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On the origin of dips in total fluorescence yield X-ray absorption spectra: Partial and inverse partial fluorescence yield at the L-edge of cobalt aqueous solution

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ABSTRACT

Dips appearing in the L-edge total fluorescence yield (TFY) spectra of transition-metal ions in aqueous solutions have been recently attributed to, orbital mixing of the solute with the solvent orbitals. Here we compare the L-edge TFY, Oxygen K_α and Co^{2+} $L_l(3s \rightarrow 2p_{3/2})$, $L_\eta(3s \rightarrow 2p_{1/2})$, $L_\alpha(3d \rightarrow 2p_{3/2})$ and $L_\beta(3d \rightarrow 2p_{1/2})$ –edge partial fluorescence yield with the transmission spectrum. We thereby confirm that these mixed orbitals lead to electron delocalization between the valence d-orbitals of the transition metal and the valence bands of the solvent molecules, quenching their X-ray fluorescence.

1. Introduction

Soft X-ray total fluorescence yield (TFY) spectroscopy as a tool to record X-ray absorption (XA) spectra has recently been demonstrated in the study of biochemical systems in solution, even at high dilutions [1–12]. In most cases it cannot be accurately interpreted without additional electronic-structure information or theoretical modeling. Recently, Aziz et al. reported on the appearance of dips in the TFY spectra of transition metal atomic and molecular ions in aqueous solution [13–15]. The dips were attributed to two concurrent mechanisms: (a) the competition between the fluorescence yield of the solvent species (i.e. oxygen) versus that of the solute and (b) a charge transfer from the metal d-orbitals to the solvent resulting from orbital mixing of the ion and the water molecules. The charge transfer would then quench the X-ray fluorescence from the X-ray excited metal d-orbitals. It was suggested that the dips could be used as a probe of this ultra-fast charge transfer. Later, Winter and Aziz explored further the nature of the underlying decay mechanism of 2p core-excited Co^{2+} in water as a model, by probing the non-radiative Auger-type electron emission channel using photoelectron spectroscopy from a liquid micro-jet [13–15]. They demonstrated that the resonant part of the dip observed in the TFY absorption spectrum is indeed associated with a metal-to-water charge transfer. Nevertheless, some uncertainty remains about the nature of the decay channels which could possibly be revealed by energy selective detection of the X-ray fluorescence stemming from the d-orbitals and comparing it with the TFY and the transmission spectra.

A method free from artefacts of TFY detection, such as reabsorption, was recently proposed for solid samples by Achkar et al. [16]. In what they termed 'inverse partial fluorescence yield' (iPFY), one uses the fact that the fluorescence of a lower-energy transition, which is not resonantly excited, is reduced, and the reduction is inversely proportional to the absorption of the resonant excitation. Very recently we extend the application of iPFY and PFY to solution using the liquid micro-jet for the first time [17]. This approach allows collection of soft X-ray spectra using a FY technique free from artefacts due to self-absorption and saturation. Furthermore it allowed us to observe Coster–Kronig transitions in 3d transition metals aqueous solution.

Here we extended this technique further and present TFY, PFY, and iPFY L-edge XA spectra of aqueous Co^{2+} ions. This choice of system is governed by the fact that: (a) Photoelectron spectra, X-ray absorption, and multiplet simulations are available for it [15]. (b) It is well established that in aqueous solution, Co^{2+} forms aqueous-complexes with water molecules coordinating to the metal [18–20]. The major emission lines that contribute to the TFY upon excitation of the Co 2p-orbitals are the $L_l(3s \rightarrow 2p_{3/2})$, $L_\eta(3s \rightarrow 2p_{1/2})$, $L_\alpha(3d \rightarrow 2p_{3/2})$ and $L_\beta(3d \rightarrow 2p_{1/2})$, in addition to the oxygen K_α emission. All have been used to record PFY and iPFY spectra. The results presented here provide further evidence for the proposed mechanism of a dark channel and go beyond the initial publication [13].

2. Experiment

The partial and inverse partial fluorescence yields were obtained using the newly developed high resolution X-ray emission

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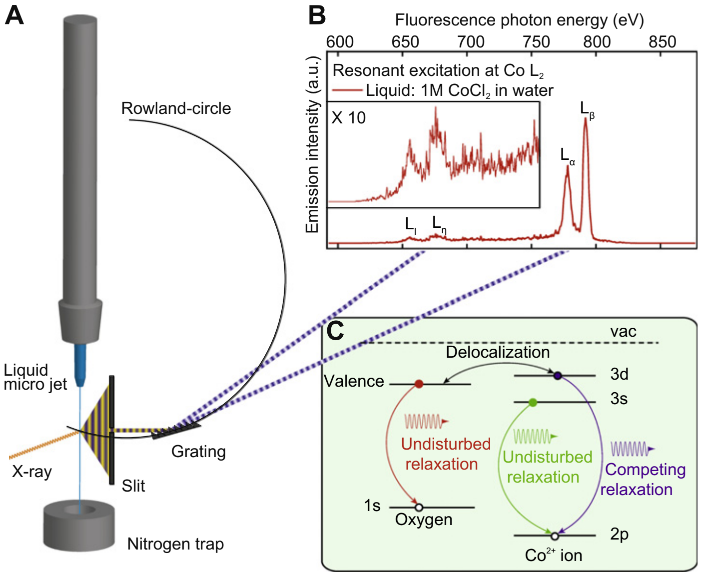

Fig. 1. **(A)** Schematic presentation for the relative positions of the micro-jet to the grating of the Rowland circle of the XES spectrometer (more details shown elsewhere [21]). **(B)** Emission spectrum as a consequence of 2p-excitation. A resolution better than 5 eV allows good separation of the emission lines. The inset shows an expanded view of the low energy region. **(C)** Schematic presentation of the fluorescence decay taking place upon the creation of a Co 2p core-hole as well as the core refill following ionization of water (O). The 2p core-hole in Co^{2+} is filled by either a 3d ($L_{\alpha,\beta}$) or a 3s ($L_{\iota,\eta}$) electron.

spectrometer (XES) and a liquid micro-jet [4,21–23]. A scheme of the micro-jet on the Rowland-circle of the emission spectrometer is presented in Figure 1A. The PFY spectra were recorded by setting the spectrometer to a given emission line and scanning the incident energy in the region of the Co^{2+} $L_{2,3}$ absorption edges [17]. The TFY spectra were measured using a flow cell equipped with Si_3N_4 membrane windows. Note that, as the TFY spectra are measured with a GaAsP photodiode, it is preferable to use the flow cell in order to reduce the noise [4]. Since the L_2-edge seemed to be rather similar for all spectroscopic methods, we used its intensity for normalization. The resolution of the emission spectrometer is approximately 0.5 eV. The transmission spectrum was measured for the sample as a drop deposited between two Si_3N_4 membranes.

3. Results and discussion

Figure 1B shows the fluorescence spectrum of aqueous Co^{2+} excited at the L_2 resonance. It exhibits the above mentioned four cobalt emission lines, recorded with a resolution of better than 5 eV, which allows us to clearly separate them. Concurrently to 2p → 3d electron excitation in the resonance energy range of the Co^{2+} L-edge of 776–800 eV ionization of the solvent will also occur, because the water ionization energy lies at 538.1 eV [24]. Figure 1C illustrates the subsequent fluorescence decay. It shows the refilling of the 2p core-hole by 3d ($L_{\alpha,\beta}$) and 3s ($L_{l,\eta}$) electrons with the energy released as an X-ray photon. Analogous processes will occur for $H_2O(aq)$, with the difference though that core refilling follows ionization of water giving rise to the oxygen K_α emission. These three main photon-out events, Co $L_{\alpha,\beta}$ and $L_{l,\eta}$ and oxygen K_α, were detected indistinguishably in the TFY using the photo-diode in our previous studies [13] and will now be detected separately in the present study.

Figure 2A shows the L-edge transmission and TFY XA spectrum of a 1 M $CoCl_2$ aqueous solution with a schematic diagram for the molecular orbitals of the ground and excited state of Co^{2+} based on Ref. [15]. The transmission XA spectrum reflects the true absorption cross section and is thereafter used as a reference. A detailed discussion of this spectrum and its comparison with the partial electron yield spectrum as well as the theoretical simulation was done by Seidel et al. [15]. The spectrum that was simulated using multiplet theory is reproduced in Figure 2A from Ref. [15]. It allows the conclusions that: (a) only considering crystal field, the

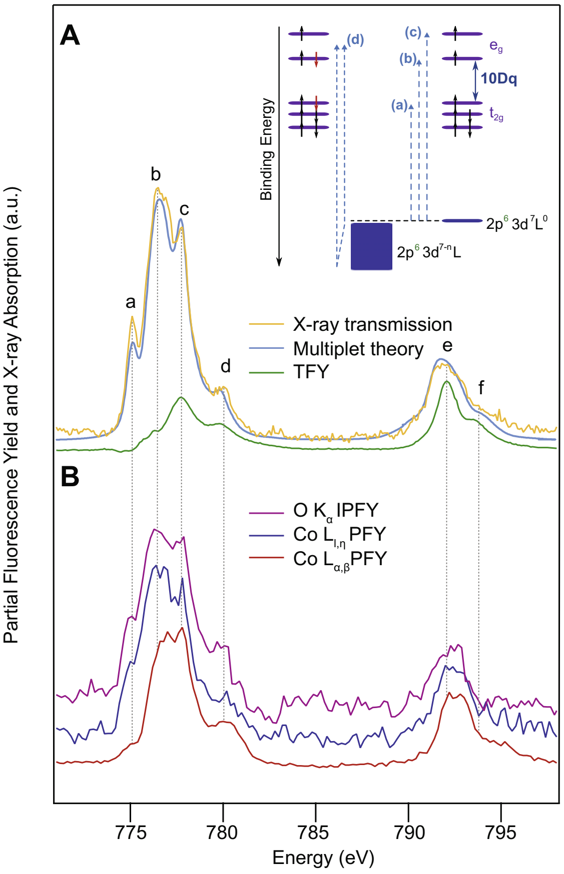

Fig. 2. **(A)** Co^{2+} L-edge transmission, simulated and experimental TFY XA spectra of a 1 M aqueous solution of $CoCl_2$ at pH 5.9, obtained with 0.5 eV resolution. **(B)** L-edge XAS PFY–$L_{\alpha,\beta}$, and $L_{\iota,\eta}$ of Co^{2+} in comparison with the iPFY–K_α.

simulated spectrum is far from being in agreement with the transmission spectrum; (b) upon inclusion of charge transfer, we found that peak a is strongly influenced by metal to ligand charge transfer (MLCT). It has to be stressed that, upon inclusion of charge transfer, one cannot distinguish the spin states in the absorption band. While the multiplet theory is a powerful tool in many applications, it does not take into account the important explicit electronic-structure interactions and orbital mixing between the solute and the water molecules. This mixing, which can be captured by quantum chemical calculations is however very crucial for an understanding of the charge transfer in aqueous solutions.

We obtained the PFY spectra by tuning the fluorescence spectrometer to individual lines of the emission spectrum (Figure 1B) while scanning across the $L_{2,3}$ absorption edges of Co^{2+} Figure 2B shows the oxygen K_α reverted PFY spectrum while the incident energy is scanned in the region of the Co L-edges. This spectrum is in good agreement with the transmission spectrum of Figure 2A. The Co $L_{l,\eta}$ PFY XA spectrum (blue trace in Figure 2B) is also in good agreement with the transmission spectrum, after area normalization. As this spectrum depends on the relaxation of the 3s-electron to the 2p core-hole, it reflects the 'undisturbed relaxation' of Figure 1C. In other words, electrons in the Co 3s orbitals relax to a core-hole giving unquenched photon-out events. Actually, measuring the Co $L_{l,\eta}$ PFY spectrum is another way of getting the true XA spectrum. The Co $L_{\alpha,\beta}$ PFY spectrum is shown as a red trace in Figure 2B. It is less noisy than the Co $L_{l,\eta}$ PFY and the oxygen K_α PFY spectra, because the $L_{\alpha,\beta}$ emission lines we tune to are more intense (Figure 1B). By normalizing at the L_2 edge this spectrum to the oxygen–PFY spectrum, we can see that contrary to the Co $L_{l,\eta}$ PFY spectrum and the transmission spectrum, band (a) is now reduced in intensity relative to the other features of the spectrum. We attribute this decrease to a quenching of the fluorescence due to non-radiative channels, such as electron transfer to the solvent. This is supported by the previous partial-electron-yield (PEY) XAS study, in which band (***a***) was also reduced relative to the transmission spectrum, due to the same mechanism [15]. The Co^{2+} hexaaqua complex is a high spin complex [15] and the analysis of the Auger spectra showed that band (**a**) corresponds to excitation of an electron from the 2p core orbital to the $d(t_{2g})$ orbitals. It was also shown that the latter lie in resonance with the orbitals of water and due to mixing with them, they will have less probability of refilling the 2p hole. At higher excitation energies where, e.g., an electron is promoted into the $d(e_g)$ orbitals, which energetically do not match well with the orbitals of water, the excited electron will promptly refill the 2p hole. This is reflected by the fact that the high-energy peaks are more radiative in the TFY.

To further support our analysis, we varied the pH of the solution from 5.9 to 1.0 (via adding a few drops of concentrated HCl) and the results are presented in Figure 3. We observe that the Co $L_{l,\eta}$ PFY spectrum, which we have shown in Figure 2B to be in good agreement with the transmission spectrum, does not change (within the noise) with pH. However, the deviations with the TFY spectrum become significantly more pronounced at pH 1.0. The deviations between the Co $L_{\alpha,\beta}$ and $L_{l,\eta}$ PFY spectra are more remarkable, where now both the (***a***) and (***b***) bands are dramatically reduced in intensity in the former, compared to the latter.

Indeed, it would be of interest to find out if one can construct the TFY spectrum from the PFY spectra. We further consider the summation of PFY spectra as mentioned to reproduce the dips in the TFY spectra. Given that the TFY and PFY were measured under somewhat different conditions (see experimental), we stress that the summation presented here is qualitative and can by no means be quantitative. In our case, the TFY can be obtained by summing up all the previous three photon-out spectra (the Co $L_{\alpha,\beta,}$ $L_{l,\eta}$ and oxygen K_α PFY's):

$$TFY = R(CoL_{\alpha\beta})I(CoL_{\alpha\beta}) + R(CoL_{l\eta})I(CoL_{l\eta}) + R(OK_\alpha)I(OK_\alpha) \quad (1)$$

where the Rs represent the detection efficiency at the energy of the corresponding emission line. As we have seen above that the reverted oxygen K_α PFY is almost a mirror image of Co $L_{l,\eta}$ PFY we have :

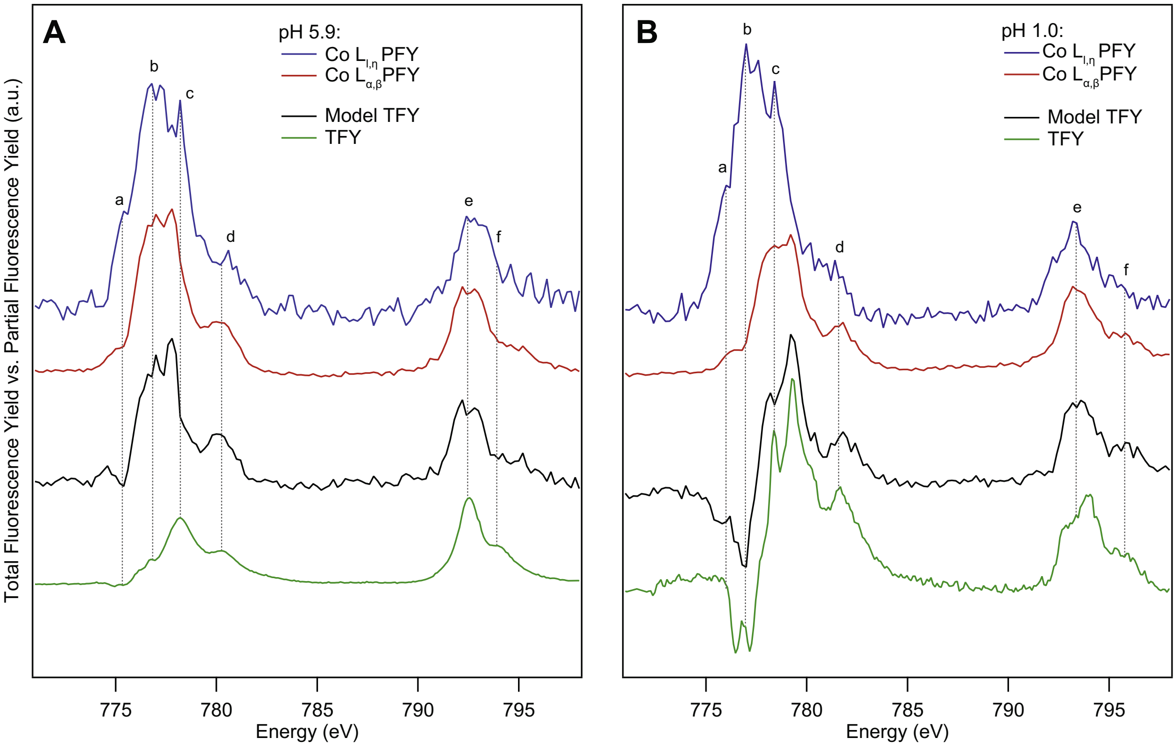

Fig. 3. **(A)** and **(B)** present the L-edge XAS PFY–$L_{\alpha,\beta,}$ and $L_{l,\eta}$ of Co^{2+} for pH 5.9 and 1.0, respectively displayed in comparison with the TFY and the model TFY for both of them.

$$I(OK_\alpha) = AI(CoL_{l\eta}), \tag{2}$$

where $A = -80$ is a normalization constant.

Dividing Eq. (1) by $R(CoL_{\alpha\beta})$

$$\frac{TFY}{R(CoL_{\alpha\beta})} = I(CoL_{\alpha\beta}) + \frac{R(CoL_{l\eta})}{R(CoL_{\alpha\beta})} I(CoL_{l\eta}) + \frac{AR(OK_\alpha)}{R(CoL_{\alpha\beta})} I(CoL_{l\eta}) \tag{3}$$

As the efficiency of the photodiode (that we used for TFY) is not the same as the efficiency of the CCD-detector of the XES analyser (that we used for PFY) we can normalize TFY by a constant $\frac{1}{R(CoL_{\alpha\beta})}$.

So when it comes to calculating the TFY spectrum, Eq. (1) becomes:

$$(TFY)_{calc.} = I(CoL_{\alpha\beta}) + \frac{R(CoL_{l\eta})}{R(CoL_{\alpha\beta})} I(CoL_{l\eta}) + A\frac{R(OK_\alpha)}{R(CoL_{\alpha\beta})} I(CoL_{l\eta}) \tag{4}$$

The TFY would then be:

$$(TFY)_{calc.} = I(CoL_{\alpha\beta}) + CI(CoL_{l\eta}) \tag{5}$$

where $C = \frac{(R(CoL_{l\eta}) + AR(OK_\alpha))}{R(CoL_{\alpha\beta})}$

The constant C should be negative as it will present a missing signal from the oxygen shaded by the Co^{2+} absorption. C is derived from the best agreement between simulated and experimental TFY, obtained by minimizing the square residual function. The simulated TFY spectra for both pHs are presented in Figure 3. Interestingly its value (-2.4) is the same at both pHs which supports our modeling of the TFY spectra. Essentially all important features are captured in the simulated spectrum. In particular, the reduction of the L_3 band compared to the L_2 band and the disappearance of the (***a***) and (***b***) bands, in particular at pH 1.0.

4. Conclusion

In summary, by detecting the X-ray fluorescence of the solvent and that of the solute separately, we confirm one of the two previously proposed scenarios that explains the occurrence of dips and distorted bands in the TFY L-edge spectra of aqueous transition metal ions. In particular, some bands are quenched by non-radiative channels leading to a reduction/disappearance of the corresponding X-ray emission. For the second mechanism, disentangling the competition between fluorescence yield of the metal and that of the solvent, which is indeed present, is very difficult and requires the present approach based on the detection of the individual X-ray emission lines.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.07.067.

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