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Electronic and Vibrational Coherences in Algal Light-Harvesting Proteins

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Abstract. We present broadband two-dimensional electronic spectra of a light-harvesting protein from photosynthetic algae. Analysis of the spectra show that the amplitude of the main cross peak oscillates as a function of the waiting time period. Both electronic coupling and intramolecular vibrational modes, and their mixture, can lead to such oscillations. Using predictions based on models of four-level systems, we describe ways to distinguish electronic from vibrational contributions to the coherence and find that both types of coupling contribute to the measured dynamics.

1 Introduction

Photosynthetic energy-transfer processes have fascinated researchers for many decades. The well-known Förster resonant energy-transfer process is just one of several theoretical treatments that have been used to understand how electronic energy flows in biological light-harvesting systems. Recent experiments using two-dimensional electronic spectroscopy (2D ES) have challenged existing models. 2D ES experiments measure many of the same dynamics as frequency-resolved pump-probe spectroscopy but have improved resolution of spectral features by accessing information about the excitation process. In particular, cross peaks between distinct excitation and emission frequencies can occur between coupled transitions.

Initial experiments found cross peaks with amplitudes that oscillate as a function of the 'waiting' time, here denoted τ_2 [1–3]. The two main phenomena that give rise to such coherent dynamics in nonlinear optical spectroscopy experiments are electronic coupling and vibrational coupling. Although the two types of coupling have distinct physical origins and vastly different consequences for energy-transfer processes, their signatures in nonlinear spectra [4, 5] are often very similar.

Spectra of pigment-protein complexes in particular can be challenging to understand because two or more organic molecules—each with multiple vibrational levels in ground and excited states—can have electronic states that couple to form exciton states which absorb incident radiation. The initial 2D ES measurements on biological pigment-protein complexes suggested that the oscillatory signals were signatures of electronic coupling among multiple chromophores [1–3]. This assignment was based on evidence from previous measurements and simulations, but direct evidence from the 2D ES experiments was not provided.

Here we use model energy-level schemes as a basis for differentiating between the two types of coherences in a direct manner in 2D ES experiments. We model electronic coherences using a pair of coupled two-level systems, and we model vibrational coherences using a four-level system having two vibrational levels in the ground electronic state and two vibrational levels in the excited

electronic state. Using these energy-level schemes, we have shown that there are three ways of differentiating between the two phenomena in 2D ES studies [6, 7]. The set of double-sided Feynman diagrams representing the third-order nonlinear signal pathways show that signatures of vibrational coherence are: oscillations in the nonrephasing component of the cross peak; two extra weak cross peaks at red-shifted emission energies; and a 180° phase shift to oscillations in the cross peak of the total 2D spectrum (the sum of rephasing and nonrephasing spectra).

2 Results

We quantitatively analyzed 2D ES measurements of the light-harvesting protein phycocyanin 645 (PC645) from *Chroomonas* sp. CCMP270. The 2D spectrum contained a well-resolved cross peak that oscillates in amplitude. Example spectra are shown in Fig. 1(a), where the cross peak coordinates are marked in the 55 fs spectra. Fig. 1(b) shows traces extracted from the rephasing (S_I) and nonrephasing (S_{II}) contributions to the cross-peak coordinates.

PC645 is a pigment-protein complex composed of eight bilin chromophores held in a protein lattice. The absorption spectrum therefore involves eight electronic peaks, which are spectrally broad due to both sample inhomogeneity and rapid dephasing of the optical coherences, and there is significant overlap among the eight transitions.

Previous studies of PC645 suggest that a modestly coupled (J ~ 10 THz) DBV chromophore pair leads to excitonic features with absorption maxima at 510 THz (588 nm) and 529 THz (567 nm) and a minimally coupled MBV chromophore pair leads to excitonic features with absorption maxima at 499 THz (601 nm) and 496 THz (604 nm) [2, 8]. The cross-peak oscillation shown in Fig. 1 (b) is the sum of at least eight frequency components, the two highest amplitude of which are at 21 and 26 THz, as indicated by the arrows in Fig. 1 (c).

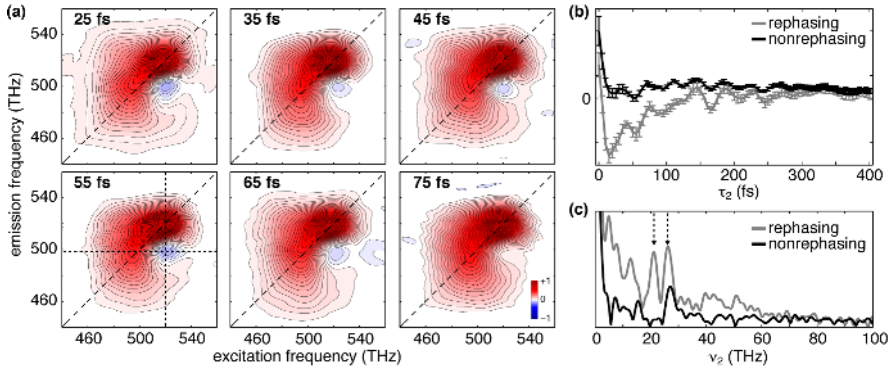

Fig. 1. 2D ES spectra from one measurement of PC645 at a temperature of 298 K. (a) The real part of the total 2D ES at representative τ_2 values; contours are linearly spaced at 3% intervals. The cross-peak location studied below is highlighted in the 55 fs spectrum. (b) Extractions from the separated nonrephasing (black) and rephasing (grey) contributions to the cross peak. The nonrephasing component oscillates; this immediately confirms the presence of vibrational coherence(s) but does not exclude possible contribution(s) from electronic coherences. Error bars are the result of statistics of ten independent measurements. (c) Fourier transforms of the oscillations. The rephasing component has two strong features at 21 and 26 THz, highlighted with dashed vertical arrows, while the nonrephasing component has only one strong feature at 26 THz. This difference, and the difference between the phases of the two oscillation frequencies (not shown), indicates that the 26 THz component is a signature of vibrational coherence while the 21 THz component is a signature of electronic coherence.

The coordinates of the cross peak indicated in the 55 fs spectrum of Fig. 1(a) suggest that the coherent oscillations are a signature of coherence between a DBV exciton and an MBV exciton, but the oscillation frequency of 21 THz indicates coherence between the two DBV excitons. Because

spectral features can overlap and lead to peaks shifted to unexpected locations, it is likely that the oscillation frequency is a more reliable indicator. Moreover, for a homodimer, the energy levels should split by twice the coupling value, which for the two DBVs in PC645 would be a split of 20 THz. This is within the 1.5 THz resolution of the measurement. Therefore, the data and analysis indicate that the electronic coupling between the two DBV chromophores is the source of the coherent oscillations in the signal at 21 THz.

3 Conclusions

Recent measurements using two-dimensional electronic spectroscopy (2D ES) have shown that the initial dynamic response of photosynthetic proteins to femtosecond laser pulse excitation may involve coherent dynamics, which may be quantum in nature [9]. Other studies were instructive reminders that intramolecular vibrational modes and electronic coupling share many spectral signatures in 2D ES measurements. We use predictions based on model energy-level schemes to differentiate between electronic and vibrational coherence in 2D ES. On that basis, we find signatures of both types of coherences in quantitative 2D ES measurements of the light-harvesting complex PC645 at ambient temperature. The electronic coherence has a dephasing time of 150±50 fs. It is clear that light-harvesting systems cannot be described completely by four-level systems; more complex models and additional analysis are needed to provide new insights into the role of vibronic coupling in 2D ES studies and in photosynthetic energy-transfer processes [10–12].

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