

THEORY OF EXCITATION ENERGY TRANSFER IN THE PRIMARY PROCESSES OF PHOTOSYNTHESIS. II. GROUP SYMMETRY ANALYSIS OF THE BACTERIAL LIGHT-HARVESTING COMPLEX

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A group symmetry analysis of the Pauli master equation for the excitation energy transfer in the cyclic arrangement of N ($N=6-36$) antenna Bchl molecules surrounding the bacterial reaction center of *Rhodospseudomonas viridis* is performed. The group theory allows to find analytic expressions for the most important observables (the antenna and reaction center fluorescence intensities and the quantum yield of the transfer to the charge transfer state) and to express their dependence on N . The time dependence of the fluorescence intensities is given by two exponentials, however, a single-exponential approximation can be used for $t > t_0 = 4-25$ ps. The quantum yield of the excitation energy transfer to the reaction center charge transfer state is high (0.71–0.98) for the whole range of physically acceptable values of the Förster radius $R_0 = 46-96$ Å.

1. Introduction

Recently, more detailed information on the structure and geometry of the light-harvesting complexes in the bacterial photosynthetic systems has been obtained (see ref. [1]). In ref. [2], we presented a general theory of the excitation energy transfer in the primary processes of photosynthesis. Geometrical information given in ref. [1] allows to carry out a more detailed analysis of the excitation energy transfer in the bacterial photosynthesis. In this paper we present the symmetry analysis of a simple model of the antenna and reaction center (RC) complex of the purple bacteria *Rhodospseudomonas viridis* and solving the Pauli master equation (PME) we find analytic expressions for the most important observables as a function of the number N of Bchl molecules in the antenna system. This makes possible to answer some important questions regarding the incoherent stage of the excitation energy transfer in the primary processes of bacterial photosynthesis.

2. Model

In our model we take into consideration the following intramolecular processes: fluorescence ($S_1 \rightarrow S_0$ transition), intersystem crossing ($S_1 \rightarrow T_1$) and phosphorescence ($T_1 \rightarrow S_0$). The intermolecular rate constants are calculated from the Förster formula [3]. The processes leading to the electron-hole pair separation are represented by means of the charge transfer state (CT) level. A more detailed description of the model is given in ref. [2].

The geometrical arrangement of the antenna bacteriochlorophyll (Bchl) molecules and RC in the photosynthetic unit (PSU) is based on the information given in ref. [1]. All the Bchl molecules in the antenna system lie in a ring of width ≈ 10 Å and radius $R_C \approx 50$ Å. The spatial arrangement of the Bchl molecules is such that it can with good accuracy be replaced by a cyclic arrangement (see fig. 1). The RC is represented by the special pair (two Bchl molecules).

The incoherent excitation energy transfer is described by the PME (see ref. [2])

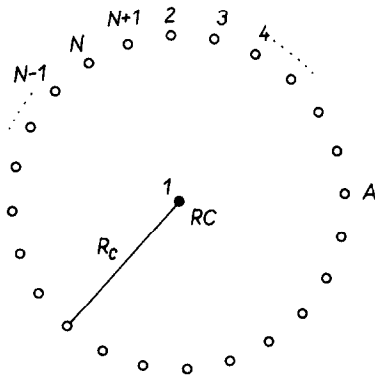


Fig. 1. The geometry of the investigated cyclic model of the PSU. The reaction center RC is surrounded by N antenna Bchl molecules, A, antenna system, $R_C = 50 \text{ \AA}$.

$$\frac{dP_m}{dt} = \sum_n F_{mn} P_n, \quad (1)$$

where $P_m(t)$ are probabilities of finding the S_1 exciton at the RC ($m=1$) or at the m th antenna Bchl molecule ($m=2, \dots, N+1$) and the intermolecular rate constants $F_{mn}=F_{nm}$ ($m \neq n$) will be derived from the Förster rate constant [2,3]

$$k = \frac{3}{2} \frac{[\mathbf{u}_m \cdot \mathbf{u}_n - 3(\mathbf{u}_m \cdot \mathbf{r})(\mathbf{u}_n \cdot \mathbf{r})]^2}{\tau_F (R_0/R)^6}. \quad (2)$$

Here, \mathbf{u}_m and \mathbf{u}_n are the unit vectors giving the direction of the $S_0 \rightarrow S_1$ transition dipole moments of the m th and n th Bchl molecule, respectively. The unit vector along the direction connecting the two molecules is \mathbf{r} , R denotes their distance, $\tau_F = 5 \text{ ns}$ is the fluorescence life time and R_0 is the Förster radius. The transition dipole moments of all the Bchl molecules in the antenna system and RC lie in the plane of the ring [4]. In order to simplify the calculation we assume that the transition dipole moments of the interacting molecules are randomly oriented in this plane. Calculating the corresponding average rate constant we get from eq. (2)

$$k = k(R) = (15/8\tau_F) (R_0/R)^6. \quad (3)$$

The intermolecular rate constants depend on R as $1/R^6$ so that we can simplify the problem by assuming only nearest neighbor interaction among the antennas. The RC consists of the two Bchl molecules so that we take the following values of the rate constants ($m \neq n$):

$$\begin{aligned} F_{mn} &= K = 2k(R_C), & \text{for } m = \text{RC}, n = \text{antenna}, \\ F_{mn} &= k = k(2R_C |\sin(\pi/N)|) & \text{for neighboring antenna molecules,} \\ F_{mn} &= 0, & \text{otherwise.} \end{aligned} \quad (4)$$

The diagonal elements of the matrix F are given by

$$F_{mm} = - \sum_{n(\neq m)} F_{mn} - k_{RC}, \quad m = \text{RC}; \quad F_{mm} = - \sum_{n(\neq m)} F_{mn} - k_A, \quad m \in A. \quad (5)$$

Here,

$$k_{RC} = k_{CT} + k_F^{RC} + k_I^{RC} \quad \text{and} \quad k_A = k_F^A + k_I^A \quad (6)$$

describe the trapping and loss processes in the PSU. The rate constants appearing in eqs. (6) are $k_{CT} = 3.3 \times 10^{11} \text{ s}^{-1}$ (the $S_1 \rightarrow CT$ reaction center state rate constant), $k_F^A = 6.7 \times 10^7 \text{ s}^{-1}$ (the $S_1 \rightarrow S_0$ antenna fluorescence), $k_F^{RC} = 1.34 \times 10^8 \text{ s}^{-1}$ (the $S_1 \rightarrow S_0$ RC fluorescence) and $k_I^A = k_I^{RC} = 1.34 \times 10^8 \text{ s}^{-1}$ (the $S_1 \rightarrow T_1$ antenna and RC intersystem crossing) [2,5]. A denotes the antenna system.

The resulting matrix F has the form

$$F = \begin{pmatrix} -k_{RC} - NK & K & K & K & \dots & K & K \\ K & -k_A - K - 2k & k & 0 & \dots & 0 & k \\ K & k & -k_A - K - 2k & k & \dots & 0 & 0 \\ K & 0 & k & -k_A - K - 2k & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ K & 0 & 0 & 0 & \dots & -k_A - K - 2k & k \\ K & k & 0 & 0 & \dots & k & -k_A - K - 2k \end{pmatrix}. \quad (7)$$

3. Group symmetry analysis

A general solution of eq. (1) can be written as [2]

$$P_m(t) = \sum_{i=1}^{N+1} c_i \exp(\lambda_i t) h_m(i), \quad m=1, \dots, N+1, \quad (8)$$

where λ_i and $h(i) = \{h_m(i), m=1, \dots, N+1\}$ are eigenvalues and eigenvectors of the problem

$$\sum_{n=1}^{N+1} F_{mn} h_n(i) = \lambda_i h_m(i), \quad m=1, \dots, N+1. \quad (9)$$

The coefficients of the linear combination c_i can be determined from the initial values of the probabilities at $t=0$.

In general, the eigenvalue problem (9) has the order $N+1$ and must be diagonalized numerically. It has been shown in ref. [2], however, that the experimental observables depend only on the eigenvalues and eigenvectors of the matrix F corresponding to the unit representation A_1 of the symmetry group. It means that introducing a symmetry-adapted basis and expressing the matrix F in this basis it is sufficient to diagonalize only one block corresponding to the A_1 representation.

The symmetry of the PSU shown in fig. 1 is D_{Nh} [6]. In our case, however, it is sufficient to consider the C_{Nv} group. The representation Γ of the C_{Nv} group corresponding to the matrix F is reducible and contains the unit representation A_1 twice,

$$\Gamma = 2A_1 + \dots \quad (10)$$

Using the projection operator technique [6] we find the following symmetry basis of the A_1 representation:

$$b_1^{(A_1)} = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad b_2^{(A_1)} = N^{-1/2} \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 1 \end{pmatrix}. \quad (11)$$

The block of the matrix F corresponding to this basis equals

$$F_{A_1} = \begin{pmatrix} -NK - k_{RC} & N^{1/2}K \\ N^{1/2}K & -K - k_A \end{pmatrix}. \quad (12)$$

Diagonalizing this matrix we obtain the eigenvalues $\lambda_{1,2}$ and eigenvectors $h(\lambda_{1,2})$ corresponding to the representation A_1 ,

$$\lambda_{1,2} = -\frac{1}{2}[(N+1)K + k_{RC} + k_A] \pm \left\{ \frac{1}{4}[(N+1)K + k_{RC} + k_A]^2 - (NK + k_{RC})(K + k_A) + NK^2 \right\}^{1/2} \quad (13)$$

and

$$h(\lambda_{1,2}) = N_{1,2} \begin{pmatrix} 1 \\ a_{1,2} \\ \vdots \\ a_{1,2} \end{pmatrix}, \quad (14)$$

where

$$a_{1,2} = (NK + k_{RC} + \lambda_{1,2})/NK \quad \text{and} \quad N_{1,2} = (1 + Na_{1,2}^2)^{-1/2} \quad (15)$$

are the normalization factors.

4. Observables

The most important observables characterizing the excitation energy transfer in the primary processes of photosynthesis are the intensities of the antenna and RC fluorescence $I_{\text{F}}^{\text{A}}(t)$ and $I_{\text{F}}^{\text{RC}}(t)$ and the time-dependent quantum yield of the transfer to the CT reaction center state $\eta_{\text{CT}}(t)$ [2],

$$I_{\text{F}}^{\text{A}}(t) = k_{\text{F}}^{\text{A}} \sum_{m=2}^{N+1} P_m(t), \quad I_{\text{F}}^{\text{RC}}(t) = k_{\text{F}}^{\text{RC}} P_1(t), \quad \eta_{\text{CT}}(t) = k_{\text{CT}} \int_0^t P_1(\tau) d\tau. \quad (16)$$

It is assumed in eqs. (16) that only a single photon is absorbed at $t=0$. Definitions of other observables and their relation to those given above are discussed in ref. [2].

If we use eqs. (8), (12)–(19) these observables equal

$$I_{\text{F}}^{\text{A}}(t) = N k_{\text{F}}^{\text{A}} [c_1 N_1 a_1 \exp(\lambda_1 t) + c_2 N_2 a_2 \exp(\lambda_2 t)], \quad (17)$$

$$I_{\text{F}}^{\text{RC}}(t) = k_{\text{F}}^{\text{RC}} [c_1 N_1 \exp(\lambda_1 t) + c_2 N_2 \exp(\lambda_2 t)], \quad (18)$$

$$\eta_{\text{CT}}(t) = k_{\text{CT}} \{c_1 N_1 [\exp(\lambda_1 t) - 1]/\lambda_1 + c_2 N_2 [\exp(\lambda_2 t) - 1]/\lambda_2\}. \quad (19)$$

We see that all the three observables have a very simple double-exponential form despite of the original multi-exponential expression (8). In agreement with general conclusions given in ref. [2], it is the consequence of the invariance of the physical properties of the PSU with respect to the operations of the symmetry group since the observables must be expressed in terms of the states corresponding to the unit representation A_1 and must be therefore double-exponential. The coefficients c_1 and c_2 are given by the initial conditions, i.e. by $P_m(t=0)$.

5. Discussion

Our results will be discussed for three values of the Förster radius R_0 . As the most probable value we assume in agreement with refs. [7,8] $R_0 = 64 \text{ \AA}$. We consider also the smallest and largest physically acceptable values $R_0 = 46 \text{ \AA}$ and $R_0 = 96 \text{ \AA}$ [8].

As the experimentally most probable number of the Bchl molecules in the antenna system we assume $N = 24$ [1,4].

Table 1

The most important results for three values of R_0 and $N=24$. λ_1 and λ_2 are the eigenvalues of the matrix of the rate constants F , c_1N_1 , c_2N_2 , a_1 and a_2 are given in eqs. (17)–(19), η_{CT} denotes the quantum yield $\eta_{CT}(t \rightarrow \infty)$, $\eta_{CT}^e = \eta_{CT}^{e'}(t \rightarrow \infty)$ is the contribution of the single-exponential regime to η_{CT} , ν is the ratio of the probabilities of finding the exciton at the antenna and RC and t_0 is time from which the single-exponential approximation for the fluorescence intensities may be used. R_0 is in Å, λ_1 and λ_2 are in s^{-1} , t_0 is in ps

R_0	λ_1	λ_2	c_1N_1	c_2N_2	a_1	a_2	η_{CT}	η_{CT}^e	ν	t_0
46	-6.41×10^8	-3.41×10^{11}	1.23×10^{-3}	7.57×10^{-2}	31.18	-1.34×10^{-3}	0.709	0.633	749	25
64	-2.86×10^9	-4.10×10^{11}	7.60×10^{-3}	6.93×10^{-2}	5.14	-8.11×10^{-2}	0.934	0.877	123	17
96	-1.00×10^{10}	-1.26×10^{12}	2.95×10^{-2}	4.75×10^{-2}	1.35	-3.07×10^{-2}	0.980	0.974	32	4

The wavelength of the exciting light is large in comparison with the dimensions of the PSU so that we assume that the initial probability of finding the exciton at different Bchl molecules or RC is proportional to the value of their transition dipole moment. As the RC contains two Bchl molecules we suppose $P_1(t=0) = 2/(N+2)$ and $P_m(t=0) = 1/(N+2)$, $m=2, \dots, N+2$. The corresponding values of c_1 and c_2 are given by

$$c_1N_1 + c_2N_2 = 2/(N+2) \quad \text{and} \quad c_1N_1a_1 + c_2N_2a_2 = 1/(N+2). \quad (20)$$

The absolute value of the eigenvalue λ_1 (see table 1) lies in the range $6.4 \times 10^8 - 1.0 \times 10^{10} s^{-1}$. Similarly, $|\lambda_2|$ changes in $3.4 \times 10^{11} - 1.3 \times 10^{12} s^{-1}$. In any case, $|\lambda_2|$ is larger than k_{RC} (see eq. (13)).

The time from which the single-exponential approximation for the fluorescence intensities I_F^A and I_F^{RC} may be used is calculated from the requirement that the contribution of the second term in eqs. (17) and (18) is smaller than 1%,

$$|c_2N_2 \exp(\lambda_2 t_0) / c_1N_1 \exp(\lambda_1 t_0)| = 0.01. \quad (21)$$

The resulting values of $t_0 \approx 4-25$ ps are similar to those obtained in ref. [9]. If a similar criterion for the more intensive antenna fluorescence I_F^A were used we would get $t_0 = 4, 7$ and 1 ps for $R_0 = 46, 64$ and 96 Å, respectively. From the experimental point of view, the single-exponential form of the total fluorescence intensity $I_F^A + I_F^{RC}$ may therefore appear at shorter times than at t_0 given in table 1.

In the single-exponential regime of the transfer ($t > t_0$), the ratio of the total probability of finding the excitation in the antenna system to the probability of finding it at the RC is constant in time and equals $\nu = Na_1$ (for $N=24$ we get $\nu = 749, 123$ and 32 for $R_0 = 46, 64$ and 96 Å, respectively). The larger the Förster radius R_0 and the rate constants, the smaller the ratio ν (the probability of finding the excitation transfers from the antenna

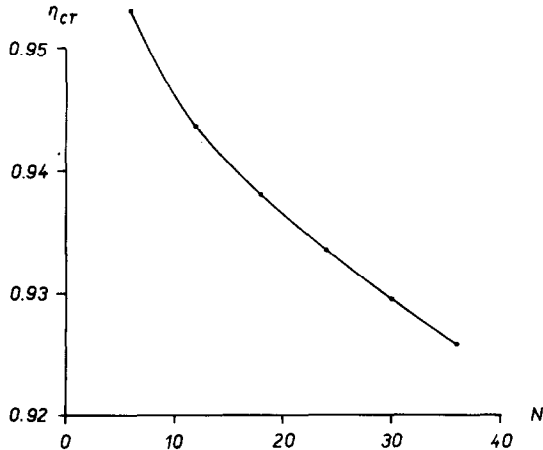


Fig. 2. The quantum yield $\eta_{CT}(t \rightarrow \infty)$ as a function of the number of the Bchl molecules N in the antenna system, $R_0 = 64$ Å.

system to the RC). The eigenvalue λ_1 and the fluorescence life time $\tau = 1/|\lambda_1|$ can be approximately calculated from [2]

$$\lambda_1 = -k_{CT}/(\nu + 1). \quad (22)$$

According to this formula, the fluorescence intensities are for $t > t_0$ single exponentials which time decay is given by the ratio $k_{CT}/(\nu + 1)$.

The quantum yield $\eta_{CT}(t \rightarrow \infty)$ is remarkably high (0.71–0.98). The calculated high efficiency of the transfer to the CT state depends only slightly on the value of R_0 and is a consequence of the large value of the capture rate of the reaction center CT state k_{CT} in comparison with the rate constants k_F^A , k_F^{RC} , k_1^A and k_1^{RC} determining the losses in the PSU. We see also from table 1 that the contribution of the single-exponential regime $\eta_{CT}^{sc}(t \rightarrow \infty) = 0.63\text{--}0.97$ to the total quantum yield $\eta_{CT}(t \rightarrow \infty)$ is dominating in agreement with ref. [2].

The last investigation made in this work is the dependence of the quantum yield $\eta_{CT}(t \rightarrow \infty)$ on the number of the antenna molecules N (see fig. 2) for $R_0 = 64 \text{ \AA}$. We see that due to the very high ratio k_{CT}/k_A ($\approx 10^3$) $\eta_{CT}(t \rightarrow \infty)$ varies only very little on the whole range of the possible values of $N = 12\text{--}36$ [4].

The geometry of the PSU assumed in this work is only approximate and should be improved when new experimental data will be available. Nevertheless, the results of this work show that the quantum yield $\eta_{CT}(t \rightarrow \infty)$ is very high and the single-exponential regime of the excitation energy transfer in the investigated bacterial photosystem is the most significant one both from the point of view of the quantum yield $\eta_{CT}(t \rightarrow \infty)$ and the form of the luminescence intensities. These conclusions are valid for the whole range of the physically acceptable values of the Förster radius $R_0 = 46\text{--}96 \text{ \AA}$.

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