Ultrafast Dynamics in Photosynthetic Protein Complexes

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Introduction

During the prior magnet-time period, ultrafast spectrally-resolved pump probe (SRPP) spectroscopy was successfully implemented at the Split Florida-Helix facility at NHMFL. This technique is highly sensitive to coherent oscillations in time-resolved spectroscopic signals, and the ability to spectrally resolve pump-probe signals allows for identification of the active electronic/vibronic bands emitting the coherent signal.

Given the sensitivity of ultrafast pump-probe spectroscopy to oscillatory signals, its setup and optimization was the first subject of the prior magnet time, and immediately following, preliminary experiments were performed on the cryptophyte algae phycobiliproteins PC577 and PC645. By comparing patterns observed for coherences in pump-probe spectra at high field to zero field, we expect to discriminate between vibrational and excitonic coherences.

Experimental

Spectrally-resolved pump-probe spectroscopy was performed with a commercial optical parametric amplifier (OPA) with a spectral bandwidth of ~20 nm FWHM and 35-40 fs pulse duration. The compressed pulses were passed through a wedged beamsplitter transmitting 99% to be used as the pump beam, leaving the front-reflected beam to be used as the probe and the back-reflected as reference. The pump was aligned through a delay stage and both beams were combined in the sample cell placed in the bore of the magnet. The probe was brought into a spectrograph where it was dispersed on a CCD camera and readout. For the protein samples, a small filament stirrer was used.

Results and Discussion

Pump-probe experiments were performed through the magnet at 0 T and 25 T. The first sample was the laser dye cresyl violet as a reference and those results collected at full field are summarized in Figure 1a) (single scan). Figure 1a) (middle) shows the kinetic traces at 497 and 490 THz where oscillations are clearly evident. Removal of the biexponential population decay leaves only the coherent features as residuals shown at the bottom of Figure1a) along with the Fourier transform (FT) which reveals the single dominant vibrational frequency.

Following cresyl violet, experiments on PC577 were done first with the OPA set to 590 at 25 T and 0 T. The 25 T results are shown in Figure 1b). For comparison with cresyl violet, the data shown for PC577 in is an average of three separate scans, and oscillations can be seen in the kinetic traces. The FT of the residuals displays a clear oscillation around 300 cm^{-1} and some smaller amplitude features at higher frequency. This is consistent with prior results done without the presence of the magnetic field.[1] Unfortunately, data taken with the same excitation conditions at 0 T were significantly noisier and precluded comparative information.

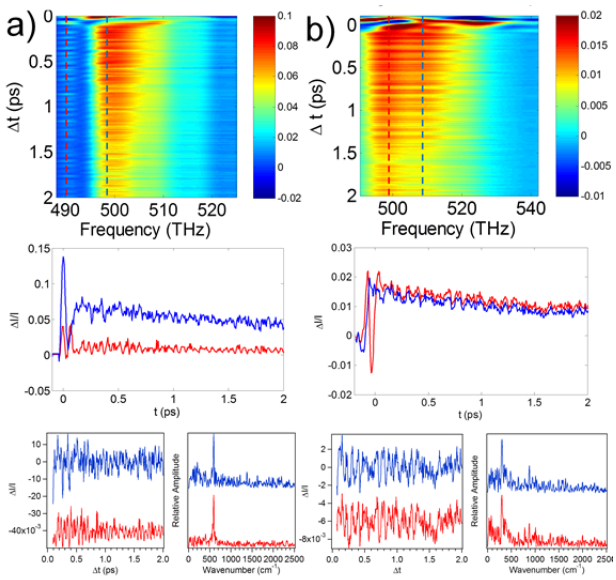

Figure 1. Pump-probe spectrum of (a) cresyl violet and (b) PC577 at 25 T with kinetic traces (middle) and residuals after subtraction of biexponential decay.

The same experiment was attempted on PC645, which displays weaker oscillations in the spectral region of interest and no reproducible coherence was detected as a result.

Acknowledgements

This work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy. The authors gratefully acknowledge Dima Seminov for designing/building a stirring probe.

References

[1] McClure, S. D.; Turner, D. B.; Arpin, P. C.; Mirkovic, T.; Scholes, G. D. *J. Phys. Chem. B* **2014**, *118*, 1296-1308.