Dips and peaks in fluorescence yield X-ray absorption are due to state-dependent decay

To the Editor — In a 2010 paper Aziz, Chergui and colleagues observe fluorescence yield (FY) detected X-ray absorption spectra that are concentration-dependent and show both dips and peaks[1]. In this comment I will show that all observed spectral features are a consequence of the relative ratio of background and edge emission, combined with energy-dependent X-ray emission decay channels.

Fluorescence yield detection can be used as the basis for an X-ray absorption measurement. The FY of an energy-dependent edge absorption ($\mu_x(\omega)$) on a constant background (μ_B) is derived in detail in the Supplementary Information (section A). It is given as:

$$I_{FY} = \frac{\mu_B \alpha_B}{\mu_x(\omega) + \mu_B + \mu_x(\omega_B') + \mu_B(\omega_B')} + \frac{\mu_x(\omega)\alpha_x}{\mu_x(\omega) + \mu_B + \mu_x(\omega_x') + \mu_B(\omega_x')} \quad (1)$$

The effective absorption coefficient μ includes the concentration of the species and α is the efficiency of the X-ray emission decay, an intrinsic property of the core hole. Note that the two denominators are different as they contain the self-absorption at the X-ray emission energies of the edge (ω_x') and the background (ω_B'). For a dilute species the effective absorption coefficient μ_x is very small, implying that the μ_x-dependent terms in the denominator can be neglected. The consequence is that the FY is proportional to the X-ray absorption coefficient of the edge absorption plus a constant background (Supplementary Information, section B). In partial fluorescence yield (PFY) an X-ray emission detector is used to select only part of the X-ray emission spectrum. In the dilute limit, the PFY intensity is directly proportional to the X-ray absorption coefficient without any background signal. Increasing the concentration does result in saturation effects in PFY experiments of concentrated samples[2,3].

If the X-ray emission of the background dominates, a negative signal for the total fluorescence yield is likely, as in the case of a dilute iron species dissolved in water as measured in ref. 1. The reason for the domination of the background X-ray emission is that the main water X-ray emission energy ω_B' has an energy below the oxygen K edge, implying that it has small self-absorption. The main iron emission energies ω_x' have an energy above the oxygen K edge and the emitted X-rays are strongly re-adsorbed by the water. Because the iron X-rays are strongly self-absorbed, the first term dominates equation (1). It can be shown (Supplementary Information, section C) that this term can be rewritten as a signal that is negatively proportional to the absorption constant, exactly as observed in ref. 1.

The negative signal from background emission and the positive signal from edge emission occur simultaneously and their relative magnitude determines the sign of the TFY signal. Increasing the edge-element concentration influences the relative values of background emission and edge emission. Because the self-absorption at the edge emission energy $\mu(\omega_x')$ is much larger than $\mu(\omega_B')$, increasing the concentration will increase the edge signal more than it will decrease the background signal. This will slowly turn a negative spectrum (dips) into a positive spectrum (peaks). In other words, an increase in the concentration will decrease the X-ray penetration depth, lowering the chances for self-absorption, which mainly affects the strongly self-absorbed iron edge signal.

The last issue to explain is the occurrence of dips and peaks in the same spectrum. Above we have implicitly assumed that the decay rate (α_x) is, over a short energy range, independent of the X-ray energy. However, it is known that in case of 3d metal L edges, the fluorescence decay can show strong variations over the edge. The fluorescence

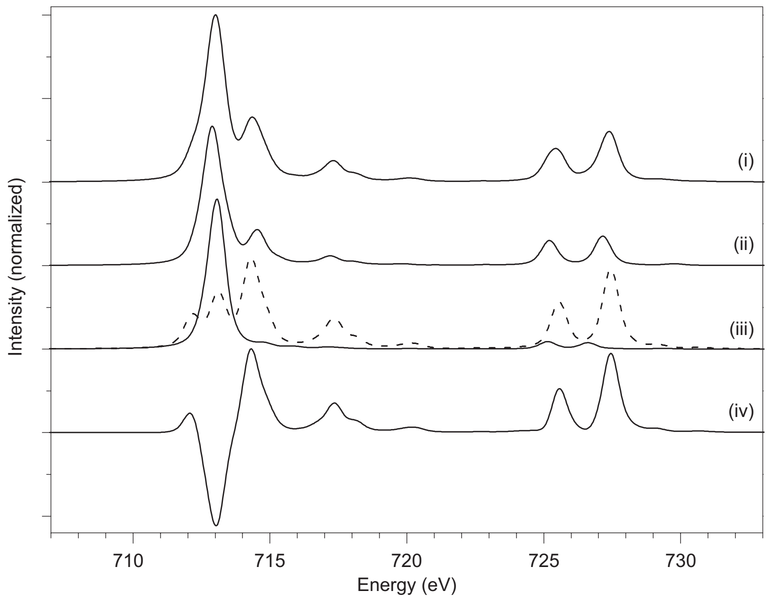

Figure 1 | Simulated state-dependent decay rates yielding dips and peaks in a FY XAS spectrum. From top to bottom (i) Atomic multiplet calculation of the iron $L_{2,3}$ X-ray absorption spectrum of Fe^{3+} ions; (ii) final states with $J = 5/2$; (iii) final states with $J = 7/2$ (solid line) and $J = 3/2$ (dashed line); (iv) Difference spectrum of the $J = 7/2$ minus $J = 3/2$ spectrum, simulating the effects of the state dependent FY decay rates.

decay for states at the high-energy side of the L_3 and L_2 edges is increased by a factor of five[4]. This effect is correlated with the total moment J value of the core-hole state. Low-J core-hole states have stronger fluorescence decay than high-J states. The low-J states occur at the high-end side of the L_3 edge implying that the high-end side of the L_3 edge will have stronger edge fluorescence, which implies a tendency to more positive intensity at the high end of the L_3 edge. Because of its $2p_{1/2}$ core hole one expects the L_2 edge to have on overall a stronger fluorescence than the L_3 edge.

In the case of iron ions in water, part of the spectrum appears as dips and other parts as peaks[1]. Using the state-dependent fluorescence decay, the simultaneous occurrence of dips and peaks appears if one assumes that the fluorescence decay is high for $J = 3/2$ states, intermediate for $J = 5/2$ states and low for $J = 7/2$ states. This behaviour is simulated in Fig. 1 and is in agreement with the experimental observations made in ref. 1. A more detailed theoretical treatment would include crystal field and charge-transfer effects and explicitly calculate the integrated FY XAS signals over the different fluorescence channels, similar to the Ni^{2+} calculations in ref. 4. Such treatment is not expected to modify the main observations made in Fig. 1.

In conclusion, it is shown that the behaviour of fluorescence yield L-edge X-ray absorption spectra is a consequence of the relative ratio of background and edge X-ray emission, combined with energy-dependent X-ray emission decay channels. The combination of these effects explains the dips and peaks of the L edge of iron in water, including their concentration dependence. Because all observations as observed in ref. 1 are naturally explained from the fundamental behaviour of fluorescence yield detection, the introduction of an alternative explanation described only in qualitative terms does not contribute to a better understanding. To study alternative phenomena, it is necessary that different predictions arise and dedicated experiments are performed to distinguish the interpretation. In all cases where FY is used the intrinsic effects of concentration dependence, combined background and edge emission and energy-dependent X-ray emission strengths must be included in such analysis. ❐

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Additional information

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