Comment on "State-Dependent Electron Delocalization Dynamics at the Solute-Solvent Interface: Soft-X-ray Absorption Spectroscopy and Ab Initio Calculations"

In a recent letter, Bokarev *et al.* [1] create a general relationship between state-dependent fluorescence yield and electron delocalization in L-edge x-ray absorption spectra based on $2p$ core-electron excitations into e_g and t_{2g} orbitals for three aqueous ionic species. In this Comment, we show that Bokarev *et al.* do not account for previous findings and that their claims are unsubstantiated.

The crucial role of state-dependent fluorescence yield was established previously [2–4]. *Ab initio* restricted active space self consistent field approaches for transition-metal L-edge spectroscopy have been reported before [5,6] and it was established that the state-dependence fluorescence yield for aqueous Cr^{3+} arises from local atomic effects [4]. In contrast to the assertions in Ref. [1] that the analysis in Ref. [4] is mostly based on semiempirical simulations of spectral line shapes, we note that the same kind of ab initio quantum-chemistry model was employed as in Ref. [1]. Furthermore, rigorous *ab initio* calculations of the fluorescence pathways are missing in Ref. [1] although they were shown to be essential for a correct interpretation of the fluorescence-yield x-ray spectra [4].

In spite of these findings and beyond the presented computational approach, Bokarev *et al.* advocate an interpretation in which the differences between total and partial fluorescence yield x-ray spectra arise, next to large x-ray optical effects, from a t_{2g}- and e_g-dependent delocalization of the core-excited electron into the water solvation shell. X-ray optical effects, including, in general, more than the mentioned solvent-background variation and, in particular, the strong polarization dependence [7,8], are not quantitatively treated although this is necessary and straightforwardly possible [4].

The interpretation by Bokarev *et al.* is based on two arguments. The first is that the covalent overlap between the oxygen $2p$ derived lone-pair state of water is larger with the Fe e_g than with the t_{2g} orbitals. Second, Bokarev *et al.* determine the time-independent dipole transition-matrix elements for the $2p^{-1}t_{2g}^1$ core-excited states as smaller than for $2p^{-1}e_g^1$. Neglecting the dominant (> 99%) nonradiative decay channels of the core-excited states, they postulate an unquantified longer lifetime of the $2p^{-1}t_{2g}^1$ over the $2p^{-1}e_g^1$ states. With these assumptions they invoke a more "pronounced" or more "complete" electron delocalization in the $2p^{-1}t_{2g}^1$ over the $2p^{-1}e_g^1$ resonances that should be visible as state depend-fluorescence yields depending on the orbital population of t_{2g} and e_g states.

The claims by Bokarev *et al.* are not sufficiently supported. First, the correlation between $2p$ excitations into t_{2g} orbitals and the appearance of spectral differences is not substantiated. Bokarev *et al.* display dominant t_{2g} occupations for Fe^{3+} in Fig. 1(b) at 709.9, 710.4, and 710.7 eV and for $[FeCl(H_2O)_5]^{2+}$ and $[FeCl_2(H_2O)_4]^{+}$ above 709 eV but the spectral distortions are minor or not present at these energies. In turn, the spectra deviate by 50% at 714.1 and 723.9 eV but no connection is made to orbital occupation. For Co^{2+} (Fig. S2) they report dominant t_{2g} occupation for only one data point (775.4 eV). Instead, strong spectral differences at higher energies contrast with a dominant e_g occupation, an inconsistency that appears to be selective interpretation. We also note that the experimental Co^{2+} spectra in Figs. S2 and 3 are shifted by 1.2–1.3 eV, impeding more detailed inspections. Second, Bokarev *et al.* estimate the lifetime of core-excited states from the minority channel of radiative decay although the lifetime is dominated by the nonradiative decays. Without calculating all decay channels and in particular the dominant Auger decays, this does not appear to be an adequate determination of the lifetime. It is important to note that the combined $2p3p3p$, $2p3p3d$, and $2p3d3d$ Auger decay channels are essentially energy independent, as has been exemplified, i.e., for the Auger decay of Ni^{2+} [3]. Third, the claim by Bokarev *et al.* that for core excitations with longer lifetimes the delocalization of the excited electron would be more pronounced or more complete appears to be mere speculation as no evidence is given to support this claim.

In summary, we show that the claim by Bokarev *et al.* that the spectral differences between fluorescence-yield x-ray spectra and the true absorption cross section are largest for excitations of the $2p$ core electron into t_{2g} orbitals and that, because the corresponding core-excited states have longer lifetimes, the core-excited electron delocalizes into the water solvation shell more "completely" is not substantiated; and that state-dependent fluorescence yield is an atomic effect without relevant electron delocalization.

A Comment by Green *et al.* [9] and the Reply by Bokarev *et al.* [10] have been published concurrently.

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