Eur. Phys. J. B **12**, 163–166 (1999)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Incoherent energy transfer within light-harvesting complexes

Julian Juhi-Lian Ting[1,a]

No.38, Lane 93, Sec.2, Leou-Chuan E. Rd., Taichung, 40312 Taiwan, Republic of China

Received 29 May 1998

Abstract. Rate equations are used to model spectroscopic observation of incoherent energy transfer in light-harvesting antenna systems based upon known structures. A two-parameter two-dimensional model is proposed. The transfer rates obtained, by matching the fluorescent decay, are self-consistent within our model.

PACS. 87.10.+e General theory and mathematical aspects – 36.40.Mr Spectroscopy and geometrical structure of clusters – 87.15.Mi Spectra, photodissociation, and photoionization; luminescence

1 Introduction

We have had a reasonably complete picture of the bacterial light-harvesting (LH) system recently [1,2]. Both the inner antenna, LH1, and the outer antenna, LH2, are assembled from the same modules to form rings. Each module consists of two short α-helical polypeptides coordinate one carotenoid and three bacteriochlorophylls (BChls). The LH2 is composed of 9 units, for *Rhodopseudomonas acidophila* [3], resemble a cylinder, with an inner diameter 36Å and an outer diameter 68Å, while the LH1 is composed of 16 units, for *Rhodospirillum rubrum* [4], in order to accommodate the reaction center (RC). The later has an outer diameter 116Å and a central diameter 68Å. However, the exact numbers of both complexes are variable [1,4,5].

Furthermore, the LH2 B850 BChl *a* form a complete over-lapping ring in a hydrophobic environment, which reduces the dielectric constant, while the B800 BChl *a* are well separated and are in a polar environment. When a BChl molecule is excited by light, the energy can reach equilibrium within about 10 ps [6]. A LH2 can function as a storage ring to store the excited singlet state energy for about 1100 ps. However, the energy will transfer to other rings before decaying. The hopping of energy continues from one ring to another one until a LH1, which contains the RC, is finally reached. The total trip lasts for about 5 to 50 ps [3,7,9]. Apparently, there is a competition between energy relaxation and energy transfer.

Historically, relatively few physicists have tackled problems of photosynthesis. Notably, Montroll used random walk concepts to model energy transfer amongst antenna rings on a lattice by considering its first passage time [10]. Later, Hemenger *et al.* proposed a more realistic model by taking inhomogeneous transfer rates and trapping of RCs into account [11]. Interestingly, it is Pearlstein's work which is most often cited in the literature [12]. In the mean time, almost all experimentalists try to find some explanations for their spectral data. However, due to lack of precise geometrical information most efforts are in vain.

Progresses in physics are often made along the line structures-energy-dynamics. A goal of researches nowadays is to find the relation between structural and spectral information obtained, expecting that the function of photosynthesis will be explained in terms of its structure, and further drawing inferences from the model by applying methods of mathematical or numerical analysis. Recently Timpmann *et al.* used a rate equation model to describe energy trapping and detrapping by the RC [13]. However, their antenna has no structure. Skála *et al.* also carried out a series of investigation by analyzing the spectrum of a more realistic LH1 model [14–16]. However, their model is incompatible with the recent structural finding. In this paper we established a two-parameter model based on recent structural data.

2 Model

With the known periodical structure, shown in Figure 1, we can built, from chemical rate equation, the following phenomenological model of energy transfer,

$$\frac{\mathrm{d}E}{\mathrm{d}t} = k' A_1 - (k'' + k_E)E, \tag{1}$$

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = kA_{16} - 2kA_1 + kA_2 - k'A_1 + k''E, \tag{2}$$

$$\frac{\mathrm{d}A_n}{\mathrm{d}t} = kA_{n-1} - 2kA_n + kA_{n+1}, \qquad n = 2...15, \tag{3}$$

$$\frac{\mathrm{d}A_{16}}{\mathrm{d}t} = kA_{15} - 2kA_{16} + kA_1, \tag{4}$$

---

[a] e-mail: `jlting@yahoo.com`

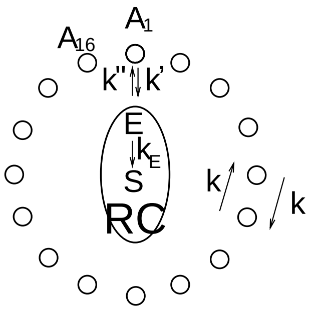

Fig. 1. Schematic plot of LH1 and definition of symbols used.

in which A_ns denote the excited BChl dimer, $E \equiv P^*BH$ is the excited state, with B representing the chlorophyll monomer within the RC, and P^* is the excited special pair of BChl molecules. It is a set of 17 coupled linear differential equations. The symmetry of this system is broken due to $k' \neq k''$. A similar model has been proposed by Skála *et al.* [15]. However, the RC and the antenna ring are connected only at one site in the present model, corresponding to the recent experimental observation.

In the homogeneous case with the same transition rate amongst the units, the characteristic polynomial of the above rate-constant-matrix can always be expressed as

$$P_{16} = P_{16}^1 P_{16}^2 P_{16}^3 P_{16}^4, \tag{5}$$

with

$$P_{16}^1 = s + 2k, \tag{6}$$

$$P_{16}^2 = s^2 + 4ks + 2k^2, \tag{7}$$

$$P_{16}^3 = s^4 + 8ks^3 + 20k^2s^2 + 16k^3s + 2k^4, \tag{8}$$

$$\begin{aligned} P_{16}^4 = {} & s^{10} + (k_E + k'' + k' + 18k)s^9 \\ & + (k'k_E + 18kk_E + 18kk'' + 16kk' + 134k^2)s^8 \\ & + 2(8k'k_E + 67kk_E + 67kk'' + 52kk' + 266k^2)ks^7 \\ & + 2(52k'k_E + 266kk_E + 266kk'' + 176kk' + 605k^2)k^2s^6 \\ & + 2(176k'k_E + 605kk_E + 605kk'' + 330kk' + 786k^2)k^3s^5 \\ & + 12(55k'k_E + 131kk_E + 131kk'' + 56kk' + 91k^2)k^4s^4 \\ & + 4(168k'k_E + 273kk_E + 273kk'' + 84kk' + 86k^2)k^5s^3 \\ & + 8(42k'k_E + 43kk_E + 43kk'' + 8kk' + 4k^2)k^6s^2 \\ & + 2(32k'k_E + 16kk_E + 16kk'' + kk')k^7s + 2k^8k'k_E, \end{aligned} \tag{9}$$

which is a consequence of the master equation used, and is independent of the detail geometrical symmetry. The mode controlling the decay to the RC is within P_{16}^4, since P_{16}^1, P_{16}^2, P_{16}^3 do not contain k', k'' and k_E. However, all four parts will be influenced by the change of k. If one solves this set of differential equations by applying the Laplace transformation method, one finds the solution divides into four distinct groups of decay channels, namely, A_5-A_{13}; E-A_1-A_9; A_3-A_7-A_{11}-A_{15}; A_2-A_4-A_6-A_8-A_{10}-A_{12}-A_{14}-A_{16}. Because the matrix of rate constants is Hermitian, all eigenvalues are negative. Furthermore, no eigenvalues are degenerated, in contrast to Skála's model which posses too high degree of symmetry [16]. Letting $k' = k''$ does not results in additional factorizability although the symmetry of our model is restored. At $k' = k'' = 0$, P_{16} becomes

$$\begin{aligned} & s(s + 2k)^2(s + 4k)(s + k_E)(s^2 + 4ks + 2k^2)^2 \\ & \qquad \times (s^4 + 8ks^3 + 20k^2s^2 + 16k^3s + 2k^4)^2 \ . \end{aligned} \tag{10}$$

It contains a zero eigenvalue, which signals the existence of a steady-state solution, as should be happened without the decay to the RC. Degeneracy of eigenvalues is introduced as the transition to the RC is decreased.

3 Spectrometry comparison

We can verify our model against experiments: The pump-probe spectroscopy measures the difference between two beams, with

$$\Delta D = \Delta\epsilon_A \sum_n A_n + \Delta\epsilon_E E \ , \tag{11}$$

being the signal measured. The symbol $\Delta\epsilon$ s are the differences in dielectrical constants between pump and probe beams of the corresponding pigments. By choosing the pump and probe laser frequencies, we can selectively detect the population changes of $\sum A_n$ or E. Summing over equations (1-4) we know that the decay of the total population should be $\mathrm{d}(\sum A_n)/\mathrm{d}t = -k'A_1 + k''E$. The measured charge separation rate is $k_E \approx 3.57 \times 10^{11}$ s^{-1} at room temperature, and increases by 2 to 4 times from 300 K to 10 K depending on the species chosen [17,18]. The ratio of the forward and backward transition to the RC is know to be about 25% [13] for an open RC, *i.e.*, the RC BChl dimer (P) is reduced and the iron quinone electron acceptor is oxidized; 40% for pre-reduced RC. The back-trapping rate can, in principle, be estimated from $k''/k' = \exp(-\Delta G/k_\mathrm{B}T)$, with ΔG the free-energy gap between A_1 and E is estimated from their absorption peaks, k_B is the Boltzmann constant, and T is the absolute temperature. However, the measured absorption peaks of the excited RC are broad and imprecise [8]. We do not know the absolute values of k' or k'' experimentally since it is difficult to tune the laser frequency to distinguish A_n from E. Nor do we know the transition rate between A_ns because transition between the same species cannot be measured directly. Furthermore, at room temperature, energy equilibrium within the antenna interferes with the trapping process. Therefore we have taken k and k' as parameters and fit the slow mode of fluorescence decay of excited population observed, *i.e.* 200 ps [6,7,9]. Thus, the absolute value of the largest eigenvalue should be about 3/200 ps $= 1.5 \times 10^{10}$ s^{-1}. A computer code is written to scan all combinations of k and k', with $k'' = k'/5$, for the largest eigenvalue to be smaller than -1.5×10^{10} s^{-1} between -10^8 s^{-1} to -10^{15} s^{-1}. Interestingly, we find all possibility happened at $k = k'$ and $k > 6.97 \times 10^{11}$ s^{-1} for $k'' = k'/5$. Presumably, it is an extremum of P_{16}^4. At the lowest k, we can match the required 200 ps decay

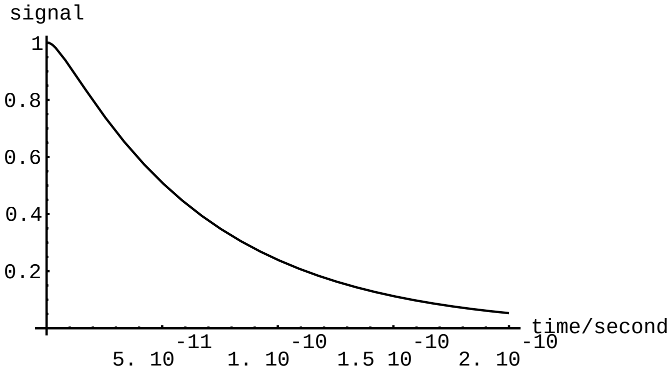

Fig. 2. Numerically calculated pump-probe signal from equation (11) at $k = 6.97\times10^{11}$, $k_E = 3.57\times10^{11}$, $k' = k$, $k'' = k'/5$, $\Delta\epsilon_A = 1$, $\Delta\epsilon_E = 0$. The initial condition is $A_5 = 0.2$, $A_7 = 0.4$, $A_{10} = 0.3$, $A_{12} = 0.1$, while other sites are not excited at $t = 0$.

whose curve is plotted at Figure 2. If $k'' = k'/4$, we obtained $k = 7.25 \times 10^{11}$ s^{-1}. That k has to be equal to k' might sound peculiar in view of the geometrical distance between A_1 and RC is less than the distance between RC and other A_ns [4]. However, the species for donor and acceptors are different at these two cases. There are possibilities that the final hopping rate are still the same.

The transfer of excitation energy requires coupling between the emitting molecule and the ground state molecule. At an intermolecular separation involved between 10 Å to 100 Å, long-range resonance transfer of electronic excitation arises from coupling between the transition dipoles of the donor and the acceptor, which is the Föster theory [19,20]. Since the BChl Q_y dipoles lie in the same plane, we have

$$k(R) \propto \frac{1}{\tau_{\mathrm{F}}}\left(\frac{R_0}{R}\right)^6, \tag{12}$$

in which R_0, measures transfer efficiency, is the Föster radius. van Grondelle gave $R_0 = 90$ Å for the BChl 875 to BChl 875 energy transfer and a fluorescence life time, τ_{F}, about 3000 ps or slightly higher [21,22]. If a putative separation distance between interacting BChl a dimers $\approx$ 17.5 Å is used [4] we obtain an estimation of $k \approx 6.17 \times 10^{12}$ s^{-1}. This number is about an order of magnitude higher than the value obtained from our model. However, the pairwise energy transfer is about 1 ps according to our calculation [9]. On the other hand, from the value of k obtained here, by fitting the 200 ps decay as well as the τ_{F}, we estimated the Föster radius to be 26.8 Å. This result is consistent within our model since we assume only nearest neighbour transition. Further, since we put the population at the antenna at $t = 0$ for our calculation,the rising time is infinitely short, instead of having some instrumental limits as observed experimentally. Although the light wave length is much larger than the ring size, the ring still might receive energy in localized form by energy transfer from other rings as the initial condition we used in Figure 2. Table 1 provides a list of all eigenvalues and corresponding amplitudes obtained from our model. From the table, we found that the largest eigenvalue mode is important, not only for its large separation from the other eigenvalues but also for its corresponding large amplitude.

amplitude	eigenvalue
-0.0070	-2.9707×10^{12}
-0.0006	-2.7443×10^{12}
0.0000	-2.6819×10^{12}
0.0221	-2.4614×10^{12}
0.0000	-2.3797×10^{12}
-0.0200	-2.0143×10^{12}
0.0000	-1.9275×10^{12}
0.0124	-1.4844×10^{12}
0.0000	-1.3940×10^{12}
-0.0086	-9.5864×10^{11}
0.0000	-8.6054×10^{11}
-0.0159	-5.5606×10^{11}
0.0000	-4.0829×10^{11}
0.0034	-3.8570×10^{11}
-0.0716	-1.4875×10^{11}
0.0000	-1.0611×10^{11}
1.0858	-1.5107×10^{10}

Table 1. Eigenvalues for LH 1 for Figure 2. In a time-resolved experiment the relaxation rates correspond to the lifetimes observed from antenna fluorescence or bleaching kinetics.

We have also introduced inhomogeneity, due to geometrical distortion, into the rate constant. However, even at large distortion, the basic character of the spectrum is not altered considerably. If the criteria for $k = k'$ can be established, we can further reduce the free parameters in our model.

4 Conclusion

In summary, a physicist's approach [23] of incoherent energy transfer within an antenna ring is taken by considering a two-parameter two-dimensional model. This model differs from the one presented by Skála *et al.* The reality might be somewhere between these two models. In our model, we numerically found k has to be equal to k'. Furthermore, we are able to calculate analytically some of the eigenvalues and demonstrate explicitly that there is a mode for decaying to the RC and other three modes. However, this result of mode separation depends upon the exact number of unit involved in the ring. Therefore should not be important. Perhaps we should interpret the finding as: P^1_{16}, P^2_{16}, P^3_{16} are redundant, since P^4_{16} contains k_E which should be important. A ring of 16 units is huge. The only purpose for such a large antenna is to accommodate the RC.

Finally we remark that it is possible to extend a two-dimensional random walk model of energy transfer into a quasi-three-dimensional one, in view of the recent structural finding, with a recent result of random walk on bundled structures by Cassi and Regina [24]. Furthermore, this theoretical result should be able to be verified experimentally using its spectral dimension by measurements involving diffusion processes such as time-resolved spectroscopy of nearest-neighbours energy transfer. Other light-harvesting models and mechanisms are under further investigation.

References

1. W. Kühlbrandt, Nature **374**, 497 (1995).
2. X. Hu, K. Schulten, Phys. Today **8**, 28 (1997).
3. G. McDermott, S.M. Prince, A.A. Freer, A.M. Hawthornthwalte-Lawless, M.Z. Papiz, R.J. Cogdell, N.W. Isaacs, Nature **374**, 517 (1995).
4. S. Karrasch, P.A. Bullough, R. Ghosh, EMBO J. **14**, 631 (1995).
5. S.E. Bradforth, R. Jimenez, F. van Mourik, R. van Grondelle, G.R. Fleming, J. Phys. Chem. **99**, 16179 (1995).
6. K. Timpmann, A. Freiberg, V.I. Godik, Chem. Phys. Lett. **182**, 617 (1991).
7. A.Y. Borisov, A.M. Freiberg, V.I. Godik, K.K. Rebane, and K.E. Timpmann, Biochim. Biophys. Acta **807**, 221 (1985).
8. T. Pullerits, A. Freiberg, Biophys. J. **63**, 879 (1992).
9. V. Sundström, R. van Grondelle, H. Bergström, E. Åkesson, T. Gillbro, Biochim. Biophys. Acta **851**, 431 (1986).
10. E.W. Montroll, J. Math. Phys. **10**, 753 (1969).
11. R.P. Hemenger, R.M. Pearlstein, K. Lakatos-Lindenberg, J. Math. Phys. **13**, 1056 (1972).
12. R.M. Pearlstein, Photochem. Photobiol. **35**, 835 (1982).
13. K. Timpmann, F.G. Zhang, A. Freiberg, V. Sundström, Biochim. Biophys. Acta **1183**, 185 (1993).
14. L. Skala, V. Kapsa, Chem. Phys. **137**, 77 (1989).
15. L. Skala, P. Jungwirth, Chem. Phys. **137**, 93 (1989).
16. J. Dvořák, L. Skála, Chem. Phys. **191**, 31 (1995).
17. G.R. Fleming, J.L. Martin, J. Breton, Nature **330**, 190 (1988).
18. J.-L. Martin, J. Breton, A.J. Hoff, A. Migus, A. Antonetti, Proc. Natl. Acad. Sci. USA **83**, 957 (1986).
19. T. Föster, Ann. Phys. **2**, 55 (1948).
20. M.W. Windsor, in *Physics, Chemistry of the Organic Solid States* (Intersciences, New York, 1965), Vol. 2, p. 343.
21. R. van Grondelle, R., Biochim. Biophys. Acta **811**, 147 (1985).
22. J.S. Connolly, E.B. Samuel, A.F. Janzen, Photochem. Photobiol. **36**, 565 (1982).
23. S.M. Gruner, J.S. Langer, P. Nelson, V. Vogel, Phys. Today **12**, 25 (1995).
24. D. Cassi, S. Regina, Phys. Rev. Lett. **76**, 2914 (1996).