

TIME: 12:30-2:00 PM PLACE: SCIENCE HALL WEST 301
Dr. Dugan Hayes**JOSEPH KATZ FELLOW****ARGONNE NATIONAL LABORATORY****WHEN: THURSDAY, SEPTEMBER 29TH, 2016****Title: "Electronic and nuclear contributions to time-resolved optical and X-ray absorption spectra and insights into photoelectrochemical performance"**

Ultrafast time-resolved studies of photocatalytic thin films can provide a wealth of information crucial for understanding and thereby improving the performance of these materials by directly probing electronic structure, reaction intermediates, and charge carrier dynamics. The interpretation of transient spectra, however, can be complicated by thermally induced structural distortions, which appear within the first few picoseconds following excitation due to carrier-phonon scattering. Here we present a comparison of *ex situ* steady-state thermal difference spectra and transient absorption spectra spanning from near-IR to hard X-ray energies of hematite (α -Fe₂O₃) thin films grown by atomic layer deposition. Hematite is a remarkably stable and inexpensive heterogeneous catalyst for photochemical and photoelectrochemical water splitting with absorption extending to the near-IR, but its utility is limited by poor carrier mobility and an absorbed photon to current efficiency spectrum that drops to zero for energies below 2 eV. Efforts to overcome these deficiencies through nanostructuring and doping are currently impeded by the lack of a unanimous assignment of the steady state and transient optical absorption bands in the literature. Our combined spectroscopic data, which are modeled with density functional theory and full multiple scattering calculations, support an assignment of the optical absorption spectrum of hematite that includes two ligand-to-metal charge transfer bands that nearly span the visible spectrum. We also find that beyond the first few picoseconds, the transient spectra are almost entirely attributable to thermal effects as the lattice expands in response to the ultrafast temperature jump and then cools to room temperature on the microsecond timescale. At early delay times we observe a broad excited state absorption band with a 75 picosecond lifetime that we assign to free carriers and conclude that carrier recombination is complete on the sub-nanosecond timescale, in contrast to previous assignments. Our results also provide the first experimental identification of the photoelectrochemically active and inactive transitions in hematite, thereby suggesting a framework for shifting the relevant absorption bands of ferric oxide films from the near-UV further into the visible part of the solar spectrum to improve solar conversion efficiency.