Combining femtosecond hard X-ray scattering and spectroscopy to study photochemical dynamics in solution: instrumentation and recent results

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Recent development of optical pump/X-ray probe techniques at large scale facilities such as synchrotrons and X-ray free-electron laser (XFEL) sources enabled direct visualization of various fundamental ultrafast phenomena in solution photochemistry. Due to intrinsically much shorter pulses, the temporal resolution of such experiments at XFELs is over three orders of magnitude higher compared to that at conventional synchrotron sources, reaching the sub-100 fs domain – the fundamental timescale of elementary steps in photochemical dynamics.

In particular, understanding photochemistry of transition metal complexes is currently of high interest since they often are the major players in many fundamental photochemical processes that define e.g. biochemical reactivity and photovoltaic/photocatalytic functionality. In these reactions photoexcitation typically triggers ultrafast charge and spin changes of the metal center which intrinsically drives dramatic rearrangements in the structure of the molecule and its solvation shell.
Taking advantage of combining structurally and electronically sensitive probes, namely time-resolved X-ray scattering/diffraction [1], X-ray emission [2] and absorption [3] spectroscopies in one experiment [4,5], it has become possible to accurately monitor intrinsically coupled ultrafast electronic and structural transformations during e.g. ultrafast spin transitions and ligand exchange reactions in solvated iron complexes. A few examples of such studies performed at synchrotrons and XFEL sources are presented in this contribution.

The methodology of combining simultaneous structural and electronic observables is applied for experiments at the Femtosecond X-ray Experiments (FXE) instrument of the European XFEL, which came online only about 1.5 years ago. The new European XFEL source is capable of MHz pulse repetition rate thus providing a 100-fold increase in average flux over other XFELs and can deliver high X-ray photon energies up to 20-25 keV. We report on the progress of the FXE instrument commissioning over the past year, describe current capabilities of the setup as well as the first experimental results.

Figure 1. Schematic representation of the combined time-resolved X-ray methodologies at the FXE instrument.

References

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