Increased fraction of low-density structures in aqueous solutions of fluoride

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X-ray absorption spectroscopy (XAS) and small angle x-ray scattering (SAXS) were utilized to study the effect of fluoride (F^-) anion in aqueous solutions. XAS spectra show that F^- increases the number of strong H-bonds, likely between F^- and water in the first hydration shell. SAXS data show a low- Q scattering intensity increase similar to the effect of a temperature decrease, suggesting an enhanced anomalous scattering behavior in F^- solutions. Quantitative analysis revealed that fluoride solutions have larger correlation lengths than chloride solutions with the same cations but shorter compared to pure water. This is interpreted as an increased fraction of tetrahedral low-density structures in the solutions due to the presence of the F^- ions, which act as nucleation centers replacing water in the H-bonding network and forming stronger H-bonds, but the presence of the cations restricts the extension of strong H-bonds. © 2011 American Institute of Physics. [doi:10.1063/1.3597606]

I. INTRODUCTION

The interaction between ions and water, both in the bulk^{1,2} and at interfaces,^{3,4} is vital in many chemical and biological processes. Among halides, fluoride (F^-) is certainly regarded as unique in terms of its effect on the structure of the surrounding water. For example, in a chromatographic study that quantified the apparent dynamic hydration number (ADHN) of various ions, i.e., the number of water molecules bound to an ion as it eluted through the chromatographic column, F^- was determined to have an ADHN of five, in agreement with the coordination number of fluoride from neutron scattering.⁵ F^- has the highest ADHN among all singly charged ions, including small monovalent cations such as Li^+ and Na^+ . In fact, only di- and trivalent cations (e.g., Mg^{2+} , Al^{3+} , Cr^{3+}) were found to have higher ADHNs than F^- .⁶ It is the only halide with a negative hydration entropy^{7,8} and a positive Jones-Dole viscosity B coefficient;^{2,8} therefore, F^- is traditionally classified as a “structure-making” ion, while other halides are considered as “structure-breakers.”

Various experimental studies have demonstrated the strength of the interaction between water and fluoride. For instance, infrared^{9,10} and Raman¹¹ spectroscopies show a redshift in the O–D/O–H stretching band of F^- solutions and blueshift for other alkali halide solutions. The redshift in the O–H (or O–D) stretching band is commonly associated with the strengthening of H-bonds and blueshift with the weakening of H-bonds. Results from a Raman ξ -function dispersion study also suggest that F^- forms strong H-bonds with water,¹² and neutron diffraction data interpreted using the empirical potential structure refinement method¹³ indicate

that F^- enhances the structuring of the water molecules in the first hydration shell.¹⁴ Other experimental studies^{15,16} and a number of molecular dynamics simulations^{17–20} have supported this; therefore, it is generally undisputed in the literature that F^- strongly interacts with water.

The structure-making effect of F^- is generally attributed to its small size and, consequently, high charge density relative to other halides. Indeed, other ions that strongly interact with water, such as Mg^{2+} and Al^{3+} , tend to have high charge densities. The residence time of water molecules in the first hydration shell of F^- ($(20\text{--}30) \times 10^{-12}$ s) (Refs. 20–22) is longer than that of Cl^- ($(5\text{--}9) \times 10^{-12}$ s);^{20–22} however, it is still many orders of magnitude shorter than those of Mg^{2+} ($\sim 10^{-6}$ s) and Al^{3+} ($\sim 1\text{--}6$ s).^{1,23} In addition, while various studies suggest the presence of strongly bound second and third hydration shells for Mg^{2+} and Al^{3+} ,^{15,24} respectively, there is no such evidence for F^- . Therefore, water is bound more weakly to F^- than to Mg^{2+} or Al^{3+} , which can be explained by the higher charge densities of Mg^{2+} and Al^{3+} due to their smaller sizes (ionic radii of 72 pm and 54 pm, respectively) and the multiple charges compared to singly charged F^- (ionic radius of 133 pm). In addition, F^- is unique among other monatomic ions because it is capable of accepting strong H-bonds from water molecules, which leads to the water molecules in the first hydration shell only having one OH available to H-bond to another water molecule. On the other hand, the water molecules in a cation first hydration shell point their O atoms towards the cations, leaving two available H donors. Thus, the nature of the hydration shell formed by F^- differs from those formed by cations such as Mg^{2+} and Al^{3+} .

In a previous study,²⁵ we used experimental x-ray Raman scattering spectroscopy (XRS), as an alternative to conventional x-ray absorption spectroscopy (XAS), and small

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angle x-ray scattering (SAXS) to investigate the effect of Na^+ , Mg^{2+} , and Al^{3+} cations on the structure of the surrounding hydration shells. XRS/XAS probes the unoccupied orbitals of a molecule through excitation of a core electron. It is sensitive to the H-bonding environment of water in the bulk liquid phase as well as in aqueous solutions.^{26–29} In particular, the pre-edge and main edge are a signature for distorted or weakened H-bonds, while the post-edge is sensitive to strong H-bonds as in tetrahedrally H-bonded ice.^{26,28,29} This assignment of spectral features is supported by experimental^{29,30} and theoretical^{28,31–34} results, and it was proposed from experimental and theoretical XAS (Ref. 27) that the majority of water molecules in the liquid phase have asymmetrical (distorted) H-bonds, contradicting the conventional continuous tetrahedral model of water. This interpretation has initiated a strong debate,^{31,33,35–43} however, XAS has been proven a reliable method for detecting even small changes in the H-bonding environment of water.^{25,29,44–48} XAS has also been used to study the changes in the electronic structure of hydrated cations in aqueous solutions.^{49,50}

SAXS is a scattering technique that can detect density heterogeneities at the nanometer length scale in liquid samples. Recent SAXS data for liquid water at various temperatures, in combination with XRS and x-ray emission spectroscopy, suggest that there are density fluctuations in ambient liquid water due to fluctuations into structural heterogeneities.⁴⁴ These have been suggested to be related to the preference of water for either of two distinct structure modes in the bulk, namely, as low-density liquid water (LDL) with tetrahedral H-bonds minimizing the enthalpy, or as disordered high-density liquid (HDL) with distorted H-bonds maximizing the entropy.⁴⁴ However, these two structures do not exist with well-defined shapes and boundaries. Instead, the HDL species consists of a continuous, broad distribution of structures that fluctuate into the LDL species.⁵¹

We demonstrated in our previous XRS and SAXS study²⁵ that while Na^+ weakens the H-bonds between the surrounding water molecules and increases the fraction of HDL species in the solution, Mg^{2+} and Al^{3+} form stable and highly ordered high-density hydration shells with strong H-bonds between water molecules. In addition, solvated Mg^{2+} and Al^{3+} form ordered quasi-lattice structures that appear in SAXS as a diffraction peak in the intermediate Q region (before the first scattering maximum). In the present study, we use XAS and SAXS to investigate the effect of F^- solvation on water structure in comparison to strongly hydrated cations such as Mg^{2+} and Al^{3+} .

II. EXPERIMENTAL METHODS

KF, KCl, NaF, and NaCl samples at various concentrations were prepared using commercially available salts (>99% from Fisher Chemicals) dissolved in Millipore-purified H_2O ($\sim 18 \text{ M}\Omega \text{ cm}$). XAS spectra were measured in transmission mode (T-mode) at beamline (BL) 10–1 at the Stanford Synchrotron Radiation Lightsource (SSRL). Measurements were performed in a low vacuum environment ($< 1 \text{ mTorr}$) and the photon energy was scanned between 520 and 570 eV. The sample cell, prepared at the Stan-

ford Nanofabrication Facility, consisted of two $5 \times 5 \text{ mm}^2$ Si(100) pieces with $0.5 \times 0.5 \text{ mm}^2$ x-ray transparent Si_3N_4 membranes in the middle (200 nm thickness). Sputtered Au (300 nm thick) was used as spacer between the windows to satisfy the T-mode XAS sample requirements, which must be 200–500 nm in thickness. It has been found that Au coating the Si_3N_4 membrane can neutralize the charging of the membrane, and furthermore render it more chemically inert, which might otherwise potentially cause reactions between membrane and solution which might affect the spectra.⁵² The intensity of the transmitted beam was measured using a photodiode detector behind the sample for both an empty (I_0) and filled cell (I) in order to obtain the absorption coefficient μ for a sample of thickness x according to the Beer-Lambert law $I = I_0 \exp(-\mu x)$, plotted as a function of photon energy. A pinhole of 25–50 μm diameter was placed in front of the sample to reduce the beam spot size so that a uniform area of the sample could be measured. This is related to the inherent problems with the sample cells, where the thickness of the liquid sample inside the cell is not perfectly uniform. Despite inhomogeneity problems, which appear as a slight saturation effect, T-mode XAS has been proven to generate reproducible spectra for liquid water over separate experimental runs.²⁹ In addition, a previous x-ray emission spectroscopy study of water has shown that the silicon nitride membrane has no effect on the spectra.⁵³

SAXS measurements were performed at the BioSAXS beamline BL 4–2 at SSRL with beam energy of 11 keV and an optical fiber charge-coupled detector (Rayonix225HE). The sample holder consists of a quartz capillary with a diameter of 1.5 mm and the x-ray path between the sample holder and the detector was kept in 1×10^{-3} Torr vacuum in order to reduce background scattering. The scattering vector is defined as $Q = 4\pi \sin \theta / \lambda$, where λ is the wavelength and θ is one-half of the scattering angle. The scattering curves have been corrected for the primary beam intensity, absorption, and detector readout noise. The scattering of the empty capillary was observed to contribute $\sim 20\%$ of the total scattering at $Q > 0.05 \text{ \AA}^{-1}$. The scattering of water and solutions was obtained by separately measuring the scattering of the empty capillary and subtracting it from the total scattering.

III. RESULTS AND DISCUSSION

The T-mode XAS spectra of 1, 2, and 4 m KCl and KF solutions compared to that of bulk water, as well as the difference spectra (i.e., solution minus water), are displayed in Figs. 1(a) and 1(b), respectively. The spectral changes caused by KCl solvation are obvious; the pre- (535 eV) and main edge (537–538 eV) systematically increase with concentration accompanied by a decrease in the post-edge (540–541 eV). Since the pre- and main edge are sensitive to weak H-bonds and the post-edge to strong H-bonds,^{26,28,29} this intensity redistribution from the post-edge to the pre- and main edge is a signature of H-bond weakening, similar to the effect of NaCl solvation.^{25,29,46} In connection to the fluctuations between the two local favored structures in pure water,⁴⁴ this can be interpreted as an increase in the fraction of the HDL species caused by the presence of the ions, similar to

FIG. 1. (a) O 1s T-mode XAS spectra of 1, 2, and 4 m KCl solutions with their difference spectra, (b) O 1s T-mode XAS spectra of 1, 2, and 4 m KF solutions with their difference spectra and the enlarged pre-edge peaks shown in the inset, (c) the difference spectrum between 4 m KF and water (green), compared to the difference spectrum between two pure water spectrum (black), both multiplied by a factor of 4, and (d) the spectrum of pure water (black) compared to the spectrum of water plus the difference spectrum between 4 m KF and KCl, illustrating the effect of only the F⁻ anion (green). All O 1s XAS spectra in (a), (b), and (d) have been normalized by area from 532 to 550 eV.

the effect of increasing pressure as was proposed from a neutron diffraction study.⁵⁴ When the temperature of bulk water is increased, an intensity redistribution from the post-edge to the pre- and main edge is observed, similar to Fig. 1(a).^{27,29,44} However, with a temperature increase the pre-edge also shifts to lower energy, indicating the increased disorder due to the thermal excitation of the existing HDL species,^{29,44} which is not observed for the solvation of NaCl (Ref. 25) and KCl.

On the other hand, the spectra of KF solutions [Fig. 1(b)] are very similar to that of pure water and the changes in the difference spectra are very small. There is a slight increase in the pre-edge [inset of Fig. 1(b)] and a very small shift of the main and post-edge to higher energy. In addition, there is a shift of the pre-edge to higher energy as concentration increases. Figure 1(c) displays the difference spectrum between 4 m KF solution and neat water multiplied by a factor of 4 (green line). This is compared to the difference spectrum between two pure water spectra obtained separately (black line, also multiplied by a factor of 4) representing the typical experimental noise, showing that the changes induced by KF are indeed real and not simply due to noise. In order to understand these minimal spectral changes despite the presence of F⁻ ions, which interact strongly with water, we need to describe first the effect of the K⁺ cation, assuming that there is no interaction between the cation and the anion.

Previously, we have suggested²⁵ that the changes in the spectra of NaCl, MgCl₂, and AlCl₃ solutions relative to neat water are mainly due to the cations, and that the effect of the Cl⁻ anion is small. To determine the effect of the K⁺ cation in KCl solutions on water structure, we compare the spectra of 4 m NaCl and KCl to that of pure water in Fig. 2(a). While both salts have a similar effect, i.e., increased pre- and main edge and decreased post-edge, the magnitude of the changes is greater for KCl than for NaCl, as can be directly seen from the difference spectra. This trend persists also at 1 m concentration but to facilitate the comparison we show the 4 m spectra where the effect is enhanced. At the same concentration, where the Cl⁻ can be neglected, this indicates that K⁺ has a stronger effect in weakening the H-bonds of water and increasing the fraction of the HDL species. This is in agreement with previously published fluorescence yield XAS spectra of NaCl and KCl,⁴⁶ and it is also consistent with various studies that classify K⁺ as a stronger structure-breaker than Na⁺ based on their relative size and charge density, Jones-Dole viscosity B coefficient, and hydration entropy.^{2,7}

As in KCl, an increase of the pre-edge in the KF spectra, albeit very small, is also observed (inset of Fig. 1(b)), which can be attributed to the effect of K⁺. The effect of the F⁻ anion must thus be the opposite to that of K⁺; i.e., F⁻ decreases the pre- and main edge and increases the post-edge, thereby cancelling almost all of the effects of K⁺ resulting in a spectrum that resembles that of pure water. In this picture, the slightly higher pre-edge in KF solutions compared to for neat water is simply a residual effect of the K⁺ cation. Therefore, while K⁺ decreases the number of strong H-bonds in water, F⁻ increases them. The enlarged pre-edge peaks of 1 m NaF, 1 m KF, and H₂O [inset of Fig. 2(b)] show the same trend as NaCl and KCl in which the pre-edge of KF is higher than that of NaF, indicating that there is less residual effect from Na⁺ than from K⁺. Unfortunately, comparison between NaF and KF at higher concentrations is not possible because NaF reaches its saturation concentration at ~1 m.

Another spectral change observed for KF solutions is the small shift of the pre-, main, and post-edge to higher energy, shown in the inset of Fig. 1(b) for the pre-edge and as the dip at ~536.4 eV and the peak at ~542.8 eV in the enlarged difference spectrum between 4 m KF and water

FIG. 2. O 1s T-mode XAS spectra of (a) 4 m NaCl (red) and KCl (blue), and (b) 1 m NaF (red) and KF (blue) compared to the spectrum of pure water (black). The difference spectra between the solutions and water are displayed above each set of spectra. Inset: the enlarged pre-edge region of H₂O (black), 1 m NaF (red), and 1 m KF (blue). All O 1s XAS spectra have been normalized by area from 532 to 550 eV.

[Fig. 1(c)] for the main and post-edge. The shift of the pre-edge to higher energy is similar to the effect of a temperature decrease in pure water,^{29,44} which is consistent with the previous discussion that F[−] increases the number of strong H-bonds in the solution. The post-edge in the O 1s XAS spectrum of water can be described as a shape resonance, whose energy position, according to the “bond-length-with-a-ruler” principle,^{55,56} is dependent on the H-bond distance.^{29,32} This has been shown from theoretical simulations³² as well as experimental XAS spectra of protonated water.⁵⁷ In our previous XAS spectra of MgCl₂ and AlCl₃ solutions,²⁵ a shift of the main and post-edge was also observed, especially strongly for AlCl₃, which was attributed to the short H-bonds between water molecules in the first and second hydration shells, in agreement with the results of various diffraction and molecular dynamics studies.¹

For hydrated F[−], however, it is unclear whether the short H-bonds are formed between water molecules, between the anion and water in the first hydration shell, or a combination of both since F[−] is able to form relatively strong H-bonds with water. The average distance between fluoride and oxygen determined from various diffraction studies is ~ 2.7 Å,^{1,18,19,21,22,58} which is shorter than the average O–O distance in liquid water (~ 2.84 Å) (Refs. 59 and 60) and close to the H-bond distance in crystalline ice (2.75 Å).⁶¹ In addition, the O–H–F angle is found to be nearly linear,^{19,62} indicating that F[−] does indeed form strong H-bonds with water. A combination of vibrational spectroscopy and *ab initio* calculations of F[−](H₂O)_{3–5} clusters suggests that there is no water–water H-bonding in the first shell and that the interaction is, instead, dominated by anion–water H-bonding.¹⁷ Apart from this study, however, not much is known about the H-bonding between water molecules in the first and second hydration shells of fluoride.

To illustrate the effect of only the F[−] anion on water, we subtracted the spectrum of 4 m KCl from that of 4 m KF, and the difference spectrum was then added to the spectrum of pure water. This was done under the assumption that the effect of Cl[−] is negligible and that the spectrum of the salt solution is the result of a linear combination of the spectral effects of cation and anion. The resulting spectrum [green line, Fig. 1(d)] shows significant changes compared to the pure water spectrum; the pre- and main edge are decreased while the post-edge gains quite a significant intensity, the opposite of the effect of K⁺. In fact, the spectral features become more icelike,²⁹ which is consistent with our observation of the pre-edge shift implying effects corresponding to a temperature decrease. At high concentrations, solvated ions are known to form ion pairs (see, e.g., Ref. 63 for Na–Cl ion pairing). However, the trends in the spectral changes observed at 4 m concentration are also observed at 1 m, indicating that the formation of ion pairs at high concentrations does not have a significant effect on the XAS spectra.

Figure 3 shows the SAXS data of NaF compared to NaCl and of KF compared to KCl at 0.1, 0.25, 0.5, and 1 m concentrations. The data for all of the salt solutions at 1 m concentration are displayed in Fig. 4. In all of the graphs, the scattering of pure water is shown as a dashed line as a reference. The scattering structure factor $S(Q)$, plotted as a function of momentum transfer Q , was separated from the total scattering intensity using the weighted sum of the scattering factors of H₂O and of the individual ions. Note that, although the changes in the XAS spectra of KF solutions are minimal due to the opposing effects of the K⁺ cation and also that for most salts 1 m is generally the minimum concentration at which XAS spectral changes become observable, SAXS is very sensitive to the changes in the density variations in the liquid even at very low concentrations; therefore, even with the cancelling effect of K⁺ in XAS, the effect of F[−] is easily observed using SAXS. Here, the combination of experimental techniques is essential.

For all salt solutions, the scattering intensity over the measured Q range increases with concentration since more solvated ions are present as scatterers. In addition, at the same concentration KF and KCl have a higher scattering

FIG. 3. Experimental structure factors $S(Q)$ of (a) NaCl (green) and NaF (purple), and (b) KCl (blue) and KF (red) compared to pure water (black-dashed lines). The salt concentrations for each type of solution, from top to bottom, are 1, 0.5, 0.25, and 0.1 m.

intensity than NaF and NaCl due to the higher number of electrons in K^+ than in Na^+ . The most interesting observation from these SAXS curves is that with the same cation, there is a low- Q intensity enhancement for F^- compared to Cl^- at all concentrations, indicating an increase in the anomalous scattering behavior due to the formation of strongly H-bonded structures. This enhancement is very similar to the effect of decreasing temperature,⁶⁴ consistent with the XAS data in Fig. 1, which has been interpreted as an increased fraction of the tetrahedral LDL species. In addition, the scattering of Cl^- solutions shows a plateau at small angles, which was previously found to correspond to a reduced correlation length compared to pure water,⁶⁴ implying a reduced anomalous behavior of water similar to the effect of increased pressure.⁶⁵

The low- Q intensity enhancement for F^- solutions is distinctly different from the enhancement observed in the scattering data of $MgCl_2$ and $AlCl_3$, which is dominated by a pre-peak in the intermediate Q region (before the first scattering peak) related to the scattering from the quasi-lattice structure formed by the strongly coordinated cations and their hydration shells.²⁵ In agreement with the results from neutron scattering⁶⁶ and gel-sieving chromatography,⁶ it was previously determined that Mg^{2+} and Al^{3+} , respectively, stabilize an equivalent of one and one and a half hydration shells that have, on average, a higher density than bulk water. This is because there are six water molecules in the first hydration shells of Mg^{2+} and Al^{3+} with cation-oxygen

distance of 2.1 Å and 1.9 Å,¹ respectively, compared to four in water with O–O distance of ~ 2.8 Å. However, no such pre-peak is observed for F^- solution in Fig. 3, indicating that, unlike Mg^{2+} and Al^{3+} , solvated F^- does not form a quasi-lattice structure in solutions, presumably due to its smaller charge density compared to the multivalent cations.

A more detailed analysis of the SAXS data was performed using the Percus-Yevick approximation for a hard sphere fluid to describe the fraction of scattering expected from a simple liquid and the Ornstein-Zernike (OZ) approximation to describe the anomalous scattering at small angles exceeding the expectation for a simple liquid (for further details, see Ref. 64). The OZ correlation lengths ξ obtained from this method are shown in Fig. 5 plotted as a function of concentration. The correlation length ξ should not be mistaken as a specific length in the liquid; in the OZ theory, it represents the damping factor of the long-range part of the pair-correlation function. Using various approximations, it can be translated to specific sizes in real space which for water at ambient conditions gives an average of the order of 1 nm (Ref. 44) in close correspondence to the distance out to which shell structure is observed in the O–O pair-correlation function obtained from high-accuracy x-ray diffraction studies.^{67,68} For the same anion, solutions containing Na^+ have higher ξ than those containing K^+ . The reduced correlation length for K^+ compared to Na^+ is related to a decrease in anomalous behavior, which is in agreement with the XAS interpretation that K^+ has a stronger H-bond breaking

FIG. 4. Experimental structure factors $S(Q)$ of 1 m NaCl (green), NaF (purple), KCl (blue), and KF (red) compared to pure water (black-dashed line)

effect than Na^+ (i.e., an enhanced temperature and pressure increase effect). At the same concentration, the ξ values for F^- solutions are higher than those for Cl^- solutions. This is consistent with the observation of an increased anomalous scattering at small angles for F^- compared to Cl^- as shown in Figs. 3 and 4. From the SAXS study of supercooled water,⁶⁴ it was shown that decreasing temperature results in an increased correlation length. However, the ξ values of all solutions are lower than for water and they decrease as the concentration increases. Comparison between the SAXS data of HCl and NaCl (not shown) reveals that the decrease in correlation length for NaCl solution is due to the Na^+ cation while Cl^- has a minor role. Indeed, the small effect of Cl^- on the H-bonding network of the surrounding water has been proposed in our previous XRS and SAXS study,²⁵ and it has also been supported by a molecular dynamics study that found that Cl^- does not disrupt the H-bonding network of water.⁶⁹ Therefore, the reduced correlation length for NaF and KF solutions, despite the observation of an increased anomalous behavior, is due to the presence of the Na^+ and K^+ cations, which affect water structure in a manner opposite to that of F^- . It is likely that although F^- forms a strong first hydration shell due to its strong H-bond-accepting capability, the presence of the counterions weakens the H-bonding between water molecules in the first hydration shell of F^- with those outside, thereby preventing the formation of an extended hydration shell.

FIG. 5. OZ correlation length ξ , derived using the method described in Ref. 64, plotted as a function of concentration in molality for NaF (circles), KF (squares), NaCl (triangles), and KCl (diamonds). The correlation length at zero concentration is the ξ for pure water.

IV. CONCLUSIONS

In conclusion, from our combined experimental XAS and SAXS data, we observe an increased fraction of low-density tetrahedral LDL-like species in water due to the solvation of fluoride ions. XAS spectra indicate that F^- increases the number of H-bonds in the solution similar to the effect of a temperature decrease, likely due to the strong H-bonds between the anion and water. SAXS data show an intensity enhancement at low- Q with increasing concentration for F^- solutions, which is indicative of an increasing anomalous scattering behavior in F^- solutions similar to the effect of a temperature decrease. We hypothesize that F^- ions act as nucleation centers for the formation of tetrahedral LDL structures in the solution due to its ability to form strong H-bonds with water. However, the presence of the alkali cations likely prevents the formation of an extended hydration shell as observed from the smaller correlation lengths of F^- solutions compared to for neat water. Therefore, the hydration shell structure around F^- is distinctly different from the hydration shells of di- and trivalent cations such as Mg^{2+} and Al^{3+} , which were previously found to form high-density ordered structures around the cations.²⁵ In addition, unlike the first hydration shells of Mg^{2+} and Al^{3+} , which persist over a relatively long time scale (10^{-6} s for Mg^{2+} and 1–6 s for Al^{3+}),^{1,23} the hydration shell of F^- is more fleeting ($(20\text{--}30) \times 10^{-12}$ s) (Refs. 20–22) and the water molecules are, therefore, involved in normal density fluctuation as in bulk water, albeit at a longer time scale and involving shorter H-bond distances than in pure water.

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