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Tracking Excited State Dynamics in Photo-Excited Metal Complexes with Hard X-ray Scattering and Spectroscopy

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Potential energy surfaces play the central role for understanding molecular and chemical dynamics. For chemical reactions on the electronic ground state potential, transition state theory usually provides a strong foundation for understanding chemical reactivity because intra-well equilibration precedes chemical reaction and reactive trajectories proceed along adiabatic trajectories through the transition state with minimal damping. Chemical reactions on electronic excited state potentials differ fundamentally from those on the electronic ground state potential. Reactions can proceed faster than excited state equilibration and reaction dynamics often depend critically on the location of intersections between Born-Oppenheimer potentials where non-adiabatic effects dictate the transition probabilities between distinct electronic state potential energy surfaces. These so-called conical intersections can be seen as the analog of the transition state for electronic excited state chemical reactions and understanding the reaction mechanism of electronic excited states entails identifying the location of these intersections.

Robustly identifying the location of conical intersections that control the relaxation dynamics of electronic excited states has long been a goal and challenge in the chemical sciences. While ultrafast optical methods have made significant contributions to our understanding of electronic excited state reaction dynamics, the detailed interpretation of such measurements proves challenging for the majority of molecular systems. Addressing this challenge requires the development of more direct and differentiated probes of electronic and nuclear dynamics. With the advent of ultrafast x-ray laser sources, powerful x-ray scattering and spectroscopy tools for characterizing steady state nuclear and electronic structure, can now be extended to measure ultrafast electronic and nuclear dynamics.

We have utilized simultaneous K-alpha K-beta X-ray emission spectroscopy (XES) and X-ray diffuse scattering (XDS) to characterize the excited state dynamics in a range of iron-centered molecular systems, from photo-induced spin crossover in the $[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ model system, to the details of charge-separation in the photofunctional iron centered N-heterocyclic carbene systems. Combining the sensitivity of XES to the electronic spin moment on the Fe center with the sensitivity of XDS to the dominant changes in intramolecular nuclear structure places significant constraints on the possible trajectories involved in excited state cascade, demonstrating the ability of ultrafast x-ray methods to characterize electronic excited state dynamics of transition metal complexes with unprecedented detail.

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