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On the Involvement of the Water–Polaron Mechanism in Energy Trapping by Reaction Centers of Purple Bacteria

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Abstract—A locus for binding a mobile water molecule was searched for in the immediate vicinity of the special pair in the reaction center. Using the PROTEUS PC-program (a part of the GRASP package) atomic structures of the reaction centers were analyzed in purple bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides*. In both structures the loci for binding mobile water molecules were found at the distance of about 4.5 Å from the middle of the special pair in the reaction center. The reorientation of a hydrogen atom of this water molecule in the electric field of the excited special pair required energy of no less than 40 MeV that corresponded to predictions of the water-polarization model of trapping of electron excitation which was developed by M. V. Fok and one of the authors of this article.

Key words: purple bacteria, reaction centers, electron excitation trapping, water-polarization and exciton mechanisms

Based on abundant experimental data acquired starting from the mid-1960s, the following scheme of primary processes in purple bacteria was adopted in the literature on photosynthesis:

$$\text{BChl-800} \underset{K_{m1-}}{\overset{K_{m1}}{\leftarrow\!=\!\rightarrow}} \text{BChl-850} \underset{K_{m2-}}{\overset{K_{m2}}{\leftarrow\!=\!\rightarrow}}$$

$$\leftarrow\!=\!\rightarrow \text{BChl-880} \underset{K_{m-}}{\overset{K_{m}}{\leftarrow\!=\!\rightarrow}} P_2^* X \underset{K_{e-}}{\overset{K_{e+}}{\leftarrow\!=\!\rightarrow}} P_2^+ X^- ,$$

where BChl-800, BChl-850, and BChl-880 are fractions of the antennal BChl with the corresponding absorption peaks (BChl-880 is the main core-BChl); K_{m1}, K_{m2}, K_m, K_{m1-}, K_{m2-}, and K_{m-} are generalized constants of energy migration rates between the corresponding BChl fractions; X and X^- are primary electron acceptors in the normal and reduced state; K_{e+} and K_{e-} are rate constants of the forward and back electron transfer between P_2^* and X.

Abbreviations: RC) reaction center; P_2, P_2^*, P_2^+) RC special pair in normal, excited, and oxidized states; BChl) bacteriochlorophyll; SEE) singlet electron excitation.

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This model dominated until the early 1990s when the efficiency of the back electron transfer $P_2^* X \leftarrow\!= P_2^+ X^-$ was found to be very low [1-5]. This finding contradicted the model of primary processes in purple bacteria [6, 7]. To overcome this contradiction, three mechanisms have been proposed to date.

1. In works [8, 9] and then in more detail in [6, 7] was developed a "water–polaron" model of capture of singlet electron excitations (SEE) in reaction centers (RC). This mechanism suggests that the SEE entrance into the special pair of the reaction center transforms it to a strong charge transfer complex (CCT). A strong CCT means that a significant part of the excited electron has passed onto the adjacent molecule of the pair. Using the Stark effect, Moore et al. [10] found that the dipole moment of the special pair (P_2^*) of the RC was 6.6 D/*f*, where *f* was an orientation factor determined as the ratio of the local field to the external field superimposed which was approximated by a spherical cavity model $3\varepsilon/(2\varepsilon + 1)$. At the dielectric permeability coefficient $\varepsilon = 1.7$ for the spherical cavity this resulted in the dipole moment value ~8D for the excited P_2^*. For P_2 of purple bacteria the part of the charge transferred from the $P870_L$ onto the $P870_M$ molecule is $\Delta e \cong e/3$ [10, 11]. The energy required to produce in the CCT the P_2^* state of the $(+e/3)/(-e/3)$ dipole of 5 Å in length was ~150 MeV. A significant part of this energy should be compensated by dielectric polarization in the surrounding sphere of P_2 with the radius comparable to

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the length of the P_2^* dipole. The microscopic value of ε in the very hydrophobic RC globule around P_2 in the interesting time span of ~10^{-13} sec^{-1} corresponding to the time of generation and life of the CCT-state should be rather close to the light refraction (n) square for nonpolar amino acids which were dominant inside the RC globule, i.e., $n \cong 1.3$ and $\varepsilon = n^2 \cong 1.7$ [12]. Of the known atoms, only hydrogen has such low weight that it can fluctuate or be transferred over the distance of a chemical bond within the time span of ~10^{-13} sec^{-1} [13]. The electric dipole of water molecules is 1.84 D, which corresponds to the presence of +0.27 e on each hydrogen atom and of 0.54 e on the oxygen atom. To provide functions of the water–polaron model, a water molecule with the hydrogen atom(s) unbound, i.e., able to reorient in the electric field should be present in the immediate vicinity of the RC special pair. The atomic structures of the RC of purple bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* are found in works [14, 15]. The preparation of RC crystallized from *Rps. viridis* contained 202 water molecules, eight of which were at the distance of 7-10 Å from the middle of the special pair [14]. We have analyzed the data on the structure [14] using the approach described in [17] and all atoms of these water molecules were found to be bound to polypeptide atoms with the corresponding uncompensated opposite charges, i.e., their H-atoms were unable to be markedly displaced or rotated. Moreover, the calculation by the formula of the dipole–dipole interaction has shown that, on average, only about 10 MeV of the P_2^* electron energy can be expended for polarization of a mobile H-atom with ~+0.27 electron charge at the distance of 8 Å from the middle of the RC special pair. Thus, the main factor which could rehabilitate the water–polaron model is the presence of a water molecule located more closely to the center of the P_2 dipole. According to the electrostatics formula, to increase the energy portion spent for polarization of an H-atom in a water molecule in the field of the excited pair P_2^* to the level of $\Delta W_{pol} > 30$-40 MeV, this distance should be no more than 5 Å. Note, that the energy value of $\Delta W_{pol} \sim 40$ MeV is insufficient to overcome this contradiction. It was suggested that it could be completely eliminated only by a combined effect of the water–polaron and exciton mechanisms (see item 2).

2. Authors of works [18-21] and of some further works have developed an exciton variant as follows: in the presence of excitons delocalized by some core BChl molecules the migration rates of SEE onto the RC special pair and backward increase, but, first of all, the ratio of constants of these rates increases compared to those for monomeric or dimeric BChl molecules. The exciton model (if it is correct) can increase in the annular antennal structures similar to those ascribed to *Rhodospirillum rubrum* the ratio of constants of SEE migration rates from the antennal BChl onto the RC special pair and backward not more than 3.5-fold, whereas to overcome this contradiction this ratio has to be increased no less than 8-10-fold [7]. Note that by now the exciton model is also a hypothesis. Although the exciton appearance in long-wave fractions of BChl of purple bacteria is established reliably, the exciton property to concentrate several times the SEE in the RC special pairs [18-20] has not been shown experimentally to date.

3. Electron density fluctuations with frequencies of about 260 cm^{-1} were found in the excited special pairs of RC [22-24]. According to the authors of work [24], these fluctuations facilitate an excited electron to overcome the energy barrier and to be transferred onto the primary acceptor in the RC, the $P800_A$ molecule. However, a low value of the fluctuation energy (260 cm^{-1}) seems to exclude the possibility of a fundamental solution of the problem formulated above.

METHODS

To detect in the reaction center structures water molecules located at a distance less than 9 Å from the special pair, a PC-program was written which allowed us to determine the distance from water molecule oxygens to the center of the Mg–Mg section of P_2. Another program was written for determination of probable bonds of hydrogens of water molecules. This program allowed us to find the oxygen and nitrogen atoms located at a distance less than 3.5 Å from water molecule oxygens, because the mean distance between electronegative atoms producing a hydrogen bond is known to be 2.8 Å. To determine the most probable locations of hydrogen atoms of water (their coordinates could not yet be determined by X-ray crystallography), a standard PROTEUS program was used as a part of the GRASP packet [17]. The PROTEUS program allowed us to add hydrogen atoms to amino acids and water molecules, providing their orientation to minimize the free energy of their electrostatic interaction with atoms carrying an uncompensated negative charge and located nearer than 4.5 Å, first of all, with oxygen and nitrogen atoms.

COMPUTERIZED ANALYSIS OF PROBABLE HYDROGEN BONDS IN WATER MOLECULES ADJACENT TO THE RC SPECIAL PAIR

On analyzing data on the atomic structure of the RC from *Rps. viridis* present in the Brookhaven Protein Databank, identification number 1PRC, we found that oxygens in five H_2O molecules adjacent to 2P are at the distance of 7-9 Å from the middle of the section connecting Mg–Mg atoms in P_2: HOH304[1] (7.5 Å),

[1] This (and the other) numbers are not ordinal, they do not mean that the RC has more than 202 water molecules.

HOH302 (8.2 Å), HOH13 (8.4 Å), HOH32 (8.8 Å), and HOH14 (8.9 Å). Our program allowed us to determine for each of these H_2O molecules probable bonds of their H-atoms to the surrounding amino acids or cofactors, and these bonds corresponded to oxygens or nitrogens with an uncompensated negative charge which were located at the distance of no more than 4 Å from the oxygen of the water molecule considered. As in the case of the reaction center from *Rh. sphaeroides*, all these molecules are bound by two-three hydrogen bonds and are in a polar environment. We have found that the interaction energy of water hydrogen is 100 MeV, and this is much higher than the interaction energy of the H_2O dipole moment with the dipole moment of the excited special pair of the RC. Therefore, the reorientation of these five water molecules under the influence of the electric field of P_2^* which is required to provide the water–polaron mechanism of the SEE capture in the RC [6, 7] seems unlikely.

SEARCH FOR WATER MOLECULES ADJACENT TO THE RC SPECIAL PAIR

The above-described five H_2O molecules seem to be constituents of the rigid skeleton of M- and L-subunits of the RC. The total binding energy of the three atoms in these molecules with the polypeptide carriers is rather high and reaches 1.0 eV. Therefore, these molecules are maintained in the RC, whereas the more loosely bound H_2O molecules with only two bonds (or even one bond through the oxygen) of three possible bonds with the protein could be extracted during the crystallization of RC preparations. This possibility is suggested based on the findings as follows.

a) The presence of only 202 water molecules in the RC particles [16] seems to be a result of a noticeable loss of water during crystallization. The weight of 202 H_2O molecules is 3636 carbon units that corresponds ~11% of the total weight of their carriers, the M- and L-subunits of the RC. However, in intact RC the fraction of the bound water can be up to 15% [25, 26]. It should be emphasized that there is no concern of the RC quality: the authors of work [16] include biochemists, and according to their data, the preparations had a very high biochemical purity. The loss of a part of the weakly bound but functionally important water seems to be a natural consequence of the crystallization which requires uniform protein blocks. We suggested that in addition to the RC relatively weakly bound water molecules should be also present in polymolecular "machines", such as mitochondria, ATPases, etc., which are associated with charge transfers. In particular, in the RC from purple bacteria they are responsible for protein dynamics which provide the electron transfer between quinones Q_A and Q_B [27].

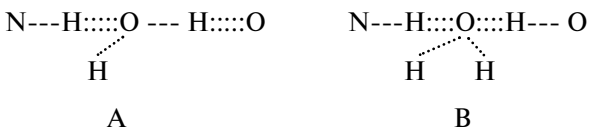
b) According to work [28], the vacuum dehydration of the RC from *Rs. rubrum* within 10-20 min when the water content was decreased about twofold, the efficiency of the energy capture in the RC decreased but recovered nearly completely on admittance of humid air to the specimens.

c) The necessity of conformational rearrangements during the electron transfer was indicated by differences in the "dark" and "light" structures of the RC from *Rh. sphaeroides* [29]. These findings were confirmed by data on the electron back transfer in purple bacteria from pheophytin molecules to the RC special pair [30-32]. In work [33] the dielectric repolarization in the active locus was shown to precede an act of the electron back transfer in the RC from *Rh. rubrum*. This topic is considered in detail in a review [34].

d) New findings from the laboratory of V. A. Shuvalov suggest a mobile water molecule in the immediate vicinity of the RC special pair. According to these findings, excitation of the RC special pair is accompanied by damped oscillations of the electric dipole of a water molecule at the frequency of 32 cm^{-1}. And this effective coupling with the electron excitation is reasonably suggested to be due to location of this water molecule immediately close to P_2 and even to be bound to the latter.

Therefore, we suggested that the rigid structures detected in works [14, 15] in crystallized RC preparations should be a markedly deformed "hardened" approximation to the intact image of this most important molecular machine. Based on the above-presented data, we suggested that *in vivo* the RC should have weakly bound water molecules with one (or two) unbound and consequently mobile hydrogen atoms.

We tried to find the probable locations of these "mobile" H_2O molecules near the special pairs of the reaction centers. With our program, the search for such locations of the water molecules was started by choosing polar atoms (oxygen and nitrogen) located at the distance less than 9 Å from the middle of the Mg–Mg section of P_2. Then among them the atoms were chosen which failed to produce obvious hydrogen bonds, i.e., lacked oxygens or nitrogens at the distance of ~3 Å to provide hydrogen bonds. For these "free" atoms chosen as described a possibility was considered to generate bonds with the environment through mobile water molecules, as shown in schemes A and B:

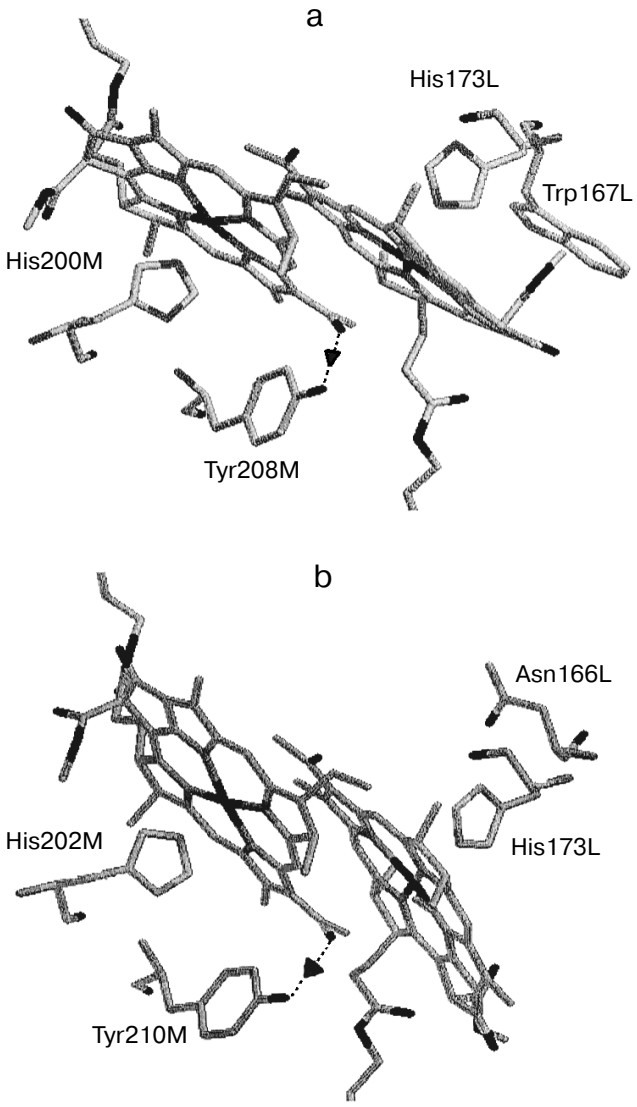


Based on these concepts, the distance between the water-coordinating polar atoms was suggested to be 5-7 Å. And it was reasonable to consider only bonds amino acid–H_2O–one of two P_2 molecules because only in this case a hypothetical water molecule could be at a suffi-

ciently little distance from P_2 and the energy of its interaction with the P_2^* dipole is comparable to the effect of the environment. After the pair of charges which were able to retain the water molecule had been found, the distance between the incorporated water molecule and the center of the Mg–Mg section in P_2 was assessed. To do this, the oxygen of H_2O was suggested to be located in the center of the section between the water-coordinating atoms. For the RC structure from *Rps. viridis* four amino acids were found which failed to produce distinct hydrogen bonds [16]. These were His173L, His200M, Trp167L, and Tyr208M (figure, panel (a)). The first two amino acids were histidines which seemed to control BChl of the RC special pair. Trp167L seemed to produce bonds through H_2O with atoms OBD or O2D of BCL602 bacteriochlorophyll (here and further the denominations are taken from Brookhaven Protein Databank, identification number 1PRC). However, the water incorporated in such a manner would be at the distance of 8.4 ± 0.2 Å from the center of the Mg–Mg section. Tyr208M could bind through water to the OBB atom of the BCL603 molecule. Such a H_2O molecule, if it existed *in vivo*, should be located at the distance of 4.6 Å from the center of the Mg–Mg section. The interaction energy of its dipole moment (ρ_w) with the dipole transient moment of the excited pair P_2^* was approximately $\rho_w\rho_{P2}/\varepsilon R^3 \cong 0.3$ eV.

Even if because of unsuccessful mutual orientation of the dipoles or of rotation of only one of two hydrogens of water molecule the change in the interaction energy were 4-5-fold lower, the resulting value would be sufficient to effect the water–polaron mechanism [6, 7, 10, 11].

To check this hypothesis, it was important to compare the structures of RC from various purple bacteria. If our hypothesis on the *in vivo* existence near the RC special pair of a water molecule with a hydrogen atom (atoms) which could be reoriented under the influence of the excited RC special pair was correct, then other RCs should also have similar landing places for the bound water at approximately the same distance from the RC special pair. Therefore, the above-described procedures were repeated for the RC from *Rhodobacter sphaeroides*. Two structures are known for its RC: in the state before the charge separation (the dark structure) and in the D^+Q^- state after the charge separation (the light structure), the identification numbers 1AIJ and 1AIG, Brookhaven Databank, from work [29], respectively. In the RC from *Rh. sphaeroides* (the dark structure 1AIJ) four water molecules (HOH30 (7.5 Å), HOH107 (8.3 Å), HOH55 (8.6 Å), and HOH28 (8.6 Å)) are also located at the distance less than 9 Å from the middle of the Mg–Mg section in P_2 BChl. As in the RC from *Rps. viridis*, all these molecules are bound through hydrogen bonds and have a polar environment, and the H_2O interaction energy with the latter is much higher than its interaction with the dipole moment of the RC special pair. This dark structure of the RC also has four amino acids which fail to generate distinct hydrogen bonds with the environment: His173L, His202M, Asn166L, and Tyr210M (figure, panel (b)). Similarly to His173L and His200M in the RC from *Rps. viridis*, these histidines also coordinate RC special pair of BChl and also seem to be conservative amino acids. Generally speaking, the OD1 atom of Asn166L can produce a bond "through water" with the OBB atom of one of the BChl, BCL2. The distance



Fragments of the atomic model of the special pair and its protein carriers in the crystallized reaction centers from purple bacteria: a) *Rps. viridis* [16]; b) *Rh. sphaeroides* [29]. The data are taken from Brookhaven Protein Databank (identification number 1PRC). ▼ indicates the location of the oxygen of a hypothetical H_2O molecule between tyrosines 208 and 210 (in panels (a) and (b), respectively) and the oxygen of the OBB chromophore of BChl $P870_M$. The distance between the oxygen of H_2O and the center of the section between $P870_M$ and $P870_L$ chromophores is ~4.5 Å

between these atoms is 6.8 Å and the distance from the water molecule thus located to the center of the Mg–Mg section of P_2 would be 5.3 Å. But amino acid Tyr210M which seems to be a structural analog of Tyr208M in the RC from *Rps. viridis* is more promising. Analysis of a possible binding through water between the OH-group of Tyr210M and the OBB atom of bacteriochlorophyll BCL3, similarly to the binding supposed by us for the RC from *Rps. viridis*, has shown the distance of 3.4 Å between these atoms in the light structure of the RC from *Rh. sphaeroides*, i.e., too little for incorporation of a water molecule. However, in the light structure (1AIG) of the same RC the distance between the corresponding atoms is 5.7 Å and the distance from the oxygen of a hypothetical water molecule incorporated between them to the center of the Mg–Mg section of the RC is 4.4 Å, which is rather close to a similar value obtained for the RC from *Rps. viridis*.

Thus, in the context of the water–polaron model of the SEE stabilization in the RC from purple bacteria the corresponding mobile water molecule are suggested to be located between the OH-group of the conservative tyrosine of the subunit M (Tyr210M in *Rh. sphaeroides* or Tyr208M in *Rps. viridis*) and the OBB atom in the adjacent BChl of the P_2 special pair (BCL3 in *Rh. sphaeroides* or BCL603 in *Rps. viridis*). And really, only the water bound to a conservative amino acid in all reaction centers of purple bacteria can be located at nearly the same distance from their special pairs and have its own dipole oriented similarly relatively to the dipole of the excited special pair and, consequently, can provide a similar interaction energy of the dipoles mentioned. In particular, the presence of such a water molecule in the subunit M seems to promote the electron transfer in purple bacteria along the chain of acceptors bound to the opposite subunit L, because water atoms with significant uncompensated charges can differently change the local values of dielectric permeability near BChl-M and BChl-L.

For these reasons, Nature is suggested to have not omitted during the evolution the possibility to generate effective "latches" for electron excitations in the reaction centers of the above-mentioned "micromachines" of organisms using the generally available water molecules which can be easily incorporated into biological structures. In photosynthesizing RC one can expect conformational transformations in the L- and M-subunits during successive transitions of the RC: $P_2 \rightarrow P_2^*HQ_A \rightarrow P_2^+H^-Q_A \rightarrow P_2^+HQ_A^-$, etc. Because the transitions between these states are associated with significant displacements of charges, the conformational transitions seem to be forced by displacements of the atoms with uncompensated charges located most closely to P_2. The $P_2^*HQ_A$ state with the lifetime of only 3 psec is an exception. This prevents pronounced displacements in the "heavy" polypeptide chains. Only the lightest hydrogen atoms can be displaced within the shorter periods as it is shown in the present work and was shown earlier in works [6, 7, 11, 12] in the framework of the water–polaron hypothesis which is mainly characterized as follows: the presence of a water molecule in the immediate vicinity of the RC special pair; a subpicosecond reorientation of the water electric dipole at the cost of low-inertial electron-deficient hydrogens. The reasons in favor of a water molecule to also have similar functions in the reaction centers of the plant photosystem-1 are presented in [35].

The present work has emphasized the importance of problems concerning the structures and functions of polymolecular "micromachines".

First, it is very likely that Nature has used the ability of water molecules to rapidly reorient their electric dipoles to organize the transforming "gates" with the functions responsible for energetic and structural coupling of different stages in the main activities of polymolecular "machines". Such mobile water molecules can also occur in the reaction centers of plants and in such biochemical "machines" as various ATPases. As V. A. Shuvalov had said in his report at the Scientific Council at the Belozersky Institute of Physicochemical Biology, Moscow State University (October 2001), a similar function could also be realized due to polarization of mobile hydrogens of $-NH_2$ and -COOH groups of amino acids near the corresponding functional loci, although their hydrogens have a lower electron insufficiency than hydrogens of water.

Second, as mentioned in [36], effective functions of proteins are impossible in static structures they but need a certain mobility and conformational rearrangements in some fragments. It seems that a water molecule with an unstable bond to protein has to be involved in such processes not only in the RC but in many "micromachines". The crystallization of such biological particles is inevitably associated with a partial loss of water just from these molecules with unstable bonds because the crystal can be built only from identical blocks. And the question is: how can such water-deficient and as a result deformed static structures be responsible for real sets of active conformations? Possibly, in the future new approaches should be developed including model calculations to establish structural states providing individual stages in charge transfer and energy transformation.

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REFERENCES

1. Clayton, R. K. (1967) *Photochem. Photobiol.*, **5**, 807-821.
2. Abdourakhmanov, I. A., Danielius, R. V., and Razjivin, A. P. (1989) *FEBS Lett.*, **245**, 47-50.
3. Timpmann, K. N., Fu Geng Zhang, Freiberg, A. M., and Sundstrem, V. (1993) *Biochim. Biophys. Acta*, **1183**, 185-193.

4. Otte, S. C., Kleinherenbrink, F. A., and Amesz, J. (1993) *Biochim. Biophys. Acta*, **143**, 84-90.
5. Bernhardt, K., and Trissl, H. W. (2000) *Biochim. Biophys. Acta*, **1457**, 1-17.
6. Borisov, A. Y., and Fok, M. V. (1999) *Biochem. Mol. Biol. Int.*, **47**, 117-125.
7. Borisov, A. Yu. (2000) *Biochemistry (Moscow)*, **65**, 1266-1271.
8. Fok, M. V., and Borisov, A. Y. (1981) *Stud. Biophys.*, **84**, 115-124.
9. Fok, M. V., and Borisov, A. Yu. (1981) *Mol. Biol. (Moscow)*, **15**, 575-581.
10. Moore, L. J., Zhou, H., and Boxer, S. G. (1999) *Biochemistry*, **38**, 11949-11960.
11. Steffen, M. A., Lao, K., and Boxer, S. G. (1994) *Science*, **264**, 810-815.
12. Borisov, A. Y., and Zuber, H. (1992) in *Research in Photosynthesis* (Murata, N., ed.) Vol. 1, Kluwer Academic Publishers, Amsterdam, pp. 117-120.
13. Eisenberg, D., and Kautzmann, W. (1969) in *The Structure and Properties of Water*, Oxford University Press, Oxford.
14. Deisenhofer, J., Epp, O., Miki, K., Huber, R., and Michel, H. (1985) *Nature*, **318**, 618-624.
15. Feher, G., Allen, J. P., Okamura, M., and Rees, D. C. (1989) *Nature*, **339**, 111-116.
16. Ermler, V., Fritzsch, G., Buchanan, S. R., and Michel, H. (1994) *Structure*, **2**, 925-936.
17. Nichols, A., and Honig, B. (1991) *J. Comp. Chem.*, **12**, 435-445.
18. Novoderejkin, V. I., and Razjivin, A. P. (1993) *FEBS Lett.*, **330**, 5-8.
19. Novoderejkin, V. I., and Razjivin, A. P. (1997) *Biofizika*, **42**, 64-168.
20. Novoderejkin, V. I., Monshouwer, R., and van Grondelle, R. (1999) *Biophys. J.*, **77**, 666-681.
21. Novoderejkin, V. I., Monshouwer, R., and van Grondelle, R. (1999) *J. Phys. Chem.*, **103**, 10540-10548.
22. Vos, M. H., Lambry, J. C., Robles, S. J., and Youvan, D. C. (1992) *J. Mol. Biol.*, **280**, 297-314.
23. Streltzov, A. M., Aartsma, T. J., Hoff, A. J., and Shuvalov, V. A. (1997) *Chem. Phys. Lett.*, **266**, 347-352.
24. Yakovlev, A. G., and Shuvalov, V. A. (2001) *FEBS Lett.*, **466**, 209-212.
25. Kononenko, A. A., Nikolaev, C. N., and Rubin, A. B. (1981) *Stud. Biophys.*, **84**, 13-14.
26. Aksenov, S. I. (1995) *Zh. Fiz. Khim.*, **69**, 1406-1409.
27. Knoks, P. P., Lukashov, E. P., Kononenko, A. A., Venediktov, P. S., and Rubin, A. B. (1977) *Mol. Biol. (Moscow)*, **11**, 1090-1099.
28. Clayton, R. K. (1966) *Photochem. Photobiol.*, **5**, 679-688.
29. Stowell, M. W. B., McFillips, T. M., Rees, D. S., Soltis, S. M., Albresch, E., and Feher, G. (1997) *Science*, **270**, 812-816.
30. Kirmaier, C., and Holten, D. (1990) *Proc. Natl. Acad. Sci. USA*, **87**, 3552-3556.
31. Muller, M. G., Grebenov, K., and Holzwarth, A. R. (1992) *Chem. Phys. Lett.*, **199**, 465-469.
32. Du, M., Rosenthal, S. J., Xie, X. L., Dimango, T. J., Schmidt, M., Hanson, D. K., Schiffer, M., Norris, J. R., and Fleming, G. R. (1992) *Proc. Natl. Acad. Sci. USA*, **89**, 8517-8521.
33. Trissl, H. W., Benhardt, K., and Lapin, M. (2001) *Biochemistry*, **40**, 5290-5298.
34. Rubin, A. B., Kononenko, A. A., Shaitan, K. V., Pashchenko, V. Z., and Riznichenko, G. Yu. (1995) *Biofizika*, **39**, 173-195.
35. Borisov, A. Y. (2000) *Membr. Cell Biol.*, **14**, 333-341.
36. Frauenfelder, H., Petsko, G. A., and Tsernoglou, D. (1979) *Nature*, **280**, 558-563.