Fluorescence Detected 2D Spectroscopy of LH2

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Fluorescence detected coherent 2D spectroscopy on peripheral light harvesting complex of photosynthetic purple bacteria LH2 reveals clean cross peaks between two major absorption bands B800 and B850. The results together with quantum dynamics simulations allow new insight to the excitation dynamics in this system.

Fluorescence and photocurrent detected 2D spectroscopies [1] are relatively recent additions to the coherent multidimensional spectroscopy family of methods. Particularly the photocurrent detection allows selectivity which enables to relate the 2D spectral evolution directly to the "action" in the material of the device which is studied – photo-generated current in a solar cell or a photo-cell. The methods provide an additional excited state absorption (ESA) pathway compared to the conventional photon echo 2D signal. The 2 ESA components have opposite signs, one of them leads to singly excited, other to the doubly excited population. In molecular aggregates like light harvesting complexes the doubly excited state rapidly relaxes to a singly excited state through exciton-exciton annihilation [2]. As a consequence the two ESA pathways give very similar signal amplitudes and because of the opposite signs, they take out each other.

Here we use fluorescence detected 2D spectroscopy to study excitons and their dynamics in LH2. Since the ESA signal is negligible, the cross peaks of the 2D spectra are very clear showing partial inter-band delocalization of the excited state (Fig.1). Quantum dynamics simulations based on hierarchy equation of motion [3] and multiconfiguration time-dependent Hartree method [4] allow to draw detailed conclusions about non-Markovian dynamics in the system.

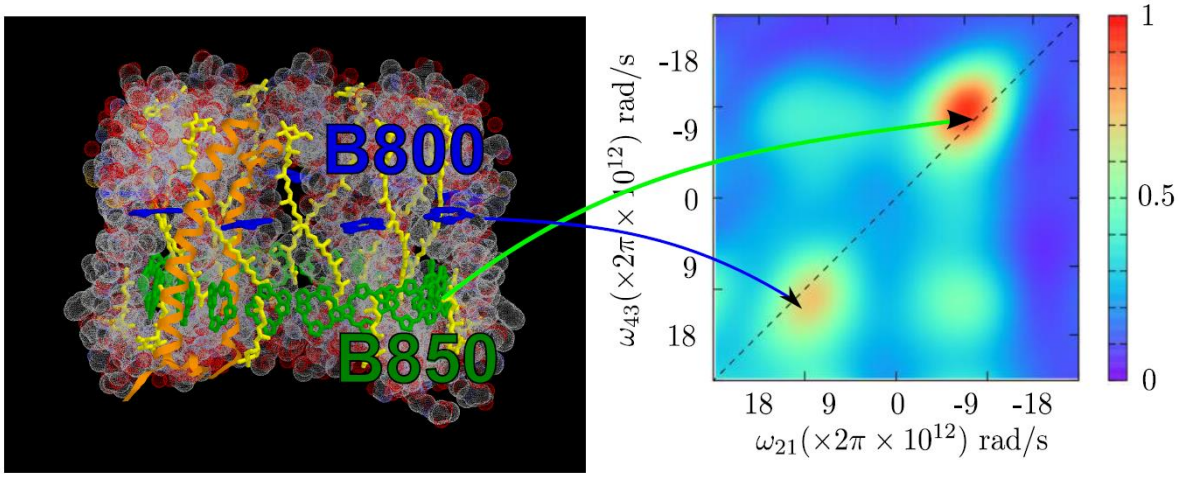

Fig.1 Left: structure of LH2. Right: Fluorescence detected 2D spectrum of LH2 at population time T = 0.

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