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Molecular orbital simulations of metal 1s2p resonant inelastic X-ray scattering

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For first-row transition metals, high-resolution 3d electronic structure information can be obtained using resonant inelastic X-ray scattering (RIXS). In the hard X-ray region, a K pre-edge (1s → 3d) excitation can be followed by monitoring the dipole-allowed Kα (2p → 1s) or Kβ (3p → 1s) emission, processes labeled 1s2p or 1s3p RIXS. Here the restricted active space (RAS) approach, which is a molecular orbital method, is used for the first time to study hard X-ray RIXS processes. This is achieved by including the two sets of core orbitals in different partitions of the active space. Transition intensities are calculated using both first- and second-order expansions of the wave vector, including, but not limited to, electric dipoles and quadrupoles. The accuracy of the approach is tested for 1s2p RIXS of iron hexacyanides [Fe(CN)6]n– in ferrous and ferric oxidation states. RAS simulations accurately describe the multiplet structures and the role of 2p and 3d spin-orbit coupling on energies and selection rules. Compared to experiment, relative energies of the two [Fe(CN)6]3– resonances deviate by 0.2 eV in both incident energy and energy transfer directions and multiplet splittings in [Fe(CN)6]4– are reproduced within 0.1 eV. These values are similar to what can be expected for valence excitations. The development opens up for the modeling of hard X-ray scattering processes for both solution catalysts and enzymatic systems.

1 Introduction

First-row transition metals are important components of many catalytic systems. Development of more efficient and selective catalysts can be aided by knowledge of the electronic structure of the metal 3d orbitals involved in catalysis. X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are widely used as element-specific probes of electronic structure. For 3d transition metals, L-edge (2p → 3d) XAS provides high-resolution information, but the strong absorption of soft X-rays from the sample environment makes it challenging to apply directly to enzymes and solution catalysts. The hard X-ray alternative is to excite into the metal K pre-edge (1s → 3d). In absorption the short life-time of the 1s core hole leads to significant lifetime broadening (1-2 eV), but high-resolution spectra can instead be obtained using resonant inelastic X-ray scattering (RIXS).

In RIXS the incident energy (Ω) is scanned over the absorption resonances, followed by emission of a scattered photon of typically a lower energy (ω). The energy transfer (Ω − ω), corresponds to the energy of the fundamental process that is probed, e.g., a core, valence or charge-transfer excitation. In the hard X-ray region, a 1s → 3d excitation can be coupled to a 2p → 1s (Kα), a 3p → 1s (Kβ main), or even a valence → 1s (Kβ2,5) emission process, see Figure 1. The lifetime broadening in the energy transfer direction does not depend on the lifetime of the 1s hole, only on the lifetimes of the final states. High-resolution energy transfer spectra can thus be obtained while still keeping the advantages of the hard X-ray probe when it comes to the sample environment.

For systems with low metal concentration, or those that rapidly damage in the X-ray beam, it is important to get a relatively intense signal. Following absorption,
Fig. 1 Two-step total energy schematic of the 1s2p RIXS process. The vertical axis shows the total energy of the electron configuration. Photon energies are for an iron complex.

it is then preferable to monitor the most intense emission channel, Kα, which is approximately ten times more intense than Kβ emission.15 The complete process is referred to as Kα or 1s2p RIXS, where the latter label indicates a 1s hole in the intermediate state and a 2p hole in the final state. High-resolution 1s2p RIXS data have been collected for several enzymes e.g., photosystem II and cytochrome c.16,26

The shape of the 1s2p RIXS spectrum depends on a number of factors, e.g., the 2p-3d and 3d-3d electron interactions, as well as the spin-orbit coupling in 2p and 3d orbitals. With hard X-ray RIXS experiments reaching 0.1 eV resolution in the energy transfer direction,1 details of the electronic structure can now be resolved. However, to extract as much information as possible requires a theoretical model. Iron 1s2p RIXS experiments have previously been analyzed using the semi-empirical charge-transfer multiplet (CTM) model.9,30 This method gives a balanced description of electron-electron repulsion and spin-orbit coupling and includes all relevant final states. Metal-ligand interactions are modeled in a configuration interaction procedure where energy differences and coupling strengths are parameters fitted to the experimental spectrum. For cytochrome c, the CTM model has been used to analyze the role of the axial ligands in the electron transfer process.26

The number of parameters in the CTM model increases with decreasing symmetry. An important consideration is that the intensity of the metal K pre edge increases significantly when the centrosymmetric environment is broken, e.g., when going from a six-coordinate to a five-coordinate site.54 The distortion allows for 3d-4p orbital hybridization and mixes in dipole-allowed 1s → 4p transitions into the pre edge. In the parameterized CTM model the addition of 4p orbitals increases the number of system parameters,2 which makes it more difficult to get stable fits. There is thus need for a parameter-free method that takes into account all the effects shaping the K-edge RIXS spectra.

Soft L-edge XAS and RIXS of several transition-metal systems have previously been simulated with the \textit{ab initio} restricted active space (RAS) approach.5,5,11,21,29,40,41,51,52 This is a multiconfigurational molecular orbital method based on the complete active space (CAS) self-consistent field (SCF) method.44,47 It can be adapted to X-ray processes by including also the core orbitals in the active space. As the number of excitations from the core orbitals can be restricted, usually to one, it becomes convenient to use the restricted active space approach.33,38 For iron L-edge XAS spectra, the RAS method has shown comparable performance to CTM.40,41 The ratio between cost and accuracy can be optimized by a proper selection of active space, basis set and computational algorithms,42 and the method can potentially be applied to both small and medium-sized systems.

Here the RAS method is used for the first time to calculate K-edge RIXS, specifically 1s2p RIXS. The difference compared to L-edge RIXS is that the orbital occupation of two different sets of core orbitals, both 1s and 2p, have to be controlled. Second, modeling K pre-edge excitations requires terms beyond the electric dipole approximation.4 We recently implemented transitions from first and second order expansions of the wave vector in the RAS framework, which in addition to the electric dipole also includes second-order terms like electric quadrupoles and magnetic dipoles. That implementation was then used to model iron K pre-edge spectra with accurate descriptions of both multiplet effects and 3d-4p mixing.17
The goal of the current simulations is to illustrate how the RAS method describes the electron-electron interactions and spin-orbit couplings that determine the shape of the 1s2p RIXS spectra. Calculations are performed for a pair of model complexes, low-spin ferrous/ferric hexa-cyanide ([Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻), for which data are available both in solid and different solvents.³⁰,³⁹ Ferrocyanide has a d⁶ electron configuration and exhibits Oᵥ symmetry. Ferricyanide has a d⁸ electron configuration, and the five electrons in three degenerate t₂g orbitals lead to a weak Jahn-Teller distortion to D₄h symmetry. The distortion has only small effects on the calculation, and the five electrons in three degenerate orbitals will be used in the discussion of the results.⁴⁰ The high symmetries are useful as they make it much easier to assign electronic transitions. The electronic structure effects on the spectra of the solids have previously been analyzed using the CTM model.³⁰ Testing the RAS approach against these well-known complexes will help to reveal its applicability for K-edge RIXS modeling of complexes with unknown geometric or electronic structure.

2 Computational details

The ferrocyanide geometry is taken from the crystal structure with an Fe-C distance of 1.913 Å.²⁸ The ferricyanide geometry was originally obtained from a CASPT2/ano-rcc-vtzp optimization using the same valence active space described above.⁴⁰ The geometry shows a Jahn-Teller distortion with four Fe-C distances of 1.916 Å and two distances of 1.939 Å.⁴⁰ This geometry deviates slightly from the one used in a recent soft X-ray RIXS study,²⁹ and the difference can be explained by an error in the definition of the carbon ano-rcc basis sets in the version of Molcas used to optimize the current structure. The minor differences in geometry, at most 0.005 Å, should not have any significant effects on the calculated spectra.⁴²

RAS calculations of ferro- and ferricyanide are performed with similar active spaces. Using labels from Oᵥ symmetry, the metal 3d eₓ orbitals mix with two symmetry-adapted linear combinations (SALCs) of filled cyanide σ orbitals to form two ligand-dominated bonding (σ) and two metal-dominated antibonding (σ*) orbitals. The Fe 3d t₂g orbitals mix weakly with SALCs from empty CN π* to form three metal-centered bonding (π, often labeled t₂g) and three ligand-centered antibonding (π*) orbitals. Together, these ten orbitals make up the RAS2 active space, see Figure 2. The 2p orbitals are placed in the RAS1 space, allowing only single excitations. As both complexes are centrosymmetric, the final states with 2p holes are the lowest states with ungerade symmetry. The 1s orbital is placed in the RAS3 space allowing two electrons in the ground and final states, and one electron in the intermediate state. This gives a total of 18 electrons in 14 orbitals for ferrocyanide, with one electron less in ferricyanide. All RAS calculations have been performed with a local development version of MOLCAS.

Although the model systems have Oᵥ or D₄h symmetry, calculations are effectively performed in the Abelian point group D₂h. In that group, Fe 1s, σ and σ*(eₓ) orbitals belong to a₁g irreducible representation. π(t₂g) and π* orbitals belong to b₁g, b₂g, and b₃g, while the Fe 2p are in the corresponding ungerade representations.

![Fig. 2 Schematic orbital diagram showing the active space of ferrocyanide. In ferrocyanide the t₂g shell is completely filled. The labels of the transitions show the irreducible representations of the final states reached after a one-electron excitation in ferrocyanide.](image-url)
state of ferrocyanide is a singlet and in ferricyanide it is a doublet. The number of intermediate states was chosen by monitoring the K pre-edge spectra until no significant changes could be detected. This required 20 by monitoring the K pre-edge spectra until no singlet. The number of intermediate states was chosen to be 60 and 80 respectively. Adding more states would only affect results in energy regions that are covered by the rising edge. To avoid orbital rotation, i.e., that hole appears in the 3s instead of the 1s orbital, 1s and 2p core orbitals have been frozen in the orbital optimization of the intermediate and final states. Relaxing the core orbitals in ferricyanide mainly affect the energy shift required to overlay calculated and experimental spectra. In a second step, dynamical correlation was included using multi-state second-order perturbation treatment (MS-RASPT2). Calculations have been performed using the default ionization-potential electron-affinity shift of 0.25 hartree, and to reduce problems with intruder states an imaginary shift of 0.3 hartree has been applied. Scalar relativistic effects have been included by using a second-order Douglas-Kroll-Hess Hamiltonian in combination with a relativistic atomic natural orbital basis set, ano-rcc-vtzp. Oscillator strengths have been calculated between orthogonal states formed from a RAS state-interaction approach that also includes spin-orbit coupling using a local implementation of the origin-independent second-order expansion of the wave vector. RIXS spectra are described using the Kramers-Heisenberg formula:

$$ F(\Omega, \omega) = \sum_{f} \sum_{n} \left( \frac{\langle f | T_e | \overline{i} \rangle \langle \overline{i} | T_a | g \rangle}{K(\Gamma)} \right)^2 \times K(\Gamma_f) $$

where the scattering intensity $F$ is a function of incident energy ($\Omega$) and emitted X-ray energy ($\omega$), the $|g\rangle$, $|\overline{i}\rangle$, and $|f\rangle$ are ground, intermediate and final states respectively. $T_a$ and $T_e$ are transition operators for the absorption and emission processes respectively. $K(\Gamma)$ depends on the resonance energy and the lifetime broadening $\Gamma$ of each state.

The current RIXS calculations use the oscillator strengths of absorption and emission processes, which means that interference effects are neglected. A Boltzmann averaging of the contributions from different initial states were made. For ferricyanide, where six initial spin-orbit states contribute, the summations then run over 640 intermediate spin-orbit states and 1920 final spin-orbit states. Transitions with low intensity were screened out in a procedure that ensures that the final RIXS planes include more than 99.9% of the total intensity.

Calculated spectra were broadened using a Lorentzian lifetime broadening of 1.25 eV full-width half-maximum (FWHM) in the incident energy direction and two different broadenings in the energy transfer direction, 0.4 eV for the $K\alpha_1$ ($L_3$) and 0.8 eV for the $K\alpha_2$ ($L_2$) region. The difference in lifetime broadening comes from an extra decay process where the states reached after $K\alpha_2$ emission $J_{2p} = 1/2$ can decay into the $K\alpha_1$ ($J_{2p} = 3/2$) final states by emitting an Auger electron (Koster-Kronig decay).

The spectra are then convoluted with experimental Gaussian broadenings of 1.06 eV FWHM in the incident energy direction and 0.4 eV in the energy transfer direction. Comparisons with experimental RIXS spectra are done using data for solid samples from reference. Energies of the calculated spectra have been aligned to the first pre-edge peak and intensities have been scaled to match the maximum of the pre-edge region.

Experimental iron L-edge XAS spectra are taken from reference. The extent of photodamage in the ferricyanide spectrum has been analyzed extensively, and that data set is within acceptable levels. Calculated spectra are obtained using the procedure described in reference. Due to the problems with the ano-rcc basis set for carbon discussed above, the current ferricyanide spectrum, calculated using the corrected basis set, shows minor differences compared to the original publication.
3 Results and discussion

3.1 RIXS planes

Experimental and calculated 1s2p RIXS spectra of ferrocyanide and ferricyanide are shown in Figure 3. The two axes are the incident energy (Ω) and the energy transfer (Ω − ω). Each plane has two separate regions, stretching roughly diagonal across the plane. The region at lower energy transfer is the Kα1 emission and these final states correspond to the L3 edge of the L-edge XAS. The upper region is the Kα2 emission, which corresponds to the L2 edge. The 12-eV splitting comes from the 2p spin-orbit coupling in the final state.

The experimental 1s2p RIXS spectrum of ferrocyanide has a single pre-edge feature at 7112.9 eV, in both the Kα1 and Kα2 emission regions, see Figure 3a. This transition can be assigned to a 1s → 3d(e_g) excitation. In the energy transfer direction, the L3 maximum is at 708.9 eV. The ferricyanide spectrum has two pre-edge features, associated with excitations to t_{2g} and e_g orbitals respectively. The t_{2g} feature, located at an incident energy of 7110.2 eV, is very sharp in the energy transfer direction. The e_g feature, with a maximum at 7113.3 eV, is much broader in both the incident energy and energy transfer directions, see Figure 3c. The two pre-edge features are both very different in shape compared to the ferrocyanide pre-edge resonance.

The calculated RAS spectra reproduce the general shapes of the experimental pre-edge peaks. In addition, both of them also have additional peaks that overlap with the rising edges in the experimental spectra. These high-energy resonances can be assigned to transitions to the empty ligand-dominated π*- orbitals, see Figure 2. For both systems, the energy splitting between the Kα1 and Kα2 regions is underestimated by 1-2 eV. This is similar to what has previously been observed for the L3-L2 splitting, and can be explained by an underestimation of the 2p spin-orbit coupling in the present scheme.\(^\text{11,40}\)

The e_g ferrocyanide pre-edge resonance is calculated to be slightly asymmetric in the energy transfer direction, with more intensity on the low-energy side of the peak, see Figure 3b. The shape is very similar to that obtained from a CTM calculation.\(^\text{30}\) The 1s → 3d(e_g) excitation leads to two degenerate \(^1E_g\) intermediate states. The 2p → 1s emission from these states lead to different 2p^53d^7 final states, and the energy differences between these states give the asymmetric spectral shape in the energy transfer direction as will be explained in more detail below.

In the ferricyanide spectrum, the t_{2g} peak is narrow in the energy transfer direction, while the e_g peak is much broader in both dimensions, see Figure 3d. The 1s → 3d(t_{2g}) excitation gives rise to a single \(^2A_{1g}\) intermediate state with an unpaired electron in the 1s orbital. From here, 2p → 1s emission leads to 2p^5\(^3t_{2g}\) final states that all have the same energy. As the t_{2g} peak is not split by any electron-electron interactions, its shape in the modeled spectra is independent of the method and only depends on the applied broadenings. The shape of the e_g peak is more complicated because the excitation leads to a large number of 1s\(^1t_{2g}\)\(^1e_g\) intermediate states, split by exchange and multiplet interactions, and even more 2p^5\(^3t_{2g}\)\(^2e_g\) final states.\(^\text{30,53}\)

The intensity pattern of the ferricyanide e_g peak is shown in more detail in Figure 4. A first-moment analysis of the experimental spectrum gives energies of 7113.3, 709.5 eV, or 3.2 eV and 3.7 eV above the t_{2g} peak along the two energy axes. Looking first at a calculation at the RASSCF level, it reproduces these energy differences with errors of -0.1 eV in the incident energy direction and 0.8 eV in the energy transfer direction. Adding dynamical correlation with RASPT2 gives errors of 0.2 eV in both directions. The improvement in the t_{2g}-e_g splitting along the energy transfer axis is similar to what has previously been observed for the L-edge XAS spectrum.\(^\text{42}\)

The RASSCF calculation gives relatively good estimates both of the intensity ratio between the two peaks and the shape of the e_g peak. Here RASPT2 does not offer any improvement and instead underestimates the relative t_{2g} intensity. It is not the total intensities of the two peaks that changes, but rather a more compact shape of the e_g resonance that increases the maximum intensity, which leads to a scaling down of the entire calculated spectrum and an apparently lower intensity of the t_{2g} peak. The CTM calculation did a better job at calculating relative peak intensities, but underestimated the e_g intensity at lower energy-transfer values.\(^\text{30}\)

As the e_g peak involves many different intermediate states it is possible that the RIXS spectrum is affected by interference effects.\(^\text{22}\) The present calculations, as well
as the previous CTM simulations, represent an isotropic averaging and do not include interference. The interference effects in the hard X-ray region have scarcely been analyzed.\(^{50}\) It is therefore not clear to what extent this neglect affects the calculated intensities, and it is an interesting future direction. Fortunately, the present study does not rely on an exact calculation of the shape of the \(e_g\) peak.

3.2 Incident energy direction

Although the RIXS planes contain a lot of information, they can be challenging to interpret. An alternative is to make cuts through the planes at constant emission energy (CEE) and constant incident energy (CIE), see Figure 3. The CEE cuts are the high-energy resolution fluorescence detected XAS spectra, and can be compared to the K-edge absorption spectra. In ferrocyanide the CEE cut through the maximum of the \(e_g\) peak gives a sharper feature and shows the structure in the rising edge more clearly than the K-edge XAS, see Figure 5. The RAS simulation includes the \(e_g\) peak but also predicts a second intense \(\pi^*\) pre-edge peak 2.5 eV higher in energy. This peak fits under the rising edge and suggests that a significant part of the intensity in this region can be assigned to this metal-to-ligand charge transfer feature.

The CEE cut through the maximum of the \(e_g\) peak in ferricyanide also gives significantly sharper spectral features than the K pre edge, especially for the \(1s \rightarrow t_{2g}\) resonance, see Figure 6. The effect is smaller for the \(1s \rightarrow e_g\) peak because it contains a large number of different states in both incident and energy transfer directions. The RAS calculation includes both these features and also a higher-lying \(\pi^*\) peak that appears as part of the rising edge. The description of the \(e_g\) peak is good but the intensity of the \(t_{2g}\) is underestimated. This is due to the underestimation of the intensity of the \(t_{2g}\) resonance in the RIXS plane, as discussed above, and partly because the CEE cut does not go through the \(t_{2g}\) maximum.

3.3 Energy transfer direction

Ferrocyanide. The full advantage of the high-resolution 1s2p RIXS experiment appears in the energy transfer direction. The \(L_3\) edge of the experimental ferrocyanide...
**Fig. 4** First-moment analysis of the pre-edge region of the 1s2p RIXS spectrum of [Fe(CN)]$_6^{3-}$ in experiment, RASSCF and RASPT2. The black line shows the intensity limit for the calculation of the first moment.

**Fig. 5** Iron K pre-edge XAS spectra and CEE cuts of ferrocyanide [Fe(CN)$_6^{4-}$] from experiment and RASPT2 modeling. The bold labels show the orbital assignment of the K pre-edge transition, while labels in normal font show the irreducible representation of the intermediate spin-orbit states in Bethe notation with the spin and symmetry of the valence electron configuration in parenthesis.

L-edge XAS spectrum has two intense features at 709.1 and 710.7 eV, see Figure 7, which can be assigned as $e_g$ and $\pi^*$ peaks. The same two peaks also appear in the L$_2$ edge. An L-edge-like spectrum is obtained by taking a CIE cut through the at 7112.9 eV, the incident energy of the 1s $\rightarrow$ $e_g$ transition. The 2p $\rightarrow$ 1s emission from this $^1E_g$ intermediate states lead to 2p$^5$3d$^7$ final states, nominally the same as in L-edge XAS, but the CIE cut gives much wider $e_g$ peaks, both in L$_3$ and L$_2$ edges, and lacks the intense $\pi^*$ peaks. The width of the $e_g$ resonance increases from the 0.8 eV in the L-edge spectrum to 1.5 eV in the CIE spectrum. As explained previously, the increased width is not due to larger broadening in the hard X-ray experiment, but rather a difference in selec-
tion rules between the two experiments.\textsuperscript{30}

Fig. 7 Iron L-edge XAS and CIE cut through the $\epsilon_g$ pre-edge peak for ferrocyanide $[\text{Fe(CN)}_6]^{4-}$ from RASPT2 modeling (top) and experiment (bottom).

The final $2p^5 1d^6 \epsilon_g^1$ electron configuration gives rise to two different states, having either $T_{1u}$ or $T_{2g}$ irreducible representation. The advantage of the molecular orbital representation is that the origin of the energy difference between the states can be easily visualized. In the spin-free representation, the simplest linear combination of the $T_{1u}$ and $T_{2g}$ final states can be written $\bar{p}_{\epsilon} d_{z^2}$ and $\bar{p}_{\epsilon} d_{x^2-y^2}$ respectively, where $\bar{p}_{\epsilon}$ represents a hole. For the $\bar{p}_{\epsilon}$ hole the attraction to the $d_{z^2}$ electron is stronger than to a $d_{x^2-y^2}$ electron because of a better overlap when the two orbitals are in the same plane, see Figure 8. The $T_{2g}$ states are thus lower in energy because of more favorable 2p-3d electron interactions. The wavefunctions with $\bar{p}_{\epsilon}$ and $\bar{p}_{\pi}$ holes are more complicated linear combinations but can, from group theory arguments, be shown to have the same energies. In the XAS process the single-photon electric dipole transitions ($T_{1u}$) only reaches $T_{1u}$ states from the $A_{1g}$ ground state. The two-photon RIXS process, electric quadrupole ($E_g+T_{2g}$) followed by electric dipole, reaches both $T_{1u}$ and $T_{2g}$ final state, and the energy differences between these states gives rise to the spectral broadening.\textsuperscript{30}

To reproduce the difference between L-edge XAS and CIE thus requires a method that accurately takes into account the multiplet structures of the final states. Starting with the L-edge XAS, the RAS simulation gives good agreement with experiment, see Figure 7, results almost identical to those in a very recent soft X-ray RIXS study.\textsuperscript{29} The relative intensities are very well described, including the fact that the $\pi^*$ peak is the most intense. The energy difference between $\epsilon_g$ and $\pi^*$ peaks is overestimated by 0.6 eV. The agreement appears to be better than for early simulations of the ferrocyanide L-edge XAS.\textsuperscript{11} The main differences are the full optimization of the valence orbitals in the excited state and inclusion of dynamical correlation through PT2 calculations. In the present simulation, staying at the RASSCF level gives an error in the $\epsilon_g - \pi^*$ splitting in the L-edge XAS of more than 2 eV.

In the CIE cut, the RASPT2 calculation reproduces the change in shape of the $\epsilon_g$ resonance with additional intensity at the low-energy side. The width is 1.6 eV, an overestimation by only 0.1 eV, similar to the error in the CTM model.\textsuperscript{30} The PT2 results are a clear improvement compared to the RASSCF level where the peak width is overestimated by 0.5 eV.

**Ferricyanide.** The experimental L-edge XAS spectrum of ferricyanide, see Figure 9, has three distinct peaks in the $L_3$ edge; a first $t_{2g}$ peak at 705.8 eV, a second $\epsilon_g$ peak with a maximum around 710 eV, and a third $\pi^*$ peak at around 712 eV.\textsuperscript{20} The $L_2$ edge has a simi-
lar structure, but the $t_{2g}$ peak is much weaker. The RAS L-edge XAS spectrum captures all the major features of the experimental spectrum, e.g., the difference in intensity of the $t_{2g}$ peaks in the two edges, the shape of the $e_g$ resonance, and the high intensity of the $\pi^*$ resonance, see Figure 9. The main deviations are the shift of the $\pi^*$ peak to higher energies by $\sim 1.5$ eV, and the usual underestimation of the splitting between the $L_3$ and $L_2$ edges by $\sim 1.0$ eV.42

The CIE cut through the RIXS $t_{2g}$ resonance at 7110.1 eV gives two sharp edges, where the $L_2$ peak is more intense than in the L-edge XAS spectrum, see Figure 9. The difference in intensity in the two experiments can only be explained by invoking the selection rules for spin-orbit coupled states.20 The spin-orbit coupling in the final state is straightforward to analyze because 2p hole in the 2p$^6t_{2g}^5$ configuration gives rise to $L=1$ and $S=\frac{1}{2}$ and, according to Hund’s third rule, the highest $J$ value ($J_{2p}^{2p}=\frac{3}{2}$) is lowest in energy because the shell is more than half-filled, see Figure 10. The initial state is slightly more complicated as it has 2p$^6t_{2g}^5$ electron configuration with the hole in $t_{2g}$. The presence of the ligands leads to a quenching of the orbital angular momentum of the 3d orbitals and in the limit of a strong ligand field, the $t_{2g}$ orbitals have an effective $l$ value of 1, the same as the

2p orbitals.49 The important difference is that the sign of the effective angular momentum operator is the opposite of the corresponding operator for the 2p orbitals. This leads to a reversal of the energy ordering of the different spin-orbit states, and for $t_{2g}$ the lowest $J$ value ($J_{3d}=\frac{3}{2}$) is lower in energy.

In the L-edge XAS a direct excitation from the $J_{3d}=\frac{1}{2}$ ground state ($\Gamma_{\frac{1}{2}}^7$ in Bethe double-group notation) to the $L_2$ $J_{2p}=\frac{1}{2}$ $t_{2g}$ peak ($\Gamma_{\frac{3}{2}}^8$) are electric dipole forbidden, see Figure 10.20 The weak intensity in the experimental spectrum can come either from distortions from $O_h$ symmetry or from Boltzmann population of the $J_{3d}=\frac{3}{2}$ states. The transition is also allowed in the two-photon RIXS experiment, see Figure 10, which explains the increase in intensity when going from L-edge XAS to RIXS. The RAS CIE cut through the $t_{2g}$ correctly predicts the increase in intensity of the $L_2$ edge in the two-photon process. This shows that the RAS state-interaction approach correctly takes into account the effects of both the weak 3d and the strong 2p spin-orbit coupling in these experiments.

The CIE cut through the $e_g$ resonance at 7113.3 eV shows a broad feature with a width of 2.7 eV in the $L_3$ edge, see Figure 9. This cut shows intensity at energies
below that of the $e_g$ peak in the L-edge, again due to the presence of new final states.\textsuperscript{30} The RAS CIE cut is in general agreement with the experiment, but the shape is not well reproduced below 709.5 eV, as could be seen already from the RIXS planes in Figure 3. As the spectral feature contains a large number of different pre-edge transitions, the CIE cuts are sensitive both to the incident and the emission energy, which makes it challenging to assign specific transitions. The important point is that the RAS reproduce the increase in width due to the new selection rules and correctly predicts that a significant part of this intensity appears below the L-edge peak.

3.4 General applicability of RAS to simulate hard X-ray RIXS

The two examples presented, ferro- and ferricyanide, arguably represent favorable cases for the application of the RAS method, mainly due to their high symmetry and relatively small size. However, the method should be applicable to a large number of small and medium-sized systems. The two main limitations are the number of atoms in the molecule and the size of the active space.

A large number of atoms, or more accurately, basis functions, primarily leads to an increase in the time for the RASPT2 calculations. Compared to calculations of ground state properties, the RIXS spectrum is much more expensive as it relies on the explicit calculation of a large number of intermediate and final states. Using a triple-zeta basis, complexes with approximately 50 atoms can be handled. One alternative is to use a small basis set, and even a double-zeta basis can give good results.\textsuperscript{42} Another alternative is to ignore the dynamical correlation added in the RASPT2 step and rely on the qualitative RASSCF results. As seen above, the two methods gave the same general description of the RIXS process, although RASPT2 in most cases gave significantly better quantitative agreement.

The second limitation is the size of the active space. Here two of the three RAS spaces are used to control the occupation of the core orbitals, leaving no flexibility in the design of the valence active space. That limitation could potentially be addressed by the use of a generalized active space approach.\textsuperscript{31} Still, a straightforward expansion from monomeric to dimeric complexes would remain challenging, both due to the large active spaces required and the need to converge a large number of complicated wavefunctions. Due to the local nature of the X-ray process, it is possible that schemes to separately describe processes on different metals could have some success.

The simulations can be applied to all possible spin states. If anything, low-spin states are more challenging to calculate because of increase in the number of configuration state functions compared to high-spin complexes with the same number of active electrons and orbitals. In addition, low-spin complexes are often highly covalent and typically require more ligand orbitals in the active space.

The high symmetries of the hexacyanides lead to significant savings in computation time. Centrosymmetry also makes it trivial to generate the final states with 2p holes as they become the lowest states with ungerade symmetry. However, the primary reason for choosing symmetric systems was the possibility to unambiguously identify electronic states and assign transitions. For systems that lack centrosymmetry it is possible to use an algorithm that gives zero weight to states without a proper core hole configuration.\textsuperscript{19} The RAS approach should then be directly applicable also to systems that lack symmetry elements. That is an important development because that makes it possible to model hard X-ray RIXS for systems where the intensity of the pre edge is strongly affected by 3d-4p orbital hybridization.

4 Conclusions

The extension of the RAS method to transition metal K pre edge makes it possible to also model hard X-ray RIXS experiments. Simulations of the iron 1s2p RIXS spectra of two model complexes show that the RAS approach includes the important interactions that determine spectral shape. The ferrocyanide results suggest that the 2p-3d multiplet interactions are well reproduced, as seen by the 0.1 eV error in the multiplet broadening of the CIE cut through the main $e_g$ pre-edge resonance. In ferricyanide, the relative energies of the $t_{2g}$ and $e_g$ pre-edge resonances are reproduced within 0.2 eV. These errors are similar to what can be expected for the description of valence excitations with RASPT2. The correct descriptions of selection rules show that the effects of both
3d and 2p spin-orbit coupling are included. Overall, the performance is similar to that of the semi-empirical CTM model, but the possibility to include also 3d-4p orbital hybridization makes RAS an attractive method to model hard X-ray RIXS processes of many different types of transition-metal complexes, including solution catalysts and enzymes.

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