New results in high-resolution X-ray fluorescence spectroscopy

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Abstract. We present some recent results dealing with resonant inelastic X-ray scattering (RIXS) on atomic targets in the 3-5 keV energy region. In this so-called tender spectral region, the K-shell fluorescence branching ratios become reasonably large, but a full vacuum enclosure is still preferable to avoid detection efficiency loss due to the sizeable arms of high resolution crystal spectrometers. By squeezing energy resolution in the fluorescence decay channel, one may improve the spectral resolution of photoabsorption, enable separation of multielectron excitation and relaxation channels, and completely eliminate the need to scan across the selected energy range of the photon probe in order to acquire the photoabsorption spectrum. On the other hand, the spectra may be untrivially modified by effects such as interference of absorption-emission paths or structured relaxation modes, and a more elaborated modelling is needed to understand the emitted signal. We illustrate these aspects by presenting four cases: the reconstruction of Ar KM and Ar KL absorption edges from a series of highly resolved emission spectra recorded at different probe energies, the reconstruction of the Xe L₃ edge from a single X-ray emission spectrum, and the analysis of the radiative Ar K-MM Auger decay preceeded by the resonant or nonresonant photon absorption.

1. Introduction

In a commonly perceived picture, the excitation-decay process induced by a weak probe consists of a more or less prompt excitation stage followed by a delay – with an average duration of the core-hole lifetime \( \tau \) – which ends by a decay of the excited quantum system to one of the allowed channels with probabilities governed by the corresponding relative decay rates. An effective time spread of the excitation stage depends on the type of the probe and on the nature of the excitation, for example, the time required for the ejected electron to leave an atom after the photoabsorption event significantly affects the probability for electronic coexcitation. This forms a basis of the Thomas model for the electron shake-up and shake-off probability \cite{1} that prevails at high electron energies, where other “mechanisms” for satellite production, such as electron knock-out, become less probable. Similar to excitation, electronic coexcitation may also occur in the decay of the core-hole in the Radiative Auger emission process (RAE), where the transition energy is shared by the emitted photon and electron. Both events, excitation and decay, may overlap more or less strongly when they lead to electron ejection: the faster (Auger) electron emitted later overtakes the slow primary ejected electron, which leads to energy...
and momentum exchange in the so-called post-collision interaction, even to such an extent that primary electron is recaptured [2]. As for the timing, the sharpest picture is obtained by resonant photoabsorption and emission in the atom: a single photon is absorbed or emitted by a single electron and no electron leaves the atom (Fig. 1a). The energy conservation in such a photon in - photon out experiment is reflected by the Raman effect, i.e., in the absence of any energy drain in the atom the energy of the emitted photon is bound to follow energy of the absorbed photon - a linear Raman dispersion. Nowadays the experiments are feasible with a combined probe and spectrometer energy resolution tighter than the core-hole natural linewidth $\Gamma$ (see for example [3]). Besides improving the spectral resolution, such experiments offer a tool to shorten an effective time between excitation and decay below $1/\Gamma$ by detuning the photon probe energy. The “core hole clock” effects are seen in the molecular and solid state physics in which the energy can be pumped from electronic to atomic degrees of freedom, and results in nonlinear energy dispersion in the resonant Auger and X-ray spectra [4].

In the following we present a few results of X-ray photon in - photon out experiments obtained at the ID26 beamline of the ESRF facility (France) with our high resolution Johansson type crystal spectrometer equipped with the position sensitive photon detector [5].

![Figure 1](image_url)

**Figure 1.** a) Schematics of the resonant photon in - photon out experiment involving creation of satellite atomic states in the excitation ($K^{-1}V^{-1}O^2$, blue (black) line), in the emission ($V^{-2}O^2$, red (gray) line) or both ($V^{-3}O^3$, green (light gray) dotted line). The dashed line denotes the final ionic $V^{-1}$ state populated by the diagram transition. b) Ar K photoabsorption (black line) and KM X-ray emission spectrum recorded at probe energy 3250 eV (gray (red)). Emission lines $\omega''_1$ pertaining to triply excited final atomic state are not yet observed (?).

2. Separation of multielectron excitations

As there is a small (positive) energy shift of the satellite line versus the diagram emission line due to the presence of an extra vacancy in the initial subshell (see Fig. 1b), high resolution spectroscopy can be employed to separate both contributions in the emission. Such an approach removes the uncertainties of the usual procedure that draws the separation line between the single- and multielectron excitations by extrapolation of the single electron contribution in the absorption spectrum. The Ar KM satellite spectrum presented in Fig. 2 results from the direct separation of the emission signal. The low energy part with two-electron excitations of the type $(1s3p)^{-1}nln'l'$ smoothly maintains intensity by opening of the $(1s3p)^{-1}nll$ shake-up and $(1s3p)^{-1}nll$ shake-off transitions which slowly saturate the signal. The lowest peak in energy corresponds to the so-called conjugate shake-up into $(1s3p)^{-1}4s^2$ state and there is a reasonably good agreement with calculated intensities according to the configuration interaction...
(CI) model with the nonorthogonal orbitals separately optimized for the ground and the excited core-hole states [6]. For more tightly bound satellites, the relative signal is smaller but the energy shift is larger and the separation of satellite structure in the emission channel can still be performed. Fig. 3 presents the Ar KL satellite signal structure. This tiny absorption signal of the order of 0.3% of the smooth background of Ar K and Ar KM signal is much easier to isolate on the high energy tail of the K-L emission line where it becomes a predominant feature at high photon probe energy (Fig. 3a). It is interesting that the absorption signal measured in the emission mode starts to agree with the photoabsorption spectrum of Deutsch et al. [7] only after taking into account that fluorescence decay rate of the singlet core hole transition \((1s^2p)^{-1} 1P \rightarrow 2p^2 \ 1S^{1}D\) is about two times larger than the rate of the triplet transition \((1s^2p)^{-1} 3P \rightarrow 2p^2 \ 3P\). (The Auger decay rates of the singlet and triplet core hole combination are approximately equal.) Still, the emission of the lowest singlet and triplet resonances reaches only about half the emission intensity with respect to the absorption signal. An extensive CI calculation including \((1s^2p)^{-1}(4p^2 + 3d^2 + 4d^4d + 3d4s + 4ds)\) configurations, higher Rydberg states, and shake-up states approximately reproduces the photoabsorption spectrum (Fig. 3b) and also shows the existence of several overlapping levels hidden underneath the two-peak resonance structure. The observed lack of intensity in X-ray emission is attributed to the destructive interference of the corresponding absorption-emission paths, similar to the HCl case [8]. The Ar KL satellites demonstrate that a substantial change of the fluorescence decay branching ratio and relatively strong interference effects may generate significant differences of the integrated emission signal with respect to the true absorption spectrum.

3. Avoiding the photon probe scan
In principle, the photoabsorption spectrum is measured by recording attenuation of the photon beam as a function of probe energy. For practical reasons, the true photoabsorption signal is often substituted by the signal of characteristic photons emitted in fluorescence decay of an inner hole, relying on the stability of the fluorescence branching ratio across the threshold. The photon yield is collected either by the solid state detector which measures the integral photon yield (TFY) or by the high resolution X-ray spectrometer equipped with the slit to detect fluorescence.
Figure 3. a) Ar K-L emission spectrum recorded at photon probe energy of 4000 eV. b) Comparison of the KL absorption signal (empty red circles, [7]) with the total fluorescence yield (filled black circles) in the KL edge energy region. Model result for the photoabsorption is shown by a thick gray (red) line. It is the sum of the resonant (thin lines) and shake-up contributions (dashed line). The (red) dotted curve shows the absorption signal multiplied by 1.87.

at a single emission energy (HERFD). On the other hand, when high resolution spectrometer is equipped by a position sensitive detector, the scanning ability of the photon probe is not a necessary requirement for acquisition of the photoabsorption spectrum. The absorption is in fact encoded in the emission spectrum and under proper conditions - normally an off-resonant negative detuning of the probe - a relation between the emission and absorption spectra is simple and straightforward [9]. In the so-called HERO (High Energy Resolution Off-resonant) spectroscopy [10], the absorption spectrum can therefore be obtained at a fixed photon probe energy (i.e., without any scanning), and is accumulated in parallel on the spectrometer CCD camera. To follow changes on the atomic level for materials submitted to variable environment or undergoing chemical reaction, one needs to acquire a full absorption spectrum in a due time. Depending on the signal emission strength and statistics required, one may be able to measure dynamics of the system with absorption frames of the order of milliseconds, which is practically impossible to achieve by moving the parts of the beamline mechanically. Another advantage of HEROS is that it allows to measure an absorption spectrum by a single (monochromatic) intense pulse of light - a must for the solid matter targets which can be severely damaged by a single pulse of intense light. In Fig 4a,b we present a recent example of HERO spectroscopy of Xe $L_3$ edge and its comparison with the HERFD spectrum acquired by scanning the beamline monochromator.

4. Avoiding the photon probe scan and separating the multielectron transitions

The above mentioned approach with an absorption encoded into the emission spectrum does not allow for a direct separation of the signal due to multielectron excitations from the underlying predominant single electron signal while the separation procedure described in Section 2. requires the photon probe energy scan. It is, however, still possible to study an isolated multielectron signal without scanning the probe when one is focusing on multielectron transitions induced by target relaxation. It is well known that RAE signal appears on the low energy tail of the diagram line. The onset of the RAE signal starts well below the diagram transition energy because the outgoing photon shares available energy with an electron, which must take away a substantial minimum amount of energy to make a quantum jump. Normally the photon probe is tuned above
the threshold and RAE spectrum starts with a sequence of emission lines where an electron has made a transition inside the atom [11]. The RAE spectrum smooths out towards lower energies corresponding to bound-continuum transition of the relaxed electron which is then ejected from the atom. Both types of RAE transitions, the resonant and the continuum one, exist also when the first step, the core-hole excitation is the resonant one. This means that high energy part of the RAE spectrum recorded with the probe energy tuned to the resonance below the edge is expected to display the Raman behavior as only the observed photon is emitted in the bound (high energy) part of the resonant RAE spectrum (RRAE). The resonant Ar K-MM (RRAE) and the continuum RAE spectra are presented in Fig. 5 with a reversed emission energy scale to emphasize the similarity with the satellite spectrum in Fig. 2. It is obvious that some of the final states with the two valence holes are populated in both cases and then $\omega_0 - \omega'_0 = \omega_1 - \omega'_1$ (Fig. 1b). However, since we deal with an integrated satellite emission yield, the satellite signal in Fig. 2 actualy reports the sum over all accessible final states at a given probe energy difference $\omega_0 - \omega'_0$ corresponding to several excited $(1s3p)^{-1}nln'\ell'$ intermediate states which are excited simultaneously due to the finite spectral width of the probe. On the other hand, the spectrum in Fig. 5 maps out directly the final states accessible from the selected $1s^{-1}4p$ excited state by RAE. Despite such an averaging the absence of certain final states in the satellite spectrum is evident: although the same selection rules apply for both chains of events, the dipole emission leads to $3p^{-2}1S^1D$ coupled valence core states only while the most probable RAE scenario - described by the sequence of the Coulomb and the dipole transition matrix elements $\langle n'\ell' D|\ell\ell\rangle (1s l|\ell\rangle (3p^{-2})$ - populates also the $3p^{-2}3P$ combination. Note also a completely different behavior of the tail of the signal which slowly saturates with an increase of the probe energy in the satellite spectrum and decays relatively fast in the RAE spectrum. According to the sudden approximation the satellite intensity relative to the single electron ionization intensity converges to the stable value at high probe energy. In RAE, the dominant dependence of intensity on the emission energy is given by the dipole matrix element describing the bremsstrahlung of an Auger electron in the atom that converts electron energy into the X-ray fluorescence and indeed has a form of the matrix element for the “reversed” photoionization.

We conclude by pointing out the possibility to observe triply excited atomic states by tuning the probe to the strongest atomic satellite energy and observe the corresponding resonant RAE
spectrum. The intense Ar KM satellites with excitation strength of the order of 10% with respect to the predominant $K^{-1}$ process display the resonant RAE spectrum with about 0.4% relative intensity. The signal of Ar KM-MMM resonant RAE spectrum leading to $V^{-3}O^3$ final states is thus expected to be of the order of $10^{-5}$ with respect to the main Ar K-L diagram line and is expected to overlap with the Ar K-MM spectrum (Fig. 5)

![Figure 5. Ar K-M X-ray emission spectrum recorded at 3240 eV. Inset: Ar K-MM Radiative Auger emission spectra: RRAE recorded at $1s^{-1}4p$ resonance at 3203.5 eV (red), RAE recorded above Ar K threshold at 3215.0 eV (black) and RAE recorded at 3240 eV (green-pink-blue). Energy positions of Ar $M^{-2}4pnl$ and Ar$^+M^{-2}nl$ states are shown for RRAE and RAE, respectively. RAE transitions into continuum are denoted by dotted curves. Inset shows the Raman shift of an onset of RRAE spectrum at three different probe detunings with respect to $1s^{-1}4p$ resonance: $\Omega=-0.3$ eV (dashed line), 0.0 eV (full line), +0.3 eV (dotted line).]

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