

Modeling charge transfer in the photosynthetic reaction center

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In this work, we present a model to elucidate the unidirectionality of the primary charge-separation process in the bacterial reaction centers. We have used a model of three sites/molecules with electron transfer beginning at site 1 with an option to proceed to site 2 or site 3. We used a stochastic model with arbitrary correlation functions. We get the quantum yields of electron escape via the sites 2,3 in two limiting cases that correspond to a spectral density of underdamped and overdamped Brownian oscillator. In the fast modulation limit of an overdamped regime we get the effect, which was named “fear of death,” in which for strong enough sink parameters the electron has a tendency to avoid the place with greater sink. The presented model was used to provide a plausible explanation of the temperature dependence of the quantum yields of the Rhodospirillum rubrum photosynthetic reaction center in the high-temperature regime.

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I. INTRODUCTION

The bacterial reaction center [1] is a membrane-bound pigment-protein complex that performs the conversion of the photon energy into the charge-separated states in a photosynthetic organism. The reaction centers (RC) of purple bacteria are composed of three protein subunits called L , M , and H [2,3]. All cofactors involved in the electron transfer (ET) are noncovalently bound to subunits L and M in two chains. Both chains of cofactors start at the bacteriochlorophyll dimer (P) that 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 macroscopic C_2 symmetry. For more details on structural arrangement, see Ref. [4]. The cofactors serve as donor-acceptor pairs in the electron transfer. In spite of the structural symmetry, only the L branch of cofactors is used for electron transfer through the protein.

To describe the first steps of electron transfer processes in the reaction centers, we have used the three-site model. We designate the special pair (P) as site 1; sites 2 and 3 then represent the molecules B_M and B_L . We forbid the direct ET between sites 2 and 3. We consider that this three-level system is coupled to a bath. We assume that the energy levels 2 and 3 have an imaginary part, which describes the interaction with the next molecules in the branch. The imaginary part of the energy level 1 describes the probability of electron deactivation to the ground state. This model was used to elucidate the unidirectionality of the primary charge separation in the bacterial RC in [5,6]. Because of the very fast primary charge-separation process, we assume that the electron transfer has a hot character. This means that ET is so fast that the bath does not have sufficient time to relax to the new thermal equilibrium before the particle moves away. The result of

this assumption is that we used the stochastic model where the fluctuations do not depend on the localization of electron in the branch.

II. THEORY

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

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

where the Hamiltonian H is divided into two parts,

$$H = H_0 + V, \quad (2)$$

where

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

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

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^\dagger (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 the 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

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$$\langle W_{ij}(t)W_{ij}(\tau) \rangle = K_{ij}(t-\tau), \quad (6)$$

where the functions K_{ij} will be defined below. Now using projection techniques [6–9] with the projector in the form

$$(DA)_{mn} = \delta_{mn} \langle A_{mm} \rangle, \quad (7)$$

we get the generalized master equations (GME) for population probabilities,

$$\frac{\partial P_i(t)}{\partial t} = -\frac{2\Gamma_i}{\hbar} P_i(t) - \sum_{\substack{j=1 \\ (j \neq i)}}^n \frac{2|V_{ij}|^2}{\hbar^2} \int_0^t \cos\left(\frac{\varepsilon_i - \varepsilon_j + \Delta_{ij}}{\hbar}(t-\tau)\right) \Theta_{ij}(t-\tau) \exp\left(-\frac{\Gamma_i + \Gamma_j}{\hbar}(t-\tau)\right) \{P_i(\tau) - P_j(\tau)\} d\tau, \quad (8)$$

$$i = 1, \dots, n,$$

where $P_i(t)$ is the population probability and

$$\Theta_{ij}(t) = \exp\left(-\frac{1}{2\hbar^2} \int_0^t \int_0^t K_{ij}(\tau_2 - \tau_1) d\tau_1 d\tau_2\right).$$

III. MODEL OF RC

In the three-site model, Eqs. (8) have the form

$$\begin{aligned} \frac{\partial P_1(t)}{\partial t} = & -\frac{2\Gamma_1}{\hbar} P_1(t) - \frac{2J_M^2}{\hbar^2} \int_0^t \cos\left(\frac{\varepsilon_M}{\hbar}(t-\tau)\right) \exp\left(-\frac{\Gamma_1 + \Gamma_2}{\hbar}(t-\tau)\right) \Theta_M(t-\tau) \{P_1(\tau) - P_2(\tau)\} d\tau - \frac{2J_L^2}{\hbar^2} \\ & \times \int_0^t \cos\left(\frac{\varepsilon_L}{\hbar}(t-\tau)\right) \exp\left(-\frac{\Gamma_1 + \Gamma_3}{\hbar}(t-\tau)\right) \Theta_L(t-\tau) \{P_1(\tau) - P_3(\tau)\} d\tau, \end{aligned} \quad (9a)$$

$$\frac{\partial P_2(t)}{\partial t} = -\frac{2\Gamma_2}{\hbar} P_2(t) - \frac{2J_M^2}{\hbar^2} \int_0^t \cos\left(\frac{\varepsilon_M}{\hbar}(t-\tau)\right) \exp\left(-\frac{\Gamma_1 + \Gamma_2}{\hbar}(t-\tau)\right) \Theta_M(t-\tau) \{P_2(\tau) - P_1(\tau)\} d\tau, \quad (9b)$$

$$\frac{\partial P_3(t)}{\partial t} = -\frac{2\Gamma_3}{\hbar} P_3(t) - \frac{2J_L^2}{\hbar^2} \int_0^t \cos\left(\frac{\varepsilon_L}{\hbar}(t-\tau)\right) \exp\left(-\frac{\Gamma_1 + \Gamma_3}{\hbar}(t-\tau)\right) \Theta_L(t-\tau) \{P_3(\tau) - P_1(\tau)\} d\tau, \quad (9c)$$

where we denote $\varepsilon_L = \varepsilon_1 - \varepsilon_3 + \Delta_{13}$, $\varepsilon_M = \varepsilon_1 - \varepsilon_2 + \Delta_{12}$, $\Theta_{12} = \Theta_M$, $\Theta_{13} = \Theta_L$, $V_{12} = J_M$, and $V_{13} = J_L$. The quantum yield (QY) Φ_i of the electronic escape via the site i can be characterized by the expression [10]

$$\Phi_i = \frac{2\Gamma_i}{\hbar} \int_0^\infty P_i(t) dt = \frac{2\Gamma_i}{\hbar} \lim_{p \rightarrow 0^+} \tilde{P}_i(p), \quad i = 1, 2, 3, \quad (10)$$

where $\tilde{P}_i(p)$ is the Laplace transformation of $P_i(t)$. The Laplace transform to Eqs. (9), with the initial conditions $P_1(0) = 1$, $P_2(0) = P_3(0) = 0$, reads

$$\begin{aligned} p\tilde{P}_1(p) - 1 = & -\frac{2\Gamma_1}{\hbar} \tilde{P}_1(p) - w_M(p) [\tilde{P}_1(p) - \tilde{P}_2(p)] \\ & - w_L(p) [\tilde{P}_1(p) - \tilde{P}_3(p)], \end{aligned} \quad (11a)$$

$$p\tilde{P}_2(p) = -\frac{2\Gamma_2}{\hbar} \tilde{P}_2(p) - w_M(p) [\tilde{P}_2(p) - \tilde{P}_1(p)], \quad (11b)$$

$$p\tilde{P}_3(p) = -\frac{2\Gamma_3}{\hbar} \tilde{P}_3(p) - w_L(p) [\tilde{P}_3(p) - \tilde{P}_1(p)], \quad (11c)$$

where

$$\begin{aligned} w_M(p) = & 2 \frac{J_M^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_M}{\hbar} t\right) \exp \\ & \times \left(-\frac{\Gamma_1 + \Gamma_2 + \hbar p}{\hbar} t\right) \Theta_M(t) dt, \end{aligned} \quad (12a)$$

$$w_L(p) = 2 \frac{J_L^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_L}{\hbar} t\right) \exp\left(-\frac{\Gamma_1 + \Gamma_3 + \hbar p}{\hbar} t\right) \Theta_L(t) dt. \quad (12b)$$

IV. OVERDAMPED REGIME

In this section, we assume that the correlation function corresponds to a spectral density of the strongly overdamped Brownian oscillator. We have [11,12]

$$K_{ij}(t) = \langle \xi_{ij}^2 \rangle_{slv} \exp(-|t|/\tau_{ij}^e). \quad (13)$$

We start with the fast modulation limit, where we assume that $\Gamma_{ij}^e \tau_{ij}^e / \hbar \ll 1$. Here $\Gamma_{ij}^e = \langle \xi_{ij}^2 \rangle \tau_{ij}^e / \hbar$. In this limit, we have

$$w_M(p) = 2 \frac{J_M^2}{\hbar^2} \frac{p + (\Gamma_1 + \Gamma_2 + \Gamma_M)/\hbar}{[p + (\Gamma_1 + \Gamma_2 + \Gamma_M)/\hbar]^2 + [\varepsilon_M/\hbar]^2}, \quad (14a)$$

$$w_L(p) = 2 \frac{J_L^2}{\hbar^2} \frac{p + (\Gamma_1 + \Gamma_3 + \Gamma_L)/\hbar}{[p + (\Gamma_1 + \Gamma_3 + \Gamma_L)/\hbar]^2 + [\varepsilon_L/\hbar]^2}, \quad (14b)$$

where we denote $\Gamma_L = \Gamma_{13}^e$, $\Gamma_M = \Gamma_{12}^e$, $\tau_L = \tau_{13}^e$, and $\tau_M = \tau_{12}^e$. Using the solution of Eqs. (11), we can compute the quantum yields. Here we present the ratio $K_{32} = \Phi_3/\Phi_2$ which characterizes the asymmetry of electron transfer through the L and M branch, and the ratio $K_{13} = \Phi_1/\Phi_3$ which characterizes the decay of the system to the ground state,

$$K_{32} = \frac{J_L^2 \Gamma_3 (\Gamma_1 + \Gamma_3 + \Gamma_L) \{ J_M^2 (\Gamma_1 + \Gamma_2 + \Gamma_M) + \Gamma_2 [(\Gamma_1 + \Gamma_2 + \Gamma_M)^2 + \varepsilon_M^2] \}}{J_M^2 \Gamma_2 (\Gamma_1 + \Gamma_2 + \Gamma_M) \{ J_L^2 (\Gamma_1 + \Gamma_3 + \Gamma_L) + \Gamma_3 [(\Gamma_1 + \Gamma_3 + \Gamma_L)^2 + \varepsilon_L^2] \}}, \quad (15a)$$

$$K_{13} = \frac{\Gamma_1 \{ J_L^2 (\Gamma_1 + \Gamma_3 + \Gamma_L) + \Gamma_3 [(\Gamma_1 + \Gamma_3 + \Gamma_L)^2 + \varepsilon_L^2] \}}{J_L^2 \Gamma_3 (\Gamma_1 + \Gamma_3 + \Gamma_L)}. \quad (15b)$$

We will analyze only the case that is interesting from a theoretical point of view. If the parameters Γ_2 , Γ_3 are very large in comparison to the parameters ε_L , ε_M , J_M , J_L , Γ_L , Γ_M , and $\Gamma_1 \approx 0$, we get

$$K_{32} = \frac{J_L^2 \Gamma_2}{J_M^2 \Gamma_3}, \quad K_{13} \approx 0. \quad (16)$$

In this limit of strong sink at place 2 (branch M) and 3 (branch L), we have inverted the regime of electron transfer. When we assume that $J_L \sim J_M$, an electron is transported mainly through the branch with a smaller value of the sink parameter. In this case, the electron has a tendency to avoid the place with greater sink parameter. A similar result was obtained in [13], where the energy transport in a semi-infinite chain with one sink was described. On the other hand, if the parameter Γ_1 is large, the electron escapes from the system through site 1. Because of small sink parameters in comparison to energy differences between molecules, these cases can be hardly realized in RC.

Now we analyze the slow modulation limit. This limit is obtained when the condition $\Gamma_{ab}^e \tau_{ab}^e / \hbar \gg 1$ is fulfilled. We have

$$w_M(p) = 2 \frac{J_M^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_M}{\hbar} t\right) \times \exp\left(-\frac{\Gamma_1 + \Gamma_2 + \hbar p}{\hbar} t - \frac{\langle \xi_M^2 \rangle}{2\hbar^2} t^2\right) dt \quad (17a)$$

$$w_L(p) = 2 \frac{J_L^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_L}{\hbar} t\right) \times \exp\left(-\frac{\Gamma_1 + \Gamma_3 + \hbar p}{\hbar} t - \frac{\langle \xi_L^2 \rangle}{2\hbar^2} t^2\right) dt \quad (17b)$$

$$K_{32} = \frac{k_L \left(k_M + \frac{2\Gamma_2}{\hbar}\right) \Gamma_3}{k_M \left(k_L + \frac{2\Gamma_3}{\hbar}\right) \Gamma_2}, \quad K_{13} = \frac{\left(k_L + \frac{2\Gamma_3}{\hbar}\right) \Gamma_1}{k_L \Gamma_3}, \quad (18)$$

where we denote $k_L = w_L(p \rightarrow 0^+)$ and $k_M = w_M(p \rightarrow 0^+)$. In the static limit, when the conditions $(2\langle \xi_L^2 \rangle)^{1/2} \gg \Gamma_1 + \Gamma_3$ and $(2\langle \xi_M^2 \rangle)^{1/2} \gg \Gamma_1 + \Gamma_2$ are fulfilled,

$$k_L = \frac{2\pi}{\hbar} J_L^2 \sqrt{\frac{1}{2\pi\langle \xi_L^2 \rangle}} \exp\left(-\frac{\varepsilon_L^2}{2\langle \xi_L^2 \rangle}\right), \quad (19)$$

$$k_M = \frac{2\pi}{\hbar} J_M^2 \sqrt{\frac{1}{2\pi\langle \xi_M^2 \rangle}} \exp\left(-\frac{\varepsilon_M^2}{2\langle \xi_M^2 \rangle}\right). \quad (20)$$

In this case we can see that the sink parameters have similar values as the constants k_L, k_M and so this limit predicts that the balance between the ET to the L and M branch can be effectively regulated also with the change of the sink parameters, in contrast to the fast modulation limit.

V. UNDERDAMPED REGIME

In the present section, we assume the regime where the correlation function corresponds to a strongly underdamped Brownian oscillator. It means that we assume the correlation function $K_{ij}(t)$ in the form [11,12]

$$K_{ij}(t) = \langle \xi_{ij}^2 \rangle_{slv} \exp(-|t|/\tau_{ij}^e) \left\{ \cos[\omega_{ij}t] + \frac{1}{\omega_{ij}\tau_{ij}^e} \sin[\omega_{ij}|t|] \right\}. \quad (21)$$

We will work in the strongly underdamped limit where the condition $\omega_{ij}\tau_{ij}^e \gg 1$ is fulfilled. In this regime, we proceed in the same way as in the previous sections,

$$w_L(p) = 2 \frac{J_L^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_L}{\hbar}t\right) \exp\left(-\frac{\Gamma_1 + \Gamma_3 + \hbar p}{\hbar}t\right) \exp\left[-\frac{\langle \xi_L^2 \rangle}{\hbar^2 \omega_L^2} \left[\frac{2t}{\tau_L} + 1 - \exp\left(-\frac{t}{\tau_L}\right) \left(\cos(\omega_L t) + \frac{3}{\omega_L \tau_L} \sin(\omega_L t) \right) \right] \right] dt \quad (22)$$

$$w_M(p) = 2 \frac{J_M^2}{\hbar^2} \int_0^\infty \cos\left(\frac{\varepsilon_M}{\hbar}t\right) \exp\left(-\frac{\Gamma_1 + \Gamma_2 + \hbar p}{\hbar}t\right) \exp\left[-\frac{\langle \xi_M^2 \rangle}{\hbar^2 \omega_M^2} \left[\frac{2t}{\tau_M} + 1 - \exp\left(-\frac{t}{\tau_M}\right) \left(\cos(\omega_M t) + \frac{3}{\omega_M \tau_M} \sin(\omega_M t) \right) \right] \right] dt \quad (23)$$

and the constant k_L can be expressed in the form

$$k_L = A_L e^{-S_L} \left\{ \sum_{k=0}^{\infty} \frac{1}{k!k!} (S_L/2)^{2k} \frac{\Omega_L + 2k/\alpha_L}{(\Omega_L + 2k/\alpha_L)^2 + p_L^2} + \sum_{k=0}^{\infty} \sum_{q=1}^{\infty} \frac{1}{k!(k+q)!} (S_L/2)^{2k+q} \left[\frac{\Omega_L + (2k+q)/\alpha_L + \frac{3q}{\alpha_L}(q-p_L)}{[\Omega_L + (2k+q)/\alpha_L]^2 + [q-p_L]^2} \right. \right. \\ \left. \left. + \frac{\Omega_L + (2k+q)/\alpha_L + \frac{3q}{\alpha_L}(q+p_L)}{[\Omega_L + (2k+q)/\alpha_L]^2 + [q+p_L]^2} \right] \right\}, \quad (24)$$

where $A_L = 2J_L^2/\hbar^2 \omega_L$, $S_L = \langle \xi_L^2 \rangle / \hbar^2 \omega_L^2$, $\alpha_L = \omega_L \tau_L$, $\Omega_L = (\Gamma_1 + \Gamma_3)/\hbar \omega_L + (2S_L/\alpha_L)$, and $p_L = \varepsilon_L/\hbar \omega_L$. Changing $L \rightarrow M$ and $\Gamma_3 \rightarrow \Gamma_2$, we get the expression for the constant k_M .

Now we will use the presented model to elucidate the observed ET in the YM210W mutant of the Rhodospirillum rubrum photosynthetic reaction center. We assume that the underdamped regime can correctly describe the ET in this reaction center. In the mutant tyrosine, M210 residue is replaced by tryptophan [14–17]. The general view is that the free energy of the state $P^+B_L^-$ has been raised in this mutant. As a result of this mutation, the observed time constant associated with the charge separation from P^* is about 70 ps at room temperature and 320–400 ps at cryogenic temperature. The decrease in the primary electron transfer rate results in a diminishing of the efficiency of $P^+Q_L^-$ formation to 80% at room temperature and 60–70% at cryogenic temperature [14,16].

To get the observed results we will examine three low-frequency modes. The numerical results are collected in Table I. In the computation, it was assumed that the expression $\langle \xi_{ij}^2 \rangle = 2E_{ij}k_B T$ is valid in the classical limit, where E_{ij} is the “reorganization” energy. In YM210W mutant the parameter $2\Gamma_3/\hbar$ was decreased, similar to the work [16], to the value $(2 \text{ ps})^{-1}$ in comparison to WT. To imitate the possible temperature dependence of the parameter $2\Gamma_1/\hbar$, we used the value $(300 \text{ ps})^{-1}$ of this parameter at temperature

200 K in the computations. The numerical computations show that the $\hbar\omega = 80 \text{ cm}^{-1}$ mode gives the results that are in the best correspondence with the observed data. The mode $\hbar\omega = 100 \text{ cm}^{-1}$ gives a small increase of QY to the L branch with a decrease in the temperature in the YM210W mutant. The mode $\hbar\omega = 50 \text{ cm}^{-1}$ can indicate that the lifetime of P^* in WT increases with a decrease in the temperature, which is not in accordance with experimental results. In the numerical computation, it was assumed that the changes of parameter $\tau_L(\tau_M)$ are small in the considered temperature range. To characterize the effect of electron-vibration coupling on the ET, we present the dependence of the effective time constant $A_L/k_L(A_M/k_M)$ on the parameters $S_L(S_M)$ and $\alpha_L(\alpha_M)$ in Fig. 1.

In the slow mutant where the lifetime of P^* is very long, there is a possibility that the ET has an incoherent character. It means that there exist vibrational modes that relax sufficiently fast after each step of electron/energy transfer. In this case, the same projector operator as in the works [18–22] has to be used.

VI. DISCUSSION

In the previous theories with more than one sink parameter, these parameters were added in the GME ad hoc, neglecting the effect of the sink parameters on the memory kernels in the GME [10]. As a result, the requirement of

TABLE I. Computed constant $1/k_L$, $1/k_M$, and quantum yields for wild type (WT) and YM210W mutant of the Rhodobacter sphaeroides RC's. The values $\hbar/2\Gamma_2=0.9$ ps, $\varepsilon_M=2000$ cm $^{-1}$, $\alpha_M=\alpha_L=20$, and $J_L=J_M=26$ cm $^{-1}$ were taken in the computations.

Sample	T (K)	$\hbar\omega^a$ (cm $^{-1}$)	S^b	$\hbar/2\Gamma_1$ (ps)	$\hbar/2\Gamma_3$ (ps)	ε_L (cm $^{-1}$)	$1/k_L$ (ps)	$1/k_M$ (ps)	ϕ_1	ϕ_2	ϕ_3
WT	300	100	30	170	0.9	430	2.57	119	0.019	0.028	0.953
WT	200	100	20	300	0.9	430	2.31	469	0.01	0.007	0.983
YM210W	300	100	30	170	2	1300	15	119	0.08	0.115	0.805
YM210W	200	100	20	300	2	1300	35.8	469	0.104	0.067	0.829
WT	300	80	30	170	0.9	430	2.34	329	0.019	0.01	0.971
WT	200	80	20	300	0.9	430	2.29	1109	0.01	0.003	0.987
YM210W	300	80	30	170	2	1280	29	329	0.143	0.073	0.784
YM210W	200	80	20	300	2	1280	97.6	1109	0.234	0.063	0.703
WT	300	50	30	170	0.9	430	2.53	1517	0.02	0.002	0.978
WT	200	50	20	300	0.9	430	3.4	3056	0.014	0.001	0.985
YM210W	300	50	30	170	2	900	33	1517	0.167	0.019	0.814
YM210W	200	50	20	300	2	900	125	3056	0.29	0.029	0.681

$$^a\omega = \omega_L = \omega_M.$$

$$^bS = S_L = S_M.$$

non-negativity of population probabilities $P_i(t)$ was not always fulfilled. The theory presented here allows computation of quantum yields of electronic escape via the branches L , M , and of direct ground-state recombination. Computed quantum yields give subsidiary information, and together with the transient state lifetimes they can help to determine the free parameters of the system. The lifetimes ought to be defined from GME. The temperature dependences of quantum yields are very important experimental data, which can be theoretically described by effective rate constants also in the case where the dynamics of electrons must be described by GME. However, it is not the case of lifetimes.

In this paper, we describe the system by a relatively

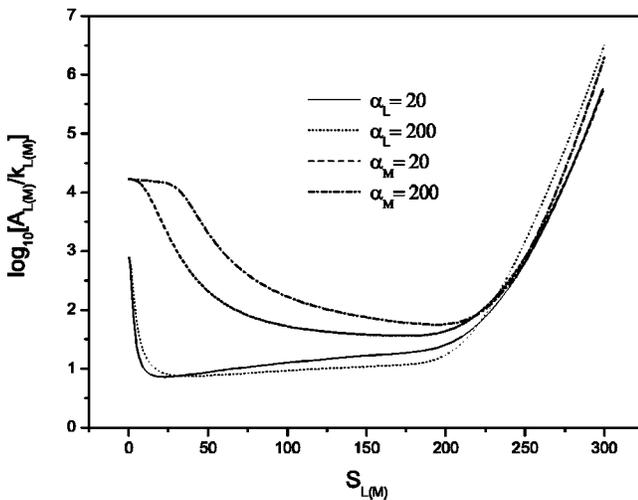


FIG. 1. Plot of $\log_{10}(A_{L(M)}/k_{L(M)})$ vs $S_{L(M)}$ with $\hbar/2\Gamma_1=170$ ps, $\hbar/2\Gamma_3=\hbar/2\Gamma_2=0.9$ ps, $\varepsilon_L=430$ cm $^{-1}$, $\varepsilon_M=2000$ cm $^{-1}$, and $\hbar\omega_L=\hbar\omega_M=80$ cm $^{-1}$ for various values of $\alpha_{L(M)}$. $k_{L(M)}$ is the effective rate constant and $A_{L(M)}=2J_{L(M)}^2/\hbar^2\omega_{L(M)}$.

simple model with one vibrational mode and symmetry in all parameters excluding energies. The obtained results are in agreement with the published experimental data [16]. Since the experiments do not give full information about the temperature dependence of quantum yields, we can compare with experimentally measured data only the temperature dependence of the computed quantum yields Φ_3 of electronic escape via the L branch. To better characterize the free parameters of the system, full information about the temperature dependence of the quantum yields is needed. This information can then show whether the presented model is realistic or not.

To describe the effective rate constant, the two-vibration modes approximation is used with high- and low-frequency modes [22–24]. The high-frequency mode is important mainly for the very fast second ET step, where there is a great free-energy gap. Using only the low-frequency mode, the second ET step is slower than the first ET step, which is not in accordance with experimental data. In contrast, in the first ET step, the high-frequency mode does not seem to be so important, thus we expect that the one-mode approximation could be realistic. The high-frequency mode can play an important role in the M -branch ET in the case of a large free-energy gap. This case can be described also in the one-mode approximation assuming asymmetry in the frequencies ω_L, ω_M .

Figure 1 shows the lack of the unidirectionality of electron transfer even when large asymmetry in the energies is present when very small or great values of the parameters $S_{L(M)}$ are used. In this study, the value of $S_{L(M)}$ corresponds to the “reorganization” energy $E_r \approx 460$ cm $^{-1}$ when the vibrational mode $\hbar\omega=80$ cm $^{-1}$ is used. With this value of $S_{L(M)}$ the difference between the calculated values k_L and k_M is sufficient to obtain the observed unidirectionality as seen in Table I. The unidirectionality was previously explained by the effective rate constants describing the first electron trans-

fer step in bacterial RC [25]. It was shown that assuming only the first ET step is not enough to elucidate the unidirectionality [22].

VII. CONCLUSIONS

This paper addresses a specific problem of the highly asymmetric ET in the photosynthetic reaction centers. Extensive experimental efforts have been devoted to the elucidation of the role of accessory bacteriochlorophyll molecules [26]. At least two alternative models have been proposed for the role of these molecules [27]. In our model, we considered that the electron is delocalized to the molecules P , B_M , and B_L . We assumed that the ET has a hot character [28]. On the studied time scale, the model excludes the repopulation processes of some electron-accepting sites. This exclusion requires the introduction of an imaginary part of the energy level. As a result of this imaginary part, we get the effect called “fear of death” that was first described in [13]. With this effect, for strong enough sink parameters the electron has a tendency to avoid the place with greater sink.

In the present work, the GME was derived to describe the primary charge transfer in the photosynthetic reaction centers. This integro-differential equation (GME) can be changed to a differential equation (master equation). To justify this change, it has to be shown that the memory kernels $w_{ij}(t)$ in Eqs. (8) fulfill certain conditions. Specifically, it has to be shown that the memory kernels damp very quickly in comparison to the relaxation of the system to the steady state. This means roughly that in the fast modulation limit the conditions $\Gamma_1 + \Gamma_3 + \Gamma_L, \Gamma_1 + \Gamma_2 + \Gamma_M \gg J_L, J_M$ must be fulfilled [29]. Here $(\Gamma_1 + \Gamma_3 + \Gamma_L)/\hbar$ and $(\Gamma_1 + \Gamma_2 + \Gamma_M)/\hbar$ characterize the loss of memory, and $J_L/\hbar, J_M/\hbar$ characterize the “coherent propagation.” In the slow modulation limit, the conditions $\sqrt{2\langle \xi_L^2 \rangle}, \sqrt{2\langle \xi_M^2 \rangle} \gg J_L, J_M$ must be satis-

fied. When these conditions are not fulfilled, ET has coherent or partially coherent (damped with oscillations) character and the GME must be used to describe the relaxation of the system to the steady state. On the other hand, we have shown in the present work that the quantum yields can be described by the parameters k_L, k_M usually used as rate constants.

We used the stochastic model where the interaction of electron with medium was described with the correlation functions (6). Similar results can be obtained when we describe the medium as the vibronic manifolds with the spectral density $J(\omega) = 2\lambda\omega/(1 + \omega^2\tau_e^2)$ [30,31] or when we use the frequency dependence of the dielectric function in the form $\text{Im } \varepsilon(\omega)/|\varepsilon(\omega)|^2 = c\omega\tau_e/(1 + \omega^2\tau_e^2)$ for the polar medium [18,32–34]. When the dielectric function in the resonance approximation is used, we can get the correlation function, which was used in the underdamped regime of the single-mode approximation [35]. The parameter $\varepsilon_L(\varepsilon_M)$ is obviously split up into the free-energy difference and the reorganization energy. This splitting in the hot electron transfer strongly depends on the medium state frozen during the ET and hardly can be verified with experiments. Thus the energy $\varepsilon_L(\varepsilon_M)$ was used as one free model parameter.

The observed L -branch electron transfer is slower in the YM210W mutant than in the wild-type bacterial RC, suggesting that the character of electron transfer reaction in the mutant and wild-type RC can be different. It would be ideal to obtain and study the M -branch electron transfer of RC mutant with the same L -branch electron transfer rate as the wild-type RC.

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