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The role of accessory bacteriochlorophylls in the primary charge transfer in the photosynthetic reaction centers

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Abstract

In this work we present a model to elucidate the unidirectionality of the primary charge separation process in the bacterial reaction centers (RCs) where two symmetric ways of electron transfer (ET), starting from the common electron donor, are possible. We have used a model of three sites/molecules with ET beginning at site 1 with an option to proceed to site 2 or site 3. The dependence of the asymmetry in ET on the value of the sink parameter, introduced through an additional imaginary diagonal matrix element of the Hamiltonian, was investigated. Results show indeed that the unidirectionality of the ET generated in the system of three molecules depends strongly on the value of the energy levels of the accessory bacteriochlorophyll molecules. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The photosynthetic reaction center (RC) [1] is a special pigment–protein complex, which functions as a photochemical trap. The RCs of a purple bacteria are composed of three protein subunits called L, M and H [2,3]. All cofactors involved in the electron transfer (ET) are non-covalently bound to subunits L and M in two chains. Both chains of cofactors start at the bacteriochlorophyll dimer (P) which is interacting with both subunits L and M. Then the cofactor chains are split and each individual one continues on subunit L and symmetrically on subunit M. Cofactors in subunit L are accessory bacteriochlorophyll ($BChl_L$), bacteriopheophytin (BPh_L) and quinone (Q_L). Identically in the M subunit are the accessory

bacteriochlorophyll ($BChl_M$), bacteriopheophytin (BPh_M) and quinone (Q_M). The arrangement of cofactors shows the local twofold symmetry which is almost perfect in the arrangement of the bacteriochlorophyll dimer. The part of the L subunit involved in ET can be superimposed onto corresponding part of the M subunit by a rotation of almost exactly 180°. For more details on structural arrangement, see [4].

The cofactors serve as a donor–acceptor pair in the ET. In spite of the structural symmetry, the RC is functionally highly asymmetric. In the primary charge transfer an electron is transferred from photoexcited special pair P, the starting point for a series of ET reactions across the membrane, to the cofactors on subunit L, to $BChl_L$, BPh_L , Q_L and Q_M [5,6]. On the other hand the chain located on subunit M is inactive in ET. The highly asymmetric functionality, however, can be decreased by amino acid mutations or cofactor modification [7]. The main goal of the present work is to compute

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the probabilities of electronic escape through the branches L and M.

2. Theory

We begin with the von Neumann equation for the density matrix ρ of the total electron-bath system

$$i\frac{\partial}{\partial t}\rho(t)=\frac{1}{\hbar}[H\rho(t)-\rho(t)H^+], \quad (1)$$

where the Hamiltonian H is divided into two parts $H=H_0+V$, (2)

where

$$H_0=\sum_{i=1}^n[h_i(\vec{R})+\varepsilon_i-i\Gamma_i]a_i^+a_i, \quad (3)$$

$$V=\sum_{\substack{i,j=1 \\ i\neq j}}^nV_{ij}(a_i^+a_j+\text{h.c.}). \quad (4)$$

We assume that the total statistical system described by the density matrix ρ consists of a system of interest (electrons) and a bath (molecules of the environment). V is a perturbation causing a transition between the eigenstates of H_0 . The ε_i and $a_i^+(a_i)$ are the site energy and the creation (annihilation) operator of the electron at site i . The parameter $\hbar/2\Gamma_i$ has a meaning of the lifetime of the electron localization at the site i in the limit of zero coupling parameter. We denote the solvent Hamiltonian when the electron is at site i by $h_i(\vec{R})$. \vec{R} denotes the coordinates of the position and orientation of the solvent molecules. We assume that

$$h_i(\vec{R})-h_j(\vec{R})=\Delta_{ij}+W_{ij}(t). \quad (5)$$

$W_{ij}(t)$ is taken to be a Gaussian–Markovian process with zero mean, and correlation function

$$\langle W_{ij}(t)W_{ij}(\tau)\rangle=\left\langle\xi_{ij}^2\right\rangle_{slv}\exp(-|t-\tau|/\tau_{ij}^e). \quad (6)$$

We start from the von Neumann equation and designate

$$\begin{aligned} \rho_I(t)=&\left[\vec{T}\exp\left(\frac{i}{\hbar}\int_0^tH_0(\tau)d\tau\right)\right]\rho(t) \\ &\times\left[\bar{\vec{T}}\exp\left(-\frac{i}{\hbar}\int_0^tH_0^+(\tau)d\tau\right)\right], \end{aligned} \quad (7)$$

$$\begin{aligned} V_I(t)=&\left[\vec{T}\exp\left(\frac{i}{\hbar}\int_0^tH_0(\tau)d\tau\right)\right]V(t) \\ &\times\left[\bar{\vec{T}}\exp\left(-\frac{i}{\hbar}\int_0^tH_0(\tau)d\tau\right)\right]. \end{aligned} \quad (8)$$

$\vec{T}(\bar{\vec{T}})$ is a time ordering operator ordering the later times to the right (left). The von Neumann equation for the density matrix in the interaction picture reads

$$\begin{aligned} i\frac{\partial}{\partial t}\rho_I(t)=&\frac{1}{\hbar}[V_I(t)\rho_I(t)-\rho_I(t)V_I^+(t)] \\ &=L(t)\rho_I(t), \end{aligned} \quad (9)$$

where $L(t)$ is the Liouville operator in the interaction picture. Now using standard projection techniques [8–10] we get

$$\frac{\partial}{\partial t}D\rho_I(t)=-DL(t)\int_0^tL(\tau)D\rho_I(\tau)d\tau. \quad (10)$$

We are using the projector in the form

$$(DA)_{mn}=\delta_{mn}\langle A_{mm}\rangle.$$

The bracket $\langle\rangle$ is the ensemble average over the solvent motion. For Eq. (10) we take the matrix elements $\langle a|\cdots|a\rangle$, $|a=1,2,\dots,n\rangle$ are the eigenstates of H_0 . We get

$$\begin{aligned} \frac{\partial P_a(t)}{\partial t}=&-\frac{2\Gamma_a}{\hbar}P_a(t)-\sum_{b(\neq a)}\frac{2|V_{ab}|^2}{\hbar^2} \\ &\times\int_0^t\cos\left[\frac{\varepsilon_a-\varepsilon_b+\Delta_{ab}}{\hbar}(t-\tau)\right]\Theta_{ab}(t-\tau) \\ &\times\exp\left[-\frac{\Gamma_a+\Gamma_b}{\hbar}(t-\tau)\right] \\ &\times\{P_a(\tau)-P_b(\tau)\}d\tau, \end{aligned} \quad (11)$$

where

$$P_a(t)=\langle\rho_{aa}(t)\rangle,$$

$$\Theta_{ab}(t)=\exp\left(-\frac{\Gamma_{ab}^e}{\hbar}\left\{t-\tau_{ab}^e\left[1-\exp\left(-\frac{t}{\tau_{ab}^e}\right)\right]\right\}\right),$$

$$a,b=1,\dots,n.$$

Here $\Gamma_{ab}^e=\langle\xi_{ab}^2\rangle\tau_{ab}^e/\hbar$. We will work in the limit of short correlation time of the solvent. It is in accordance with molecular dynamic simulations [11]. In this limit we assume that $\Gamma_{ab}^e\tau_{ab}^e/\hbar\ll 1$.

3. Model of RC

To describe the first steps of ET processes in the RCs we have used the three-sites model. Let us designate the special pair (P) as site 1, the sites 2 and 3 then represent the molecules of accessory bacteriochlorophyll on the branches M and L. We assume that the hopping terms between molecule 1 and molecule 2 or 3 on both branches are the same. We forbid the direct ET between sites 2 to 3. We assume that the energy levels 2 and 3 have imaginary part which describes the interaction with the next molecule in the branch. The imaginary part of the energy level 1 describes the probability of electron deactivation to the ground state. In this three-sites model, Eq. (11) has the form

$$\begin{aligned} \frac{\partial P_1(t)}{\partial t} = & -\frac{2\Gamma_1}{\hbar}P_1(t) - \frac{2J^2}{\hbar^2} \int_0^t \cos\left[\frac{\varepsilon_M}{\hbar}(t-\tau)\right] \\ & \times \exp\left[-\frac{\Gamma_1 + \Gamma_2 + \Gamma_M}{\hbar}(t-\tau)\right] \\ & \times \{P_1(\tau) - P_2(\tau)\} d\tau \\ & - \frac{2J^2}{\hbar^2} \int_0^t \cos\left[\frac{\varepsilon_L}{\hbar}(t-\tau)\right] \\ & \times \exp\left[-\frac{\Gamma_1 + \Gamma_3 + \Gamma_L}{\hbar}(t-\tau)\right] \\ & \times \{P_1(\tau) - P_3(\tau)\} d\tau, \end{aligned} \quad (12a)$$

$$\begin{aligned} \frac{\partial P_2(t)}{\partial t} = & -\frac{2\Gamma_2}{\hbar}P_2(t) - \frac{2J^2}{\hbar^2} \int_0^t \cos\left[\frac{\varepsilon_M}{\hbar}(t-\tau)\right] \\ & \times \exp\left[-\frac{\Gamma_1 + \Gamma_2 + \Gamma_M}{\hbar}(t-\tau)\right] \\ & \times \{P_2(\tau) - P_1(\tau)\} d\tau, \end{aligned} \quad (12b)$$

$$\begin{aligned} \frac{\partial P_3(t)}{\partial t} = & -\frac{2\Gamma_3}{\hbar}P_3(t) - \frac{2J^2}{\hbar^2} \int_0^t \cos\left[\frac{\varepsilon_L}{\hbar}(t-\tau)\right] \\ & \times \exp\left[-\frac{\Gamma_1 + \Gamma_3 + \Gamma_L}{\hbar}(t-\tau)\right] \\ & \times \{P_3(\tau) - P_1(\tau)\} d\tau, \end{aligned} \quad (12c)$$

where we denote $\varepsilon_L = \varepsilon_1 - \varepsilon_3 + \Delta_{13}$, $\varepsilon_M = \varepsilon_1 - \varepsilon_2 + \Delta_{12}$, $\Gamma_L = \Gamma_{13}^e$, $\Gamma_M = \Gamma_{12}^e$ and $V_{12} = V_{13} = J$. The quantum yield (QY) Φ_i of the electronic escape via the site i can be characterized by the expression [12]

$$\begin{aligned} \Phi_i &= \frac{2\Gamma_i}{\hbar} \int_0^\infty P_i(t) dt \\ &= \frac{2\Gamma_i}{\hbar} \lim_{p \rightarrow 0^+} \tilde{P}_i(p), \quad i = 1, 2, 3, \end{aligned} \quad (13)$$

where $\tilde{P}_i(p)$ is the Laplace transformation of $P_i(t)$. The quantum yields Φ_i must fulfill the expression $\Phi_1 + \Phi_2 + \Phi_3 = 1$. It means that electron can escape from the system through the branch L, M or the system decay to the ground state which characterize the quantity Φ_1 . Assuming the initial conditions

$$P_1(0) = 1, \quad P_2(0) = P_3(0) = 0,$$

we can solve Eqs. (12a)–(12c) in Laplace transformation. Using the solution, we can compute the quantum yields. Generally the analytical results are cumbersome. Here we present some special cases where we describe the main characteristics of the process. We assume that $\Gamma_1 = 0$, $\Gamma_2 = \Gamma_3 = \Gamma$. In this case we compute parameter $K = \Phi_3/\Phi_2$ that characterized the ratio between the probability of electronic escape through the L and M branches of RC. We have

$$K =$$

$$\frac{(\Gamma + \Gamma_L)[J^2(\Gamma + \Gamma_M) + \Gamma(\Gamma^2 + 2\Gamma\Gamma_M + \Gamma_M^2 + \varepsilon_M^2)]}{(\Gamma + \Gamma_M)[J^2(\Gamma + \Gamma_L) + \Gamma(\Gamma^2 + 2\Gamma\Gamma_L + \Gamma_L^2 + \varepsilon_L^2)]}. \quad (14)$$

We can see that at $\Gamma \rightarrow \infty$ is $K \approx 1$. It means that when the electron escapes from the system very quickly the asymmetry of the electron distribution cannot be achieved. For a very slow escape, when $\Gamma \rightarrow 0$ and $\Gamma_L = \Gamma_M = 0$, we get

$$K = \frac{J^2 + \varepsilon_M^2}{J^2 + \varepsilon_L^2}. \quad (15)$$

At this limit steady state does not exist. The asymmetry in the electron distribution is caused by the asymmetry arrangement of the energy levels.

If Γ_L , Γ_M are not zero the system can achieve the steady state. The probability to find electron at sites 2 and 3 is raising asymmetrically. From Eq. (13) we can see that the probability of electronic escape depends on the history of the system. Because the steady state is fully symmetric in this case the asymmetry in the quantum yields depends on

the parameters which caused the asymmetry in the relaxation and does not depend on the steady state. For large ε_L , ε_M from Eq. (14) we get

$$K = \frac{(\Gamma + \Gamma_L)\varepsilon_M^2}{(\Gamma + \Gamma_M)\varepsilon_L^2}. \quad (16)$$

At this limit asymmetry in the relaxation is caused by the asymmetry in parameters which characterized the energy level fluctuations. For large Γ_L , Γ_M we have

$$K = \frac{\Gamma_M}{\Gamma_L}. \quad (17)$$

In this case the electron is transported mainly through the branch with smaller fluctuation of the energy level. For small Γ and large Γ_L , Γ_M when conditions $J^2\Gamma_L \gg \Gamma(\Gamma_L^2 + \varepsilon_L^2)$ and $J^2\Gamma_M \gg \Gamma(\Gamma_M^2 + \varepsilon_M^2)$ are fulfilled we have ET with $K \sim 1$. At this limit the system reached the steady state very fast. The quantum yields are determined by the steady state. We have the same probability of the electronic escape through the branches L and M. From Eqs. (14)–(17) we can see that the main effect on the unidirectionality of ET has asymmetry of the energy levels. The quantum yields do not depend on the sign of the energy level.

The implementation of the theory requires information regarding energetic parameters, such as the energy gap between the equilibrium nuclear configuration between P^* and $P^+BChl_{L(M)}^-$ which, in spite of recent progress, cannot be reliably calculated. The energy level of $P^+BChl_L^-$ in RCs of *Rb. sphaeroides* is about 50 meV below P^* [13]. Another calculation shows that this energy level is about 30 meV above the special pair [14]. Theoretical calculation, using the *Rp. viridis* RC crystal structure suggested that the $P^+BChl_M^-$ state is 240 meV higher than P^* [15]. The $(200 \text{ ps})^{-1}$ P^* internal conversion rate is the average of the values of $(90\text{--}350 \text{ ps})^{-1}$ that have been estimated from measurements in wild-type (WT) RCs [13]. The decay time of $P^+BChl_L^-$ in *Rp. viridis* is 0.65 ps [13]. The transfer integral J is estimated to be about 2.5 meV [16–18]. We have chosen the next parameters which characterized the WT of RC in our model. The energy levels are $\varepsilon_M = 250 \text{ meV}$, $\varepsilon_L = 50 \text{ meV}$, hopping term is $J = 2.5 \text{ meV}$, rate constants are $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = 2\Gamma/\hbar \approx (0.65 \text{ ps})^{-1}$.

We assume, as in [16], that Γ_1 is smaller than the Γ_2 , Γ_3 by about two orders of magnitude. This also followed from experimental data [13,19]. We used in computations the next values of parameters which characterized the noise and the decay of the system to the ground state: $\Gamma_L = \Gamma_M = 25 \text{ meV}$ and $2\Gamma_1/\hbar = (200 \text{ ps})^{-1}$ for wild type (WT) of RC. We get the following quantum yields for WT of RC in our simulation: $\Phi_1 = 0.03$, $\Phi_2 = 0.05$, $\Phi_3 = 0.92$.

4. ET reactions in modified RC

The highly asymmetric functionality can be changed by amino acid mutations or cofactor modifications [7,13,20–26]. These mutants have provided insights into key factors impacting the directionality and yields of ET in the RC by changing the relative free energies of the participating states. ET to the L- versus the M-sides in the RC may be substantially modulated by the relative free energies of $P^+BChl_L^-$ and $P^+BChl_M^-$.

A drastically reduced quantum yield is observed in RCs where substantially different chromophores were in the different binding pockets of the electron acceptors. In [23] ET in a series of *Rhodobacter capsulatus* RC mutants is reported. In the G(M201)D/L(M212)H double mutant 15% ET to M-side bacteriopheophytin, 70% ET to the L-side cofactors and 15% deactivate to the ground state. It is proposed that the Asp at M201 raised the free energy of $P^+BChl_L^-$. In the S(L178)K/G(M201)D/L(M212)H triple mutants 62% ET to the L-side BPh, 23% ET to the M-side bacteriopheophytin and 15 % return to the ground state. In the S(L178)K/G(M201)D/L(M212)H triple mutants the S(L178)K mutation might lower $P^+BChl_M^-$ in free energy and increasing the yield of ET to BPh_M in comparison to the G(M201)D/L(M212)H double mutant. ET along the M-side was observed in the H(M182)L mutant of *Rb. sphaeroides* [24]. In this mutant bacteriopheophytin (referred to as Φ_M) is incorporated in place of $BChl_M$. One would expect that the $P^+\Phi_M^-$ state would be considerably lower in energy than $P^+BChl_M^-$, thus enhancing the probability of M-side ETs. The yield of the $P^+\Phi_M^-$ state is apparently 30–40%.

The exchange of histidine to leucin in RCs of *Rp. viridis* (mutant denoted as L153HL) caused the incorporation of a bacteriopheophytin b instead of a bacteriochlorophyl b molecule (referred to as B_L). As a consequence of this chromophore exchange, the energy level of the ET state $P^+B_L^-$ is lowered in comparison to $P^+BChl_L^-$ in WT. The quantum yield of $P^+B_L^-$ in this mutant is reduced to 50%.

When we increase the energy ε_L in the theoretical simulations, as in the G(M201)D/L(M212)H *Rhodobacter capsulatus* RC double mutants, we get the following QY: $\Phi_1 = 0.14$, $\Phi_2 = 0.14$, $\Phi_3 = 0.72$. We use the parameters: $\varepsilon_M = 250$ meV, $\varepsilon_L = 100$ meV, $J = 2.5$ meV, $2\Gamma_2/\hbar = (0.65 \text{ ps})^{-1}$, $2\Gamma_3/\hbar = (3.25 \text{ ps})^{-1}$, $\Gamma_L = \Gamma_M = 25$ meV, $2\Gamma_1/\hbar = (130 \text{ ps})^{-1}$. If we decrease the energy ε_M as in S(L178)K/G(M201)D/L(M212)H triple mutant in comparison to double mutant we get the following QY: $\Phi_1 = 0.13$, $\Phi_2 = 0.20$, $\Phi_3 = 0.67$. We use the parameters: $\varepsilon_M = 200$ meV, $\varepsilon_L = 100$ meV, $J = 2.5$ meV, $2\Gamma_2/\hbar = (0.65 \text{ ps})^{-1}$, $2\Gamma_3/\hbar = (3.25 \text{ ps})^{-1}$, $\Gamma_L = \Gamma_M = 25$ meV, $2\Gamma_1/\hbar = (130 \text{ ps})^{-1}$. We lowered here the rate from molecules 3 which agree with experimental results [7,23].

When we considerably decrease the energy ε_M in comparison to WT as in the H(M182)L mutant of *Rb. sphaeroides* where bacteriopheophytin is incorporated in place of $BChl_M$ we get the following QY: $\Phi_1 = 0.04$, $\Phi_2 = 0.33$, $\Phi_3 = 0.63$. We use the parameters: $\varepsilon_M = -75$ meV, $\varepsilon_L = 50$ meV, $J = 2.5$ meV, $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = (0.65 \text{ ps})^{-1}$, $\Gamma_M = \Gamma_L = 25$ meV, $2\Gamma_1/\hbar = (130 \text{ ps})^{-1}$.

When we considerably decrease the energy ε_L in comparison to WT as in the L153HL mutant of *Rp. viridis* where bacteriopheophytin is incorporated in place of $BChl_L$ we get the following QY: $\Phi_1 = 0.16$, $\Phi_2 = 0.42$, $\Phi_3 = 0.42$. We use the parameters: $\varepsilon_M = 225$ meV, $\varepsilon_L = -225$ meV, $J = 2.5$ meV, $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = (0.65 \text{ ps})^{-1}$, $\Gamma_M = \Gamma_L = 25$ meV, $2\Gamma_1/\hbar = (260 \text{ ps})^{-1}$.

5. Conclusions

This Letter addresses a specific problem of the highly asymmetric ET in the photosynthetic RCs.

Because of very fast primary charge separation process we use the stochastic model with the memory functions equally for the forward and backward ETs. When conditions $\Gamma_2 = \Gamma_3 = \Gamma_1 = 0$, $\Gamma_M \neq 0$ and $\Gamma_L \neq 0$ are fulfilled we get the fully symmetric steady state. It means that electron occupation probabilities $P_i(t)$ relax to the equilibrium distribution $P_i(\infty) = 1/3$. When one of the parameters Γ_M , Γ_L is also zero, for instance, $\Gamma_M = 0$ we have an asymmetric steady state with equilibrium occupation probabilities $P_1(\infty) = P_3(\infty) = (\varepsilon_M^2 + 2J^2)/\{2(\varepsilon_M^2 + 3J^2)\}$ and $P_2(\infty) = J^2/(\varepsilon_M^2 + 3J^2)$. At this limit when $\varepsilon_M = 0$ the fully symmetric steady state is restored. On the other hand when $\varepsilon_M^2 \gg J^2$ we get $P_1(\infty) = P_3(\infty) \rightarrow 1/2$ and $P_2(\infty) \rightarrow 0$. In this case the M-branch is practically inactive and we get the steady state as in the stochastic two-sites models [27–30].

Extensive experimental efforts have been devoted to elucidation of the role of accessory bacteriochlorophyll molecules. At least two alternative models have been proposed for the role of these molecules [18]. In our model we considered that the electron is delocalized to the molecules P, $BChl_M$ and $BChl_L$. Electron density depends on the parameters which characterized the three-molecules system. The data show that the free energy of the intermediates $P^+BChl_L^-$, $P^+BChl_M^-$ is of major importance. For instance, if the free energy of $P^+BChl_L^-$ is raised relative to that of WT RC (as, likely, if negative charge is introduced in the mutant L153HE), the quantum efficiency is lowered considerably. In our work we have showed that there is a correlation between shift of energy levels of accessory bacteriochlorophyll molecules and quantum yields. Theoretical simulations are in correspondence with experimental results. The influence of energy fluctuations must not be neglected. When we assume asymmetry in the parameters which characterized the fluctuations ($\Gamma_M = 0$, $\Gamma_L = 25$ meV) we get the following quantum yields in WT of RC: $\Phi_1 = 0.034$, $\Phi_2 = 0.001$, $\Phi_3 = 0.965$. To elucidate the unidirectionality the Markovian approximation was used in the previous Letters. It must not be proper for describing the primary charge transfer processes in the RC. In [31,32] it was shown that different hopping terms (ET integrals)

in the branches can result in the asymmetry of charge separation across the L and M branches of the RC. In the present work we have demonstrated that for the asymmetric ET it is not sufficient to consider only an asymmetry in ET integrals. For example, in the case of small Γ , the system approaches to the quasi-steady state, where asymmetry is determined by equilibrium electron density distribution and does not depend on an ET integral.

We have mutants, where hopping integrals are not changed significantly, and unidirectionality is lowered considerably [20]. It is in contradiction with [33], where the unidirectionality is explained only through the asymmetry of the transfer integrals in the L- and M-regions. The results of [34] suggest that the dimer is playing the decisive role in the vectorial charge separation. There are mutations where the dimer is not changed and we have strong changes in unidirectionality [7,23,25]. The hopping terms asymmetry contributes to unidirectionality. It was not assumed in our work.

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