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An exciton model to calculate spectra, intra- and intercomplex energy transfer rates of photosynthetic light harvesting antenna

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Introduction

Light harvesting in photosynthesis is a magnificent example of a sequence of multiple events in a complex biological system that guarantees arrival of sun's energy to the photosynthetic reaction centre at about 98% efficiency. The photosynthetic unit (PSU) of purple bacterium contains a number of laterally distributed peripheral LH2 antenna and the core antenna LH1 surrounding the reaction centre (RC) all fixed in the cell membrane. In the PSU light is transferred through the peripheral LH2 network via the LH1 to the reaction centre. Light harvesting antenna consists of aggregates of bacteriochlorophylls (BChl *a*) imbedded in protein. The LH2 antenna of *Rps. acidophila*

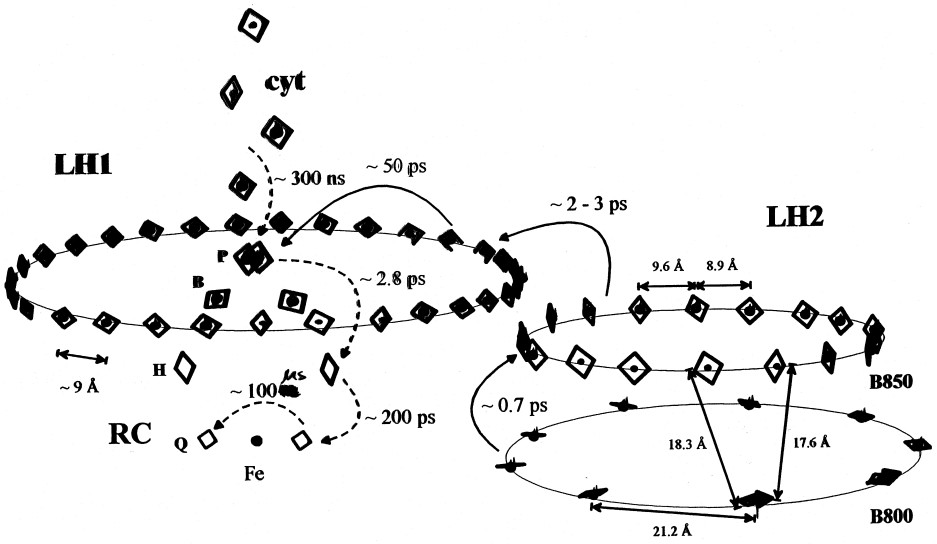

Fig. 1. A schematic presentation of chromophores of the photosynthetic unit of purple bacterium Rps. acidophila. LH2 and LH1 refer to peripheral and core light harvesting antenna, Respectively and RC to the reaction center. Experimental energy transfer time constants and most important distances are given .

contains two circular BChl *a* aggregates, the B800 ring with nine weakly interacting BChl *a*'s and the B850 ring with 18 Bchl *a*'s with strong interaction (Fig.1.). In LH2 of *Rs. molischianum* the corresponding numbers are eight and 16, respectively. The LH1 antenna has only one ring with 32 BChl *a*'s (Fig. 1). The atomic structures of LH2 and LH1 antenna and the RC are known at atomic detail (see Sundström 1999).

Methods

We have developed and tested a systematic computational method that can not only predict spectroscopic properties of light harvesting antenna, but also ultrafast excitation energy transfer rates in the bacterial PSU (Fig. 1). In the CIEM-method quantum chemical configuration interaction calculations (in this case ZINDO/S CI method) are used to obtain dimeric interaction energies as well as site energies (Linnanto 1999). Local protein environment, the amino acids in the neighbourhood of the chromophores, is included in the optimisation processes. Inhomogeneous broadening of the spectral lines is included by varying the diagonal and off-diagonal matrix elements of the exciton Hamiltonian according to Gaussian random distribution. Experimental homogenous and inhomogeneous line widths are used as input parameters, as well as the value of 6.1 D of the transition moment of BChl *a*. Spectra and excitation energy transfer rates are calculated for some 5000 configurations. For calculation of excitation energy transfer rates excitonic wavefunctions that reproduce the experimental spectra and Fermi's Golden rule with the dipole – dipole operator are used. General expression for calculation of the rates was

$$W_{fi} = \frac{2\pi}{\hbar}\left|\langle\varphi_f|\hat{T}|\varphi_i\rangle\right|^2 \delta\left(E_f - E_i\right)$$

$$= \frac{2\pi}{\hbar}\left|\langle\varphi_f|\hat{V}|\varphi_i\rangle + \sum_m \langle\varphi_f|\hat{V}|\varphi_m\rangle \frac{1}{E_i - E_m \pm i\varepsilon}\langle\varphi_m|\hat{V}|\varphi_i\rangle\right.$$

$$\left. + \sum_m \sum_n \langle\varphi_f|\hat{V}|\varphi_m\rangle \frac{1}{E_i - E_m \pm i\varepsilon}\langle\varphi_m|\hat{V}|\varphi_n\rangle \frac{1}{E_i - E_n \pm i\varepsilon}\langle\varphi_n|\hat{V}|\varphi_i\rangle + \langle\varphi_f|\hat{T}^{(4)}|\varphi_i\rangle\right|^2 \delta\left(E_f - E_i\right)$$

The first term in the equation is the traditional Fermi's 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 represent the transition via two different intermediate states *m* and *n*. $\hat{V}$ is the interaction operator. The last term involves the higher order terms of the transition operator $\hat{T}$. It turned out that second and third terms produced only small effects on the calculated rates and hence they were omitted. Kinetic constants of all transitions from the prepared excited states to the probed, final states are evaluated. Comparison of calculated distribution of kinetic constants to the experimentally determined constants is done by using exponential fits (Linnanto 2000).

The method developed is general and may be used to calculate spectra and energy transfer rates of any photosynthetic antenna system the structure of which is known, such as PSI and PSII for which the atomic co-ordinates are becoming available (Jordan 2001). The method may be used to model other biochemical processes besides photosynthesis, like electron and proton transfer reactions. The development of the model has taken place in close contact with experimental work both within our own group but also with several collaborators abroad.

Results

Simulation of absorption and CD-spectra. Absorption and CD - spectra of peripheral LH2 antenna complexes of purple bacteria *Rps. acidophila* and *Rs. molischianum*, absorption spectra of five mutated LH2 antenna of *Rps. acidophila*, the core antenna LH1 and the reaction centre were simulated. The main purpose was to obtain understanding of the underlying physical reasons that shift the B800 and B850 absorption bands of LH2 towards red with respect to the BChl *a* monomer absorption at 773 nm. Extensive work on aggregation of Chl's (Linnanto 1998) and BChl's in solution suggests that in the B850 ring of strong chromophore – chromophore interactions give rise to most of the spectroscopic shift. Fine tuning is due to the nearby amino acids. As dipole-dipole interaction fails to describe

such effects, the interaction energies of the two dimers present in the B850 ring were determined by using the semiempirical ZINDO/CI method. Geometry minimisation included the nearby amino acids of the BChl *a*'s. Interaction energies in the αβ-protomer of 622 cm^{-1} and 756 cm^{-1} and in between the protomers of 562 cm^{-1} and 570 cm^{-1} in *Rps. acidophila* and in *Rs. molischianum* were obtained, respectively. The monomer site energies of BChl *a*'s of the B850 ring became 784 nm and 768 nm for BChl *a* - $B850_{\beta}$ and 779 nm and 763 nm for BChl *a* - $B850_{\alpha}$, in *Rps. acidophila* and in *Rs. molischianum,* respectively. By using these parameters absorption and CD-spectra of both bacteria were correctly predicted. The simulation of the CD spectrum of *Rs. molischianum* was done by using a fully excitonic model for the first time (Linnanto 2001).

In the B800 ring the chromophore - chromophore interaction is weak, and it can not explain the spectroscopic shift of about 385 cm^{-1} from the monomer transition energy of BChl *a*. The shift must originate from the protein. The transition energies of the BChl *a* -B800 were estimated by including the nearby protein environment of the chromophore within 7Å radius in semiempirical ZINDO/CI calculations. Site energies of 797 nm and 798 nm of the BChl *a* - B800 in *Rps. acidophila* and in *Rs. molischianum,* respectively, consistent with the experiment were obtained. A nice example of local protein interactions was obtained from simulations of the spectra of five genetically modified LH2 antenna of *Rps. Acidophila*

In the modified antenna the chromophores of the BChl *a* - B800's were exchanged, while BChl *a* - B850's were left in place. The modified antenna shows widely varying absorption wavelengths of the B800 ring, from 670 to 800 nm, depending on the exchanged dye. According to simulations the interaction of BChl *a* with the local protein environment was strongest, the weakest interaction was observed for Chl *a*. Simulations produced the spectra shown in Fig. 2., in nice agreement with experimental spectra.

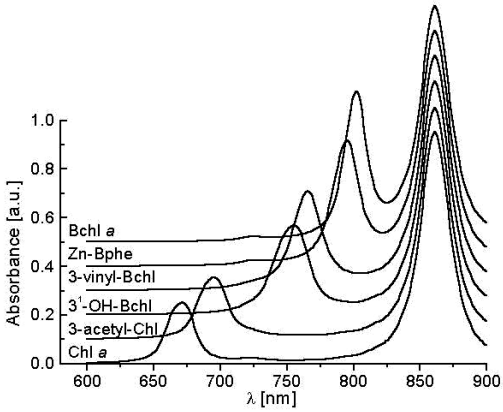

Fig. 2. *Simulated absorption spectra of mutated LH2 antenna of Rps. acidophila. The BChla - B800 chromophores were exchanged by chromophores shown above each curve on the left side.*

(Herek 2000).

Simulation of excitation energy transfer rates. Most important excitation energy transfer rate constants of the PSU of *Rps. acidophila* resolved until today are shown in Fig. 1. The excitonic wavefunctions that predicted the absorption and CD-spectra of the light harvesting complexes correctly were used for estimation of rates of intra - and inter - complex energy transfer rates in the PSU of *Rps. acidophila*. The B800 to B850 energy transfer rates of LH2 of *Rs. molischianum* as well as of five above mentioned LH2 mutants of *Rps. acidophila* were evaluated. Calculations were performed at zero phonon coupling limit.

Energy transfer rates from the B800 ring to the B850 ring of LH2 of *Rps. acidophila* and *Rs. molischianum* of 0.5 ps and 1.0 ps, respectively, were predicted in good agreement with observed rates. The reason for the difference of the energy transfer rates is that *Rps. acidophila* has two but *Rs. molischianum* only one excitonic acceptor state below and in the neighbourhood of the B800 exciton manifold. In LH2 of *Rs. molischianum* wavelength dependence of the transfer rate was predicted. B800 to B850 excitation transfer rates in five mutated LH2 complexes of *Rps. Acidophila* were also calculated. Transfer rates for the antenna with exchanged chromophores showing strong protein - chromophore interaction were correctly predicted, the rates for weakly interacting chromophores became slightly too slow. In the weakly interacting chromophores probably vibronic couplings contribute to transfer rates.

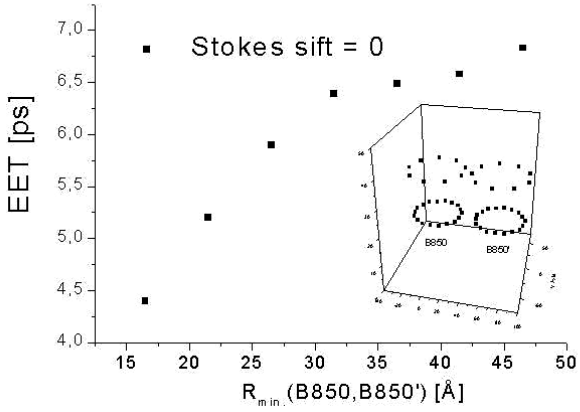

Fig. 3. Dependence of excitation energy transfer rate on lateral inter LH2 distance

Simulated inter antenna transfer rates in the PSU of *Rps. acidophila*, between peripheral LH2 to LH2 antenna, from LH2 to LH1 antenna and from LH1 to the reaction centre were in good agreement with the experimental results. According to simulations energy transfer rates between adjacent LH2's are not strongly dependent on the Stokes shift and lateral (**Fig. 3.**) or vertical inter antenna distances in the photosynthetic membrane.

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According to calculations open ring structure of the LH1 antenna does not much distort energy transfer efficiency from LH2 to LH1 and from LH1 to the RC. Calculations indicate that the observed ultrafast rate constants depend on the overlap of the excitation pulse and the excited states and on probing conditions. Experimental evidence of such dependencies was obtained in LH2 of *Rs. molischianum.*

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