<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Journal of Physical Chemistry A*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Guo, M., Erik, K., Sørensen, L K., Delcey, M G., Pinjari, R V. et al. (2016)
Molecular orbital simulations of metal 1s2p resonant inelastic X-ray scattering.
Journal of Physical Chemistry A, 120(29): 5848-5855
<http://dx.doi.org/10.1021/acs.jpca.6b05139>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-302165>

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

Meiyuan Guo,^a Erik Källman,^a Lasse Kragh Sørensen,^a Mickaël G. Delcey,^{a,b} Rahul V. Pinjari,^{a,c} and Marcus Lundberg^{*a}

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 ($1s \rightarrow 3d$) excitation can be followed by monitoring the dipole-allowed $K\alpha$ ($2p \rightarrow 1s$) or $K\beta$ ($3p \rightarrow 1s$) 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 $[\text{Fe}(\text{CN})_6]^n$ 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 $[\text{Fe}(\text{CN})_6]^{3-}$ resonances deviate by 0.2 eV in both incident energy and energy transfer directions and multiplet splittings in $[\text{Fe}(\text{CN})_6]^{4-}$ 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 ($2p \rightarrow 3d$) 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 ($1s \rightarrow 3d$). 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).¹⁵

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).^{1,13,24,27} The energy transfer ($\Omega - \omega$), corresponds to the energy of the fundamental process that is probed, e.g., a core, valence or charge-transfer excitation.^{6,7,23,43} In the hard X-ray region, a $1s \rightarrow 3d$ excitation can be coupled to a $2p \rightarrow 1s$ ($K\alpha$), a $3p \rightarrow 1s$ ($K\beta$ main), or even a valence $\rightarrow 1s$ ($K\beta_{2,5}$) emission process, see Figure 1.³⁶ 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.^{8,18} 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.¹

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,

^aDepartment of Chemistry-Ångström laboratory, Uppsala University, SE-751 20 Uppsala, Sweden.; E-mail: marcus.lundberg@kemi.uu.se.

^bPresent address: Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA and Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA. ^cPresent address: School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431606, Maharashtra, India.

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, $K\alpha$, which is approximately ten times more intense than $K\beta$ emission.¹⁵ The complete process is referred to as $K\alpha$ 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 *ab initio* restricted active space (RAS) approach.^{3,5,11,21,29,40,41,51,52} 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 hexacyanide ($[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$), for which data are available both in solid and different solvents.^{30,39} Ferrocyanide has a d^6 electron configuration and exhibits O_h symmetry. Ferricyanide has a d^5 electron configuration, and the five electrons in three degenerate t_{2g} orbitals leads to a weak Jahn-Teller distortion to D_{4h} symmetry. The distortion has only small effects on the calculated spectra and O_h symmetry 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 O_h symmetry, the metal 3d e_g 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^* , often labeled e_g) orbitals. The Fe 3d t_{2g} orbitals mix

weakly with SALCs from empty CN π^* to form three metal-centered bonding (π , often labeled t_{2g}) 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 O_h or D_{4h} symmetry, calculations are effectively performed in the Abelian point group D_{2h} . In that group, Fe 1s, σ and $\sigma^*(e_g)$ orbitals belong to a_{1g} irreducible representation. $\pi(t_{2g})$ and π^* orbitals belong to b_{1g} , b_{2g} , and b_{3g} , while the Fe 2p are in the corresponding ungerade representations.

Fig. 2 Schematic orbital diagram showing the active space of ferricyanide. In ferrocyanide the t_{2g} shell is completely filled. The labels of the transitions show the irreducible representations of the final states reached after a one-electron excitation in ferricyanide.

RASSCF orbital optimizations have been performed using the state average (SA) formalism. For ground and valence excited states, averaging was made over 20 states in each irreducible representation. The ground

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 states for $[\text{Fe}(\text{CN})_6]^{4-}$ and 80 states for $[\text{Fe}(\text{CN})_6]^{3-}$.¹⁷ All intermediate states have the same spin multiplicity as the ground state because the spin-orbit coupling is weak in these states, and the spin-selection rule is therefore largely valid. In the final state, strong 2p spin-orbit coupling gives extensive mixing of states of different multiplicity and triplet states were included for ferrocyanide and quartet states for ferricyanide. The number of states per irreducible representation were 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.⁴²

In a second step, dynamical correlation was included using multi-state second-order perturbation treatment (MS-RASPT2).³² Calculations have been performed using the default ionization-potential electron-affinity shift of 0.25 hartree,¹⁴ and to reduce problems with intruder states an imaginary shift of 0.3 hartree has been applied.¹² 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-vtzip.^{10,19,45,46}

Oscillator strengths have been calculated between orthogonal states formed from a RAS state-interaction approach that also includes spin-orbit coupling,^{34,35} using a local implementation of the origin-independent second-order expansion of the wave vector.^{4,17}

RIXS spectra are described using the Kramers-Heisenberg formula:

$$F(\Omega, \omega) = \sum_f \left| \sum_n \frac{\langle f | T_e | i \rangle \langle i | T_a | g \rangle}{K(\Gamma_i)} \right|^2 \times K(\Gamma_f) \quad (1)$$

where the scattering intensity F is a function of incident energy (Ω) and emitted X-ray energy (ω), the $|g\rangle$, $|i\rangle$, 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 Γ 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.^{25,37} 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 reference³⁰. 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 reference²⁰. The extent of photodamage in the ferricyanide spectrum has been analyzed extensively,⁴⁸ and that data set is within acceptable levels. Calculated spectra are obtained using the procedure described in reference⁴². 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.⁴⁰

3 Results and discussion

3.1 RIXS planes

Experimental and calculated 1s2p RIXS spectra of ferro- and ferricyanide are shown in Figure 3. The two axes are the incident energy (Ω) and the energy transfer ($\Omega - \omega$). Each plane has two separate regions, stretching roughly diagonal across the plane. The region at lower energy transfer is the $K\alpha_1$ emission and these final states correspond to the L_3 edge of the L-edge XAS. The upper region is the $K\alpha_2$ emission, which corresponds to the L_2 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 $K\alpha_1$ and $K\alpha_2$ emission regions, see Figure 3a.³⁰ This transition can be assigned to a $1s \rightarrow 3d(e_g)$ excitation. In the energy transfer direction, the L_3 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 $K\alpha_1$ and $K\alpha_2$ regions is underestimated by 1-2 eV. This is similar to what has previously been observed for the L_3 - L_2 splitting, and can be explained by an underestimation of the 2p spin-orbit coupling in the present scheme.^{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.³⁰ The $1s \rightarrow 3d(e_g)$ excitation leads to two degenerate 1E_g intermediate states. The $2p \rightarrow 1s$ emission from these states lead to different

$2p^5 3d^7$ 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 $1s \rightarrow 3d(t_{2g})$ excitation gives rise to a single $^2A_{1g}$ intermediate state with an unpaired electron in the 1s orbital. From here, $2p \rightarrow 1s$ emission leads to $2p^5 t_{2g}^6$ 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 $1s^1 t_{2g}^5 e_g^1$ intermediate states, split by exchange and multiplet interactions, and even more $2p^5 t_{2g}^5 e_g^1$ final states.^{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.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.³⁰

As the e_g peak involves many different intermediate states it is possible that the RIXS spectrum is affected by interference effects.²² The present calculations, as well

Fig. 3 Experimental and RASPT2 calculated 1s2p RIXS planes of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. Experimental spectra are taken from reference³⁰. The RAS spectra only includes pre-edge absorption and the rising edges are not described.

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 π^* 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 π^* 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 $[\text{Fe}(\text{CN})_6]^{3-}$ 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 $[\text{Fe}(\text{CN})_6]^{4-}$ 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.

Fig. 6 Iron K pre-edge XAS spectra and CEE cuts of ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ 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 π^* 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 π^* 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.³⁰

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

The final $2p^5 t_{2g}^6 e_g^1$ electron configuration gives rise to two different states, having either T_{1u} or T_{2u} 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_{2u} final states can be written $\bar{p}_z d_{z^2}$ and $\bar{p}_z d_{x^2-y^2}$ respectively, where $\bar{p}_z$ represents a hole. For the $\bar{p}_z$ 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_{2u} states are thus lower in energy because of more favorable 2p-3d electron interactions. The wavefunctions with $\bar{p}_x$ and $\bar{p}_y$ 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_{2u} final state, and the energy differences between these states gives rise to the spectral broadening.³⁰

To reproduce the difference between L-edge XAS and CIE thus requires a method that accurately takes into ac-

Fig. 8 Difference in molecular orbital interactions between T_{1u} and T_{2u} multiplets of the 1s2p RIXS final states of ferrocyanide reached after 1s to e_g excitations.

count 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.²⁹ The relative intensities are very well described, including the fact that the π^* peak is the most intense. The energy difference between e_g and π^* peaks is overestimated by 0.6 eV. The agreement appears to be better than for early simulations of the ferrocyanide L-edge XAS.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 e_g - π^* 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 e_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.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 e_g peak with a maximum around 710 eV, and a third π^* peak at around 712 eV.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 π^* resonance, see Figure 9. The main deviations are the shift of the π^* peak to higher energies by ~ 1.5 eV, and the usual underestimation of the splitting between the L_3 and L_2 edges by ~ 1.0 eV.⁴²

Fig. 9 Iron L-edge XAS and CIE cuts through the t_{2g} and e_g pre-edge peaks for ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ from RASPT2 modeling (top) and experiment (bottom).

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 $2p^5 t_{2g}^6$ configuration gives rise to $L=1$ and $S=\frac{1}{2}$ and, according to Hund's third rule, the highest J value ($J_{2p}=\frac{3}{2}$) 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 $2p^6 t_{2g}^5$ 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

Fig. 10 Selection rules among spin-orbit coupled states in ferricyanide for L-edge XAS (electric dipole) and 1s2p RIXS (electric quadrupole followed by electric dipole) processes. Orbital occupations and spin-orbit energies are shown for ground state and t_{2g} final states. Completely filled and empty orbitals are not shown.

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}^5 the lowest J value ($J_{3d}=\frac{1}{2}$) is lower in energy.

In the L-edge XAS a direct excitation from the $J_{3d}=\frac{1}{2}$ ground state (Γ_7^+ in Bethe double-group notation) to the L_2 $J_{2p}=\frac{1}{2}$ t_{2g} peak (Γ_6^-) 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.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.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.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.¹⁷ 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.

5 acknowledgement

We acknowledge financial support from the Marcus and Amalia Wallenberg Foundation, the Swedish Research Council, and the Knut and Alice Wallenberg Foundation (Grant No. KAW-2013.0020). The computations were performed on resources provided by SNIC through Uppsala Multidisciplinary Center for Advanced Computational Science (UPPMAX) and the National Supercomputer Centre at Linköping University (Triolith).

References

- Luuk JP Ament, Michel van Veenendaal, Thomas P Devereaux, John P Hill, and Jeroen van den Brink. *Rev. Mod. Phys.*, 83(2):705–767, 2011.
- M-A Arrio, S Rossano, Ch Brouder, L Galois, and G Calas. *Europhys. Lett.*, 51(4):454–460, 2000.
- Kaan Atak, Sergey I Bokarev, Malte Gotz, Ronny Golnak, Kathrin M Lange, Nicholas Engel, Marcus Dantz, Edlira Suljoti, Oliver Kühn, and Emad F Aziz. *J. Phys. Chem. B*, 117(41):12613–12618, 2013.
- Stephan Bernadotte, Andrew J Atkins, and Christoph R Jacob. *J. Chem. Phys.*, 137(20):204106–204121, 2012.
- Sergey I Bokarev, Marcus Dantz, Edlira Suljoti, Oliver Kühn, and Emad F Aziz. *Phys. Rev. Lett.*, 111(8):083002–083007, 2013.
- SM Butorin, J-H Guo, Martin Magnuson, Pieter Kuiper, and J Nordgren. *Phys. Rev. B*, 54(7):4405–4408, 1996.
- SM Butorin, DC Mancini, J-H Guo, N Wassdahl, J Nordgren, M Nakazawa, S Tanaka, T Uozumi, A Kotani, Y Ma, and KE Myano. *Phys. Rev. Lett.*, 77(3):574–577, 1996.
- Frank MF De Groot. *Chem. Rev.*, 101(6):1779–1808, 2001.
- Frank MF De Groot. *Coordin. Chem. Rev.*, 249(1):31–63, 2005.
- Marvin Douglas and Norman M Kroll. *Ann. Phys.*, 82(1):89–155, 1974.
- Nicholas Engel, Sergey I Bokarev, Edlira Suljoti, Raul Garcia-Diez, Kathrin M Lange, Kaan Atak, Ronny Golnak, Alexander Kothe, Marcus Dantz, Oliver Kühn, and E.F Aziz. *J. Phys. Chem. B*, 118(6):1555–1563, 2014.
- Niclas Forsberg and Per-Åke Malmqvist. *Chem. Phys. Lett.*, 274(1):196–204, 1997.
- Faris Gel'mukhanov and Hans Ågren. *Phys. Rep.*, 312(3):87–330, 1999.
- Giovanni Ghigo, Björn O Roos, and Per-Åke Malmqvist. *Chem. Phys. Lett.*, 396(1):142–149, 2004.
- Pieter Glatzel and Uwe Bergmann. *Coordin. Chem. Rev.*, 249(1):65–95, 2005.
- Pieter Glatzel, Henning Schroeder, Yulia Pushkar, Thaddeus Boron III, Shreya Mukherjee, George Christou, Vincent L Pecoraro, Johannes Messinger, Vittal K Yachandra, Uwe Bergmann, and J Yano. *Inorg. Chem.*, 52(10):5642–5644, 2013.
- Meiyuan Guo, Lasse Kragh Sørensen, Mickaël G Delcey, Rahul V Pinjari, and Marcus Lundberg. *Phys. Chem. Chem. Phys.*, 18(4):3250–3259, 2016.
- K Hämäläinen, DP Siddons, JB Hastings, and LE Berman. *Phys. Rev. Lett.*, 67(20):2850–2853, 1991.
- Bernd A Hess. *Phys. Rev. A*, 33(6):3742–3748, 1986.
- Rosalie K. Hocking, Erik C. Wasinger, Frank MF de Groot, Keith O. Hodgson, Britt Hedman, and Edward I. Solomon. *J. Am. Chem. Soc.*, 128:10442–10451, 2006.
- Ida Josefsson, Kristjan Kunnus, Simon Schreck, Alexander Föhlisch, Frank de Groot, Philippe Wernet, and Michael Odelius. *J. Phys. Chem. Lett.*, 3(23):3565–3570, 2012.
- Amélie Juhin, Christian Brouder, and Frank Groot. *Open. Phys.*, 12(5):323–340, 2014.
- C-C Kao, WAL Caliebe, JB Hastings, and J-M Gillet. *Phys. Rev. B*, 54(23):16361–16364, 1996.
- Akio Kotani and Shik Shin. *Rev. Mod. Phys.*, 73(1):203–246, 2001.
- Manfred Otto Krause and JH Oliver. *J. Phys. Chem. Ref. Data*, 8(2):329–338, 1979.
- Thomas Kroll, Ryan G Hadt, Samuel A Wilson, Marcus Lundberg, James J Yan, Tsu-Chien Weng, Dimosthenis Sokaras, Roberto Alonso-Mori, Diego Casa, Mary H Upton, and Hedman B. *J. Am. Chem. Soc.*, 136(52):18087–18099, 2014.
- Thomas Kroll, Marcus Lundberg, and Edward I. Solomon. John Wiley & Sons, Ltd, Hoboken, 2016.
- Juraj Kuchar, Juraj Cernak, and Werner Massa. *Acta Crystallogr. C*, 60(8):418–420, 2004.
- Kristjan Kunnus, Wenkai Zhang, Mickaël G. Delcey, Rahul V. Pinjari, Piter S. Miedema, Simon Schreck, Wilson Quevedo, Henning Schroeder, Alexander Föhlisch, Kelly J. Gaffney, Marcus Lundberg, Michael Odelius, and Philippe Wernet. *J. Phys. Chem. B*. doi: 10.1021/acs.jpcc.6b04751, 2016.
- Marcus Lundberg, Thomas Kroll, Serena DeBeer George, Uwe Bergmann, Samuel A Wilson, Pieter Glatzel, Dennis Nordlund, Britt Hedman, Keith O Hodgson, and Edward I Solomon. *J. Am. Chem. Soc.*, 135(45):17121–17134, 2013.
- Dongxia Ma, Giovanni Li Manni, Jeppe Olsen, and Laura Gagliardi. *J. Chem. Theory. Comput.* doi: 10.1021/acs.jctc.6b00382, 2016.
- Per-Åke Malmqvist, Kristine Pierloot, Abdul Rehaman Moughal Shahi, Christopher J Cramer, and Laura Gagliardi. *J. Chem. Phys.*, 128(20):204109–204119, 2008.
- Per-Åke Malmqvist, Alistair Rendell, and Bjoern O. Roos. *J. Phys. Chem.*, 94(14):5477–5482, 1990.
- Per-Åke Malmqvist and Björn O Roos. *Chem. Phys. Lett.*, 155(2):189–194, 1989.
- Per-Åke Malmqvist, Björn O Roos, and Bernd Schimmelpfennig.

-
- Chem. Phys. Lett.*, 357(3):230–240, 2002.
- 36 Drew A Meyer, Xuena Zhang, Uwe Bergmann, and Kelly J Gaffney. *J. Chem. Phys.*, 132(13):134502–134510, 2010.
- 37 Masahide Ohno and Grant A van Riessen. *J. Electron. Spectrosc.*, 128(1):1–31, 2003.
- 38 Jeppe Olsen, Bjo:rn O. Roos, Poul Jørgensen, and Hans Jørgen Aa. Jensen. *J. Chem. Phys.*, 89(4):2185–2192, 1988.
- 39 Thomas James Penfold, Marco Reinhard, Mercedes Hannelore Rittmann-Frank, Ivano Tavernelli, Ursula Rothlisberger, Christopher J Milne, Pieter Glatzel, and Majed Chergui. *J. Phys. Chem. A.*, 118(40):9411–9418, 2014.
- 40 Rahul V Pinjari, Mickaël G Delcey, Meiyuan Guo, Michael Odelius, and Marcus Lundberg. *J. Chem. Phys.*, 141(12):124116–124127, 2014.
- 41 Rahul V Pinjari, Mickaël G Delcey, Meiyuan Guo, Michael Odelius, and Marcus Lundberg. *J. Chem. Phys.*, 142(6):069901, 2015.
- 42 Rahul V. Pinjari, Mickaël G. Delcey, Meiyuan Guo, Michael Odelius, and Marcus Lundberg. *J. Comput. Chem.*, 37(5):477–486, 2016.
- 43 PM Platzman and ED Isaacs. *Phys. Rev. B*, 57(18):11107–11114, 1998.
- 44 Bjorn O. Roos. John Wiley & Sons, Inc. Hoboken, NJ, USA, 1987.
- 45 Björn O Roos, Roland Lindh, Per-Åke Malmqvist, Valera Veryazov, and Per-Olof Widmark. *J. Phys. Chem. A.*, 108(15):2851–2858, 2004.
- 46 Björn O Roos, Roland Lindh, Per-Åke Malmqvist, Valera Veryazov, and Per-Olof Widmark. *J. Phys. Chem. A.*, 109(29):6575–6579, 2005.
- 47 Björn O Roos, Peter R Taylor, and Per E M Siegbahn. *Chem. Phys.*, 48(2):157–173, 1980.
- 48 MM van Schooneveld and S DeBeer. *J. Electron Spectrosc.*, 198:31–56, 2015.
- 49 Satoru Sugano, Yukito Tanabe, and Hiroshi Kamimura. Academic Press, INC, New York., 1970.
- 50 György Vankó, Frank MF de Groot, Simo Huotari, RJ Cava, Thomas Lorenz, and M Reuther. *arXiv preprint arXiv:0802.2744.*, 2008.
- 51 Ph Wernet, Kristjan Kunnus, Ida Josefsson, Ivan Rajkovic, Wilson Quevedo, Martin Beye, Simon Schreck, Sebastian Grübel, Mirko Scholz, and Dennis Nordlund. *Nature.*, 520(7545):78–81, 2015.
- 52 Philippe Wernet, Kristjan Kunnus, Simon Schreck, Wilson Quevedo, Reshmi Kurian, Simone Techert, Frank MF de Groot, Michael Odelius, and Alexander Föhlisch. *J. Phys. Chem. Lett.*, 3(23):3448–3453, 2012.
- 53 Tami. E. Westre, Pierre. Kennepohl, Jane. G. DeWit, Britt. Hedman, Keith. O. Hodgson, and Edward. I. Solomon. *J. Am. Chem. Soc.*, 119(27):6297–6314, July 1997.
- 54 Tami E Westre, Pierre Kennepohl, Jane G DeWitt, Britt Hedman, Keith O Hodgson, and Edward I Solomon. *J. Am. Chem. Soc.*, 119(27):6297–6314, 1997.
-