

## 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 RAS-SCF 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 [1] that the analysis in [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 [1]. Furthermore, rigorous ab initio calculations of the fluorescence pathways are missing in [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 (TFY) and partial fluorescence yield (PFY) 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: Firstly, that 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. Secondly, 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 %) non-radiative decay channels of the core-excited states, they postulate an un-quantified 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 shall 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 Fig. S2 and Fig. 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 non-radiative 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, 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.

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[1] S. I. Bokarev, M. Dantz, E. Suljoti, O. Kühn, E. F. Aziz, Phys. Rev. Lett. **111**, 083002 (2013).

[2] F. M. F.de Groot, Nat. Chem. **4**, 766-767 (2012).

[3] F.M.F. de Groot, Solid State Commun. **92**, 991-995 (1994).

- [4] Ph. Wernet, K. Kunnus, S. Schreck, W. Quevedo, R. Kurian, S. Techert, F. M. F. de Groot, M. Odelius, A. Föhlisch, *J. Phys. Chem. Lett.* **3**, 3448 (2012).
- [5] I. Josefsson, K. Kunnus, S. Schreck, A. Föhlisch, F.M.F. de Groot, Ph. Wernet, M. Odelius, *J. Phys. Chem. Lett.* **3**, 3565 (2012).
- [6] M. Roemelt, D. Maganas, S. DeBeer, F. Neese, *J. Chem. Phys.* **138**, 204101 (2013)
- [7] R. Kurian, K. Kunnus, Ph. Wernet, S. M. Butorin, P. Glatzel, F. M.F. de Groot, *J. Phys.: Condens. Matter* **24**, 452201 (2012).
- [8] R. Mitzner, J. Rehanek, J. Kern, S. Gul, J. Hattne, T. Taguchi, R. Alonso-Mori, R. Tran, C. Weniger, H. Schröder, W. Quevedo, H. Laksmono, R. G. Sierra, G. Han, B. Lassalle-Kaiser, S. Koroidov, K. Kubicek, S. Schreck, K. Kunnus, M. Brzhezinskaya, A. Firsov, M. P. Minitti, J. J. Turner, S. Moeller, N. K. Sauter, M. J. Bogan, D. Nordlund, W. F. Schlotter, J. Messinger, A. Borovik, S. Techert, F. M. F. de Groot, A. Föhlisch, A. Erko, U. Bergmann, V. K. Yachandra, Ph. Wernet, J. Yano, L-edge X-ray Absorption Spectroscopy of Dilute Systems Relevant to Metalloproteins Using a X-ray Free-Electron Laser, *J. Phys. Chem. Lett.* **4**, 3641-3647 (2013).