Femtosecond Spin State Changes – Implications for Photocatalysis

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This proposal seeks to deliver a motion picture of the interplay between the nuclear, electronic and spin degrees of freedom during the course of a chemical reaction. The coupling of nuclear and electronic dynamics also governs the light harvesting and catalytic conversion in molecular systems. Understanding the mechanisms by which electronic excitation energy is converted to energy-rich electrons and eventually to energy-rich molecules (photocatalysis) is critical for the development and optimization of efficient molecular-based light energy converters. While many aspects of relaxation phenomena are known in organic photochemistry, the photochemical relaxation dynamics of transition metal complexes, widely used as photocatalysts, remain largely unknown. This lack of knowledge reflects the greater complexity of d-electron based electronic structure and the important role of ligand field states. This highlights the importance of tracking the charge, spin, and covalent interaction between the metal and ligands to gain a mechanistic understanding of de-excitation in coordination chemistry. While femtosecond-resolution optical spectroscopy can accurately determine the kinetics and time scales of the relaxation, such spectroscopy cannot directly determine these key degrees of freedom, and consequently does not allow accurate determination of the reaction mechanism.

For this purpose we aim to combine, for the first time in a single experiment, x-ray emission spectroscopy (XES) with x-ray scattering (XRS) to directly measure the time evolution of both charge redistribution and nuclear motion. This methodology will allow disentangling the sequence of events leading to the product state in photochemical reactions. We propose to exploit this capability by studying the early events in a photocatalytic active bi-metallic bipyridine-based Ru-Co compound. This study aims to observe in real-time the photoinduced i) Ru to Co charge transfer, which leads to ii) a reduction of the Co ion, which partially undergoes a iii) spin transition. Since XES tools are sensitive to spin changes in the central atom, both the charge transfer as well as the spin conversion can be monitored on the femtosecond time scale. Simultaneous XRS will identify the nuclear motion, especially between both Ru and Co atoms.

The above methodology will be calibrated by studying the metal center charge and spin multiplicity, next to metal-ligand bond length during a laser induced spin crossover in Fe(II)-tris-bipyridine. Since both XES and XRS deliver complementary information, their combination in a simultaneous measurement will allow us to unravel the interplay between nuclear movements and electronic interactions. [Fe(bpy)3]2+ is a model system for the photoinduced transition from a low spin (LS, S=0) to a high spin state (HS, S=2).