Direct Evidence of Orbital Mixing between Water and Solvated Transition-Metal Ions: An Oxygen 1s XAS and DFT Study of Aqueous Systems

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We have studied the chemical bonding of water in the first hydration sphere to transition-metal ions in aqueous solutions by using X-ray absorption spectroscopy (XAS) combined with density functional theory calculations (DFT). The experimental technique is for the first time applied to the study of the oxygen K-edge absorption of liquid water in the presence of dissolved ions. We successfully resolved the electronic structure of water in the first hydration sphere. Features in the oxygen 1s XAS pre-edge region in Cr3+ and Fe3+ solutions are interpreted as mixing between the molecular orbitals of water and the open d shell of the transition-metal ion. These features are absent for Al3+ solutions. Effects on the electronic structure from anions in the first hydration sphere are also described.

1. Introduction

The essential role of water as a solvent in chemical processes is closely connected to the properties of the hydration spheres of aqua ions. The chemical interaction between the ion of an element and water as a ligand gives essential information not only on the aqueous chemistry of the element but also on the chemical properties of the element in general. For example, the vast differences in thermodynamics and kinetics of hydrated ions in aqueous solution when replacing a coordinated water molecule with another ligand or for the deprotonation of water ligands to give hydroxo species are controlled to some extent by the charge density on the central atom but also by electronic factors, in particular, ligand field effects for transition-metal ions.1 Another factor of primary importance for the properties of aqueous solutions is the nature of the hydrogen bonding, which is strongly influenced by the presence of ions. It is well known that the conformation of proteins and nucleic acids, for example, the structure of DNA and its functions, depends on the nature of the ionic solution.2

Because of the importance of the ion—solvent interaction, a large number of experimental techniques, primarily EXAFS, X-ray, and neutron diffraction, have been applied to obtain direct structural information on the ion—water interaction. Structural and dynamic information is also available from NMR, infrared, and Raman spectroscopic methods as well as from theoretical calculations and computer simulations, but direct measurements of the local electronic structure of the water molecules in the solution have proven difficult. In surface science, near-edge X-ray absorption fine structure spectroscopy (NEXAFS, or more simply X-ray absorption spectroscopy, XAS)3 is widely used to study the nature of the bonding between adsorbates and the surface. However, the extension to low-energy measurements at the oxygen K edge in aqueous solution has long been a challenge because of the high vapor pressure of the liquid. The requirement of a vacuum environment when the measurements are performed using electron detection has led to the construction and application of differentially pumped systems.4 In those cases, the measurements have typically been done on a thin film of liquid, which is constantly replenished. With the advent of third-generation synchrotron light sources, improved detection techniques, and the possibility to make ultrathin windows to separate the ultrahigh vacuum of the beamline from a high-pressure cell, measurements under ambient conditions have now become possible. Recently, we were able to apply high-resolution XAS to the oxygen K edge of liquid water using a fluorescent photon detection mode in a helium atmosphere.5 The electronic structure of the liquid was compared to that in the solid state, which, in combination with theoretical calculations of spectra, lead to the spectroscopic identification of specific hydrogen-bonding situations.6–7 In the present work, we will extend this analysis to specific effects on the electronic structure of water as a ligand to metal cations in aqueous solution.

XAS involves the excitation of a core electron into unoccupied orbitals. The experiments show chemical specificity because the core-level positions depend strongly on the element and are furthermore sensitive to the chemical environment. Finally, the extreme spatial localization of the core orbital involved in the transition makes X-ray absorption an extremely local probe of the electronic structure at a specific atomic site.

The excitation process obeys the dipole selection rule,3 which for an atom strictly limits the change in the angular momentum quantum number (Δl) to ±1. For K-shell transitions of molecular

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systems, the spatial localization of the 1s orbital involved in the excitation results in the spectrum being completely dominated by transitions to molecular orbitals with a local p-orbital contribution, although the overall symmetry is not atomic-like. For an oxygen 1s electronic excitation, the features in the XAS spectrum will thus reflect only the local atomic p contribution to the excited orbital. Moreover, because of the short time scale of the excitation process (less than 1 fs, i.e., much faster than the vibrational and translational motions), the spectrum becomes the sum of snapshot contributions from individual molecules in their instantaneous environments.

In our earlier work we could, with the help of density functional theory (DFT) spectrum calculations for specific hydrogen-bonding situations, assign the XAS spectral features of the liquid to two different situations: (1) water molecules having one hydrogen bond broken at the donor side (D-ASYM) and (2) tetrahedral coordination (SYM) and unsaturation on the acceptor side (A-ASYM), where the latter two gave similar spectrum contributions (Figure 1). In the present paper, we will follow a similar strategy—combining XAS and DFT to study the local structure of water in transition-metal solutions. In particular, we will show that the molecular orbitals of water ligands in the first hydration sphere mix with the d orbitals of the metal ion, giving rise to low-intensity pre-edge features in the XAS spectrum. We propose that these features, which we have found for solutions of Cr^{3+} and Fe^{3+} but not for Al^{3+} (see Figure 1), are related to the electronic structure of the solvated trivalent transition-metal ions. Furthermore, we find these features to be sensitive to the composition of the first hydration sphere (e.g., the presence of inner-sphere chloride coordination as well as deprotonation of the water ligands give clear spectroscopic signals that serve to fingerprint these species).

2. Experimental Section

2.1. Experimental Technique. The oxygen 1s X-ray absorption spectroscopy (O 1s XAS) spectra were collected on beamline 8.0 at the Advanced Light Source (ALS) in Berkeley, CA. Because the method of detection is based on measuring fluorescence, it requires a high-flux undulator-based soft X-ray beamline. We have used the Soft X-ray Endstation for Environmental Research (SXEER) that makes it possible to separate the liquid under atmospheric pressure and room temperature in the sample chamber from the vacuum in the synchrotron beamline. The chamber is filled with helium gas that is transparent to soft X-rays in the energy range of interest for O 1s XAS. Furthermore, by maintaining a constant flow of helium gas through the chamber, we continuously removed the water vapor; this is necessary because water vapor will contribute spectral features to the spectrum in the same energy range as liquid water. The XAS spectra are obtained in fluorescence mode, and the photons are detected with a GaAs photodiode. The spectra are normalized by the incident photon intensity, I_0, monitored with a gold mesh in the beamline. The I_0-normalized spectrum is also normalized with an XAS spectrum of the Si_3N_4 window that separates the helium atmosphere from the vacuum. This is necessary because of adsorbed water molecules on the window. The spectra are then calibrated with the peak photon absorption energy of the water vapor features (O 1s → 4a_1 at 534.20 eV, O 1s → 2b_1 at 536.10 eV, and O 1s → 2b_2 at 537.25 eV), known from earlier experiments, before subtracting the gas-phase contributions from the spectrum. Figure 2 demonstrates for pure water the steps involved to obtain the final XAS spectrum.

The geometry of the sample with respect to incoming and emitted X-rays is very important in order to avoid saturation effects, which arise when the detection depth is deeper than the absorption depth (i.e., when all photons are absorbed in the volume from which the fluorescence can escape and reach the detector). Saturation effects affect the spectra in the energy range where the intensity is high, and in the case of pure water, where the mean free path of the fluorescence is long, saturation effects may be present above 536 eV. The saturation effect can be reduced by maximizing the penetration depth of the X-ray beam and by minimizing the detection depth by letting the X-ray photons impinge the sample normal to the surface and then collecting the fluorescence at a grazing angle. To achieve such a geometry, the detector is placed perpendicular to the incoming photon beam, and a 0.4-mm slit is placed in front of the detector. The slit will screen off most of the fluorescence and give a detection angle of only 1–2°. Whether this arrangement is sufficient to eliminate the saturation effect completely in pure water is still under debate. In the present case, however, where metal chloride salts are dissolved in the water, the saturation effect is entirely eliminated by the present geometry because the chloride ions, with L-edge absorption, reduce the fluorescence mean free path in the sample. We will focus further on the origin of the low-intensity features below the pre-edge found for solutions containing transition-metal ions (Cr^{3+} and Fe^{3+}), and in that energy region, no saturation effects have been noticed even in the pure liquid water case. Thus, a comparison between the different spectra is valid in this energy region, whereas a discussion of the solution-induced differences at higher energies, although highly interesting, must be investigated further.

2.2. Samples. The samples are prepared from commercially available salts from Sigma-Aldrich: chromium(III) chloride
alkaline earth metal 

trans-

fresh, the

Solutions of Trivalent Metal Ions 

TABLE 1: Samples in the O 1s XAS Study of Aqueous 

Figure 2. Recorded XAS spectra of (a) the sample, (b) the 

Figure 3. Structures of selected cluster models used in the DFT calculations: (a) [M(H2O)6]3+, (b) [MCl(H2O)5]2+, (c) [FeCl2(H2O)4]+, (d) [Fe(OH)2(H2O)4]2+, and (e) [M(H2O)9]3+ (M = trivalent metal ion).

hexahydride, CrCl3·6H2O; aluminum chloride hexahydride, 

AlCl3·6H2O; iron(II) chloride hexahydride, FeCl3·6H2O, aluminum perchlorate, Al(ClO4)3·9H2O; and iron(III) perchlorate, Fe(ClO4)3·10H2O. The salts were dissolved in deionized water without any further preparation, except in the case of FeCl3 (low pH, aq) where a few droplets of concentrated hydrochloric acid, HCl, are added before dissolving the salt. The sample notation, concentration, and color of the sample at the time of the XAS measurement are presented in Table 1.

2.3. Speciation. Aluminum. The small size of the Al3+ ion leads to extensive hydrolysis of its aqueous solutions, but at the high (~1 M) concentration of aluminum chloride hexahydride, AlCl3·6H2O(s), the dominating species is the hexaaquaaluminum ion [Al(H2O)6]3+.1,29

Chromium. When chromium chloride hexahydride, CrCl3·6H2O(s), is dissolved in water, the solution will contain different species of Cr—Cl inner- and outer-sphere complexes. When fresh, the trans-dichlorotetraaquochromium(III) ion, [CrCl2(H2O)4]2+, gives the solution a dark green color, but within 1 h, the solution gradually changes to light green because of the replacement of one of the chloride ligands by a water mol-
This calculation results in a discrete set of energy levels, each associated with a specific oscillator strength. The obtained oscillator strengths are then convoluted with Gaussians of linearly increasing full width at half-maximum (fwhm) to obtain the spectra. Effective core potentials (ECP), eliminating the O 1s level on all oxygen atoms but the core-excited one, were used to simplify the definition of the core hole. The core-excited oxygen was described using the IGLO-III all-electron basis set of Kutzelnigg et al.26 For the chlorine and metal atoms, TZVP and DZVP all-electron basis sets27 were used, respectively. The calculations were performed using a double basis set technique where in the spectrum calculation the normal molecular basis is augmented by a large diffuse basis (~150 functions) to improve the description of the Rydberg and continuum states.28

4. Results and Discussion

With the experimental setup described in the Experimental Section, we were recently able to probe the electronic structure in liquid water successfully by using XAS at the oxygen K edge.5 An experimental O 1s XAS spectrum of pure water5 is presented in Figure 1, and the spectral features (the strong pre-edge peak at 535 eV, an enhancement at 537 eV, and a less pronounced structure at 542 eV compared to bulk ice) were shown to be sensitive to the specific bonding of the hydrogens (donating H-bond) but not of the oxygen lone pair. The reason for this is that XAS measures the unoccupied 2p character at the oxygen of the probed water molecule, which gives a very low intensity for excitations involving the essentially doubly occupied lone pairs. Three different bonding situations of the water molecules were considered in ref 5: saturated fully coordinated (SYM), unsaturated with a missing hydrogen bond at the acceptor side (A-ASYM), and unsaturated with a missing hydrogen bond at the donor side (D-ASYM). Because the SYM and A-ASYM species were found to give similar contributions to the spectrum, we can distinguish spectroscopically only whether the H-bonding at the hydrogen side is saturated. The results in the previous work indicate that the unsaturated donating H-bonding environment applies to a dominating fraction of the water molecules.

O 1s XAS spectra of aqueous solutions of metal ions have overall similar features to those of pure water. There are small changes in the intensities and the peak positions, showing that the metal ions affect the H-bonding in water. In the present paper, however, we will focus our interest on the new features that appear in the pre-edge region of the O 1s XAS spectra of aqueous solutions of transition-metal ions. (See the shaded areas in Figure 1.) In FeCl3(aq), there are extra features that are not present in pure water. New features are also present in FeCl3-(low pH, aq) and Fe(CIO4)3(aq), but they not as clear as those in the FeCl3(aq) solution, and in CrCl3(aq), the pre-edge seems to be slightly shifted to lower energy. The aluminum(III) solutions, Al(CIO4)3(aq) and AlCl3(aq), do not show any major differences from pure water. Because these features appear in aqueous solutions of Fe3+ and Cr3+, but not Al3+, they should be related to the electronic structure of the transition-metal ions and the specific bonding in their coordination sphere.

The d orbitals are strongly influenced by the surrounding ion. The hexaaquaion complex [Cr(H2O)6]3+ is the most inert hydration complex of the first-row trivalent transition-metal ions mainly because of its large ligand-field activation energy.14,29 In the current experiment, we can expect that a certain amount of the monochloro complex, [CrCl(H2O)5]3+, is present in addition to the hexaaquaion complex, [Cr(H2O)6]3+. The inner-sphere chloro ligand in the [CrCl(H2O)5]3+ complex can have

\[ I_d \propto |\langle \psi_d | \mu | \psi_d \rangle|^2 \] (1)

Within the transition-potential approach,24 the initial and the final states are obtained from the same wave function, characterized by a half-occupied core hole. The transition-element calculation for transition between the core level and an unoccupied orbital is thus simplified:

\[ I_i \propto |\langle \phi_i | \mu | \phi_i \rangle|^2 \] (2)

Figure 4. Calculated spectra of [Fe(H2O)6]3+ (—) and [Fe(H2O)6]3+ (—) show that the interaction between the water molecule and the metal d orbitals is very local in nature and that the spectra of the two calculated cluster sizes do not differ in the low-energy region (530–535 eV). At higher energies, there are some differences because the excited water molecule in the first solvation sphere has a different local hydrogen bond structure in these two cases.
some effect on the XAS spectra, which will be analyzed on the basis of the theoretical calculations below.

The main-group Al\(^{3+}\) metal ion with the closed-shell [Ne] electronic configuration binds the first-sphere water molecules octahedrally with almost the same metal-oxygen distance as Cr\(^{3+}\): 1.88 and 1.96 Å, respectively. (The size of the water ligand is 1.34 Å.\(^{29,30}\) For both ions, the mean metal ion-oxygen distance to the second solvation sphere is about 4.0–4.2 Å.\(^{8,9,11,29,31–35}\) The geometrical differences in the hydration spheres of the cations are thus small enough that the comparison should provide useful information pertaining mainly to the differences in electronic structure.

Experimental O 1s XAS spectra of water with dissolved aluminum chloride, AlCl\(_3\) (aq), and water with dissolved chromium chloride, CrCl\(_3\) (aq), are shown in the inset of Figure 5, covering the energy range of 531–536 eV. (Note the more extended energy range than that shown in Figure 1.) It is clearly seen that AlCl\(_3\) (aq) has a double pre-edge peak with a shoulder at 534.3 eV and maximum at 535.1 eV that differs from the spectrum of pure water, presented in Figure 1. The present interpretation is that this difference is due to changes in the distribution of the D-ASYM water species in the bulk caused by the ion hydration. CrCl\(_3\) (aq) has the same feature but shifted to lower energy by 0.1 eV. This is actually not a shift in peak position but a shift due to extra features in the energy range of 532–536 eV. Because the new features in CrCl\(_3\) (aq) appear very close to the pre-edge, we have used a subtraction procedure to enhance them. A difference spectrum between the CrCl\(_3\) (aq) spectrum and the AlCl\(_3\) (aq) spectrum is presented in Figure 5 showing three peaks at 533.8, 534.5, and 535.8 eV. The computed spectrum for the [CrCl\(_2\) (H\(_2\)O)\(_4\)]\(^{2+}\) complex is compared with the experimental difference spectrum in the Figure. It is clear that the two features at 533.8 and 535.8 eV are well reproduced by the computed spectrum. To assign the feature at 534.5 eV, we turn to the computed spectra of chloro complex [CrCl(H\(_2\)O)\(_5\)]\(^{3+}\), also shown in Figure 5, where we consider the inclusion of one chloride in the first solvation sphere (Figure 3). We find that the chloro ligand induces an upward shift of the spectrum by about 1 eV as well as a slight compression of the features. The comparison with experiment suggests that the feature at 534.5 eV should be assigned to the t\(_{2g}\) component of the [CrCl(H\(_2\)O)\(_5\)]\(^{3+}\) complex. The corresponding e\(_g\) component...
to two peaks in the XAS spectrum. In the case of a parallel-spin core-electron excitation, the transition into the 3d orbitals is forbidden in the Fe$^{3+}$ ion, but it is allowed for Cr$^{3+}$ because of its d$^3$ configuration. The two e$_g$ orbitals in the Cr$^{3+}$ ion are completely empty and free for excitation of both parallel and antiparallel-spin core electrons.

From a simple consideration of the number of empty t$_{2g}$ and e$_g$ levels, one could expect corresponding intensity ratios of 3:2 for Fe$^{3+}$ and 3:4 for Cr$^{3+}$; these are not obtained from the calculations. To understand this, it must be remembered that the ligand-field splitting of the t$_{2g}$ and e$_g$ levels is due to the interaction between the OH lone pairs of the coordinated water molecules. The e$_g$ orbitals are pointing against the oxygen lone pairs, but the t$_{2g}$ orbitals are not, resulting in different interactions. If we anticipate that the observed orbitals are antibonding, we can expect that the more strongly interacting e$_g$ will be at higher energy and contain a larger water contribution. This will lead to the observed energy splitting and a larger intensity for the e$_g$ interacting orbitals in the spectra. Hence, the intensity ratios of the d-orbital interaction-derived features are different than expected. The extra, low-energy features, as can be seen in Figures 5 and 6, can originate from the d-orbital interactions between the water molecules and the trivalent d-metal ion. Finally, the energy shift of about 2 eV between the d-orbital interaction features of the [Cr(H$_2$O)$_6$]$^{3+}$ and the [Fe(H$_2$O)$_6$]$^{3+}$ clusters is due to the different energy of the d levels in Cr and Fe where the higher nuclear charge of the Fe atom leads to a greater stabilization and thus a lower energy for transitions into the 3d levels of Fe$^{3+}$.

To show that the mixing between the molecular orbitals of water and the Cr$^{3+}$ d orbitals represents a general case in all transition metals, we have also studied aqueous iron(III) solutions. Figure 7 (left) includes the experimental O 1s XAS spectra of FeCl$_3$(aq), Fe(ClO$_4$)$_3$(aq), and FeCl$_3$(low pH, aq). As compared to Fe(ClO$_4$)$_3$(aq) or FeCl$_3$(low pH, aq), the shapes of the d-orbital features are quite distinct in the FeCl$_3$(aq) spectrum but also more complicated. The difference between the FeCl$_3$(aq) and AlCl$_3$(aq) spectra (Figure 8, bottom) displays local maxima at 530.0, 531.6, and 532.8 eV. Figure 7 (right) shows the computed X-ray absorption spectrum of oxygen in the OH$^-$ ligands of the [Fe(OH)(H$_2$O)$_6$]$^{3+}$ and [Fe(OH)(H$_2$O)$_6$]$^{3+}$ clusters (Figure 3). The agreement indicates that the first peaks in the FeCl$_3$(aq) spectrum, at 530.0 and 531.6 eV, respectively, are due to the interaction between the OH$^-$ molecular and the d orbitals in the metal. A confirmation of this is the absence of these two peaks in the experimental spectra of the FeCl$_3$ solution at low pH (Figure 7, left). The broad peak at 532.9 eV is then assigned to the d interaction of the water molecules in the Fe$^{3+}$ ion solvation sphere. The yellow-brown color of the FeCl$_3$(aq) solution indicated that a colloidal precipitate had formed to some extent. Equilibrium calculations indicate that a substantial fraction of the iron would be present in amorphous iron(III) hydroxides or crystalline solid compounds such as Fe(OH)$_3$·xCl$_3$(s) and that the dominating solution species would be [FeCl$_2$(H$_2$O)$_4$]$^{3+}$ and [FeCl$_3$(H$_2$O)$_5$]$^{2+}$. Thus, it is likely that the observed features are due to the hydroxo groups in the solid precipitates.

By adding HCl to the iron(III) chloride solution to prevent the precipitation of iron(III) (oxy)hydroxides, the speciation will be simplified, and hydrolysis is suppressed. The experimental O 1s XAS spectrum of water with dissolved ferric chloride at low pH, FeCl$_3$(low pH, aq), is shown in Figure 7 (left). The features in the energy range of 531–534 eV look similar to those for the aqueous iron(III) perchlorate solution, Fe(ClO$_4$)$_3$ $(aq)$, but are somewhat shifted to higher energy. Calculations in Figure 7 (right) show the theoretical spectrum of the [Fe(H$_2$O)$_6$]$^{3+}$, [FeCl(H$_2$O)$_5$]$^{2+}$, and [FeCl$_2$(H$_2$O)$_4$]$^{+}$ complexes indicate that the presence of the chloro ligands in the first solvation sphere is responsible for the shift to higher energy of the d-orbital-derived features.
iron(III) perchlorate, Fe(ClO$_4$)$_3$ (aq), is shown in Figure 7 (left). The oxygen atoms in the ClO$_4$$^-$ ion will also be excited and give features in the XAS spectra, but not in the area of interest for the d-orbital interaction and will not affect our analysis (Figure 9). To ascertain that there are no intensity contributions from the oxygens of the counterion in the lower-energy region of the spectra, the Fe(ClO$_4$)$_3$ (aq) spectrum is compared to an O 1s XAS spectrum of water with dissolved Al(ClO$_4$)$_3$ (aq) (Figure 7 (left)). Calculations of XAS spectra for the ClO$_4$$^-$ ion also show that the perchlorate does not give any contribution in the region below 535 eV (Figure 9 inset). A difference spectrum of Al(ClO$_4$)$_3$ (aq) and AlCl$_3$ (aq) showing the ClO$_4$$^-$ (aq) contribution to the spectrum supports the conclusions from the calculations, as shown in Figure 9. The features at 530.5–533.5 eV must then be due to the interaction between the water molecule and the d orbitals in the Fe$^{3+}$ ion.

The difference between the Fe(ClO$_4$)$_3$ (aq) and Al(ClO$_4$)$_3$ (aq) spectra is shown in Figure 8 (top) together with the corresponding difference between the FeCl$_3$ (low pH, aq) and AlCl$_3$ (aq) spectra. The first difference curve displays d-orbital structure from 531 to 533.6 eV, and the second shows d-orbital structure from 531.3 to 533.7 eV. The shape is somewhat different; Fe(ClO$_4$)$_3$ (aq) has rather uniformly distributed features of the d-orbital structure, but FeCl$_3$ (low pH, aq) has more intensity at higher energy. This experimental evidence further supports our assertion that the shift to higher energy is due to the presence of chloro ligands in the inner solvation sphere of Fe$^{3+}$.

5. Conclusions

In this work, we have demonstrated the utility of X-ray absorption spectroscopy, in combination with DFT calculations of the spectral contributions, in studying the electronic structure of water in the first hydration sphere of metal ions. In our study, we focused our attention on the interaction between M$^{3+}$ transition-metal ions and the water molecules in their first solvation sphere, resulting in characteristic peaks in the O 1s XAS spectral pre-edge region. In particular, the peaks below 536 eV in the spectra of Cr(III) and Fe(III) aqueous solutions but missing in the case of Al(III) provide evidence for the existence of orbital mixing between the d orbitals of the metals and the molecular orbitals of the solvating water. This interaction between the water and the metal d orbitals is certainly anticipated in the literature, even though direct experimental electronic structure proof is missing. In fact, no technique other than XAS, combined with DFT calculations, is sensitive and selective enough to use as a direct experimental probe of the local orbital changes resulting from such a weak interaction.

Moreover, XAS shows great sensitivity to the local environment of the solvated metal ion, and the formation of metal–chlorine inner-sphere complexes is fingerprinted by a chemical shift in the position of the d-orbital interaction-derived features. In the case of the complex FeCl$_3$ (aq) solution, the peaks located in the 530–532 eV region could be assigned to the excitation of the oxygens in the hydroxyl groups resulting from the hydrolysis of water molecules and the probable formation of Fe(OH)$_2$.$\gamma$Cl$_0$.3(s) solid precipitates.

In addition to the pre-edge region, aqueous solution XAS spectra also differ slightly from the pure bulk water spectrum at higher energies. Although we did not focus on this part of the spectra in the present work, the information contained there is indeed interesting and will be the aim of further investigations.

Combined XAS-DFT is a powerful tool for providing insight into the local electronic structure of a hydrogen-bonded liquid, and we successfully applied it for the first time on water showing a great sensitivity to the symmetry and the saturation of the local hydrogen bond structure. Now this technique is extended to the case of transition-metal aqueous solution, and for its unique capacity of probing the local electronic structure around the central ion, it holds the promise of becoming an important tool, in addition to EXAFS and neutron and X-ray diffraction, for the study of aqueous solutions in chemistry, biology, and environmental science.

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