Chapter 16
High-Energy Resolution XAS

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16.1 Introduction

High-energy resolution X-ray absorption refers to the measurement of XANES spectra with the use of a detector signal that is measured coherently with the XANES measurement. The detector signal can be fluorescence, which is known under the name High-Energy Resolution Fluorescence Detected (HERFD) XANES. Similarly one can define High-Energy Resolution Auger Detection (HERAD) XANES.

The first HERFD experiments have been performed by Hamalainen and coworkers [1]. They recorded the dysprosium L_3 edge by detecting the 2p3d fluorescence with an energy resolution better than the core hole lifetime broadening. They indeed observed a much more structured spectral shape with respect to the conventional XANES spectrum. A similar experiment was performed on the Mn K pre-edge [2]. The first spectra using nonradiative decay channels have been published by the groups of Sham [3] and Drube [4, 5].

## 16.2 Principle of High-Resolution XANES

In a HERFD experiment, a XANES spectrum is measured with a resolution that appears sharper than the lifetime broadening of the core hole. HERFD spectra are popular for the K edges of 3d transition metals and also for the $L_{2,3}$ edges of rare

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Fig. 16.1 HERFD XANES
(*top*) and normal XANES
(*bottom*) at the iron K edge
of Fe_2SiO_4 [6]
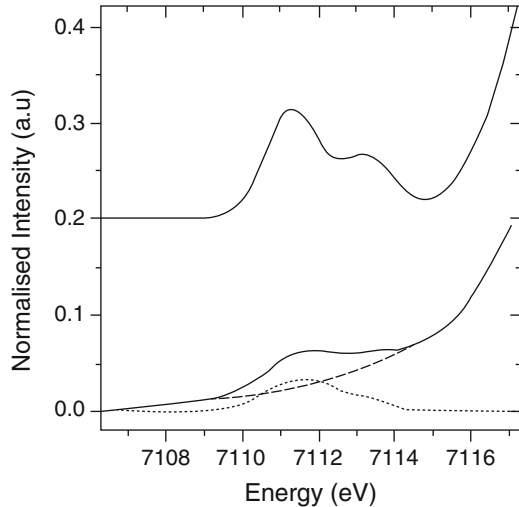
earths and actinides. The quadrupole pre-edge structures in these edges appear much sharper in the HERFD spectra, see for example the iron pre-edge of Fe_2SiO_4 in Fig. 16.1 [6]. The sharper features allow for a much more detailed analysis.

The main principle of HERFD XANES can best be described assuming a single 1s resonance state at the edge that is linked to a single 1s2p X-ray emission decay final state [7]. By tuning the incident photon energy close to the 1s absorption state, the X-ray absorption and X-ray emission processes occur coherently and the overall 1s2p process is described by the Kramers–Heisenberg formula:

$$F(\Omega, \omega) = \sum_j \left| \sum_i \frac{\langle j|T_2|i\rangle\langle i|T_1|g\rangle}{E_g + \hbar\Omega - E_i + i\Gamma_i} \right|^2 \delta(E_g + \hbar\Omega - E_j - \hbar\omega)$$

This formula forms the basis of all resonant X-ray processes. The scattering cross section F is given as a function of the excitation energy (Ω) and the emission energy (ω). The ground state (g) is excited to an intermediate state (i), characterized by a 1s core hole via the dipole operator (T_1). The second dipole operator (T_2) describes the X-ray emission decay to the final state (j) with a 2p core hole. The denominator contains the binding energy of the core hole state and its lifetime broadening. A resonance occurs if the excitation energy is equal to the 1s edge. The general spectral landscape can be viewed as a two-dimensional space with axis Ω and ω.

Figure 16.2 shows a contour-plot of the resonant inelastic X-ray scattering (RIXS) plane indicating a single core hole resonance coupled to a single final state [8]. The gray area is the peak maximum, which is set at 100. The first contour-line is set at 64 and each following line represents respectively 32, 16, 8, etc., as indicated in the figure. The horizontal axis shows the X-ray excitation energy. The X-ray absorption spectrum consists of a single resonance with an
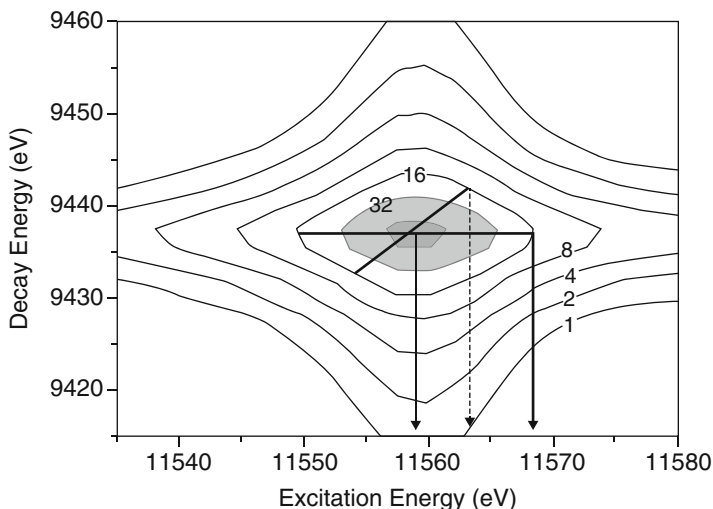
Fig. 16.2 Two-dimensional contour plot of the RIXS plane of a single resonance and a single final state [8]

energy of approximately 11,560 eV. The vertical axis shows the final state energies with a maximum of the X-ray emission decay at 2123 eV.

Instead of normal X-ray absorption, one can measure the X-ray absorption spectrum at a fixed emission energy. This relates to the diagonal line in Fig. 16.2. The effective lifetime related broadening can be derived from the figure, and is given by

$$\Gamma = 1/\sqrt{\Gamma_i^{-2} + \Gamma_j^{-2}}$$

If the intermediate state lifetime broadening is much large than the final state lifetime broadening the total HERFD lifetime is approximately equal to the final state lifetime broadening. The Lorentzian broadening thus decreases in comparing normal X-ray absorption and selective X-ray absorption. In case of a single resonance this is a real effect that can be exploited in HERFD experiments.

In the case of a series of resonances with, in particular a series of different final state energies, the situation becomes more complex. Figure 16.3 shows the experimental data of 2p4f quadrupole pre-edge of LaF_3 at 460 eV [9]. The vertical X-ray emission axis shows the 2p5d decay channel centered at 0 eV. Detecting the HERFD XANES with such RIXS plane yields a number of pre-edge peaks related to the multiple X-ray emission channels, as indicated in the panel on the right. Note that this HERFD XANES spectrum is NOT the same as the XANES spectrum itself. The XANES spectrum consists of only a single peak at 460 eV; all the other
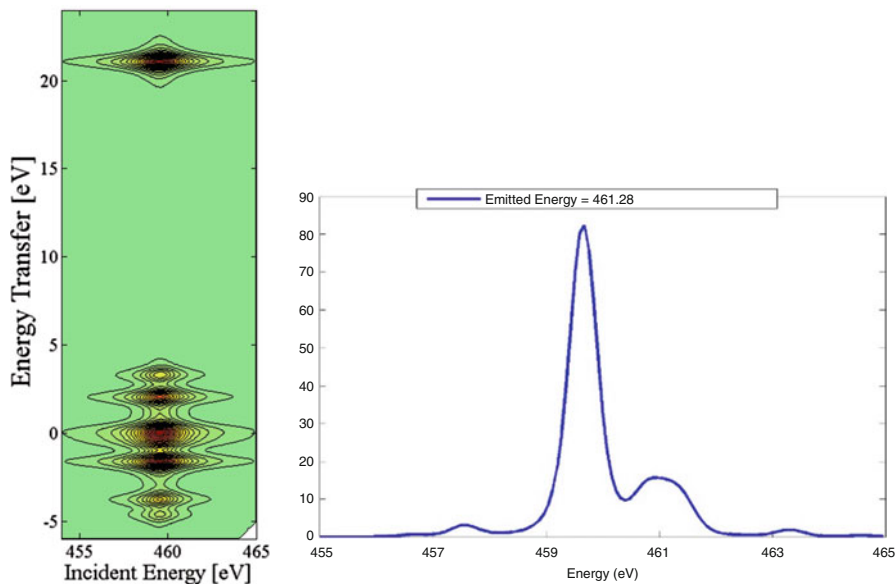
Fig. 16.3 Two-dimensional contour plot of the 2p5d RIXS plane of a single XANES excitation at 460 eV coupled to multiple X-ray emission final states. The HERFD cross section yields a spectrum with many peaks, which in this example is not the same as the XANES spectrum [9]

structures are tails from different X-ray emission channels. This is an important warning that HERFD spectra should always be treated carefully in their approximation as pure XANES spectra.

16.3 Resonant Inelastic X-ray Scattering

A general way to present RIXS is by showing 2D plots that provide a comprehensive picture of the 1s X-ray absorption and the 1s2p X-ray emission processes. For quantitative purposes it is, however, more convenient to compare 1D spectral shapes. There are a number of ways one can create spectral shapes out of the 2D images [10]. In Fig. 16.4, three cross sections are shown, respectively:

- The constant incident energy (CIE) spectrum, a vertical cross section at fixed excitation energy (7112 eV in the figure). This relates to resonant X-ray emission spectra.
- The constant transferred energy (CTE) spectra, a horizontal cross section at a constant transferred energy in Fig. 16.4a. In Fig. 16.4b, the CTE scan is a diagonal cross section. A constant transferred energy implies that for all excitation energies the same final states are probed. This could also be called constant final state (CFS) spectra.
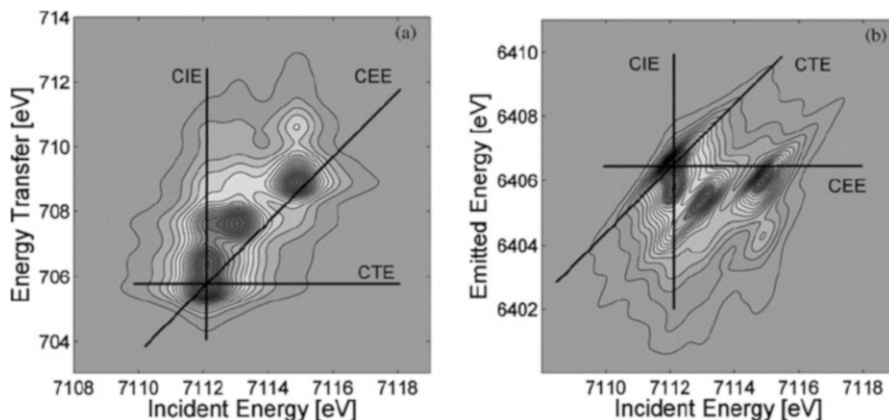
Fig. 16.4 Two-dimensional contour plot of the 1s2p RIXS plane of an iron compound. RIXS planes can be given with two different choices for the axes, where the vertical axis can be used for the energy transfer (*left*) or for the emitted energy (*right*). Three cross sections can be made, respectively the constant emission energy (CEE) that identifies with the HERFD spectrum, the constant incident energy (CIE) spectrum and the constant transfer energy (CTE) spectrum [10]

- The constant emission energy (CEE) spectra: a diagonal cross section at a constant emission energy in Fig. 16.4a. In Fig. 16.4b, the CEE scan is a horizontal cross section at fixed emission energy. This relates to the HERFD spectrum the so-called "lifetime."

16.4   Using the Chemical Options of the RIXS Plane

There are a number of ways in which one can use the RIXS planes to derive detailed information. We will briefly mention these options:

16.4.1   Valence Selective X-ray Absorption

If there is a valence shift in the X-ray emission energies of for example Fe^{2+} and Fe^{3+}, one can use the separate resonances to selective detect the XANES spectra of Fe^{2+} and Fe^{3+} in the same material. This has been demonstrated for the case of Prussian blue that contains a combination of Fe^{2+} and Fe^{3+} sites [11]. In case of an active catalyst one can track both signals and as such follow the time-evolution of the valence selective XANES spectra. In principle this also applies for the EXAFS spectra as has been shown in Ref. 11.

16.4.2   Spin Selective X-ray Absorption

Using the 1s3p X-ray emission channel, the main peak and the satellite are correlated with the spin state of the metal ion. As such one can distinguish different spin states in the X-ray absorption spectrum. It can be shown that spin selective X-ray absorption relates to the local spin moment and is essentially the same for a paramagnet and a ferromagnet [12].

16.5   Analysis of HERFD Spectra of the Pre-edge Peaks of Transition Metal K Edges

Over the last years, the use of HERFD XANES has greatly improved our knowledge of the 3d transition metal K pre-edge structures. In short the pre-edges can be understood as follows. For all systems there is the 1s3d quadrupole transition directly into the empty 3d states. This is essentially an atomic transition that has the same strength for any 3d valence hole. The pre-edge fine structure can be calculated with crystal field multiplet models. At higher energy there is the 1s4p dipole transition that defines the main K edge. The main K edge structure can be calculated with, for example, DFT based models such as band structure and multiple scattering [13].

Next there are a few options:

(a) If the system is divalent, has a metal ion with inversion symmetry, and has isolated transition metal ions, no additional features are present.
(b) If the metal ion has no inversion symmetry, the metal 3d states mix with the metal 4p states. This implies that there are dipole transitions to the pre-edge and the pre-edge intensity will strongly increase in intensity.
(c) If the metal ion has a trivalent or tetravalent nature, contains ligand bridged metal sites, and has inversion symmetry, non-local peaks will appear in the pre-edge region. The non-local peaks typically appear at 2.5 eV higher energy, and this energy difference is related to the additional core hole potential of the 3d excitonic states.

Figure 16.5 shows the RIXS planes of two low-spin Co(III) systems. The system that contains isolated Co ions only shows the quadrupole peak. The solid state oxide system that contain close Co-O-Co bonds show an additional peak at 2.5 eV higher excitation energy, related to a non-local excitation: The 1s core hole is dipole excited to a 4p state that hybridizes with the 3d-band of a cobalt ion that is close by. The energy of this non-local peak has higher excitation energy because the local 1s3d quadrupole peak is pulled down by the core hole potential [14].
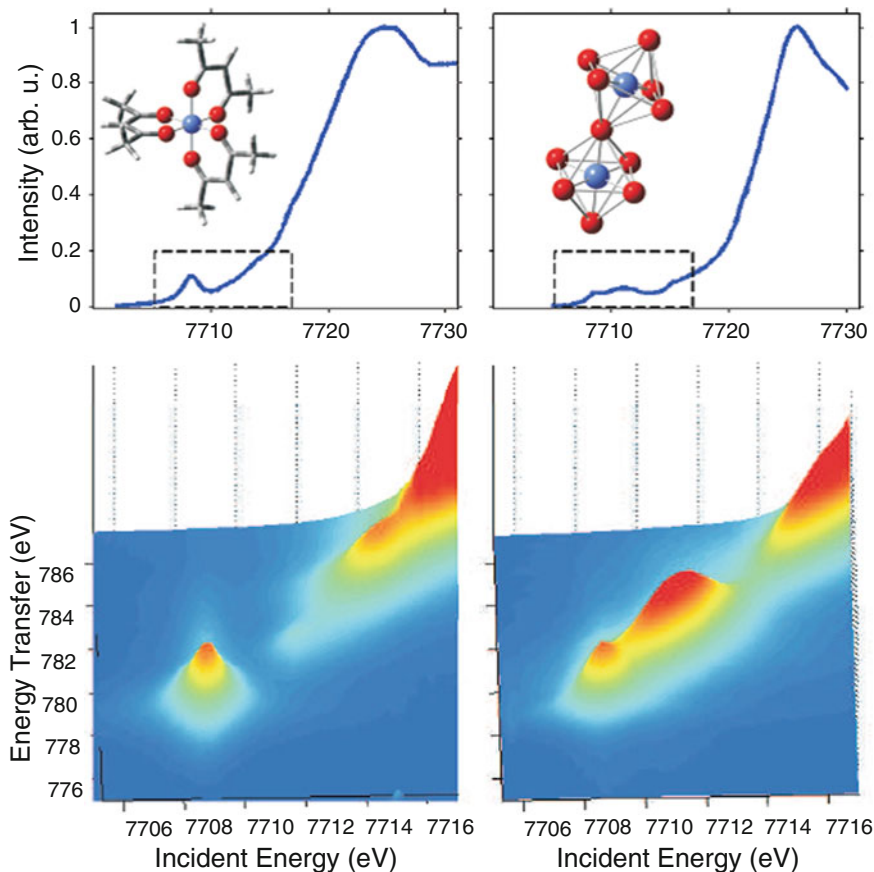
Fig. 16.5 Two-dimensional contour plot of the 1s2p RIXS plane of two low-spin Co(III) systems, an isolated molecular system (*left*) and a solid state oxide system (*right*). The solid state spectrum has an additional peak related to the non-local transition [14]

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