

# Spin Sensitivity in the X-ray Emission of Iron Compounds

S. Lafuerza<sup>1</sup>, A. Carlantuono<sup>2</sup>, P. Glatzel<sup>1</sup>, M. Retegan<sup>1</sup>

<sup>1</sup>ESRF-The European Synchrotron, 71, Avenue des Martyrs, Grenoble, France

<sup>2</sup>Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

[marius.retegan@esrf.fr](mailto:marius.retegan@esrf.fr)

Core-to-core  $K\alpha$  and  $K\beta$  X-ray emission lines have long been recognized as markers of the local spin states in transition metal complexes [1]. As such, changes in the spectral envelope have been successfully used to track the spin dynamics of short-lived excited states or to quantify local spin moments [2]. However, the spin-related spectral changes, which are intrinsically related differences in the exchange interaction between the core and valence electrons, can be obscured by the changes due to different chemical environments around the metallic center. Also, as the magnitude of the exchange interaction is different in  $K\alpha$  and  $K\beta$ , their spin sensitivity will be different.

To address these points, we have carried out a systematic experimental and theoretical investigation of the  $K\beta$  and  $K\alpha$  XES spectra on a wide range of iron compounds with different oxidation states (+2, +3, +4, and mixed-valence), spin states (high spin, low spin, and mixed-spin), coordinating ligands (fluorides, oxides, sulfides, etc.), and local symmetry (octahedral and tetrahedral). We have retrieved the spin evolution between complexes by determining various parameters commonly used in X-ray emission studies ( $K\beta_{1,3}$ -first moment,  $K\alpha_1$ -full width half maximum, and integrated absolute difference (IAD) [3]). Our analysis reveals a significant spread of these parameters even at fixed nominal spin values. Using semi-empirical multiplet calculations we were able to show that this results from changes in the intra-atomic exchange interaction arising from metal-ligand covalency.

## References

[1] - P. Glatzel and U. Bergmann, *Coord. Chem. Rev.* **249**, 65 (2005).

[2] - W. Zhang et al., *Nature* **509**, 345 (2014).

[3] - G. Vankó et al., *J. Phys. Chem. B* **110**, 11647 (2006).