



Modelling excitonic energy transfer in the photosynthetic unit of purple bacteria

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ABSTRACT

Molecular mechanics and quantum chemical configuration interaction calculations in combination with exciton theory were used to predict vibronic energies and eigenstates of light harvesting antennae and the reaction centre and to evaluate excitation energy transfer rates in the photosynthetic unit of purple bacteria. Excitation energy transfer rates were calculated by using the transition matrix formalism and exciton basis sets of the interacting antenna systems. Energy transfer rates of 600–800 fs from B800 ring to B850 ring in the LH2 antenna, 3–10 ps from LH2 to LH2 antenna, 2–8 ps from LH2 to LH1 antenna and finally 30–70 ps from LH1 to the reaction centre were obtained. Dependencies of energy transfer rates on lateral and vertical inter-complex distances were determined. The results indicate that a fair amount of spatial heterogeneity of antenna complexes in the photosynthetic membrane is tolerated without much loss in excitation energy transfer efficiency.

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1. Introduction

Three light harvesting (LH) antenna complexes LH1, LH2 and LH3 have been isolated from various species of photosynthetic purple bacteria. In the core complex of photosynthetic unit (PSU) the LH1 antenna surrounds the reaction centre (RC), and contains 24–36 bacteriochlorophyll (Bchl) *a* or *b* molecules depending on species [1]. The LH1 antenna absorbs at about 875 nm at room temperature (RT) [2]. The peripheral antenna complexes have two absorption bands each, LH2 at about 800 and 850 nm and LH3 at 800 and 820 nm [2,3]. Electron microscopy, AFM and X-ray studies reveal closed and open ring structures with circular or elliptical shape of the LH1 antenna in the core complexes [1,4–9]. The LH2 and LH3 complexes are laterally distributed around the LH1–RC core complex in the cell membrane to allow for non-interrupted energy transfer from the peripheral LH's to the RC [10]. AFM studies suggest inter-complex LH2–LH2 and LH2–LH1 distances of 15–38 and 35 Å, respectively [11–13]. The density of the peripheral antenna complexes in the PSU depends on growth conditions [10]. These complexes contain 24 or 27 Bchl *a* molecules in two separate circular arrangements, called the B800 Bchl *a* and B820 Bchl *a* or B850 Bchl *a* rings according to their maximum absorption wavelength in the *Q_y* region [11,12,14–16]. Detailed atomic structures of the RC of the purple bacteria *Rhodospseudomonas* (*Rps.*) *viridis* and *Rhodobacter* (*Rb.*) *sphaeroides* have been published about 20 years ago [17–20]. The RCs have three major absorption bands a 750–800, 800–850 and 870–1000 nm, corresponding absorption of the monomeric Bphe's and

accessory Bchl's and the Bchl dimer, respectively [21–25]. Atomic structures of the LH2 of *Rps. acidophila* [14], of the LH1 complex of *Rb. sphaeroides* by Schulten et al. [26] and of the RC of *Rb. sphaeroides* [19] were used in the calculations. The open LH1 complex was generated by removing 8 Bchl *a* molecules from Schulten's ring structure.

Ultrafast spectroscopic techniques have been used extensively to determine relevant time scales of intra- and inter-complex excitation energy transfer (EET) in PSU of purple bacteria [3,27–55]. Sundström et al. have reported an energy transfer rate from B800 Bchl *a* to B875 Bchl *a* of LH1 of 12 ps at 77 K [30,31]. A summary of published intra- and inter-complex EET rates looks as follows: 0.7 ps for B800 Bchl *a* → B850 Bchl *a* transfer in LH2 at RT, 1–10 ps for LH2 → LH2 transfer, 2–13 ps for B850 Bchl *a* of LH2 → B875 Bchl *a* of LH1 transfer and finally 35 ps for LH1 → RC transfer [3,30–36,38–47]. At low temperatures the B800 Bchl *a* → B850 Bchl *a* transfer rates in LH2 are slightly reduced, at 77 K to about 1.5 ps and at 4 K to about 2 ps [30,35,37,38,41–43,48–53]. Several time-resolved and hole-burning experiments have suggested the presence of intra-B800 Bchl *a*, intra-B850 Bchl *a* and intra-B875 Bchl *a* relaxation processes with rates of a few hundred femtoseconds or faster [32,35,40,56–64].

Gillbro et al. [43] have reported that the B800 Bchl *a* → B800 Bchl *a* excitation energy transfer rate in LH2 of *Rps. acidophila* is wavelength dependent and suggested involvement of several excitonic states in this process. Förster model was unable to describe the EET [43]. Sundström et al. [65] studied a series of mutated LH2 antenna of *Rps. acidophila* by using Förster model and obtained rates that were five times slower than the experimentally recorded B800 Bchl *a* to B850 Bchl *a* EET rates. An advanced approach to calculate EET rates was proposed by Fleming et al. who used

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ab initio transition density cube method to estimate most important chromophore–chromophore interaction constants in the LH2 antenna of *Rps. acidophila*, and Förster approach to calculate EET rates from B800 Bchl *a* to B850 Bchl *a* pigments [66,67]. Mukamel et al. used the collective electronic oscillator approach that gave for the B800 Bchl *a* → B850 Bchl *a* EET rates about 0.44–0.70 ps for *Rhodospirillum (Rs.) molischianum* in agreement with experimental results [68,69]. Schulten et al. have used an effective Hamiltonian to calculate B800 Bchl *a* → B850 Bchl *a* EET rates 0.39–0.53 ps for the LH2 antenna of *Rs. molischianum* [70]. Sumi et al. have studied EET rates in the LH2 antenna by assuming that transfer takes place from individual bacteriochlorophylls of the B800 Bchl *a* ring to the excitonic B850 Bchl *a* system but rates were underestimated by an order of magnitude [71,72]. In subsequent work Sumi et al. emphasize the excitonic role of the EET mechanisms that contains both exciton – phonon and exciton – disorder interactions and obtained an improved B800 Bchl *a* to B850 Bchl *a* EET of 1 ps [73,74]. They suggested that the broad excitonic manifolds of the B850 Bchl *a* of LH2 and B875 Bchl *a* of LH1 provide a spectrally broad channel for the initial excitation in the antenna to find its way to the RC efficiently. Kakitani et al. used the generalized master equation to calculate EET rates in mutated LH2 antenna of *Rps. acidophila* and reported rate constants in agreement with experimental observations [75]. In our previous studies of the LH2 antenna complexes of *Rps. acidophila* and *Rs. molischianum* the experimental B800 Bchl *a* → B850 Bchl *a* EET rates were correctly predicted as well as its wavelength dependence. The calculations indicated involvement of higher exciton states of B850 Bchl *a* pigments in the B800 Bchl *a* → B850 Bchl *a* EET process [36,76–79].

One of the most discussed topics in energy transfer of ring like antenna systems is the question of the identity of the antenna states that finally receive and transfer sun's radiation. It is not clear how many pigments receive the excitation and how such excitation relaxes within a single ring system and/or how energy is transferred from one ring system to another? It is a debated question, whether the initially prepared excitation is localized on a single chromophore or is it spread over the entire ring aggregate or is it something in between [76,80–84]. Energetic disorder is needed to allow preparation of coherent localized excitations in a pigment aggregate. This may be created by local interactions of individual chromophores with nearby amino acids of the antenna protein. Local interactions may create heterogeneity both in internal pigment organization in the aggregate and/or deform the over all geometry of the aggregate into circular or ellipsoidal, closed or open. The results from single-molecule spectroscopy suggest that the excited states of individual LH2 and LH1 complexes indeed vary from complex to complex [85–91]. Extent of localization of the initial excitation strongly affects the EET properties of a light harvesting antenna system. The theoretical approach to be used in the EET analysis has to be able to describe such effects as well as experimentally observed wavelength dependence of EET [30,31,36,43,44,48].

In the present paper we model intra- and inter-complex energy transfer by introducing vibronic transitions and what we call the 'protein phonons'. First temperature dependence of the absorption spectrum of the B800 Bchl *a* aggregate of LH2 of *Rps. acidophila* was modelled. Strong coupling between the B850 pigments, weak coupling between the B800 pigments and between the B800 and the B850 pigments were assumed. Exciton couplings between the pigments located in separate antenna complexes were assumed to be weak and calculated as dipole–dipole interactions. It is noted that the strong intra-antenna couplings in the B850 Bchl *a*, the B875 Bchl *a*, and the RC complexes have no effect on inter-antenna exciton couplings, but they determine the density of states of the exciton manifolds of the LH and the RC complexes, respectively [78]. Following these assumptions LH2–LH2, LH2–LH1 and LH1–RC EET rates were then calculated.

2. Theoretical approach

2.1. Transition rates

In the Schrödinger picture the state vectors are time dependent, whereas the operators are time independent [92,93]. The time evolution of the system in the Schrödinger picture is described by

$$i\hbar \frac{\partial}{\partial t} |\Psi_S(t)\rangle = \hat{H} |\Psi_S(t)\rangle, \quad (1)$$

where the Hamiltonian \hat{H} is assumed to have no explicit time dependence and it can be expressed as the sum of two terms (subscript *S* in the state vector denotes the Schrödinger picture)

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (2)$$

where \hat{H}_0 acting alone yields a soluble problem and operator \hat{H}_1 represents the interactions. A formal solution of Eq. (1) is obtained by writing

$$|\Psi_S(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar} |\Psi_S(t_0)\rangle, \quad (3)$$

where the state $|\Psi_S(t_0)\rangle$ is the initial state at t_0 . Using the interaction picture then the probability amplitude for finding the system in the state $|\varphi_f\rangle$, which is the eigenstate of \hat{H}_0 at any time t is

$$P_f = \langle \varphi_f | \Psi_I(t) \rangle, \quad (4)$$

where the interaction state vector (subscript *I*) is defined by

$$|\Psi_I(t)\rangle \equiv e^{i\hat{H}_0 t/\hbar} |\Psi_S(t)\rangle. \quad (5)$$

Using Eq. (4) the transition rate may be written as

$$W_{fi} \equiv \frac{d}{dt} |P_f|^2 = \frac{d}{dt} |\langle \varphi_f | \Psi_I(t) \rangle|^2. \quad (6)$$

From scattering theory and properties of the Green's function then the transition rate becomes ($\hat{V} \equiv \hat{H}_1$) [77,94]

$$\begin{aligned} W_{fi} &= \frac{2\pi}{\hbar} |\langle \varphi_f | \hat{T} | \varphi_i \rangle|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar} \left| \langle \varphi_f | \hat{V} | \varphi_i \rangle + \sum_m \langle \varphi_f | \hat{V} | \varphi_m \rangle \frac{1}{E_i - E_m \pm i\epsilon} \langle \varphi_m | \hat{V} | \varphi_i \rangle \right. \\ &\quad \left. + \sum_m \sum_n \langle \varphi_f | \hat{V} | \varphi_m \rangle \frac{1}{E_i - E_m \pm i\epsilon} \langle \varphi_m | \hat{V} | \varphi_n \rangle \right. \\ &\quad \left. \times \frac{1}{E_i - E_n \pm i\epsilon} \langle \varphi_n | \hat{V} | \varphi_i \rangle + \langle \varphi_f | \hat{T}^{(4)} | \varphi_i \rangle \right|^2 \delta(E_f - E_i). \quad (7) \end{aligned}$$

The first term in the Eq. (7) is the traditional Fermi Golden rule, the second term corresponds to transitions between initial state *i* and the final state *f* via an intermediate state *m*. The third term represents the transition via two different intermediate states *m* and *n*. The last term involves the higher order terms of the transition operator (\hat{T}). In this work only the first term (Fermi Golden rule) was used for EET rate calculations.

2.2. The model Hamiltonian for molecular aggregates

Consider a system of *N* molecules that form an aggregate. Assuming that there are *A* relevant molecular vibronic transitions from the ground to the excited states, only one particle-hole excitation and *M* phonons with linear exciton–phonon coupling the Hamiltonian takes the form

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{ph} + \hat{H}_{ex-ph}^{(1)} + \hat{H}_{ex-ph}^{(2)}, \quad (8)$$

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