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Time resolved resonant inelastic X-ray scattering: A supreme tool to understand dynamics in solids and molecules

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ABSTRACT

Dynamics in materials typically involve different degrees of freedom, like charge, lattice, orbital and spin in a complex interplay. Time-resolved resonant inelastic X-ray scattering (RIXS) as a highly selective tool can provide unique insight and follow the details of dynamical processes while resolving symmetries, chemical and charge states, momenta, spin configurations, etc. In this paper, we review examples where the intrinsic scattering duration time is used to study femtosecond phenomena. Free-electron lasers access timescales starting in the sub-ps range through pump-probe methods and synchrotrons study the time scales longer than tens of ps. In these examples, time-resolved resonant inelastic X-ray scattering is applied to solids as well as molecular systems.

1. Introduction

Resonant inelastic X-ray scattering (RIXS) has the potential to give access to dynamic phenomena of matter on a vast range of time scales even suited for processes faster than a femtosecond. For time resolved pump-probe RIXS, the advent of brilliant short pulse X-ray sources allows to use RIXS as a probe for transiently excited states of matter and their dynamics. Here the development of sources, beam lines and spectrometers will bring us toward the Fourier limit in pulse length and energy resolution of around $\Delta E \Delta t \approx 1\,\text{eV} \cdot 1\,\text{fs}$.

Combining time-resolved methods with the capability of RIXS to probe electronic, orbital, magnetic and lattice excitations in an element specific and chemical selective manner provides unique detail. Governed by the scattering geometry all these properties can be accessed as a function of momentum transfer on solids. Thus the symmetry and q-dependence of low energy excitations provide unique insight into matter.

Applied to molecules, RIXS discovers the local symmetry of atomic centers as seen through crystal and molecular field split parameters. To date the field of molecular dynamics is largely unexplored, where the charge and spin configuration in combination with the ligand field parameters are provided by RIXS. Here also the intrinsic time scale of RIXS brings unique insight to the dynamic pathways on the multidimensional and intersecting potential energy surfaces.

We will thus focus in our discussion on dynamics in solid and molecular systems. In solids, we have to deal with the projection of the delocalized, strongly interacting electronic states onto the core hole produced in a RIXS process, while the situation in isolated molecules can be treated more rigorously by theory.

The discussion of these two classes of matter, where RIXS studies can be fruitfully applied, is interwoven with two different approaches to study dynamics with RIXS. Using the intrinsic duration of the scattering process, dynamical evolutions during the core hole lifetime contribute to the signal and processes on the femtosecond time scale are studied. Detuning the excitation from resonances effectively shortens the scattering duration time and gives access to even faster dynamics. We can study processes that intrinsically evolve in the sample independent of the RIXS process, as will be exemplified for electron–phonon scattering studies on silicon. In molecules, the core hole produced in the RIXS process is not as well screened as in solids, so that the main contribution to the RIXS dynamics is induced by the core hole. This allows for the accurate mapping of potential energy surfaces in the electronic ground and excited states, as will be shown for molecular oxygen.

In another group of examples, pump-probe RIXS is used to access longer time scales and slower dynamics. In a prototypical pump-probe experiment, an ultrashort laser pulse, the pump (usually shorter than 100 fs) excites the dynamics and is probed at specific delay times with short X-ray pulses [1]. The induced dynamics is usually rather complex and evolves in parallel in many degrees of freedom, so that the specificity of RIXS is very important for a full understanding of the underlying processes.

For the study of sub-ps dynamics, an X-ray source is needed that provides a high photon flux in sub-ps pulses. Nowadays only

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free-electron lasers (FELs) can fulfill this condition and provide pulses of 10–100 fs lengths with orders of magnitude higher photon numbers than at synchrotrons [2–4]. The achieved time resolution allows to access time scales typically longer than 100 fs [5], while attempts are made to improve the resolution to the 10 fs level [6].

With their constantly high repetition rate, synchrotrons provide a high enough photon flux to study dynamics slower than tens of ps (the typical pulse length at a synchrotron) equally well with time resolved RIXS by using pump lasers with high repetition rates matched to the storage ring pulse pattern [7].

By combining this full suite of pump-probe methods and resolutions down to 10 fs, with studies relating to the intrinsic femtosecond duration of RIXS, the full range of relevant electron and atom driven dynamics is in the reach of RIXS studies.

As examples for pump-probe experiments with RIXS on solids, we will describe the ultrafast non-thermal melting of silicon after laser excitation [8]. On molecules, we highlight a pump-probe hard X-ray RIXS study from a storage ring by Vanko et al. [7]. As a last example, we feature a combination of a solid with a molecular system – a surface science example – where RIXS has been used to follow in detail the desorption dynamics of carbon monoxide from a ruthenium surface.

2. Dynamics in solids

With its chemical selectivity and the specific information that can be obtained about lattice, spin and electronic excitations, RIXS is particularly valuable for solids in which these different degrees of freedom interact in a complex manner. Analyzing the momentum transfer through the soft X-ray photons, RIXS can easily map out dispersion relations of excitations across the whole Brillouin zone [9–11].

In correlated materials, the complex interaction between those degrees of freedom leads to a low energy landscape [12] with often complex phase diagrams, that is intimately linked to emergent phenomena of functionality, like superconductivity, colossal magnetoresistance, multiferroic effects etc. In turn, the low-energy landscape makes the systems highly susceptible to external stimuli and the dynamics following impulsive stimulation can ideally be followed in time. Here, the selectivity of time resolved RIXS is well suited to single out the important contributors to the dynamics and understand how functionality is enabled in these materials.

Dynamics that follow impulsive excitation have been studied with optical lasers for a while and more recently with photoelectron spectroscopy (see for example the reviewing book [13] and references therein) and X-ray diffraction methods [14–16]. While optical methods probe essentially integral properties and the diffraction methods are mainly sensitive to long-range order, photoelectron spectroscopy and RIXS are directly sensitive to the site-specific electronic state. The central limitation of photoelectron spectroscopy, however, is the fairly low pump fluence that can be used before space charge formation heavily distorts the spectrum (for soft X-ray probes, see e.g. [17]). Here, time-resolved RIXS appears as the ideal tool. It is both, highly specific and – as only photons are involved – not sensitive to space charge effects. Another important aspect is that the understanding of RIXS data from correlated solids has improved enormously in the last years such that a precise quantitative interpretation of the data has become possible. For a review, see [10].

2.1. Lifetimes and scattering rates of low energy excitations

In the model system of silicon, the electron–phonon scattering rates can be estimated by making use of the intrinsic duration of the RIXS event. Furthermore, the selectivity of RIXS allows to estimate different rates of electron–phonon scattering where either crystal or angular momentum is transferred. First, we will describe how the crystal momentum transfer rate through phonon scattering can be quantified with RIXS, before we show how we can also address and quantify the transfer of angular momentum, which turns out to be a factor of 50 slower. With RIXS on the silicon L edges, the momentum transfer through photons can be neglected. Ideally, the spectra would therefore only reflect states with the same value in k-space as selected by the excitation into a specific part of the conduction band (see Fig. 1). The whole process has to be described as a coherent process, and the crystal momentum is conserved.

In contrast to this coherent process, the scattering of the electrons with phonons during the apparent lifetime of the core excited state (in the following, we will call this the scattering duration time) can randomly alter the crystal momentum of the involved electrons, while the energy is only negligibly changed. The resulting spectra thus show an average over all crystal momenta, and reflect the k-integrated density of states. Scattering with phonons disturbs the coherence in the RIXS process, so that the spectra show no dependence into which point in k-space the core electron has been excited.

In reality, spectra show contributions from both process and can be decomposed into parts with and without phonon scattering during the scattering duration time. The contribution without phonon scattering is called the “coherent part” and often shows distinct peaks, where bands cross the selected k-value. Phonon scattering leads to spectra that reflect the Brillouin zone integrated density of states, the “incoherent part” (see Fig. 1) [18–20]. When the excitation energy is tuned away far above the absorption edge such that the electron is excited into the continuum, no k-value is selected and the spectra reflect the k-integrated density of states, similar to the incoherent part. With this method, one contribution to the resonant excited spectra can be selectively measured and the decomposition into the coherent and incoherent parts is straightforward.

The relative spectral weights of the coherent and incoherent parts are connected to the probability of electron–phonon scattering during the scattering duration time. In the time average, this probability is directly related to the relative rates of core decay or electron–phonon scattering. If the electron–phonon scattering rate is much higher than the duration of the RIX scattering, one expects spectra dominated by the incoherent part, whereas the coherent part will be dominating when the electron–phonon scattering is much slower than the RIXS duration time.

With this method, we can quantitatively determine the crystal momentum transferring electron–phonon scattering rate. To justify this approach, we can shorten the effective scattering duration time by detuning the excitation energy from the resonance (the effective scattering duration time τ is a function of the energetic detuning from resonance Ω, following $\tau(\Omega)=\hbar\left(\Omega^2+\Gamma^2\right)^{-1/2}$ [21], where the lifetime of the core excited intermediate state is expressed in its natural lifetime broadening Γ (HWHM)). Detuning from resonance therefore allows to access dynamics on shorter time scales than the core hole lifetime.

Quantitatively, we expect the electron–phonon scattering rate to be independent of the detuning of the excitation energy from the resonance, as long as the same resonance gets excited. On solids, this is typically the case for detuning below the absorption edge. As the scattering duration time gets shorter for detuned excitation, the coherent contribution to the spectra grows and less phonon scattering events take place during the scattering duration time. Correctly calculating the effective scattering duration time for detuned excitations then yields similar electron–phonon scattering rates as for resonant excitation, as shown in Fig. 1.