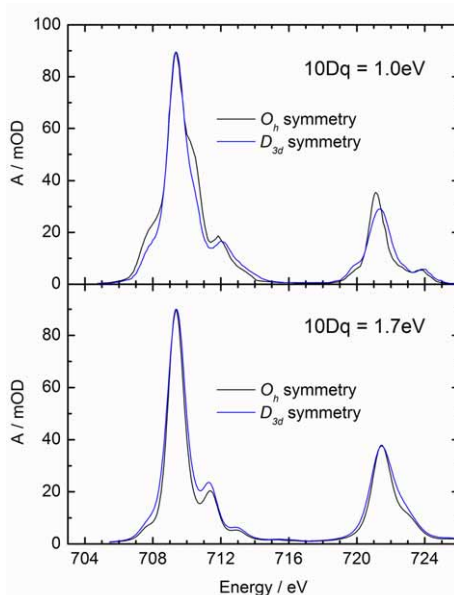


Ligand-field Symmetry Effects in Fe(II) Polypyridyl Compounds Probed by Transient X-ray Absorption Spectroscopy

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Supplementary Material

10 We have performed charge transfer multiplet (CTM) calculations in order to access what effect symmetry reduction has on the L-edge line shapes and in particular, on the branching ratio $r_3 = I(L_3)/[I(L_2)+I(L_3)]$.



15 **Fig. S** Charge transfer multiplet (CTM) calculations for a low-spin Fe^{II} compound with crystal fields in O_h - and D_{3d} -symmetry. The value describing the additional D_{3d} -symmetry crystal field is $10D_s = 2.0$ eV. The resulting branching ratios are (top panel) 0.78 and 0.75 for O_h - and D_{3d} -symmetry, respectively, and (bottom panel) 0.66 for both, O_h - and D_{3d} -symmetry.

20 The CTM approach is based on atomic theory, with the addition of crystal field interactions, and the CTM model of Thole and co-workers.^{S1,S2} The CTM many-body Hamiltonian includes the on-site correlation energy U of the Fe $3d$ level, the $3d3d$ electron-electron interaction within the $3d$ shell and the $2p3d$ multiplet interaction between the $2p$ and $3d$ shells, as well as

the spin-orbit coupling in each subshell. The atomic values have been used for the $2p3d$ and $3d3d$ interactions and for the $2p$ and $3d$ spin-orbit coupling. As one possible variation, the Fe environment was simulated using crystal fields with O_h -symmetry (defined by the parameter $10Dq$) and with D_{3d} -symmetry (with an additional value for $10Ds = 2.0$ eV). Covalent mixing between the metal $3d$ -orbitals with the ligand valence $2p$ -orbitals was taken into account by charge-transfer between the $3d^6$, $3d^5L^-$, and $3d^7L^+$ configurations (the latter two describing π -back-bonding and σ -donation, respectively).

10 The branching ratio r_3 can be used as a measure of the spin-state^{S2} but for a polyatomic system is also affected by other factors such as valence orbital mixing and structural variations. It is apparent from Fig. S that the change in branching ratio r_3 of the Fe^{II} L-edges in the singlet ground state is clearly affected for a crystal field parameter $10Dq = 1.0$ eV (top panel in Fig. S) 15 while for the larger value $10Dq = 1.7$ eV no substantial change in the branching ratio is observed between octahedral and trigonal symmetry (bottom panel in Fig. S). From these empirical calculations we tentatively deduce that for the difference in branching ratio r_3 of the investigated compounds, the varying deviation from octahedral symmetry is not the main 20 reason.

References

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