresponding to the first (II) shell of Mg^{2+} .

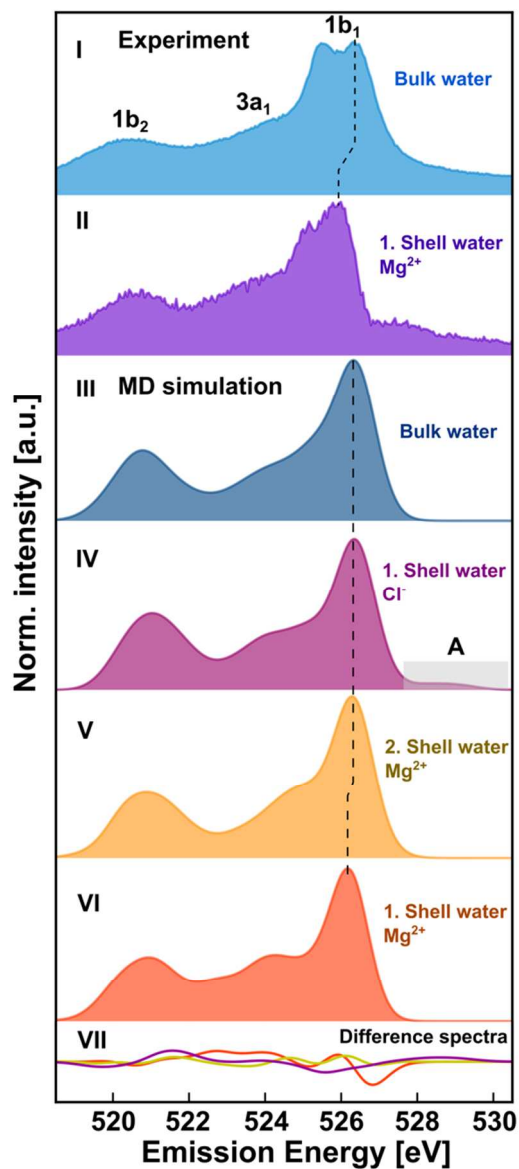


Figure 3: *Ab initio* spectra of pure water clusters compared with the first and second solvation shell of water around Mg^{2+} and first shell around Cl^- ions with experimental results of pure water and the first around Mg^{2+} ion. The dashed line is a guide to the eye to illustrate the shift of the $1b_1$ peak position. Tier VII shows color coded the difference spectra of the solvation shells to bulk water for the theoretical results.

As can be seen, the calculation reproduces the different $1b_1$, $3a_1$, $1b_2$ orbital contribution that are seen in the measured spectrum. The split peak of the $1b_1$ part is not reproduced by the calculation. As discussed before, this feature might stem from proton dynamics during the core hole lifetime⁴¹ that are not included in our calculation. Alternatively, the fine structure might

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3 stem from two different structural motifs in the local hydrogen bond structure. However, in our
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5 calculation these structural motifs may not be correctly reproduced by the utilized force field
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7 approach. Therefore, we cannot give a satisfactory answer on the origin of the peak splitting.
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10 Apart from this discrepancy, we think that the calculation shows overall good agreement with the
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12 measured spectrum, that allows us to understand the qualitative salt-induced changes.
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15 For the fluorescence spectrum of the salt solution, we classify the calculated fluorescence
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17 spectrum for water molecules ionized in the first and second solvation shell of Mg^{2+} and first
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19 solvation shell around Cl^- , respectively. Thus, we can identify the impact of the ions on the
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21 fluorescence spectrum as a function of distance to the different ions. As can be seen, for all the
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23 different water molecule classes, the $1b_2$ and $3a_1$ orbital contributions are rather unaffected. For
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25 the first hydration shell (IV) around Cl^- and the second solvation shell (V) around Mg^{2+} the
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27 calculated spectrum is very similar to the calculated pure water spectrum, whereas the first
28
29 solvation shell (VI) around the Mg^{2+} ions, the $1b_1$ orbital contribution is red-shifted, which is
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31 also mirrored in the difference spectra in tier VII. In the difference spectra are noticeable changes
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33 in the second solvation shell around the Mg^{2+} observed. However, they are much weaker
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35 compared to the first solvation shell modifications. The red shift can be explained by the Mg^{2+}
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37 induced polarization changes of water molecules. The lone pair orbital points towards the cation
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39 such that the electrostatic interaction between the water molecules and the Mg^{2+} cation lowers
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41 the energy of the lone pair orbital and hence lowers the emitted X-ray for a re-occupation of the
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43 core hole from this orbital.
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50 For the fluorescence spectrum of the water molecules in proximity to Cl^- ions we see an
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52 additional shoulder above 528eV, see tier IV A in Figure 3. This additional contribution was
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54 reported in a previous calculation⁴⁵ and has also been observed before in the three component
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3 spectra fit of the aqueous solution spectrum based on the water model (1).³⁷ Closer inspection of
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5 the electronic structure reveals that this fluorescence signal stems from molecular orbital
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7 representing the 3p shell of Cl⁻ with slight contribution in the valence orbitals of the ionized
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9 water molecules. We can therefore assign it to a refilling of the oxygen core vacancy from the Cl⁻
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11 anion.
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15 Taken altogether, our calculations show that, indeed, Mg²⁺ affects mainly the electronic
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17 properties of water molecules in close proximity. Whereas the water molecules close to Mg²⁺
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19 ions have a bathochromic 1b₁ shift, water molecules close to Cl⁻ show more or less an
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21 undistorted pure water XE spectrum augmented by an additional shoulder at 528eV. Therefore,
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23 the additional shoulder in the experimental difference spectrum at ~ 528eV which we in Figure 3
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25 tentatively assigned to the first solvation shell of Mg²⁺ must be attributed to the water molecules
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27 in the vicinity of Cl⁻ anions.
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31 In the comparison, we assumed that the solvation structure around Mg²⁺ is independent of the
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33 salt concentration. However, for the high salt concentration investigated here, it is conceivable
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35 that water molecules are in direct contact with an Mg²⁺ and Cl⁻ ion. Considering that the overall
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37 ion impact on the XE spectra is rather small we speculate that the ion's impact is additive and in
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39 this case a water molecule may show both ion induced features, for further discussion see SI.
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44 In experimental XE studies, noticeable distortion in the electronic properties of water is only
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46 observed at high salt concentration.^{28, 37-39} Theoretical results show significant changes in the
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48 electronic properties of water molecules in proximity of the ions. For water molecules in the
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50 second solvation shell of the ion and beyond, the electronic properties of water show negligible
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52 distortions compared to bulk water. Based on these facts, we conclude that ions mainly influence
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54 the electronic properties of water molecules in close vicinity. Soft XES is therefore particularly
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3 sensitive to the local environment of the ion and less sensitive to the geometrical arrangement of
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5 water molecules in the bulk far from the ion.
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8 In summary, we compared the XE spectrum of 4M MgCl₂ solution with that of pure water, and
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10 revealed significant differences in the electronic properties of water. Results from *ab initio*
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12 electronic structure calculations agree with our experimental findings, except for the fine
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14 structure of the 1b₁ peak region which is likely due to the lack of explicit core-hole excited-state
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16 dynamics in the spectra calculations.⁴¹ Because of this agreement, the simulation results serve to
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18 explain the observed differences in terms of a microscopic model. Accordingly, it is mainly the
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20 water molecules in the immediate vicinity of the salt ions whose electronic properties are
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22 markedly affected thereby defining the sensitivity of our probe.
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27 Our results show that salt ions have indeed a significant impact on the electronic properties and
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29 that cation and anion have ion specific influence on the electronic states of water, such that
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31 anionic and cationic effects leave different fingerprints on the XE spectra. The interaction of the
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33 first solvation shell water molecules with Cl⁻ anions leads to an additional signal at ~ 528 eV. In
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35 the first solvation shell around Mg²⁺ ion the lone pair orbital of water is bathochromatically
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37 shifted. Furthermore, the origin of the specific ions effects can be explained by Mg²⁺ cation
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39 induced polarization changes in water and contributions of the 3p shell of Cl⁻ anions.
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43 We think that the combination of soft X-ray spectroscopy with MD sampled *ab initio* electronic
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45 structure calculations developed and demonstrated here, can serve to probe molecular interaction
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47 in a broad range of different condensed matter systems, including highly complex biomolecular
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49 structures.
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Experimental and Simulation Method

The experiments were performed at the beamline U41 of BESSY II synchrotron at the Helmholtz Zentrum Berlin using the FlexRIXS endstation⁴⁶ and at P04 of PETRA III using the ChemRIXS⁴⁷ setup. For excitation, a monochromatic soft X-ray beam has been utilized. The MgCl₂ solution was prepared from >99.0 % MgCl₂·6H₂O (Magnesium Chloride Hexahydrate) from Sigma - Aldrich at least 24 hours prior to the experiment. The non-resonant excitation energies have been selected from the X-ray absorption (XA) spectra of water and aqueous solutions recorded in the total fluorescence yield mode, see SI. XA and XE spectra of pure water were recorded periodically to confirm the stability of the setup, see SI. The resolution of the spectrometer was ~ 0.4 eV at 530 eV (oxygen K-edge). The elastic peaks have been used for energy calibration.

To perform ab-initio calculation of the XE spectrum of liquids we have sampled molecular geometries from molecular dynamics calculations. The MD calculations have been conducted using the gromacs 4.5.5 program⁴⁸ employing the Particle-Mesh-Ewald method ($r_{\text{cutoff}} = 0.85$ nm, fourier spacing = 0.12 nm) with Noose-Hoover temperature coupling ($\tau = 0.1$ ps) and Parinello-Rahman pressure coupling ($\tau = 4.0$ ps). The flexible Ferguson force-field⁴⁹ has been used with a time-step of 0.5 fs. For pure water, we have performed a 100ps-MD simulation of a box containing 1410 water molecule at a temperature of 300 K and a pressure of 10^5 Pa.

Since we expect the impact of the ions to be restricted to the first solvation shells, we have performed simulations at low salt concentration. The same setup as before has been used to conduct 100ps-MD simulations for a box containing 1426 water molecules with a single Mg²⁺ ion and two Cl⁻ ions. The interaction of the ions with the water molecules was described using the gromos45a3 force field.⁵⁰ For the discussion of the validity utilizing this force field approach see SI. From these MD simulations, water molecules have been randomly picked at different

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3 snapshots to sample the local environment around the ionized water molecule. For the
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5 calculations of the XE spectrum, clusters around the ionized water molecule have been
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7 constructed that include neighboring water molecules (oxygen-oxygen distance smaller than 3.5
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9 Å) and neighboring ions (oxygen-ion distance smaller than 4 Å). These clusters have been
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11 considered explicitly in the electronic structure calculations while molecules and ions within a
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13 sphere of 10 Å around the ionized oxygen were included as point charges in the electronic
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15 structure calculations via electrostatic embedding.
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19 For each of these molecule clusters restricted Hartree Fock orbitals with localized core orbitals
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21 have been calculated employing a 6-31G(d)⁵¹ basis set using the psi3 electronic structure
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23 package.⁵² Using this orbital set the initial core ionized electronic state Ψ_i has been described
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25 using a configuration interaction (CI) calculation involving all configurations with single
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27 excitations from the water valence orbitals into virtual orbitals, while the core hole orbital on the
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29 core ionized oxygen atom has been kept singly occupied. The final valence-ionized state has
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31 been described using a CI calculation involving all possible valence orbital vacancies and
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33 reoccupied core orbital. From these CI solutions the transition rate for fluorescence has been
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35 evaluated from
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$$40 \quad I_0 = \frac{4}{3} \alpha^3 \omega^3 \sum_{j=x,y,z} |\langle \Psi_i | d_j | \Psi_f \rangle|^2$$

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42 where d is the dipole moment operator and $\omega = E_i - E_f$, with E_f and E_i being the final and initial
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44 state energies from the CI solutions, respectively. Finally, the obtained fluorescence line
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46 spectrum has been convoluted with a Gaussian function of 1eV FWHM to account for
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48 vibrational broadening effects and accumulated for the various water clusters. To distinguish the
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50 different chemical effects, the XE spectra have been assembled for water molecules in different
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52 chemical environments. For water molecules in the first solvation shell around Mg^{2+} , Cl^- , and for
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3 water molecules in the second solvation shell of Mg^{2+} , as well as for water molecules stemming
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5 from the neat water simulation, the XE spectrum has been assembled from ~80 different water
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7 clusters, respectively.
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10 All calculated spectra have been shifted by 0.2 eV to lower energies for a better comparison with
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12 the experimental spectra.
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38 [†]Z. Yin and L. Inhester contributed equally to this work.
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ASSOCIATED CONTENT

Additional experimental and theoretical data as mentioned in the text.

ABBREVIATIONS

XES, XAS, HB

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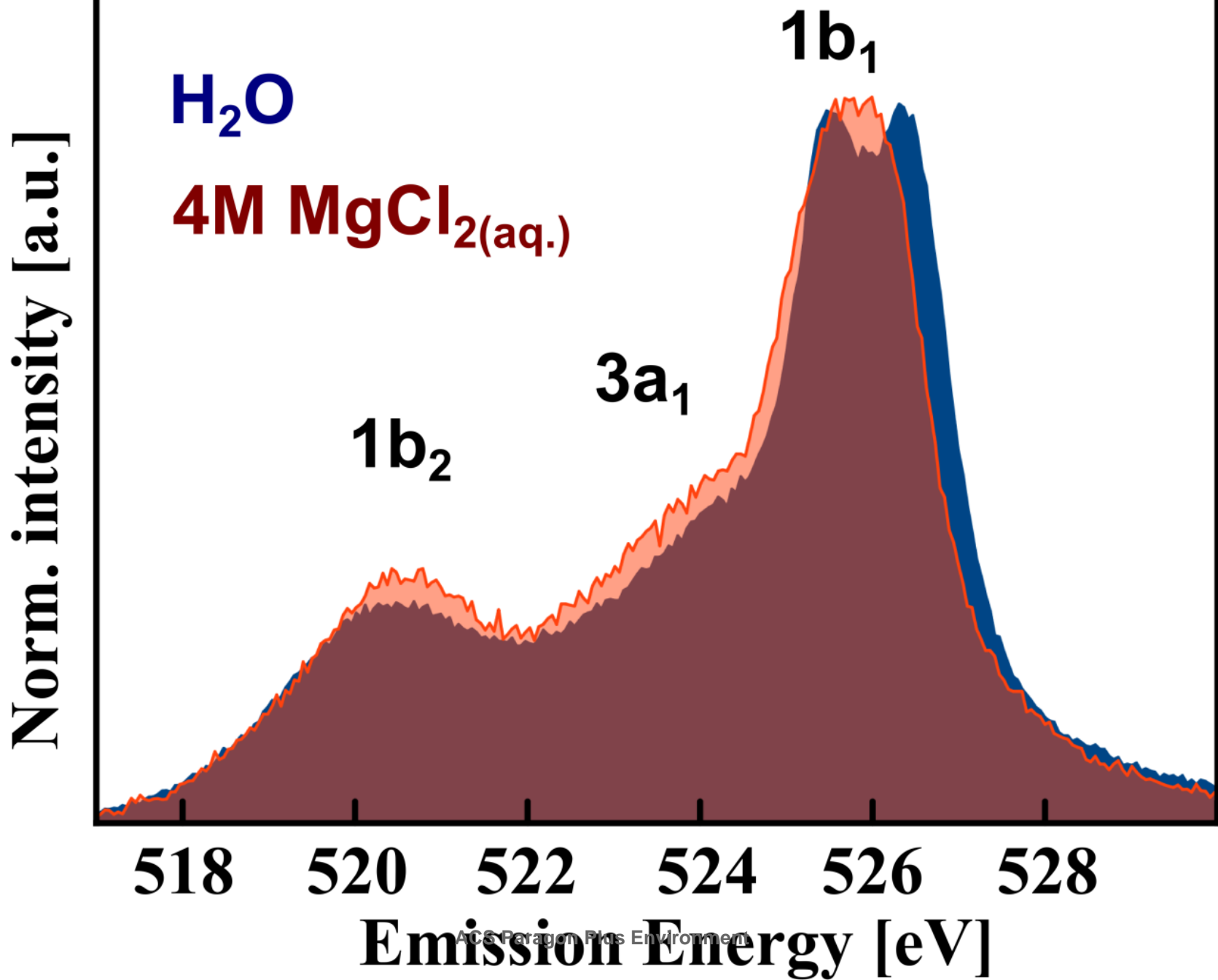
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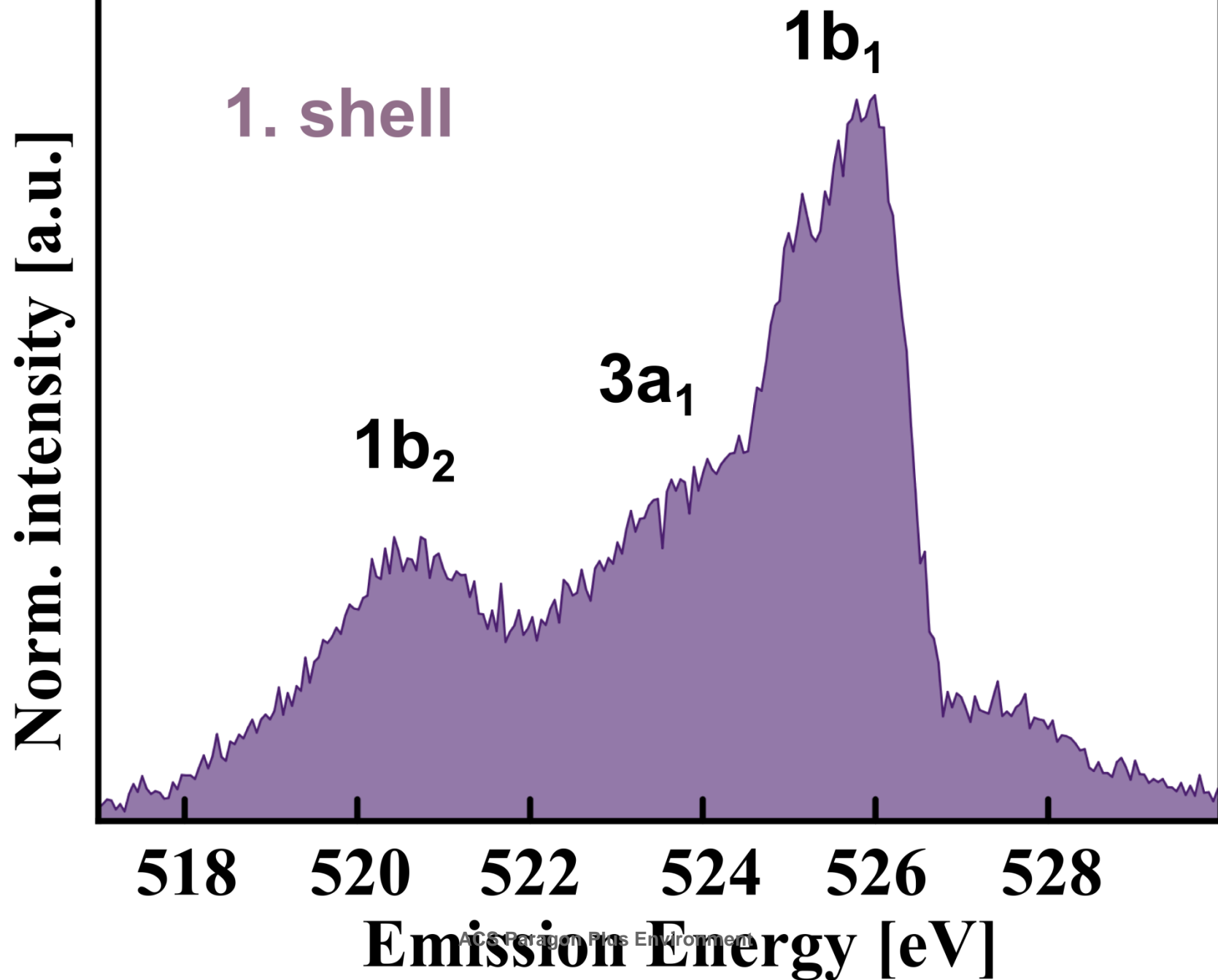
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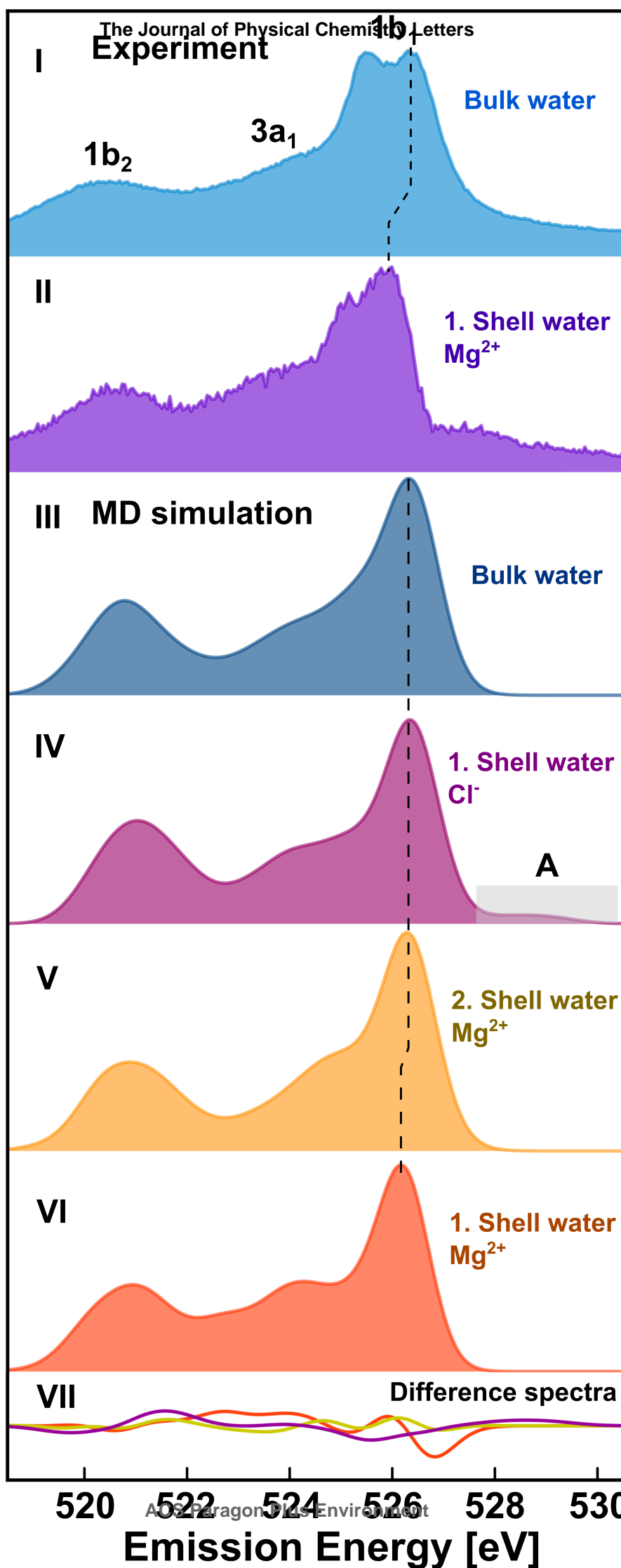
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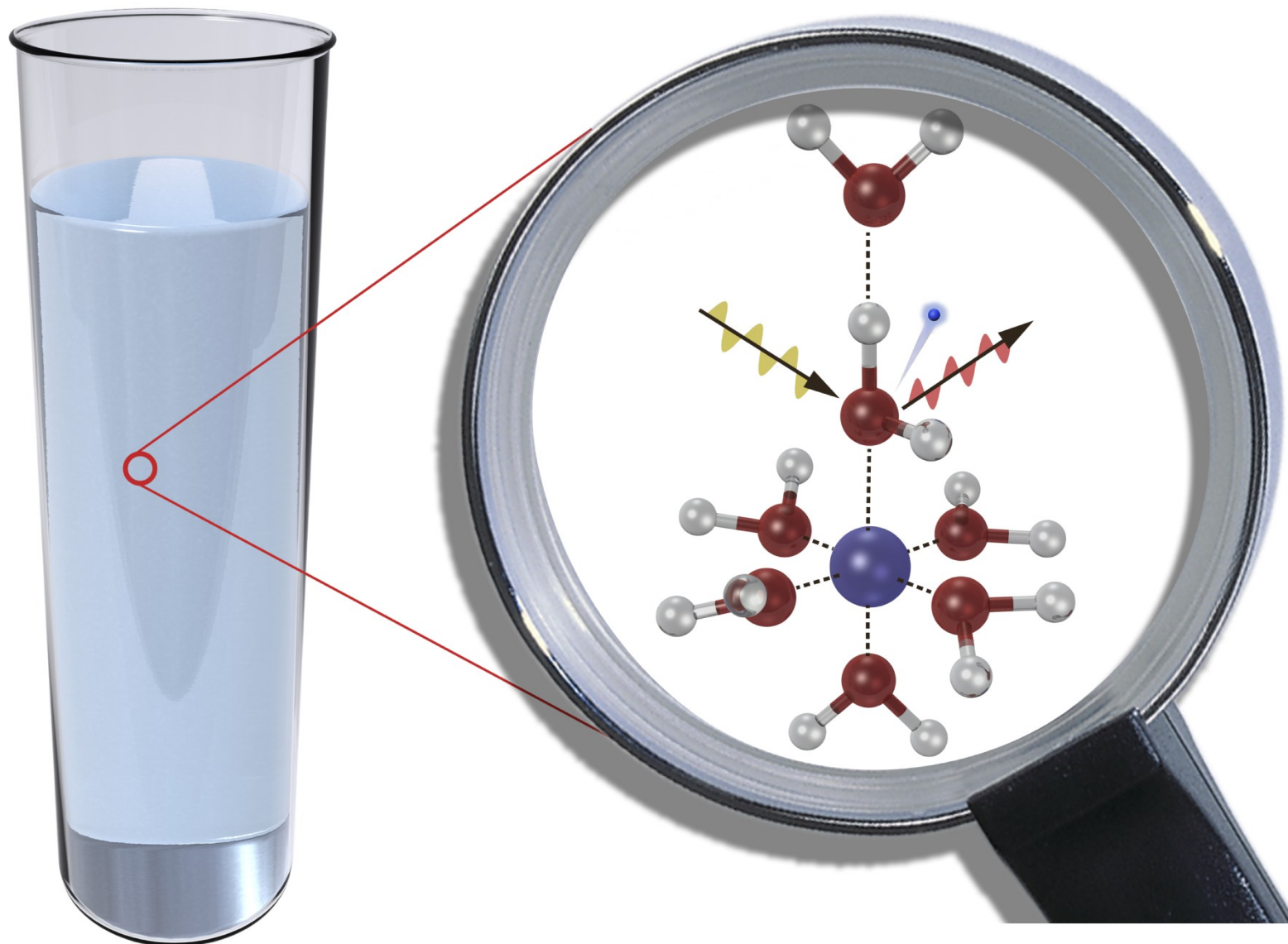


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