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Mapping Ultrafast Energy Transfer Across Electronic and Nuclear Degrees of Freedom

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Abstract: This work reinvestigates the subpicosecond energy transfer (ET) dynamics of light-harvesting complex II with two-dimensional electronic-vibrational spectroscopy (2DEV). With the help of a straightforward theoretical model, emphasis is also more generally placed on the manifestation of ET in 2DEV. © 2020 The Author(s)

1. Introduction

Light-harvesting complex II (LHCII) is the most important light-harvesting complex on the planet. The complex, found natively as a trimer, binds the majority of chlorophyll (Chl) *a* and Chl *b* pigments found in green plants. These Chls serve as the primary light-harvesting pigments that absorb sunlight and ultimately transfer it as electronic excitation energy to the photosynthetic reaction center, Photosystem II [1]. While our understanding of how these Chl pigments transfer excitation energy has improved since the earliest ultrafast experiments on LHCII [2], largely as a result of the application of multidimensional spectroscopy [3,4], these new experiments have also created more questions. In trying to understand the interplay between the energetic and spatial landscapes of LHCII, the observation of quantum beats in the two-dimensional electronic spectroscopic studies of this pigment-protein complex has led to an extensive debate on the origin of these observed features—are they electronic, vibronic, or vibrational in nature? Beyond this question lies an even more difficult one—how does the spectroscopic observation of these beats connect to their mechanistic function in photosynthetic light-harvesting?

Here, we reinvestigate the subpicosecond energy transfer (ET) dynamics of LHCII trimers at 77 K with two-dimensional electronic-vibrational spectroscopy (2DEV) [5] and discuss how this technique has the potential to significantly improve our understanding of the ET mechanism of photosynthetic light-harvesting.

2. Results and Discussion

In order to better interpret how ET manifests in 2DEV spectra (particularly of LHCII), we rely on a straightforward heterodimer model consisting of two electronically coupled monomers, each with one electronic and one vibrational degree of freedom (DoF). As in the LHCII experiments, the vibrational mode in the model is taken to be highly local. This is particularly advantageous because when the probed modes are highly local and not anharmonically coupled to lower frequency modes (e.g. the carbonyl and chlorin C=C stretching modes of Chl [6]), any observed oscillatory features (in both the peak amplitude and CLS) will be free of purely vibrational character. Therefore, if oscillatory features are observed, they can only be electronic or vibronic in origin. The model (Figure 1), although an approximation in comparison to LHCII, elucidates many of the distinct signatures of ET observed in the experimental spectra of LHCII (Figure 2). Among the most notable of these features is the emergence of distinct excited state absorption (ESA) quartets (Figure 1b-c versus Figure 2a-b). The model also illuminates three other key dynamical manifestations of energy transfer: 1) oscillatory ESA peak amplitudes (at frequencies matching excitonic energy gaps), 2) spectral evolution that results in an increasing degree of “mirror symmetry” between bands along the excitation axis (due to population relaxation), and 3) CLS (proportional to the vibrational frequency-electronic frequency correlation function) that oscillate at the frequency of energy gaps between excitonic states (Figure 1e and g versus Figure 2d and f) and which exhibit highly complementary behavior. The manifestation of population transfer in 2DEV is counterintuitive in that energetically higher-lying bands appear to grow in over time. For example, in the model (Figure 1b-c), the B excitonic band mirrors the A excitonic band as the spectra evolves. This is because as population is transferred from $|B\rangle$ to $|A\rangle$ during the waiting time, modes that form the manifold of A

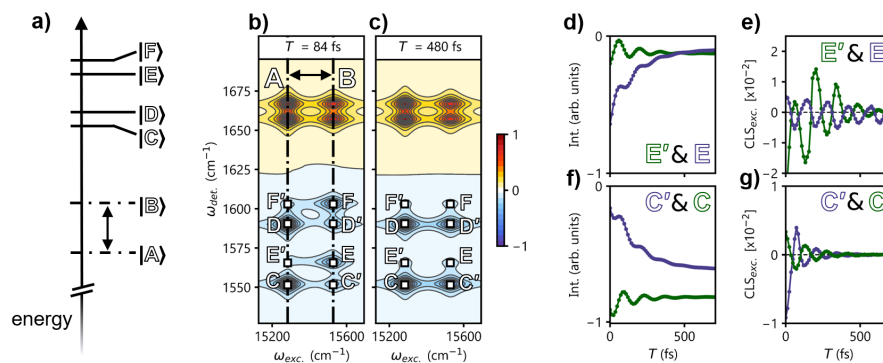


Figure 1. a) Excited state manifold of the heterodimer model (ground state manifold omitted for clarity). b)-c) Model 2DEV spectra at waiting times of 84 fs and 480 fs. Red features indicate ground state bleaches and the blue features indicate excited state absorptions (ESAs). The two prominent ESA quartets are labeled as F', F, D, and D' and as E', E, C, and C'. The two excitonic bands along the excitation axis have also been labeled as A and B. d) and f) Oscillatory peak intensity dynamics for selected ESAs. e) and g) Oscillatory center line slope dynamics belonging to selected ESAs.

states will appear along the detection axis. For the same reason, the two highest-lying bands along the excitation axis present in the 2DEV spectra of LHCII (Figure 2a-b), which grow in during the waiting time and closely mirror the two lowest-lying bands, indicate that population is rapidly transferred from the higher-lying vibronic states of mixed Chl character to the lower-lying Chl *a* and *b* states. Lastly, out of all of these features, it should be noted that the CLS is a particularly promising new measure of ET, as it can be an electronic/vibronic coherence-specific measurement because it is free of population dynamics that complicate peak amplitudes.

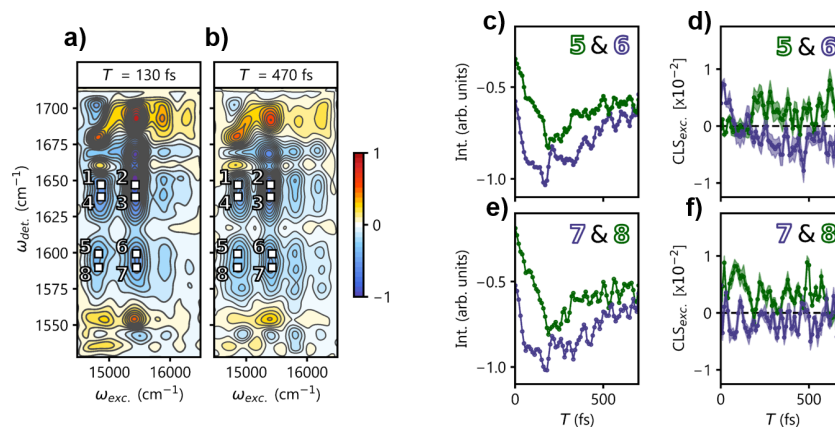


Figure 2. a)-b) 2DEV spectra of LHCII at 77 K at waiting times of 130 fs and 470 fs, respectively. Red features indicate ground state bleaches and the blue features indicate excited state absorptions (ESAs). The two prominent ESA quartets are labeled 1-4 and 5-8. The visible excitation spectrum was centered at ~ 15565 cm^{-1} and spanned $14350\text{--}16775$ cm^{-1} , covering the Q_y bands. The IR detection spectrum was centered at ~ 1620 cm^{-1} , probing the carbonyl and chlorin C=C stretching modes. More detail on the 2DEV experiment can be found in Ref. [7]. c) and e) Oscillatory peak amplitudes belonging to the lower-lying quartet ESAs. d) and f) Oscillatory center line slope dynamics of the lower-lying quartet ESAs. The shaded light green and purple regions indicate the standard error of the fit used to calculate the slope of the feature.

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