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Cite as: Struct. Dyn. 7, 044102 (2020); https://doi.org/10.1063/4.0000022
Submitted: 07 May 2020 . Accepted: 18 June 2020 . Published Online: 06 July 2020

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Submitted: 7 May 2020 · Accepted: 18 June 2020 ·
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ABSTRACT
Recently, coherent structural dynamics in the excited state of an iron photosensitizer was observed through oscillations in the intensity of Kα x-ray emission spectroscopy (XES). Understanding the origin of the unexpected sensitivity of core-to-core transitions to structural dynamics is important for further development of femtosecond time-resolved XES methods and, we believe, generally necessary for interpretation of XES signals from highly non-equilibrium structures that are ubiquitous in photophysics and photochemistry. Here, we use multiconfigurational wavefunction calculations combined with atomic theory to analyze the emission process in detail. The sensitivity of core-to-core transitions to structural dynamics is due to a shift of the minimum energy metal–ligand bond distance between 1s and 2p core-hole states. A key effect is the additional contraction of the non-bonding 3s and 3p orbitals in 1s core-hole states, which decreases electron–electron repulsion and increases overlap in the metal–ligand bonds. The effect is believed to be general and especially pronounced for systems with strong bonds. The important role of 3s and 3p orbitals is consistent with the analysis of radial charge and spin densities and can be connected to the negative chemical shift observed for many transition metal complexes. The XES sensitivity to structural dynamics can be optimized by tuning the emission energy spectrometer, with oscillations up to ±4% of the maximum intensity for the current system. The theoretical predictions can be used to design experiments that separate electronic and nuclear degrees of freedom in ultrafast excited state dynamics.

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I. INTRODUCTION
Transition-metal complexes are key components in many photocatalytic processes. An area of intense interest is the conversion of solar to chemical energy stored in fuels.1,2 A solar fuel system consists of three major components, a photosensitizer, a catalyst for reductive fuel formation, and a catalyst for the oxidation of an electron donor. The photosensitizer absorbs a photon to form a long-lived valence-excited state, from which an electron can be transferred to the fuel-forming reaction. As many photosensitizers are metal complexes, detailed characterization of charge-transfer excited states of such systems is not only of interest for fundamental research but also directly applicable to light-harvesting applications.3,4

To understand the efficiency of the charge transfer process, the electronic and structural dynamics along the excited state relaxation pathway must be probed. X-ray spectroscopy is ideally suited for this task as it is possible to selectively probe a specific site in a complex environment. With the use of laser pumps in combination with ultrafast x-ray probes, it is also possible to study processes on very short time scales. For ultrafast time-resolved experiments, nonresonant x-ray emission spectroscopy (XES), both Kα (2p → 1s) and Kβ (3p → 1s), has been successfully used to study transitions between electronic states.5–11 This relies on the sensitivity of XES to the metal oxidation state and spin multiplicity.12–14 Complementary to XES, structural dynamics can be probed by elastic x-ray scattering.15–22 XES and scattering can also be detected simultaneously, making it possible to probe the connection between electronic and structural dynamics.7,10,23

The most commonly used photosensitizers are ruthenium coordination complexes. However, for large-scale applications, catalysts based on widely abundant non-toxic base metals such as iron are desirable.24–26 Iron carbenes have attracted considerable interest due
to the possibility to design systems with extended excited state lifetimes and high electron injection efficiencies. This is due to the strong σ-donor binding associated with carbene ligands, which leads to a destabilization of the metal-centered (MC) states that are involved in rapid recombination. Instead, this gives long lifetimes for the metal-to-ligand charge-transfer (MLCT) states, from which electrons can be transferred.

A prominent example of an Fe carbene photosensitizer is [Fe(bmip)2]2+ [bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine]. The COOH-functionalized derivate of this complex can inject electrons into a TiO2 substrate with very high efficiency. This complex was recently probed using the combination of femtosecond Kα and Kβ XES with x-ray solution scattering (XSS). To be more precise, Kα XES was measured at a fixed emitted photon energy, corresponding to the maximum of the Kα1 XES peak, while the Kβ signal was integrated over the full spectral range. These measurements show temporal oscillations in the XES and XSS difference signals with the same 278 fs period oscillation (see Fig. 1). By combining the results from these two experiments, the oscillatory signal is assigned to a vibrational wavepacket along a Fe-ligand stretching mode on a triplet metal-centered (MC) excited state surface. This was the first observation of purely structural dynamics with core-to-core x-ray emission.

Understanding the origin of this structural sensitivity is important for further development of femtosecond time-resolved XES methods and, we believe, generally necessary for interpretation of XES signals from highly non-equilibrium structures that are ubiquitous in photophysics and photochemistry. Core-hole spectroscopy can probe metal-ligand interactions due to the strong interactions between core and valence electrons, but core-to-core XES is largely considered an atomic phenomenon because transitions occur between two core orbitals that are not directly involved in metal-ligand bonding. The sensitivity of Kα (and Kβ) XES to nuclear wavepacket dynamics can therefore be considered unexpected and requires a detailed explanation. A better understanding of this phenomenon can also be useful in the interpretation of other experimental data that show time-resolved oscillations. As first shown in Ref. 23, this sensitivity appears to be a result of the relative displacement (vibronic coupling) of the associated core-ionized potential energy surfaces. However, the detailed physical origin of this vibronic coupling and its dependence on the chemical bonding is still not established. In this work, we use the example of [Fe(bmip)2]2+ to explain the structural sensitivity of the core-to-core x-ray emission spectra and discuss in detail the effect of various metal-ligand electronic interactions.

Electronic and geometric structures are connected to XES spectra through multiconfigurational calculations based on the ab initio restricted active space (RAS) approach. This method includes a formally correct coupling of the multiple open shells created during the x-ray process, while at the same time, it directly describes metal-ligand interactions in a molecular orbital picture. We recently introduced efficient algorithms to control the occupation numbers of multiple core orbitals, which makes it possible to simulate core-to-core XES processes. The goal of this contribution is to convert the multiconfigurational results into an intuitive physical explanation for the shift by connecting it to a more straightforward atomic model.

II. COMPUTATIONAL DETAILS

The geometries for the ground state (GS) and 3MC energy minima were obtained from density-functional theory (DFT) PBE0/6-311G(d,p) optimizations, including the MeCN solvent through the polarizable continuum model. Two additional geometries were created on each side of the 3MC energy minimum by changing the geometry along the GS—3MC distortion coordinate, with Fe-ligand distances changing on average by −0.01 Å for 3MC short and by +0.025 Å for 3MC long. These two geometries represent the extreme turning points of the average oscillation of the Fe-ligand bond length according to wavepacket quantum dynamics simulations and XSS measurements. The GS minimum structure belongs to the D3 point group, but as the iron is six-coordinated, O8 point group labels will be used to describe the metal orbitals. The Cartesian coordinates of the four structures are given in the supplementary material.

Kα emission spectra were calculated using the RAS approach in the OpenMolcas package (version v18.0.0180105–1800). All calculations use the ANO-RCC basis set with polarized double-zeta contraction (ANO-RCC-VDZP) and the atomic compact Cholesky decomposition. Orbital optimizations were performed using the state-average RAS self-consistent field (SCF) formalism, separately for each spin multiplicity. The sensitivity of the results with respect to adding dynamic correlation was tested at the GS and 3MC minimum geometries through second-order perturbation theory with the RASPT2 method (see Sec. I in the supplementary material for more details).

The valence active space consisted of 10 electrons distributed in 10 orbitals, five Fe 3d dominated orbitals and five corresponding orbitals (see Fig. 2). These orbitals can be classified in two filled Fe-ligand σ-bonding orbitals together with two metal-dominated e_g orbitals forming σ* orbitals with the ligand and three filled metal-dominated non-bonding t_2g orbitals together with three empty orbitals that can correlate with the filled t_2g orbitals (see Fig. 2). These are
metal 4d orbitals that describe the double-shell effect. These orbitals were placed in the RAS2 space, where all possible excitations were allowed.

The Fe 1s orbital was placed in the RAS3 space, allowing for a maximum of two electrons, while the three Fe 2p orbitals were placed in the RAS1 space, allowing for a maximum of one hole (see Fig. 2). To model the core-ionized states and ensure the hole stayed in the core orbitals instead of higher-lying orbitals, the core hole orbitals were kept frozen in the RASSCF optimizations of the 1s and 2p core-ionized states. To avoid calculating all lower-lying excited states, we have used a projection operator technique, along the lines of the core-valence separation technique, which sets the configuration interaction (CI) coefficients of all unwanted configurations with doubly occupied core orbitals to zero.

To select relevant spin multiplicities, the spin-selection rules of the electric dipole transitions (AS = 0) and the selection rules for the spin–orbit operator (AS = 0, ±1) were considered. The valence electronic states were calculated with the singlet and triplet spin multiplicities, while the core-ionized states were calculated with doublet and quartet spin multiplicities. For the 3MC states, the 1s core hole was averaged over 9 doublet and 6 quartet states. For the 2p core-hole states, 50 doublet and 18 quartet states were used. To be able to converge the CI calculations, we have used our recently developed CI algorithm designed for use with a large number of states, which puts a cap on the number of CI vectors and then dynamically allocates more CI vectors to states that have not yet been converged.

Spin–orbit coupled states were obtained using a Douglas–Kroll–Hess Hamiltonian and atomic mean field integrals by the RAS state-interaction (RASSI) approach. In addition to calculate the spin–orbit coupling, the RASSI method is also used to calculate electric dipole oscillator strengths. The photoionization process for the closed-shell ground state has been calculated using the Dyson-orbital formalism, recently implemented for closed-shell species in OpenMolcas. For triplet initial states, a statistical ratio of 4:2 for quartet and doublet core-excited states has been assumed.

For comparison to experiment, RAS spectra were broadened with a Gaussian of 0.39 eV half-width-at-half-maximum (HWHM) and Lorentzian function of 0.81 eV HWHM. The spectrum for the GS geometry was shifted by 17.35 eV to align with the experimental Kα emission maximum, and the intensity was scaled by 1/0.067 so that the GS maximum intensity is 1. The same energy shift and intensity scaling factor were then used for all calculated spectra. The RASSCF wavefunctions were analyzed by examining the orbital composition and by calculating the radial electron density using the Multiwfn program.

Calculations of atomic ions have been performed using the CTM4XAS interface to an atomic multiple code. This makes it possible to connect the multiconfigurational wavefunction results with this commonly used method to describe x-ray spectra. In this method, energies are obtained from Hartree–Fock calculations, with electron correlation approximated by scaling down the electron–electron repulsion integrals to 80%.

III. RESULTS AND DISCUSSION

The first part of this section analyzes the simulated Kα XES spectra in detail, with focus on different contributions from intermediate core-ionized states. The emission from these states is then analyzed in detail, with regard to their sensitivity to the geometric structure. In the next step, spin and charge densities in the important core-excited states are analyzed in order to connect the changes in emission spectra to metal–ligand bonding characteristics and the chemical shift. Finally, the general requirements to observe structural dynamics are outlined and discussed in relation to other types of complexes and emission processes.

A. X-ray emission spectra

Experimentally, the ground state has a Kα1 intensity maximum at 6404.3 eV, with the Kα2 maximum at 12.8 eV lower in energy. From the closed-shell valence configuration of the ground state, 1s photoemission only reaches one doublet intermediate state, and no significant shake-up transitions are observed. From this state, the only important transitions are those to states with a 2p hole coupled to the closed-shell valence. These final states are split by 0.1 eV due to deviations from the 2p-degeneracy in formal O3g symmetry and then further by the 2p spin–orbit coupling, leading to the simulated spectrum in Fig. 4 (gray line). After aligning the energy of the Kα1 peak to experiment, the agreement is very good, as can be expected from such a relatively simple process. The energy of the Kα2 peak is slightly too high, which is likely due to limitations in the description of the strong 2p spin–orbit coupling.

The 3MC valence excited states reached after photoexcitation have a formal 12g 1e2g orbital occupation, which gives rise to six different states (see Fig. S1 in the supplementary material). 1s ionization from any of the six 3MC states leads to doublet and quartet core-ionized intermediate states. Figure 4 presents here the Kα emission for the lowest-energy 3MC state, via the doublet 3MC(D) and quartet 3MC(Q) 1s core-ionized intermediate states. There are significant differences in the emission spectra of different intermediate states. The 3MC(Q) spectrum shows a significant blueshift of the emission peak, while the 3MC(D) spectrum shows a significant redshift of the emission peak. As the quartet contribution dominates, the 3MC emission spectrum is blue shifted relative to the GS. The 3MC contributions are generally broad, especially for the 3MC(D) state. All of this leads to a significant drop in intensity at the GS Kα maximum energy when measuring the

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**FIG. 2.** Restricted active space used in the calculations of Kα x-ray emission. The electron configuration represents the 1s core-hole intermediate of the ground state.
3MC emission. To test the robustness of the results with respect to the state character (or the valence electronic configuration), we have also calculated the emission spectra for the two following higher-energy 3MC states; the data are gathered in Fig. S2 in the supplementary material. Although there are some differences between the three 3MC states, these are much smaller than the differences between the contributions from intermediate states of different spin multiplicities.

As shown previously by XSS measurements and wavepacket quantum dynamics simulations, upon photoexcitation, the system evolves on a 3MC excited state surface and oscillates along a Fe-ligand stretching mode. To model the sensitivity of XES to structural dynamics, we calculated emission spectra at several geometries, in addition to the GS minimum energy geometry, in the vicinity of the 3MC minimum around which the vibrational wavepacket oscillates (see Fig. 5). These calculations show that although the spectral shapes do not change much, there is a clear blueshift of the emission energies as the Fe-ligand distance increases. It is noted that the emission spectra at different 3MC geometries seem to cross at specific energies. However, these are not isosbestic points but are rather due to the relatively small shift in emission energy between the three curves, which

![Active orbitals in the ground state placed in the RAS2 space: $\sigma$, $t_2g$, $e_g$, and 4d (the radial nodes of the latter are difficult to see here).](image-url)
makes different two-curve crossings appear close in energy. The energies of the Kα emission maxima as a function of the Fe-ligand distance are shown in Figs. 6. The corresponding data for the higher-lying 3MC states are shown in Fig. S3 in the supplementary material.

Two possible explanations can be proposed to rationalize these results, either a redistribution of intensities between different final states or more simply an energy shift of the dominant transitions. A detailed analysis of the emission spectra at different geometries shows that, despite the contribution from a very large number of transitions, it is possible to identify the major contributions to intensity in the different parts of the spectra and to follow them as the geometry changes; all transitions show a clear blueshift with the increasing Fe-ligand distance, therefore validating the second of our possible explanations.

B. Analyzing structural sensitivity of emission intensity

Let us now look at the emission intensity at the energy of the GS Kα maximum (6404.3 eV), which is experimentally observable. Figure 7 shows the intensities as a function of the Fe-ligand distance for the GS, 3MC(D), and 3MC(Q) states. Because of the energy shift of the GS emission spectrum as the Fe-ligand distance increases, the intensity of the GS spectrum decreases at the reference energy of 6404.3 eV. At the GS minimum geometry, the 3MC(Q) emission spectrum is blue shifted with respect to the GS emission spectrum. Since it gets further blue shifted as the Fe-ligand distance increases, the intensity of the 3MC(Q) spectrum decreases further at the reference energy.

The 3MC(D) emission spectrum is however red shifted with respect to the GS emission spectrum. Since it gets blue shifted as the Fe-ligand distance increases, the intensity of the 3MC(D) spectrum actually increases at the reference energy. The increase is small due to the rather flat shape of the 3MC(D) spectra in this energy range.

The sensitivity of the emission intensity to structural changes shown in Fig. 7 can be expressed as

$$\frac{\delta I(E)}{\delta r} = \frac{\delta I(E) \delta E_{max}}{\delta E_{max} \delta r}$$

The first factor \(\frac{\delta I(E)}{\delta E_{max}}\) is the change in intensity with respect to an energy shift of the emission curve. For small changes, this can be approximated as the negative value of the slope of the emission intensity at a given energy. This will be exemplified by the GS spectrum. At 6404.3 eV, the curve has a positive slope for the 3MC minimum structure (see Fig. 5). A shift of the emission curve to higher energies then leads to a decrease in the intensity [negative \(\delta I(E)/\delta E_{max}\)]. Numerical values for different states, all obtained at the 3MC minimum energy structure, are given in Table I. The shape of the spectrum...
spectra of the intermediate states is very different, which in turn leads to large effects on the sensitivity. For the \(^3\)MC(Q) intermediate, the value is negative, while the \(^3\)MC(D) has a smaller positive value as the former contributes more, this leads to an overall negative value for the \(^3\)MC emission.

The second factor, \(\Delta E_{\text{max}}/\Delta r\), shows the sensitivity of the emission peak energies with regard to structural changes. As the shapes of the emission spectra are constant for oscillations around the \(^3\)MC minimum, this can be approximated by the slope of the emission maximum with respect to distance (see Fig. 6). These values are similar for different intermediate states, with all showing a positive slope between 2.3 and 4.4 eV \(\cdot \) \(\text{Å}^{-1}\) (see Table I). The origin of these peak shifts and whether similar shifts can be expected in general are analyzed in more detail below.

We note a good agreement between the global sensitivity extracted from Fig. 7 and the value obtained by taking the products of the two contributing factors (see Table I). This validates the qualitative interpretation of the sensitivity of emission intensity to distance changes in terms of simpler physical concepts.

**C. Origin of structural sensitivity**

From the previous analysis, it is clear that the maximum of the XES spectra of all involved states shifts to higher energy with the increasing metal–ligand bond distance. As the most important states involved in the emission process stay the same, at least for smaller geometry changes, following the energy of these states gives potential energy surfaces of the core-excited states (see Fig. 8). The results in this figure are similar, but not identical, to the ones in Ref. 23 because here we do the analysis at the level of spin-free states rather than spin–orbit coupled states. The former are used here because they facilitate comparisons between intermediate states with different spin-couplings. This additional transparency is helpful as the simulations do not explicitly treat the electron dynamics of the short-lived 1s core-excited state.

In the RASSCF calculations, the minimum of the \(^3\)MC valence state is at 2.11 \(\text{Å}\), slightly higher than the DFT optimized structure used as the \(^3\)MC reference. In both 1s and 2p core-hole states, this minimum shifts to much shorter distances. The state with a 1s hole has a minimum 0.08 \(\text{Å}\) shorter than the valence \(^3\)MC state. Furthermore, there is also a clear difference in the potential energy surface (PES) depending on the location of the core hole, with the 1s hole giving the shortest distance by a margin of 0.019 \(\text{Å}\). The curvatures of the PES of the core-hole states are very similar, with force constants \(k\) of 162.2 and 157.3 eV \(\cdot \) \(\text{Å}^{-2}\) for 1s and 2p holes, respectively. The curvature for the valence state is smaller (114.1 eV \(\cdot \) \(\text{Å}^{-2}\)).

The increase in emission energy for longer distances during the coherent structural dynamics on the \(^3\)MC PES can be understood using the difference in the position of the energy minima \(\Delta r = r_{\text{max}} - r_{\text{min}}\). As the PESs are approximately quadratic near their minima, \(E = \frac{1}{2}k(r - r_{\text{min}})^2 + E_{\text{min}}\), the energy difference between the 1s and 2p states becomes larger for longer distances even if the curvature would be the same. Assuming that the force constant is equal in the core-excited states \(k_{\text{1s}} = k_{\text{1p}} = k_{\text{2p}}\) gives the following expressions for the sensitivity of the emission energy to the structure:

**TABLE I.** Sensitivity of emission intensity to distance changes \(\partial I/\partial r\) and its two contributing factors. Two sensitivity values are shown, both the product of the two factors and the fitted value from Fig. 7.

| Factor | GS | \(^3\)MC(Q) | \(^3\)MC(D) | \(^3\)MC |
|--------|----|-------------|-------------|---------|
| \(\Delta I/\Delta E_{\text{max}}\) (eV\(^{-1}\)) | -0.52 | -0.33 | +0.04 | -0.21 |
| \(\Delta E_{\text{max}}/\Delta r\) (eV \(\cdot \) \(\text{Å}^{-1}\)) | 3.3 | 2.3 | 4.4 | 3.0 |
| \(\Delta I/\Delta r\) (\(\text{Å}^{-1}\)) (Product) | -1.72 | -0.76 | +0.18 | -0.63 |
| \(\Delta I/\Delta r\) (\(\text{Å}^{-1}\)) (Fit) | -1.51 | -0.97 | +0.11 | -0.61 |
\[ E(r) = (E_{1s} - E_{2p}) = k_{ce} r \Delta r + E_{\text{constant}}, \]

\[ \frac{\delta E}{\delta r} = k_{ce} \Delta r. \]

Using the values of \( k_{ce} \) and \( \Delta r \) in the above equation, we get a value of \( \delta E/\delta r \) of 3.0 eV \( \cdot \) A\(^{-1}\), in very good agreement with Fig. 6 and Table I. The sensitivity to the structure can thus be simply explained by the shift in the potential energy curves between states with different core holes. The effects of the core holes on metal–ligand bonding are therefore analyzed in detail below.

### D. Core-hole effects on metal–ligand bonding

The core-hole effects on the valence orbitals are analyzed using the radial charge and spin densities of the \(^3\)MC state with and without core holes [see Fig. 9(a)]. As expected, the valence-electron distribution is shifted more toward the metal in the core-hole states. The effect on the charge and spin densities upon creation of a core hole is well understood in the molecular-orbital picture. Creation of a positive hole leads to a strong attractive force and a significant contraction of all metal orbitals. To illustrate these effects, orbital energies and pairwise interactions for the M-shell (3s, 3p, 3d) orbitals in an iron(II) atomic ion have been calculated using the atomic multiplet model (see Table II). Creation of a positive core hole lowers the orbital energy of all these orbitals. The increase in electron–nuclei interactions shows that the shift in orbital energies are not mainly due to a decrease in electron–electron repulsion but rather a contraction of the entire shell, just as seen in the charge-density plots.

#### TABLE II. Orbital energies and electron-nuclei interactions for an iron(II) atomic ion in the ground (GS) and core-excited (CE) states with 1s and 2p holes.

| Orbital | GS (eV) | CE-1s (eV) | CE-2p (eV) | GS (eV) | CE-1s (eV) | CE-2p (eV) |
|---------|---------|------------|------------|---------|------------|------------|
| 3s      | -134.3  | -160.6     | -158.5     | -874.5  | -895.8     | -890.7     |
| 3p      | -93.8   | -120.3     | -117.6     | -819.3  | -850.1     | -842.4     |
| 3d      | -34.5   | -56.3      | -56.9      | -679.4  | -738.6     | -739.4     |
Furthermore, looking into the radial charge distribution, it is clear that the 1s hole leads to a more contracted valence shell. This is also expected from a pure atomic analysis. Since orbitals behave as \( r^n \) close to the nucleus, the lower the \( l \) value of an orbital (s,p,d,f), the higher the density at the nuclei. Electron–electron interactions are especially large when two electrons are close to the nuclei, and therefore, bound electrons in general interact stronger with 1s than 2p particles.\(^5\) This effect is seen in Table III, where the pairwise interactions for all M-shell electrons are stronger with 1s compared to 2p electrons in all states. However, it should be noted that the difference is much smaller for 3d compared to 3s and 3p electrons.

To further analyze the effects of the core holes on the molecular complex, the radial spin density was analyzed [see Fig. 9(b)]. As before, the core orbitals are not included in the calculations, so the analysis of the core-excited states reflects the non-zero spin in the \( t_{2g} \) and \( e_g \) subshells. The spin-density analysis thus gives equal weight to the metal 3d-dominated orbitals, while largely ignoring the other shells. There is a clear contraction of the density upon creation of the core hole, just as for the charge density. However, when looking at the spin density, it is further away from the metal in the 1s hole state than in the 2p state. The spin-density trend between the states thus deviates from the trend in the calculated PES minima in Fig. 8 and is in apparent contradiction with the stronger 1s core–hole interactions.

![3MC valence state](image1)

To reconcile these observations, we first look at the orbital energies in Table II in more detail. This shows that although 3s and 3p shells have significantly lower energies in the 1s core-hole state, the energy of the 3d shell actually increases. Using the electron–nuclei interaction as an indication of the orbital radius, these values show that 3s and 3p electrons are more contracted in the 1s state, while the 3d electrons are less contracted. The reason for this counter-intuitive effect is the significant spatial overlap of the M shells. The additional contraction of the 3s and 3p orbitals in the 1s core-hole state leads to an increased shielding of the nuclear charge for the 3d orbitals. This shielding leads to an expansion of the 3d orbitals, which dominates over the contraction effect from the slightly stronger 1s core-hole attraction. The radial charge and spin densities are thus fully consistent with a simple atomic analysis.

Still, the relation between electron density and the relative positions of the PES minima needs to be explained. For this purpose, we have used a simple two-configuration model. As the complex is dominated by \( \sigma \)-donor bonding from low-lying filled ligand orbitals, lowering the metal levels upon creation of a core hole decreases the energy difference between metal and ligand configurations (see Fig. 10). This improved match gives stronger mixing and a more covalent bond, as seen from the increased covalency of the \( \sigma \) and \( e_g \) orbitals (see Table IV). Furthermore, contraction of the entire valence shell leads to a smaller ionic radius, which can give a shorter bond without directly affecting its character. The relative magnitude of these two contributions to the observed bond-length contraction of 0.06–0.08 Å upon core-hole creation is difficult to separate.

When comparing the two core-hole states, the shorter bond distances in the 1s core-hole states do not seem to match with the observation that the atomic 3d orbitals expand in this state. Bond-length shortening must therefore come from significant contraction of the non-bonding 3s and 3p electrons. One possibility is that this contraction reduces the Coulomb repulsion with the ligand electrons, which leads to better overlap between metal 3d and ligand levels and consequently larger off diagonal elements in the two-configuration model (see Fig. 10). The 1s core-hole state also has slightly larger \( \sigma \) and \( e_g \) covalencies, more pronounced at shorter distances (see Table IV). A

![3MC core-hole states](image2)

| Orbitals | GS | CE-1s | CE-2p |
|----------|----|-------|-------|
|          | 1s | 2p    | 1s    | 2p    |
| 3s       | 43.4 | 39.6 | 45.2 | 41.3 | 44.8 | 40.8 |
| 3p       | 42.3 | 38.1 | 44.9 | 40.4 | 44.3 | 39.8 |
| 3d       | 33.8 | 33.0 | 37.9 | 36.9 | 37.9 | 36.9 |

FIG. 10. Two-configuration model explaining increased covalency in core-hole states and differences between 1s and 2p holes.
E. Connection to the chemical shift in Kα emission

The importance of 3s and 3p orbitals in Kα XES of transition metals is already well established from analyses of the chemical shift. For light elements, oxidation leads to a positive shift in the Kα emission energies. The removal of a valence electron decreases the electron density near the nucleus, and as the interactions are more favorable with a 1s compared to a 2p hole, this leads to higher energy for the 2p → 1s transition.55,59 However, transition metal compounds typically show negative shifts upon oxidation.60–62 This can be explained by the presence of two counteracting effects, a first-order effect coming from the direct loss of 3d electron density and a second-order effect coming from the compression of all metal orbitals, especially 3s and 3p, upon the loss of the 3d electron. As 3s and 3p electrons interact more strongly with the core holes than the 3d electrons, their negative contribution dominates the Kα shift for 3d transition metals. The experimental observation of a negative chemical shift for transition metals shows that 3s and 3p electrons can have dominant influences on Kα XES even if they are not directly involved in redox activity or chemical bonding.

F. Predicting sensitivity of Kα XES to structural dynamics

For future applications of XES to study structural dynamics, it is important to predict conditions that will show a large sensitivity to such changes. To detect the wavepacket dynamics, the emission intensity must then be sensitive to the structural variations (δI/δr). This sensitivity can be predicted from the XES spectra for the relevant states. To be completely general, we call these states 1 and 2, although in the current example these are the GS and 3MC states, respectively. Figure 11 (gray and purple curves, right y-axis) shows the changes in emission intensity (ΔI) as a function of the emission energy for the two different states, calculated using a maximum oscillation of the nuclear wavepacket of 0.025 Å.23 A high sensitivity to structural dynamics in state 2 (3MC) is found at 6404.5 eV, which is close to the value chosen in the experiment (6404.3 eV). Sensitivity is actually even larger, up to 4% of the maximum intensity, when measuring on the high-energy side of the XES spectrum, around 6406.0 eV.

Tuning the emission spectrometer also makes it possible to switch between observing electronic and structural dynamics. At certain energies, the emission intensities of the two states are equal, making the XES signal independent of the electronic state [see Fig. 11 (black curve, left y-axis)]. At the same time, the signal should be off resonance for at least one state, in this example state 1, leading to sensitivity to geometric structure changes. Further increasing the emission energy again leads to sensitivity to electron dynamics.

To illustrate how the emission energy affects the experimental observable, time-dependent XES spectra have been simulated for three different emission energies (see Fig. 12). The emission energies are chosen based on the results in Fig. 11 and represent situations ranging from minimum to maximum sensitivity to structural dynamics. For simplicity, the simulations assume a two-state system with a 100% quantum yield and an infinite lifetime of the final state. However, as the magnitude of the oscillations is proportional to changes in the bond distance, the simulations require time-dependent bond distances. Here, this information is taken from previous wavepacket simulations of [Fe(CN)(bmip)]2+, including the additional Gaussian broadening of 100 fs (FWHM) to account for experimental time-resolution.23

The first example represents the commonly chosen experimental condition where data are collected at the emission maximum of state 1 (GS at 6404.3 eV). The initial intensity is then unity and drops to below 0.6 as the system transfers to state 2 (3MC). Note that the intensity difference between the states is not exactly the same as in Figs. 4

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**TABLE IV. Orbital covalency analysis for the metal–ligand orbitals in different states.**

| State | GS geometry | 3MC geometry |
|-------|-------------|--------------|
|       | σt | t2g | eg | Σt | t2g | eg |
| 3MC   | 18.8 | 92.7 | 77.3 | 9.2 | 91.7 | 89.9 |
| 3MC 1s hole | 22.4 | 93.1 | 73.3 | 15.7 | 95.7 | 79.3 |
| 3MC 2p hole | 21.8 | 94.8 | 72.3 | 15.3 | 95.7 | 79.2 |

aData from Ref. 23.
and Fig. 11 because the current modeling also includes changes in geometry. At this emission energy, there is significant structural sensitivity, with the largest oscillations of around ±2%. These oscillations then decrease with time as the wavepacket dephases. If the emission energy instead moves to the maximum emission intensity of state 2 (3MC at 6405.2 eV), the transfer from state 1 to state 2 increases the intensity, but there is no structural sensitivity as the derivative of the intensity with respect to energy is zero at the maximum. Finally, increasing the emission energy to the point of maximum sensitivity of state 2 (6406.1 eV) leads to low total intensities but large oscillations, around ±4%. Together, these three examples show how the emission energy can be used to modulate the structural sensitivity of the experiment. This in turn opens up for separation of electronic and geometric degrees of freedom in XES studies of ultrafast dynamics.

G. Other systems and detection methods

These time-dependent XES simulations using data from [Fe(II)(bmip)]_2 provide a framework for discussing if structural sensitivity of Kα XES is important for a wider range of systems. The present theoretical analysis has identified the following factors that need to be considered: (i) large differences in metal–ligand equilibrium distances between 1s and 2p core-hole states (large Δr, see Eq. 3), (ii) strong metal–ligand bonds in the core-excited states (large k_v), and (iii) emission energy properly tuned to detect the oscillations.

The first factor, Δr of the core-excited states, is predicted to be general because its main origin is an atomic effect. It should therefore not vary significantly between systems or electronic states. For [Fe(II)(bmip)]_2, the effect is similar for both GS and 3MC electronic states, even if these states have very different metal–ligand bonding. The dependence of the oscillations on the force constant means that the systems with strong metal–ligand bonds, such as those from the strong σ bonding in the carbenes, are more sensitive. Still, as the effect is linear, significant oscillations should appear also in other systems. These values can be obtained from DFT or time-dependent DFT simulations of the targeted excited states and compared to the force constant of 2000 Nm⁻¹ extracted from these simulations. Finally, the selected emission energy is possibly the most sensitive variable. To design new experiments targeting electronic and structural dynamics in excited states, this emission energy can be chosen based on theoretical predictions as in Fig. 11. Although the theoretical analysis here indicates the possibility of fluctuations up to 4% of the maximum emission intensity, the generality of these findings will have to be tested through further theoretical and experimental work on coherently excited states.

In addition to the predicted structural sensitivity in Kα XES, an important question is whether effects can also be expected in Kβ XES. For [Fe(II)(bmip)]_2, there are indications that oscillations occur also in the Kβ signal, although the low signal-to-noise ratio prevents a definitive confirmation. Here, we can only observe that the factors outlined for structural sensitivity of Kα XES cannot be directly transferred to Kβ XES. First, the radial distribution of the 3p hole overlaps more directly with the valence orbitals, which can lead to effects on chemical bonding beyond the predominantly atomic effects of the deeper core holes. The shifts in the PES surfaces of different core hole states can therefore be more dependent on the metal-ligand bonding characteristics. Second, the Kβ and Kα emission data were collected in different experimental setups. As mentioned above, Kα XES was detected using a Johann spectrometer, which is sensitive to a narrow emission energy range. The Kβ signal is collected using a dispersive von Hamos spectrometer. The experimental signal-to-noise ratio does not allow the extraction of intensity trends at specific energies, but weak oscillations appear by integrating over the full spectral range. Due to the lower Kβ fluorescence yield, the experimental signal-to-noise ratio in that particular experiment was about 10 times lower compared to Kα XES. If the main effect is an energy shift, the integrated signal would only be sensitive to the difference in intensity changes at the two ends of the emission energy interval, where the signal is already weak. For [Fe(II)(bmip)]_2, it is thus possible that the Kβ oscillations reflect changes in spectral intensity instead of an energy shift. To understand the sensitivity of Kβ XES to structural dynamics requires further simulations of that particular process.

IV. CONCLUSIONS

The sensitivity of XES emission to excited-state structural dynamics in an iron photosensitizer is due to the shift of the minimum metal-ligand bond distance between 1s and 2p core-hole states. A key effect comes from contraction of the non-bonding 3s and 3p orbitals in 1s core-hole states, which decreases electron-electron repulsion and increases overlap in metal–ligand bonding. The difference between the 1s and 2p core hole potentials explains trends in radial charge densities, the shapes of the PES of the core-hole states, and the subsequent shift in the emission energy with the metal–ligand distance. The explanation is also consistent with the negative chemical shift observed in transition metal complexes. The atomic origin of the process predicted here suggests that the structural sensitivity of Kα emission is a general effect and should be observed in other molecular systems. Furthermore, the sensitivity to electronic and structural dynamics in different states can be tuned by changing the emission energy, making it possible to selectively study either oscillations between electronic states or structural changes in a specific state. The results show how modeling can be used to predict sensitivity as a function of emission
energy and thus help to improve experiments designed to follow ultra-fast excited state dynamics.

SUPPLEMENTARY MATERIAL

See the supplementary material for the effects of dynamic correlation on the emission spectrum, the description of other 3MC intermediate states, their emission spectra, the energies of their emission maximum, and Cartesian coordinates of the different nuclear geometries used.

ACKNOWLEDGMENTS

We acknowledge financial support from the Knut and Alice Wallenberg Foundation (Grant No. KAW-2013.0020) and the Foundation Olle Engkvist Byggmästare (No. 183–0403). The computations were performed on resources provided by SNIC through the National Supercomputer Centre at Linköping University (Tetralith) under Project snic-2018-3–575. K.K. and K.J.G. acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. This work was supported by the EU through the European Regional Development Fund under Project No. TK141 (No. 2014–2020.4.01.15–0011). We thank Oscar Sommerbo for comments on the revised manuscript.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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