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Exciton self-trapping in bacterial antennas promotes light harvesting efficiency

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Introduction

Photosynthesis starts with light absorption by antenna complexes. The energy of the excited state thus formed is then transferred from one antenna complex to another until it reaches the reaction center where the energy is stored. The process of energy transfer depends on resonance between the acceptor and donor excited state energies. In the weak coupling Förster formalism, this is determined as the overlap integral between the donor fluorescence spectrum and the acceptor absorbance spectrum. A number of lines of evidence have shown that there is considerable heterogeneity in the spectra of individual antenna units. This is best characterized in LH2 photosynthetic antenna complexes from purple bacteria, where both single complex fluorescence excitation and emission studies (Tietz et al., 1999; van Oijin et al., 1999) have shown that individual antenna complexes can have substantially shifted spectra at low temperatures. This type of spectral heterogeneity is likely present also at physiological temperatures. And yet, the energy transfer between neighboring LH2 antenna units is very fast occurring in picosecond time range even at low temperatures (Timpmann et al., 2000). How, then, is this rapid energy transfer accomplished when the transition energies are so distinctly different? Here, we show that the relaxed excited states of LH2 complexes can be described as medium-range, one-dimensional excitons dynamically self-trapped by coupling to nuclear vibrations. The self-trapping results in a broad fluorescence spectrum, considerably improving energy resonance between heterogeneous antenna complexes.

Disparity between the absorption and emission spectra of LH2 complexes

It is presently well established that the non-relaxed excited states of LH2 antenna complexes have substantial exciton character. Depending on the exciton-phonon coupling strength, two limiting views concerning the origin of the emitting state(s) can be distinguished: (i) the emitting states are the molecular (commonly called Frenkel) exciton states in thermal equilibrium; (ii) the emitting states are the exciton polaron states self-trapped by coupling with nuclear vibrations. In the former case, one expects a very small Stokes shift between the absorption and emission spectra due to the momentum conservation law. In the latter, more realistic case, the emitting states are localized and a substantial Stokes shift may be observed.

Figure 1 shows the steady-state absorption and emission spectra of excitons in the LH2 antenna complex from *Rhodobacter (Rb.) sphaeroides* at low temperature.

Presented is only this part of the spectrum that is related to the Q_y electronic

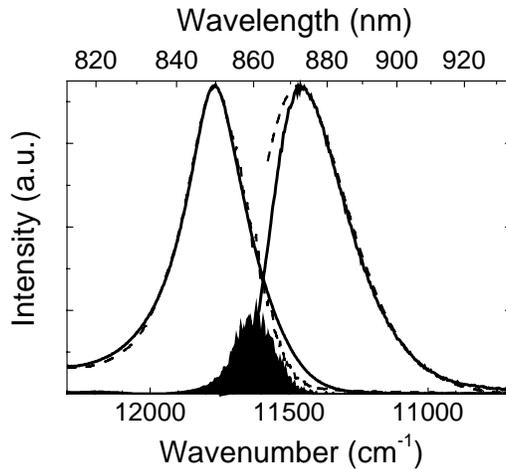


Fig. 1. Peak-normalized absorption (left side, measured at 10 K) and excited at 832 nm emission (right side, 5 K) spectra of isolated LH2 complexes from *Rb. sphaeroides*. Dashed curves show the corresponding ensemble-averaged simulated spectra. Filled area represents the distribution of the lowest Frenkel exciton transitions.

notice a discrepancy between the related spectral band shapes in Fig. 1. The emission band is over two times broader than the ensemble-averaged $k = 0$ absorption band, which is unexpected. A homogeneous nature of the emission spectrum has recently been established by fluorescence line narrowing and emission rise and decay kinetics measurements (Timpmann et al., submitted). If one takes into account the observed ~ 1.5 ns lifetime of the exciton in the LH2 complex and assumes a lifetime-limited width of the $k = 0$ transitions, the above ratio might, in principle, grow to an astonishing $\sim 10^5$ for a single member of the ensemble. The broad emission spectrum, the presence of which is confirmed by single-complex emission studies (Tietz et al., 1999), is thus strikingly different from the narrow $k = 0$ absorption line expected from the disordered Frenkel exciton theory. Finally, an appreciable Stokes shift of ~ 150 cm^{-1} should also be noticed in Fig. 1.

These observations strongly suggest that the absorbing and emitting states of the B850 aggregate are qualitatively different. It was proposed previously that the free exciton created by light dynamically (within 100-200 fs) localizes due to coupling to nuclear vibrations (Timpmann et al., submitted). Such self-trapping, inherent for one-dimensional excitons, should occur at any non-vanishing value of electron-nuclear coupling energy (Rashba, 1982). In what follows, a model of exciton self-trapping in disordered one-dimensional molecular aggregates is described. The details of the evaluation will be presented elsewhere.

Self-trapping of excitons in disordered one-dimensional aggregates

By careful inspection of the spatial shape of the low-energy exciton wave functions simulating the B850 aggregate absorption spectrum (Freiberg et al., 1999), it is revealed that the exciton is invariably localized of on a small segment of the B850 ring. The distribution of the segment sizes (defined as a double variance of the distribution of the pigment site populations (squared amplitudes of the wave function)) for the lowest eigenstate in the ensemble of B850 aggregates has a maximum at ~ 4.5 sites. The second lowest eigenstate, which also becomes expressing

transitions of bacteriochlorophyll *a* (Bchl) molecules in the B850 circular aggregate of LH2. Owing to the specific orientation of transition bacteriochlorophyll *a* (Bchl) molecules in the B850 circular aggregate of LH2. Owing to the specific orientation of transition dipoles of the Bchl molecules almost on the B850 ring plane, the lowest ($k = 0$) exciton transition in perfect aggregates would be very weak. In disordered aggregates, these transitions gain appreciable intensity, as shown by the filled area in Fig. 1, calculated according to the disordered Frenkel exciton model (Freiberg et al., 1999). One can

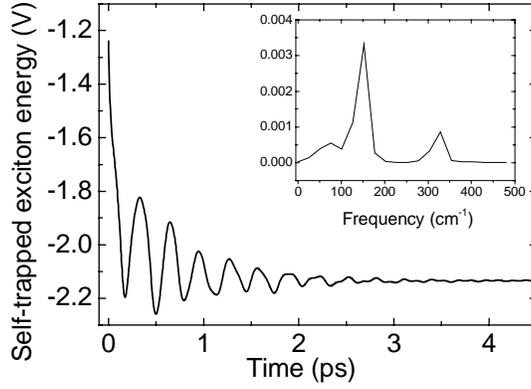


Fig. 2. Time dependence of self-trapped exciton energy in a 6-site aggregate. Note a drop of energy in femtosecond time scale and relaxation oscillations around the new equilibrium energy. The inset shows the power spectrum of oscillations. The simulation parameters: the site energies in units of V with corresponding initial occupation probabilities in parenthesis: 0.36 (0.1), -0.38 (0.2), -0.67 (0.25), -0.58 (0.22), 0 (0.13), 0.1 (0.1); $\chi=2$; $V=375 \text{ cm}^{-1}$.

emission simulations as a manifestation of a strong vibronic coupling present in disordered aggregates and that was not accounted for in the applied model. A further localization (self-trapping) of excitons is expected due to this vibronic coupling.

The simplest dynamic model of exciton self-trapping concerns a homogeneous molecular dimer whose site excitations are coupled to classical intramolecular vibrations (Kenkre and Wu, 1989). An extension of this model for the disordered chain of molecules is straightforward:

$$i\dot{c}_m = \varepsilon_m c_m + V(c_{m-1} + c_{m+1}) + \gamma c_m q_m \quad (1)$$

$$\dot{q}_m = -\Gamma q_m - \delta |c_m|^2. \quad (2)$$

Here, c_m and ε_m are the excitation amplitude and energy of the m -th molecule, correspondingly, q_m is the displacement, γ is the rate of change of site energy due to vibronic coupling, $\Gamma = \omega^2 / a$ is the vibrational relaxation rate (ω and a are the oscillator frequency and the damping coefficient, respectively) and δ is the proportionality coefficient. Equation (2) describes fast energy dissipation to the environment at a given molecule. Notice that eqs (1) and (2) asymptotically approach the states described by the non-linear Schrödinger equation. The non-linearity parameter $\chi = \gamma\delta / \Gamma$ has a meaning of double Huang-Rhys factor. The system of eqs. (1) and (2) shows a very robust dynamics of site occupations and energies for $V < 0$. Irrespective to initial conditions, the exciton is effectively localizing on only 3 molecular sites. The site with the lowest energy enjoys the highest occupation

probability, while the occupation of the remaining molecules of the aggregate is vanishing small. The most excited molecule is also the one that acquires the largest

broadening, has a maximum performed implies that (i) the part of the B850 ring, rather than the portion of the lowest exciton state at low temperatures. In this case, the calculation of the shape of the vibrational molecular aggregates

perfect fit of the red side of the spectrum. Compared with the simulations performed in Fig. 1, the fit is expected to provide an excellent fit to the experimental data. The theory: the inter-pigment coupling, σ . The best fit of the experimental data in Fig. 1 gives $\sigma = 220 \text{ cm}^{-1}$, in contrast to the value of 10 cm^{-1} in the model of Freiberger et al., 1999). This indicates that the different origin compared to the model of Freiberger et al. gained from the

displacement. As can be seen in Fig. 2, the shift to the new equilibrium position of this molecule occurs on a very short time scale followed by damped irregular oscillations. This rapid spectral shift can be related to the observed subpicosecond rise of the emission (Timpmann et al., submitted).

This model, implying that the emitting state in the B850 ring always stems from a Bchl trimer, naturally explains the observed homogeneous character of the emission as well as its weak temperature dependence. The functional importance of self-trapping is not limited with promoting energy resonance between heterogeneous LH2 antenna complexes. The red shift of the LH2 emission spectra also improves overlap with the core LH1 antennas. Exciton self-trapping is thus part of nature's strategy to increase the speed and efficiency of energy transfer in photosynthesis.

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