

# Coherent Control of Chirality-Induced 2D Electronic Spectroscopy Signals

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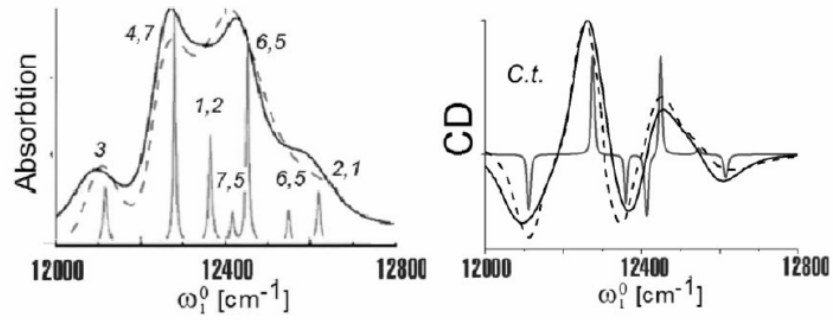
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**Abstract.** Chirality-induced 2D electronic spectra, calculated to first order in the optical wavevector, reveal new features, not available from non-chiral signals. Coherent control is used to optimize the resolution of various energy transfer pathways in the Fenna-Matthews-Olson complex from photosynthetic green sulfur bacteria.

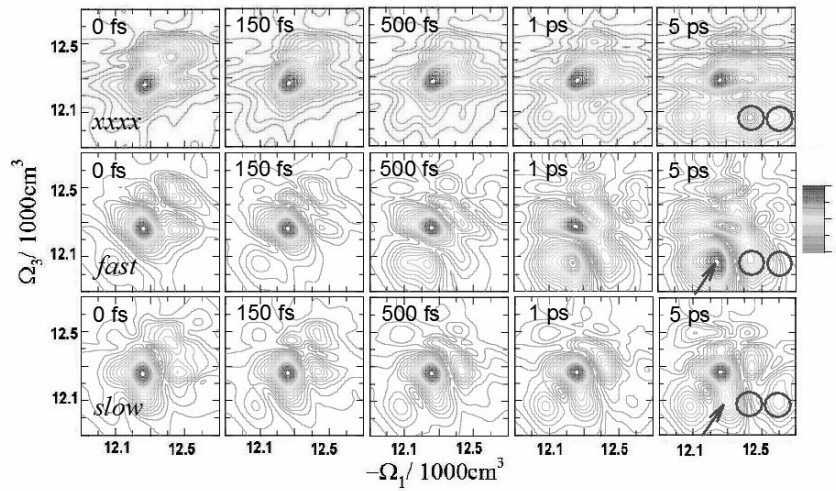
Ultrafast 2D electronic spectroscopy recently performed on several photosynthetic systems provides valuable insights into the mechanisms of light harvesting [1-4]. Energy transfer pathways can be directly observed through the temporal evolution of the cross peaks [1, 5], and oscillations of these provide information on electronic quantum coherences [2]. The spectra of photosynthetic molecular aggregates consist of bands of closely-lying excited states. Spectral congestion due to the large number of states and the solvent and protein environments complicates the analysis. Weak cross-peaks overlap with strong diagonal peaks preventing the unambiguous assignment of exciton features. 2D four-wave mixing (FWM) spectroscopy provides rich information through snapshots of vibrational and electronic dynamics. These can be considerably simplified by using coherent control techniques which manipulate the interference of various Liouville space pathways [6].

We have recently demonstrated the simplification of 2D spectra at zero population delay time ( $t_2$ ) in a chiral porphyrin dimer by designing linear combinations of two-dimensional electronic chirality-induced (2D ECI) tensor components, which lead to the control of spectral features through interferences [7]. Linear combinations of 9 2D ECI tensor components were optimized using genetic algorithm. The ratios of the amplitudes of weak cross peaks were chosen as control targets. Here we apply this method to simulate  $t_2$ -dependent 2D electronic spectra of the light-harvesting Fenna-Matthews-Olson (FMO) complex from the photosynthetic green sulphur bacteria *Chlorobium tepidum*. We use the Hamiltonian obtained by fitting the linear and 2D xxxx spectra by Brixner et. al [1] and an overdamped Brownian oscillator bath spectral density. The 7 one-exciton states contributing to the linear absorption and circular dichroism spectra are shown in Figure 1. At 77 K the linear absorption spectra form 2 overlapping peaks and 2 shoulders. The peaks are labelled 1 to 7 increasing in energy. The largest contributions of the 7 constituent bacteriochlorophyll (BChl) molecules (numbered 1 to 7 according to Fenna et. al. [8]) to the exciton states are indicated on each peak (in decreasing order of strength). The simulated linear absorption and CD fit the experiments well. CD provides a better resolution of the exciton states. We extend the CD technique to the nonlinear regime, and apply coherent control algorithms to simplify the chiral 2D spectra.



**Fig. 1.** Linear absorption and circular dichroism (CD) spectra of the FMO complexes from the *Chlorobium tepidum* green sulfur bacteria: experimental (dashed) and simulated (solid) spectra. An overdamped Brownian oscillator model at 77 K ( $\Lambda^{-1} = 100$  fs,  $\lambda = 55$  cm $^{-1}$ ) was used for the line broadening. Stick spectra are shown in red. BCHs with the largest contributions to the corresponding exciton states are indicated on each peak (in decreasing order of the contribution)

The couplings between the various BCHs of the complex, observed as cross-peaks in the 2D spectra, determine the energy flow timescales and the efficiency of photosynthesis. Two main energy transfer pathways are revealed in time-resolved electronic 2D spectra of FMO, which are spatially separated and occur on different time scales. Analysis of exciton delocalization patterns in 2D ECI spectra allows to visualize the energy transfer through space, and reveals the slower energy transfer pathway which was not well resolved in the non-chiral 2D xxxx spectra shown in Figure 2.



**Fig. 2.** Coherent control of energy transfer in FMO. Absolute magnitude of 2D signals: non-chiral xxxx and optimized 2D ECI (fast) and (slow) pathways

The xxxx spectra are dominated by strong diagonal peaks, and clearly indicate only the fast energy transfer pathways (left circle). Using coherent control with a genetic learning algorithm, we have separated different energy transfer channels by optimizing a linear superposition of tensor components. The control target aims at manipulating various peaks in these 2D spectra. We chose it to be the ratios of cross peak absolute values of the 2D signals at delay time  $t_2 = 5$  ps.

The two cross peaks contributing to the fast and slow energy transfer pathways (1,5) and (1,7) are marked in Figure 2. by the left and right circles, respectively. These cross peaks are due to energy transfer from higher to lower energy states and they grow as a function of  $t_2$ . The coefficients obtained from the optimizations at  $t_2 = 5$  ps were then used to obtain the 2D spectra at other  $t_2$ -delay times. In the optimization of the fast energy transfer pathway, the ratio of (1,5) to (1,7) is maximized. The left circle and arrow indicate cross peaks (1,5) and (1,2), respectively. The states 1, 2, and 5 are involved in the fast pathway and the corresponding cross peaks are enhanced. For the slow pathway the ratio of (1,7) to (1,5) is maximized. The right circle and arrow indicate cross peaks (1,7) and (1,3), respectively. These participate in the slow energy transfer pathway. As a result both pathways are separately optimized and well-resolved. In addition, there is a new spectral feature in the fast pathway: a node between the arrow and the left circle, corresponding to the elimination of the (1,3) cross peak of the slow pathway. Similarly, in the optimization of the slow pathway we see nodes corresponding to the elimination of the (1,2) and (1,5) cross peaks of the fast pathway.

Using a coherent control algorithm we demonstrated optimal laser polarization configurations which enhance chirality-sensitive spectral features, revealing a slow energy transfer pathway which was not resolved in the xxxx spectra.

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