Structural Dynamics of Charge Transfer in Photocatalytic Solar Fuel Production

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Femtosecond Stimulated Raman Spectroscopy

Funded by the DOE ANSER Center equipment grant, the new lasers for the FSRS instrument began to arrive in July 2010. The experimental setup developed over the course of the Booster Award is shown below in the photo and illustration. We have successfully integrated the entire system via a homebuilt LabVIEW code, and recent data show significant improvements in performance and signal-to-noise (PDI data shown below).

[FeFe] Hydrogenase Active Site Photocatalysts

[In collaboration with Prof. Michael Wasielewski]

Using femtosecond visible-pump mid-infrared-probe spectroscopy, we studied the vibrational motions of the photodriven reduction of a diiron complex (NMI-Fe_2S_2(CO)_6) modeled on the active site of the [FeFe] hydrogenases. We were able to monitor the carbonyl stretches of the diiron complex (left) and the naphthalene-monoimide (NMI) backbone (right) upon photoexcitation of the zinc porphyrin electron donor moiety and subsequent electron transfer in CH_2Cl_2. The ground state bleach and appearance of both the reduced diiron complex and NMI peaks were simultaneously observed, indicating that electron density of [NMI-Fe_2S_2(CO)_6]^-1 is spread across the naphthalene backbone and the diiron active site. The mechanistic details of electron transfer in photocatalytic reactions are critical in designing more efficient photocatalysts, and such information would not have been obtainable with visible transient absorption alone.