

# Electron Transfer and Quantum Yields of Charge separation in Bacterial Photosynthetic Reaction Centers

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**Abstract.** A description of electron transfer (ET) by the incoherent sequential model was employed to elucidate the unidirectionality of the primary charge separation process in bacterial photosynthetic reaction centers (RC). Analysis shows that employed model can successfully explain the asymmetry of primary electron transfer both in the wild type ( WT ) of RC and F(L121)D mutant of *Rhodobacter capsulatus* reaction centers. The dependence of the asymmetry of the electron transfer on the temperature was also evaluated.

## 1 Introduction

The problem of bacterial photosynthesis has attracted much interest since the reaction centre (RC) of bacteria provides an interesting system for studying a high-efficiency electron transfer in an organized molecular complex. The photosynthetic reaction centre [1] is a special pigment-protein complex, which functions as a photochemical trap. The reaction centres (RC) of a purple bacteria are composed of three protein subunits called L, M and H [2,3]. All cofactors involved in the 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 ( $B_L$ ), bacteriopheophytin ( $H_L$ ) and quinone ( $Q_L$ ). Identically in the M subunit are the accessory bacteriochlorophyll ( $B_M$ ), bacteriopheophytin ( $H_M$ ) and quinone ( $Q_M$ ). The arrangement of cofactors shows the local twofold symmetry. For more details on structural arrangement, see [4](Fig. 1). The cofactors serve as a donor-acceptor pairs in the electron transfer. In spite of the structural symmetry, the RC is functionally highly asymmetric. To describe the asymmetry of ET it was assumed that the first step of primary ET in bacterial photosynthesis has hot character [5,6]. It means that ET is so fast that system does not have sufficient time to relax to the thermal equilibrium. In this paper we attempt to analyse the possibility that ET asymmetry can be described by incoherent sequential model which assumes, contrary to the coherent model, that there exist the vibrational modes which has a sufficient time for relax to the thermal equilibrium after each ET step.

**Fig.1.** The RC of a purple bacteria are composed of three protein subunits called L,M and H. Dimer P is describing by molecule 2. Cofactors in the subunits L are: 3 represent ( $B_L$ ) molecule 4 ( $H_L$ ) and 5 is ( $Q_L$ ) and identically in the subunits M. Molecule 1 describes Cytochrom C which serve as a source of electrons for RC.

## 2 Model of RC

To describe the first steps of electron transfer processes in the reactions centres we have used the 6-sites model. Similar model was developed in the work [7]. We designate the special pair  $P$  as site 1, the sites 2 and 3 represent the molecules  $B_M$  and  $B_L$ , the sites 4 and 5 then represent the molecules  $H_M$  and  $H_L$ . Site 6 represent the quinone molecule  $Q_L$  (Fig. 2). We consider that this system is coupled to a bath (medium). Based on experimental observations of ET in RC it is expected that bacteriochlorophyll play a crucial role in ET. In this 6-sites model we have assumed that ET in RC is sequential where  $P^+B^-$  is a real chemical intermediate and also that the repopulation of accessory bacteriochlorophyll ( $B_L$ ) from molecule of bacteriopheophytin ( $H_L$ ) is possible because of the small energy difference between states  $P^+B_L^-$  and  $P^+H_L^-$  in mutation F(L121)D [12]. The repopulation of accessory bacteriochlorophyll ( $B_M$ ) from molecule of bacteriopheophytin ( $H_M$ ) is neglected because of the large energy difference between molecules. The imaginary part of energy level 1 describes the probability of electron deactivation to the ground state. Another imaginary parts of energy levels are neglected. We describe the ET in RC by the following kinetic model

**Fig.2.** Kinetic scheme for the primary electron transfer in bacterial photosynthetic reaction centers.

$$\begin{aligned}
\partial_t P_1(t) = & -\frac{2\Gamma_1}{\hbar} P_1(t) - \int_0^t W_{12}(t-\tau) P_1(\tau) d\tau \\
& - \int_0^t W_{13}(t-\tau) P_1(\tau) d\tau + \int_0^t W_{21}(t-\tau) P_2(\tau) d\tau \\
& + \int_0^t W_{31}(t-\tau) P_3(\tau) d\tau
\end{aligned} \tag{1a}$$

$$\begin{aligned}
\partial_t P_2(t) = & - \int_0^t W_{24}(t-\tau) P_2(\tau) d\tau - \int_0^t W_{21}(t-\tau) P_2(\tau) d\tau \\
& + \int_0^t W_{12}(t-\tau) P_1(\tau) d\tau
\end{aligned} \tag{1b}$$

$$\begin{aligned}
\partial_t P_3(t) = & - \int_0^t W_{35}(t-\tau) P_3(\tau) d\tau - \int_0^t W_{31}(t-\tau) P_3(\tau) d\tau \\
& + \int_0^t W_{13}(t-\tau) P_1(\tau) d\tau + \int_0^t W_{53}(t-\tau) P_5(\tau) d\tau
\end{aligned} \tag{1c}$$

$$\begin{aligned}
\partial_t P_5(t) = & - \int_0^t W_{53}(t-\tau) P_5(\tau) d\tau - \int_0^t W_{56}(t-\tau) P_5(\tau) d\tau \\
& + \int_0^t W_{35}(t-\tau) P_3(\tau) d\tau
\end{aligned} \tag{1d}$$

Where  $P_i(t)$  is occupation probability of site  $i$  and  $W_{ij}(t)$  is a memory function [7].

### 3 Electronic escape through the branches

The quantum yields (QY's)  $\phi_L$ ,  $\phi_M$  of electronic escape via branch L, M and the quantum yields  $\phi_G$  of direct ground state recombination can be characterized by the expressions

$$\phi_G = \frac{2\Gamma_1}{\hbar} \int_0^\infty P_1(t) dt = \frac{2\Gamma_1}{\hbar} P_1(s \rightarrow 0^+) \tag{2a}$$

$$\phi_M = \int_0^\infty \int_0^t W_{24}(t-\tau) P_2(\tau) d\tau dt = k_{24}(s \rightarrow 0^+) P_2(s \rightarrow 0^+) \tag{2b}$$

$$\phi_L = \int_0^\infty \int_0^t W_{56}(t-\tau) P_5(\tau) d\tau dt = k_{56}(s \rightarrow 0^+) P_5(s \rightarrow 0^+) \tag{2c}$$

where  $P_i(s)$ ,  $k_{ij}(s)$  are the Laplace transformation of  $P_i(t)$  and  $W_{ij}(t)$ . The quantum yields must fulfill the expression  $\phi_G + \phi_M + \phi_L = 1$ . We assume that the memory function which characterize ET can be described by both a low frequency medium vibrational mode and a high frequency intramolecular

vibrational mode. At a high temperature regime the constant  $k_{ij}(s \rightarrow 0^+)$  is in the form [8]:

$$k_{ij} = \int_0^\infty W_{ij}(t)dt = \frac{2\pi}{\hbar} V_{ij}^2 \left( \frac{1}{4\pi\lambda_{mij}k_B T} \right)^{1/2} \exp(-S_{cij}) \times \sum_{n=0}^\infty \frac{S_{cij}^n}{n!} \exp\left[ \frac{(G_{ji} + \lambda_{mij} + n\hbar\omega_{cij})^2}{4\lambda_{mij}k_B T} \right] \quad (3)$$

Here,  $G_{ij} = \epsilon_i - \epsilon_j$  and  $S_{cij} = \frac{1}{2\hbar} m_{cij} \omega_{cij} (d_{ci} - d_{cj})^2$  is the scaled reorganization constant for the high frequency  $ij$ -th mode which is nonzero when electron is transferring from state  $|i\rangle$  to state  $|j\rangle$ , and  $\lambda_{mij} = \frac{1}{2} m_{mij} \omega_{mij}^2 (d_{mi} - d_{mj})^2$  is the reorganization energy of the low-frequency mode when electron is transferring from state  $|i\rangle$  to state  $|j\rangle$ . In derivation of constants  $k_{12}$ ,  $k_{13}$  it was assumed that  $\Gamma_1 \ll \hbar\omega_{12}, \hbar\omega_{13}$ . For our goals these two parameters are of principal importance

$$K = \frac{\Phi_L}{\Phi_M}, \quad R = \frac{\Phi_L}{\Phi_G} \quad (4)$$

which express the asymmetry in probabilities of electronic escape through branches  $L$  and  $M$ . We can solve equation (1) in Laplace transformation. Using this solution, we have

$$K = \frac{k_{13}(\exp(\frac{-G_{12}}{k_B T})k_{12} + k_{24})k_{35}k_{56}}{k_{12}k_{24}[k_{35}k_{56} + \exp(\frac{-G_{13}}{k_B T})k_{13}(\exp(\frac{-G_{35}}{k_B T})k_{35} + k_{56})]} \quad (5)$$

$$R = \frac{k_{13}k_{35}k_{56}}{\frac{2\Gamma_1}{\hbar}[k_{35}k_{56} + \exp(\frac{-G_{13}}{k_B T})k_{13}(\exp(\frac{-G_{35}}{k_B T})k_{35} + k_{56})]} \quad (6)$$

Here we denote  $k_{ij}(s \rightarrow 0^+)$  as  $k_{ij}$ . It was assumed that electron is localized on the first molecule at initial time. The implementation of the theory, requires information regarding energetic parameters, the medium reorganization energies, the high frequency modes, low frequency modes and electronic coupling constants. We utilize the following parameters to describe the electron transfer in wild type (WT) of reaction centers [9,10]: the high frequency modes have the same value  $\hbar\omega_{cij} = 1500cm^{-1}$  besides one which is  $\hbar\omega_{c56} = 1600cm^{-1}$ , values  $V_{12} = V_{13} = 32cm^{-1}, V_{24} = V_{35} = 59cm^{-1}$  and  $V_{56} = 4.8cm^{-1}$  for the electronic coupling constants and  $S_{cij} = 0.5$  for the scaled reorganization constants for the high frequency  $ij$ -th mode with only one distinguished value which is  $S_{c56} = 1$ . The energetic parameters for WT of RC at room temperature are:  $\epsilon_1 = 0$ ,  $\epsilon_3 = -450cm^{-1}$ ,  $\epsilon_2 = 800cm^{-1}$ ,  $\epsilon_4 = -1000cm^{-1}$ ,  $\epsilon_5 = -2000cm^{-1}$ ,  $\epsilon_6 = -7200cm^{-1}$  and the medium's low

frequency vibrational modes have the same value for each step of electron transfer  $\lambda_{mij} = 800cm^{-1}$  except one  $\lambda_{m56} = 4800cm^{-1}$ . The P\* internal conversion rate is  $\frac{2T_1}{h} = (170ps)^{-1}$ . We assume similarly as in work [11] for WT of RC that the free energy of  $P^+H_M^-$  is about  $1000cm^{-1}$  above  $P^+H_L^-$ . In this case the *M*-branch is practically inactive. In a series of Rhodobacter capsulatus RC mutants [12] the F(L121)D mutant shows 78% of electron transfer to the L-side cofactors and 22% recombination to the ground state at room temperature. The suggested model for the F(L121)D mutant assumed that the  $P^+H_L^-$  has higher free energy than in wild-type of RCs and so we had to increase the energy  $\epsilon_5$  from the value  $\epsilon_5 = -2000cm^{-1}$  to the value  $\epsilon_5 = -450cm^{-1}$ . To characterize the structural changes on the *L* branch in the F(L121)D mutant we also slightly change the free energy of the  $P^+B_L^-$  state and in computation we used the value  $\epsilon_3 = -350cm^{-1}$ . Experimental observations in the F(L121)D mutant at low temperature (77K) show 88% quantum yield via the L-side in comparison to 78% at room temperature. The results of our numerical computations for WT and mutant RC's are collected in the Table 1. In both branches only the incoherent sequential mechanism was assumed.

Table 1: Computed constants  $1/k_{ij}$  and quantum yields for wild type and F(L121)D mutant of RC's.

Sample	T	$\epsilon_3$	$\epsilon_5$	$1/k_{12}$	$1/k_{24}$	$1/k_{13}$	$1/k_{35}$	$1/k_{56}$	$\Phi_G$	$\Phi_M$	$\Phi_L$
	(K)	( $cm^{-1}$ )	( $cm^{-1}$ )	(ps)	(ps)	(ps)	(ps)	(ps)			
WT	295	-450	-2000	96.7	1.02	2.35	0.9	200	0.01	0.02	0.97
	200			508	1.2	2.11	1.1	186	0.013	0.002	0.985
F(L121)D	295	-350	-450	96.7	1.02	2.65	1.2	205	0.11	0.13	0.76
	200			508	1.2	2.53	1.42	195	0.07	0.02	0.91

## 4 Conclusions

We have not included superexchange mechanism of ET into our model because it was showed in the work [7] that it have not considerable effect on the QY's at high temperature regime. The change of the free energy of the states  $P^+B_L^-$ ,  $P^+B_M^-$  significantly influence the QY's. The free energies arrangement can be verified by the determination of the temperature dependence of QY's. For this purpose we have used the present model to predict the change of QY's with temperature. We get the results which are in a good agreement with observed data at high temperature regime and could elucidate observed data also in the low temperature regime (77K). To get the numerical results at low temperature regime we have to used the formula for  $k_{ij}$  where also the low frequency mode is described quantum mechanically and consequently compare computed results with the observed quantum yields [11–13]. Application of incoherent sequential model to ET in some mutants of RC can not

describe the directionality of ET and it can also indicate that ET in RC can have coherent or hot character at the first stage [5,6,14].

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