Bokarev *et al.* Reply: In the Comment [1] Föhlisch *et al.* claim that our recently proposed model explaining the role of electron delocalization into the solvation shell after core-level excitation [2] is not substantiated by the provided experimental and theoretical data. The Comment is based on three aspects: the nature of the core-hole excited state, the interplay between time scales of electron delocalization and radiative or nonradiative core-hole decay, and the role of x-ray optical effects. In the second comment [3], Green *et al.* put forward a simpler explanation of the observed differences between partial fluorescence yield (PFY) and x-ray absorption spectroscopy (XAS) L-edge spectra. They invoke ligand field multiplet theory to conclude that the differences are "consequences of the different formalisms which govern PFY and XAS."

Föhlisch *et al.* endeavor to invalidate our findings arguing that state-dependent fluorescence yield is an atomic effect without relevant electron delocalization. Their conclusion has been drawn on the basis of spectroscopic and theoretical investigations of Cr^{3+}(aq) [4]. Reference [4] does, however, lack a discussion of the underlying resonant x-ray emission spectra, which allow for tracking orbital mixing by experiment as we have recently demonstrated for Fe^{2+}(aq) [5]. Furthermore, recent resonant photoelectron studies of Fe^{3+}(aq) [6] and Co^{2+}(aq) [7] have revealed orbital mixing between metal ion and surrounding water molecules, associated with electron delocalization upon core-hole excitation. The effect is especially pronounced for Fe^{3+}(aq) in which case strong intensity enhancement at the energetic position of the water $3a_1$ orbital occurs [6].

In their multiconfigurational second-order perturbation theory restricted active space (RASPT2) and restricted active space self-consistent field (RASSCF) calculations, Wernet *et al.* [4] included the influence of the ligands beyond the crystal field electrostatic effect, i.e., one-electron orbital mixing. Their RASPT2 calculations account for ligand-metal electron correlation via excitations from and to ligand orbitals. The relevance of these correlation and exchange effects between metal and ligands is a clear manifestation of the nonatomic character of the wave function. Nevertheless, even though Wernet *et al.* admit the notable orbital mixing and substantial changes upon inclusion of metal-ligand electron correlation (Fig. 1 in [8]), they insist that orbital delocalization does not play a role in interpreting the experimental data. The arguments of [3,4] are based on atomic ligand multiplet theory [9]. It is interesting that our data can be reproduced by a well-established semiempirical theory, which is atomic in nature and contains a number of empirical parameters that cannot be consistently obtained from *ab initio* theory. However, the fact that the data can be fitted by an equation that is *a priori* biased towards an atomic model cannot be taken as a falsification of our unbiased *ab initio* methodology.

Although the methodology and results in [4] are correct, the interpretation leaves room for discussion as it is based on the isolated case of Cr^{3+}, and therefore cannot be considered as general. Wernet *et al.* do not provide the careful analysis of states that we present for the first time. Specifically, we suggest a system-dependent interpretation showing that state-dependent effects on fluorescence decrease in a series $Fe^{3+} > Co^{2+} > Fe^{2+}$ [2], and local atomic and intermolecular effects could be more intertwined [5,10]. As shown in [2], the RASSCF wave function has a complex multiconfigurational nature. To allow for simple and straightforward interpretation, we used a reduced representation of the nature of the states by means of orbital occupation numbers. Occupancies presented in Figs. 1 and S2 in [2] show the difference in core-excited and ground state occupation numbers, thus illustrating the localization of the core-excited electron. We emphasized the separation between the fraction of $2p \to 3d(t_{2g})$ transitions (prepeak of L_3) and the rest of the L_3 band, which has a more complex nature [1]. This allows for looking specifically at t_{2g} localized states separated from more intense $2p \to e_g$ transitions. In this respect Fe^{3+}(aq) can be clearly distinguished from Fe^{2+}(aq) and Co^{2+}(aq). We suggest an interpretation where the isolated t_{2g} states in Fe^{3+}(aq) exhibit different behavior when compared to the rest of the L_3 edge due to stronger electron delocalization.

In previous works [4,8,11] delocalization has been rationalized within a stationary picture where electronic relaxation effects (like orbital mixing) are completed. In [2], we instead shift the focus on the time-dependent interpretation, following recent works by Cederbaum *et al.* [12,13], who showed that charge migration after the instantaneous ionization or interatomic Coulombic decay takes place on a time scale comparable to the core-excited state lifetime of a few femtoseconds. This suggests the importance of the interplay between delocalization and radiative or nonradiative core-excited state decay, which is governed by the ratio of the respective time scales.

As correctly pointed by Föhlisch *et al.* [1], the total lifetime of the core-excited state depends mostly on the nonradiative (Auger-type) decay rate, whereas radiative decay is a minor channel. However, the particular decay channel is not essential for our interpretation. To quantify our argument we have fitted the total lifetime broadening of RASSCF results to the partial-electron-yield x-ray absorption spectrum of Fe^{3+} (aq) [6]. We find that the lifetime of isolated t_{2g} states in the 707–709 eV spectral region exceeds that of the e_g states above 709 eV by 3 fs. As a possible reason for the longer lifetime, we consider the variation of Auger decay rate due to the state-dependent $2p3d3d$ channel [14]. Based on this lifetime estimate and the characteristic time scales for electron wave packet dynamics, we conclude that the delocalization will be more pronounced for t_{2g} than for e_g states.

Finally, Föhlisch *et al.* [1] anticipate strong polarization effects similar to the solid state phase [15]. However, these findings cannot be readily transferred to the present solution-phase situation [10,16–19] (see discussion in Supplemental Material [20]).

In summary, we do not agree with the criticism put forward in Refs. [1,3]. Based on our multispectroscopic experimental approach and a comprehensive *ab initio* theory, we demonstrated that state-dependent electron delocalization is a possible electron pathway of the $2p$ core-excited state at the L_3 edge of aqueous transition metal ions.

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