Coherence Signatures in the Cryptophyte Protein PC645 in a 25 T Magnetic Field

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Introduction

Since the discovery of long-lived electronic coherences in light-harvesting proteins,[1] there has been intense interest in understanding the mechanisms and implications of these quantum effects on energy transfer processes.[2] The phycocyanin protein PC645 from the cryptophyte algae *Chroomonas mesostigmatica* (CCMP 269) has been shown to exhibit electronic coherence signatures utilizing 2D electronic spectroscopy,[3] owing to the strong coupling of the dihydrobiliverdin (DBV) pigment pair. This strong coupling yields two excitonically coupled states (DBV^+ and DBV^-). There is, however, great difficulty in distinguishing vibrational coherence from electronic coherence, as they can both result in oscillatory signals of similar frequencies. A high magnetic field is expected to modify relative energies of the aforementioned exciton states differently than states corresponding to vibrational coherences. Progress toward differentiating and better understanding these coherent processes could help to resolve long-standing questions in this field.

Experimental

Spectrally-resolved femtosecond pump-probe transients of PC645 were measured in the 25 T Split-Florida Helix Magnet utilizing a multichannel (CCD), balanced detection system developed by McClure *et al*.[4] The relatively high signal-to-noise ratio afforded by this method allows the measurement of the small oscillations (coherence signatures) superimposed on the pump-probe transients in time-frames that are reasonable for high-field work. The CCD detection implemented in this experiment allows for simultaneous detection of pump-probe signals from all the wavelengths within the bandwidth of the 35-femtosecond laser pulse.

Results and Discussion

Fig. 1a shows frequency-resolved pump probe spectra of PC645 at room temperature in a 25 T magnetic field. The purely oscillatory components of the pump-probe signal were analyzed by subtracting the biexponential population response, which were fit at each frequency value, and performing a Fourier transform on these residuals. The pump-probe transients at zero field exhibited no oscillatory components, while a low frequency oscillatory component was apparent at 25 T across a range of emission frequencies under identical conditions (see Fig. 1b). The frequency of this mode correlates well to a Zeeman splitting of a typical spin ½ system in a 25 T magnetic field. The relatively long damping time (>2 ps) suggests that the coherence signal is vibrational in nature. It is therefore plausible that this oscillatory component revealed under a 25 T magnetic field could be due to splitting of a degenerate or near-degenerate electronic or vibronic state.

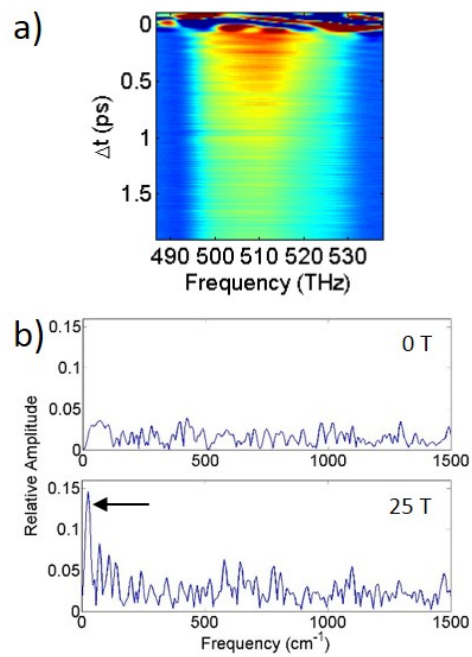

Fig.1 (a) Frequency-resolved pump-probe spectra of PC645 at room temperature. (b) Fourier transforms of the population-subtracted time resolved pump-probe signal. The arrow points to the low frequency mode identified in the text.

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