Dissecting Exciton Dynamics Pathways in Electronic Multidimensional Spectroscopy by Pulse Polarizations

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Abstract. A simulation study shows how coherent exciton dynamics in photosynthetic complexes may be revealed in two-dimensional photon-echo signals by specific laser pulse polarization configurations. Dynamics of single-exciton density matrix cohenrences shows strong signatures of excitonic coherences prior to energy relaxation.

Introduction

Multidimensional correlation spectroscopies are valuable probes of dynamical processes in molecules, which provide detailed dynamical information on complex structures: proteins, excitons, and semiconductors [1]. These techniques are performed by applying four well-separated chronologically-ordered ultrashort laser pulses as shown in Fig. 1.

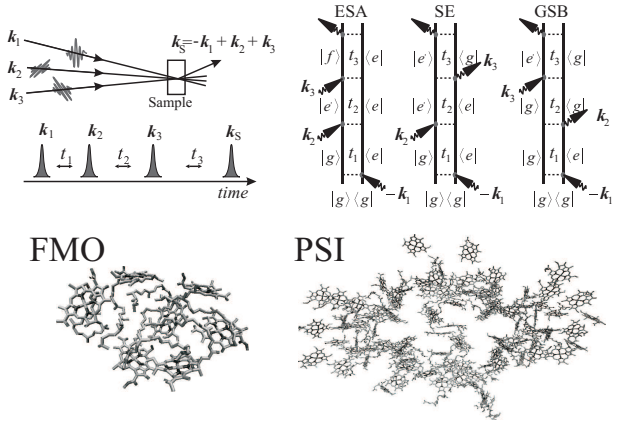

Fig. 1. Top row: Scheme of the coherent third order photon echo technique (left) and the Feynman diagrams of the contributing Liouville space pathways (right). Bottom row: Configurations of BChls in photosynthetic complexes FMO (left) and PSI (right); scales are different.

We consider the photon-echo signal generated in the phase-matching direction $-\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3$, where the delay times between pulses, t_1 , t_2 and t_3 serve as control parameters. A double Fourier transform with respect to $t_1 \rightarrow \Omega_1$ and $t_3 \rightarrow \Omega_3$ at fixed delay t_2 is used to display the two-dimensional coherent spectra (2D CS). Diagonal ($-\Omega_1 = \Omega_3$) peaks carry similar information as linear absorption: peak positions correspond to excitation

energies. However, unlike linear techniques, the homogeneous and inhomogeneous broadenings in 2DCS show up in anti-diagonal and diagonal directions, respectively, and can be separated. Crosspeaks ($-\Omega_1 \neq \Omega_3$) carry novel information about couplings and correlations of different states [2]. We show how symmetry properties of these signals with respect to pulse polarization configurations (PPC) may be used to probe the system's density matrix coherences [3].

Signatures of density matrix coherences

In broad-band impulsive optical techniques, when the pulses are resonant with interband transitions, the signal is proportional to the third order response function $S^{(3)}$ at the photon echo phase-matching direction [5]. The response function is given by a sum over three Liouville space pathways (LSP): excited state emission (ESE), ground state bleaching (GSB) and excited state absorption (ESA) (Fig. 1). We classify the LSPs as follows [4]: coherence (population) pathways, when *bra* and *ket* are different (same) during t_2.

The following set of transitions is characteristic to the population pathways: the population is created from the ground state by two transitions to the same initial state i, it relaxes to a final f state during t_2, and f is deexcited to any other state. The population LSP contains the product $\langle \boldsymbol{\mu}_f^{\nu_4} \boldsymbol{\mu}_f^{\nu_3} \boldsymbol{\mu}_i^{\nu_2} \boldsymbol{\mu}_i^{\nu_1} \rangle$; here $\boldsymbol{\mu}_i$ ($\boldsymbol{\mu}_f$) is the excitation (deexcitation) transition dipole. Angular brackets denote orientational averaging and $\nu_4\nu_3\nu_2\nu_1$ ($\nu = x,y,z$) denote the laser pulse PPC. For three basic tensor components of the response function we have [3]:

$$\langle \boldsymbol{\mu}_f^x \boldsymbol{\mu}_f^x \boldsymbol{\mu}_i^y \boldsymbol{\mu}_i^y \rangle = 15^{-1}(2\boldsymbol{\mu}_f^2 \boldsymbol{\mu}_i^2 - (\boldsymbol{\mu}_f \cdot \boldsymbol{\mu}_i)^2), \tag{1}$$

$$\langle \boldsymbol{\mu}_f^x \boldsymbol{\mu}_f^y \boldsymbol{\mu}_i^x \boldsymbol{\mu}_i^y \rangle = \langle \boldsymbol{\mu}_f^x \boldsymbol{\mu}_f^y \boldsymbol{\mu}_i^y \boldsymbol{\mu}_i^x \rangle = 30^{-1}(-\boldsymbol{\mu}_f^2 \boldsymbol{\mu}_i^2 + 3(\boldsymbol{\mu}_f \cdot \boldsymbol{\mu}_i)^2). \tag{2}$$

We found that the following combination $B \equiv S^{(3)}_{xyxy} - S^{(3)}_{xyyx}$ cancels for all population LSPs [3]. For localized excitons we would have $\boldsymbol{\mu}_i \equiv \boldsymbol{\mu}_f$ and therefore B also vanishes. The B signal therefore solely shows the coherence LSPs of delocalized excitons.

Results and Discussion

We study coherent exciton dynamics in two photosynthetic complexes: the Fenna-Matthews-Olson (FMO) complex of a green sulfur bacteria and the Photosystem I (PSI) photosynthetic complex of a cyanobacteria *Thermosynechococcus elongatus* [4]. Simulations were performed using the Frenkel exciton model of coupled two-level molecules as described in previous publications [3,6]. The FMO complex is one of the most extensively studied photosynthetic pigment-protein complexes. It is a trimer of small noninteracting identical subunits, each consisting of seven bacteriochlorophyll (BChls) molecules (see Fig. 1). The broad absorption spectrum extends from 12000 cm^{-1} to 13000 cm^{-1} (see Fig. 2). The B signal at different t_2 delay times is shown in Fig. 2 (top row). We see well-resolved offdiagonal peaks, which oscillate with t_2. Peak positions can be correlated with the excitons and their wavefunctions. Only highly delocalized excitons contribute to the signal, while the lowest-energy peak (localized exciton) is not observed.

The PSI complex is a larger energy-conversion apparatus appearing in trimeric and monomeric forms. The absorption band of the PSI monomer with 96 chlorophylls

extends between 13500 – 15500 cm^{-1}. The B signal of PSI [Fig. 2 (bottom row)] at $t_2 = 0$ contains unresolved features at the bulk antenna region. A distinct pattern of exciton density matrix appears at later delay times. The two well-resolved crosspeaks at 100 fs can be related to the reaction center, which contains very strong couplings between molecules and its excitons are delocalized.

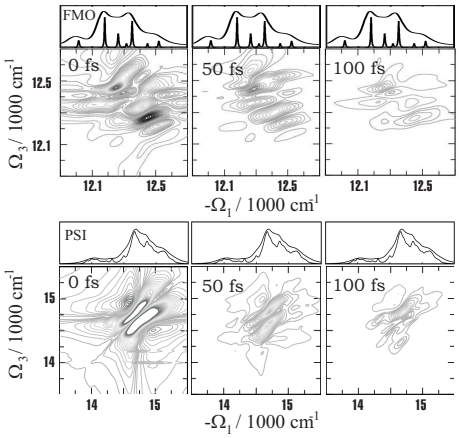

Fig. 2. Absorption and two dimensional photon echo technique $B \equiv S^{(3)}_{xyxy} - S^{(3)}_{xyyx}$ for two photosynthetic complexes: FMO and PSI at various t_2 delay times.

In summary, the single-exciton density matrix can be directly probed by two dimensional signals through crosspeaks in 2D CS using PPCs. The oscillatory pattern of the signal with the delay time t_2 follows propagation of density matrix coherences. It implies exciton delocalization since localized excitons are filtered out by the B signal.

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