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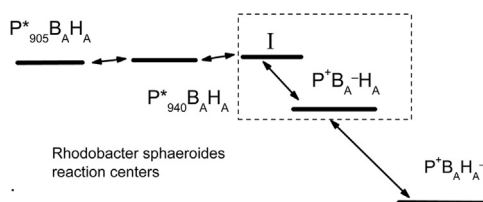
Modeling of reversible charge separation in reaction centers of photosynthesis: An incoherent approach

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HIGHLIGHTS

- Primary charge separation in photosynthetic reaction centers can be modeled by kinetic equations with time-dependent rate constants.
- The model consisting of two excited and three charge separated states is in good accordance with experimental data.
- The intermediate states in the model act as fast mediators.
- In the model the oscillations in the population kinetics arise from the external modulation of the reaction energetics.
- The oscillations in the population kinetics of the excited and charge separated states of reaction centers may have an incoherent nature.

GRAPHICAL ABSTRACT



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ABSTRACT

Primary charge separation in reaction centers (RCs) of bacterial photosynthesis is modeled in this work. An incoherent population dynamics of RCs states is formulated by kinetic equations. It is assumed that charge separation is accompanied by regular motion of the system along additional coordinates. This motion modulates an energetics of the reactions, and this modulation causes femtosecond oscillations in the population of the states. The best qualitative and quantitative accordance with experimental data on native, modified and mutant RCs of *Rba. sphaeroides* is achieved in the five states model that includes two excited states $P_{905}^* B_A H_A$ and $P_{940}^* B_A H_A$ 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 electron acceptors, monomeric bacteriochlorophyll and bacteriopheophytin in active A-branch respectively). The excited states emit at 905 and 940 nm and have approximately the same energy and high interaction rate. The intermediate state I is populated earlier than the $P^+ B_A^- H_A$ state and has energy close to the energy of the excited states, a high rate of population and depopulation and spectral identity to the B_A^- . A sum of the I and $P^+ B_A^- H_A$ populations fits the experimental kinetics of the B_A^- absorption band at 1020 nm. The model explains an oscillatory phenomenon in the kinetics of the P^* stimulated emission and of the B_A^- absorption. In the schemes without the I state, accordance with the experiment is achieved at unreal

Nonmathematical abbreviations: ΔA , Absorbance change (light minus dark); BChl, Bacteriochlorophyll; B_A , Monomeric BChl in A-branch; H_A , Bacteriopheophytin in A-branch; ET, Electron transfer; P, Primary electron donor, bacteriochlorophyll dimer; P_A and P_B , BChl molecules constituting P; Q_A , Primary quinone; RC, Reaction center; Rba., Rhodobacter

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parameter values or is not achieved at all. A qualitative agreement of the model with the experiment can be achieved at a wide range of parameter values. The nature of the states I and $P_{940}^*B_AH_A$ is discussed in terms of partial charge separation between P and B_A and inside P respectively.

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1. Introduction

Photosynthesis is a global biological process of conversion of light energy into chemical energy. The synthesis of organic matter by photosynthetic bacteria, algae, and plants is a basis of life on Earth. Photosynthesis is responsible for the production of oxygen and the fixation of atmospheric carbon dioxide, which both are of great importance for life. In photosynthesis, absorption of a photon by pigment molecules creates an excited state whose energy is used to transfer an electron across the photosynthetic membrane. This primary electron transfer or charge separation occurs in reaction centers (RCs) which are pigment–protein complexes of a photosynthetic membrane. The primary charge separation process triggers a sequence of chemical and biological processes which complete photosynthesis.

In RCs of purple bacteria *Rhodobacter (Rba.) sphaeroides* the charge separation consists in electron transfer from an excited dimer of bacteriochlorophyll P^* to bacteriopheophytin H_A with the participation of monomeric bacteriochlorophyll B_A (reviews and references to original works are in (Shuvalov, 2000; Parson and Warshel, 2009)). At room temperature $P^* \rightarrow B_A$ reaction occurs within ~ 3 psec, while $B_A^- \rightarrow H_A$ reaction occurs faster within ~ 1 psec. Then the electron is transferred to the primary quinone Q_A within ~ 200 psec. At cryogenic temperatures all reactions are accelerated by 2–3 times. The quantum yield of charge separation is close to unity. Charge separation is accompanied by oscillations of a population of RC states when RCs are excited by femtosecond (< 30 fsec) light pulses. These oscillations are observed during 1–2 psec after excitation in the stimulated and spontaneous emission band of P^* in the range of 900–960 nm (Vos et al., 1994a, 1993, 1994b, 1996, 1998; Spörlein et al., 1998, Stanley and Boxer, 1995; Rischel et al., 1998), in the B_A^- absorption bands at 805 (Streltsov et al., 1997, 1998) and 1020 nm (Yakovlev et al., 2000, 2002), in the H_A absorption band at 760 nm (Yakovlev et al., 2002) and in the electrochromic shift of the B_A band at 788 nm (Vos et al., 2000). A Fourier transformation of the oscillations revealed several bands in the range of 10–400 cm^{-1} with the most intensive broad band with a substructure at 130–150 cm^{-1} (period of 220–260 fsec). The oscillations with this period have opposite phases at wavelengths shorter and longer than 920 nm. These oscillations are observed in both native and mutant RCs in a wide range of temperatures, from cryogenic to room.

One of the possible mechanisms of the oscillations can be a wavepacket formed by simultaneous population of several vibronic levels of the P^* excited state (Vos et al., 1994a, 1993, 1994b, 1996, 1998). This idea is strongly proved by the fact that the 220–260 fsec oscillations are not observed when only one vibronic level of P^* is populated by a narrowband femtosecond pulse (Vos et al., 1994a). The wavepacket periodically moves in the P^* potential well within the 130–150 cm^{-1} frequency equaled to the fundamental mode frequency. The wavelength of the wavepacket emission depends on time, due to the mutual space shift of the P and P^* potential surfaces. As a result, the oscillations in the short- and long-wavelength parts of the P^* emission band have opposite phases. When the wavepacket appears in the intersection area of the P^* and $P^+B_A^-$ potential surfaces, a partial leaking of it into the charge separated state can occur (Novoderezhkin et al., 2004). This may explain the oscillations in the population of the primary photoproduct. Note that the wavepacket can be formed in the ground state P as well.

Quantum beats between two levels with close energies are another coherent mechanism that may lead to the oscillations (Shchepetov et al., 2009a, 2009b). Theoretically, the amplitude of these beats reaches 100% when the levels have exactly the same energy. In this case, the frequency of the beats V/h depends on the energy of electron coupling V only. Increase of the energy difference of the two levels leads to a decrease in the amplitude of the beats and to an increase in their frequency. Summation of the beats between the pairs of the vibrational levels provides the damped oscillations in the populations of the states. In contrast to the wavepacket mechanism, the mechanism of quantum beats is almost inertialess, being based on electron motion. Recently, the long-lived (> 1 psec) electronic coherence between the two excited states B^* and H^* was found in chemically oxidized *Rba. sphaeroides* RCs by 2D electron spectroscopy (Westenhoff et al., 2012).

Theoretical analysis of the coherent electron transfer was performed on the basis of Redfield theory (Redfield, 1965) in (Jean and Fleming, 1995) and with a dispersed polaron model (Ando and Sumi, 1998). 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 (Gu et al., 1995; Lin et al., 1995; Leegwater, 1995). In (Gu et al., 1995; Lin et al., 1995) a simple exponential decay of the vibrational coherence was assumed. In (Leegwater, 1995) the processes of the vibrational coherence transfer caused by relaxation were taken into account and the P^* vibrational dynamics was calculated by the Redfield theory in the secular approximation. The vibrational dynamics of the P^* and $P^+B_A^-$ bands coupled to the $P^* \rightarrow P^+B_A^-$ reaction was studied using the Redfield theory and the approach of a single nuclear mode coupled to the two electronic states (Jean and Fleming, 1995; Jean et al., 1992; Jean, 1994). In these works the time dependence of the reaction coordinate and the corresponding population dynamics of the P^* state were calculated. The Redfield theory permits one or two modes to be included as system coordinates. For a larger number of modes, a dispersed polaron model can be used (Ando and Sumi, 1998). This model allows calculation of the time evolution of the electron transfer coordinate for the P^* state including oscillations and vibrational relaxation. The theory of electron or energy transfer in the dispersed polaron model is currently developed only for equilibrated vibrational modes (Zhang et al., 1998), and therefore the semiclassical approach is widely used for calculations of electron transfer dynamics. In this approach, the coherent dynamics of the P^* state determines an oscillating rate constant for the $P^* \rightarrow P^+B_A^-$ reaction.

Stochasticity is a factor that can strongly limit the life time of coherent phenomena. At room temperature the quantum oscillations should be damped very quickly due to thermal motions (Lucke et al., 1997). The molecular dynamics calculations show that at room temperature the difference of the electrostatic energies of the P^* and $P^+B_A^-$ states fluctuates with an amplitude of ± 2 kcal/mol (700 cm^{-1}) and a mean period of 50 fsec (Warshel and Parson, 2001). This amplitude is more than three times greater than phonon energy $k_B T \sim 200$ cm^{-1} and is comparable with the $P^*/P^+B_A^-$ energy gap ~ 350 – 550 cm^{-1} (Shuvalov and Yakovlev, 1998; Nowak et al., 1998). Also, this amplitude is greater than the wavepacket energy ~ 150 cm^{-1} (Yakovlev et al., 2002). On the other hand, the molecular dynamics calculations revealed a number of classical vibrational modes in RCs at 20–200 cm^{-1} (Parson et al., 1998). These modes can have an influence upon the energetics of the $P^* \rightarrow P^+B_A^-$ reaction (Parson et al., 1998). The

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