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Resonant inelastic soft X-ray scattering applied to molecular materials

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ABSTRACT

A brief overview is given of opportunities for resonant inelastic soft X-ray scattering applied to molecules and molecular materials, in the light of upcoming diffraction limited storage rings, X-ray free-electron lasers, and novel instrumentation.

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1. Introduction

The development of X-ray sources gives new opportunities for spectroscopy. For resonant inelastic soft X-ray scattering (RIXS) the strive toward ultimate storage rings where the emittance is only limited by diffraction is especially promising. The high brilliance of such sources implies that a primary high-flux beam of low-bandwidth photons can be focussed into a small spot on a sample, facilitating high-precision analysis of the secondary photons. With the development of matching experimental equipment not only will the RIXS technique fulfill many of its long-standing promises but also open the door to new applications [1–6].

For investigations of liquids and molecular systems the method combines the assets of core-level methods with the ability to probe low-energy excitations in neutral systems. As the resonances in RIXS are due to quasi-atomic core excitations the method is inherently site-specific on the atomic length scale. In contrast to other core-level-based methods, however, the final states probed are property-determining low-energy excitations in the neutral system. The results should thus be compared with low-energy spectroscopies working in the IR and the visible range. Such comparisons become relevant for the first time when the new technical advances allow the energy resolution in RIXS to reach the natural spectral width. The natural width is not set by the finite lifetime of the core hole state, as was earlier commonly held, but by the natural width of the *final* states. This paper is focussing on RIXS excited in the range of the core levels of carbon, nitrogen, and

oxygen, the species which are the main constituents of most important molecules. Today, the overall experimental resolution achieved with the SAXES instrument [7] at the ADDRESS beam line [8] of SLS is around 50 meV at the oxygen edge, allowing for separation of individual vibrations [9,10] and Rydberg states [11]. There are several large scale projects at the new-generation synchrotrons aiming at further improved performance, and we may expect considerable advances in a not too distant future. This will give access to a number of interactions and processes which have so far been out of reach, e.g., collective excitations like phonons in molecular crystals. As the momentum transfer can be varied via the scattering angle in many new set-ups one anticipates that the phonon dispersion can be monitored.

X-ray free-electron lasers (FEL) provide high-intensity X-ray pulses, and non-linear X-ray scattering, like multi-photon excitation and stimulated RIXS (s-RIXS), opening a fascinating new field for fundamental atomic and molecular physics, into which the first steps have just been taken [12,13]. Non-linear inelastic X-ray scattering has already been shown to create secondary intense laser radiation based on atomic processes, and the opportunity to use non-linear effects in dense media to influence the FEL pulse shape [14,15] may find applications in future experimental schemes. An attractive feature of s-RIXS is the low-emittance secondary radiation which can be used to substantially refine RIXS experiments. The direct application of non-linear molecular RIXS for investigation of technically relevant materials requires insights gained in studies of smaller model systems. A vision is to control the dynamics in the scattering process itself during its femtosecond duration.

The short duration of the FEL pulses also give new opportunities for time-resolved RIXS (t-RIXS), and it has already been demonstrated that pump-probe experiments give information on timescales which are chemically relevant [16–18]. The prospects for

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applied t-RIXS experiments are appreciated as “molecular movies” visualizing the time-evolution of local electronic structure in complex molecules may be realized. Of immediate interest in basic molecular physics is the feasibility to perform t-RIXS experiments in the time domain of the scattering duration.

In the context of upcoming diffraction limited storage rings, X-ray FEL:s, and novel instrumentation, molecular RIXS is still a maturing technique, with new phenomena being revealed as the spectra are refined. This is of direct significance in fundamental molecular physics, and has potential for new applications in chemical physics in a wide sense.

2. Electronic structure

The interpretability of RIXS spectra is one of their principal assets. It relies on the applicability of a number of approximations. The scattering event can often be described in a two-step model where the absorption (SXA) and emission (SXE) events are treated separately. Both processes have in common that they can be used to investigate atomic-site specific local properties as they connect quasi-atomic core levels and the outermost states, and they are complementary in the sense that absorption and emission reflect the unoccupied and occupied valence states, respectively. Both SXA and SXE spectra project the local electronic structure around specific atomic species.

This notion is very useful for the investigation of larger molecules in which specific functional groups leave spectral fingerprints. Indeed, this may be exploited for chemical analysis, not only for free molecules but also for molecules in solution, for adsorbates, molecules at buried interfaces, and bulk molecular materials. Fingerprinting of functional groups also opens the door to spectromicroscopy with chemical sensitivity. As opposed to X-ray absorption spectroscopy, however, a comprehensive SXE database that facilitates quantitative chemical analyses in general is not yet established. This has been impracticable as the spectral quality and thereby also the standards are steadily improving with technical advances. In addition, SXE spectra are dependent on the means of excitation, and a rich phenomenology is encountered when excited with synchrotron radiation of well defined and varied energy and polarization state. The general description of the excitation–emission event as a RIXS process indeed captures this multi-dimensional dependence, while uncomplicated interpretability is retained to the extent that a quasi-two-step model can be maintained. Multidimensional RIXS maps [19] not only provide fingerprints of chemical groups [20,21], but reflect details of their local interactions [22].

2.1. Energy transfer

The intrinsic energy selectivity in SXE spectra is due to the core level binding energies which clearly separates emission from different species, in the same way as SXA spectra. Following core *ionization* the final states of the emission are typically single-valence hole states, the same states which are reached in direct photoemission. The intensities are, however, different in the two spectroscopies since the SXE process renders the *local* projection of the valence states. This is very useful when investigating systems where the important species is in minority, e.g., when it is an impurity, a solute or an adsorbate. Whereas the specific signal in a global method like photoemission tends to be overshadowed it is highlighted in core-level methods such as SXE and SXA spectroscopy.

When the excitation energy is tuned below ionization thresholds the final states are typically the same neutral states which are reached in direct Raman and low-energy absorption. However,

the selectivity is further enhanced as the core electron now can be excited to specific unoccupied orbitals in the first step. Often the approximation that the excited electron stays as a pure spectator during the second step of the process is valid, thus making it possible to selectively emphasize specific neutral final states. If the excited electron populates a Rydberg orbital or a state with small coupling between the local electron system, the spectrum simulates spectra excited above the ionization limit (see Fig. 1). If the excited electron couples strongly with the remaining electrons the corresponding RIXS spectrum shows less similarities with the spectrum excited above threshold. Thus, each molecule, and each functional group reach out with many different fingers for the fingerprint to ensure specificity, and details in the local interactions can be addressed.

The same species in different functional groups often give rise to different resonances in the SXA spectrum. This gives the opportunity to *site-selective excitation*, so that corresponding RIXS spectra reflect the local electronic structure at corresponding to specific sites. In a molecule with oxygen atoms in –OH and =O and –OO[−] groups each site can be studied selectively [20], and in-gap resonances due to crucial defect states at specific sites in amorphous molecular materials [23] can be studied separately.

It is a direct consequence of energy conservation in the scattering process that the sharpness of RIXS features is ultimately limited only by the intrinsic broadening of the final states. The width of features narrower than the natural width of the intermediate state are often referred to as “sub-natural”, while the width of the intermediate state was earlier believed to put an ultimate limit to spectral fine structure. It is only recently, however, that the experimental energy resolution has become sufficient to make detailed comparisons to low-energy methods. Whereas the goal to reach the natural widths in spectra of small molecules will remain elusive for years to come (see Fig. 1, it may be within reach for spectra of many liquids and molecular materials at the next generation synchrotron radiation facilities. Conceptually, RIXS has many features in common with resonant photoemission. In the two-step picture they have the first excitation step in common, while a photon or an electron, respectively, is emitted in the second decay step. Although this leads to similar phenomenology in spectra of free molecules, it is very different in spectra of liquids and molecular materials. The change of charge state associated with the electronic decay leads to intermolecular screening and relaxation and a consequential spectral shift and broadening. RIXS is a core-level process which does not change the charge state, and the natural widths are much smaller than in photoemission. Albeit less pronounced than when a charge is removed, local electronic excitations indeed also give rise to broadening due to intermolecular relaxation, and vibrational excitations in large molecules often include a quasi-continuum of soft vibrational modes. For vibrational excitations in the electronic ground state and phonon excitations in molecular crystals (see below) we believe that the experimental resolution will continue to limit the spectral width.

The feasibility to resolve individual vibrational excitations [9,10,24] gives access to local potential surfaces of the *electronic ground state* (Fig. 2) in complex systems. While local modes can often be isolated and identified in low-energy Raman, the RIXS process is intrinsically local, and whereas in IR Raman the first vibrational excitation and a few overtones are observed, a core excitation often initiates rather violent nuclear rearrangement, and therefore RIXS spectra map a large part of the local potential surface of the electronic ground state, with a large number of vibrational excitations, sometimes all the way to dissociation [25], with the prospect of giving a picture of the local chemical bond in complex systems. By tuning the excitation energy one can emphasize various parts of the potential landscape, and e.g., focus on regions where the electronic–vibronic coupling is large at avoided crossings and

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