



Hard X-ray photon-in photon-out spectroscopy

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ABSTRACT

Spectroscopic techniques to study the electron configuration and local coordination of a central atom by detecting inner-shell radiative decays following photoexcitation using hard X-rays are presented. The experimental setup requires an X-ray spectrometer based on perfect crystal Bragg optics. The possibilities arising from non-resonant and resonant X-ray emission spectroscopy are discussed when the instrumental energy broadenings of the primary (beamline) monochromator and the crystal spectrometer for X-ray emission detection are on the order of the core hole lifetimes of the intermediate and final electronic states. The small energy bandwidth in the emission detection yields line-sharpened absorption features. In transition metal compounds, electron–electron interactions as well as orbital splittings and fractional population can be revealed. Combination with EXAFS spectroscopy enables to extend the *k*-range beyond unwanted absorption edges in dilute samples that limit the EXAFS range in conventional absorption spectroscopy.

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1. Introduction

Photon-in photon-out techniques are targeted at applications where the sample environment cannot be chosen freely, i.e. UHV conditions suitable for photoemission experiments are not possible. This applies in particular to catalysis research where the aim is to study the catalyst under working conditions. The most popular *in situ* X-ray spectroscopy technique to study the element-specific electronic structure and local coordination is X-ray absorption spectroscopy (XAS) [1,2]. The X-ray absorption near edge structure (XANES) is often used to obtain oxidation states but 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 absorption range (EXAFS) is well developed theoretically and experimentally but the technique has its inherent limitations (e.g. differentiation of elements close in atomic number) 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 X-ray techniques that either provide a means to verify the results obtained from XAS or yield additional information concerning local coordination and electronic structure.

An X-ray absorption spectrum arises from excited states that subsequently decay either non-radiatively by emitting an electron (Auger decay) or radiatively (fluorescence). The fluorescence or, more general, the X-ray emission exhibits a chemical sensitivity when recorded with an instrumental energy bandwidth that is on the order of the lifetime broadenings [3–5]. The required energy resolution can be achieved by employing an X-ray emission spectrometer based on perfect-crystal Bragg optics (Fig. 1) [6–8].

High-brilliance, tunable X-ray sources that are nowadays available allow to study the X-ray emission with unprecedented energy resolution and sensitivity resulting in a wealth of new applications [3]. The emission spectrometer installed at a synchrotron radiation beamline acts as a secondary monochromator for the emitted X-rays with an instrumental energy broadening that is similar to the primary crystal monochromator that selects the incident energy. Non-resonant X-ray emission spectroscopy (XES) provides information on occupied electron orbitals in the valence shell. By tuning the incident energy to an absorption edge, i.e. to a resonant state, and observing the X-ray emission one takes advantage of the properties of resonant X-ray emission (RXES) or resonant inelastic X-ray scattering (RIXS) [5,9]. As a result, a spectral sharpening occurs that can reveal previously unobserved features giving valuable input for a detailed analysis.

The main strength of XES is that the electronic structure can be studied element-selectively and under *in situ* conditions. XES is thus complementary to XAS which mainly addresses the local coordination (EXAFS) or provides only basic information on the

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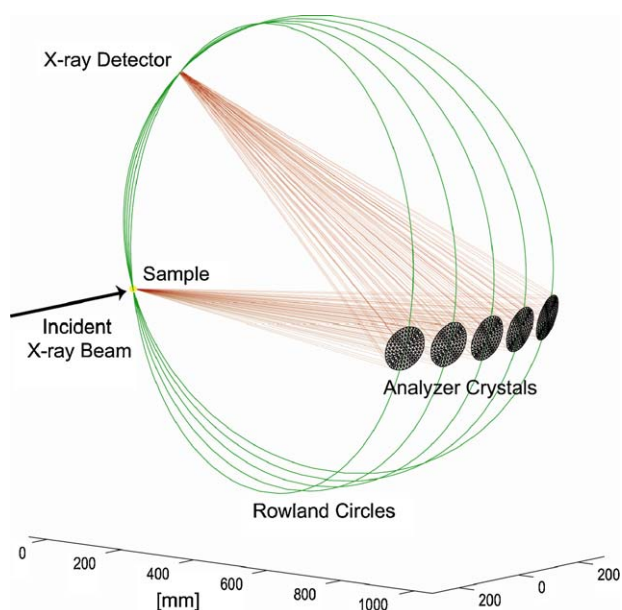


Fig. 1. X-ray emission spectrometer with vertical scattering geometry employing five analyzer crystals. The focusing (Rowland) circles are shown.

electronic structure, e.g. an oxidation or reduction of the metal. The activity of catalytic sites and reaction kinetics depend on the electronic structure and the potential of X-ray emission spectroscopy to study chemical reactions is considerable. The aim of this contribution is therefore to give an overview of the technique and we hope to give some ideas for experiments to the inclined reader. The paper is organized as follows. We first outline some basic aspects of resonant and non-resonant XES. We then give examples that demonstrate the possibilities of XES. This section is divided into non-resonant XES, i.e. fluorescence lines, and resonant XES (RXES or RIXS).

2. X-ray emission spectroscopy with lifetime resolution

The energy level diagram in Fig. 2 schematically describes the energy levels that are involved in absorption and emission spectroscopy. We use a multi-electron scheme where the vertical axis denotes the total energy of the entire system including all electrons that are possibly involved in the photoabsorption process. An absorption edge is formed by discrete resonances (e.g. 3d transition metal K pre-edges) as well as broad excitations

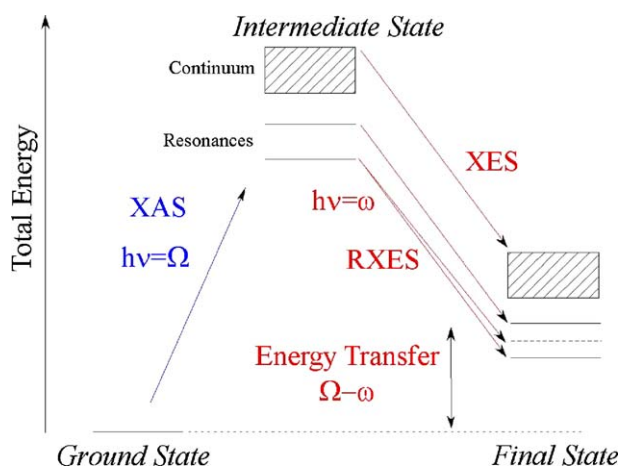


Fig. 2. Energy scheme for X-ray absorption and emission.

into a band or the continuum. A radiative decay from a continuum state gives rise to a non-resonant X-ray emission or fluorescence line. We define high-energy-resolution X-ray emission measurements as detecting the fluorescence line with an energy bandwidth on the order or below the core hole lifetime broadening.

The physics involved in a two-level photon scattering process (second-order optical process) are described by the Kramers–Heisenberg equation [9]. The scattered X-ray intensity is a function of two experimental energies, the incident X-ray energy Ω and emitted X-ray energy ω , as well as the energies of the electronic configurations. It is useful to define the energy transfer $\Omega - \omega$ in order to relate the energies of all intermediate and final states to the same reference energy, i.e. the ground state energy.

The model energy diagram in Fig. 2 shows two resonant intermediate states of which the lower decays into two final states. The final state that is represented by a dashed line is due to the so-called final state effects. These are electron interactions that occur only in the final and not in the intermediate state. We now translate this energy diagram into a contour plot where the incident energy points along the horizontal axis and the energy transfer or final state energy points along the vertical direction (Fig. 3). Comparisons between different spectra and a quantitative analysis are usually made for line plots. We therefore show some possibilities for extracting line plots from the full RIXS plane. When the incident energy is plotted versus the energy transfer, both lifetime broadenings extend perpendicularly to each other in the RIXS plane. The broader intermediate state lifetime stretches along the incident energy axis. Scans of the emission energy (constant incident energy scans) yield spectra that are broadened by the final state lifetime broadening that is usually smaller than for the intermediate state.

It is important to note that terminology like “lifetime suppressed” that is sometimes found in the literature does not mean that the lifetime broadenings are reduced or even disappear in resonant spectroscopies. The lifetime broadenings are always there as the RIXS plane shows (Fig. 3). All the experimentalist can do (apart from de-convoluting the spectra [10]) is scan through the RIXS plane such that the line broadening is minimized. This is in many cases achieved using a diagonal cut through the RIXS plane as shown in Fig. 3. Experimentally, this means that the emission energy is fixed while the incident energy is scanned (constant emission energy scan). This resembles an absorption scan and was done by Hämäläinen et al. on dysprosium [11].

A comparison between an absorption and a constant emission energy scan requires some further discussion. First, the constant emission energy scan shows a feature at 4969 eV which is absent in the absorption scan. One may be led to conclude that the reduced lifetime broadening reveals this absorption feature. While this feature is indeed revealed by using an instrumental energy bandwidth below the lifetime broadening there is, however, no absorption resonance at 4969 eV. This may appear counter-intuitive since the intermediate states are reached via absorption of a photon. Comparison of the RIXS plane with the energy diagram in Fig. 2 shows that, in fact, the feature at 4969 eV is due to the absorption resonance at 4968 eV that causes via the final state effect and the lifetime broadening a peak at higher incident energy. The limitations in interpretation of constant emission scans as absorption scans have been pointed out by Carra et al. [12] as well as Loeffen et al. [10]. Secondly, the pre-edge features show a stronger intensity relative to the main edge in the high-resolution scan. This has also been observed experimentally in Fe systems [13,14].

The fact that the lifetime broadenings do not disappear in RIXS spectroscopy has important ramifications. A large number of resonant states with an energy splitting that is considerably smaller than their intermediate and final state lifetime broadenings cannot

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