



Use of a system of differential equations to analyze the functioning of a catalytic bio macromolecule under non equilibrium conditions



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ARTICLE INFO

Keywords:

Biophysics
Electron-conformational sub states
Structural self-regulation
Reaction centers of *Rhodobacter sphaeroides*
Electron transport
Mathematical model

ABSTRACT

The aim of the work is to analyze the response of a biomolecule to an external influence based on the study of its hidden states by identifying differential equations with constant coefficients.

The relevance of the work lies in the fact that often the main reaction of an object to an external action can be represented as a sum of various exponential functions with a common starting point and a material balance equation. In this case, the response of an object to an external action corresponds to a system of differential equations with constant coefficients. This character of the main reaction may be due to the influence of the hidden properties of the object, which play the role of regulatory parameters.

The problem is that the hidden factors and the system of differential equations are not identified. As an object, isolated reaction centers (RC) of the bacteria *Rhodobacter sphaeroides*, which possess the above properties, has been used. Their structure is well studied.

As result of studying of photo excitation processes of the reaction center has shown that electron transfer kinetics (the main reaction) can be approximated by three normalized exponential functions. Program was developed to identify for four differential equations of electron transfer and the balance equation, the behavior of hidden states of the reaction center.

It was concluded that time the dependence the probability density of finding an electron in different conformational states of the reaction center characterizes the space-time changes in the structure of the reaction center.

1. Introduction

Spatiotemporal movements of biological macromolecules have complex multi component kinetics, which experimentally manifests itself as the main reaction of the system to the action of the control parameter. The dynamic properties of macromolecules are important for their functioning. The study of these properties is a relevance task, but they are difficult to measure. This situation has been observed for the well-known isolated RCs of photosynthetic bacteria *Rhodobacter sphaeroides*, whose electronic states simultaneously affect and depend on the conformational state of RC protein complex. When RC has been illuminated with a light pulse, the absorption of RC decreases (on the 865 nm line). After the end of the illumination, the absorption of RC has been restored. The intensity of the spectral line of 865 nm is associated with electron photo transfer from a bacteriochlorophyll dimer (P) to a secondary acceptor

(Q_B). The transfer of an electron from a donor to an acceptor goes with high efficiency over a distance of 40 nm. As a result, the protein structure of RC is out of equilibrium. The energy of protein reorganization is changing, which leads to a change in the kinetics of electron transfer. The interrelation of electron transfer processes and changes in the protein structure of RC [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] appears. The kinetics of electron transfer acquires a multi exponential character. We used long-term illumination (100 s) of the reaction center, at which multiple, reversible electron transfer takes place in RC. As a result, there are significant changes in the protein structure of RC. Characteristic relaxation times of the protein reach values of 1–100 s. Such slow transitions of molecules on excited states can be modeled using the methods of classical kinetics. Therefore, RCs of the bacteria *Rhodobacter sphaeroides* has been chosen as the object for the development of a program for studying macromolecules. The kinetics of the main reaction of RC during

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<https://doi.org/10.1016/j.heliyon.2019.e02108>

Received 12 July 2018; Received in revised form 13 May 2019; Accepted 15 July 2019

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illumination and after illumination has usually approximated by the sum of various exponential functions with a negative exponent [11, 12, 13]. The parameters of the normalized exponential functions has used to analyze the main reaction, identify the conformational states of an object, and the effects of structural self-regulation of the main reaction. Often the values of weights and decrements of the exponential components depend on each other and the characteristics of the control parameter of the main reaction [14, 15, 16, 17]. This makes their interpretation difficult. There is a need to move from the parameters of the exponential components of the main reaction to the rate constants of kinetic reactions.

It is known from mathematics that the solution of a system of differential equations with constant coefficients is expressed as a certain sum of exponential functions. If the experimental kinetics of the main reaction is described as the sum of exponential functions, then it can correspond to a certain system of differential equations. Such differential equations may correspond to independent subsystems of the object. The experimental kinetics of cyclic electron transfer RC was approximated by the sum of three exponential functions, with a material balance equation. They determined the number of differential equations. The parameters of the exponential functions were used to determine the values of the coefficients of the three differential equations, which were equal to the algebraic sum of the reaction rate constants for the balance equations RC. The values of the rate constants of the balance equations were found by solving the optimization problem using the coordinate descent method. The solution of the system of differential equations determined the kinetics of populations of RC substations. All this allows us to determine the number of balance equations, the number and kinetics of the behavior of sub states (subsystems) of an object.

The task was to create a computer program (Delphi7) to identify four differential equations with constant coefficients with material equation for balance. The algorithm developed using the electron transfer kinetics of the reaction center. Another task was to determine the kinetics of electron transfer between the hidden states of the reaction center. The results obtained compared with the results of the study of the reaction center using the method of two exposures.

As a result shown that the experimental kinetics of cyclic transfer of electrons of the reaction center was approximated the sum of three different exponential functions that had negative exponents. The values of reaction rate constants were determined for the stage of illumination of RC ($I = 7.2 \text{ mW/cm}^2$, $T_{\text{exp}} = 100 \text{ s}$) and for the stage of relaxation of RC after turning off the light. It is obtained that the maxima of the population of the states of RC correspond to a time of $3 \div 140 \text{ s}$ from the moment of switching on (off) the exciting light.

The aim of the work is to analyze the response of an object to an external action based on the study of hidden states of objects by identification differential equations with constant coefficients.

2. Materials and methods

Isolated reaction centers (RC) of *Rhodobacter sphaeroides* bacteria, which provided by the Department of Biophysics of Moscow State University M.V. Lomonosov. They suspended in 0.01 M Na-P buffer, pH 7.2, which contained 0.05% LDAO. A two-channel PC-based spectrometer developed for the study. The first channel for measuring RC absorption used light with a frequency of 5 kHz with an intensity of $0.2 \mu\text{W/cm}^2$ at a wavelength $\lambda = 865 \pm 10 \text{ nm}$. The measurement accuracy of the absorption was $\pm 0.0005 \text{ cm}^{-1}$ in the absorption range $0 \div 1 \text{ cm}^{-1}$. In another channel, light was used to excite RC with a wavelength $\lambda = 865 \pm 50 \text{ nm}$ with an intensity of $0 \div 10 \text{ mW/cm}^2$ with a step of $5 \mu\text{W/cm}^2$. The time sampling of signals varied from 0.01 to 1 s, depending on the rate of change of the signal. The size of the cuvette is $3 \times 2.5 \times 1 \text{ cm}$. The RC suspension was prepared at a concentration of 10^{-6} M , kept in the dark at temperature (20°C) for 12 hours (dark RC-adapted state). The state of the reaction center adapted to light formed using a light pulse with duration of 100 s and an intensity of 7.2 mW/cm^2 . After the photo excitation of the reaction center was completed and the absorption

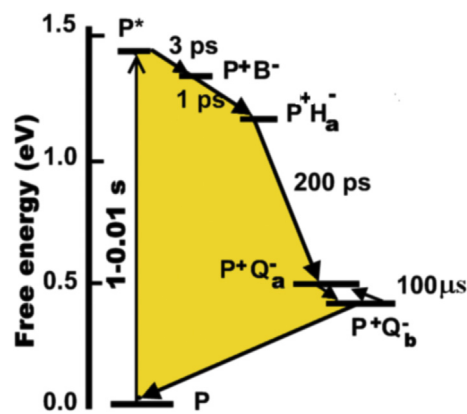


Fig. 1. Shows the levels of free energy and the time of cyclic electron transfer between the ion-radical states of the RC.

reached a dark value, the reaction center solution additionally kept in the dark for 1500 seconds to reach an equilibrium state. Then re-illumination of the reaction center took place. It is important to note that, unlike most studies of RC reactions to pulsed excitation, we study the effects of continuous excitation of RC of a certain duration and intensity, because only then the effects of the conformational rearrangements of the RC become especially significant. As is known [18, 19], the reaction center consists of three polypeptides, called H, L and M, which contain 10 co-factors. These are four bacteriochlorophylls (BChl), two bacteriopheophytin (BPhe), two ubiquinones Qa, Qb, one photoprotective carotenoid and a non-heme iron atom. The complex also contains a large number of bound water molecules, some of which play functional roles, for example, in the reduction and protonization of Qb of ubiquinone [19]. Electron transfer occurs from the primary electron donor, excited bacteriochlorophyll dimer (BChl), to the quinone acceptor secondary acceptor ubiquinone Qb through the sequential formation of several intermediate states with a separated charge [20]. Fig. 1 shows a diagram of cyclic electron transfer with long-term excitation of the RC. The intensity of the exciting light determines the re-excitation time of the RC. Changes in the RC structure affect the electron return time of the acceptor.

The intensity of the 865 nm line of the absorption spectrum of RC is associated with electron transfer from the donor to the acceptor (from the acceptor to the donor). It characterizes the time dependence the probability density finding electron at the donor (population of such a state of RC when the electron is on the donor). The analysis of the experimental dependences of electron transfer carried out in several stages. At the first stage, the kinetic curve ($X_1(t)$) of the photo induced electron transfer RC was divided into the region the electron excitation (the oxidation of donor) and the region the electron recombination (recovery of donor) after the light was turned off. These stages of the kinetic curve has approximated by sums of exponential components with a positive weight and a negative value of the decrement [21]:

$$X_1(t) = \sum_i A_i e^{-d_i t}; \quad \sum_i A_i = 1 \quad i = 1, 2, 3 \quad (1)$$

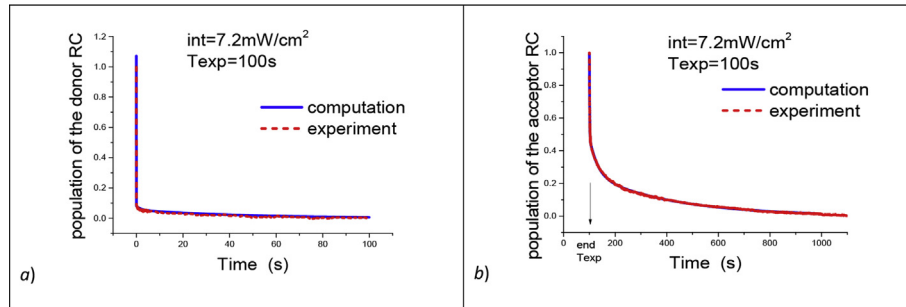
The program independently found the number of exponential components, which has a minimum approximation error. The analyzed signal had a text format in the form of two columns. The first column contains the time portion of the signal. The second column contains the signal size in arbitrary units. The magnitude of the signal should constantly decrease in time. After starting the program, the process of decomposition of the original signal into exponential components occurred within a few minutes.

After completing the approximation, the exponent parameters will be shown in the menu table. The results of the decomposition in text format can be stored in two files: in the form of signal approximation for visual inspection and in the form of Table 1 of the parameters of exponential

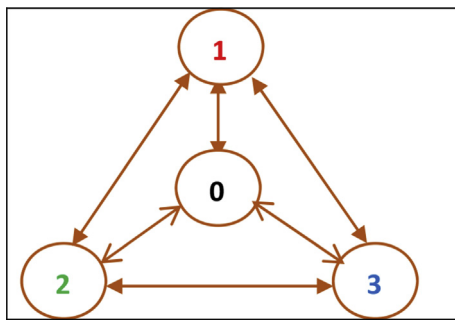
Table 1

Parameters of the exponential components of the kinetics of electron transfer RC.

The electron transfer	d_1 (s ⁻¹)	A_1 (rel. un)	d_2 (s ⁻¹)	A_2 (rel. un)	d_3 (s ⁻¹)	A_3 (rel. un)	dispersion
Exposure of RC	123.62	0.9925	0.5397	0.0249	0.0235	0.0548	0.00443
After the exposure of RC	1.10	0.512	0.0342	0.2264	0.0034	0.2538	0.00118

**Fig. 2.** Approximation of the electron transfer kinetics RC by the sum of three exponentials; a) -the time dependence the probability density of finding an electron on donor under illumination ($\lambda = 865\text{nm}$) RC. b) -the time dependence the probability density of finding an electron on acceptor after the illumination RC.

functions. Fig. 2 shows the normalized graph of the kinetics of electron transfer in the RC photoexcitation process (experiment) and the signal approximation curve by three exponential functions. Analysis of various regions (oxidation, donor reduction) of kinetic curves for different parameters of photoexcitation RC showed that the experimental curves well approximated by the sum of three exponentials [22]. It known that a system of N homogeneous differential equations with constant coefficients, with an equation the material balance has a solution in the form of the sum $(N-1)$ of exponential functions. It can assumed that the kinetic curves, presented as a sum of three normalized exponential components with balance equation, can correspond to the solution of a system of four differential equations with some kinetic constants. Fig. 3 shows the kinetic form of electron transfer in RC, where the electron-conformational states of RC are shown. The state (0) of RC corresponds to the condition when electron is on donor of RC. The states (1, 2, 3) of RC correspond to the states when electron is on acceptor. Unfortunately, mathematics does not allow us to speak in more detail about the structure of these states. In the second stage, a gradient method for solving the

**Fig. 3.** Kinetic scheme of electron transfers in RC *Rhodobacter sphaeroides*. The arrows in the diagram show the electron-conformational interaction of the RC-complex. Arrows indicate the rate constants of the reactions (k_{ij}) (12 pieces) of four differential equations in the figure. They represent the rate of charge transfer between the states of the reaction center.**Table 2**The rate constants of the differential balance equations for the stages of oxidation of the donor RC (line 2), restoration of the donor RC (line 3). The intensity of the exciting light is 7.2 mW/cm^2 , the exposure time of the RC (T_{exp}) is 100s.

k_{ij} (s ⁻¹)	k_{01}	k_{10}	k_{12}	k_{21}	k_{23}	k_{32}	k_{02}	k_{20}	k_{13}	k_{31}	k_{03}	k_{30}	dispersion
oxidation	112.6	9.3	0.07	0.375	1E-5	1E-5	1.18	1E-6	1E-5	1E-5	0.446	1E-5	4E-5
recovery	0	0.01	0.007	1E-6	1E-6	0.143	0	0.003	0.024	0.315	0	0.635	2.1E-6

optimization problem was used, which (see Table 2).

In the second stage, a gradient method for solving the optimization problem was used, which consisted in determining the values of the coefficients of the system of differential equations for which the kinetics of donor population (donor population, state 0) RC coincided with the experimental absorption kinetics of the RC. This task is reverse and ill conditioned. For the direct task, when the kinetic constants of the system of differential equations have known, there is a one-to-one correspondence between the constants of the differential equations and the solution of equations. The system has a unique solution. The differential equations of electron transfer in RC and the equation of state have the following form:

$$\begin{aligned}
 dX_0/dt &= -(k_{01}+k_{02}+k_{03})X_0 + k_{10}X_1 + k_{20}X_2 + k_{30}X_3 \\
 dX_1/dt &= k_{01}X_0 - (k_{10}+k_{12}+k_{13})X_1 + k_{21}X_2 + k_{31}X_3 \\
 dX_2/dt &= k_{02}X_0 + k_{12}X_1 - (k_{20}+k_{21}+k_{23})X_2 + k_{32}X_3 \\
 X_0+X_1+X_2+X_3 &= 1
 \end{aligned} \quad (2)$$

Where $X_j(t)$ is the time dependence of the probability density of finding an electron in the j -state of RC (population of the states of the RC), $j = 1, 2, 3, 4$.

The initial conditions of the populations of the states of RC during exposure are:

$$X_0(0) = 1, X_1(0) = 0, X_2(0) = 0, X_3(0) = 0 \quad (3)$$

The initial conditions of the populations of the states of the RC after the exposure of RC are equal to the populations of the states of RC at the end of the exposure:

$$X_0^{\text{rel}}(0) = X_0(T_{\text{exp}}), X_1^{\text{rel}}(0) = X_1(T_{\text{exp}}), X_2^{\text{rel}}(0) = X_2(T_{\text{exp}}), X_3^{\text{rel}}(0) = X_3(T_{\text{exp}}) \quad (4)$$

The solution of the system (2) is:

$$X_j(t) = \sum C_{j,i} \exp(-d_i t) \quad X_3(t) = 1 - \sum X_j(t) \quad i = 1, 2, 3; j = 0, 1, 2 \quad (5)$$

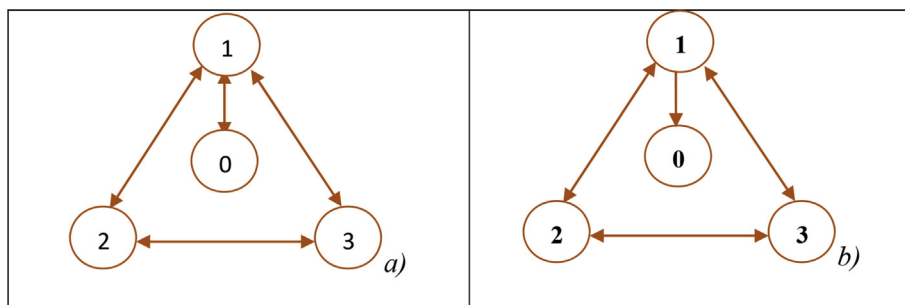


Fig. 4. The kinetic scheme is of the initial stage of determining the rate constants. a) The initial values constants of the rate the reaction of differential equations when illuminating the RC: $k_{02} = k_{03} = 0$, $k_{01} = k_{10} = 0.01 \text{ c}^{-1}$, $k_{20} = k_{30} = k_{31} = 10^{-8} \text{ c}^{-1}$, $k_{12} = 10^{-9} \text{ c}^{-1}$, $k_{21} = k_{13} = k_{32} = k_{23} = 10^{-6} \text{ c}^{-1}$. b) The initial values constants of the rate the reaction of differential equations after illuminating the RC. $k_{02} = k_{03} = k_{01} = 0$, $k_{10} = 0.01 \text{ c}^{-1}$, $k_{20} = k_{30} = k_{31} = 10^{-8} \text{ c}^{-1}$, $k_{12} = 10^{-9} \text{ c}^{-1}$, $k_{21} = k_{13} = k_{32} = k_{23} = 10^{-6} \text{ c}^{-1}$.

Figure 5 displays the menu of a program for calculating reaction rate constants. The interface includes several input fields and tables for parameters.

Texp number: 0

parameters of the experimental curve

	d1	weight-1	d2	weight-2	d3	weight-3
Oxidation data	-0	0	-0	0	-0	0
Calcul of oxidation	0	0	0	0	0	0
Recovery data	0	0	0	0	0	0
Calcul of recovery	-0	-0	-0	-0	-0	-0

initial parameters of the optimization process

i\j	1-2	2-1	1-3	3-1	1-4	4-1	2-3	3-2	2-4	4-2	3-4	4-3
K _{0ij}	0.01	0.01	0.000000	0.000000	0.000000	0.000000	0.000000	0.000001	0.000001	0.000000	0.000001	0.000001
dK _{ij}	0.1	0.01	0.001	0.001	0.0011	0.0011	0.001	0.001	0.0011	0.0011	0.001	0.0011

output parameters

	k1-2	k2-1	k2-3	k3-2	k3-4	k4-3	k1-3	k3-1	k2-4	k4-2	k1-4	k4-1
Oxidation	0	0	0	0	0	0	0	0	0	0	0	0
Recovery	0	0	0	0	0	0	0	0	0	0	0	0

Buttons: Calculation, Save K(i,j), Upload, Cleaning, Save File, No delta1, T=f(1/T), Close

Fig. 5. Menu is of program for "calculating reaction rate constants for a system of three differential equations".

d_i - are equal to the eigenvalues of the matrix of constants of differential equations; C_{ji} - are constants defined by the coordinates of the eigenvectors of the matrix of differential equations and the initial conditions of the states of RC.

The eigenvalues of the matrixes of coefficients of differential equations for photoexcitation and relaxation processes RC should not be equal to zero ($d_i \neq 0$). This imposed a restriction on the initial values of the constants of differential equations (Fig. 4a, b).

The optimization process, using the method of coordinate descent, proceeded as follows. First, the values of the constants of the differential equations of the photo transfer of an electron were found for the stage of illumination of the reaction center. We used the initial values of the constants k_{ij} , d_{ij} (Fig. 4). Differential equations (direct problem) the solution was sought using the matrix method. The solution of the equations was sought as the sum of three exponential functions with parameters $A_i d_i$ (Formula 1). The difference between the experimental (A_i^0 , d_i^0) (Table 1) and calculated A_i^x , d_i^x parameter values of the exponential functions was used as the objective function (Δx). It is defined as:

$$\Delta x = \sum \frac{(A_i^0 - A_i^x)^2}{(A_i^0)^2} + \frac{(d_i^0 - d_i^x)^2}{(d_i^0)^2} \quad i = 1, 2, 3 \quad (6)$$

In the beginning, the value of the constant k_{01} optimized for the initial values of other constants. Then the optimal value of k_{10} was

determined at the optimal value of k_{01} and the initial values of the other constants. For the optimal values of k_{01} and k_{10} , the values of the constants k_{02} , k_{20} , k_{03} , k_{30} , k_{12} , k_{21} , k_{13} , k_{31} , k_{23} , k_{32} were sequentially optimized. A set of parameters that had the smallest error was recorded each time. The search for constant values was carried out with a variable step in the double range of values of the greatest decrement. The objective function had numerous local minima. The process was repeated 50 times in the same order of work with k_{ij} . As a result, we obtained a set of k_{ij} values with the smallest error. The solution of a system of differential equations with an optimal set of constants determined the population of all states of the reaction centers during photoexcitation. The population of the states obtained at the end of the RC illumination was used as initial conditions for analyzing the stage of relaxation of the reaction center (after turning off the light). For this stage, we used our own set (Table 1) of the parameters of the exponential components of the experimental kinetics of electron transfer, and set, k_{ij} (Fig. 4), of the initial values of the reaction rate constants. The values of k_{ij} determined using the above method.

3. Results and discussion

In Fig. 5 shows menu of program for identifying a system of differential equations of photo stimulated electron transfer in RC.

The kinetics of photo stimulated electron transfer (Fig. 6) as the sum

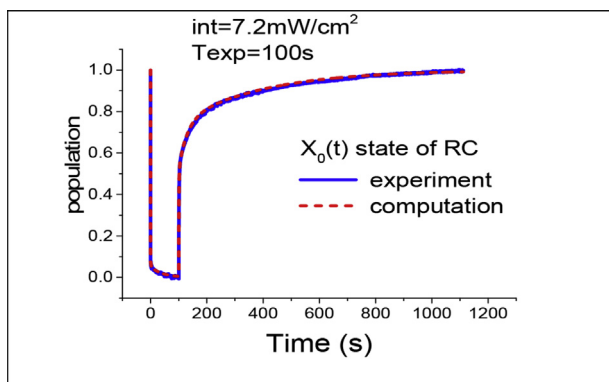


Fig. 6. Photo stimulated electron transfer RC. Experimental and calculated dependence of the population $X_0(t)$, which was obtained as a result of solving a system of differential equations.

of three exponential functions has represented by data in two columns (time, signal magnitude). Data on the exposure time, on the parameters of the exponential functions of the kinetics of electron transfer during illumination and after illumination of the reaction center, on the location of the analyzed signal introduced into the program menu (Fig. 5). The procedure for determining the values of the rate constants for the reactions of differential equations has initiated using the "Calculation" button. In the course of calculations, the data displayed in the upper cells of the table. After the end of the program, the values of the reaction rate constants shown in the table "output parameters". The solution of the system of differential equations of electron transfer obtained by the matrix method based on the calculated values of reaction rate constants. This solution shown in the table "parameters of the experimental curve." The calculation results saved in two text format files.

The program was used to determine the values of the constants for matrices of differential equations, the kinetics of the substation population

of RC in various photo stimulation modes of the RC. In most cases, a good agreement can be obtained between the experimental and calculated kinetics $X_0(t)$ of the RC population over the entire time interval of photo stimulation and relaxation of the RC. In Fig. 6 shows the experimental kinetics of the population of the state $X_0(t)$ for two stages of photoexcitation of the RC. The stage of illumination of the RC (donor oxidation) and the stage of relaxation of the RC (donor recovery) after the illumination of the RC. The same figure shows the kinetics of the population of this state of the RC, obtained by the program "Calculation of the constants of the system of differential equations". In Fig. 7 shows the experimental for $X_0(t)$ and the calculated kinetics of populations for $X_0(t)$, $X_1(t)$, $X_2(t)$, $X_3(t)$ of RC states. A single light pulse excited RCs with an intensity of 7.2 mW/cm² of 100 s. The mean-square error (dispersion) of calculations was $4 \cdot 10^{-5}$ for the stage of illumination of the RC for the stage of relaxation of the RC, dispersion = $2.1 \cdot 10^{-4}$. The computation time was about 10 minutes. As can be seen from Fig. 7, the kinetics of the population of states of the RC has features, the character of which depends on the parameters of the photo stimulation of the RC. The analysis showed that, unlike the state of $X_0(t)$, the kinetics of the population of states $X_1(t)$, $X_2(t)$, $X_3(t)$ has features. In the photo excitation mode of the RC, the maximum values of the set of states $X_0(t)$ $X_1(t)$ are 0.06 and 6 s after turning on the light. In the RC relaxation mode, the maxima of the $X_1(t)$ and $X_3(t)$ state populations were recorded after 3 and 47 s. Their population decreased to zero within 3 and 140 s, although the relaxation time of the RC was > 1000 s.

The maxima of the RC state population show the presence of opposite processes in the kinetics of the RC substations with their photo excitation and relaxation. These processes may be is caused by the RC structural changes in photo stimulated charge transfer. Studies of the kinetics [20] of photo stimulated charge transfer in RC using two consecutive light pulses with a variable interval between them showed the absence of a monotonic dependence of the exponential component of the kinetics on the interval between pulses. This method, like the previous one, allows determining the time parameters of the electron-conformational interactions in RC.

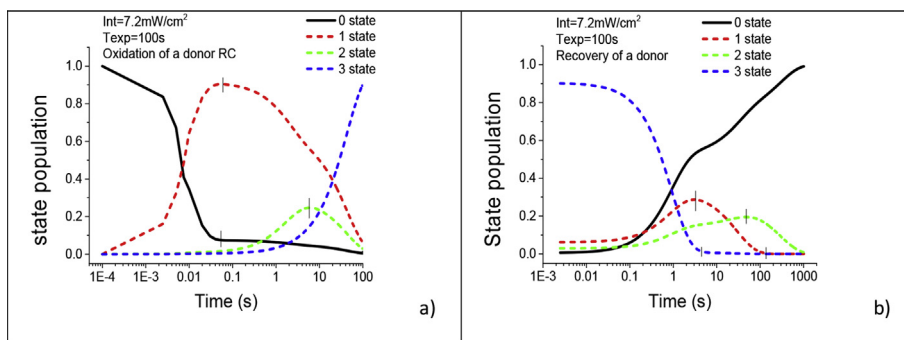


Fig. 7. Kinetics of the population of sub states of the RC as a result of solving the system of differential equations, a) - region of photo excitation of the RC, b) - region of relaxation of the RC.

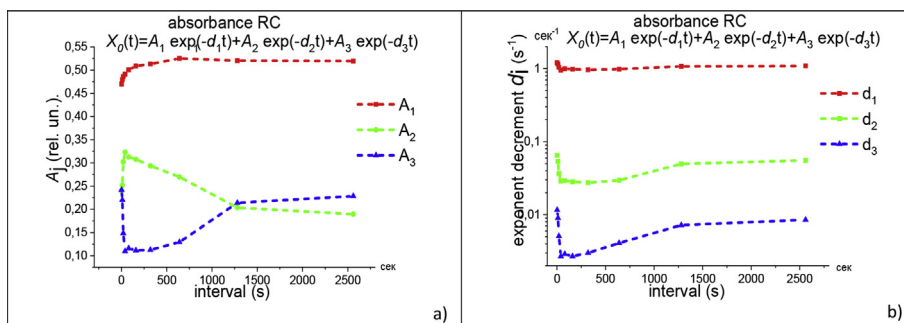


Fig. 8. Method of two exposures RC. Change in the parameters of the exponential components of photo induced electron transfer after the second light pulse, depending on the value of the interval between the first and second light pulses of the PC stimulation photo; a) changes in the weights (A_i), b) of the decrements (d_i) of the exponential components of relaxation RC. The pulse intensity is 7 mW/cm², the duration is 50 s.

Comparison of the results obtained by these methods (Figs. 7, b, 8 a, b) shows their coincidence. Time intervals (3, 47 and 140 s), corresponding to maxima of populations $X_2(t)$ and $X_3(t)$ during RC relaxation, coincide in order of magnitude with time intervals (4–200 s) between the excitation light pulses at which the parameters of the exponential components of the relaxation process RC have extreme values. This confirms the assumption that the appearance of the features the kinetics of the populations of the states of the RC substrates during photo stimulated charge transfer is associated with changes in their structure. Consideration of the physical nature of the electron-conformational states of the reaction center requires additional analysis and is beyond the scope of the work.

4. Conclusions

The photo kinetics of stimulated electron transfer in isolated reaction centers of *Rhodobacter sphaeroides* satisfactorily described by a system of three differential equations with two sets of constant coefficients and an equation of state.

The process of photo stimulated charge transfer in the RC satisfies models of the four independent states of the RC, which correspond to four interconnected electron-conformational interactions.

The kinetics of the RC state in photoexcitation and relaxation processes has clearly defined extremes (0.06, 3 ÷ 140 s), which are caused by the effects of the structural self-regulation of the main reaction because of the space-time movements of the RC macromolecule.

The program is designed for determine the values of the rate constants of reactions of differential equations, when the reaction of an object to an external action is represented as three exponential functions with a negative indicator and equation a material balance.

Declarations

Author contribution statement

Yuriy M. Barabash: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Taisiia V. Serdenko: Performed the experiments.

Peter P. Knox: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Alexander A. Golub: Conceived and designed the experiments; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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