

Characterization of Intermediates in Photocatalytic Hydrocarbon Oxidation Using Tabletop Femtosecond XANES

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Scientific Accomplishments

In Year 2 of this grant, we completed our spectroscopy of transition metal porphyrins, which are useful model complexes for understanding photocatalysts. Ni(II) octaethylporphyrin (NiOEP) has been widely studied using hard x-ray transient absorption and scattering techniques, but there is still considerable uncertainty about the electronic structure in the first tens of ps after photoexcitation. Specifically, initial ligand-based $\pi \rightarrow \pi^*$ excitation is thought to lead to a metal-centered excited state accompanied by elongation of the Ni-N bonds. However, whether the metal-centered state has singlet or triplet multiplicity remained an open question.

To resolve this issue, we combined femtosecond M-edge XANES spectroscopy, which probes the $3p \rightarrow 3d$ transition in first-row transition metals, with femtosecond UV/Visible spectroscopy, which probes the electronic structure of the porphyrin π system (*J. Phys. Chem. A* 2019, 123, 25, 5214-5222). As shown in Figure 1, π - π^* excitation of the porphyrin ligand forms the metal-centered triplet state within 100 fs, without any observable charge transfer state or metal-centered singlet. This rapid spin-state change is mediated by spin-orbit-vibronic coupling, and forms a highly vibrationally excited triplet that relaxes in tens of ps.

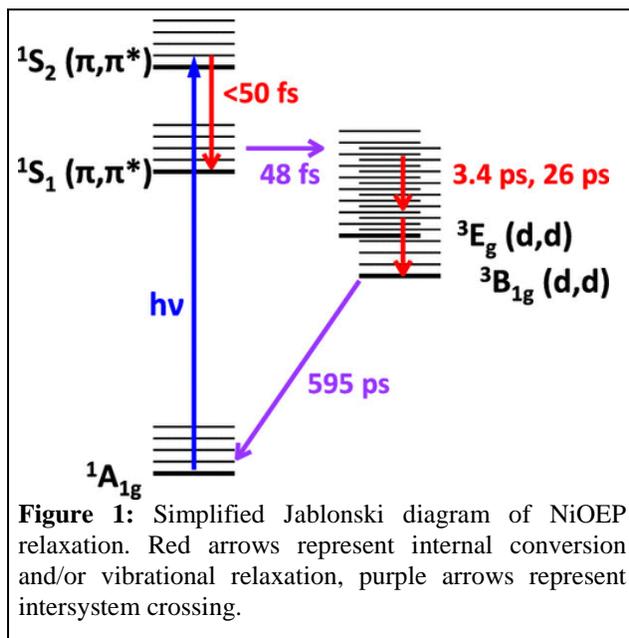


Figure 1: Simplified Jablonski diagram of NiOEP relaxation. Red arrows represent internal conversion and/or vibrational relaxation, purple arrows represent intersystem crossing.

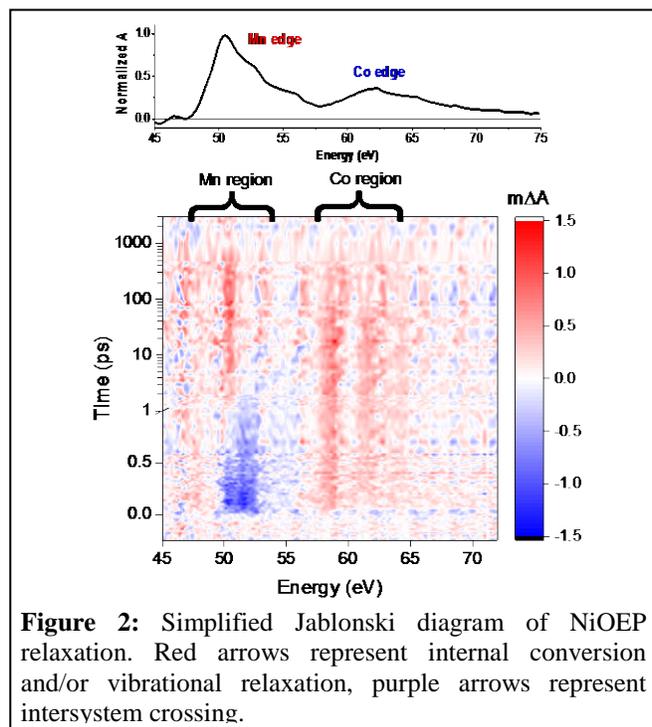


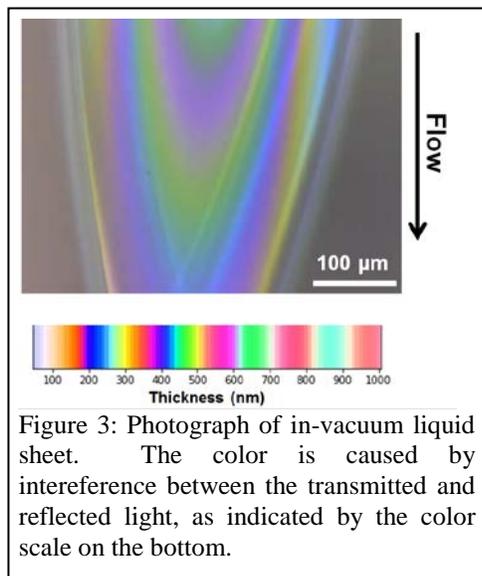
Figure 2: Simplified Jablonski diagram of NiOEP relaxation. Red arrows represent internal conversion and/or vibrational relaxation, purple arrows represent intersystem crossing.

From a photochemical perspective, this result showed that solvent or substrate ligation to the Ni center in the excited state is the *result* of the spin-state change, and not the *cause* of this change.

With this work complete, we progressed to studying the photophysics of bimetallic complexes. In a collaboration with a synthetic chemist (Prof. Connie Lu) and a theorist (Prof. Laura Gagliardi), both at the University of Minnesota, we measured the ground- and excited-state electronic structure of a CoMn complex with approximately C_{3v} symmetry. High-level calculations indicate that this molecule has strongly multireference character, so it eluded characterization with traditional experimental techniques. Using a combination of X-ray photoelectron spectroscopy, M-edge XANES, and L-edge XANES, we showed that this complex is well described as high-spin Co(II), high-spin Mn(II). As shown in Figure 3, the M-edge XANES spectrum shows the Mn $3p \rightarrow 3d$ transition at 50-55 eV and the Co $3p \rightarrow 3d$ transition at 60-65 eV. This spectral separation enabled us to observe distinct changes to each metal's electronic structure after photoexcitation, as shown by the heat map. We continue to analyze this data, but our preliminary

calculations suggest that the initial photoexcitation at 435 nm is a ligand-to-Mn charge transfer transition that rapidly converts the Mn to a low-spin excited state. We are currently synthesizing single-metal tripodal complexes as models for these potential excited states in order to support this assignment.

Technical Accomplishments: Extending M-edge XANES to the Solution Phases



We also continued our efforts to move M-edge XANES into the solution phase (all spectra presented above are with vapor deposited thin films). The entire XUV transient absorption system is in high vacuum (10^{-6} torr) because the 40-80 eV photons have a short penetration depth in air. In Year 1 of this grant, we fabricated a microfluidic flow cell with silicon nitride windows. While this cell was successful in maintaining the sub-micron path length required for XUV transmission, we found that photodeposition of reaction products on the silicon nitride made it unusable for pump-probe spectroscopy. We therefore collaborated with the Sample Delivery Team at the Linac Coherent Light Source to implement an in-vacuum liquid sheet. In this device, a cylindrical liquid jet is shaped into a sheet by two jets of He gas. We measure the thickness of the film using visible-light interferometry. As shown in Figure 3, we can now achieve stable films of molecules such as Fe tetraphenyl porphyrin chloride in dichloroethane solvent, with a width of ~200 microns and a thickness of 200-500 nm.

Impact on Student Development

This project funded the graduate studies (including conference travel) of Liz Ryland. Liz was the primary driver of the porphyrin project, and graduated in Fall 2019 with her Ph.D. in Physical Chemistry. She accepted a postdoctoral fellowship at the Naval Research Laboratory, using two-dimensional infrared spectroscopy to measure excited-state dynamics of polarons in optical cavities. Kris Benke and Aastha Sharma presented their work on this project at the International Symposium on Molecular Spectroscopy and the ACS Great Lakes Regional Meeting. Kris is scheduled to graduate this year with his Ph.D. and is seeking positions in science policy, including the ACS Science Policy Fellow program.