ISEN Award: “Near-Infrared Spectrometer” (M. R. Wasielewski)

Electron transfer reactions are essential to the efficient capture and storage of excitation energy following light absorption by these complex systems. Unambiguous identification and structural characterization of the short-lived intermediates produced by energy and electron transfer are critical to determining the mechanisms of solar energy capture, charge separation and storage in these molecular systems. Ultrafast femtosecond transient absorption spectroscopy is one of the most important spectroscopic tools used to characterize energy and electron transfer in molecular systems for solar fuels and solar electricity research.

Femtosecond transient near-infrared absorption spectroscopy is a powerful spectroscopic technique wherein a chromophore is excited using a femtosecond pulse at a specified visible wavelength and the resulting excited state population is probed with a femtosecond near-infrared (NIR) continuum. This effectively generates the absorption spectrum of the transient species, and varying the delay between the excitation and the probe pulses allows for the dynamics following the excitation to be followed in real time. Typical NIR transient absorption data are shown below for an organic donor-bridge-acceptor species. In this sample, perylene-xylene-(perylene-diimide), the visible excitation results in a transfer of an electron from the perylene donor to the perylene-diimide (PDI) acceptor. The anion and cation signals are known from spectroelectrochemistry; the PDI radical anion has a strong absorption around 950 nm, while perylene cation has significant absorption in the NIR. The formation of the PDI anion signal accompanies a decay of the excited $^1$PDI absorption, allowing determination of the charge separation time. The signal then decays with the charge recombination time. The incorporation of NIR sensitivity to our existing femtosecond transient absorption apparatus thus allows us to better distinguish between various charged and excited states for many of the molecular systems we utilize in our research.

![Experimental layout for NIR transient absorption](image)

Femtosecond near-infrared (NIR) transient absorption spectra of a perylene-xylene-(perylene-diimide) (Per-Xy-PDI) donor-bridge-acceptor species.