

# Picosecond Resolved X-Ray Absorption Spectroscopy of Laser-Excited Organometallics in Solution

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Our understanding of fundamental properties in physics and chemistry relies on our knowledge of the inherent electronic and geometric structure of compounds. Consequently, mature experimental tools like X-ray absorption spectroscopy (XAS), X-Ray, neutron and electron diffraction spectroscopies permit us to investigate different aspects of the structural details. XAS methods have been widely exploited to reveal the local electronic structure of complex systems around a selected atom (via XANES) together with its local geometric structure (via EXAFS). Simultaneously, femtosecond laser spectroscopies elucidated the electronic changes upon impulsive photoexcitation, which is a prerequisite for our understanding of the making and breaking of bonds. With increasing complexity of the system, optical methods can no longer unambiguously determine how the molecule changes its structure, and direct structural tools as the probing sensor are desired.

We have started to combine laser excitation and X-ray probing spectroscopies in order to deliver the missing local structural and electronic information via time-resolved X-ray absorption spectroscopy. Hereby we have focused on the photoexcited kinetics of aqueous tris-(2,2'-bipyridine) ruthenium (II) ( $=\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ ) as a test bench of this new technique. Upon impulsive photoexcitation with 400 nm light, an electron from the Ru<sup>II</sup> central ion is moved to one of its bipyridine ligands on a 300 fs time scale in a metal-to-ligand charge transfer (MLCT) reaction. This excited state radiatively decays to the ground state on a 100-300 ns time scale.

Using 60 ps hard x-ray pulses we have followed the kinetics of this model system on a picosecond and nanosecond time scale. Hereby XANES spectra around the Ru  $L_3$  and  $L_2$  edges at a fixed time delay were recorded in order to determine the electronic structure of the transient species, e.g., the oxidation state of the central metal atom. A new absorption feature has been discovered at the  $L_2$  edge, which might be due to the distorted symmetry of the intermediate compound thus pointing to a geometric modification. Time-resolved EXAFS experiments are currently underway to support this interpretation.

The experimental setup has been upgraded to allow sensitive measurements down to the shot-noise level of the bend magnet source, and with a temporal resolution corresponding to the SR pulse width. With this setup a large variety of chemical systems can now be studied on a sub-100 ps time scale, where optical-only methods can no longer provide required structural information.