A SEMI-CLASSICAL MODELING OF REVERSIBLE CHARGE SEPARATION IN REACTION CENTERS OF PHOTOSYNTHESIS.

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In photosynthesis, the primary charge separation occurs in reaction centers (RCs) which are pigment-protein complexes of a photosynthetic membrane. In RCs of purple bacteria *Rhodobacter (Rba.) sphaeroides* this process consists in electron transfer from excited dimer of bacteriochlorophyll P* to bacteriopheophytin H_A with a participation of monomeric bacteriochlorophyll B_A. Charge separation is accompanied by oscillations of a population of RC states when RCs are excited by femtosecond (<30 fsec) light pulses. In the present work the charge separation dynamics of native, modified and mutant *Rba. sphaeroides* RCs is modeled in terms of the kinetics equations for the populations with rate constants depended on time through the dependence on "slow" coordinates. This approach is based on the Marcus theory and on its application to charge separation in RCs. A goal of the work was to build up a more realistic model of incoherent charge separation for qualitative and quantitative explanation of oscillatory phenomena at early times of this process. A success in this way would mean that the observed femtosecond oscillations of the populations of the RC states may have incoherent nature too. The simplest case of regular changes of the "slow" coordinates with time was studied in the model. It was found that the five states model $P*_{905}B_AH_A \leftrightarrow P*_{940}B_AH_A \leftrightarrow I \leftrightarrow P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$ adequately explains the experimental kinetics of ΔA at t > 150 fsec. In the five states model two different excited states of P* and three charge separated states I, $P^+B_A^-H_A$ and $P^+B_AH_A^-$ were used. The new intermediate state I was assumed to be populated earlier than the $P^+B_A^-H_A$ and $P^+B_AH_A^-$ states. The simplest three states model $P*B_AH_A \leftrightarrow P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$ does not provide the correct form of the oscillations and does not explain the out-of-phase oscillations of the P* stimulated emission at 905 and 940 nm. The four states model $P*_{905}B_AH_A \leftrightarrow P*_{940}B_AH_A \leftrightarrow P^+B_A^-H_A \leftrightarrow P^+B_AH_A^-$ well explains the oscillatory features of the P* stimulated emission

kinetics. A drawback of the four states model is the unacceptably large amplitude of the oscillations of the reaction energetics and the wrong position of the $P^+B_A^-$ level higher than the $P^*_{905}B_A$ and $P^*_{940}B_A$ levels. In the model the oscillations in the population kinetics arise from the external modulation of the reaction energetics leading to the modulation of the rate constants. The qualitative agreement of our model with the experimental data can be reached in the wide range of the parameters. This indicates the stability of the solution founded in the model against the parameter fluctuations. In our opinion, the most interesting result of the modeling is a conclusion about a possibility of an existence of the new intermediate states participating in primary charge separation. We signed these states as $P^*_{940}B_AH_A$ and I. The first state is presumably associated with the P* stimulated emission band at 940 nm. The 940-nm band might be ascribed to the $P_A^{\delta+}\,P_B^{\delta-}$ state with partial charge separation between P_A and P_B. This hypothesis is indirectly confirmed by the quantum-mechanical calculations of the electron-spin density shift from P_A to P_B in P* and by the IR spectroscopy data. The intermediate state I was introduced in the model in order to co-ordinate the position of the $P^+B_A^-$ level below the P*B level by several hundreds of cm^{-1} with the presence of the deep oscillations in the population of the $P^+B_A^-$ state. The dynamics of the I state population in the model mainly coincide with the oscillatory component of the experimental B_A^- absorption band dynamics. These means that the state I may be the $P^{\delta+}B_A^{\delta-}$ state with partial charge separation between P* and B_A. The main advantage of the presence of the $P^*_{940}B_AH_A$ and I intermediates seems to consist in the very high rates of the primary reactions. The $P^*_{940}B_AH_A$ and I states act as mediators which quickly receive an electron from the previous state and quickly pass it to the next state. Based on the numerous data one can conclude that shortly after the excitation of P by <30-fsec pulse the nuclear motion inside P has a coherent character. If the coherent nuclear wavepacket is quickly damped then the nuclei would continues the incoherent motion. The model presented here describes the influence of this incoherent component of the nuclear motion on primary charge separation in native and mutant RCs of *Rba. sphaeroides*. The closeness between the calculated and measured kinetics at t >150 fsec demonstrates a possibility of incoherent nature of the observed oscillations.