

Ultrafast Electronic and Nuclear Structural Dynamics of Excited State Transition Metal Centers for Solar Energy Conversion

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The long term goal of the research is to structural dynamics of the transition metal excited states during photochemical processes and effects of coherent electronic and nuclear motions in the excited state to the excited state relaxation pathways which if understood, can be used to guide synthesis to control excited state relaxation pathways in favor of driving photochemical reactions with minimal loss in the energy converted from photons. In this presentation, we will focus on two systems, Cu(I) diimine complexes and Pt(II) complexes which may function as sensitizers in solar energy conversion and as catalysts for photochemical transformation. A series of Cu(I) complexes and a series of platinum pyrazolate bridged dimers are selected as a platform of structural tuning for optimal excited state pathways for desirable functions. These complexes display progressing changes in optical properties, energy levels and excited state pathways with absorption/emission peaks strongly dependent upon the structures in the ground and excited state, such as the angle between two ligand planes in the Cu(I) complexes and the Pt-Pt distances in the ground state.

The MLCT structural dynamics of Cu(I) diimine complexes in different solvents are studied by both optical and X-ray transient absorption, from which the structural dependent MLCT state formation kinetics and interfacial electron injection to TiO₂ nanoparticles are studied. The MLCT formation time in some complexes is a sub-ps process rather than “instantaneous” as expected revealing electronic and nuclear interactions and internal motions in these molecules within 1 ps after the photoexcitation.

To follow the excited state trajectory of Pt dimer complexes, we recently carried transient absorption measurements on the aforementioned Pt-dimer complexes using sub-30 fs laser pulses in a transient grating setup and found long-lived wave-packet oscillations along the Pt-Pt stretching coordinate. These oscillations imply that the coherence prepared upon the excitation of the singlet MLCT state survives ISC and is transferred from the ¹MMLCT state to the ³MMLCT state. As the Pt-Pt distance decreases, the lifetime of wave-packet motion is dramatically shortened, indicating a strong dependence of energy relaxation dynamics in the MMLCT state on the energy level of the excited state controlled by the Pt-Pt distance. The coherent vibrational wave-packet dynamics observed in this study suggest that the Pt-Pt distance controls the electronic coupling between singlet and triplet MMLCT states which

could have significant influence on the excited state lifetime and dynamic energetics of the molecules. Future studies include wave-packet motion phase related photoinduced energy and electron transfer processes in these complexes. These studies are combined with recent femtosecond X-ray absorption/emission/scattering measurements at the LCLS to detect structural evolution in the excited state. Preliminary results will be presented.

These studies will provide new insight into excited state potential energy surface and excited state pathways and guidance for molecular design in order to optimize excited state energy for useful solar energy conversion process for solar fuel and electricity generation.

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