3D12

位相変調２次元蛍光分光を用いた光合成光捕集系のエネルギー移動の研究

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Exploring Energy Transfer in Light Harvesting Systems by using Phase-Modulation Two-Dimensional Fluorescence Spectroscopy

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Introduction

Light harvesting system of purple bacteria (LH2) has been studied by a wide variety of experimental and theoretical works because of the importance of the system as a model for exploring energy transfer process. LH2 from *Rps. acidophila* has a ring structure of 9 pairs of α helixes, each pair binds 3 bacteriochlorophyll (Bchl) *a*. The Bchls form 2 rings of 9 and 18 molecules known as B800 and B850 according to their respective absorption bands (Fig. 1 and 2). It is well known that energy transfer between B800 and B850 occurs on a timescale of 1 ps at room temperature [1]. The transfer can be described by either Förster or Redfield theories, or their modifications. The physics of the dynamics in various models is very different. In Förster theory the coupling to the bath is included exactly by using experimentally observed absorption and fluorescence spectra, whereas electronic coupling enters perturbatively via Fermi Golden rule (FGR) expression. On the other hand, in Redfield theory the electronic coupling between molecule is diagonalized out exactly whereas the coupling to the bath is acting as a perturbation entering a FGL-like expression [2]. Various "hybrid" representations between these two theories exist and have provided basic understanding of the process. However, the possible role of coherence to the transfer step is still an open question. Electronic two-dimensional (2D) spectroscopy is a promising way to shed further light to this issue [3]. 2D spectroscopy gives the information of the correlation between excitation and emission frequencies in 2D map. From the 2D spectra, we can get the insight of dynamics between resonant states, e.g. the coupling strength, the timescale of energy transfer between states and the time constant of dephasing. In this contribution, we use a new type of 2D spectroscopy, namely phase-modulation 2D fluorescence spectroscopy (PM-2DFS) [4].

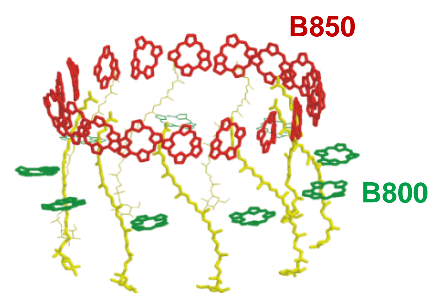

Figure 1. The molecular structure of LH2. 9 and 18 Bchl molecules form 2 rings of B800 (green) and B850 (red), respectively. Yellow strings are carotenoid molecules. α helixes are not shown here.

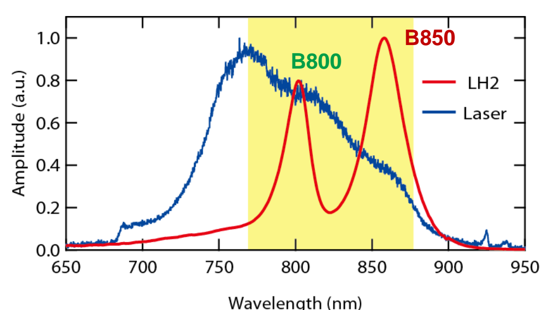

Figure 2. The absorption spectrum of LH2 (red) and the spectrum of laser which we used (blue). The frequency range of 2D spectra that we show is colored by yellow.

Experimental Setup

A sequence of 4 laser pulses interacts with the electronic states of LH2. The pulses have broad spectra which cover both B800 and B850 (Fig. 2). Unlike usual 2D electronic spectroscopy that detects a coherently generated optical signal [3], we detect an incoherent fluorescence signal [4]. All possible combinations of interactions of the pulses with LH2 can lead to fluorescence. By using phase modulation of the pulses introduced by acousto-optic modulators (AOMs) and by mixing the reference signal, we can separate the part of the fluorescence which corresponds to desired Liouville pathways (Fig. 3). By changing time intervals between 1st and 2nd laser pulses (t_1, coherence time) as well as 3rd and 4th (t_3, detection time), and taking Fourier transform over them, we obtain 2D fluorescence spectra. A time interval between 2nd and 3rd laser pulses (t_2, population time) is fixed for each measurement of 2D spectrum.

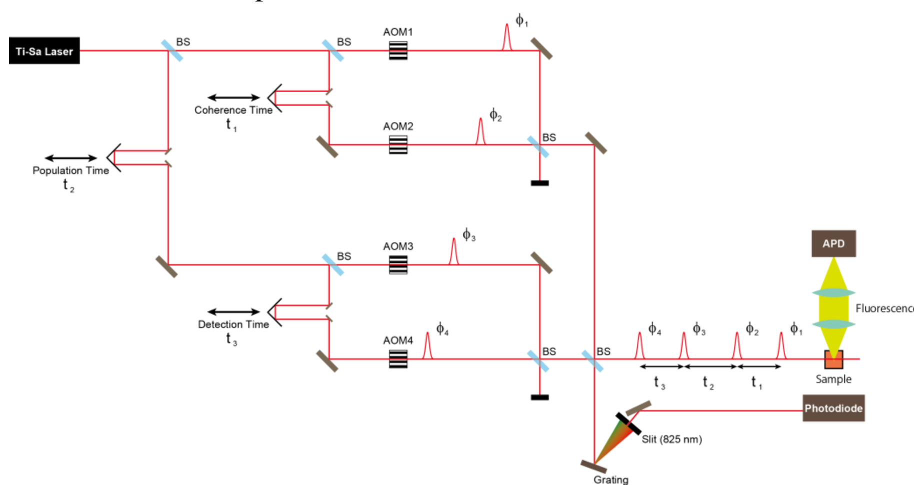

Figure 3. The experimental setup of PM-2DFS. We introduce phase modulation to each laser pulse using AOM. The intensity of fluorescence changes in time with the frequency of phase modulation.

Result

The 2D spectra are shown in Fig. 4. We can see cross-peaks even when t_2 = 0 fs. This suggest that there is mixing of wave functions between B800 and B850. While we can see the elongation of the peak of B800 along the diagonal direction when t_2 = 0fs, the peak of B800 when t_2 = 60 fs is circular. This shows the dephasing of electronic excited state of B800 may be faster than this time scale.

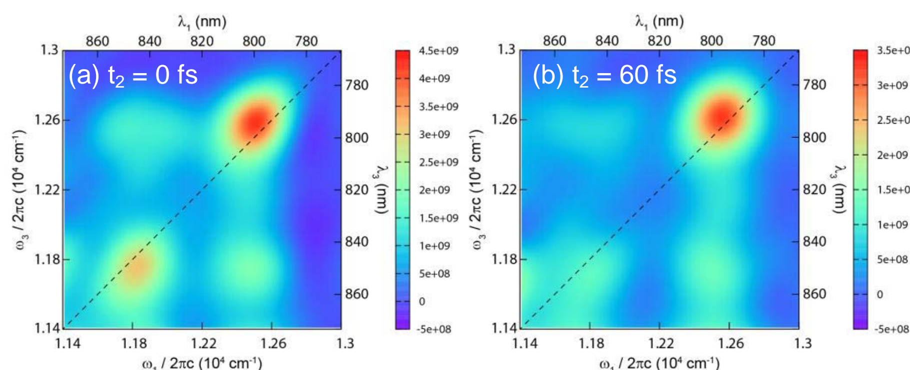

Figure 4. The 2D spectra of LH2.
(a) t_2 = 0 fs
(b) t_2 = 60 fs

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