

# RESONANT X-RAY EMISSION SPECTROSCOPY UNVEILS FINE DETAILS OF COBALT 1s PRE-EDGES

**G. Vankó<sup>1\*</sup> and F.M.F. de Groot<sup>2</sup>**

<sup>1</sup> MTA KFKI Research Institute for Particle and Nuclear Physics  
H-1525 Budapest, P. O. Box 49, Hungary

<sup>2</sup> Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University,  
Sorbonnelaan 16, 3584 CA Utrecht, Netherlands

*Keywords: transition metals, electronic structure, X-ray absorption, resonant X-ray emission, nonlocal transitions*

*\*) e-mail: vanko@rmki.kfki.hu*

X-ray absorption spectroscopy (XAS) at the 3d metal K edges can be separated into a pre-edge region and an edge region. The pre-edge is rich in information, as it reflects valence and spin state, coordination number and local symmetry simultaneously. However, there are several obstacles to address the fine details of the pre-edge, including its low intensity, the poor separation from the tail of the main edge, and the smearing due to the large lifetime broadening of the 1s core hole in the XAS final state. Combination of absorption and emission spectroscopy, the resonant X-ray emission spectroscopy (RXES) can overcome these problems and can unveil the details of the underlying transitions [1]. This will be demonstrated by applying RXES 1) to resolve resonances of different sites that happen to appear at the same incident energy in Co<sub>3</sub>O<sub>4</sub>, 2) to disprove an assignment based on deceptive XAS spectral shapes in LaCoO<sub>3</sub>, and 3) to study nonlocal 1s3d transitions to 3d orbitals of the neighbouring metal atoms. The latter will constitute the main part of the talk, and thus it is described in more details in what follows.

Over the last five decades, the pre-edge is ascribed to 1s3d quadrupole transitions to the empty 3d (or mixed 3d-4p) states and the edge region to the onset of 1s4p transitions to the (4p) conduction band. Accumulating theoretical and experimental evidence indicate that this description is incomplete, and non-local (off-site) transitions to neighbouring metal 3d orbitals may also take place [2,3]. We performed a detailed investigation of pre-edges on compounds containing (almost centrosymmetric) CoO<sub>6</sub> clusters with high-resolution 1s2p RXES [4]. Our strategy to search for non-local excitations was to vary the Co(4p)–O(2p)–Co'(3d) mixing by varying the Co–O bond length and the Co–O–Co angle: optimal mixing is expected at short bond lengths and linear Co–O–Co arrangement. We found that non-local effects are visible for all low-spin Co(III) oxides, where the intensity of the non-local peak is larger for the corner-sharing oxides LaCoO<sub>3</sub> and EuCoO<sub>3</sub> versus the edge-sharing oxides LiCoO<sub>2</sub> and AgCoO<sub>2</sub>. In addition, angular dependent experiments reveal the different origin of the pre-edge features: while the local

transition is quadrupolar, the non-local one shows a dipolar character, as expected. The absence of the non-local peak for Co(acac)<sub>3</sub>, a low-spin Co(III) system with isolated Co-ions, further supports its non-local nature (see Figure 1). The non-local peaks are neither visible for CoO, a high-spin Co(II) system with significantly longer Co–O bond distances. The absence of non-local effects and the rich multiplet structure makes CoO the ideal system to show the improvement in the resolving power of our RXES experiment with 0.3 eV (FWHM) energy resolution as well as to demonstrate the coherent second-order nature of the underlying scattering process. These results have important consequences on the interpretation of the pre-edges (and thus the lowest-lying excitations) of highly correlated transition metal compounds with a short metal-ligand distance. In these, typically high-valent systems, the usual interpretation of quadrupole pre-edge plus dipole edge fails and the dominant pre-edge structure can be the non-local dipole feature.

The offered interpretation of the pre-edges has far reaching implications within physics, but also in many applied fields. Our results suggest that application of resonant techniques are in many cases indispensable to the understanding of the pre-edge region, whose intuition-based analysis can otherwise fail.

## References

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