

Effects of Cations on the Hydrogen Bond Network of Liquid Water: New Results from X-ray Absorption Spectroscopy of Liquid Microjets

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Oxygen K-edge X-ray absorption spectra (XAS) of aqueous chloride solutions have been measured for Li⁺, Na⁺, K⁺, NH₄⁺, C(NH₂)₃⁺, Mg²⁺, and Ca²⁺ at 2 and 4 M cation concentrations. Marked changes in the liquid water XAS are observed upon addition of the various monovalent cation chlorides that are nearly independent of the identity of the cation. This indicates that interactions with the dissolved monovalent cations do not significantly perturb the unoccupied molecular orbitals of water molecules in the vicinity of the cations and that water–chloride interactions are primarily responsible for the observed spectral changes. In contrast, the addition of the divalent cations engenders changes unique from the case of the monovalent cations, as well as from each other. Density functional theory calculations suggest that the ion-specific spectral variations arise primarily from direct electronic perturbation of the unoccupied orbitals due to the presence of the ions, probably as a result of differences in charge transfer from the water molecules onto the divalent cations.

Introduction

Obtaining a clear understanding of the molecular scale interactions between inorganic salts and water molecules that occur during ionic solvation is fundamental to understanding the role of ions in chemical and biological systems and processes. Both anion- and cation-specific effects are important in determining many physical phenomena associated with aqueous solutions. In 1888, Hofmeister arranged some common cations (and anions) according to their ability to precipitate, or salt-out, hen egg white proteins from solution and determined that^{1–3}



where Gdm⁺ indicates the guanidinium ion (C(NH₂)₃⁺). The Hofmeister series is generally thought to be related to the degree of hydration of the cations. In addition to the ability of cations to salt-out proteins, they are often also classified based on, e.g., their abilities to denature proteins,^{2,4–6} their varying entropies of solvation,⁷ or their effect on the viscosity⁸ and surface tension^{2,9} of water.

Although it is often stated that anion effects are more important than cation effects,² relatively large, systematic variations that depend on the cation identity are also observed, especially in going from the monovalent to the divalent cations. The first ions (e.g., Ca²⁺) in the above Hofmeister series are often considered “structure-makers”, and those at the end (e.g., Gdm⁺), “structure-breakers”,^{2,7} a classification that is primarily based on their relative entropies of solvation. The differences between the ion behaviors in solution are generally understood as resulting from variations in the microscopic interactions

between the ions and the water molecules in the first solvation shell of the ion and from the interactions between these first shell water molecules and the bulk liquid. However, despite intensive study over the last century, the ion specificity inherent in the Hofmeister series still “remain[s] unexplained by present theories of physical chemistry”.¹⁰

Core level X-ray absorption spectroscopy (XAS) is a powerful tool for understanding details of the microscopic interactions between water molecules and dissolved solutes because XAS is an element-specific probe of the local electronic environment experienced by molecules.¹¹ For example, we have demonstrated that clear differences in the oxygen K-edge XA spectrum of aqueous sodium halide solutions exist that depend explicitly upon the identity of the halide anion and that these spectral variations arise largely as a result of differing direct electronic interactions between the anions and the unoccupied molecular orbitals of water molecules in the vicinity of the anion.¹² Also, spectral features in the XA spectrum of aqueous transition metal solutions (Fe³⁺ and Cr³⁺) have been interpreted as indicating that interactions between these cations and water molecules in the first solvation shell depend on mixing between the molecular orbitals of water and the open d shell of the transition-metal ion.¹³

Given the dependence of so many physical properties of aqueous solutions on the identity of the cation,² we might similarly expect to see obvious variations in the XA spectra of different cation chloride solutions due either to direct electronic perturbation of the unoccupied molecular orbitals of solvation shell water molecules or to geometric distortion (i.e., structure making or structure breaking) of the hydrogen bond network. However, as will be demonstrated below, the effect of *monovalent* cations (Li⁺, Na⁺, K⁺, NH₄⁺, and Gdm⁺) on the XA spectrum of liquid water is essentially independent of the cation identity, indicating the negligible overall influence of monovalent cations on the liquid water XA spectrum. In striking contrast, for *divalent* cations (Mg²⁺ and Ca²⁺) distinct cation

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dependent differences are observed in the XA spectrum. Charge transfer from the solvating water molecules to the cation is identified as an important factor in determining the observed spectral variations. These experiments therefore provide an important contribution toward unraveling the microscopic interactions that engender the Hofmeister effects.

Methods

Experimental. Our liquid microjet X-ray experiment has been described in detail in previous manuscripts.^{12,14,15} Briefly, the total electron yield (TEY) soft XA spectra from pure water and aqueous LiCl, NaCl, KCl, NH₄Cl, CN₃H₅·HCl (gaumidium chloride), MgCl₂, and CaCl₂ solutions at 2 and 4 M concentrations were measured on Beamline 8.0.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The TEY was measured by collecting the electrons produced from interaction of the X-rays with the liquid sample on a copper electrode biased at +90 V. XA spectra of liquid water and aqueous solutions measured via TEY provide a probe of the bulk electronic structure.¹⁶ Liquid microjets were used to introduce the liquid sample ($T \sim 285$ K) into the high vacuum environment, thereby allowing for detection of the electrons and for rapid renewal of the liquid sample on a millisecond time scale. XA spectra were collected from 531–560 eV at a step size of 0.1 eV, with a resolution of $E/\Delta E \sim 4000$. All measured spectra were normalized to the incident X-ray flux, as measured on a gold mesh located ~ 3 m from the interaction region. A small ($\sim 3\%$) subtraction of the residual vapor phase contribution to the liquid TEY-XA spectrum was performed to allow for accurate comparison between different liquid spectra. All comparisons between experimental spectra were made using spectra obtained under constant experimental conditions. Under these conditions, the experimental spectra are highly reproducible. To facilitate comparison between the different spectra, all spectra were additionally area normalized over the energy range 529–549 eV, according to the Thomas–Reiche–Kuhn sum rule.¹¹

Computational. The calculated XA spectra were generated using the StoBe-DeMon 2.0 program to calculate oscillator strengths of specific oxygen K-edge transitions.¹⁷ The oscillator strengths and transition energies were calculated from density functional theory (DFT) using a linear combination of Gaussian type orbitals (LCAO) approach. The RPBE gradient-corrected exchange functional and the PBE correlation functional were used as provided. All calculations were performed using the transition potential method¹⁸ under the half core hole approximation.¹¹ For all oxygen atoms, besides the water molecule of interest, an effective core potential (ECP) was used to simplify the definition of the core hole and allow for determination of the XA spectrum of the central molecule.¹⁹ For the cations, no ECPs were used because none were available for lithium, magnesium, or calcium. Therefore, for all calculations involving a Na, K, Mg, or Ca cation, the half core hole was placed on the second lowest energy orbital, which corresponded to the oxygen atom of interest. For calculations with Li, the half core hole was placed on the lowest energy orbital. All calculated energies were shifted to lower energy by 1.7 eV for comparison with experimental values. This value was chosen to align the first calculated transition for the H₂O molecule with the first experimental gas-phase feature (534.1 eV). It is not possible to calculate transition widths a priori, and therefore, a broadening scheme, based on previous experience,¹² was chosen for presentation of the spectra and for comparison with experiments. For the molecular clusters (≥ 23 molecules), a full width at half-maximum (fwhm) value of 0.6 eV is used below 538 eV

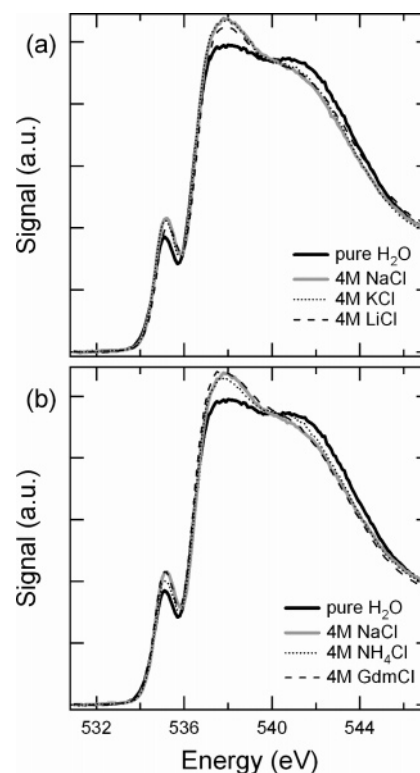


Figure 1. (a) Experimental TEY-XA spectra of aqueous 4 M LiCl, NaCl, and KCl solutions compared to pure water. (b) Experimental TEY-XA spectra of aqueous 4 M NH₄Cl and GdmCl solutions compared to pure water and 4 M NaCl.

(unshifted energy) and a fwhm of 3 eV is used above 540 eV (unshifted). The fwhm is linearly varied from 0.6 to 3 eV from 538 to 540 eV. For the cation–water dimer calculations, a constant fwhm of 1 eV was used.

XA spectra were calculated for 23 water molecule/1 cation clusters obtained from snapshots from an MD simulation of 1.2 M NaCl in liquid water, provided by Doug Tobias (UC Irvine). These clusters were selected based on a criterion wherein the six Na⁺ near-neighbor water molecules were identified. For each of these cation near-neighbor water molecules, the 22 nearest water molecules, as determined from the oxygen–oxygen distance (R_{OO}), were selected, along with any Na⁺ or Cl[−] ions within the sphere defined by the maximum R_{OO} . Only those clusters containing one Na⁺ ion were selected for the XA calculations. For the other (spherical) cations, the Na⁺ ion in the Na⁺/water clusters was replaced by a K⁺, Li⁺, Ca²⁺, or Mg²⁺ ion at the same ion position rather than using configurations specific to the different cations obtained. Although this simplification undoubtedly introduces some limitations into the analysis, this has the benefit of focusing attention specifically on the differences in the nature of the direct electronic interactions between the different cations and the near-neighbor water molecules by separating out potentially important differences in the hydrogen bond network restructuring effects of the cations. Additional calculations were performed using cation–water molecule dimers, as will be discussed further below.

Experimental Results

The oxygen K-edge TEY-XA spectra for 4 M aqueous solutions of monovalent cations are shown in Figure 1. Clear changes in the pure liquid water XA spectrum associated with the addition of monovalent cation chloride salts at 4 M concentrations are evident. The addition of monovalent cation

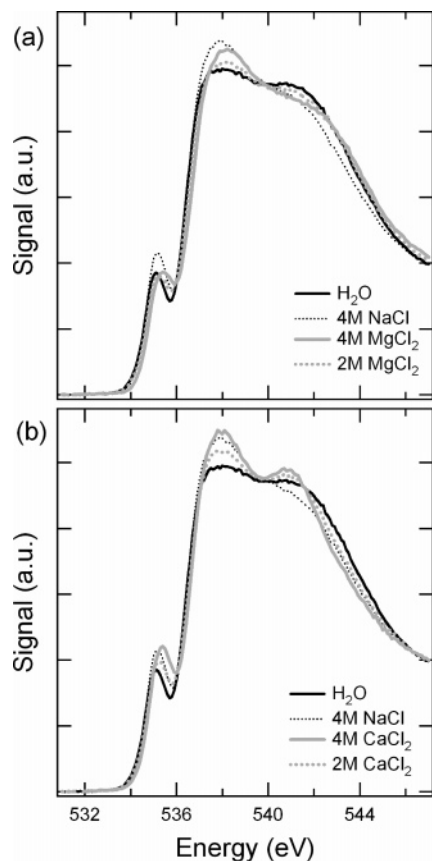


Figure 2. (a) Experimental TEY-XA spectra of aqueous 2 and 4 M MgCl_2 solutions compared to pure water and 4 M NaCl. (b) Same as part a, but for CaCl_2 .

chlorides engenders an increase in the pre-edge (~ 535 eV) and main-edge (~ 537 eV) features and a decrease in the post-edge (~ 541 eV) feature, as previously observed for aqueous NaCl ^{12,20,21} and KCl ²¹ solutions. It is of particular interest that the changes in the XA spectra induced by the various monovalent cation species are nearly identical. Specifically, this experimental result indicates that *the perturbation of the overall liquid water electronic structure by the addition of monovalent cations is essentially independent of the identity of the cation*. This is true both within the alkali metal series (Li^+ , Na^+ , and K^+) and for the NH_4^+ and Gdm^+ ions. Minor differences between some of the cation spectra are observed; however, no systematic trends can be identified. This suggests that either (i) both the direct electronic perturbation of the unoccupied molecular orbitals of the cation near-neighbor water molecules and the geometric distortion of the hydrogen bond network induced by the presence of the cation are the same for all monovalent cations, (ii) these two perturbations to the overall electronic structure of water cancel identically for these monovalent cations, or (iii) the overall influence of monovalent cations on the unoccupied orbitals of water molecules is negligible. These second two possibilities would indicate that the major observed spectral changes arise predominately from perturbation of water molecules by the Cl^- anion.

The TEY-XA spectra for 2 and 4 M MgCl_2 and CaCl_2 are shown in Figure 2. In striking contrast to the monovalent cations, the addition of the divalent Mg^{2+} or Ca^{2+} cations engenders unique spectral changes in the XA spectrum that depend explicitly upon the cation identity. The divalent cation XA spectra are also different than the monovalent XA spectra at both 2 M salt concentrations (where the chloride ion concentration is 4 M) and 4 M salt concentrations (where the cation

concentration is 4 M). Additionally, the changes effected due to both Mg^{2+} and Ca^{2+} addition are distinct from those caused by changing the temperature of liquid water.^{22,23}

The addition of MgCl_2 has a minor effect on the pre-edge intensity of liquid water, although the pre-edge feature is broadened and becomes less well resolved from the main edge. The main-edge intensity increases, the post-edge intensity decreases, and both features exhibit a slight blue-shift.

The addition of CaCl_2 leads to an increase in both the pre-edge and main-edge features, similar in nature to the effects of monovalent cations. However, at the post-edge, there is a unique increase in intensity at lower energies (~ 541 eV) but a decrease in intensity at higher energies (~ 543 eV), compared to pure water. For both Mg^{2+} and Ca^{2+} , a 0.3 eV blue-shift of the pre-edge feature, compared to pure water, was observed. The strong spectral differences at 4 M salt concentrations are already apparent at 2 M concentrations, indicating that the difference between the divalent and the monovalent cations is not simply a function of the larger Cl^- concentration at 4 M salt.

Discussion

Monovalent cations. It is interesting that the addition of any of the monovalent cation chlorides has generally the same perturbative effect on the oxygen K-edge spectrum of water. This is in stark contrast to the differing effects of both divalent cations and monovalent halide anions (e.g., Cl^- , Br^- , and I^-),¹² each of which has a unique effect on the XA spectrum of liquid water. For the anions, it was determined that the differences between the anion species results primarily from variations in the direct electronic perturbation of the unoccupied orbitals of the surrounding water molecules. Likely, the unoccupied molecular orbitals of the solvating water molecules are distorted from those of the pure liquid as a result of the change in the local electric field due to the presence of the ions, thereby engendering noticeable spectral changes in the case of the halide anions. Differences in how the halide anions affect the hydrogen bonding interactions among water molecules were determined to be of secondary importance. This is consistent with recent findings from classical molecular dynamics (MD) simulations, where it was concluded that the presence of a halide anion has only a minor effect on how water molecules in the first solvation shell interact with bulk water molecules,²⁴ and with ultrafast pump-probe vibrational spectroscopy of aqueous inorganic salt solutions ($\text{Mg}(\text{ClO}_4)_2$, NaClO_4 , and Na_2SO_4), wherein wavelength dependent differences of the rotational dynamics were interpreted as indicating that ions have no effect on the hydrogen bond network outside of the first hydration shell.²⁵

In previous work, we demonstrated that the direct electronic perturbation of the unoccupied water orbitals by Na^+ is small by comparison of calculated XA spectra of water molecules around a Na^+ ion making two donor hydrogen bonds to similar water molecules in pure water.²⁰ The calculated average spectra of these “double donor” molecules in both the Na^+ and pure water environments were very similar, indicating the negligible direct perturbation of the Na^+ ion. Here, we have also calculated average XA spectra of water molecules in the first solvation shell of Li^+ and K^+ ions for comparison to Na^+ , as shown in Figure 3a. A total of 10 spectra were averaged for each cation considered. Given the limited number of total configurations used in determining the average spectrum and that the molecular configurations used are independent of the cation identity, no attempt has been made to either quantitatively or qualitatively reproduce the observed aqueous solution XA spectra. However, qualitative comparisons can nonetheless be made between the

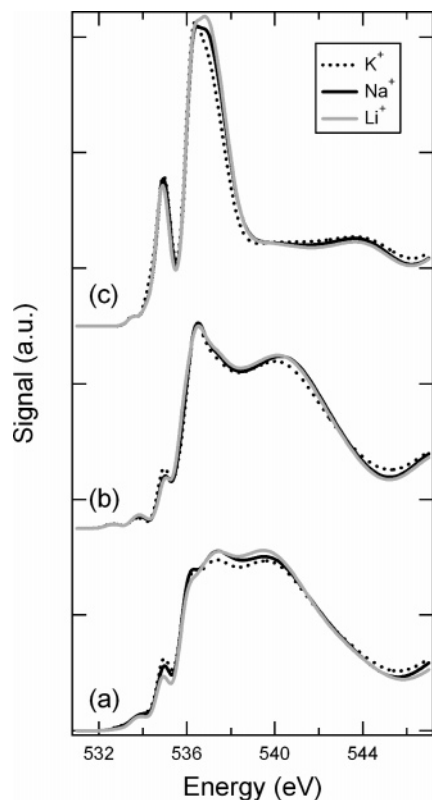


Figure 3. (a) Calculated average XA spectrum for water molecules in the first solvation shell of Li^+ , Na^+ , and K^+ , from 10 individual configurations. All cluster configurations were obtained from a snapshot from a classical MD simulation of $\text{NaCl}_{(\text{aq})}$, and the cation identity was changed to Li^+ or K^+ . (b) Calculated XA spectrum for a specific “double donor” configuration and (c) for a “no donor” configuration.

various calculated spectra to assess the influence of the cation identity on the direct electronic perturbation of solvation shell water molecules. In general, for the monovalent cations considered in the calculations (Li^+ , Na^+ , and K^+), the perturbation of the unoccupied orbitals of the near-neighbor water molecules by the cation, as reflected in the calculated XA spectra, is similar for each of the ions. Minor differences in intensity in some spectral regions are found; however, the overall spectral shape is independent of the alkali metal cation identity. This same conclusion is reached if the individual, rather than the average calculated, XA spectra are considered. This is shown for a double donor (Figure 3b) and a “no donor” (Figure 3c) solvation shell water molecule. The (small) direct electronic perturbation of the unoccupied orbitals of the solvating water molecules by monovalent alkali metal cations is independent of the cation identity. Although we have not carried out explicit calculations for NH_4^+ or Gdm^+ ions, the strong similarity of all of the measured monovalent cation chloride aqueous solution XA spectra suggests that this is a general property of all simple monovalent cations.

Despite the small direct electronic perturbation of solvation shell water molecules by monovalent cations,²⁰ the similarity of the respective XA spectra is quite surprising, given the importance of the monovalent cation identity in determining numerous properties within the Hofmeister series.² The most striking example is found when considering the similarity of the Gdm^+ XA spectrum to the other monovalent cation spectra, particularly Li^+ . Gdm^+ is one of nature’s strongest denaturing cations and is a “salting-in” agent²⁶ (e.g., it increases the solubility of benzene in water), whereas Li^+ has a strong “salting-out” effect.²⁷ Also, recent neutron diffraction measure-

ments revealed that Gdm^+ has no recognizable hydration shell because of the low charge density of the ion and its planar structure in solution.²⁸ Simulations based on these results suggest that water molecules do accept hydrogen bonds to some extent from the hydrogen atoms of Gdm^+ ions that are in the molecular plane of the ion, but these are not bound strongly enough to constitute a true solvation shell.^{28,29} Water molecules are effectively excluded from the “hydrophobic” ion face around the carbon atom and, in relatively concentrated Gdm^+ solutions (3 M), the Gdm^+ ions efficiently stack parallel to the water-deficient ion faces to form contact ion pairs.²⁹ This is markedly different than solvation of, e.g., the Li^+ ion, for which the charge density is high and a well-defined, relatively symmetric hydration shell exists around the ion with water molecules in a tetrahedral arrangement, as indicated from neutron diffraction measurements³⁰ and MD simulations.³¹

Given the high sensitivity of the liquid water XA spectrum to relatively small changes in the local electronic environment (e.g., temperature dependent geometric distortions of the hydrogen bond network),²² one might expect that the differences in the hydration environment of these cations that are thought to be responsible for the ion-specific Hofmeister effects should induce noticeable differences in the XA spectrum of liquid water. However, the experimental XA spectra of, e.g., 4 M LiCl and GdmCl aqueous solutions are nearly identical, indicating that water molecules around these different cations actually exist in very similar hydrogen bonding environments, particularly with respect to the formation of donor hydrogen bonds (the XA spectrum of water has been shown to be most sensitive to the geometric distortion of donor, rather than acceptor hydrogen bonds³²). If this were not the case, distinct and systematic spectral differences would be observed between the different monovalent cations. *There is therefore no long-range effect on the hydrogen bond network of water due to the presence of monovalent cations*, consistent with the interpretation of the IR pump–probe measurements of Omta et al.²⁵ These results indicate that the observed XA spectral changes that occur upon addition of monovalent cation halide salts are instead driven by interactions of water molecules with the halide anions. We further propose that it is unlikely that each of the different monovalent cations would engender an identical distortion of the donor hydrogen bonds formed by water molecules in the first solvation shell of the cation; accordingly, we conclude that the nature of the donor hydrogen bonds formed by these solvation shell waters is not significantly different from those formed by bulk water molecules. This conclusion is consistent with the *ab initio* MD simulation of Na^+ in water by White et al.,³³ who find no significant change in the water–water hydrogen bonding interactions of solvation shell water molecules as compared to bulk water molecules. However, this conclusion does contrast the results from several classical MD simulations, which deduce that Na^+ has a clear effect on water structure. For example, Grossfield concludes, based on calculated oxygen–oxygen radial distribution functions of water molecules in the first solvation shell of ions compared to bulk water using a polarizable force field, that the presence of cations, but not anions, disrupts the water–water structure around the ions and that the extent of disruption is larger for Na^+ than for K^+ .²⁴ Obst and Bradaczek find a maximum in the number of acceptor hydrogen bonds formed by water molecules in the *second* solvation shell of Na^+ ,³⁴ and Tongraar et al. find, using mixed quantum mechanics/molecular mechanics methods, that Na^+ can orient water molecules beyond the first solvation shell whereas K^+ cannot.³⁵ Yet, as discussed above, the observed XA spectra

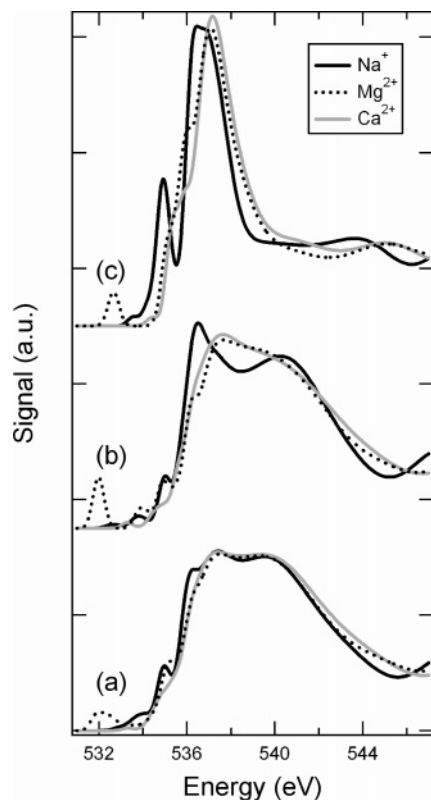


Figure 4. (a) Calculated average XA spectrum for water molecules in the first solvation shell of Mg^{2+} and Ca^{2+} compared to Na^+ , from 10 individual configurations. (b) Calculated XA spectrum for a specific “double donor” configuration and (c) for a “no donor” configuration.

of $\text{NaCl}_{(\text{aq})}$ and $\text{KCl}_{(\text{aq})}$ solutions exhibit negligible differences, which indicates that Na^+ and K^+ do not have very different effects on the nature of hydrogen bonds formed around these ions, which is inconsistent with many simulation results. This suggests that, for the monovalent cations (especially the alkali metal ions), some effect other than geometric distortion of the local hydrogen bond network leads to the observed Hofmeister ordering.

Divalent Cations. In contrast to the monovalent cations, the divalent cations Mg^{2+} and Ca^{2+} exhibit marked differences in their relative influence on the experimental XA spectrum of liquid water, both between each other and relative to the monovalent cations. The ways in which the Mg^{2+} and Ca^{2+} ions affect the liquid water XA spectrum are very different from those caused by simple geometric distortion of the hydrogen bond network effected by, e.g., increasing temperature.^{22,23} From this, we deduce that the major effects associated with Mg^{2+} and Ca^{2+} addition predominately arise from direct electronic interactions with the solvation shell water molecules, although the potential influence of geometric distortion should not be completely neglected. We explore the role of the direct electronic interactions further by calculating XA spectra of divalent cation/water clusters, again using the same (Na^+) cluster geometries as for the monovalent cations considered above. The average XA spectra calculated for the divalent cation near-neighbor water molecules are noticeably different from the monovalent spectra, especially in the pre-edge and far post-edge regions (Figure 4a). The differences are particularly evident when spectra for specific individual configurations are compared (e.g., a double donor configuration in Figure 4b and a no donor configuration in Figure 4c). This suggests that direct electronic distortion of the unoccupied orbitals of solvation shell water

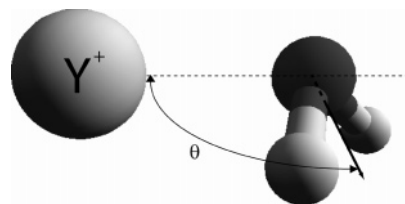


Figure 5. Tilt angle for water molecules in the first solvation shell of a cation.

molecules by the divalent cations is fundamentally different than that effected by monovalent cations.

We are unable at present to explain why, in the calculations for Mg^{2+} clusters, very low-energy features before the pre-edge are observed. Because no new low-energy features are actually observed in the experimental XA spectra of MgCl_2 solutions, we conclude that the very low calculated absolute energies of these orbitals are probably an artifact of the electronic structure calculations and, in part, lead to the difference between the calculated Mg^{2+} and Ca^{2+} spectra in the pre-edge region. Recall, however, that definite spectral differences in the pre-edge region are observed between Mg^{2+} and Ca^{2+} solutions. Calculations of XA spectra of different sized water/cation clusters (from 6 to 23 total water molecules, not shown) indicate that this anomalous feature is not a result of the finite size of the studied clusters. We note the general similarity of the main-edge and post-edge structures in the calculated average XA spectra for both Mg^{2+} and Ca^{2+} solvation shell water molecules, despite the presence of these low-energy features for Mg^{2+} . Additionally, the calculated core level ionization potentials for water molecules solvating either Mg^{2+} or Ca^{2+} differ by only ~ 0.15 eV, suggesting that the presence of the low-energy peak for Mg^{2+} does not have a dramatic affect on the overall electronic structure of the cluster. Thus, valid *qualitative* comparisons between the higher energy regions of the calculated XA spectra can still be made.

In contrast to the experimental observations, there is a general similarity between the calculated divalent cation spectra for the Mg^{2+} and Ca^{2+} clusters (not considering the differences in the calculated pre-edge feature). Although the calculated spectra are not meant to quantitatively reproduce the observed spectra, the differences between the calculated divalent and monovalent cation spectra nonetheless do not resemble the differences in the experimental spectra. One possible reason for this is that the relative orientations of the water molecules with respect to the cation have been constrained by using configurations taken from a classical MD simulation of the *sodium ion* in water. The particular orientation (with respect to both the cation and other water molecules) of water molecules within the first solvation shell may be important in determining the specific nature of the direct electronic distortions of the unoccupied water orbitals by the cations. Ab initio MD simulations indicate that water molecules in the first solvation shell of the magnesium ion in solution orient with one of the lone pairs pointed toward the cation.³⁶ (We note that the solvation environment around Ca^{2+} is less well-known, with different ab initio MD simulations yielding very different results in terms of the cation–oxygen $g(r)$ and coordination number.^{37,38}) In contrast, ab initio simulations of sodium ions in liquid water indicate that water molecules in the first solvation shell of sodium ions exhibit a broad distribution of tilt angles between the vector defined by the cation and the oxygen atom and the dipole moment of the water molecule, with approximately equal probability of finding the tilt angle between $120^\circ < \theta < 180^\circ$ and a slow decay to zero at 75° (see Figure 5 for a definition of the tilt angle).³³ However,

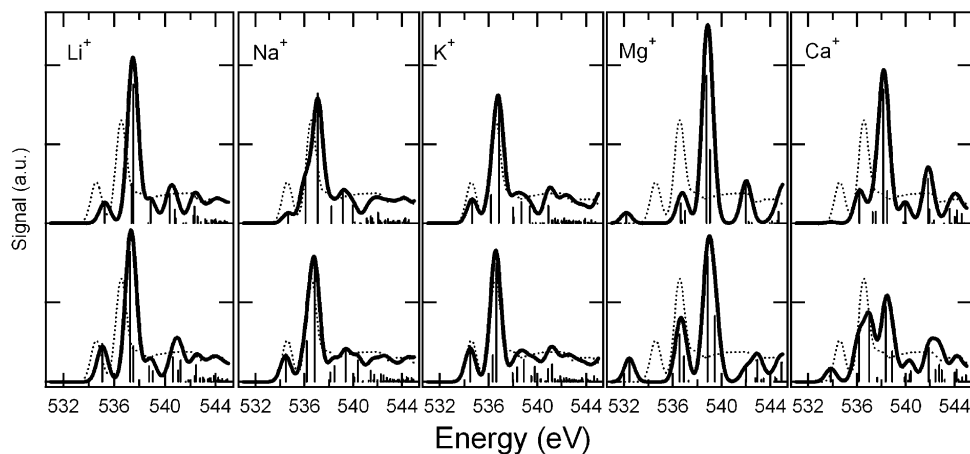


Figure 6. Calculated XA spectra for (from left to right) $\text{Li}^+-\text{H}_2\text{O}$, $\text{Na}^+-\text{H}_2\text{O}$, $\text{K}^+-\text{H}_2\text{O}$, $\text{Mg}^{2+}-\text{H}_2\text{O}$, and $\text{Ca}^{2+}-\text{H}_2\text{O}$ dimers and the associated stick spectra. The Y^+-O distance for the dimers was determined based on the maximum in the $g_{\text{YO}}(r)$ for each cation. The calculated spectrum for the hydrogen bond acceptor molecule in the water dimer is shown for comparison (dotted line). The spectra at the top of each panel were calculated with the cation–water tilt angle at 180° , and for the spectra at the bottom of each panel, the tilt angle was 109° . All spectra were shifted to lower energy by 1.7 eV and broadened with a constant Gaussian fwhm value of 1 eV.

TABLE 1: First Maximum in the $g_{\text{YO}}(r)$ (r_{max}) Obtained from ab Initio MD Simulations Used to Specify the Ion–Water Separation in the Cation–Water Dimer Calculations

	r_{max}	ref
Li^+	1.96	31
Na^+	2.49	33
K^+	2.88	49
NH_4^+	2.7	50
Mg^{2+}	2.13	36
Ca^{2+}	2.45	38

the distribution of angles from classical MD simulations (such as the one used here to obtain the cluster geometries) tends to be strongly peaked at 180° and decreases to near zero by 90° , although the details depend importantly on the particular simulation force field used.^{24,33,39,40} Thus, the orientation of water molecules with respect to the cation in the clusters used here (obtained from classical MD simulations) may not provide a completely accurate representation of the relative orientations between the *divalent* cations and the solvating water molecules. However, these calculations should provide a reasonable first approximation of the direct electronic perturbation by the divalent cations.

As a starting point for understanding the possible influence of the orientation of water molecules within the first solvation shell of cations on the XA spectra, we have calculated spectra for various cation–water dimers, where the tilt angle is specified at 180° (linear) and at 109° (bent) (Figure 6). All cation–oxygen distances were set at the value corresponding to the first maximum in the $g_{\text{YO}}(r)$ for the specific cation, as determined from ab initio MD simulations (Table 1). For each of the monovalent cations considered (Li^+ , Na^+ , and K^+), the dimer spectrum is nearly independent of the tilt angle and there is a strong similarity between the calculated spectra for the different monovalent cations (as found with the larger clusters). Also, the calculated water molecule XA spectra for the monovalent cation–water dimers exhibit only slight differences from the H-bond acceptor molecule water dimer XAS. This result again indicates that monovalent cations have a negligible direct influence on the unoccupied water orbitals. In contrast, some of the features in both the $\text{Mg}^{2+}-\text{H}_2\text{O}$ and $\text{Ca}^{2+}-\text{H}_2\text{O}$ spectra are very sensitive to the tilt angle, particularly so for Ca^{2+} , and large calculated spectral differences from those of the water dimer acceptor are observed. For Ca^{2+} , the calculated XA

spectrum for the linear dimer is similar to the monovalent cation dimer spectra; however, the bent $\text{Ca}^{2+}-\text{H}_2\text{O}$ dimer spectrum exhibits notable differences. This suggests that, in the above calculations using larger clusters, the geometries of which were obtained from a classical MD simulation of NaCl in water, the spectra associated with Mg^{2+} and Ca^{2+} only provide a first order estimate of the spectral perturbation associated with these ions. This is because, for the divalent cations, the direct electrostatic distortion of the unoccupied orbitals appears to be intimately linked to the orientation of water molecules within the first solvation shell. This may be a result of the larger charge density and stronger interaction of the divalent cations with the solvating water molecules. The nature of this orientational effect is difficult to quantitatively assess from these calculations. In particular, whether the observed spectral variations arise due to induced differences in the formation of donor hydrogen bonds by the first solvation shell waters (i.e., geometric distortion) or only from orientation-sensitive direct perturbation of the electronic structure by the divalent cation (as with the dimers). However, it does suggest that differences in the structure of the first solvation shell of Mg^{2+} and Ca^{2+} in solution exist which give rise, in part, to the experimentally observed spectral differences between these divalent cations. This is in accord with calculations of the successive cation–water binding energies in $\text{Mg}^{2+}(\text{H}_2\text{O})_m$ and $\text{Ca}^{2+}(\text{H}_2\text{O})_n$ clusters, where $m = 1-7$ and $n = 1-8$, which demonstrate that coordination of Mg^{2+} to more than six water molecules is highly unfavorable (in these clusters), whereas for Ca^{2+} such higher coordination is possible.⁴¹

Origin of the Differences between Monovalent and Divalent Cations. Any attempt to understand the nature of specific perturbations of cations on the XA spectrum of liquid water must account for the marked differences observed between spectra of the monovalent and divalent cations. Particularly, the observation that the distortion of the electronic structure by monovalent cations is independent of the cation identity must be reconciled with the observation that the divalent cations exhibit unique spectral effects with respect to each other, similar to the recently reported¹² effects of anions. Many properties associated with the dissolution of cations in aqueous solution, such as changes in the surface tension,⁴² molal fluidity elevations,⁸ and NMR relaxation times,⁴³ generally indicate that the effects of divalent cations are larger than those of monovalent cations; however, for these same properties, the magnitude of

TABLE 2: Charge-to- r_{ion} Ratio⁵¹ for the Alkali and Alkaline Earth Metal Cations and the Halide Anions^a

	excited state (half core hole)			ground state			
	Z/r_{ion} (1/Å)	q_{ion}	q_{oxygen}	q_{hydrogen}	q_{ion}	q_{oxygen}	q_{hydrogen}
Li ⁺	1.69	0.98	-0.35	0.43	0.95	-0.62	0.34
Na ⁺	1.01	0.98	-0.32	0.42	0.94	-0.58	0.32
K ⁺	0.73	0.99	-0.32	0.41	0.96	-0.58	0.31
Be ²⁺	12.50	1.72	-0.16	0.47	1.55	-0.33	0.39
Mg ²⁺	2.78	1.87	-0.29	0.46	1.74	-0.50	0.38
Ca ²⁺	2.00	1.95	-0.35	0.45	1.87	-0.60	0.36
Cl ⁻	-0.55	-0.75	-0.20	0.15/0.30	-0.86	-0.53	0.18/0.20
Br ⁻	-0.51	-0.75	-0.18	0.13/0.30	-0.87	-0.52	0.19/0.20
I ⁻	-0.45	-0.65	-0.17	0.05/0.27	-0.78	-0.52	0.12/0.19
H ₂ O (A)			-0.25	0.37		-0.53	0.27
H ₂ O (D)			-0.22	0.31/0.35		-0.53	0.27/0.24

^a Also shown are the Mulliken charge populations for the ion (q_{ion}), oxygen atom (q_{oxygen}), and hydrogen atoms (q_{hydrogen}) calculated for the ground and excited state ion–water dimers using the StoBe-deMon program.¹⁷ The ion–oxygen distance for each dimer was set to the maximum in the appropriate pair correlation function.⁴⁸ For the pure water dimers, (A) indicates the acceptor water molecule and (D), the donor molecule.

the variations between different divalent cations is typically not much larger than those found between the monovalent cations. As another example, the electronic polarizabilities of the monovalent and divalent cations vary over the same range of values, dependent primarily on the ion size, and are therefore not the basis for the observed differences in the XA spectra.⁴⁴ We must therefore look for properties of dissolved ions for which the monovalent cations exhibit only small differences while the divalent cations exhibit large variations between each other in order to explain the measured aqueous solution XAS.

One possible explanation for the observed differences is that, due to their small ionic radii and 2+ charge state, the Mg²⁺ and Ca²⁺ cations have large charge-to- r_{ion} ratios, while the charge-to- r_{ion} ratios for the monovalent cations are all smaller (Table 2). In turn, these differing charge-to- r_{ion} ratios engender differing magnitudes of charge transfer (CT) from the solvating water molecules to the cation.^{41,45} Mulliken population analyses, performed using the StoBe program,¹⁷ of the metal atom charges (q_{ion}) in both ground and core-excited state cation–water dimers indicate that transfer of negative charge to the divalent metal cations from the water molecule is significant, while for the monovalent metal cations it is small (Table 2). Differences in the amount of CT to the Mg²⁺ and Ca²⁺ ions are found, with a greater reduction of the Mg²⁺ ion charge than the Ca²⁺ ion charge due to the presence of the water molecule, consistent with previous analyses.⁴¹ Even for larger clusters, where a full first solvation shell of six water molecules is considered, the average magnitude of CT from each water molecule to the cation is larger for Mg²⁺ ($0.71/6 = 0.12$) than for Ca²⁺ ($0.44/6 = 0.07$).⁴¹ This suggests that variations in the observed XA spectrum upon addition of divalent cations results in large part from a redistribution of charge among the water molecules that act to solvate the divalent cations. When CT is smaller, as with the monovalent cations, perturbation of the unoccupied water molecular orbitals is minor, as evidenced by the negligible variation of the charge on the water oxygen (q_{oxygen}) or hydrogen (q_{hydrogen}) atoms between the monovalent cations (Table 2). For the divalent cations, q_{oxygen} becomes less negative as the charge-to- r_{ion} ratio increases. For the cations, the calculated CT is somewhat greater for the ground state dimers than for the core-excited state dimers (as indicated by a smaller q_{ion}). CT to the divalent cations causes the partial charge on the ground state oxygen atom of solvating water molecules to be somewhat less

negative than for bulk water molecules (as approximated as the acceptor molecule in the pure water dimer), thereby making it more difficult to remove an electron from these solvation shell water molecules than from bulk water molecules. This is evidenced by a calculated core level ionization potential (IP) in the cation–water dimers that is ~ 13 eV greater for the divalent cation dimers than for the pure water dimer, yet only ~ 5 eV greater for the monovalent cation dimers. Full solvation of the central molecule will tend to decrease the calculated IPs. However, the calculated average IP for waters in the vicinity of divalent cations is still ~ 4 eV larger than that for monovalent cations. We note that the calculated average IPs of the solvating water molecules around Mg²⁺ and Ca²⁺ ions are very similar, both inducing a strong upward shift from the bulk water IP, even though CT to the Mg²⁺ ion is greater than to the Ca²⁺ ion.

Effects of Halide Anions. Given the above insights, we have additionally calculated the Mulliken charge populations for ground state and core-excited halide anion–water dimers, wherein the water is bound to the anion through a single hydrogen atom rather than through the oxygen. CT from halide anions to water molecules has been previously identified as an important factor in determining the halide anion–water dimer –OH stretching spectrum.^{46,47} Similarly, our DFT based analysis indicates that transfer of negative charge from the monovalent anions to the adjacent water molecule is substantial (Table 2), consistent with previous high-level ab initio calculations of CT in water–anion dimers.⁴⁶ Comparing to the partial charges on the donor molecule in the pure water dimer, the excess charge from the anion is more localized on the hydrogen atoms, thereby leaving the partial charge on the oxygen atom essentially unchanged from pure water in the ground state. Opposite to the cations, CT in the anion–water dimers is greater for the core-excited state than for the ground state and a considerable asymmetry in the q_{hydrogen} values is observed for the core-excited state but not for the ground state. This suggests a dramatic restructuring of the electron density around the water molecule on the time scale of the excitation due to the presence of the anion, which precipitates large changes in the XA spectrum of liquid water. The effect of the halide anions is thus to both change the static electronic structure of the solvent molecules and to strongly influence how the electronic structure relaxes upon excitation and formation of a core hole.

Our results stand in direct contrast to the conclusions of Näslund et al., who exclude Cl⁻ as a source of the experimental XA spectral variations, based upon the observation that KCl and NaCl solutions exhibit changes opposite to those of AlCl₃ solutions and that the overall spectral changes associated with AlCl₃ addition are small at 1 M concentrations.²¹ We contend that this does not actually indicate that Cl⁻ has a negligible effect on the XA spectrum but, instead, that extensive CT to the highly charged Al³⁺ ions engenders spectral changes that are opposite to those of Cl⁻ ions such that at 1 M concentrations the observed spectral variations are small. At higher concentrations, the direct perturbation due to Al³⁺ overwhelms that due to Cl⁻, leading to the observed decrease in the pre-edge and increase in the post-edge intensity. A similar effect was recently invoked to explain the observed spectral variations for aqueous HCl solutions.²⁰ Additionally, the interpretation of Näslund et al. in terms of strict “breaking” of hydrogen bonds as the source of the observed spectral variations completely neglects the important direct electronic distortion of the unoccupied molecular orbitals and leads to the unsupported conclusion that water molecules in the first hydration shell of strongly hydrated ions

(Al³⁺) have fewer broken hydrogen bonds than bulk water while molecules around weakly hydrated ions (Na⁺ and K⁺) have more broken hydrogen bonds.

Conclusions

We have presented comprehensive measurements of TEY X-ray absorption spectra of aqueous monovalent (Li⁺, Na⁺, K⁺, NH₄⁺, and Gdm⁺) and divalent (Mg²⁺ and Ca²⁺) chloride solutions at the oxygen K-edge. Upon addition of the monovalent cation chloride salts, marked changes are effected in the liquid water XA spectrum. However, a negligible dependence on the monovalent cation identity was observed. This experimental result, compared with DFT calculations of the XAS of water molecules around monovalent ions, indicates that the overall influence of monovalent cations on the unoccupied molecular orbitals of liquid water is small and that both direct electronic distortion and geometric distortion of the hydrogen bond network by monovalent cations are negligible. As a result, the spectral variations observed upon addition of *monovalent* cation halide salts to liquid water are dominated by the water–anion interactions, in disagreement with the recent conclusions of Näslund et al.¹³

In contrast, *divalent* cations engender unique changes to the liquid water XA spectrum. These spectral variations result from the strong interactions between the dissolved cations and water molecules in the first solvation shell. The high charge density of the divalent ions facilitates significant charge transfer from the solvating water molecules, thereby strongly distorting the unoccupied molecular orbitals of the solvation shell waters. Charge transfer to Mg²⁺ occurs to a much greater extent than it does to Ca²⁺, such that the identity of the divalent cation is important, whereas charge transfer to the monovalent cations is small and the cation identity is essentially irrelevant. DFT calculations of XA spectra for cation–water dimers also indicate that the specific orientation of water molecules within the first solvation shell of divalent cations may be an important factor in determining the nature of the overall direct electronic perturbation and that the arrangement of water molecules in the first solvation shell of these ions is different. We suggest that studies of Be²⁺ and Sr²⁺ or Ba²⁺ chloride salts would be informative, because charge transfer to Be²⁺ is even greater than that to Mg²⁺, whereas charge transfer to Sr²⁺ and Ba²⁺ is likely to be small. Additionally, Be²⁺ is thought to be coordinated with a first solvation shell comprising four waters in a tetrahedral arrangement, whereas Sr²⁺ and Ba²⁺ have first solvation shells that contain many waters due to their large sizes and low charge densities.⁴⁸

Our calculations suggest that charge transfer is also important in the perturbation of local water molecules by the halide anions and that the variation in the XA spectrum is strongly related to how the perturbed unoccupied orbitals relax under the influence of a core hole. For the cations, the influence of the cation on the unoccupied orbitals is primarily determined prior to the excitation event.

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