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$^{3+}$(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 \textit{ab initio} theory. However, the fact that the data can be fitted by an equation that is \textit{a priori} biased towards an atomic model cannot be taken as a falsification of our unbiased \textit{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$^{3+}$ [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 $2p \rightarrow 3d(t_{2g})$ 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 $2p \rightarrow e_g$ 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 L₃ edge of aqueous transition metal ions.

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