Introduction. This report summarizes the achievements for the ISEN Booster Award in the Co Lab from 6/1/2010 to 2/29/2012 with a total funding amount of $45,000. We have been investigating the post photoexcitation nuclear motions of novel photocatalysts relevant to solar fuel production. Here I will present the progress that we have made in (1) constructing the femtosecond stimulated Raman spectroscopy (FSRS) instrument, (2) obtaining first FSRS data on a perylenediimide chromophore, (3) elucidating the photoinduced structural dynamics of a zinc porphyrin-hydrogenase active site mimic dyad using femtosecond vibrational spectroscopy, and (4) understanding ultrafast phonon dynamics in CdSe quantum dots using FSRS. Using preliminary results from the ISEN-funded project, I have successfully secured external funding from The Camille and Henry Dreyfus Foundation Postdoctoral Program in Environmental Chemistry to support a postdoctoral fellow for 2 years (totaling $120,000). The title of the award is "Ultrafast Structural Dynamics of Interfacial Photoinduced Electron Transfer in Hybrid Semiconductor Quantum Dots." We will be collaborating closely with Asst. Prof. Emily Weiss and Asst. Prof. Richard Schaller on that project (Benchmark 3 in original proposal). The postdoctoral research fellow for the Dreyfus fellowship started in my group on Feb. 1, 2012. The additional funding and extension approved by ISEN provided much needed continuity for the project. I am indebted to ISEN for supporting this project and allowing me to compete with tenure-track applicants for funding from prestigious agencies.

Femtosecond Stimulated Raman Spectroscopy (FSRS). Funded by the DOE ANSER Center equipment grant, the new lasers for the FSRS setup began to arrive in July 2010. The FSRS apparatus is a Ti:sapphire based system comprised of a MaiTai SP oscillator (780-820 nm, < 25 fs), Spitfire Pro XP amplifier (4 mJ/pulse, 1 kHz), Second Harmonic Bandwidth Compressor (SHBC) and TOPAS-400 optical parametric amplifier (OPA) for the Raman pump pulse (290-2600 nm, < 20 cm⁻¹), and TOPAS-C OPA for the femtosecond actinic pump (470-2600 nm, 100 fs). The experimental setup developed by Co, Smeigh, and Kim over the course of the year is shown in Figure 1. We have successfully integrated the entire system via a new homebuilt LabVIEW code, and recent data show significant improvements in performance and signal-to-noise, as illustrated by the first results on the time-resolved FSRS studies of perylenediimide shown in the section below.

FSRS of Perylenediimide. Perylenediimides (PDIs) are commonly used as chromophores in donor-bridge-acceptor systems, light harvesting materials, and self-assembling structures because of their strong absorptivity, high fluorescence quantum yields, high photochemical and thermal stability, strong hydrophobic π-π stacking interactions, and semiconducting properties. However, the structural dynamics of this ubiquitous chromophore’s excited state(s) and subsequent electron transfer reactions in D-B-A systems are poorly understood. Figure 2 shows the raw transient FSRS...
spectra of PDI as a function of delay times after photoexcitation at 525 nm. The Raman pump wavelength was set to 640 nm in order to be near resonance to the $S_n \leftrightarrow S_1$ transition while still keeping the Stokes-side Raman modes accessible to the Raman probe spectral range (<750 nm). Interesting Raman features to note are the perylene core stretching modes of the PDI $S_1$ state (labeled with the dotted lines and stars) and the ground state solvent (chloroform) peaks at 669, 672, and 694 nm that are persistent in all traces. The broad feature centered near 700 nm and spanning the entire spectral window is the “bleach” of the PDI $S_1$ excited state. Even at 640 nm where the absorption from the $S_1$ state is low, absorption of the Raman pump is competitive with the Raman transitions. Monitoring the amplitude of the core stretch peak at 713 nm (1607 cm$^{-1}$) yields kinetics in excellent agreement with known PDI $S_1$ lifetimes (2.75 ns). Using PDI as a benchmark molecule, we were able to demonstrate the feasibility of using FSRS to obtain high quality Raman spectra of solution-phase organic dye molecules (Benchmark 1 in original proposal). We are currently investigating the vibrational dynamics of PDI in a covalently linked Perylene-Ph-PDI D-A system to further understand the structural evolution of electron transfer reactions.

**Vibrational Dynamics of [FeFe] Hydrogenase Mimics.** [In collaboration with Prof. Michael Wasielewski] Using femtosecond visible-pump infrared-probe spectroscopy, we studied the vibrational motions of the photodriven reduction of a diiron complex (NMI-Fe$_2$S$_2$(CO)$_6$) modeled on the active site of the [FeFe] hydrogenases. We were able to monitor the carbonyl stretches of the diiron complex and the naphthalenemonoimide (NMI) backbone upon photoexcitation of the zinc porphyrin electron donor moiety and subsequent electron transfer in CH$_2$Cl$_2$. Figure 3. The negative features correspond to the bleaches of the ground state Fe$_2$S$_2$(CO)$_6$ and NMI C=O stretches, respectively. The red-shifted positive peaks correspond to the C=O vibrational modes of the reduced species, which are both in excellent agreement with spectroelectrochemistry data. The key discovery here is that the ground state bleach and appearance of both the reduced diiron complex and NMI peaks were simultaneously observed, which indicates that electron density of [NMI-...
Fe$_2$S$_2$(CO)$_6$] is spread across the naphthalene backbone and the diiron active site. This perhaps should not have come as a surprise as the NMI-[FeFe] complex is among the most easily reduced hydrogenase mimics (-0.74 V vs. SCE) reported to date. We are currently working on quantifying the amount of “leakage” of the electron density onto the NMI backbone. The mechanistic details of electron transfer in photocatalytic reactions are critical in designing more efficient photocatalysts. Such comprehensive picture of the reduction of a photocatalyst was previously prohibitive since electronic transitions probed in visible transient absorption are largely insensitive to nuclear motions. We believe this represents an important advance in the development of photocatalysts for hydrogen production (Benchmark 2 in original proposal).

Ultrafast Phonon Dynamics of CdSe Quantum Dots. [In collaboration with Prof. Richard Schaller] Using femtosecond stimulated Raman spectroscopy, we monitored the ultrafast dynamics of the low-frequency longitudinal optical phonon mode (~200 cm$^{-1}$) in CdSe semiconductor quantum dots of various sizes (radii 1.5 nm – 3.5 nm). Preliminary time-resolved Raman spectra (probed at 650 nm) of 3.5 nm radius QD as a function of delay time after photoexcitation at 400 nm are shown in Figure 4. Interestingly, the anti-Stokes feature near -200 cm$^{-1}$ has the opposite sign of what one would expect from a typical FSRS anti-Stokes mode. We are currently working on the theoretical explanations for that observation. Upon photoexcitation, the Stokes LO phonon mode gets entirely annihilated and recovers, though not completely, with a time constant in the range of 7 – 200 ps depending on the size of the QD. The recovery time gets longer with larger QDs. These results have never been observed in the literature, and we are working on understanding the measurements via additional control experiments and theoretical modeling of FSRS lineshapes. The current hypothesis is that the transient melting of the QD lattice structure caused by the fs actinic pump suppresses the LO phonon modes, and the Raman-active mode recovers as the heat dissipates and lattice relaxes. These studies are important in elucidating the ultrafast structural dynamics of QDs as we begin to study the interfacial photoinduced electron transfer reactions (Benchmark 3 in original proposal) in hybrid QDs.

Figure 4. Raw transient FSRS spectra of 3.5-nm-radius CdSe quantum dots in toluene as a function of delay times after photoexcitation at 400 nm. Raman pump wavelength was 650 nm.