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Free-electron laser based resonant inelastic X-ray scattering on molecules and liquids

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ABSTRACT

The unprecedented beam properties of free-electron laser based X-ray sources enable novel resonant inelastic X-ray scattering (RIXS) experiments. Femtosecond time-resolved RIXS can be used to follow charge, spin and structural dynamics of dilute solute molecules in solution. Ultrashort X-ray pulses allow probing of highly radiation sensitive states of matter such as the metastable phase of supercooled liquid water. Nonlinear X-ray probes like amplified spontaneous emission and stimulated resonant X-ray scattering provide an enhanced selectivity and sensitivity as well as a path to control radiation damage and increase the photon yields in RIXS experiments.

1. Introduction

The first free-electron laser based X-ray light source (XFEL) became available for user experiments a decade ago (FLASH at Hamburg, Germany [1]). Since then the XFELs LCLS [2], Fermi [3] and SACLA [4] have come online and several other XFEL facilities are currently being constructed or planned (European XFEL, LCLS-II, SwissFEL and others). These developments are driven by the unprecedented X-ray beam properties provided by XFELs, which have opened a wealth of new possibilities for experimental X-ray science. XFELs deliver X-ray pulses with 10^3 times shorter pulse duration and 10^{10} times higher peak brilliances than typical 3rd generation synchrotron light sources, i.e. around 10^{13} photons in 100 fs or shorter X-ray pulses (nominal parameters of the LCLS [5]). Thus XFELs provide drastically different experimental conditions for X-ray spectroscopy and scattering methods that have since 1970s and 1980s matured at synchrotron radiation sources.

In this work we review the experimental efforts undertaken at XFELs utilizing resonant inelastic X-ray scattering (RIXS) and X-ray emission spectroscopy (XES). RIXS [6–11] is the X-ray analog of conventional resonant Raman scattering [12–14] widely established at optical and infrared frequencies [15,16]. Hence, it combines the element and site selectivity of X-rays with the ability of Raman scattering to probe low energy excitations of matter. These are excitations of a few eV and less, which is much smaller than the scattered X-ray photon energy. XES, corresponding to above resonance continuum excitation is the analog of optical fluorescence spectroscopy and conceptually a special case of RIXS. XES is often also referred to as X-ray fluorescence spectroscopy. The unique features of RIXS have been applied to map out magnetic [17–19], charge [11,20], orbital [21,22] and structural excitations [23,24] as well as complex potential energy surfaces [25,26] of functional materials. The focus of this review is molecular systems in the gas and liquid phase, which include solutions as well as bulk liquids. We show how RIXS/XES at XFELs allows addressing major scientific questions in these systems and exploring new physical phenomena that have so far been out of experimentalists reach.

RIXS experiments that have until now been carried out at XFELs can be classified into three categories based on which unique feature of the XFEL X-ray beam they make use of. First, femtosecond X-ray pulses from an XFEL can be synchronized to an external optical pump laser for carrying out femtosecond time-resolved pump-probe RIXS (fs-RIXS) experiments. This method can be used for tracking ultrafast changes of the electronic structure in an element- and site-specific manner at intrinsic femtosecond time scales of photoinduced dynamics. Currently, fs-RIXS experiments are only feasible at XFELs. Synchrotron radiation sources have too long X-ray pulses (typically with durations around 100 ps) to address femtosecond time scales, whereas other existing femtosecond X-ray sources (laser-based plasma sources and

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synchrotron-based slicing sources) lack sufficient photon flux or tunability in photon energy. In Section 3 two fs-RIXS/XES experiments conducted so far are reviewed, one addressing ligand exchange dynamics in $Fe(CO)_5$ ethanol solution with soft X-ray fs-RIXS [27] and second utilizing hard X-ray fs-XES to study excited state spin dynamics in $[Fe(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) water solution [28]. We note that fs-RIXS at XFELs has been also successfully applied for studies of chemical reactions on surfaces [29–32] and of the ultrafast optical induced melting of crystalline silicon [33].

Second, femtosecond pulses can be used for steady state experiments in order to probe the unperturbed ground state of systems that otherwise suffer from ultrafast X-ray induced electronic and structural modifications. This is the "probe-before-destroy" principle that is the foundation for many experiments at XFELs concerning imaging of biomolecules, viruses and cells [34]. However, this principle is relevant not only for structural studies, but also for spectroscopic studies directly probing the electronic structure. For the spectroscopic studies it is necessary to "outrun" not only the overall structural damage, but also local chemical and electronic changes at the relevant atomic site. A prominent example is the efforts related to understanding the electronic structure of the Mn_4CaO_5 cluster of photosystem II during the photosynthesis cycle. It has been shown that 50 fs X-ray pulses from XFEL are able to probe the inherent redox state of the Mn_4CaO_5 cluster, which is not possible with the longer X-ray pulses at a synchrotron radiation source [35]. Recently, ultrashort X-ray pulses were applied in a RIXS investigation of a metastable phase of liquid water [36]. Here, 100 fs X-ray pulses from XFEL were utilized to measure RIXS of supercooled liquid water before it crystallizes as a result of X-rays. We discuss this experiment in Section 4.

Third, the extremely high peak brilliance delivered by XFELs provides experimental means to explore the nonlinear regime of X-ray-matter interaction. Using XFEL pulses several nonlinear processes have been detected in the X-ray photon energy range. Glover et al. have demonstrated X-ray/optical sum frequency generation (SFG) and mixed 8 keV XFEL photons with 1.5 eV optical laser photons in a diamond crystal [37]. Recently, diamond was also used for generating a second harmonic of 7.3 keV photon energy XFEL beam [38]. Two-photon X-ray absorption has been demonstrated at the germanium K-edge in the solid state [39] and saturable X-ray absorption was detected at the iron K-edge (7.1 keV) from an iron foil [40]. Concerning RIXS, we review in Section 5 experiments on stimulated resonant X-ray scattering and amplified spontaneous emission (ASE) [41,42]. In addition, at high incident intensities X-ray reabsorption mechanisms may modify the RIXS spectral shape as was recently observed in an experiment on liquid water [43].

2. Instrumentation for RIXS on liquids at XFELs

2.1. Liquid jet techniques

One of the central challenges of any XFEL experiment concerns sample handling. First, it is necessary to constantly replenish the sample to avoid accumulation of degraded sample. Second, in case of liquids, one cannot use reservoirs or cuvettes to contain the sample, as the extremely high intensity XFEL pulses will damage these. Therefore experiments on liquids at XFELs typically use liquid jet sample handling techniques. Here, the sample is introduced into the interaction region in form of a free flowing stream of liquid, thus constantly replenishing the sample and eliminating the need for a reservoir. Flow rate and dimensions of the jet are crucial experimental parameters. They determine the rate of sample replenishment, which should be ideally equal or higher than the XFEL repetition rate, and they determine the total volume of sample consumed during the experiment. The consumed sample volume can become a serious constraint for the experiment if the sample material is available only in limited quantities. Several different liquid jet techniques have been applied at XFELs so far. The simplest form of it is a Rayleigh jet [44]. This jet exhibits a uniform laminar flow region before it breaks up into droplets. The size of the jet in the laminar flow region corresponds to the diameter of nozzle used to inject the liquid. Typical nozzle diameters are 10–25 μm and volumetric flow rates are around 1 ml/min. This corresponds to flow speeds up to 100 m/s, which in an illuminated height of the jet of 100 μm replenishes the sample at 1 MHz rate. This is sufficient sample replenishing rate for warm linac based XFELs, such as the LCLS with 120 Hz repetition rate, but also for superconducting linac based XFELs, such as the upcoming LCLS-II and European XFEL with up to 1 MHz repetition rate. The comparable high volumetric flow rates of a Rayleigh jet result in a significant sample consumption of about 1 l for 12-h experimental run. This can be compensated by recycling the liquid, since, given the parameters above, at the LCLS less than 0.01% of the sample interacts with X-rays in one cycle through a jet. Recently a technique for recirculating in-vacuum liquid jets has been developed [45]. For studies of, e.g. biomolecules or proteins even the recirculating sample volume exceeds the available sample quantities by far. For such experiments very volume-efficient liquid jet techniques have been introduced [46]. A jet from a gas dynamic virtual nozzle (GDVN) can operate at volumetric flow rates around 10 μl/min [47,48]. The GDVN uses a co-flowing gas stream to reduce the diameter of the jet below the diameter of the nozzle orifice. Typical GDVN jet diameter are a few microns (flow speed 10 m/s), but diameters as small as 0.3 μm are possible (flow speed 100 m/s) [49]. Even lower volumetric flow rates (below 1 μl/min) can be achieved by electrostatically charging the liquid in so-called electrospinning technique [50]. At low XFEL repetition rates droplet jets provide a path to reduce sample consumption. The drop-on-demand (DOD) injector technique uses a pressure wave created by a piezo transducer to push out liquid from a capillary at a controlled rate [51]. Droplets with 10 μm diameter are created which corresponds to 100 nl/min flow rate at 120 Hz [46]. Currently, the low flow rate jet techniques are primarily developed for the crystallography and imaging experiments at XFELs. RIXS experiments carried out so far at XFELs have primarily made use of Rayleigh jets.

2.2. Soft X-ray RIXS endstation

The experimental endstation used for soft X-ray RIXS experiments on liquids at XFELs combines a vacuum environment, required for soft X-rays, with a liquid jet sample delivery system and a soft X-ray emission spectrometer (Fig. 1) [52]. This endstation has been successfully used in experiments [27,36,43,52,53] at the SXR instrument of the LCLS [54]. Using a Rayleigh-type liquid jet system in this endstation results in pressures in the range of 10^{-4}–10^{-3} mbar in the experimental main chamber. Differential pumping toward the beamline realizes pressures better than 10^{-8} mbar at the upstream end of the endstation. The soft X-ray emission spectrometer is a Nordgren-type grazing incidence spectrometer accommodating three gratings that cover the photon energy range from 50 to 900 eV with 1000 resolving power [55]. Hence the spectrometer provides chemical sensitivity at C, N and O K-edges as well as at 3d transition metal L-edges. The position-sensitive detector unit consisting of a MCP stack, phosphorus screen and a charge-coupled device has single photon sensitivity and multihit capability with read-out rates compatible for single-shot experiments at warm-linac based XFELs (120 Hz at LCLS). The overall detection efficiency of the spectrometer is around 10^{-7} due to the comparable small solid angle. An integrated count rate of ~10 counts per pulse over the whole 2p3d RIXS spectrum was detected