Measuring the Time-Dependent Exciton Delocalization Size in the B850 Band of Purple Bacterial LH2

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Abstract: Several ultrafast coherence spectroscopies are employed to study initially delocalized excitons and their subsequent sub-100 fs localization dynamics in LH2. Rigorous simulations of the exciton relaxation process allow determination of the time-dependent exciton size.
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The characterization of exciton dynamics in light harvesting (LH) complexes is of great interest [1]. Two factors have motivated the enormous attention that biological and physical scientists have paid to this system in recent years. First, because LH complexes trap photons that are used to drive the endothermic chemical reactions of photosynthesis, they play a key role in a process that is essential to most life on earth. Second, the highly symmetric arrangement [2] and strong intermolecular couplings [3] of the bacteriochlorophyll (BChl) chromophores in LH rings provide a unique opportunity to study the effects of delocalization on the dynamics of Frenkel (i.e., molecular) excitons. While interchromophore interactions are of comparable magnitude in J-aggregates, their structures are not well-defined [4]. Molecular crystals have high symmetry, but the weak coupling between adjacent lattice sites means that cryogenic temperatures are required to observe exciton delocalization [5]. For these reasons, it might be expected that light harvesting complexes exhibit novel photophysics.

Considerable debate exists on the extent to which the B850 exciton of the LH complex II (LH2) is delocalized over the aggregates's 18 BChl chromophores. Delocalization is of primary importance in optical spectroscopy because the transition dipole moment of a molecular aggregate in enhanced over that of the constituent monomer by a factor equal to the square root of the exciton delocalization size [6]. Two-photon absorption [7] and circular dichroism [8] studies have suggested that the exciton is delocalized over the majority the B850 ring, while measurements of the rate of superradiant emission indicated a coherence length of 3-4 BChl's [9]. The delocalization size can be rigorously defined as the inverse participation ratio, $P(t)$, of the one-exciton density matrix [10]:

$$P(t) = \frac{\left[\sum_{mn} \left|N_{mn}(t)\right|\right]^2}{L\sum_{mn} \left|N_{mn}(t)\right|^2} \tag{1}$$

where the N_{mn}'s are elements of the one exciton density matrix in the site (real-space) representation and L is the total number of chromophores in the aggregate. It should be noted from this definition that the delocalization size depends on the magnitudes of the off-diagonal elements of the density matrix; the more correlated the dynamics are among different monomers in the ring, the larger the delocalization size will be. Since the density matrix elements are time-dependent, *the delocalization size is time-dependent*. In any measurement of the delocalization size, the timescale of the experiment must be taken into account for a proper interpretation of the result.

We have measured transient grating, pump-probe anisotropy and photon echo signals from LH2 with 18 fs pulses from a Ti:sapphire laser. Fig. 1 shows the transient grating signal from B850, and for comparison, the corresponding signal for monomeric BChl dissolved in tetrahydrofuran (THF). For BChl in solution, the signal consists of an initial ultrafast component followed by a slow decay modulated by high-frequency oscillations. The initial ultrafast response can be attributed to the nearly instantaneous dephasing of a quasi-continuum of medium to high frequency vibrational modes [11]. The slower decay reflects solvation dynamics while the underdamped oscillations correspond to coherently excited high frequency vibrations. The B850 signal is quite different; it is

dominated by a decay that causes the signal to decrease to about 40% of its maximum value in about 175 fs. The time constant of this component is 53 fs, significantly longer than the 22 fs instrument response function. Because this decay is not pulsewidth limited, it cannot be attributed to a coherent-coupling artifact. We have determined, on the basis of frequency-resolved stimulated photon echo measurements of BChl/THF and B850, that the aggregate has significantly smaller exciton-vibrational coupling compared to the monomer. This is analogous to the observation that the emission spectra of molecular crystals with large exciton bandwidths exhibit weak phonon sidebands [12]. Therefore, the transient grating decay cannot be explained by fast vibrational dephasing. This feature also cannot be due to population relaxation to the ground state or a fast Stokes shift, as the fluorescence lifetime of B850 is almost a nanosecond and the Stokes shift is less than 150 cm^{-1} [9] (well within the laser spectral width) .

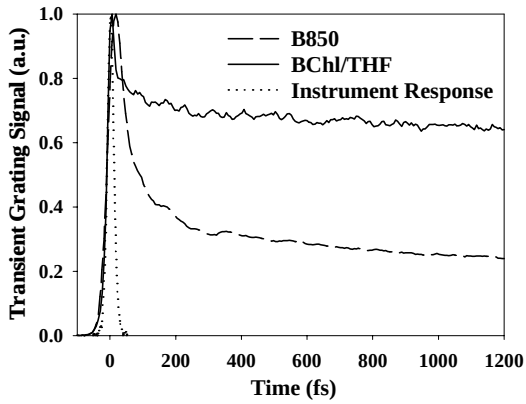

Figure 1. Transient grating signals from the B850 band of LH2 and bacteriochlorophyll dissolved in THF.

The most likely explanation for this 53 fs decay is dephasing-induced contraction of the B850 transition dipole moment. At the instant when B850 absorbs a photon, the magnitudes of the off-diagonal elements of the one-exciton density matrix will be at their peak values, meaning that at this time the delocalization size and the transition dipole strength of the exciton will achieve their highest values. As the delay time in the transient grating experiment is increased beyond zero, homogeneous and inhomogeneous dephasing processes manifest themselves and the density matrix becomes less and less coherent. Thus as the dynamics of the chromophores in the B850 ring become less correlated with each other, the delocalization size and transition dipole moment of the exciton decrease. Because the transient grating signal scales as the square of the transition dipole of the system at the time of interaction with the probe pulse, we interpret the decay of the B850 signal in Fig. 1 as a direct observation of exciton localization.

These experimental data provide essential constraints for the theoretical simulation of exciton dynamics in B850. Proper modeling of ultrafast four-wave mixing in molecular aggregates requires considerably more effort than do calculation of these signals for isolated two-level systems. All optically accessible one- and two-exciton levels must be accounted for, in addition to exciton-phonon coupling and inhomogeneous broadening. Mukamel and co-workers have developed a theory that rigorously includes all of these elements [13,14]. The exciton-phonon interaction is modeled with arbitrary spectral densities between all pairs of electronic levels in the aggregate. We are performing calculations within this formalism in order to develop a realistic model of time-dependent exciton dynamics in B850. As a starting point, we simplify the choice of spectral densities by assuming that the nuclear fluctuations acting on different chromophores are identical and uncorrelated. Furthermore, we assume that the spectral density for these fluctuations corresponds to that of an overdamped Brownian oscillator:

$$C(\omega) = 2\lambda \frac{\omega\tau_1}{\omega^2\tau_1^2 + 1} \tag{2}$$

Inhomogeneous broadening is taken into account by averaging over a large number of realizations of static disorder, each realization being formed by choosing the transition energies of the uncoupled chromophores from a Gaussian distribution of a particular width. Assigning the spectral density parameters λ and τ to be 240 cm^{-1} and 130 fs, respectively, and assuming an inhomogeneous width of 530 cm^{-1}, a good fit is made to the linear absorption

spectrum. Fig. 2 shows experimental and calculated frequency-resolved pump-probe signals for B850 at delay times of zero and 1 ps. The calculated shapes of the induced-transmission (i.e., positive-going) portions of the signals are in excellent agreement with the experimental data, and the relative signal levels at the two delays are reproduced fairly well. The disparity between experiment and theory in the excited-state absorption region (i.e., negative signal) is due to the omission of a third electronic level in the BChl monomer. Note that exciton localization is the only mechanism in the calculations that can cause a decline in absolute signal level. These simulations demonstrate that this process provides a plausible explanation for the experimental data. Further refinement of these calculations should enable the determination of the delocalization size as a function of time elapsed since creation of the exciton.

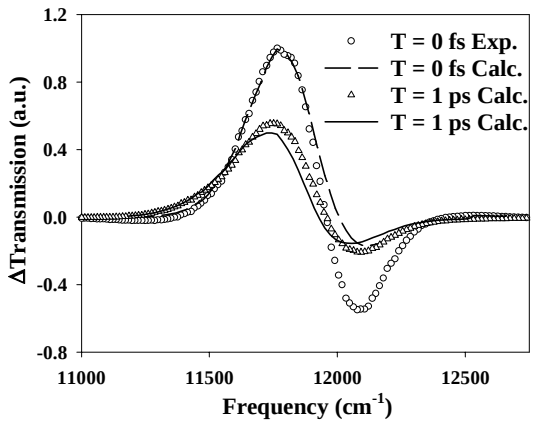

Figure 2. Experimental and calculated frequency-resolved pump-probe signal from the B850 band of LH2.

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