Bressler / ISSRNS 2008: Extended Abstracts / Synchrotron Radiation in Natural Science Vol. 7, No. 1 – 2 (2008) 84-86

L30

FEMTOSECOND AND PICOSECOND X-RAY SPECTROSCOPY STUDIES

C. Bressler [1,2*], **R. Abela** [2], **and M. Chergui** [1]

[1] Laboratoire de Spectroscopie Ultrarapide (LSU), Ecole Polytechnique Fédérale de Lausanne (EPFL),
BSP, CH-1015 Lausanne, Switzerland
[2] Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen-PSI, Switzerland

Keywords: ultrafast x-ray absorption spectroscopy, chemical dynamics, spin crossover

**) e-mail: christian.bressler@epfl.ch*

Time-resolved x-ray absorption fine structure (XAFS) spectroscopy with picosecond temporal resolution is a new method to observe electronic and geometric local structures of short-lived reaction intermediates [1]. While it adds to the information available by established ultrafast laser spectroscopies, the combination of both methodologies to the system under investigation can deliver a rather complete picture of the underlying mechanisms. We have implemented ultrafast XAFS at a synchrotron and successfully applied it to different condensed phase chemical systems.

The basic experimental setups used at the Advanced Light Source and at the Swiss Light Source (SLS) have been described previously [2-5], and will be only summarized here for the SLS setup. Briefly, x-rays from a Si(111) monochromator enter the experimental hutch, where they are focused to ca. 50 µm diameter onto the sample with a pair of Kirkpatrick Baez (KB) mirrors (Fig. 1). X-ray signals are detected with 4 large-area avalanche photodiodes (APD), one each for transmission (I_1) and for the incident signal scattered off a thin metal (Cr) foil (I_0), and via two fluorescence APDs (I_{F1}, I_{F2}) for the x-ray fluorescence emitted from the sample. The sample consists of a free-flowing liquid jet (with an adjustable thickness in the 0.1-0.5 mm range), which is excited by an amplified fs laser system. Spatial overlap (including a measurement of the spot sizes) on the sample between both laser and x-ray beams is set via steering the laser beam onto the x-ray spot on sample and monitored with an imaging CCD camera. The amplified laser used for sample excitation is synchronized to one specific x-ray pulse from the storage ring [4,5] at 1 kHz repetition rate. For femtosecond XAFS experiments we exploit so called time-sliced x-radiation, which delivers ca. 160 fs x-ray pulses at 2 kHz into the beamline [6].

Electronic structure modifications can be observed in charge transfer processes via XANES. Fig. 2 shows the example for aqueous Ru(bpy)$_3$, in which a laser photon promotes a metal-centered electron from the crystal field split and fully occupied $4d(t_{2g})$ level onto the bpy ligand system in a metal-to-ligand charge transfer (MLCT) process. For the x-ray probe process this opens up a new absorption channel, $2p_{3/2,1/2}$ (L_3, L_2 edges, respectively) → $4d(t_{2g})$ (labeled *A*' in Fig. 2b), right below the $2p_{3/2,1/2}$ → $4d(e_g)$ absorption (labeled *B*, *B*' for the ground and excited state absorptions, respectively).

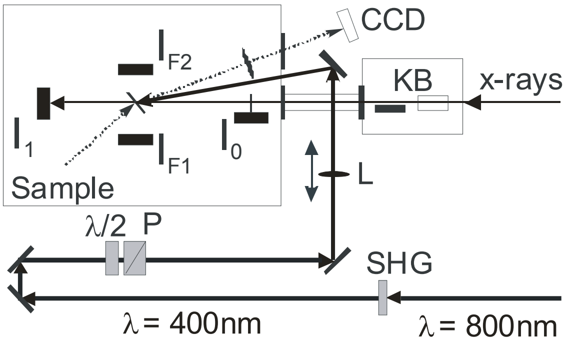

Figure 1. Top view of the experiment with overlapping laser pump and x-ray probe beams on the liquid sample sheet. 4 detectors (I_0, I_1, I_{F1}, I_{F2}) are used for measuring the XAFS, and an imaging CCD detector monitors spatial overlap and beam sizes. 400 nm light (after frequency-doubling (SHG) the 800 nm fundamental beam) is adjusted for pulse energy with a $\lambda/2$ waveplate and polarizer (P) combination before being focused (with the lens L) onto the sample with spot sizes typically around 100-500 µm. The x-ray beam is focused to ca. 50 µm diameter with the KB optics.

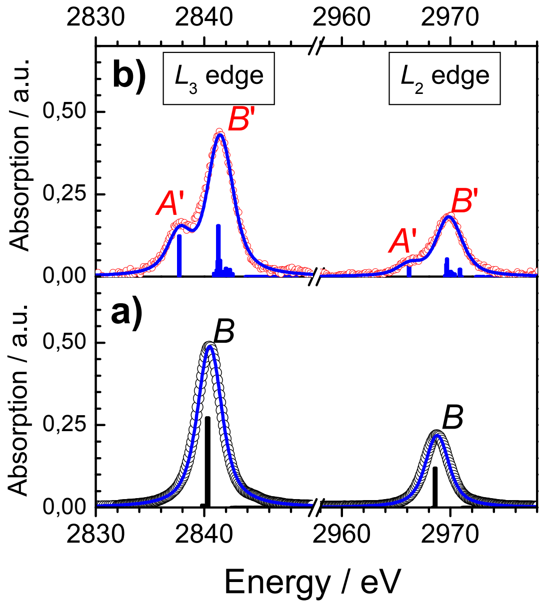

Figure 2. a) $L_{2,3}$ edge XAFS of aqueous $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$ in its ground state (open circles) together with a simulation (vertical bars) for the bound-bound transitions, which were convoluted with the lifetime width of Ru (blue curve). b) same as in a), but 50 ps after laser excitation.

From this study we also obtained the crystal-field splitting of the 4*d* levels in the excited state for the first time, and exploited this value to derive the geometric structure (here: the Ru-N distance), which is slightly shorter than in the ground state species [7].

Time-resolved XANES can also serve to observe (optically) dark species. We have probed the population of nascent I^0 species, by X-ray absorption spectroscopy at the L_1 and L_3 edges, 50 ps, and later, after electron detachment from I^- by the pump laser [8]. At the L_1 edge (Fig. 3a) one observes a small blue shift of the first transient peak around 5186 eV shown in Fig. 3b with increasing delay time. Since we know that iodine radicals react towards more complex products on a diffusion-governed time scale, we have to take these processes into account, and the following reactions also occur on the pico- to nanosecond time scales following photoionization:

$$I^- + h\nu \rightarrow I^0 + e^- \tag{1}$$

$$I^0 + I^- \rightarrow I_2^- \tag{2}$$

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \tag{3}$$

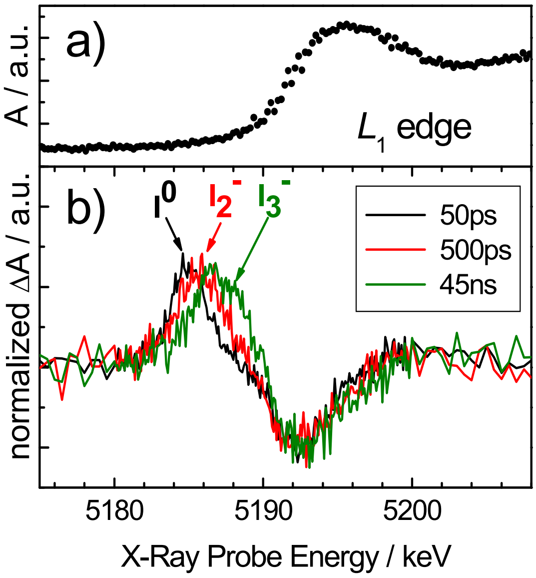

Figure 3 a) Static x-ray absorption spectrum of aqueous iodide. b) Transient absorption spectra of photoexcited iodide after 50 ps (black), 500 ps (red), and 45 ns (green), showing nascent atomic radicals, and subsequent bimolecular products.

As a last example we have observed the ultrafast magnetization process in photoexcited aqueous $Fe(bpy)_3$ (Fig. 4) exploiting time-sliced x-radiation at the microXAS beamline of the Swiss Light Source [6]. $[Fe^{II}(bpy)_3]^{2+}$ represents the simplest molecule of iron-based light-induced spin-cross over complexes, itself being a typical example of a low spin (LS) compound, which can undergo a spin change to a high spin (HS) quintet state upon irradiation [9]. The optical absorption spectrum of aqueous $[Fe^{II}(bpy)_3]^{2+}$ is characterized by an intense broad band centred at 520 nm due to the singlet Metal-to-Ligand-Charge-Transfer (^{1}MLCT) state. Photoexcitation into this band (or to higher energies) is followed by a cascade of intersystem crossing (ISC) steps through singlet, triplet and quintet MLCT and ligand-field (LF) states, which brings the system to the lowest-lying (HS) quintet state, $^5T_2$, with almost unit quantum yield in ca. 1-2 ps [10]. This state relaxes non-radiatively to the LS ground state within 0.6 ns in aqueous solutions at room temperature. Using picosecond XAS, we recently determined that in the HS state, an elongation of ca. 0.2 Å of the Fe-N bond distances occurs [11].

However, the pathway and time scale of the cascade from the intitially excited ^{1}MLCT to the $^5T_2$ state are still not known, as ultrafast optical spectroscopy can neither resolve the intermediate steps nor determine their structures. In order to address these issues and to probe the relaxation processes, we have implemented femtosecond XANES spectroscopy.

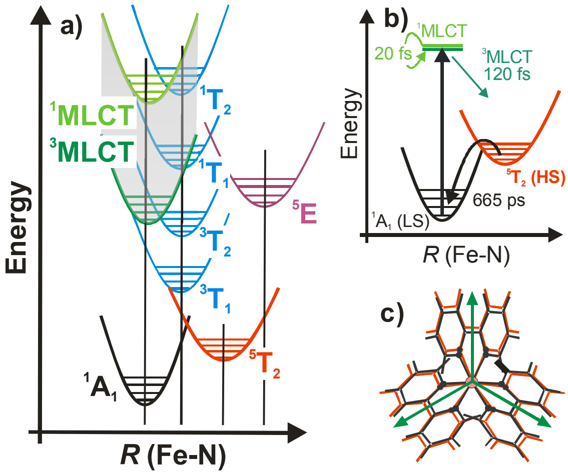

Figure 4 Generic potential energy curves of Fe(II)-SCO complexes as a function of the Fe-N bond distance (a)- The manifold of metal-to-ligand-charge-transfer (MLCT) states is shown by a shaded area. The metal-centred (MC) states are represented by their symmetry character (T and E) in the D_3 group of $[Fe(bpy)_3]^{2+}$. The LS $^1A_1$ ground state has a completely filled $t_{2g}{}^6$ subshell, while the antibonding e_g level is empty. For each electron that is promoted from the t_{2g} subshell to the e_g orbital the metal-ligand bond length increases. For the $[Fe(bpy)_3]^{2+}$ complex in its low-spin $^1A_1(t_{2g}{}^6)$ ground state, the bond length is 1.97 Å (Fe-N), in its high-spin $^5T_2$ $(t_{2g}{}^4 e_g{}^2)$ the bond length increases by ca 0.2 Å (c), as measured in picosecond XAS experiments. The arrows (b) show the relaxation cascade as determined by ultrafast laser spectroscopy.

Hereby the strongest absorption change at a multiple scattering edge feature near 7126 eV (not shown here) reflects the altered Fe-N bond distance (and thus the molecular structure), which increases by 0.2 Å in the HS state [11]. We therefore used this feature to investigate the temporal evolution of the relaxation process from the ^{1}MLCT to the $^5T_2$ by scanning the laser-x-ray time delay, which also confirms that this process terminates below 300 fs (Fig. 5). In order to quantify the time required for this spin crossover process, we have calculated the rate equations for this process. Hereby the following reaction cycle using the input from our optical studies [10] (Fig. 4b) was applied (using the indicated lifetimes and an overall cross correlation time of 250 fs [6]):

$$^1\mathrm{GS} + h\nu\ (400\ \mathrm{nm}) \rightarrow {}^1\mathrm{MLCT}\ (20\ \mathrm{fs}) \rightarrow {}^3\mathrm{MLCT}\ (120\ \mathrm{fs}) \rightarrow {}^5\mathrm{T}\ (665\ \mathrm{ps}) \rightarrow {}^1\mathrm{GS} \qquad (4)$$

With this we calculated the population dynamics of all intermediate states given above, and determined the final HS signal, which is shown in Fig. 5 together with the data. In addition, we fit the final arrival time to the ^{5}T state (previously fixed to the ^{3}MLCT departure time of 120 fs) yielding 130 (60) fs. This result implies that the electron back transfer from the ligand system simultaneously triggers the excitation of a second electron from the bonding t_{2g} orbital, so that both electron spins are parallel in the antibonding e_g orbital, together with two unpaired electrons ramaing from the bonding t_{2g} orbitals (thus changing the spin by $\Delta S = 2$). Any possible intermediate steps (in the metal-centered states) are considerably faster than 60 fs according to this fit procedure.

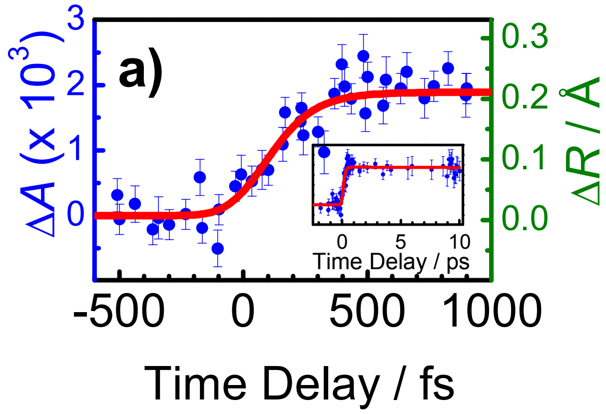

Figure 5. Transient x-ray absorption signal of photoescited aqueous Fe(bpy)$_3$, measured near the Fe K edge, together with a simulation to its ultrafast magnetization from the reactant low spin to the high spin states. The right axis shows the Fe-N bond elongation during this process, which is roughly proportional to the absorption change (and amounts to 0.2 Å in the HS state). The inset shows an expanded time scale out to 10 ps.

Acknowledgements: This work was funded by the Swiss National Science Foundation (FNRS), via contracts 200020 – 116023, PP002 – 110464, 200021 – 107956, 620-066145, and 200021-105239.

References

[1] C. Bressler, R. Abela, M. Chergui, "Exploiting EXAFS for time-resolved molecular structures in liquids", *Z. Kristallogr. 223* (2008) 307-321.

[2] M. Saes, R. Abela, D. Grolimund, S.L. Johnson, P.A. Heimann, C. Bressler, M. Chergui, "Ultrafast time-resolved x-ray absorption spectroscopy of chemical systems", *Synchr. Rad. News* **16** (2003) 12-20.

[3] M. Saes, F. van Mourik, W. Gawelda, M. Kaiser, M. Chergui, C. Bressler, D. Grolimund, R. Abela, T.E. Glover, P.A. Heimann, R.W. Schoenlein, S.L. Johnson, A.M. Lindenberg, R.W. Falcone, "A setup for ultrafast time-resolved x-ray absorption spectroscopy", *Rev. Sci. Instrum.* **A75** (2004) 24-30.

[4] W. Gawelda, C. Bressler, M. Saes, M. Kaiser, A. N. Tarnovsky, D. Grolimund, S. L. Johnson, R. Abela, M. Chergui, "Picosecond Time-resolved x-ray absorption spectroscopy of solvated organometallic complexes", *physica scripta* T**115** (2005) 102-106.

[5] W. Gawelda, V.-T. Pham, A. El Nahhas, M. Kaiser, Y. Zaushitsyn, S.L. Johnson, D. Grolimund, R. Abela, A. Hauser, C. Bressler, M. Chergui, "Capturing transient electronic and molecular structures in liquids by picosecond x-ray absorption spectroscopy", *AIP Conf. Proc.* **882** (2007) 31-36.

[6] G. Ingold, R. Abela, P. Beaud, S. L. Johnson, U. Staub, "Towards pump-probe resonant x-ray diffraction at femtosecond undulator sources", *Z. Kristallogr.* **223** (2008) 292-306

[7] W. Gawelda, M. Johnson, F. M. F. deGroot, R. Abela, C. Bressler, M. Chergui, "Electronic and molecular structure of photoexcited [Ru^{II}(bpy)$_3$]$^{2+}$ probed by picosecond x-ray absorption spectroscopy", *J. Am. Chem. Soc.* **128** (2006) 5001-5009.

[8] V.-T. Pham, W, Gawelda, Y. Zaushitsyn, M. Kaiser, D. Grolimund, S. L. Johnson, R. Abela, C. Bressler, M. Chergui, "Observation of the solvent shell reorganization around photoexcited atomic solutes by picosecond x-ray absorption spectroscopy", J. *Am. Chem. Soc.* **129** (2007) 1530-1531.

[9] A. Hauser, C. Enachescu, M.L. Daku, A. Vargas, N. Amstutz, "Low-temperature lifetimes of metastable high-spin states in spin-crossover compounds: The rule and exceptions to the rule", *Coord. Chem. Rev.* **250** (2006) 1642-1652.

[10] W. Gawelda, A. Cannizzo, V.-T. Pham, F. Van Mourik, C. Bressler, M. Chergui, "Ultrafast nonadiabatic dynamics of [FeII(bpy)3]2+ in solution". *J. Am. Chem. Soc.* **129** (2007) 8199-8206.

[11] W. Gawelda, V.-T. Pham, M. Benfatto, Y. Zaushitsyn, M. Kaiser, D. Grolimund, S.L. Johnson, R. Abela, A. Hauser, C. Bressler, M. Chergui, "Structural determination of a short-lived excited iron(II) complex by picosecond x-ray absorption spectroscopy", *Phys. Rev. Lett.* **98** (2007) 057401.