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REVIEW

Mechanisms of Excitation Trapping in Reaction Centers of Purple Bacteria

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Abstract—The contradiction between two groups of experimental data, which fails to be resolved within the framework of the widely accepted model of excitation migration and trapping (at least in case of purple bacteria), is discussed in the introduction to this review. Three directions of studies intended to resolve this conflict are reviewed in the three further sections: II. Exciton models; III. Water-polarization (water-latch) mechanism of excitation trapping; IV. Quantum-mechanical models. The maximum efficiency of these models in resolving the contradiction mentioned above was assessed. The advantages and disadvantages of the mechanisms described in sections II, III, and IV are discussed in the last section of this review. It is concluded that none of these mechanisms taken alone is able to solve this problem. Therefore, the fundamental problem of the primary excitation conversion in reaction centers remains unsolved and requires additional experimental research.

Key words: purple bacteria, reaction center, electronic excitation energy migration and trapping

I. IS THE SYNOPSIS OF EXPERIMENTAL DATA AVAILABLE FROM THE LITERATURE INCONSISTENT WITH THE CONVENTIONAL MODEL OF THE PRIMARY PROCESSES IN PURPLE BACTERIA?

For many years, the primary processes of migration of electronic excited states (EES) and their trapping in reaction centers (RC) of purple bacteria have been interpreting within the scope of the model schematically shown in Fig. 1. There is a large body of experimental evidence that EES migration from bacteriochlorophylls (BChl-800) of the accessory antenna complexes LH-2 to BChl-850 and from the additional pair BChl P800 to the RC special pair P870 occurs within fractions of one picosecond; the process of migration from the fraction BChl-B850 in LH-2 to core-BChl-880 of the main antenna LH-1 surrounding RC occurs within 5-10 psec; whereas the EES transfer from core-BChl-880 to the RC special pair P870 occurs within 50-60 psec (provided that the RC special pair P870 is in its active state) (for more detail see reviews [1-3]). It was also found that in the majority of purple bacteria, the EES energy levels in antenna core-BChl and in the RC special pair are approximately equal to each other [1, 2]. It was shown in [4, 5] that the quantum yield of EES trapping in P870 was more than 0.8, whereas according to the results reported in [6, 7], this value was more than 0.9. For many years, the aggregate of these results has been safely interpreted within the scope of the model schematically shown in Fig. 1. However, the results reported in [5, 8-10] and in earlier work of Clayton et al. [11] are inconsistent with this model. It was shown in these works that in purple bacteria containing BChl-a no more than 10-15% EES could migrate from excited RC pair back to core-BChl. It obviously follows from these data that the rate constant **k(rc,a)** of EES transfer from excited special pair of reaction centers (P870*) back to antenna core-BChl should be substantially lower than the rate constant **K(e+)** of EES trapping in P870 (Fig. 1). It was shown in [12, 13] that this requirement was in obvious disagreement with other kinetic data.

The physical sense of the controversy was discussed in [13]. In accordance with [14], let the molecules of core-BChl in *Rhodospirillum rubrum* be arranged as a symmetric ring (around P870) composed of 16 αβ-het-

Abbreviations: RC) reaction center; BChl) bacteriochlorophyll; numbers at BChl-800, BChl-850, and BChl-880 indicate approximate position of long-wavelength absorption maximums; core-BChl) the main fraction of light-harvesting antenna bacteriochlorophyll BChl-880; P870, P870*, and $P870^+$) special RC pair in the ground, excited, and oxidized states, respectively; EES) (singlet) electronic excited state; **t(a)**) EES life-time; **k(a,rc)**, **K(rc,a)**) rate constants of EES migration from core-BChl to special RC pair and back, respectively; **K(e+)**) rate constant of electron transfer from excited special RC pair P870* to the primary acceptor molecule (X).

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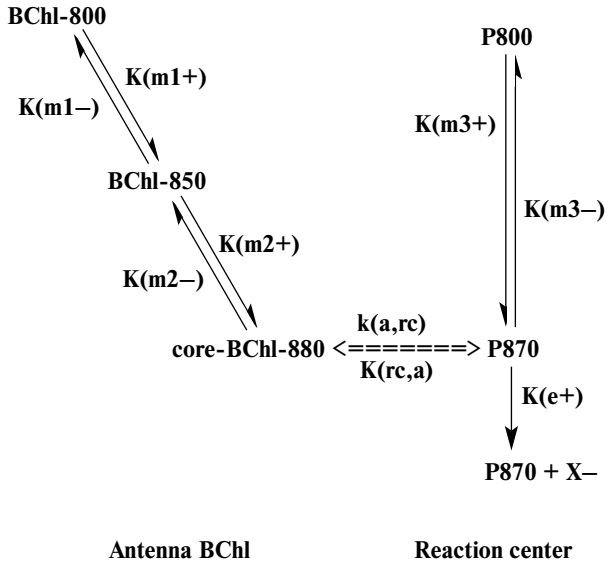


Fig. 1. Scheme of the primary processes of photosynthesis in purple bacteria. **K(m+)** and **K(m–)** are the rate constants of electronic excitation energy migration in forward and reverse directions, respectively; **k(a,rc)** and **K(rc,a)** are the rate constants of electronic excitation energy migration from core-BChl to special RC pair and back, respectively; P870, P870*, and $P870^+$ are the ground, excited, and oxidized states of special RC pair, respectively; X is the primary acceptor; **K(e+)** is the rate constant of electron transfer from excited special RC pair P870* to the primary acceptor molecule.

erodimers of BChl. Such a system of molecules is characterized by symmetry of at least C-2 type and can be described by a set of nine simultaneous linear differential equations. To obtain the required estimates, we developed a mathematical method of reduction to a simpler system of expressions. This method is based on the following three simplifications [13].

1. EES energy levels in P870* and dimers of core-BChl B880* are equal to each other.

2. All αβ-heterodimers of core-BChl are characterized by the rate constants of EES transfer to P870 (therefore, the rate constants of EES transfer from P870* back to any of the αβ-heterodimers B880) are equal to the values of the rate constant in two αβ-heterodimers, whose transition dipole moments have optimum orientation relative to that in the special RC pair P870 (but no less than $2 \cdot 10^{11}$ sec^{-1}).

3. Electron transfer from the excited special RC pair P870* to the primary acceptor (rate constant **K(e+)** in Fig. 1) is considered to be irreversible.

The fact that the resulting mathematical model has no obvious physical sense is not of principal importance. This model is described by only three simple differential equations, which can be solved even analytically. It is important to note that all the simplifications listed above cause an increase both in the rate of EES transfer from core-BChl to P870 and in the efficiency of EES trapping in RC. **Therefore, it would be realistic to expect that the EES life-time in core-BChl calculated from the reduced model was shorter than the experimentally measured value (i.e., <50-60 psec).** However, the results of our calculations [13] quite surprisingly gave an opposite result.

Taking into consideration the suggestions 1-3 listed above and complying with the principle of detailed equilibrium, the ratio of the rate constants of EES transfer from any core-BChl-880* dimer to P870 dimer and back from P870* to the whole complex core-BChl-880 should be equal to:

$$\mathbf{k(a,rc)/K(rc,a) = n(rc)/N(a)} = 2/32 = 1/16, \qquad (1)$$

where **n(rc)** and **N(a)** are the numbers of BChl molecule and core-antenna, respectively.

However, the ratio (1) is not associated with specific properties of core-BChl, whose molecules are arranged as a ring around P870 and can donate EES to P870 as could be formally expected from Fig. 1. We also analyzed two intermediate models and even an extreme case, according to which only one dimer in core-BChl serves as a bridge between P870 and the other dimers of core-BChl. The process of EES transfer between this dimer (d_1) and P870 can be described by the following expression:

$$\mathbf{k(d_1,rc) = k(rc,d_1) = n(d_1)/n(rc)} = 2/2 = 1.$$

*It should also be taken into account that EES in core-BChl is located in the dimer d_1 only during a fraction of the time interval 2/N(a). The other dimers of core-BChl are unable to transfer EES to P870. Therefore, the value of the rate constant **k(a,rc)** averaged over the whole antenna complex is described by expression (1) even at the highest values of the rate constant of EES migration. The results of mathematical simulation agreed with this conclusion.*

In accordance with results reported in [8-11], let the fraction of EES capable of migrating from P870* back to antenna BChl-880 in purple bacteria be equal to 0.1-0.15, which gives:

$$\mathbf{K(rc,a)} = (0.1\text{-}0.15)\ \mathbf{K(e+)} = (0.1\text{-}0.15)\ (3\ \text{psec})^{-1} =$$

$$(20\text{-}30\ \text{psec})^{-1}.$$

Then, substitution of **N(a) =** 32 and **n(rc)** = 2 to Eq. (1) gives:

$$\mathbf{k(a,rc) = K(rc,a)}/16 = (20\text{-}30\ \text{psec})^{-1}/16 =$$

$$(320\text{-}480\ \text{psec})^{-1}.$$

The value of the rate constant **k(a,rc)** mainly represents the mean jump-time of the EES transfer from antenna BChl to P870, whereas the reciprocal rate constant $\mathbf{k(a,rc)^{-1}} \cong$ 360-480 psec is close to the mean life-time **t(a)**

of EES in antenna BChl (according to the more rigorous equation derived in [13], these estimates are accurate to 6%). However, it was shown in many independent studies that in purple bacteria containing BChl-a this time was only 50-60 psec [1-3]. Thus, the controversy mentioned above is observed even in case of the reduced model of the photosynthetic unit, because experimentally measured mean value of EES life-time in core-BChl, **t(a)**, differs from the theoretically calculated value (50-60 and 360-480 psec, respectively). It should be noted that the simplifications listed above facilitated EES energy migration to P870 and decreased the calculated value of **t(a)** at least by a factor of 1.35. Therefore, to resolve this controversy, the obtained value of $\mathbf{k(a,rc)} \cong (40\text{-}45\ \text{psec})^{-1}$ should be about an order of magnitude smaller.

The exactness of experimentally measured values $\mathbf{K(e+)} \cong (3\ \text{psec})^{-1}$, **t(a)** = 50-60 psec, N(a) ≅ 30, and n(rc) = 2 is beyond doubt. The controversy would be even aggravated if actual characteristics of complexes LH-1 + RC of purple bacteria were taken into account [13]. Therefore, new ideas are required to resolve this controversy. The following directions of studies intended to resolve this conflict have been suggested in the literature so far.

Exciton models. Substantiation of the possibility of delocalization of excitons over several molecules of core-chlorophyll as assessed by a significant increase in the rate constant of energy migration from core-BChl-880 to special RC pair, which should cause a proportional decrease in the calculated value of **t(a)**.

Water-polarization (water-latch) mechanism of excitation trapping. Substantiation of the ability of hydrogen atoms of water molecules located in the immediate vicinity of P870 to change orientation of their dipoles in the electric field of the excited state of P870 (P870*) during the time interval substantially shorter than $\mathbf{(K(e+))^{-1}} \cong$ 3 psec, hampering thereby the process of electronic energy migration from P870* back to core-BChl.

Quantum-mechanical models. Construction of quantum-mechanical models accounting for (if possible) the energy of interaction between all chromophores and charged groups in the ensemble core-BChl + RC.

Both advantages and disadvantages of these models are discussed in this review by the example of purple bacteria. It should be noted that purple bacteria are the most comprehensively characterized in terms of the composition and, in some cases, the structure of the pigment–protein complexes of antenna and RC, as well as the energy and kinetic characteristics of EES migration and trapping.

II. EXCITON MODELS

The first evidence of the existence of excitons in chlorophyll-containing complexes of photosynthesizing organisms was obtained by Robinson [15] on the basis of comparison between absorption spectra of chlorophyll (Chl)-a *in vivo* and *in vitro*. The fact of the presence of excitons delocalized over several molecules of BChl antenna in purple bacteria is also beyond doubt. This fact was first demonstrated by kinetic data obtained in [16, 17] and some further studies (for review see [1, 2]).

A number of similar exciton models of EES migration in core-BChl and between core-BChl and special RC pair were suggested by Novoderezhkin and Razjivin [18, 19] and later by some other researchers [20-28] (for review see [29, 30]). By analogy with the structure of accessory light-harvesting complex LH-2 [31] and in conformity with later X-ray diffraction data on the structure of the light-harvesting complex LH-1 from *Rhodospirillum rubrum* [14], it was suggested in [18-21] that molecules of the main light-harvesting BChl-a pigment antenna complex LH-1 surrounding RC in purple bacteria were arranged as a ring structure. Exciton calculations in such a symmetric structure revealed that many split singlet levels S_1* were degenerated. As a result, it was impossible to obtain the theoretical absorption spectrum of such model system, which would be close to the absorption spectrum observed *in vivo*. Therefore, dynamic and static uncertainty of the value of energy of interaction between neighboring molecules of the ring (300-400 cm^{-1}) was suggested in [19-21, 29]. Models were considered in which excitons were delocalized over several molecules of the ring (from two to all). It was concluded in [19-21] that the models suggested in these works provided a satisfactory fit of a number of experimental data (e.g., shape and long-wavelength shift of absorption spectrum of core-BChl, EES life-time, and size of minor EES fraction capable of returning from the excited special RC pair back to core-BChl). The validity of the last statement was questioned in [13] (see below).

A simplified variant of the exciton concept, which was in [18-21] and some further works to resolve the controversy mentioned above, is considered below. Let a set of particles bearing three mutually arranged identical aromatic molecules M_1, M_2, and M_3 each (or triples of identical dimers of these molecules) be arranged at a small distance from each other to provide fast and effective EES exchange by the Förster induction resonance mechanism [32] (Fig. 2a). The EES concentrations in the groups of molecules M_1, M_2, and M_3 under conditions of light-induced excitation of such a molecular ensemble are obviously equal to each other regardless of the distance between the molecules ($R_{1,2}$, $R_{2,3}$, and $R_{3,1}$) and parameters of surrounding medium. Let us consider a similar molecular ensemble, in which molecules M_2 and M_3 are brought closer to one another and bond energy in these pairs is as high as giving rise to delocalized excitons. It follows from the theory of molecular excitons [33] that the first excited singlet level (S_1*) of such pair is split into two levels: $S_1^* \pm h\cdot\Delta\nu$, where h is the Planck constant, $2\Delta\nu$ is the frequency shift between the energy levels; and

$h\cdot\Delta\nu$ is equal to the energy of interaction between molecules M_2 and M_3. The oscillator strengths of the two levels in this case are determined by mutual orientation of transition dipoles of molecules M_2 and M_3. If dipole moments of transitions $S_0 \rightarrow S_1^*$ in molecules M_2 and M_3 are parallel to one another, the long-wavelength state $S_1^* - h\cdot\Delta\nu$ is dominant in their common absorption spectrum, whereas the short-wavelength state $S_1^* + h\cdot\Delta\nu$ is dominant in case of orthogonal orientation (bond energy in this case is substantially reduced).

Let the dipoles of the molecules M_2 and M_3 be parallel. The second power of the sum dipole transition moment of the exciton $S_1^* - h\cdot\Delta\nu$ in this case is equal to the sum of squares of their values in isolated molecules M_2 and M_3. Let also the energy of the bond between molecules M_2 and M_3 be small (no more than 10-20 cm^{-1}), i.e., $h\cdot\Delta\nu < k$T, where k is the Boltzmann constant and T is room temperature. Then, the EES energy values in monomer M_1^* and in exciton pair $[M_2 \sim M_3]^*$ are virtually equal to each other. According to the Förster theory of induction resonance energy migration [32], the rate constants of EES transfer from molecule M_1^* to the exciton pair $[M_2 \sim M_3]$ and back are equal to the product of squares of dipole transition moments of molecule M_1^* exciton pair $[M_2 \sim M_3]^*$. In other words, these values in opposite directions are equal to each other. **Therefore, in contrast to the ensemble of monomeric molecules, the concentration of EES in molecules M_1^* and in exciton-bound pairs $[M_2 \sim M_3]^*$ should be equal, because the fraction of molecules M_1 providing absorption of 1/3 of all light photons would contain 1/2 rather than 1/3 of the total amount of EES. Thus, formal application of the Förster theory to exciton-bound molecules gave rise to the conclusion that light-generated EES were concentrated in the fraction of individual molecules by the expense of EES absorption in the group of exciton-bound molecules.** In more complicated ensembles, excitons can be delocalized over a larger number of molecules. According to the results obtained in [18-21], a similar process of concentration of EES in individual molecules or their dimers could be even more pronounced, and this effect was used in [18-21] and some further works for resolving (at least in the authors' opinion) the controversy inherent in data obtained in purple bacteria.

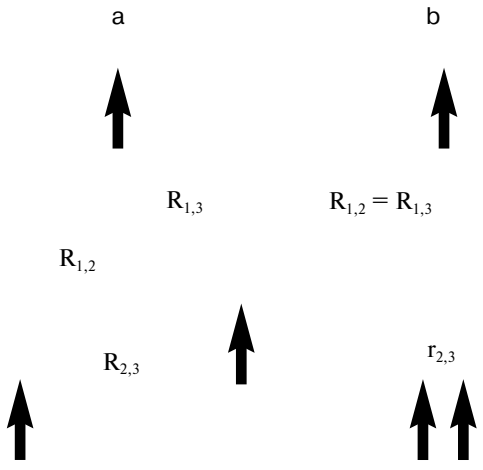


Fig. 2. Two variants of mutual orientation of transition dipole moments in triplets of interacting molecules (indicated by arrows): a) molecules are at the Förster distance from each other ($R_{1,2}$, $R_{1,3}$, $R_{2,3}$ ~ 20-50 Å); b) molecules are at the "exciton" distance ($r_{2,3}$) from each other ($8 < r_{2,3} < 12$ Å).

Later this important problem was also studied by several independent groups of researchers (for review see [29, 30]). Ring structures of core-BChl were considered almost universally in all these works. The following variants of EES localization were analyzed in models of excitons in LH-1 complexes of purple bacteria: EES delocalized over two BChl molecules (e.g., one αβ-heterodimer) [34, 35], two neighboring αβ-heterodimers [23, 28, 36, 37], or up to the entire ring [25-27, 38-40].

Let us now consider experimental data. In LH-1 complexes the number of core-BChl molecules, over which exciton was delocalized at room temperature, was determined experimentally under conditions of photoexcitation of preparations with high-power laser pulses and measurement of stimulated luminescence [23, 24], differential absorption changes at 820 nm [21], and amplitude of absorption decrease at 870 nm [17]. The number of such core-BChl molecules was estimated by different authors as 3-4 [23, 24], 5 ± 1 [21], or 4-6 [17]. Therefore, the estimated number of αβ-heterodimers did not exceed 2-3. The results obtained in [41] were an exception to this rule. In this work, the core-BChl complex of purple bacterium *Rhodobacter sphaeroides* was modified by introducing a strongly quenching center (BChl molecule with Mg atom replaced by Ni). The number of core-BChl molecules, over which exciton was delocalized at the initial moment of time was estimated in this system as 20 ± 1. However, the estimated life-time of the exciton does not exceed 1 psec, and on a longer time scale is should most probably interact with phonons and be localized in a significantly smaller group of molecules. It should also be taken into account that in the presence of 32 core-BChl molecules in the purple bacterium *Rs. rubrum* [14, 42], the dipole transition moments of neighboring molecules are shifted at an angle of $360°/32 \cong 11.2°$. As a result, the value of **k(a,rc)** and ratio **k(a,rc)/K(rc,a)** in excitons delocalized over 2-3 heterodimers of the LH-1 ring should increase by a factor of 1.7-2.4 rather than 2-3.

It is obvious that a 1.7- to 2.4-fold gain in the rate constant k(a,rc) is insufficient to resolve the controversy mentioned above.

The following comments to the conclusions drawn in [18-29] and some other works of this series should be made.

1. On the basis of a large body of experimental data obtained in aromatic molecules, the theory of molecular excitons claims that in case of medium-strength molecular bonds, the exciton at the initial moment of time is delocalized and can be considered as a wave packet or a coherent exciton. However, after a time interval of about 1 psec (life-time of phase memory, according to the theory put forward in [43-45]), the exciton interacts with a phonon and is localized in an individual molecule [46]. The value of the transition dipole moment obviously declines from the multimolecular exciton level to the level typical of monomeric molecule or associate of no more than 2-4 molecules (?). This statement is inconsistent with the exciton models intended to resolve the controversy mentioned above. Indeed, these theories require that the life-time of the multimolecular exciton, whose transition dipole moment increased many times, should be at least larger than the life-time of EES in core-BChl (i.e., more than 100 psec). Given the fact of considerable static and dynamic instability of the core-BChl structure (~300 cm^{-1} [18-21, 30, 41]), it seems fairly unrealistic that long-living delocalized excitons can be formed in such systems.

2. Possible use of the main idea put forward in [18-21] raises the problem of conformity of such an interpretation of the main points of the exciton theory [13] with the laws of thermodynamics. In particular, it remains uncertain if the process of EES concentration in individual molecules by the expense of exciton-bound molecular associates causes a decrease in the entropy of the system. In the broad sense, the following statement should be declared: if a problem system (e.g., the system shown in Fig. 2b) is constructed on the basis of the idea put forward in [18-21], this problem is pertinent not only to the idea in general but also to other models constructed on its basis. *It seems that theoretical studies alone are unable to answer this question (more than twenty of such works are presently available in the literature). New experimental research is required to demonstrate directly if EES are concentrated in individual molecules or dimers at the expense of EES concentration in more abundant multimolecular exciton-bound fractions.*

III. WATER-POLARIZATION (WATER-LATCH) MECHANISM

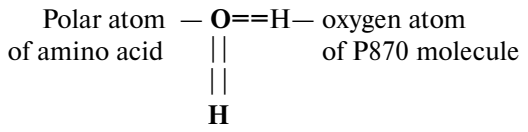
1. This was chronologically the earliest concept [47, 48]. A hypothetical water-polarization (water-latch) mechanism of EES energy trapping in RC of purple bacteria was suggested in these works. It is well known that upon absorbing a quantum of electronic excitation the special RC pair is converted virtually immediately into a charge-transfer state. A fraction of electron charge in this state is shifted from special RC pair, $P870_A$, to molecule $P870_B$ [49] at the distance between the centers of their chromophore groups of about 7 Å. Although neighboring charges should be shifted by the electric field of the charge-transfer state, this process lags behind the process of reorientation of hydrogen atoms, the lightest charge-bearing particles. The process of reorientation of hydrogen atoms may take up to 100 fsec [50]. Five variants of mutual orientation of dipoles of P870* and mobile water molecule were analyzed in [47, 48]. The oxygen atom in these variants of orientation was at a distance of 6 Å from the center of the special RC pair. It was arbitrarily assumed that the charge of the dipole of excited special RC pair P870* was equal to the whole electron charge, which is not true. For example, it was shown in [51] that the fraction of electron transfer in P870* was about 30%. Therefore, the estimates of energy expenditure (up to 0.25 eV) for reorientation of water molecule at a distance of 6 Å from P870 obtained in [47, 48] should be regarded as overestimated.

Further advancement of the idea of water latch was made in [13, 52]. Water molecules located at a distance of <9 Å from the special RC pair center were suggested to be the molecules capable of being reoriented by electric dipole. X-Ray diffraction analysis of atomic structure of RC crystals from *Rhodopseudomonas viridis* revealed five water molecules in the special RC pair vicinity [53]. However, further analysis of the atomic structure of RC of *Rps. viridis* based on the Brookhaven Protein Databank information [54] showed that all hydrogen atoms of the five water molecules should bind to oppositely charged nitrogen and oxygen atoms of nearby amino acids located at a distance of 3.0-3.5 Å from the hydrogen atoms. Therefore, the hydrogen atoms of the water molecules should not be reoriented in the electric field. Although these findings seem to dispel the water-polarization (water-latch) hypothesis, new ideas put forward in [54] may provide a new insight into this problem.

2. Search for "invisible" water molecules. It was suggested in [54] that the water molecules playing the role of water-latch could be lost during crystallization of RC. In the five water molecules discussed above, the sum bond energy of the three atoms with RC polypeptides is large. Therefore, these water molecules are not lost during crystallization, whereas less strongly bound (therefore, mobile) H_2O molecules having one or two possible bonds with RC polypeptides might be extracted during crystallization of RC preparations. The following data can be regarded as evidence in favor of this suggestion: 1) presence of only 202 water molecules in RC particles from *Rps. viridis* [54], which can be probably attributed to substantial losses of water during crystallization of RC preparations. Molecular weight of 202 H_2O molecules is 3636 atomic carbon units (D), which accounts for ~8% of molecular weight of M- and L-subunits of RC (of 24 and 26 kD, respectively). However, for intact protein particles content of bound water can approach 15% [55]. Perhaps, loss of a fraction of weakly bound water is an inevitable

side-effect of crystallization, because it requires uniform protein units; 2) according to the results reported in [56], mild 15-min vacuum dehydration of *Rs. rubrum* RC preparations reduced the content of RC-bound water by about one-half and caused a significant decrease in the efficiency of energy trapping in RC. Subsequent exposure to humid air was accompanied by virtually complete restoration of the efficiency of this process; 3) the difference between structures of dark-adapted and light-adapted RC complexes from *Rb. sphaeroides* [57] is evidence for conformational transitions associated with electron transfer processes. This conclusion is confirmed by the results of studies of back reactions of electron transfer from bacteriopheophytin molecules to special RC pair in purple bacteria [58, 59]. It was shown in [60] that the event of back electron transfer in RC *Rs. rubrum* was preceded by dielectric polarization in the active RC locus.

Based on these findings, it was suggested in [54] that the binding sites of such hypothetical water molecules were either in contact with special RC pair or in the vicinity of the pair. A special computer program was used to locate the binding sites. This program selected the polar atoms (nitrogen and oxygen) of the RC polypeptide that did not produce hydrogen bonds and were located closer than 5 Å from the center of the Mg–Mg segment of P870. The free polar atoms selected using this procedure were tested for possible formation of bonds with a water molecule of the following type:



These bonds were tested because a water molecule in this case might be located at a sufficiently short distance from P870, whereas the energy of its interaction with P870* is comparable with the energy of interaction with surrounding medium. For *Rps. viridis* RC structure [61] it was shown that for Tyr208M it is energetically beneficially to form a bond via a water molecule with $BChl_M$ P870. The oxygen atom of such a water molecule would be at a distance of 4.6 Å from the center of the Mg–Mg segment of the RC special pair P870. The energy of interaction between total dipole moment of this water molecule and dipole moment of excited P870* was calculated in [54] as 0.23 eV. If only one of two hydrogen atoms of the water molecule is mobile or mutual orientation of dipoles is disadvantageous, the energy value may decrease to 0.04-0.05 eV. Similar calculations were performed in [54] using structural data obtained for *Rb. sphaeroides* [57]. An appropriate site for the energy-advantageous binding of a water molecule through a hydrogen bond with the Tyr210M residue was found in the active dark-adapted structure of the RC of *Rb. sphaeroides*. The oxygen atom of such a hypothetical water molecule proved to be at a distance of 4.4 Å from the center of the Mg–Mg segment of the RC special pair P870, which was quite close to similar estimates obtained for RC of *Rps. viridis*. No such binding site was found in the light-adapted structure of the RC [57] (!), which implies that the structure of these micromolecular machines is dynamic rather than rigid. This also indicates that RC conformation in crystals may differ from that in their natural environment. Therefore, according to the concept suggested in [54], mobile water molecules in the active RC might be located between the O-H groups of conservative tyrosine residues of the M-subunit (Tyr210M in *Rb. sphaeroides* and Tyr208M in *Rps. viridis*) and oxygen atom of ODD BChl molecule of special RC pair P870. It was also suggested in [54] that location of such water molecule in the M-subunit underlay the fact that the electron transport activity in purple bacteria RC is inherent in the acceptor chain associated with the L- rather than the M-subunit.

New experimental findings of Shuvalov et al. [62] can also be regarded as indirect evidence of the existence of the water molecule in the immediate vicinity of the special RC pair. According to these results, strong damped oscillations of an electric dipole of a water molecule with a frequency of 32 cm^{-1} are observed in *Rb. sphaeroides* R-26 RC under conditions of excitation with femtosecond laser pulses [62]. It can be concluded from these results that this water molecule is directly bound to the special RC pair, whereas its oscillation (it was suggested in [62] that this molecule rotated) is an indication of mobility. The results reported in [62] were interpreted in [54] as evidence of the existence of a water molecule that should play a decisive role in the water-polarization mechanism of EES energy trapping in the special RC pair of purple bacteria.

It was noted by a reviewer of this work in *Biochemistry (Moscow)* that the well-known fact of coincidence of BChl-a fluorescence life-time in RC preparations (~3 psec) with the characteristic time of the primary electron transfer was hardly compatible with the water-polarization (water-latch) mechanism. However, this coincidence may indicate that isolation of RC preparations is accompanied by conformational changes of RC particles and loss of weakly bound water without inhibition of the primary reactions of charge separation. Perhaps the femtosecond kinetics predicted in [13, 47, 48, 52, 54] should be sought in chromatophores or intact cells of purple bacteria.

Rejection of the water-polarization (water-latch) mechanism returns us back where we started, because the exciton mechanism is able to provide only 2.4-fold gain in the rate constant (instead of required 8-10-fold), which is obviously insufficient to resolve the controversy mentioned above and to resuscitate the conventional scheme of the primary processes of photosynthesis.

IV. QUANTUM-MECHANICAL MODELS

When the three-dimensional structure of some pigment–protein complexes of green bacteria, purple bacteria, and plants had been resolved in the 1970-1990s with atomic resolution using X-ray diffraction analysis, it became possible to construct quantum-mechanical models of the primary processes of photosynthesis. These data provided a basis for many theoretical studies of the processes of EES migration and trapping in various chlorophyll-containing ensembles of photosynthesizing organisms [63-71]. Comprehensive theoretical analysis of these processes in the photosynthetic unit of purple bacteria was given by Schulten et al. This analysis was based on high-resolution three-dimensional structure of the light-harvesting complexes LH-1 and LH-2 of *Rb. sphaeroides* available from the literature. These structural data were subjected to global quantum-mechanical analysis by constructing a Hamiltonian of virtually all non-negligible intermolecular interactions between chromophore molecules (BChl-a and carotenoids) in the photosynthetic unit of *Rb. sphaeroides* including LH-1, LH-2, and RC [63, 67, 68]. The instability of interaction energy was taken to be 300 cm^{-1} [67, 68]. However, according to estimates obtained in [63], this factor had virtually no effect on the results of calculations. The problem of EES energy migration from carotenoids and LH-2 to LH-1 is beyond the scope of this review. Only the most important aspects of the problem associated with energy and dynamic characteristics of EES transfer from LH-1 to special RC pair are discussed. It was suggested in [63] that in addition to EES energy migration from core-BChl from LH-1 directly to special RC pair P870 there was an additional channel of EES energy transfer between these centers through an intermediate bridge (chromophores of RC monomers P800 located 7 Å closer to core-BChl than chromophores of P870). The estimates of the rate constants of EES energy transfer along this pathway led to quite a surprising conclusion that the characteristic time of energy transfer through P800 was 35 psec, whereas the process of direct EES transfer to P870 was an order of magnitude slower (characteristic time of several hundreds of picoseconds) [63]. However, these estimates were revised in further work of the same authors [68]: the process of direct EES transfer from core-BChl-875 to P870 was concluded to be the most effective (reciprocal value of corresponding rate constant was estimated as 15-102 psec rather than several hundreds of picoseconds, as in [63]).

On one hand, the fact of construction of comprehensive quantum-mechanical models [63, 67, 68, 71] of such complicated actual systems containing thousands of atoms and realistic spectral and kinetic characteristics calculated from these models is evidence of significant progress in modern quantum-mechanical methods. On the other hand, these approaches were originally designed to obtain adequate results by adjusting model parameters. The prognostic capacity of these models is presently restricted only to estimation of ranges of values of certain parameters (dielectric permittivity, static and dynamic instability, and energy of interaction between molecules), within which these methods give realistic estimates of other parameters (position of spectral bands and EES relaxation time). So far, the accuracy of these methods does not exceed one order of magnitude. Perhaps, this explains an order of magnitude discrepancy between the estimates of the rate constant of EES transfer from core-BChl to P870 obtained in [18-21, 63, 68]. It should be noted that accurate estimation of this rate constant is of cardinal importance for resolving the controversy mentioned above. The range of possible values of this rate constant reported in [68] also spanned about an order of magnitude. Perhaps, there are different methods of estimation of instability of the energy of interaction between neighboring molecules of core-BChl and local dielectric permittivity. This may also increase the total error value. It should also be noted that the models suggested in [63, 67, 68, 71] were not tested for consistency with experimental data reported in [6, 8-11], according to which the efficiency of EES migration from P870 back to core-BChl was very low.

The following general remarks to a large group of theoretical studies of ring models of core-BChl can be made.

1. Actual evidence in favor of formation of core-BChl rings around the RC in purple bacteria is less convincing than would be desired by the authors of the models. The most convincing evidence of the ring structure was obtained in the purple bacterium *Rs. rubrum* using X-ray diffraction analysis of very small crystals [15]. However, it was shown in [60, 72] that the groups of proteins of core-BChl around RC in *Rs. rubrum* are characterized by C-6 symmetry. It is obvious that the C-6 type of symmetry is hardly consistent with the presence of a ring of 32 molecules of core-BChl. The results reported in [73] suggested that the structure of the LH-1 complex could be quadratic. It was suggested in [74-76] that the LH-1 "rings" in the purple bacteria *Rhodobacter capsulatus* and *Rb. sphaeroides in vivo* were not closed as a result of incorporation of PUF-x proteins, which were required to provide access of charge transfer carriers from cytochromes to RC. Because the element of such crystalline structure is very elaborate both in terms of the number of incorporated atoms and in terms of the number of possible variants of interaction between individual αβ-heterodimers, their antenna ensemble, and pigment–protein units of the L- and M-subunits of RC incorporated in this ensemble, it can hardly be certain if these data correspond to the RC structure *in vivo*.

2. Although the problem of EES transfer to RC in plant photosystems is even more demanding than in pur-

ple bacteria, because each RC serves more than 150-250 molecules of Chl-a, circular arrangement of Chl molecules around the RC has not been demonstrated in either of the two photosystems [77, 78]. Indeed, the radius of the ring of 100 Chl molecules is too large to provide effective EES migration to special RC pair located at the center of the ring. However, two or three concentric rings around the RC could provide a sufficiently strong effect of EES concentration in special pair (provided that the exciton mechanism of EES concentration is indeed valid). If the efficiency of the exciton-mediated EES transfer to RC were so high, it would be very strange of Nature not to transfer such an effective mechanism from bacteria to plants.

3. Symmetric circular arrangement of core-BChl seems to be far from ideal in terms of implementation of high-efficiency EES trapping by special RC pair. For example, in *Rs. rubrum* the intermolecular distance in core-BChl is 9.2-9.3 Å [30] and the number of BChl molecules is 32 [14], which corresponds to the ring length and radius of 295 and 47 Å, respectively. High quantum yield of EES trapping in RC can hardly be provided at such a long distance to the special RC pair. If this mechanism were valid, the question would arise: why is the main molecular ensemble of light-harvesting antenna separated from the RC special pair P870 by such large distance? Moreover, it should be expected that during evolution at least a fraction of core-BChl molecules moved closer to rather than farther from the special pair. Indeed, the distance between BChl-a molecules in neighboring protein globules in some cases is one-half this value. For example, the distance between BChl-a molecules in neighboring protein globules in FMO-complexes of green bacteria is 24 Å [79].

The following conclusions can be drawn from these facts and their analysis.

1. The aggregate of experimental data available from the literature is not fully consistent with the conventional model that has been used over the last 30-35 years for describing the primary processes of energy migration to special RC pair and electronic excitation trapping in RC. To make this model more or less consistent with experimental data, it should be supplemented with two hypothetical molecular mechanisms (exciton and water-polarization).

2. The validity of neither the exciton mechanism (Section II) nor the water-polarization mechanism (Section III) of electronic excitation trapping in RC has yet been proved experimentally. Therefore, they should be regarded only as hypothetical. There is a large body of experimental evidence that excitons are delocalized over two to four (definitely, no more than six) molecules of core-BChl. According to our estimates, the exciton (Section II) or water-polarization (Section III) mechanisms of EES delocalization are able to provide only 1.7- to 2.4-fold or 4- to 5-fold gain in the efficiency of energy trapping, respectively, each alone being insufficient to resolve the controversy mentioned above (Section I).

3. New experimental data are urgently required to test the validity of the two models, to provide reliable assessment of the extent of the exciton-induced stimulation of EES migration from antenna chlorophylls to special RC pair, and to evaluate the efficiency of mechanisms of EES energy trapping and primary conversion in photosynthetic reaction centers. In this context, new spectroscopic data on femtosecond oscillation processes in RC preparations of purple bacteria are very promising [62, 80].

4. There has been considerable progress in construction of quantum-mechanical models of complicated molecular systems containing thousands of atoms (Section IV). In principle, these models are capable of providing the most comprehensive information about mechanisms of EES energy migration, trapping, and conversion in the photosynthetic unit. However, the presently available calculations obtained within the framework of these models give only semiquantitative estimates. It should be noted that these approaches are based on structural data of X-ray diffraction analysis of crystals of various BChl–protein complexes. Perhaps, the conformational state of antenna particles and reaction centers *in vivo* may differ from the conformational state of the complexes in crystals.

5. Conventional approaches to this problem based on the Förster theory of induction resonance energy migration should not also be discarded. According to the results obtained in [43-45], this theory is able to provide correct estimates even in case of moderate values of energy of dipole–dipole interaction, at which excitons are delocalized over groups of molecules within the first moments after absorption of the light quantum. Although neither detailed information about the position of individual molecules and atomic groups in the structure of Chl–protein complexes nor energy of interaction between these molecules or atomic groups are used in the models of this type, these models are based on reliable measurements of kinetic, spectral, and energy characteristics. It should be emphasized that structural characteristics are indirectly accounted in kinetic, spectral, and energy parameters, which increases the accuracy of the estimates obtained on their basis.

It should be noted that the problem of effective transfer of the energy of the electronic excited states generated by light absorption in molecular antenna complexes from light-harvesting chlorophyll molecules of bulk antenna to reaction centers discussed in this review is inherent not only in purple bacteria, but also in plant photosystems.

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