

# Charge transfer to solvent identified using dark channel fluorescence-yield L-edge spectroscopy

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**Aqueous ions are central to catalysis and biological function and play an important role in radiation biology as sources of damage-inducing electrons. Detailed knowledge of solute-solvent interactions is therefore crucial. For transition-metal ions, soft X-ray L-edge spectroscopy allows access to *d* orbitals, which are involved in chemical bonding. Using this technique, we show that the fluorescence-yield spectra of aqueous ionic species exhibit additional features compared with those of non-aqueous solvents. Some features dip below the fluorescence background of the solvent and this is rationalized by the competition between the fluorescence yields of the solute and solvent species, and between the solute radiative (fluorescence) and non-radiative channels; in particular, electron transfer to the water molecules. This method allows us to determine the nature, directionality and timescale of the electron transfer. Remarkably, we observe such features even for fully ligated metal atoms, which indicates a direct interaction with the water molecules.**

Water is the most important solvent in nature, and the interactions of ionic species with water molecules govern a wide range of chemical and biological phenomena, such as catalysis, electrochemical processes at interfaces, acid-base reactions, oxidation-reduction reactions, ion transport through membranes and enzymatic processes<sup>1,2</sup>, as well as phenomena in radiochemistry and radiobiology<sup>3</sup>. A detailed understanding of the electronic structure of ions when interacting with water molecules and the resulting solvent-shell structure is therefore important to the description of chemical and biochemical processes. In this respect, core-level spectroscopies are among the most powerful tools for the investigation of charge delocalization and transfer in chemical bonds<sup>4,5</sup>. In particular, X-ray absorption spectroscopy (XAS) at the L<sub>2,3</sub> edges of transition metals accesses the valence *d* orbitals (which are those involved in chemical bonding) from the 2*p*<sub>1/2,3/2</sub> core orbitals. The L edges of most transition-metal ions are less than 1,000 eV, but experiments on liquid samples at high vapour pressures (for example, volatile solutions) are now possible and studies of atomic cations in solutions<sup>6,7</sup> and, more recently, of proteins in physiological solutions have been reported<sup>8,9</sup>.

One of the most commonly used methods to obtain soft X-ray absorption spectra of low-dilution species is the fluorescence-yield method, which records the light emitted from a sample as a function of the incident photon energy. In such measurements, apart from any resonant transition of the solvent and/or the solute, a continuous background signal is detected. This results from light emitted and/or scattered elastically by the solvent. At a resonance, the solute absorbs light and both its fluorescence and light (emitted and/or scattered) from the solvent are detected. Provided the yield of fluorescence is independent of the incident photon energy, the fluorescence-yield spectra mirror the absorption spectra. Deviations between fluorescence yield and absorption spectra, however, are reported in molecular systems<sup>10</sup>, proteins<sup>11</sup>, solids<sup>12</sup> and transition-metal ions in solution<sup>6,7</sup>, and show up

mainly as different intensity ratios of the L<sub>3</sub> to L<sub>2</sub> edges and their satellite bands. The deviations found in previous studies, however, were not exploited to extract information about the nature and fate of the final states.

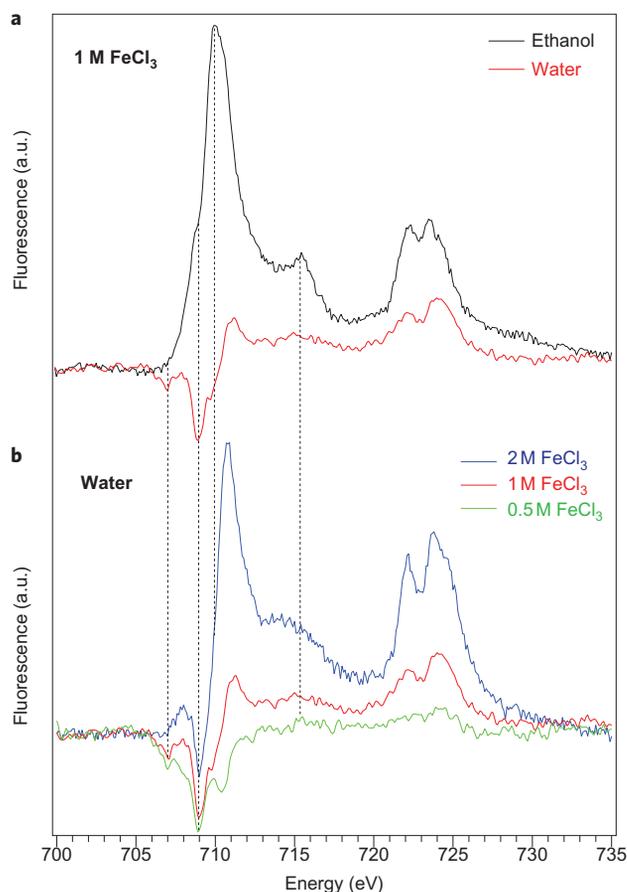
Also, spectral features that do not appear in non-aqueous solutions were observed specifically in aqueous solutions. Näslund *et al.*<sup>13</sup> reported a fluorescence-yield study of the oxygen K-edge absorption of an aqueous solution of Fe<sup>3+</sup> ions. Weak bands were observed in the pre-edge region, which they assigned, using density functional theory (DFT), to orbitals of the water molecules in the first hydration shell mixing with the iron *d* orbitals. However, the exact nature of the mixing remained unclear.

Here we report a case of extreme deviations in which, in addition to spectral components that show up in the L<sub>3,2</sub> spectra of aqueous ferric and ferrous species (as atomic or molecular ions), several components dip below the background level in the fluorescence-yield spectra. This is dependent on the solute and on its concentration, which suggests a partial extinction of the fluorescence channel from the solute. The origin of this extinction is identified as competition between the fluorescence yield of the solvent molecules and that of the solute, and to an electron transfer from the solute to the water molecules.

## Results

Figure 1a illustrates the L<sub>3,2</sub> spectrum of Fe<sup>3+</sup> ions in ethanol<sup>6</sup> and compares it with the spectrum in water at a similar concentration. Figure 1b shows concentration-dependent fluorescence-yield spectra of the same species in water. The intensity of the fluorescence bands decreased with dilution over the whole range, but the features at the L<sub>3</sub> edge were affected most, to the point that some bands dipped below the background level and truncated the main peak (at around 710 eV), which also dipped at the lowest concentration. The background level did not change with concentration (see Supplementary Fig. S1 for a plot on an absolute scale), and the

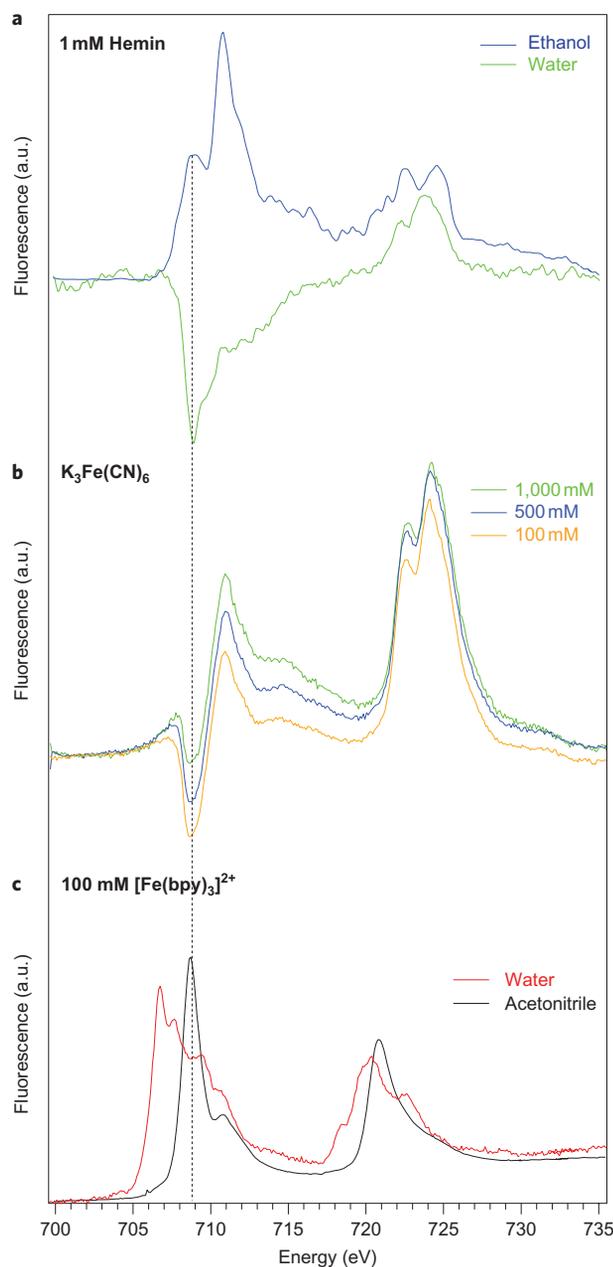
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**Figure 1** | Fluorescence-yield spectra in the  $L_{2,3}$ -edge region of  $\text{Fe}^{3+}$  ions in different solvents and for different  $\text{FeCl}_3$  concentrations. **a, b**, In ethanol (reproduced from Bonhommeau *et al.*<sup>6</sup>) (**a**) and in water (**b**) at various concentrations (see Supplementary Fig. S1 for the same spectra on an absolute scale). The dashed vertical lines show the correspondence between the features of the spectra. a.u. = arbitrary units.

dips represented an intensity decrease of  $\leq 3.5\%$ , with respect to the background level. Furthermore, the concentration effect was counter to the expected trend<sup>14,15</sup> in that the most dilute sample deviated most from the ethanol spectrum. This suggested that the changes were more pronounced the higher the number of coordinating water molecules. Compared with the ethanol spectrum, new features appeared at 707 eV and at 709 eV, and these values were concentration independent.

Sub-background spectral features also occurred in metal-containing molecular complexes. Figure 2a shows the case of the iron-containing porphyrin hemin in ethanol<sup>8,9</sup> and in water. Although the ethanol spectrum only showed bands, in water the entire  $L_3$ -edge region dipped below the background level, but at the  $L_2$  edge the relative intensities of the doublet changed, and there seemed to be a weak shift to lower energies. Hemin is penta-coordinated to the porphyrin nitrogen atoms and to the chlorine ligand atom, so our results showed that one molecule of water was sufficient to modify the spectrum dramatically. This is the case even for a fully (hexa)coordinated metal ion, such as  $[\text{Fe}(\text{CN})_6]^{3-}$ , for which again the changes in the spectra were more pronounced the lower the concentration (Fig. 2b). Also, these spectra were very different to those of  $\text{Fe}^{3+}$  ions in water, as they showed clear  $L_2$  features and no structure at 707 eV. Furthermore, they differed strongly from that of crystalline  $\text{K}_3\text{Fe}(\text{CN})_6$  (ref. 16). Evidently, in the case of  $[\text{Fe}(\text{CN})_6]^{3-}$  the water molecules were close enough to the iron centre to affect the  $L_3$ -edge fluorescence yield. Steric



**Figure 2** | Fluorescence-yield spectra in the  $L_{2,3}$ -edge region of iron in different molecular systems. **a**, The iron-containing hemin porphyrin in water and ethanol. **b**,  $[\text{Fe}(\text{CN})_6]^{3-}$  ions in water as a function of concentration. **c**,  $[\text{Fe}(\text{bpy})_3]^{2+}$  dissolved in water and acetonitrile (the intensities of the two spectra are not comparable). The dashed vertical lines show the correspondence between the features of the spectra. a.u. = arbitrary units.

constraints to the interaction of water with the iron centre were observed in iron trisbipyridine,  $[\text{Fe}(\text{bpy})_3]^{2+}$  (Fig. 2c), which is a hexacoordinated, but trigonally distorted, octahedral complex. There were strong differences between the  $[\text{Fe}(\text{bpy})_3]^{2+}$  spectrum in water and that in acetonitrile – additional bands appeared in the former and all the bands seemed broader. This could occur only if the molecules intercalated between the ligands, and the interaction here was not strong enough to produce dips. Indeed, steric constraints meant the probability that water molecules were close to the iron centre was higher in  $[\text{Fe}(\text{CN})_6]^{3-}$  than that in  $[\text{Fe}(\text{bpy})_3]^{2+}$ .

We also checked that:

- changing the detection angle with respect to the incident beam did not affect the spectra, contrary to the effect in solids (Eisebitt *et al.*<sup>14</sup>);
- decreasing the incoming flux by three orders of magnitude also did not affect the spectra;
- switching from the GaAs detector (with sensitivity to visible light) to a silicon diode equipped with a 0.15  $\mu\text{m}$  thick aluminium foil window (that is, only sensitive to X-rays, see Fig. S2) did not change the spectra, which implied that the background resulted predominantly from soft X-ray photons scattered and/or emitted by the solvent.

Therefore, we excluded the saturation effect<sup>14</sup>, which is caused by reabsorption of the fluorescence photons in the sample and distorts the fluorescence-yield spectra, depending on the angle of incidence of the X-ray beam, the angle of observation and the solute concentration. In particular, the dips were more pronounced the lower the concentration (Fig. 2). For hemin in water and in ethanol the concentrations were in the millimolar range (Fig. 2a). In addition, for a given solute concentration the spectra in water were different to those in alcohols<sup>6</sup>. Finally, a saturation effect cannot give rise to new bands (for example, at 707 eV (Fig. 1)). Also, such effects were excluded for  $\text{Ni}^{2+}$  ions in solution<sup>7</sup> and for  $\text{Na}^+$  ions in water<sup>17</sup>, for which the spectral changes were attributed to modifications of the symmetry or electronic structure of the solutes with concentration.

In summary, the two main observations were that:

- some (but not all) spectral features became dips;
- new spectral features appeared specifically in water solutions (see Figs 1 and 2).

Therefore, the origin of the sub-background signals was linked to the nature of the solute and its interaction with water molecules<sup>13</sup>.

## Discussion

In the soft X-ray regime, fluorescence is a minority channel and decay is mainly through Auger processes, the yield of which is over 99% for O(1s) and Fe(2p). As established above, the background is related to fluorescence and/or scattered photons from the O(1s) decay of water. The fluorescence yield could be several 100 eV higher in energy compared with that of the near-edge region because shake-up and shake-off processes provide additional valence holes. The iron  $L_3$ -edge yield is slightly below the oxygen K-edge yield of water<sup>18</sup>, so the fluorescence of the absorbing iron ions has a lower yield than that of the surrounding oxygen atoms and, therefore, a dip occurs in the spectrum. This is less likely at the  $L_2$  edge because its fluorescence yield is higher<sup>18</sup>. This hypothesis is supported by the fluorescence-yield spectra of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions (Supplementary Fig. S3): for  $\text{Cu}^{2+}$ , the  $L_3$ -edge fluorescence yield is larger than that of the oxygen K-edge and, therefore, only bands are produced, but for  $\text{Cr}^{3+}$  it is the opposite and only dips occur.

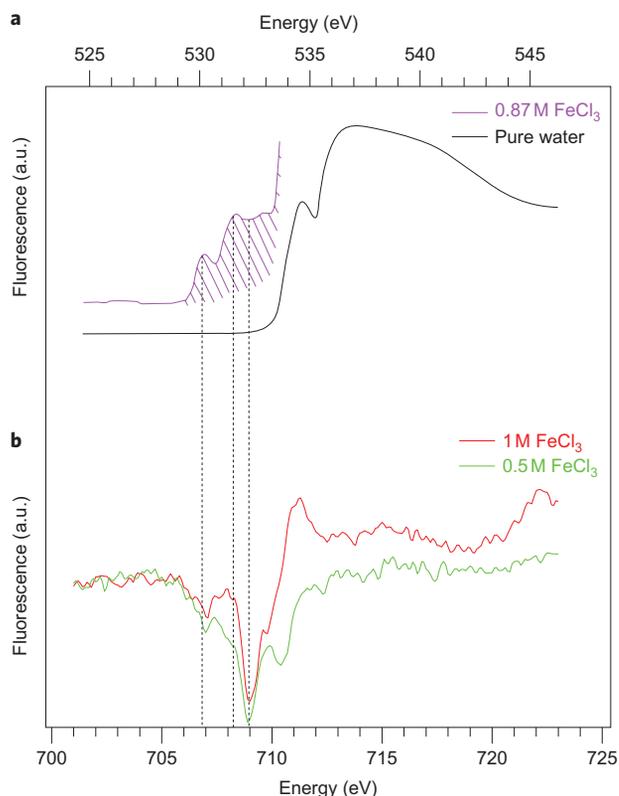
The above explanation is, however, not the whole story because only some of the features of the  $L_3$ -edge spectra appear as dips. Furthermore, neither the difference between the  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{bpy})_3]^{2+}$  spectra nor the appearance of extra spectral features in aqueous solutions can be rationalized in this way. Sub-background spectral lines are reported in the vacuum ultraviolet excitation spectra of molecules in the condensed phase<sup>19</sup>, which occur because of competition between radiative (fluorescence) and non-radiative processes. In the present case, we believe that the non-radiative channel is an electron transfer to the water-solvent molecules from the orbitals of the solute excited by the X-rays. The arguments in favour of this scenario are:

- Of all solvents used, water has the smallest negative effective charge at the oxygen site.
- For electron transfer to occur with aqueous  $\text{Fe}^{3+}$  ions, the binding energies of the metal  $d$  orbitals must lie close to those of the empty orbitals of water. The binding energy of the lowest empty orbital of water ( $4a_1$ ) lies at 3.1 eV in liquid water<sup>20</sup> and is in the same range as that for the metal  $d$  orbitals<sup>21,22</sup>.
- A good overlap between the metal  $d(e_g)$  and water orbitals (in this case the  $4a_1$  lowest unoccupied molecular orbital (LUMO)+1) should occur, which is the case as  $\sigma$  backbonding is the dominant metal-to-ligand charge transfer (MLCT)<sup>6</sup>.
- DFT calculations show that orbital mixing occurs<sup>13</sup>.
- All of our observations indicate that the  $L_3$ -edge features are affected more than the  $L_2$ -edge features. The core-hole lifetime ( $\sim 0.7$  fs) of the  $L_2$  edge is shorter than that of the  $L_3$  edge ( $\sim 2$  fs) (ref. 23), so it is likely that  $L_2$  is affected less by electron transfer because of its higher radiative decay rate. This also sets an upper limit of  $\sim 1$ – $1.5$  fs for the transfer time of the electron to the solvent.
- Although electron transfer can also take place in alcohols, the interaction of the ions with the oxygen of alcohol is known to be weaker than that with the oxygen of water<sup>24</sup>. In addition, the larger size of the alcohol molecules compared with those of water imposes a steric hindrance that further weakens the interaction of the molecular orbitals of alcohols with the ions.

Based on the above, we propose that the feature at 707 eV (Fig. 1) correlates with the first pre-edge feature of the oxygen K-edge spectrum of  $\text{Fe}^{3+}$ -containing aqueous solutions reported by Näslund *et al.*<sup>13</sup>, and in Fig. 3 we align the two spectra accordingly. It appears that the features of the iron  $L_3$  edge in the low-concentration spectrum (green trace, Fig. 3b) have corresponding features in the pre-edge region of the oxygen K-edge spectrum (Fig. 3a). The identical splitting between these supports the correspondence predicted by DFT simulations<sup>13</sup>. A similar situation is encountered in solid  $[\text{Fe}(\text{CN})_6]^{3-}$  (ref. 25), in which the lowest energy band at the  $L_3$  edges of iron and at the K edge of nitrogen have a common origin and are associated with core transitions to the partly filled  $2t_{2g}$  molecular orbitals. It is interesting that the additional spectral features with the lowest energy became dips first (in Figure. 1b).

The gradual prominence of sub-background features on dilution of  $\text{FeCl}_3$  in water can be correlated to the increase in MLCT from the iron orbitals. At the lowest concentration, coordination by water molecules is complete and it appears that electron transfer is at its maximum. However, we stress that the process does not scale simply with the number of coordinating water molecules, as shown for hemin (Fig. 2a). The case of  $[\text{Fe}(\text{CN})_6]^{3-}$  (Fig. 2b) is even more extreme in this respect, and the changes that occur imply that the water molecules come close enough to the  $\text{Fe}^{3+}$  centre for their oxygen side to point towards it. In a recent quantum mechanical/molecular mechanics simulation of ruthenium trisbipyridine  $[\text{Ru}(\text{bpy})_3]^{2+}$  in water, Moret *et al.*<sup>26</sup> found that the first solvation sphere consists of chains of hydrogen-bonded water molecules inserted between the bipyridine ligands, with their oxygen atoms pointing to the  $\text{Ru}^{2+}$  central ion ( $\text{Fe}^{2+}$  in the case of the  $[\text{Fe}(\text{bpy})_3]^{2+}$ ).  $[\text{Fe}(\text{CN})_6]^{3-}$  has smaller ligands and an octahedral symmetry, and thus it can accept water molecules between its ligands more easily than  $[\text{Fe}(\text{bpy})_3]^{2+}$  can. Therefore, full coordination of the metal ion is not a condition that hinders the strong interaction with water molecules that leads to intermolecular electron transfer, although the water molecules need to be close to the metal centre.

An additional argument to support the view that the origin of the dips is electron-transfer related is based on the sub-background spectral features reported by Sham and co-workers in the soft X-ray spectra of ruthenium- and iridium-polypyridine



**Figure 3 | Comparison of the oxygen K-edge with the iron L<sub>3</sub>-edge fluorescence-yield spectra of aqueous solutions of FeCl<sub>3</sub>.** **a**, Pre-edge of the oxygen 1s XAS at a salt concentration of 0.87 M FeCl<sub>3</sub> (from Näslund *et al.*<sup>13</sup>); the spectrum is multiplied by 5 to allow comparison with the spectrum of pure water (energy scale on the top axis). The shaded areas represent spectral features that appear only in the presence of the Fe<sup>3+</sup> metal ions. **b**, The red and green traces represent the iron L<sub>3</sub>-edge spectra for salt concentrations of 1 M and 0.5 M, respectively. The dashed vertical lines show the correspondence between the pre-edge features at the oxygen K edge and at the iron L<sub>3</sub> edge. a.u. = arbitrary units.

complexes<sup>27,28</sup>, but not discussed by them. They compared the yields of total electron and X-ray fluorescence spectra to the yield of X-ray enhanced optical luminescence spectra for these complexes, for which optical luminescence is caused by the triplet (intramolecular) <sup>3</sup>MLCT states<sup>29</sup>. When scanning across the L<sub>2,3</sub> edges of ruthenium to detect optical luminescence, they observed bands above the background (although with some deviations between absorption, total electron yield, fluorescence yield and optical luminescence yield spectra), but when scanning across the K edges of the bipyridine carbons and nitrogen atoms, they obtained an inverted spectrum with spectral lines that appeared as dips on the background. This behaviour can be understood by considering electron-transfer processes: X-ray excitation of the ruthenium atom leads to electron transfer from the metal to the bipyridine ligands (just as with optical excitation<sup>30</sup>), to yield the <sup>3</sup>MLCT luminescence. Excitation of the ligand atoms leaves the electron within the ligand and cannot lead to the formation of an MLCT state. The ligand atoms thus absorb X-ray light without giving rise to an optical luminescence. In our case, no optical luminescence is at stake, and the intermolecular electron transfer from the metal to the water molecule reduces the X-ray fluorescence yield from the metal, and the water molecule (or molecules) that receives the electron cannot fluoresce (it has no empty core levels), but can decay by Auger processes.

In a further example, Schnadt *et al.*<sup>31</sup> identified electron transfer from an aromatic ruthenium–polypyridine adsorbate to a TiO<sub>2</sub>

substrate and compared the resonant photoemission spectrum with the X-ray absorption spectrum at the K edge of nitrogen. The deviation that appeared was the disappearance of the LUMO+1 and LUMO+2 bands in the resonant photoemission spectrum, but no such effect was observed on the LUMO band. The latter lies below the substrate conduction band and the former lie within it. In the presence of the core hole an electron that resides in the LUMO therefore cannot be transferred into the substrate, but for an electron in the LUMO+1 and LUMO+2 a transfer is feasible energetically. Based on the core-hole lifetime, Schnadt *et al.*<sup>31</sup> estimated the timescale for electron injection into the substrate to be <3 fs.

In this work, we report two main observations on aqueous metal-based atomic and molecular ions: spectral features appear in their L-edge spectra that are not in the spectra of non-aqueous solvents, which stresses that water molecules affect the electronic structure of the solute through complex formation. In addition, some of the spectral components lie below the background of fluorescent light from the solvent. The latter behaviour is attributed to competition between the fluorescence yields of the solvent and the solute, as well as to an electron transfer from the X-ray excited state of the solute to the solvent molecules. In our study, the electron transfer occurs from core excited states that delocalize in the electronic structure of the water continuum. This behaviour is not limited to aqueous environments and the observation of sub-background features in fluorescence-yield spectra represents a novel and relatively simple method to identify the interaction of solutes with their environment in solutions and in heterogeneous media, such as interfaces, and to determine the direction of the electron transfer.

## Methods

The iron L<sub>2,3</sub>-edge XAS measurements were carried out at the U41-PGM high-flux undulator beamline at BESSY II (Berlin). The set-up is described elsewhere<sup>7</sup>. Briefly, the solution circulates in an ultrahigh vacuum chamber within stainless-steel tubing at a speed of 1 l min<sup>-1</sup>, and the sample refreshed constantly. The sampler is irradiated by the soft X-ray radiation behind a transparent 150 nm thick Si<sub>3</sub>N<sub>4</sub> membrane. The spectra were recorded in total fluorescence yield using either a 5 × 5 mm<sup>2</sup> GaAsP photodiode, or a silica diode equipped with a 150 nm thick aluminium-foil filter (see Supplementary Fig. S2 for the transmission curves of the aluminium foils). The attenuation length of soft X-rays in condensed matter is of the order of a micron, so the detection method is primarily bulk sensitive. The resolution of the experiment was better than 200 meV at 700 eV. The fluorescence-yield spectra were divided by a reference for the incoming flux taken from a refocusing mirror before the sample (see Supplementary Fig. S3).

Before each experiment, the samples were freshly prepared from highly purified, commercially available anhydrous FeCl<sub>3</sub> (>99.8%, Sigma-Aldrich). The salt concentration was variable and the measurements were carried out at room temperature. The pH was maintained well below one to avoid the formation of species such as FeOH<sup>2+</sup> and Fe(OH)<sub>2</sub><sup>+</sup>, so mainly [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (obtained in the best-available commercial purity (>99%)) was in the solution<sup>32</sup>. Hemin was prepared in ethanol and in water (a very basic solution, pH 11 and 1 M NaOH). [Fe(CN)<sub>6</sub>]<sup>3-</sup> samples were prepared by dissolving the K<sub>3</sub>Fe(CN)<sub>6</sub> salt directly in water, and diluting it *in situ*. For the [Fe(bpy)<sub>3</sub>]<sup>2+</sup> samples, a salt of tris(2,2'-bipyridine)iron(II) chloride hexahydrate ([Fe(2,2'-bipyridine)<sub>3</sub>]Cl<sub>2</sub>•6H<sub>2</sub>O) was dissolved in deionized water or acetonitrile at the required concentration. The liquid samples were prepared under a hood at room temperature, green light and helium atmosphere. The samples were transferred directly to the liquid container outside the chamber and circulated through capillary tubes (Teflon) within the chamber under dark conditions.

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### Author contributions

E.F.A. conceived and designed the experiments, E.F.A., M.H.R.F. and K.M.L. performed the experiments, E.F.A., S.B. and M.C. analysed the data and E.F.A. and M.C. co-wrote the paper.

### Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper at [www.nature.com/naturechemistry](http://www.nature.com/naturechemistry). Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>. Correspondence and requests for materials should be addressed to E.F.A. and M.C.