

HARD X-RAY PHOTON-IN-PHOTON-OUT SPECTROSCOPY WITH LIFETIME RESOLUTION – OF XAS, XES, RIXSS AND HERFD

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A photon-in-photon-out technique using hard x-rays is most suitable for applications where the sample environment cannot be chosen freely, *i.e.* UHV conditions necessary for photoemission experiments are not possible, or when a truly bulk sensitive probe is desired. The preferred X-ray spectroscopy technique to study element specifically electronic structure and local coordination is X-ray absorption spectroscopy (XAS). The near edge structure (XANES) is mainly used to obtain oxidation states, even though XANES also contains information on the local geometry and coordination. A detailed analysis of the XANES structure is a complex task because of the numerous interactions that contribute to its shape. The spectroscopy using the extended range (EXAFS) is well developed theoretically and experimentally but the technique has its inherent limitations (*e.g.* differentiation of elements close in atomic number Z) and the ideal experimental conditions (*e.g.* sample thickness, homogeneity) for a correct EXAFS analysis are not always given. It is thus desirable to introduce other techniques that either provide a mean to verify the results obtained from XAS or yield additional information on the sample in particular with respect to electronic structure.

An X-ray spectrometer based on perfect crystal Bragg optics opens up new possibilities for X-ray spectroscopy. Detecting the emitted X-rays with an instrumental energy bandwidths on the order of the core hole lifetime broadening enables to resolve fine structure in the X-ray emission spectrum. This fine structure contains information on the electronic configuration and chemical environment of the emitting atom that is complementary to what can be obtained in XAS [1, 2]. Such a secondary monochromator provides an additional tunable energy detection to the primary monochromator of the synchrotron radiation source. X-ray emission spectroscopy (XES) thus adds a dimension to XAS. The techniques arising from such an experimental setup have been named non-resonant XES, resonant XES or resonant inelastic X-ray scattering (RIXS) spectroscopy and high-energy-resolution fluorescence detection (HERFD). They will be discussed in this contribution. Another technique, non-resonant X-ray Raman scattering, will be left out to be discussed by others [3].

The experimental setup requires monochromatization of the emitted X-rays using perfect Bragg optics. Many instruments use a Rowland geometry with spherically bent Si or Ge wafers either in Johann or Johansson geometry (Fig. 1). An energy scan can be performed either point-by-point or single shot where the emission energy is dispersed over a position sensitive detector [4].

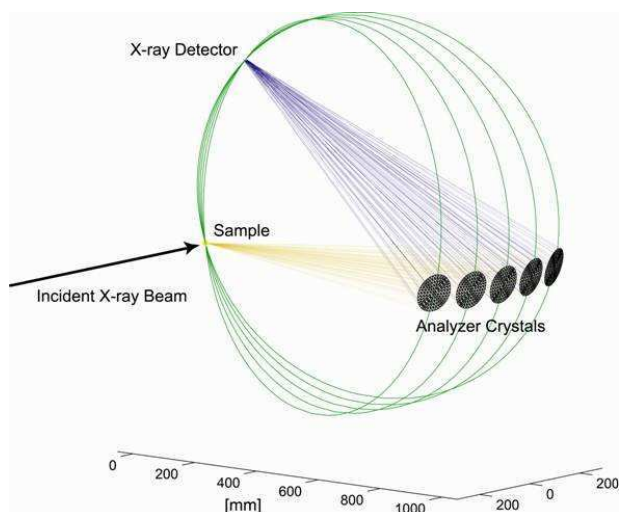


Figure 1. Setup for x-ray emission spectroscopy. Five spherically bent analyzer crystals monochromatize and focus the X-rays on a photon counting detector. The Rowland circles that define the focusing condition are shown.

An important feature and difference to standard XAS of x-ray emission detection with lifetime resolution is the strong sensitivity to electronic structure. The emission lines just below the Fermi level reflect the projected density of occupied electronic states (Fig. 2). The final states electron configuration is formally identical to valence band photoemission even though different selection rules yield different relative spectral intensities. A comparison between absorption and emission spectra can provide an element specific band gap. This is routinely done in soft x-ray spectroscopy and will now be combined with hard x-rays in order to have more freedom

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with respect to sample environment and to have access to a larger range of momentum transfer. Bergmann and co-workers showed the sensitivity of the $K\beta$ cross-over peak to the atomic charge of the ligand [5]. It is thus possible to distinguish between O, N and F as ligands to the metal atom which is difficult or impossible using other techniques.

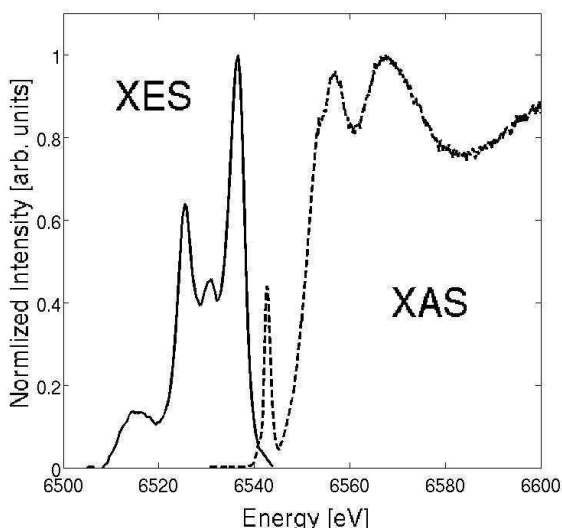


Figure 2. X-ray absorption (dashed) and X-ray emission spectra (full) in a Mn(III) nitrido complex.

The $3p$ to $1s$ transitions ($K\beta$ main lines) in $3d$ transition metals at lower energies have been used by many authors to address the metal atom spin state [6, 7]. The spin-sensitivity in the emission can also be exploited to record spin-selective absorption spectra [8]. This can be used to elucidate the origin of the spectral features in the K absorption pre-edge. Based on this technique, it was straight forward to prove the existence or absence of a $3d^4$ high-spin configuration, *i.e.* a high-spin Fe(IV) species, in catalytic systems [9] and the presence of a non-local excitation in hematite (Fe_2O_3) [10].

In a seminal study, Hämäläinen showed that spectral features with a broadening that is lower than the absorption core hole lifetime broadening can be obtained using high energy resolution fluorescence detected (HERFD) absorption spectroscopy [11]. More than 10 years later, this technique found its way to the applied sciences and was for example used to study the chemical behaviour of Au nanoparticles in the oxidation of carbon monoxide (Fig. 4) [12]. For this technique to yield spectra that can be analyzed using the theory of X-ray absorption it is necessary that final state effects in the X-ray emission process can be neglected. This is fortunately the case for the $L\alpha$ decay channels in $5d$ transition elements.

Many pitfalls can surprise the scientist who uses high energy resolution emission detection. Some of them have been first pointed out by Carra, Fabrizio and Thole [13]. Based on this paper the problems have been illustrated by

the present author and it is strongly recommended to record full intensity planes with incident and emitted energy as energy axes in order to unequivocally identify the origin of a spectral feature (*cf.* Fig. 3 and Ref. [1]). Many years of experience does not prevent erroneous assignment of spectral features as the present author had to experienced.

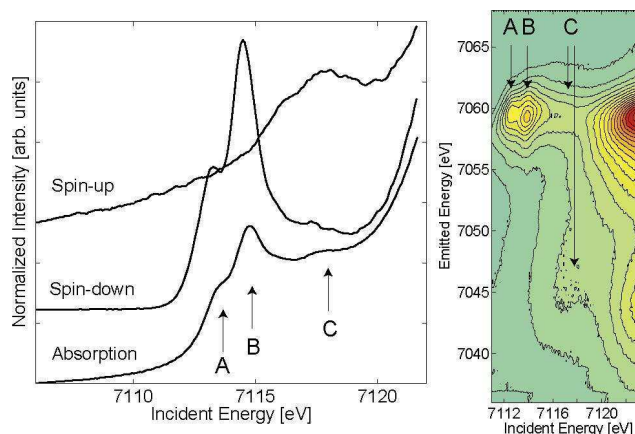


Figure 3. Left: Total and spin-selective absorption in Fe_2O_3 for $\epsilon \perp c$. Right: $1s3p$ RXES plane for polycrystalline Fe_2O_3 . The spin-up and spin-down excitations occur around 7045 and 7059 eV emitted energy, respectively.

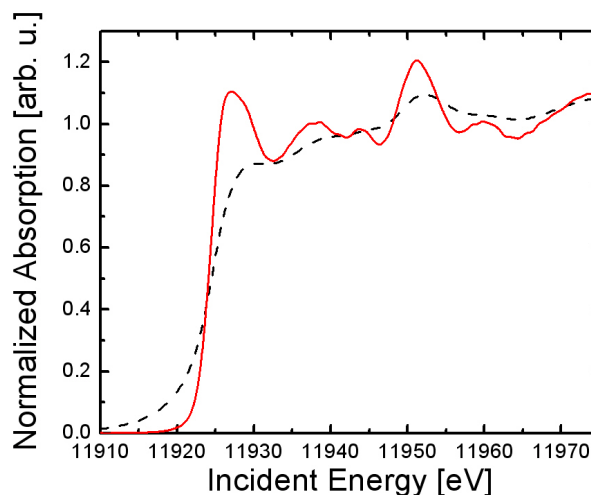


Figure 4. The L_3 absorption edge of a Au foil detected in transmission mode (dotted) and using the HERFD technique (solid).

The fundamental problem and hold-up in the progress of X-ray spectroscopy to study electronic structure is the theoretical modelling of the spectra. While the interpretation of EXAFS to obtain structural information is well developed, only few experiments that address the electronic structure are well understood based on an established theoretical framework. This is mainly due to the complexity of the problem. There are excellent research groups who do theoretical spectroscopy and

produce outstanding results. However, this is by far not enough to match the ever growing number of experimental spectra that require interpretation. X-ray emission spectrometers are either planned or being constructed at all of the new European synchrotron radiation sources. At first this will aggravate the problem but also gives rise to the hope that a larger user community will push for greater efforts in theoretical modelling in order to have more resources devoted to this field.

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