

Scientific Accomplishments

This year has focused on expanding 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 is an open question. We used femtosecond M-edge XANES spectroscopy, which probes the $3p \rightarrow 3d$ transition in first-row transition metals, to answer this question.

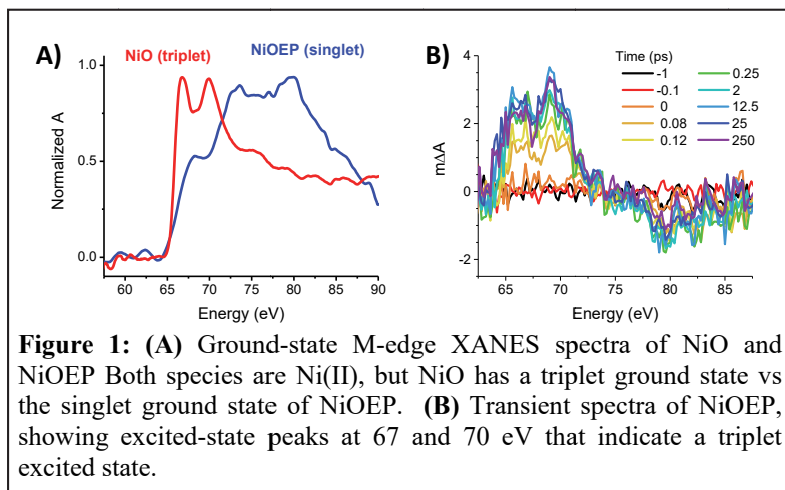


Figure 1: (A) Ground-state M-edge XANES spectra of NiO and NiOEP. Both species are Ni(II), but NiO has a triplet ground state vs the singlet ground state of NiOEP. (B) Transient spectra of NiOEP, showing excited-state peaks at 67 and 70 eV that indicate a triplet excited state.

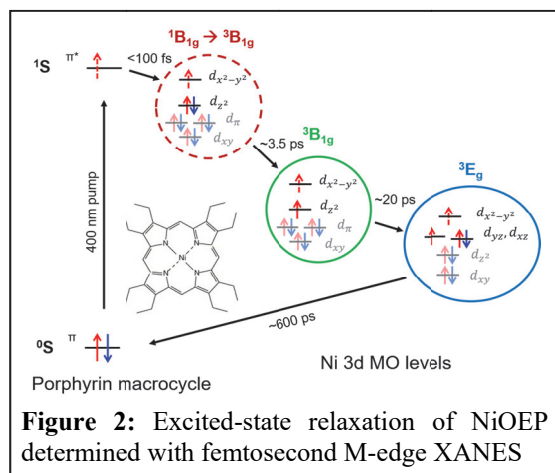


Figure 2: Excited-state relaxation of NiOEP determined with femtosecond M-edge XANES

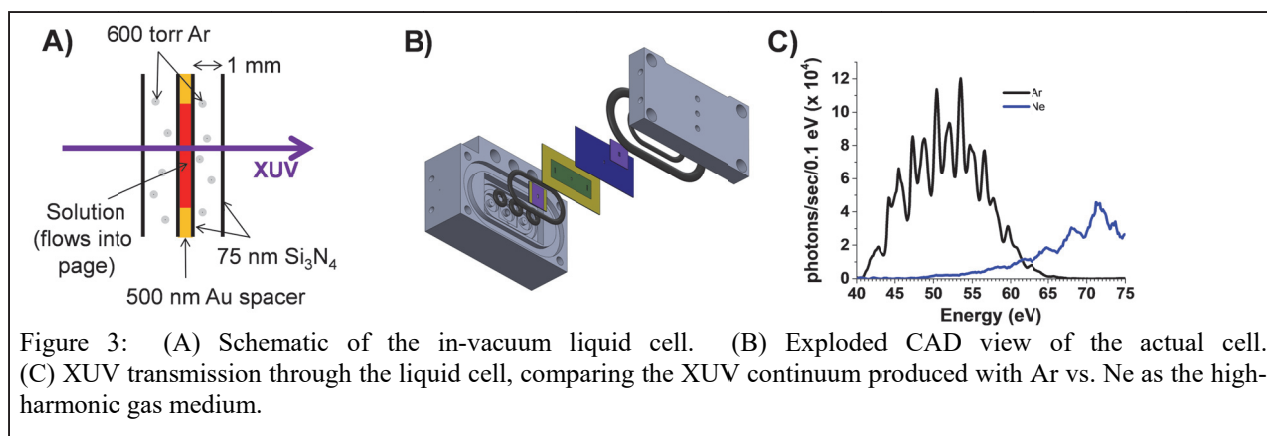
intermediate states and produce the relaxation diagram shown in Figure 2. We are currently drafting a manuscript about these results that will be submitted to the Journal of Physical Chemistry.

We continue to study the photophysics of other single-metal transition metal complexes, and have collected transient spectra of Mn and Co porphyrins that we are evaluating using models similar to that shown above. We have also initiated a collaboration with Prof. Connie Lu from the University of Minnesota to study heterobimetallic complexes as the next step in complexity towards heterobimetallic protein active sites. Over the next year, we will measure metal-to-metal charge transfer in MnCo tripod complexes and unravel relaxation within both d manifolds.

As shown in Figure 1A, M-edge XANES is sensitive to the spin state of the metal center. NiOEP is a ground-state singlet, while NiO is a ground-state triplet. Both are Ni(II), so their $3p \rightarrow 3d$ absorption edge rises at about 65 eV. The shape of the two spectra are completely different, however, due to strong p-d coupling. The NiO spectrum is characterized by two sharp peaks at 67 and 70 eV, while NiOEP shows three features at 68, 73, and 80 eV. Figure 1B shows the transient absorption spectra of NiOEP after 400 nm excitation. A two-peak excited-state absorption signal between 65 and 70 eV strongly resembles the NiO triplet ground-state spectrum, indicating that the excited state is in fact a triplet. The precise shape of the excited-state spectrum changes over time, indicative of a cascade through different d-orbital occupations within the triplet manifold. Using semiempirical ligand field multiplet simulations, we were able to assign these

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

We also continue 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. Figure 3 shows our microfluidic flow cell, in which the solution is contained between two 75 nm thick Si_3N_4 windows. These windows are flexible due to their thinness so under vacuum they stretch outward, turning a 500 nm path length of solvent into a 5,000 nm path length. To avoid this problem, a second set of windows is placed outside the “cuvette” windows and the interstitial space is filled with Ar gas at the vapor pressure of the solvent. This balances the forces on the inner windows and allows us to fine-tune the solvent path length. Figure 3C shows the XUV flux through this cell using Ne and Ar gas as the high-harmonic generation medium. The Ne continuum extends to ~ 100 eV, but is blocked beyond 75 eV in this experiment by an Al filter in the beam path that blocks other scattered light. We have begun to use this liquid cell for transient absorption studies, but are currently struggling with photodeposition of reaction products on the



windows; graduate student Kris Benke is attempting to deposit fluorosilanes onto the membrane to avoid this problem (essentially putting a Teflon coating on the inside of the flow cell).

Impact on Student Development

This project has funded the graduate studies (including conference travel) of Liz Ryland and travel to a Gordon Conference for graduate student Kris Benke. Liz has been the primary driver of the porphyrin project, and presented her results talks at the 2018 Fall ACS conference, the 2018 International Symposium on Molecular Spectroscopy (ISMS), and a poster at the 2018 Gordon Conference on Donor-Acceptor Interactions. She has received significant recognition for her work, winning a poster prize award at the Gordon Conference, the Rao Prize for best student talk at the ISMS, and the UIUC Geerdes award for excellence in graduate research. She is now applying for postdoctoral jobs, and already has an offer from the Naval Research Lab. She will graduate in Spring 2019. Kris was recognized with a talk at the Graduate Research Symposium at the Donor-Acceptor Gordon Conference.