

Incoherent Oscillations Accompanying Charge Separation in Photosynthetic Reaction Centers

A. G. Yakovlev¹, V. A. Shuvalov^{1,2}

¹A.N. Belozersky Institute of Physico-Chemical Biology, Moscow State University, Moscow, Russia

²Institute of Basic Biological Problems, Russian Academy of Sciences, Moscow, Russia

Email: yakov@genebee.msu.su, shuvalov@issp.serpukhov.su

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ABSTRACT

Early events of charge separation in reaction centers (RCs) of bacterial photosynthesis are modeled by kinetic equations with time-dependent rate constants. An illustrative case of regular motion along a “slow” coordinates leading to oscillations in the kinetics is examined. Different schemes of charge separation are investigated. A good fitting of experimental kinetics of native *Rba. sphaeroides* RCs is achieved in the five states model $P^*_1 B_A H_A \leftrightarrow P^*_2 B_A H_A \leftrightarrow I \leftrightarrow P^+ B_A^- H_A \leftrightarrow P^+ B_A H_A^-$ with two excited states $P^*_1 B_A H_A$ and $P^*_2 B_A H_A$ and three charge separated states I , $P^+ B_A^- H_A$ and $P^+ B_A H_A^-$ (P is a primary electron donor, bacteriochlorophyll dimer, B_A and H_A are an electron acceptor, monomeric bacteriochlorophyll and bacteriopheophytin in active A-branch, respectively). In the model only the first excited state is directly populated by optical excitation. The emission of the two excited states is assumed to be at 905 and 940 nm, respectively. The intermediate state I is assumed to absorb at 1020 nm as well as the $P^+ B_A^- H_A$ state. The model explains the deep oscillations in the kinetics of the $P^*_{1,2}$ stimulated emission and of the B_A^- absorption. In the simpler schemes without the I state or with only one excited state the accordance with the experiment is achieved at unreal parameter values. A possible nature of the I and $P^*_2 B_A H_A$ states and a possible incoherent nature of the oscillations are discussed.

Keywords: Photosynthesis; Charge Separation; Reaction Center; Electron Transfer

1. Introduction

In reaction centers (RCs) of purple bacteria *Rhodobacter (Rba.) sphaeroides* primary charge separation consisted in electron is transferred from excited dimer of bacteriochlorophyll P^* to monomeric bacteriochlorophyll B_A within ~ 3 psec and from B_A^- to bacteriopheophytin H_A within ~ 1 psec at room temperature (for reviews see [1,2]). Then electron is transferred to primary quinone Q_A within ~ 200 psec. At cryogenic temperatures these reactions are accelerated by 2 - 3 times. Excitation of RCs by broadband femtosecond light pulses leads to oscillations in the kinetics of P^* emission [3] and of B_A^- absorption [4] with a frequencies at 10 - 400 cm^{-1} (peak at 130 - 150 cm^{-1}). These oscillations are observed in various native and mutant RCs in a wide range of temperatures. According to modern ideas, a vibrational or electronic (or both) coherence is a possible explanation of the oscillatory phenomena in the kinetics of the excited and charge separated states. A periodical motion of a vibrational wavepacket [5] or a quantum beats between the levels with close energies [6] can produce the damped oscillations in the populations of the RC states. Analysis

of the coherent electron transfer was performed on the base of Redfield theory in [7] and in the dispersed polaron model [8]. The oscillations in the P^* stimulated emission band were theoretically studied by an approach of single electronic transition coupled to one or two vibrational modes [9-11]. At room temperature the quantum coherence should be destroyed very quickly due to thermal motions [12]. On the other hand, the molecular dynamics calculations revealed a number of classical vibrational modes in RCs at 20 - 200 cm^{-1} [13]. These modes can reflect the nuclear motions in protein matrix as well as inside the RC pigments. A classical stochastic Langevin equation was used to calculate the oscillatory dynamics of the $P^* \rightarrow P^+ B_A^-$. Reaction controlled by protein relaxation [14] in modified RCs with blocked electron transfers to H_A .

In the present work the incoherent charge separation dynamics of native *Rba. sphaeroides* RCs is modeled by the kinetic equations with time-dependent rate constants. This approach is based on the Marcus theory [15]. An aim of the work was to study a possibility of incoherent origin of the oscillatory phenomena observed at early

times of charge separation.

2. Model

According to Marcus theory [15], electron or energy transfer reaction occurs at the intersection of the potential energy surfaces of the initial and final states of the system. In harmonic approximation these surfaces are paraboloids shifted one from another: $U_{in} = 1/2m\omega^2x^2 + 1/2M\Omega^2X^2$; $U_{fin} = 1/2m\omega^2(x - x_0)^2 + 1/2M\Omega^2(X - X_0)^2 + \Delta G$. Here x and X are effective coordinates of fast (thermal) and slow (relaxation) motion, respectively; m and M are effective masses, ω and Ω are self-frequencies, x_0 and X_0 are the potential surface displacements along the x and X coordinates, ΔG is the free energy change of the reaction. In the high-temperature limit, the rate constants of the forward and backward reaction can be written as follows:

$$K_f = K_0 \exp(-E/k_B T); K_b = K_f \exp(G/k_B T).$$

Here the activation energy $E = 1/4\lambda(1 + G/\lambda)^2$; the energy gap $G = \Delta G + \lambda_1 - 2\lambda_1 X/X_0$; the fast reorganization energy $\lambda = 1/2m x_0^2$; the slow reorganization energy $\lambda_1 = 1/2M\Omega^2 X_0^2$; k_B is the Boltzmann constant; T is a temperature; K_0 is a constant. After an averaging over the fast coordinate x the dynamics of the energy gap $G(t)$ and of the activation energy $E(t)$ is determined by the dynamics of the slow coordinate $X(t)$. Thus, the rate constants $K_{f,b}$ are time-dependent in this approach. In our model we examine a simplest illustrative case of damped cosine dependence of X on time. We studied the schemes of three ($P^*B_A H_A \leftrightarrow P^+ B_A^- H_A \leftrightarrow P^+ B_A H_A^-$), four ($P_1^* B_A H_A \leftrightarrow P_2^* B_A H_A \leftrightarrow P^+ B_A^- H_A \leftrightarrow P^+ B_A H_A^-$) and five ($P_1^* B_A H_A \leftrightarrow P_2^* B_A H_A \leftrightarrow I \leftrightarrow P^+ B_A^- H_A \leftrightarrow P^+ B_A H_A^-$) states. The coordinates of each reaction were assumed to be independent. The incoherent dynamics of relative populations of these states was described by kinetic equations.

3. Results and Discussion

3.1. The Modeled Kinetics

The results of the modeling of the five states scheme (Figure 1) are shown in Figure 2 for native RCs of *Rba. sphaeroides*. The calculation parameters are as follows: temperature $T = 90$ K, energy difference $G_{12}^0 = 35$ cm⁻¹, $G_{23}^0 = 85$ cm⁻¹, $G_{34}^0 = -400$ cm⁻¹, $G_{45}^0 = -900$ cm⁻¹; reorganization energy $\lambda_{12} = 80$ cm⁻¹, $\lambda_{23} = 100$ cm⁻¹, $\lambda_{34} = 450$ cm⁻¹, $\lambda_{45} = 1500$ cm⁻¹; reaction rate $K_{12}^0 = 26$ psec⁻¹, $K_{23}^0 = 34$ psec⁻¹, $K_{34}^0 = 12$ psec⁻¹, $K_{45}^0 = 40$ psec⁻¹; $G_{12}(t) = 50$ cm⁻¹ exp(-3.5t)(sin(30.5t - 1.2) + sin(25.5t - 1.2)); $G_{23}(t) = 60$ cm⁻¹ exp(-2t)(sin(22.5t - 0.1) + sin(27.5t - 0.1)) + 20 cm⁻¹ exp(-9t); $G_{34}(t) = -600$ cm⁻¹ exp(-5t) + 320 cm⁻¹ exp(-0.5t) sin(12t - 2.4); $G_{45}(t)$

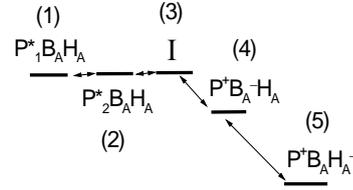


Figure 1. An illustrative scheme of the energy levels of the states at zero oscillations.

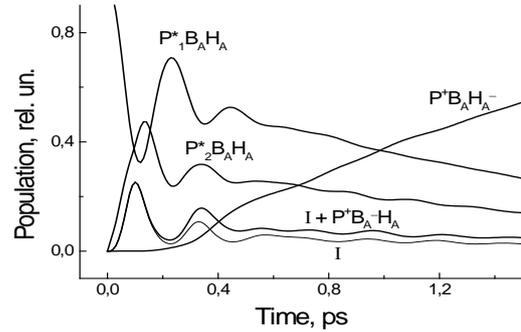


Figure 2. The modeled kinetics of the relative populations of the $P_1^* B_A H_A$, $P_2^* B_A H_A$, I , $I + P^+ B_A^- H_A$ and $P^+ B_A H_A^-$ states of the native *Rba. sphaeroides* RCs. For details see the text.

= 0; time t is given in psec. The calculated kinetics of the states are similar with the experimental ones at $t > 150$ fsec [2-4,16]. A decay of the P^* stimulated emission at 905 and 940 nm (the $P_1^* B_A H_A$ and $P_2^* B_A H_A$ states in the model, respectively) and a bleaching of the H_A absorption band at 760 nm (the $P^+ B_A H_A^-$ state) occur within ~ 1.5 psec in native RCs at 90 K. These processes are accompanied by the formation of the B_A^- absorption band at 1020 nm. The modeled sum of the I and $P^+ B_A^- H_A$ populations is close to the experimental kinetics of the B_A^- absorption band. This means that the I state absorb at 1020 nm. The pronounced damped oscillations with the ~ 220 fsec period are observed in the kinetics of the P^* stimulated emission and of the B_A^- absorption. The main contribution to the B_A^- oscillations is provided by the I state. The oscillations are completely damped within ~ 600 fsec. The P^* oscillations at 905 and 940 nm have the opposite phases, while the B_A^- absorption oscillates in phase with the P^* oscillations at 940 nm.

3.2. The Parameters of the Calculations

The parameter values used in the model are in accordance with the extensive theoretical and experimental studies reviewed in [1,2,5,14]. According to different estimations, in *Rba. sphaeroides* RCs the $P^+ B_A^- H_A$ and $P^+ B_A H_A^-$ energy levels are placed below the $P^* B_A H_A$ energy level by 300 - 700 and 900 - 2000 cm⁻¹, respectively. In our model the energies of the $P_1^* B_A H_A$, $P_2^* B_A H_A$ and I states are different by less than 100 cm⁻¹.

The rates of the forward and backward reactions between these states oscillate with approximately opposite phases (**Figure 3**). Such correlation between the dynamics of the forward and backward reactions leads to the deep oscillations in the populations.

The molecular dynamics calculations estimate the reorganization energy of the $P^*B_A \rightarrow P^+B_A^-$ and $P^*H_A \rightarrow P^+H_A^-$ reactions by $\sim 700 \text{ cm}^{-1}$ [17] and $\sim 2000 \text{ cm}^{-1}$ [18], respectively. In our model the fast reorganization energy of the $I \rightarrow P^+B_A^-H_A$ (450 cm^{-1}) and $P^+B_A^-H_A \rightarrow P^+B_AH_A^-$ (1500 cm^{-1}) reactions is much greater than that of the $P_1^*B_AH_A \rightarrow P_2^*B_AH_A$ (80 cm^{-1}) and $P_2^*B_AH_A \rightarrow I$ (100 cm^{-1}) reactions. This means the small displacement between the potential surfaces of the $P_1^*B_AH_A$, $P_2^*B_AH_A$ and I states.

If we assume $X/X_0 = 1$ for convenience, then the slow reorganization energy $\lambda_1 = 25, 40, 460, 0 \text{ cm}^{-1}$ for the $P_1^*B_AH_A \leftrightarrow P_2^*B_AH_A$, $P_2^*B_AH_A \leftrightarrow I$, $I \leftrightarrow P^+B_A^-H_A$ and $P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$ reactions, respectively. Thus, the main part of the slow reorganization is corresponded to the $I \leftrightarrow P^+B_A^-H_A$ reaction, and the noticeable part of this reorganization (160 cm^{-1}) is corresponded to the aperiodic motion.

In the model the values $K_0 = 26, 34, 12$ and 40 cm^{-1} were used for the $P_1^*B_AH_A \leftrightarrow P_2^*B_AH_A$, $P_2^*B_AH_A \leftrightarrow I$, $I \rightarrow P^+B_A^-H_A$ and $P^+B_A^-H_A \rightarrow P^+B_AH_A^-$ reactions, respectively. In the adiabatic approximation these K_0 values are corresponded to the effective frequency $\nu = 400 - 1300 \text{ cm}^{-1}$. In the nonadiabatic approximation in high temperature limit these K_0 values together with the λ values give the electron coupling energy for the above mentioned reactions $V = 74, 89, 77$ and 190 cm^{-1} . The estimations of the V value for the $P^*B \leftrightarrow P^+B_A^-$ and $P^+B_A^- \leftrightarrow P^+H_A^-$ reactions are varied from 5.4 cm^{-1} [19] to 80 cm^{-1} [20] and from 15 cm^{-1} [21] to 480 cm^{-1} [20], respectively.

The qualitative agreement of our model with the experimental data can be achieved in the wide range of the parameters that indicates the stability of the model against the parameter fluctuations. The two-fold change of the

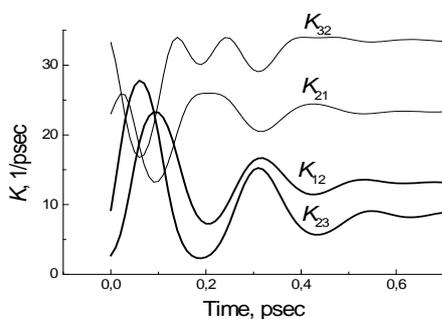


Figure 3. The calculated dependences of the forward K_{12} , K_{23} and backward K_{21} , K_{32} reaction rates (1– $P_1^*B_AH_A$, 2– $P_2^*B_AH_A$, 3–I) on time for the native *Rba. sphaeroides* RCs. For details see the text.

energy differences, reaction rates or reorganization energies causes minor quantitative changes in the kinetics shown in **Figure 2**.

3.3. Different Reaction Schemes

Calculation shows that the simplest scheme of three states $P^*B_AH_A \leftrightarrow P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$ produces more smooth oscillations than it is in experiment. In this scheme very large amplitude of the energetics changes $\sim 1000 \text{ cm}^{-1}$ is necessary to obtain the oscillation amplitude comparable with experimental one. It is clear that this scheme does not explain the out-of-phase oscillations of the P^* stimulated emission at 905 and 940 nm. These out-of-phase oscillations can be explained by the scheme of four states $P_1^*B_AH_A \leftrightarrow P_2^*B_AH_A \leftrightarrow P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$. In this scheme the oscillatory behavior of the $P^+B_A^-H_A$ state can be explained if to assume that the energetics of the $P_2^*B_AH_A \leftrightarrow P^+B_A^-H_A$ reaction oscillates with unreal amplitude $\sim 1400 \text{ cm}^{-1}$ or that the $P^+B_A^-H_A$ energy level is higher than the $P_1^*B_AH_A$ and $P_2^*B_AH_A$ levels. The last assumption contradicts to the number of theoretical and experimental works [5,17,22, 23]. An insertion of the intermediate state I between the $P_2^*B_AH_A$ and $P^+B_A^-H_A$ states helps to explain the oscillatory kinetics of the B_A^- absorption if to suppose that the I energy is close to the $P_2^*B_AH_A$ energy and that the I state has spectral properties of the B_A^- .

3.4. A Possible Nature of the $P_2^*B_AH_A$ and I States

In our model the $P_2^*B_AH_A$ state is presumably associated with the P^* stimulated emission band at 940 nm. This band is spectrally and temporally differ from the initially excited P^* emission band at $\sim 905 \text{ nm}$ (P_1^* in the model) and is clearly observed in native and mutant RCs at room and low temperatures [3,24]. In the experimental ΔA spectra the 940-nm emission band forms a long-wavelength tail of the broadband negative signal mainly consisted of the P absorption band bleaching at $\sim 870 \text{ nm}$. The nature of 940-nm emission band is not well understood. The visible and IR transient spectroscopy indicates that this band may be ascribed to the state with partial charge separation inside the dimer P [24-26]. From the other hand, the hole burning experiments at low temperatures show an absence of the P^* conversion into another state on a time scale much shorter than 1 psec [27,28]. The possible charge transfer character of the P^* state may be a result of the electron-spin density shift from P_A to P_B in P^* calculated by quantum-mechanical methods [29]. The appearance of the delayed 940-nm feature in the P^* emission spectra may originates from vibrational relaxation or electronic relaxation (or both) or from excitation energy redistribution over vibrational modes in the

P* state. It is clear that further studies are need in this question.

As it was mentioned above, the I state was introduced into the model for better fitting of the experimental B_A^- absorption kinetics at 1020 nm. The population dynamics of the I state is close to the oscillatory component of the experimental B_A^- absorption band dynamics. The calculated sum of the I and $P^+ B_A^- H_A$ populations is close to the experimental B_A^- kinetics. These results indicate that the I state may contain B_A^- or $B_A^{\delta-}$. One may speculate that I is the state with charge transfer character between P* and B_A . To distinguish the I and $P^+ B_A^- H_A$ states in experiment is very difficult because of their spectral and temporal closeness. No clear experimental evidence of the I state existence is available now.

In our opinion, an advantage of the schemes with the $P_2^* B_A H_A$ and I intermediates consists in the high rates of the reactions in which these states are involved. The $P_2^* B_A H_A$ and I states act as fast mediators between the initially excited ($P_1^* B_A H_A$) and charge separated states. A stabilization of electron occurs lately in the $P^+ H_A^-$ state and partially in the $P^+ B_A^-$ state.

3.5. A Nature of the Oscillations

In our model the oscillations in the populations are caused by external modulation of the reaction energetics. A nature of this modulation is beyond the scope of the model. The nuclear motion (not only inside P) can be a possible source of this modulation. Shortly after the excitation of P by broadband femtosecond pulse the nuclear motion has a coherent character. When the coherence is rapidly damped this motion may continue incoherently due to the nuclear inertia. One can speculate that the incoherent motion may exist a longer timescale than the coherent one, but the latter produces the greater amplitude of the oscillations. The observed oscillations may reflect both the coherent and incoherent motion. The presented model shows that at $t > 150$ fsec the oscillatory features observed in the kinetics of the excited and charge separated states can be explained by incoherent modulation of the reaction energetics.

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