## Supporting information for "Simulations of iron K pre-edge X-ray absorption spectra using the restricted active space method"

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Table 1: Geometries used in the K pre-edge simulations.

Bond <sup>a</sup>	$[\text{FeCl}_6]^{3-}$	$[\text{FeCl}_6]^{4-}$	$[\text{FeCl}_4]^{1-}$	$[\text{FeCl}_4]^{2-}$	$[\text{Fe(CN)}_6]^{4-}$	$[\mathrm{Fe(CN)}_6]^{3-}$
Fe-Cl	2.400	2.510	2.186	2.292	-	-
Fe-C	-	-	-	-	1.913	1.936/1.916
C-N	-	-	-	-	1.161	1.178/1.180

<sup>a</sup> Bond distances are taken from crystal structures (Ref.[43-47]) for all complexes except  $[Fe(CN)_6]^{3^-}$ , where the geometry is from a CASPT2/ANO-RCC-VTZP(9,0,0;0,10,0) optimization. Jahn-Teller distortions due to uneven occupation of near-degenerate 3*d* orbitals are expected for  $[FeCl_6]^{4^-}$ ,  $[FeCl_4]^{2^-}$ , and  $[Fe(CN)_6]^{3^-}$ . In  $[Fe(CN)_6]^{3^-}$ , where calculations are performed on the distorted geometry, the effects on the final X-ray spectrum of the Jahn-Teller distortion is small. For  $[FeCl_4]^{2^-}$  geometry optimization using CASPT2/ANO-RCC-VTZP(12,0,0;0,11,0) did not give any significant distortion, and the experimental (non-distorted) geometries are used for both  $[FeCl_4]^{2^-}$  and  $[FeCl_6]^{4^-}$ . The  $O_h$  and  $D_{4h}$  systems are calculated in  $D_{2h}$  symmetry and the  $T_d$  systems in  $D_2$  symmetry. In both these point groups the final states can belong to four different irreducible representations.

Table 2: Oscillator selected X-ray absorption resonance different strengths for from  $(f^{\mu}\mu),$ contributions:electric-dipole-electric-dipole electric-quadrupole-electric-quadrupole  $(f^{mm}),$  $(f^{\mu O}).$  $(f^{QQ}),$ magnetic-dipole-magnetic-dipole electric-dipole-electric-octupole electric-dipole-magnetic-quadrupole ( $f^{\mu M}$ ). Threshold for printing these contributions is  $10^{-12}$ 

	Excitation states	$f^{\mu\mu}$	$f^{QQ}$	$^{\mathrm{a}}f^{mm}$	$f^{\mu O}$	$f^{\mu M}$
$[\text{FeCl}_6]^{3-}$	${}^{5}T_{2g}(7112.8 \text{ eV})$	0.00	3.94E-06	0.00	0.00	0.00
	${}^{5}E_{g}(7114.2 \text{ eV})$	0.00	3.39E-06	0.00	0.00	0.00
$[\text{FeCl}_6]^{4-}$	${}^{4}T_{1g}(7111.3 \text{ eV})$	0.00	4.20E-06	0.00	0.00	0.00
-	${}^{4}T_{2g}(7112.0 \text{ eV})$	0.00	3.39E-06	0.00	0.00	0.00
	${}^{4}T_{1g}(7113.5 \text{ eV})$	0.00	3.59E-06	0.00	0.00	0.00
$\left[\mathrm{FeCl}_4\right]^{1-}$	${}^{5}E(7112.5 \text{ eV})$	0.00	3.97E-06	0.00	0.00	0.00
	${}^{5}T_{2}(7113.2 \text{ eV})$	2.27E-05	3.27E-06	0.00	2.73E-07	$9.37 \text{E}{-}08$
$[\text{FeCl}_4]^{2-}$	${}^{4}A_{2} (7110.8 \text{ eV})$	0.00	3.65E-06	0.00	0.00	0.00
-	${}^{4}T_{2}(7111.6 \text{ eV})$	1.06E-05	3.00E-06	0.00	1.16E-08	4.40E-08
	${}^{4}T_{1}(7112.0 \text{ eV})$	1.05E-05	2.99E-06	0.00	1.09E-08	4.91E-08
$[\text{Fe(CN)}_6]^{4-}$	$^{2}E_{g}(7112.9 \text{ eV})$	0.00	6.51E-06	0.00	0.00	0.00
$[{\rm Fe(CN)}_{6}]^{3-}$	$^{1}A_{1g}(7110.1 \text{ eV})$	0.00	3.43E-06	0.00	0.00	0.00
	$^{3}T_{1g}(7112.9 \text{ eV})$	0.00	3.75E-06	0.00	0.00	0.00

<sup>a</sup> The selection rules for allowed magnetic-dipole-magnetic-dipole transitions are  $\triangle J=0,\pm 1$  and no parity change. For  $1s \rightarrow 3d$  transition,  $\triangle J=2$ , and for  $1s \rightarrow 4p$ , then parity is changed.

Table 3: Parameters (in eV) for the semi-empirical CTM simulations. All parameters are taken from earlier fits to the L-edge XAS spectra, Ref. [34,35].

		Configuration separations				LM	CT	MLCT	
	10Dq	EG2	$\mathrm{EF2}$	EG3	EF3	$T(t_{2g})$	$T(e_g)$	$T(t_{2g})$	$T(e_g)$
$[\text{FeCl}_6]^{3-}$	1.20	0.10	-2.20	-	-	0.90	1.75	-	-
$[\text{FeCl}_6]^{4-}$	0.60	2.25	1.75	-	-	0.45	0.9	-	-
$[\text{Fe(CN)}_6]^{4-}$	3.90	2.06	1.56	-2.00	-0.00	0.00	1.90	1.60	$0.00/1.00^{\rm a}$
$[\text{Fe(CN)}_6]^{3-}$	4.00	1.00	0.50	-1.00	-1.50	0.60	2.10	2.00	$0.00/0.90^{\rm a}$

<sup>a</sup> Different parameters in initial and final states.

Table 4: Intensities, average scaling factors and energy shifts(eV).

	Intensity		Average scalin	g factor	Energy	shift
	$RAS^{a}$	Experiment <sup>b</sup>	RAS	CTM	RAS	DFT
$[\text{FeCl}_6]^{3-}$	$1.57 \times 10^{-5}$	$6.06 \times 10^{-2}$	$2.57 \times 10^{-4}$	11.0	-18.71	171.6
$[\text{FeCl}_6]^{4-}$	$1.28 \times 10^{-5}$	$4.97 \times 10^{-2}$	$2.57 \times 10^{-4}$	11.0	-18.30	172.0
$[\text{FeCl}_4]^{1-}$	$7.26 \times 10^{-5} (1.62 \times 10^{-5})^{c}$	$2.81 \times 10^{-1}$	$2.57{ imes}10^{-4}$	11.0	-20.01	171.3
$[\text{FeCl}_4]^{2-}$	$4.63 \times 10^{-5} (1.36 \times 10^{-5})^{c}$	$1.65 \times 10^{-1}$	$2.57{ imes}10^{-4}$	11.0	-20.13	171.5
$[\text{Fe}(\text{CN})_6]^{4-}$	$1.03 \times 10^{-5}$	$6.21 \times 10^{-2}$	$2.57 \times 10^{-4}$	11.0	-18.35	172.4
$[{\rm Fe}({\rm CN})_{6}]^{3-}$	$1.43 \times 10^{-5}$	$7.55 \times 10^{-2}$	$2.57 \times 10^{-4}$	11.0	-18.38	171.9

<sup>a</sup> Sum of oscillator strengths, not including LMCT or MLCT contributions. The intensity is integrated over the energy range from 7109 to 7116 for [FeCl<sub>6</sub>]<sup>3-</sup> and [FeCl<sub>6</sub>]<sup>4-</sup>, from 7109 to 7115.5 for [FeCl<sub>4</sub>]<sup>1-</sup> and [FeCl<sub>4</sub>]<sup>2-</sup>, from 7110 to 7114.8 for [Fe(CN)<sub>6</sub>]<sup>4-</sup>, from 7108.5 to 7115.8 for [Fe(CN)<sub>6</sub>]<sup>3-</sup>.
<sup>b</sup> Integrated pre-edge area from the edge subtracted spectra.

<sup>c</sup> The sum of oscillator strength for quadrupole contributions.

Table 5: Selected metal-ligand covalencies (in % metal content) from RAS (ground and excited states), CTM and DFT calculations. For the  $T_d$  symmetric complexes the amount of 4p character is shown in parenthesis.

	RAS ground		RAS excited		CTM ground <sup>a</sup>		B3LYP ground		BP86 ground <sup>a</sup>	
	$t_{2g}$	$e_g$	$t_{2g}$	$e_g$	$t_{2g}$	$e_g$	$t_{2g}$	$e_g$	$t_{2g}$	$e_g$
$[\text{FeCl}_6]^{3-}$	97.9	82.7	95.5	61.1	95	70	94	72	85	64
$[\text{FeCl}_6]^{4-}$	97.5	91.6	96.9	61.4	96	88	98	91	94	83
$[\text{Fe}(\text{CN})_6]^{4-}$	92.5	64.8	90.4	69.8	-	45	69	59	77	57
$\left[\mathrm{Fe(CN)}_6\right]^{3-}$	95.5	61.3	93.0	67.8	60	47	77	72	75	54
	$t_2(4p)$	e	$t_2(4p)$	e	$t_2(4p)$	e	$t_2(4p)$	e	$t_2$	e
$\left[\mathrm{FeCl}_4\right]^{1-}$	81.1(1.1)	95.9	70.8(1.3)	94.5	76	89	76(2.6)	89	68	77
$[\text{FeCl}_4]^{2-}$	91.4(0.7)	97.4	67.6(0.8)	96.3	87	93	80(1.5)	91	84	89

<sup>a</sup> Ref.[34,35]



Figure 1: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(11,0,2:0,10,1) calculation of  $[FeCl_6]^{3-}$  with 30 final states.



Figure 2: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(12,0,2:0,10,1) calculation of  $[FeCl_6]^{4-}$  with 20 final states.



Figure 3: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(13,0,2:0,11,1) calculation of  $[\text{FeCl}_4]^{1-}$  with 30 final states.



Figure 4: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(14,0,2:0,11,1) calculation of  $[FeCl_4]^{2-}$  with 30 final states.



Figure 5: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(12,0,2:0,10,1) calculation of  $[Fe(CN)_6]^{4-}$  with 20 final states.



Figure 6: Selected active orbitals in the ground state (top line) and excited state (bottom line) for the RAS(11,0,2:0,10,1) calculation of  $[Fe(CN)_6]^{3-}$  with 80 final states.



Figure 7: K pre-edge XAS spectra of  $[\text{FeCl}_6]^{3-}(\text{left})$  and  $[\text{FeCl}_6]^{4-}(\text{right})$  with different number of excited states in each of the four final-state irreducible representation  $(a_{1g}, b_{1g}, b_{2g}, \text{ and } b_{3g})$ .



Figure 8: K pre-edge XAS spectra of  $[\text{FeCl}_4]^{1-}(\text{left})$  and  $[\text{FeCl}_4]^{2-}(\text{right})$  with different number of excited states in each of the four final-state irreducible representation  $(a, b_1, b_2, \text{ and } b_3)$ . Quadrupole (solid line) and dipole (dash line) contributions are calculated separately.



Figure 9: K pre-edge XAS spectra of  $[Fe(CN)_6]^{4-}(left)$  and  $[Fe(CN)_6]^{3-}(right)$  with different number of excited states in each of the four final-state irreducible representation  $(a_{1g}, b_{1g}, b_{2g}, and b_{3g})$ .



Figure 10: Experimental iron K pre-edge spectra for the six iron complexes in the present study.



Figure 11: Peak fitting of the K-edge XAS spectra (black) of  $[\text{FeCl}_6]^{3-}$  (left) and  $[\text{FeCl}_6]^{4-}$  (right). The smoothed second derivative of the K-edge XAS is shown in blue and fitted peaks with dashed green lines. Fitting of K pre-edge features was performed using the EDG-FIT module of the EXAFSPAK suite using pseudo-Voigt line shapes with a fixed 50:50 ratio of Lorentzian to Gaussian functions where the peak positions, width and intensities were varied. Two functions are used to model the the rising edge.



Figure 12: Peak fitting of the K-edge XAS spectra (black) of  $[\text{FeCl}_4]^{1-}$  (left) and  $[\text{FeCl}_4]^{2-}$  (right). For a detailed description of the fitting procedure see the caption of Figure 11.



Figure 13: Peak fitting of the K-edge XAS spectra (black) of  $[Fe(CN)_6]^{4-}(left)$  and  $[Fe(CN)_6]^{3-}(right)$ . For a detailed description of the fitting procedure see the caption of Figure 11.

High-spin d<sup>6</sup> systems  $(1s \rightarrow 3d(e_g) \text{ excitations})$ 

Low-spin d<sup>5</sup> systems (1s $\rightarrow$ 3d(e<sub>g</sub>) excitations)

$$\begin{split} {}^{3}T_{1}(\gamma,M_{s}=1) &= \left| \xi \eta \overline{\eta} \xi \overline{\xi} v \right| \\ {}^{3}T_{2}(\zeta,M_{s}=1) &= \left| \xi \eta \overline{\eta} \xi \overline{\xi} u \right| \\ {}^{3}T_{1}(\beta,M_{s}=1) &= \frac{1}{2} \left( - \left| \xi \overline{\zeta} \eta \xi \overline{\xi} u \right| - \sqrt{3} \left| \xi \overline{\zeta} \eta \xi \overline{\xi} v \right| \right) \\ {}^{3}T_{1}(\alpha,M_{s}=1) &= \frac{1}{2} \left( - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi u \right| + \sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{1}(\alpha,M_{s}=1) &= \frac{1}{2} \left( - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi u \right| + \sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| - \left| \xi \overline{\zeta} \eta \overline{\eta} \xi v \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) &= \frac{1}{2} \left( -\sqrt{3} \left| \xi \overline{\zeta} \eta \overline{\eta} \xi \xi u \right| \right) \\ {}^{3}T_{2}(\xi,M_{s}=1) \\ {}^{3}T_{2}(\xi,M_{$$

Figure 14: The wavefunctions of  $T_{1g}$  and  $T_{2g}$  states for high-spin  $d^6$  system and low-spin  $d^5$  system.



Figure 15: RAS simulations of the K pre-edge of  $[Fe(CN)_6]^{4-}$  (left) and  $[Fe(CN)_6]^{3-}$  (right) with the  $\pi^*$  orbitals in the active space (black) and without (red). For  $[Fe(CN)_6]^{4-}$  spectra are calculated with 20 states per irreducible representation and for  $[Fe(CN)_6]^{3-}$  with 60 states per irreducible representation.



Figure 16: RAS simulations of the K pre-edge of  $[Fe(CN)_6]^{3-}$  with 80 states in each of the four final state (black) and only single excitations allowing into  $e_g$  and  $\pi^*$  orbitals (red). The orbital analysis is performed on the calculation with single excitations.



Figure 17: Correlation between the experimental integrated pre-edge area and RAS intensities (left), and between the two different ways to estimate the experimental pre-edge areas, for details see the Computational details.