

Disentangling Electronic and Vibrational Coherence in the Phycocyanin-645 Light-Harvesting Complex

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Abstract: We selectively excite coherence pathways in the light-harvesting complex PC645 and with wavelength and polarization control identify contributions from both electronic and vibrational coherences. Insight into the interactions between excited electronic and vibrational states follows.

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1. Introduction

Energy transfer between chromophores in photosynthesis proceeds with near unity quantum efficiency. Understanding the precise mechanisms of these processes is made difficult by the complexity of the electronic structure and interactions with different vibrational modes. Two-dimensional spectroscopy has helped resolve some of the ambiguities and identified quantum effects that may be important for highly efficient energy transfer [1,2]. Many questions remain, however, including whether the coherences observed are electronic and/or vibrational in nature and what role they play. We utilise a two-colour four-wave mixing experiment with control of the wavelength and polarization to selectively excite specific coherence pathways and identify the nature of these coherences in the PC645 light-harvesting complex from cryptophyte algae.

Previous work has reported coherences at several different frequencies in the vicinity of the blue band in the absorption spectrum [2,3]. The electronic states in this vicinity are predicted to be the excitonic states, labeled DBV+ and DBV-, resulting from the strongly coupled DBV chromophores. The precise spectral location of these excitonic states, and indeed the other electronic states in the complex, is unclear, which increases the difficulty in attributing coherences to electronic, vibrational or vibronic coherent superpositions. In this work we focus on this blue spectral region to better understand the excited state structure and the nature of coherences observed.

2. Results and Discussion

The two-color four-wave mixing experiment can selectively excite coherence pathways when the wavelengths of first two pulses are different. The subsequent evolution of this coherence is probed by the third pulse arriving a variable time later [4,5]. With the pulses set to 2.179eV and 2.066eV, close to the DBV absorption bands, previous work has reported extended coherence signals lasting beyond 1ps [4]. In the present work we varied the wavelength of the first two pulses in this vicinity and reveal a ladder of discrete states separated by 24meV that are coherently coupled and produce coherence signals that persist for several hundred femtoseconds[5]. We attribute this ladder of states to a vibrational mode with energy 24meV. This is consistent with a vibrational mode identified in previous Raman experiments in similar bili-proteins[6].

An additional coherence with energy difference of 100meV is also consistently present and is the longest and strongest signal we measure. Fig.1a shows this coherence for the case when the excitation energies were 2.179 and 2.091eV. It can also be seen in this figure that there are other signal contributions in this vicinity with different coherence energies and coherence times.

To help separate these different contributions we performed an additional experiment where the polarizations of the excitation pulses and signal were oriented in a configuration (0°, 90°, -45°, 45°). In this configuration signal pathways where the first two pulses and the second two pulses interact with transitions dipoles that are parallel are eliminated [5]. This polarization scheme is thus predicted to eliminate purely vibrational coherences. Fig.1b shows the result of these experiments. The long-lived 100meV coherence is removed, but there remain clear signal contributions at ~86meV and ~108meV. It is evident then that these coherences involve states with non-parallel

transition dipoles, while the 100meV coherence involves states with parallel transition dipoles and is likely due to an additional vibrational mode. Indeed, previous work [6] on similar complexes has shown a vibrational mode at around this energy. The coherence at 86meV is attributed to electronic coherence between the two DBV excitonic states, while the 108meV coherence is expected to involve these same electronic states, but an additional excitation of the 24meV vibrational mode identified earlier[5].

Based on these two electronic states and two vibrational modes we are able to determine an energy level scheme that explains all of our results in this spectral range, as well as the results observed by other groups exploring coherences in PC654. Furthermore, the 86meV coherence also closely matches a coherence seen by Turner et al. [3] in PC645 that they suggested may be electronic based on comparisons of rephrasing and non-rephrasing data.

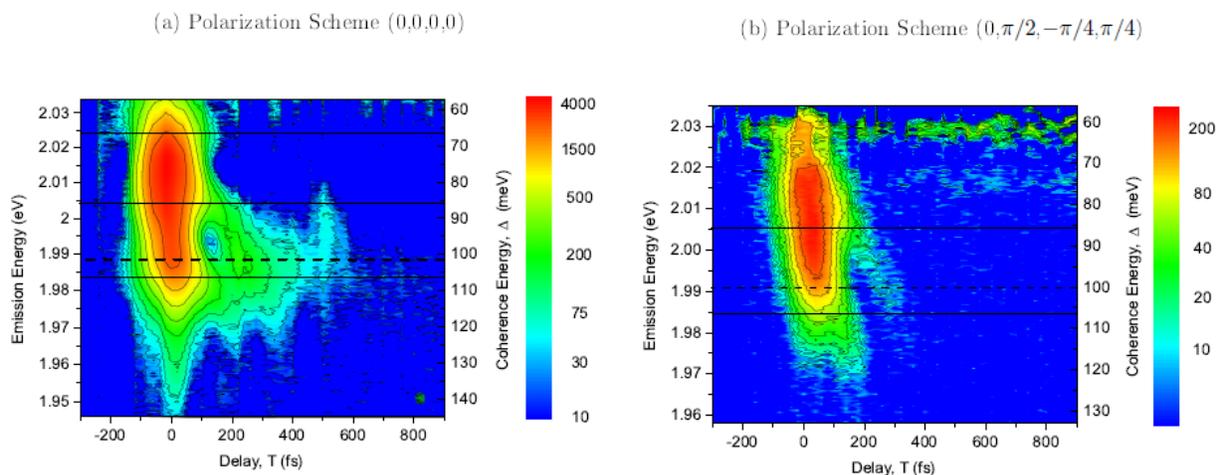


Fig. 1. The measured signals for pulse energies $(E1, E1, E2, E3) = (2.179 \text{ eV}, 2.091 \text{ eV}, 2.091 \text{ eV})$ with (a) all pulses polarized parallel $(0,0,0,0)$ and (b) the cross-polarized scheme, $(0; 90; -45; 45)$, as described in the text. In (a) extended signals at coherence energies 66 meV, 86 meV and 106 meV (black solid lines) are seen in addition to the long-lived signal at 100 meV (dashed line). In (b) the long-lived signal is eliminated but extended coherences at 86 meV and 106 meV remain present, indicating coherence between non-parallel transition dipoles.

One additional factor that is raised by these experiments is the extent to which electronic and vibrational degrees of freedom can be separated. It would appear from these results and previous works that they are strongly coupled and so it may be more appropriate to think of these states as vibronic rather than electronic states. In which case, the question of whether the coherences observed are electronic or vibrational in nature becomes misleading and unhelpful. Rather, perhaps the question we should be asking, and which we begin to explore with these results, is how the interactions between the electronic and vibrational degrees of freedom modify the excited state landscape and potentially enhance energy transfer in light harvesting complexes.

3. Conclusions

The ability to selectively excite coherence pathways has allowed us to separate and identify both electronic and vibrational coherences and observe their evolution. In the present work this has allowed us to determine a self-consistent energy level-scheme that describes all reported observations of coherences in PC645. This is based on two electronic states separated by 84 meV, which we attribute to the DBV+ and DBV- states, and two vibrational modes with energy 23 meV and 100 meV. With the approach used we are able to reveal more spectral details than broadband experiments and have greatly enhanced the understanding of the excited state structure. Further questions remain, however, regarding the role of the strong electronic-vibrational coupling observed, the coherent evolution of these coupled states, and their significance for energy transfer.

4. References

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