Probing the Hofmeister Effect with Ultrafast Core–Hole Spectroscopy

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ABSTRACT: In the current work, X-ray emission spectra of aqueous solutions of different inorganic salts within the Hofmeister series are presented. The results reflect the direct interaction of the ions with the water molecules and therefore, reveal general properties of the salt–water interactions. Within the experimental precision a significant effect of the ions on the water structure has been observed but no ordering according to the structure maker/structure breaker concept could be mirrored in the results indicating that the Hofmeister effect—if existent—may be caused by more complex interactions.
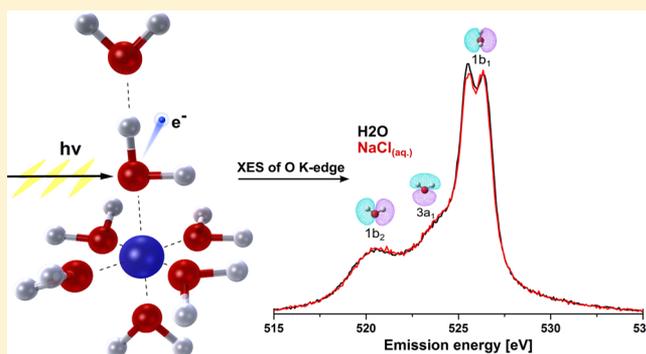
INTRODUCTION

At the end of the 19th century, Franz Hofmeister discovered that common anions and cations could be classified according to their ability to salt in/salt out proteins, in detail to enhance aggregation and precipitation of proteins dissolved in aqueous solution; see Scheme 1.[1]

Scheme 1. Partial List of Salts, Which Are Ordered According to Their Kosmotrop/Chaotropic Characteristics

$$\text{Cation: } NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$$

$$\text{Anion: } SO_4^{2-} < CH_3COO^- < Cl^- < NO_3^- < Br^- < I^-$$

By now, the so-called Hofmeister effect has been observed in a number of systems ranging from atmospheric aerosols up to whole biological entities such as cells, proteins, etc.[2,3] The salting in/out effect even plays an essential role in the metabolism of eukaryotic cells and in the case of mammalians it can lead to critical aggregation effects which were discussed as various prestages of diseases.[4,5] However, the question concerning the effect's origin remains unanswered. Two common models to explain it are (i) water interacting with the hydrated ions and causing precipitation or (ii) a consequence of the direct binding of the salt ions to the biomolecule by electrostatic interactions.[6]

The first model leads to the concept of structure makers/structure breakers (SMB), depending on the anions and cations used. According to this concept, cations and anions stabilize or destabilize the long-range water structure in aqueous solutions,[7] which is conventionally interpreted as strengthening and weakening of the hydrogen bond structure.[8] Theories based on molecular dynamic calculations have been introduced to explain the nature of the effect, some supporting the concept of structure breaking and making,[9–11] some contradicting.[12–15] However, there is a lack of understanding on the molecular level, since SMB is based on experimental observations of macroscopic properties.[16,17] Several experiments have been performed recently regarding the validation of SMB on the molecular level, which reveal objecting results.[8,18–30] Yet, the influence of salt ions on the electronic redistribution of water is unclear. In order to probe the electronic influence of salt ions on the water structure and therefore, if the SMB concept can be pictured on the molecular orbitals of the aqueous systems, core-hole X-ray emission spectroscopic (XES) measurements have been performed on the oxygen K-edge of pure water and aqueous salt solutions.

In XES, a core electron is excited with a monochromatic X-ray source to an unoccupied molecular orbital or above the ionization threshold to create a vacancy. The excited system relaxes via valence electrons filling the core-hole under emission of a photon containing information about the electronic structure of the molecules under investigation. XES is further divided into resonant XES (RIXS) and nonresonant XES. In RIXS, the core electron excitation to an unoccupied state and the following fluorescence are coupled events.[31,32] The nonresonant XES is a two-step process, where the absorption and the emission are decoupled processes.[31,32] An illustration of the molecular orbital and the difference between resonant and nonresonant XES are shown in Figure 1.
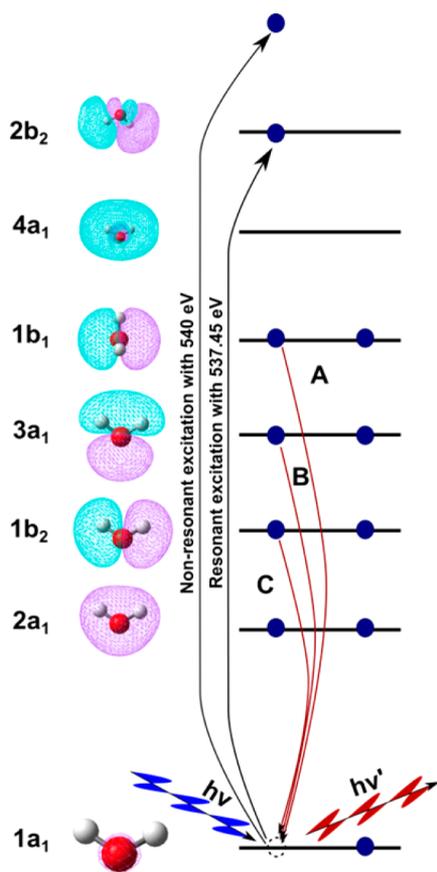
Figure 1. Schematic description of RIXS and nonresonant XES. The molecular orbitals were calculated using the RHF/6-31G** basis set from Gaussian. The transition from $2a_1$ to the core level is unlikely due to selection rules.

XES is sensitive to the element and the chemical environment.[32–41] Moreover, photons offer bulk information as the penetration length is much larger compared to electrons. The aim of the current study is to further elucidate if and how the presence of salt ions can influence the water clusters and the origin of the Hofmeister effect.

The experiments presented here are the first XES measurements on aqueous salt solutions from the Hofmeister series using the liquid jet technique.[42,43]

■ EXPERIMENTAL SECTION

The experiments were performed at the beamline U49/2-PGM 1 of BESSY II synchrotron at the Helmholtz Zentrum Berlin

using the FlexRIXS endstation. For excitation, a monochromatic X-ray beam with $\sim 10^{12}$ photons per second on the sample has been utilized. A detailed description of the liquid jet system and the FlexRIXS endstation can be found elsewhere.[42,44] For sample supply a 20 μm diameter liquid jet has been used. The jet system consists of a mixer, a degasser and an HPLC pump (JASCO). The implementation of the liquid jet provides continuously fresh samples and avoids radiation damage during the experiment. In contrast to a liquid flow cell,[45] the liquid jet also prevents interaction of X-ray and samples with the cell membrane and also prevents further loss of photon flux.

The 2 M NaCl and 1 M $MgCl_2$ concentrated aqueous salt solutions were prepared from commercially available salts of highest purity from Sigma - Aldrich at least 12 h prior to the experiment, since Na^+ is single and Mg^{2+} double charged. The resonant and nonresonant excitation energies have been selected from the X-ray absorption spectra (XAS) of water and aqueous solutions recorded in the total fluorescence yield mode. XAS and XES spectra of pure water were recorded periodically to confirm the stability of the setup. The monochromator slit was set to 150 μm corresponding to an energy bandwidth of approximately 0.4 eV. The resolution of the grating spectrometer was 0.4 at 530 eV (oxygen K-edge). The elastic peaks were used for energy calibration and the absolute energy scale in this experiment has been adjusted to Tokushima et al.[38]

■ RESULTS AND DISCUSSION

Figure 2 shows the X-ray emission spectra for nonresonant as well as resonant excitation at the oxygen K-edge for pure liquid water and aqueous NaCl solution with 2 M concentration.

Resonant excitation at 537.45 eV (Figure 2a) corresponds to a promotion of a core electron into the second LUMO (lowest unoccupied molecular orbital) of oxygen in water, the $2b_2$ orbital. Nonresonant excitation at 540 eV (Figure 2b) leads to the ionization of the water molecule; see Figure 1. The emission spectra have been area-normalized to provide an accurate comparison of relative intensities. All emission spectra show a multipeak structure. Peak A can be correlated to the lone pair electron $1b_1$, peak B and C to the covalent bonding electron pairs in the $3a_1$ and $1b_2$ orbitals, respectively (see Figure 1). For both excitation energies the intensities in peak A′ of the 2 M salt solution are equal to water but a significant drop in intensities is observed at peak A″ compared to pure water.

With a 2 M salt concentration and a maximum water concentration of 55.5 M, every salt molecule is surrounded by 27–28 water molecules. As X-ray diffraction experiments have shown, Na^+ and Cl^- are coordinated by six water molecules each.[18] This means that 12 out of 28 water molecules are in the first solvation shell and in direct interaction with either the cation or the anion. The 16 water molecules left are in the second solvation shell of either the cation or anion, where they are potentially able to attract up to 12 water molecules each.

In the case of 1 M $MgCl_2$ solution, there are 55–56 water molecules for one salt moiety. Considering the coordination number for Mg^{2+},[18] 18 water molecules are in the first solvation shell of the ions, resulting in 37–38 water molecules forming the second solvation shell.

The anions are bonded to water molecules via the hydrogen; hence the oxygen lone pair electrons of water are not directly interacting with the anions. The positively charged cations however, are attracting the negative polar charged oxygen in
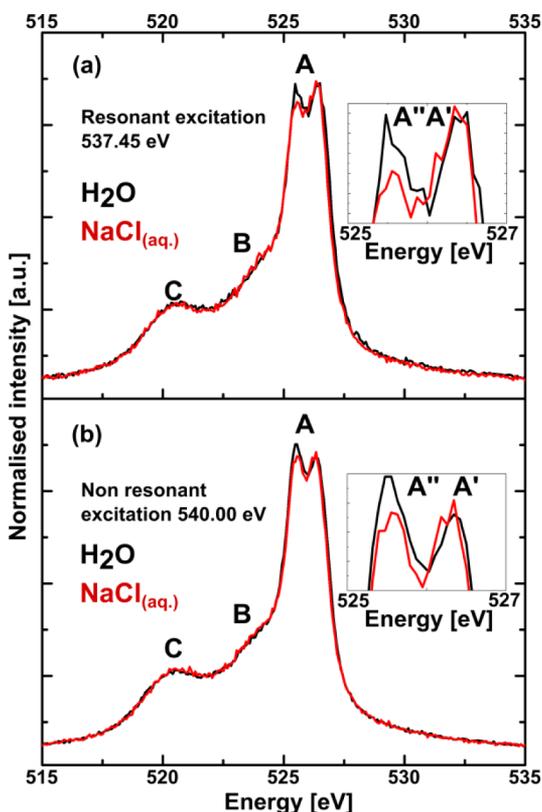
Figure 2. X-ray emission spectra of pure water and 2 M NaCl(aq). (a) Spectra for resonant excitation energy. (b) Spectra for nonresonant excitation energy.

water.[46] Thus, the oxygen lone pair electrons are responsible for the water coordination around the cations and changes in the oxygen emission spectra of the aqueous salt solutions, especially in the lone pair region are anticipated. The presence of 2 M NaCl and 1 M MgCl$_2$ seem not to affect the covalent bonding electrons (peak B and C), as can be seen in Figure 2 and 3.

Measurements of NaCl(aq) and MgCl$_2$(aq) at lower concentrations of 500 mM showed no effect in the spectra,
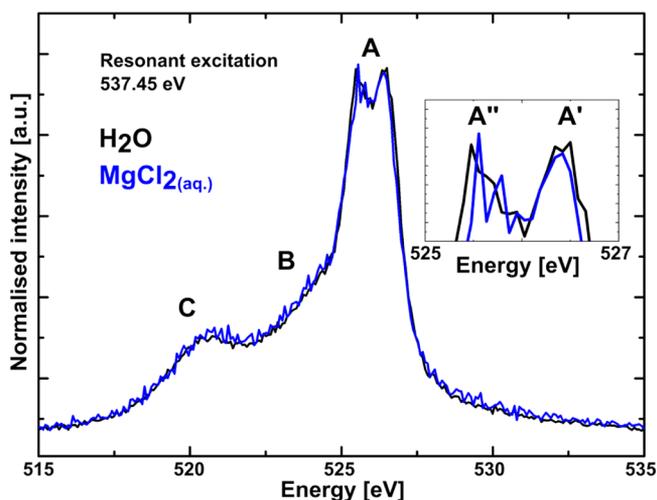
Figure 3. Resonantly excited emission spectrum of pure water compared to 1 M MgCl$_2$ solution. Within the statistical uncertainty the peak position and intensity remain constant.
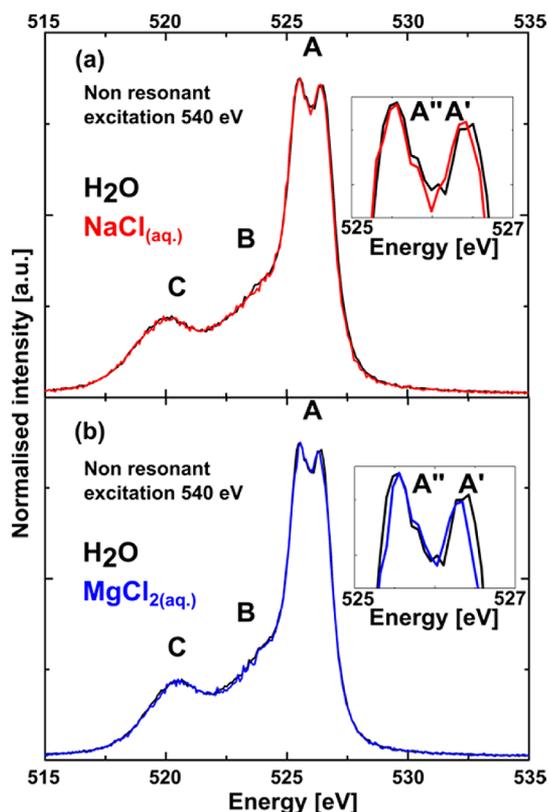
Figure 4. Nonresonant X-ray emission spectra on the oxygen K-edge of pure water compared to (a) 500 mM NaCl and (b) 500 mM MgCl$_2$ solution. No significant changes are observed, therefore a negligible cooperative effect on the electronic structure is deduced.

see Figure 4. For 500 mM NaCl and MgCl$_2$ solutions there are around 110 water molecules for one salt moiety. Since only 12 H$_2$O are in the first solvation shell for NaCl(aq) and 18 for MgCl$_2$(aq), around 100 or 90 water molecules, respectively, are left to form higher solvation shells and separate the ions from each other. Therefore, we assume changes on the electronic structure caused by cooperativity to be negligible in the case of NaCl and MgCl$_2$ solutions.

An interesting feature is the pronounced splitting of the lone pair 1b$_1$ line, both for pure water and aqueous solutions. According to Guo et al.,[35] the splitting of the oxygen lone pair orbitals was reported previously for NaCl(aq) and AlCl$_3$(aq), but not for pure water. Consequently, it has been concluded that the origin of this effect is caused by the presence of salt ions. However, in contrast to Guo et al.[35] later XES experiments showed a clear double peak even for pure water[36−40] so this cannot be an effect caused by the salt. The exact nature of the splitting is still an ongoing debate.

The fine structure is either ascribed to a dissociation into OH$^-$, which is a dynamical effect during the core-hole lifetime of around 4 fs[37,47−49] or to two different structural motifs with thetrahedral and distorted configuration.[38,40,50]

Furthermore, molecular dynamic (MD) calculations can qualitatively reproduce the fine structure without including a two component model of liquid water, rather based on ultrafast dynamics during the core-hole lifetime.[48,49]

Conclusively, this would predict that the splitting in A is due to different molecular orbitals. Forsberg et al.[39] reported an angular dependence of A′ and A″ which supports the theoretical concept described by Odelius,[48,49] whereas Tokush-

ima et al.[40] reported the negligible effect of different polarization in the XES spectra. Regardless of the double peak structure's origin, the presented data of aqueous salt solutions are interpreted within both frameworks. Within our experimental resolution, significant changes in relative intensities of the double peak features have been observed.

If the splitting is rooted in the dynamical process during the core-hole lifetime, where A′ is from intact water molecules and A″ from dissociated OH^-, we would expect that Na^+ reduces the acceptor characteristic of the water molecules due to the steric hindrance and thus, lead to less dissociations, which would be mirrored in less intensity of A″. The anion Cl^- is connected to the hydrogen site of water. Therefore, the water molecules around the anion still can act as donor and acceptor. The spectra in Figure 2 show a drop of peak A″ of the salt solution compared to pure water, which would indicate a reduced rate of dissociations of H_2O. In the concept of structure maker and structure breaker, Cl^- is a structure breaker, Na^+ is a borderline, but also conventionally referred as a breaker[6] and Mg^{2+} is a known structure maker ion.[51] According to the Hofmeister categorization, Cl^- and Na^+ break the water structure and thus, decrease the number of dissociations, which is in agreement with Figure 2. With a structure maker like Mg^{2+} an enhancement of hydrogen bonding and therefore an increasing rate of dissociations is expected. Figure 3 shows the O K-edge emission spectra of 1 M concentrated $MgCl_2(aq)$ solution in comparison to pure water. The splitting in A is clearly observable. The intensities of A′ and A″ are roughly the same in comparison to pure water, which contradicts the characteristics of $MgCl_2(aq)$ as a structure maker, where a significant change in the emission spectra of aqueous salt solution compared to pure water is anticipated. If the SMB concept is valid, the peak A″ would increase further, since a strengthening of hydrogen bonds would lead to a higher rate of dissociations. One reason for a lack of changes in the X-ray emission spectrum might be the lower concentration of $MgCl_2(aq)$. But this is also in contradiction to the SMB concept, since the latter is conventionally assumed to change the long-range structure of water.[7]

In case of the fine structure A′ and A″ being rooted in the two structural motifs, which explains the origin of peak A″ from tetrahedral coordinated water molecules and peak A′ from distorted order, the conclusion regarding the validation of SMB does not change. Within this framework, the lower intensities of A″ in NaCl(aq) can be understood by having less water molecules in tetrahedral formation due to the coordination of the salt, which is in agreement to Na^+ being a structure breaker. The presence of Mg^{2+} as a structure maker is supposed to increase intact hydrogen bonding and thus, reduce the number of distorted water molecules resulting in a significant lower intensity of A′ with respect to A″. But this is not reflected in the data, see Figure 3. Noticeably, no significant influence of the $MgCl_2$ is observable.

By choosing the same kind of anion Cl^-, the effect presented in Figure 2 can be fully deduced to the influence of changing the cationic species of Na^+ and Mg^{2+} in solution. Since the number of Cl^- is the same for $NaCl_{(aq.)}$ and $MgCl_2(aq)$, cooperative effects can be neglected. This conclusion is compliant to former experiments which report no significant effects of Cl^- on the hydrogen bond network.[25,52]

We also conclude that the Hofmeister series based on the structure maker and breaker concept is not mirrored in the electronic structure of the water molecules.

■ SUMMARY

We have presented the first X-ray emission spectroscopy data of two aqueous salt solutions from the Hofmeister series on the oxygen K-edge using the liquid jet method. The experimental results reflect the direct influence of salt ions on the water molecules. X-ray emission spectra of oxygen K-edge from pure water, 2 M NaCl, and 1 M $MgCl_2$ aqueous salt solutions show significant differences within the experimental conditions. We conclude that the presence of salt ions in aqueous solution do not cause the peak splitting at peak A and that NaCl(aq) (i) reduces dissociations in the water structure or (ii) cause less tetrahedral coordinated water molecules, which in both cases is an effect caused by Na^+ and not by Cl^-. Additionally, this indicates a breaking of hydrogen bonds in agreement to the conventional picture of Na^+ as a structure breaker. However, no significant changes are observed in the emission spectra of the 1 M $MgCl_2$ solution in disagreement with the characterization of $MgCl_2$ as a structure maker. The salting in/salting out of proteins in aqueous salt solutions seems not to originate in the structure maker and structure breaker concept. The microscopic understanding (the "local" view) of precipitation of macromolecules caused by salts needs further investigation.

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Z.Y. analyzed the data and prepared the manuscript. Z.Y., K.K., I.R., A.P., and W.Q. performed the experiment. P.W., A.F., and S.T. designed the FlexRIXS endstation. All authors discussed the results and commented on the manuscript.
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

XES, X-ray emission spectroscopy; SMB, structure makers/ structure breakers; XAS, X-ray absorption spectra; RIXS, resonant XES

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