

Probing ultrafast solvation dynamics with high repetition-rate laser / X-ray methodologies

February 20 2013, by Vic Comello

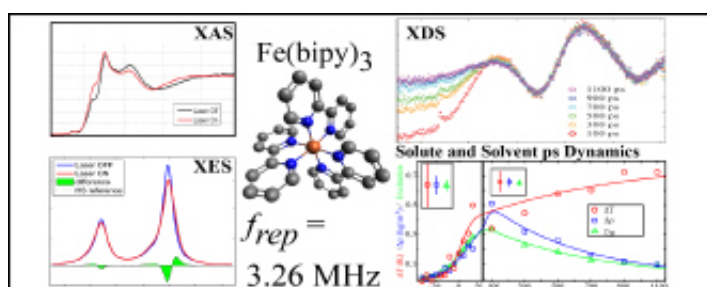


Figure 1: X-ray absorption, emission and diffuse scattering data acquired in a single experiment using MHz pump-probe repetition rates. By including x-ray diffuse scattering, the researchers could detect an ultrafast change in the solvent density (lower right, blue points) upon photo-excitation of the solute.

The chemical reactivity of molecules in solution critically depends on a complex interplay among intramolecular processes and interactions with the caging solvation shell, which surrounds a solute molecule.

Accordingly, the influence of solvation on the reactivity of chemical and biological molecular species has been the subject of increasingly intense research. Ultrafast time-resolved x-ray measurement techniques that combine picosecond lasers and short-pulse x-rays in laser pump/x-ray probe experiments are powerful tools for studying this interplay in photo-active molecular systems. In a typical laser pump/x-ray probe experiment, a laser pulse excites a molecular sample to create a transient

state; an x-ray pulse follows to probe the transient state at a fixed time delay relative to the laser pulse. X-ray spectroscopy and/or scattering signals can then be accumulated over many thousand such pump/probe cycles to satisfy signal-to-noise requirements. Doing so at a series of different time delays then reveals the temporal evolution of the transient state(s).

Such time-resolved laser pump/x-ray probe experiments have been carried out at [synchrotrons](#) for several years; however, few have been able to make use of the full x-ray flux available, often because of the low (kHz) repetition rate of amplified laser systems. Thanks to implementation of a high-repetition-rate (54 kHz–6.5 MHz), high-power (>10 W) laser system at the X-ray Science Division 7-ID-D [beamline](#) at the [Advanced Photon Source](#) (APS), it has become possible to fully match the repetition rate of the laser to the 6.5-MHz rate of the [x-rays](#), and thus to more efficiently use the flux provided by the APS.

This has enabled laser pump/x-ray probe measurements incorporating simultaneous x-ray spectroscopy and x-ray scattering techniques to study light-induced intramolecular processes and solvent interactions in challenging molecular systems. It is accomplished by simultaneous, time-resolved utilization of several complementary analytical techniques that all take advantage of the thousand-fold increase in useful x-ray flux provided by the MHz scheme.

The superior signal statistics permitted the extraction and analysis of ultrafast solute-solvent dynamics for the first time, thanks to the simultaneous inclusion of both x-ray spectroscopy and x-ray scattering tools into a single experimental setup. This facilitated the analysis of otherwise quite complex data by using complementary information extracted from each tool as a vital cross-check of the analysis.

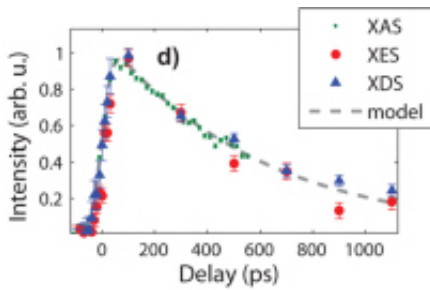


Fig. 2. Excitation fractions derived from the three methods used in the experiment, showing very good agreement. Fitting the excitation fractions revealed both the $[\text{Fe}(\text{bpy})_3]^{2+}$ HS lifetime (~ 600 ps) and the average x-ray pulse width during the experiment (~ 75 ps FWHM).

Researchers from the Technical University of Denmark, the Hungarian Academy of Sciences, the European XFEL at DESY (Germany), Argonne National Laboratory, the University of Copenhagen, SLAC National Accelerator Laboratory, and Lund University (Sweden) designed such an experiment for a highly detailed study of the photoinduced low-spin (LS) to high-spin (HS) conversion of iron(II)-tris(2,2'-bipyridine), $[\text{Fe}(\text{bpy})_3]^{2+}$, in aqueous solution, to provide information on the interplay between intramolecular dynamics and the caging solvent response on a 100-ps time scale.

The setup allowed simultaneous acquisition of x-ray emission spectroscopy (XES), x-ray absorption near edge spectroscopy (XANES), and x-ray diffuse scattering (XDS) data. These complementary spectroscopic and scattering techniques are sensitive to, respectively, the spin state and configuration of the electron system, the electronic and local structure around the absorbing atom, and the global molecular structure, including the solvation shell. The combined setup thus allowed simultaneous characterization of both the electronic and geometric degrees of freedom, while making full use of the intensity of the APS for a time-resolved experiment.

By combining information from the photon-hungry techniques of XES and XDS, the excitation fraction, as well as the temperature and density changes of the solvent, were closely followed on the sub-nanosecond time scale of the HS lifetime, allowing the detection of an ultrafast change in bulk solvent density (Fig. 1).

While initially surprising, this ultrafast bulk-density increase was shown to be consistent with recent theoretical predictions from high-level molecular dynamics simulations.

Tight focusing of both the laser (

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