



Spin-state studies with XES and RIXS: From static to ultrafast

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ABSTRACT

We report on extending hard X-ray emission spectroscopy (XES) along with resonant inelastic X-ray scattering (RIXS) to study ultrafast phenomena in a pump-probe scheme at MHz repetition rates. The investigated systems include low-spin (LS) Fe^{II} complex compounds, where optical pulses induce a spin-state transition to their (sub)nanosecond-lived high-spin (HS) state. Time-resolved XES clearly reflects the spin-state variations with very high signal-to-noise ratio, in agreement with HS–LS difference spectra measured at thermal spin crossover, and reference HS–LS systems in static experiments, next to multiplet calculations. The 1s2p RIXS, measured at the Fe 1s pre-edge region, shows variations after laser excitation, which are consistent with the formation of the HS state. Our results demonstrate that X-ray spectroscopy experiments with overall rather weak signals, such as RIXS, can now be reliably exploited to study chemical and physical transformations on ultrafast time scales.

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1. Introduction

The spin state of transition metal ions affects the properties of their compounds both on macroscopic and microscopic levels, as it has a large influence on ionic and thus molecular size, lattice unit cell volume, density, transport, magnetic and vibrational properties. Particularly interesting are cases where the spin state can be changed by external stimuli, with implications in atomic, molecular and solid state physics, geophysics, chemistry, and biochemistry. Molecular systems that can be switched between their different spin states are especially intriguing for their potential applications in high-density molecular storage devices, and the photochemical properties may prove to become useful in novel light-energy converters based on Fe-containing molecules. At low temperatures many low-spin (LS) Fe^{II} complex compounds can be switched by

light to a high-spin (HS) state [1,2]; however, the detailed mechanism of the LS to HS switching process is still under debate [3–5], despite the recent developments [6–9]. Tools sensitive to the electronic structure and the spin state, which can also be utilized on the femtosecond (fs) to nanosecond (ns) time scales, can shed light on the yet unknown details of the relevant intermediate steps involved in the spin-state switching process. Previously, fs laser spectroscopy has been used for this purpose, which has delivered a rich picture of the ultrafast events taking place on the first few hundred fs [6,10–13]. These tools are, however, rather insensitive to the changes in the spin state next to the concomitant geometric structure changes.

Hard X-ray spectroscopies can provide unique insights into the electronic and geometric structure, combined with element-, spin-, orbital-, and orientation sensitivity [14–16]. These techniques probe the bulk properties of the entire sample, and are even compatible with extreme conditions due to the large penetration depths [17]. X-ray Absorption Spectroscopy (XAS) with its variants X-ray Absorption Near Edge Structure (XANES) and Extended

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X-ray Absorption Fine Structure (EXAFS) have proven their utility in determining the unoccupied electron states and the local structure, respectively [18–21]. X-ray Emission Spectroscopy (XES) and Resonant Inelastic X-ray Scattering (RIXS) are very powerful in elucidating the electronic structure, providing information on the electron energies, local geometry, spin and charge states [14,22–28]. These tools can thus deliver complementary information to the usually employed ultrafast laser spectroscopies, when implemented in a pump-probe experiment with a laser pump and a time-delayed X-ray probe pulse.

The extension of hard X-ray techniques to the ultrafast time domain has been initiated at synchrotron radiation sources about a decade ago, with a pulse limited time resolution of ca. 50–100 ps, due to the intrinsic X-ray pulse width. Such time-resolved studies have employed XAS [29–31] or X-ray scattering (XRS) techniques [30,32–38] only and have been, with few exceptions [39–42], limited to low repetition rates (1–2 kHz) by using Ti:sapphire (or Nd:YLF) based amplified laser systems. These deliver a sufficient number of optical photons to match the number of ground state molecules in the laser beam [29]. In this way, photoexcitation of a sufficient fraction of the sample was ensured for each laser pulse. This strategy was necessary, since the number of probing X-ray photons/pulse are orders of magnitude lower, which so far hampered a wide-spread use of such structural X-ray techniques due to the low signal-to-noise (S/N) ratio. More flux demanding experiments, such as X-ray emission spectroscopy (XES) or even the very low cross section inelastic X-ray scattering techniques thus remained out of reach. However, a recent pioneering kHz laser pump-X-ray probe experiment successfully recorded transient XES spectra on photoexcited aqueous $[\text{Fe}(\text{bipy})_3]^{2+}$ (bipy:2, 2'-bipyridine) at the Fe $K\alpha_1$ emission line, which reflected a line shape variation characteristic for the LS to HS transition [43].

The above work also showed that the integrated number of X-ray photons available for such pump-probe studies is the bottleneck for time-resolved X-ray techniques, and in consequence we have developed a setup employing a high-power MHz laser, which allows for a substantial increase in collection efficiency due to a closer match between the repetition rates of both the synchrotron and the laser source. The increase in pump-probe efficiency scales with the repetition rate if we assume that the excitation rate as well as the number of photons per pulse are preserved as well. (Note that high-energy storage rings, such as ESRF and APS, deliver more photons per pulse than low-energy synchrotrons.) This strategy now permits having ca. 10^{13} monochromatic X-ray photons impinging on the sample per data point in a few seconds. With this approach at high-energy storage rings (APS, ESRF) one can now envision to employ multiple X-ray structural tools simultaneously on the sample during the course of a light-triggered chemical reaction or physical transition, with quasi-static S/N.

In this paper we report the first time-resolved RIXS and good quality XES, obtained in pump-probe scheme at MHz repetition rates. No advance is reported here concerning the mechanism of the switching of the Fe(II) complexes; the choice of these systems was for a proof-of-principle. However, this work should pave way for making extensive use of hard X-ray techniques in ultrafast studies; these techniques can be particularly useful in revealing the elementary steps of the LS to HS switching in the very first ps after the excitation.

2. Experimental methods

We have extended the capabilities of such laser-X-ray studies towards MHz pump-probe repetition rates, both at ID26 of the European Synchrotron Radiation Facility (ESRF) and at sector 7-ID

of the Advanced Photon Source (APS). By tailoring the laser repetition rate to that of the X-rays, the full flux of these high-energy synchrotrons can be utilized and the S/N for time resolved data can match that for static experiments.

Both beamlines use undulator radiation, which is monochromatized using the (1 1 1) reflection of either diamond (7-ID) or Si (ID26) crystals of a double crystal monochromator. At 7-ID [44] beamline (resp. ID26), the X-rays were then focused down to $7\ \mu\text{m} \times 8\ \mu\text{m}$ FWHM spot size (resp. $600\ \mu\text{m} \times 100\ \mu\text{m}$) at the sample by Kirkpatrick-Baez mirrors. At ID26 beamline, the beam size is further tailored with downstream slits to a spot of $500\ \mu\text{m} \times 100\ \mu\text{m}$ in order to optimize the overlap with the laser beam. Time-resolved experiments are most conveniently performed at both synchrotrons in equidistant bunch filling modes, namely in the standard 24-bunch mode at the APS, and the special 16-bunch mode at the ESRF. In the 24-bunch mode at a ring current of 102 mA and for the X-ray energies between 7.5 keV and 8.2 keV, the X-ray incident flux on 7-ID is ca. 5×10^5 photons that are delivered to the sample in the ~ 80 ps FWHM X-ray pulse at a repetition rate of 6.52 MHz. At ID26 beamline and in the 16-bunch mode (90 mA, 5.68 MHz), 2×10^6 photons are delivered to the sample in ~ 100 ps X-ray pulse FWHM.

Aqueous solution of $[\text{Fe}(\text{bipy})_3]^{2+}$ (with concentrations between 12 mM and 25 mM) in form of a $100 - \mu\text{m}$ thick sheet from a liquid jet was used as sample in both experiments. From the APS experiment, we also report here time-resolved 1s2p RIXS taken on a 20 mM solution of $[\text{Fe}(\text{terpy})_2]^{2+}$ (terpy:2, 2':6', 2''-terpyridine). The laser installed in the APS 7-ID-D hutch [40] was operated at a 3.26 MHz repetition rate. Radiation at 532 nm was produced by second harmonic generation in a nonlinear crystal; the sample was pumped with 5.85 W power, corresponding to pulse energies of $1.8\ \mu\text{J}$. The pulse width was 10 ps, and was focussed to a $100\ \mu\text{m} \times 80\ \mu\text{m}$ FWHM spot size on the sample, and spatial and temporal stability were $5\ \mu\text{m}$ and 10 ps over several hours [40]. At ID26, we used a mobile fs laser system described by the following parameters: repetition rate 1.42 MHz, wavelength 515 nm (output power of 10 W, which corresponds to a pulse energy of $7\ \mu\text{J}$ at this repetition rate), pulse length 280 fs. Cylindrical lenses were used to achieve an elliptical beam profile of ca. $125\ \mu\text{m} \times 600\ \mu\text{m}$, which provided a good overlap with the X-ray spot size on the sample. HS populations achieved under these conditions reached around 40% (20%) at 7-ID (ID26) at 80 ps delay. Note that at such repetition rates and spot sizes, the jet speed of a few m/s is not sufficient to completely replace the sample between two laser pulses. However, the molecular systems studied here decay back rapidly to the ground state (with a lifetime close to 1 ns), and they do not show any degradation; therefore, possible repeated excitations of the same molecule do not lead to any artefacts in the data.

Fig. 1 shows the schematic experimental setup. The laser and X-ray beams impinge almost collinearly (5 degrees angle of separation) on a fast-flowing $100 - \mu\text{m}$ thick liquid jet mounted at 45° with respect to the beam propagation direction. The tilted angle permits simultaneous recording of both XES and XAS and forward XRS; the XRS and XAS results are beyond the scope of the present article and will be published elsewhere. A detector was mounted on one side of the sample in order to record the XAS signal in total fluorescence yield (TFY) mode. On the other side, a wavelength-dispersive crystal spectrometer was constructed at 7-ID (in the horizontal plane) to measure the XES signal using a spherically bent analyzer crystal of 10-cm diameter positioned at a 90° scattering angle, and an avalanche photodiode (APD) detector at its focus, such that the sample-analyzer-detector setup constituted a 1-m Rowland circle. At ID26, the permanent five-crystal spectrometer of the beamline, built in the vertical plane, was used [45]. A thin plastic bag filled with He was installed inside

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