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Resonant inelastic X-ray spectroscopy of atoms and simple molecules: Satellite features and dependence on energy detuning and photon polarization

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ABSTRACT

We summarize recent results dealing with high resolution (resonant) X-ray spectroscopy of atomic and molecular targets in the tender X-ray energy region. We comment on advantages, new possibilities and problems related to RIXS spectroscopy with respect to the standard photoabsorption technique, where scanning the probe energy is the only option. In particular, three research areas are covered: X-ray emission mediated by energy dependent photoabsorption to multi-electron excited states, the Cl K core-hole clock studies exemplified by systematic study of chloro(fluoro)-hydrocarbon targets and the polarization dependent X-ray emission studies. Due to its spectral selectivity and simultaneous detection capability, high resolution wavelength dispersive X-ray spectroscopy has the capability to resolve structural and dynamical properties of matter within new instrumentation frontiers.

1. Introduction

One of the aims of physics is to understand and determine structural parameters of matter on a quantum level. With an era of synchrotron light sources, the photoabsorption technique was established as one of the most useful tools to look for the short range order in different kinds of materials. Although the technique is being constantly developed towards larger sensitivity and tighter time resolution, its use remains limited to the diluted ("optically" thin) samples. It is well-known that for thick targets the photoabsorption measurements can be mimicked by observation of the total fluorescence yield emitted in the backward direction. While photoabsorption experiment deals with measuring the attenuation of an incoming X-ray beam by the target as a function of the initial photon energy ω and polarization $\vec{e}$, a high resolution resonant inelastic X-ray spectroscopy (RIXS) belongs to the class of the photon-in photon-out experiments which aim to capture energy ω', angle and polarization distribution $\vec{e}'$ of emitted photons. Here we exemplify some opportunities and problems that can emerge when the target fluorescence is observed with a high spectroscopic resolution.

It is well-known that X-ray scattering by multiply excited electronic states leads to the emission of X-ray (satellite) lines that are blue-shifted with respect to the diagram lines emitted after the single core hole ionization. As shown recently, the analysis of the acquired sequence of highly resolved emission spectra allows for an experimental separation of the satellite signal [48] which can be further split on the resonant and the continuum (shake-up and shake-off) part due to characteristic energy dependence of the latter [27,31,49]. Besides a genuine interest in a few-body physics that governs multi-electron transitions, an accurate knowledge of

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the multi-electron signal component is desired to improve reliability of structural information extracted from the photoabsorption spectrum (EXAFS).

For some time we are aware that energy dispersive spectrometers offer an opportunity to improve resolution of the absorption spectrum beyond the photoabsorption limit represented by the core-hole lifetime broadening [21], the so-called HERFD technique (High Energy Resolution Fluorescence Detection). Due to energy conservation in the photon in – photon out experiment, a substantial energy uncertainty introduced by an intermediate short-lived core-hole state does not affect the spectral resolution. The latter depends only on lifetime broadening of the initial and final state involved in the RIXS process and, of course, on the experimental resolution of the incoming photon beam and X-ray spectrometer. HERFD spectrum is obtained simply by collecting energy resolved X-ray signal at emission energy corresponding to the energy difference E_{if} of the intermediate and final state while scanning the photon excitation energy. If available, HERFD spectrum can be also extracted from the measured RIXS intensity map $I(\omega, \omega')$ by performing a cut along the excitation energy axis with X-ray emission energies limited to a narrow band of energies around E_{if}.

Another way to obtain the photoabsorption spectrum without the core-hole state broadening is to set the photon impact energy below the LUMO energy and record X-ray spectrum for an extended set of emission energies. If the detuning is large enough, all the resonances are weakly excited because for each of them the probe energy hits only the tail of the corresponding Lorentzian excitation profile. Such a spectrum may be obtained by a cut of the RIXS map along the emission energy axis at a fixed “red shifted” excitation energy. Compensating for the effect of the strong and unequal resonance detuning by multiplying the spectrum with an inverse Lorentzian tail correction function and shifting the emission energy scale $\omega' \rightarrow \omega - \omega' + E_{if}$ one obtains the so-called HEROS spectrum which is in close correspondence with the HERFD spectrum [30]. HEROS (High Energy resolution Off-resonant Spectroscopy) technique was introduced recently [44] and is free from target self-absorption effects [2]. In principle, HEROS allows to reconstruct a highly resolved photoabsorption spectrum in a sub-second time, because no movements of the set-up are required, either of the beamline monochromator, or the spectrometer. As shown recently, with high resolution X-ray emission spectrometry (XES) one can access chemical state of the target averaged over time period corresponding to the pulse duration, which is typically of the order of tens of femtoseconds for the free-electron laser light source [33]. Very recently it was shown that a full photoabsorption spectrum can be built-up upon the off-resonant target excitation by a single intense X-ray pulse [45]. HEROS therefore represents another technique to capture target state before its destruction. Finally, it has to be mentioned that although HERFD and HEROS techniques may not always yield a true photoabsorption spectrum. For example, the final state multiplet splitting may mask spectral features arising from the intermediate states causing differences between the spectra corresponding to different radiative decay channels and the interferences between the absorption–emission paths may modulate the signal when the resonances are strongly overlapping.

Another approach to chemical sensitivity is based on X-ray Raman Scattering (XRS) where the structure of the ionization edge is observed at photon impact energies much higher than LUMO, making the momentum and energy dependent measurements of inelastically scattered photons truly bulk sensitive. A strong space focusing combined with a spectroscopic power of hard X-ray energy dispersive detectors has led to a “direct tomography” with chemical bond contrast in light elements identifying allotropes down to the micrometer scale [24].

Core-hole creation in molecules can trigger dissociation dynamics which encodes emission spectra taken in the vicinity of the resonant energy condition $\omega \approx E_R$ [12]. The effect causes nonlinear dispersion and linewidth variation of the emission signal which can be modeled to extract Franck-Condon spectral broadening depending on the dissociative potential curve of the intermediate core-excited molecular state [40,36,4]. Acquisition of RIXS spectral map may be thought of as a ready-made pump-probe experiment performed in the energy domain. The delay of the photon emission with respect to the absorption event depends on the decay rate Γ of the core-hole and the longest achievable delays are of the order of the core-hole lifetime Γ^{-1} [13]. The effective delay τ_{eff} of the emission event with respect to the photon absorption is controlled by energy detuning $\Omega = \omega - E_R$, and τ_{eff} reduces as $|\Omega|^{-2}$ when energy detuning is large, $|\Omega| \gg \Gamma$. Besides the dissociation, the vibrational structure of the molecule can also make an imprint on the high resolution RIXS: as the potential well of the core-hole excited state differs from the potential of the ground/final state, X-ray scattering may lead to redistribution of the vibrational population. This is reflected in the elastic resonant scattering giving an asymmetric lineshape at small energy detuning when there is enough time for the excited wave packet to evolve before it is projected back on the manifold of the initial vibrational states [3]. By comparing mission spectra measured at different angles one can also study interferences of Thompson and the resonant elastic scattering [8]. Moreover, linear dichroism extracted by polarization-dependent RIXS measurements has been shown to sensitively probe molecular field effects on the electronic structure of isolated molecules [15,16,6].

2. Instrumentation for highly resolved X-ray spectrometry

For ground state photoabsorption followed by the core-valence photon emission, the RIXS spectral sharpness crucially depends on the available spectroscopic resolution because the lifetime broadening of the initial (ground) and final (valence) state can usually be neglected. The sharpening effect of HERFD technique depends on the ratio of the available resolution of the spectrometer versus core-hole lifetime broadening and becomes significant when this ratio is smaller than one. For light elements the K core hole linewidths [34] go up to 0.24 eV (Ne) and the L_{23} core-hole linewidths up to 0.13 eV (Ar). The spectrometers in the matching soft X-ray energy range (0.1–1 keV) work with gratings in the glancing angle configuration and feature relatively small acceptance solid angle ($\sim 10^{-5}$ efficiency), reaching at the same time a few tens of meV spectral resolution [39]. With long spectrometer arms the resolving power in the soft X-ray energy region can be pushed up to 17000 and 12000 for L_3 core hole emission of Ti (470 eV) and Cu (930 eV), respectively [14]. Higher up, from 1 to 5 keV extends the so-called tender X-ray region which covers K-edges of low-Z elements (Ne to V) and L-edges of 4d-transition metal elements (Y to Xe), for which the core hole linewidths are of the order of 0.25–3 eV. In this energy region the spectrometer vacuum enclosure is still necessary to suppress photon absorption on their way to the target and from the target to the detector. Quasi perfect crystals are available as dispersion devices and a major source of energy spread is given by the Bragg reflection bandwidth: for Si(3 1 1) crystal at 4.5 keV the Darwin broadening is as small as 0.14 eV and goes up to 0.40 eV for Si(1 1 1) at 2.6 keV. A scheme of the crystal spectrometer is given in Fig. 1. In the tender energy range high resolution spectrometers work either in von Hamos [22,20], Johann [26,41], or Johansson geometry [29] with typical efficiency of the order of $\sim 10^{-7}$, and the experimental resolving power of up to ~ 7000 for low density (extended) atomic and molecular targets, going up to 10^4 for the multi-crystal point-to-point focusing spectrometer arrangements [42]. Hard X-rays spectrometers that are used to analyze radiation in the 7–100 keV photon energy are normally fully

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