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The revision of the model of primary energy conversion in purple bacteria

A.Y. Borisov[a,*], Y.M. Sidorin[b,†]

[a] A.N. Belozersky Institute of Physico-Chemical Biology, M.V. Lomonosov Moscow State University 119899, Moscow, Russia
[b] Physical faculty of M.V. Lomonosov Moscow State University, 119899 Moscow, Russia

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Abstract

A simulation method is suggested which enables one to check whether a model for excitation energy exchange in an ensemble of dye molecules fits available experimental data. In particular, this method may deal with photosynthetic units (PSUs) in which excitation migration in antenna chlorophylls and their substantial trapping in reaction centers (RCs) take place. Its application to the purple bacteria has proved that the model, which was generally accepted during the last 20–30 years, is in contradiction with recent experimental facts and thus requires modernization. Two physical mechanisms are discussed: femtosecond polarization of mobile hydrogen atoms near the reaction center special pair (“water latch”), and the presence of excitons delocalized over several core-bacteriochlorophylls (BChls). Our considerations give evidence that neither of these mechanisms alone can resolve the conflict, but their cumulative action appears to be sufficient. Unfortunately, these mechanisms were as yet only partially addressed experimentally.

Keywords: Purple bacteria; Core-BChl; Reaction center; Energy trapping

1. Introduction

All photosynthesizing organisms are known to form phospholipid membranes which contain chlorophyll–protein complexes, i.e., light-harvesting complexes (LHC) and reaction centers (RC). In photosynthetic bacteria, algae, and plants tens to hundreds of light-harvesting (bacterio)chlorophylls [(B)Chls] serve on the average one energy-converting reaction center (reviewed in Refs. [1,2]). Thus, the problem arises how absorbed light energy is transferred from the numerous “antenna” pigments to RCs. It was clearly demonstrated that this energy transfer is achieved via singlet electronic excitations ([3], reviewed in Refs. [1,2]), in particular, in purple bacteria within the antenna BChls and from their long wavelength core fractions to RCs. Duysens [3] was the first to suggest the inductive-resonance mechanism for this action, which was developed by Foerster [4]. Subsequently, many authors have used the Foerster theory, often without due consideration whether its application is justified. Later extensive application of kinetic methods of high time resolution has elucidated the most important characteristics of these processes. Excitation lifetimes of about 50 ps were found in antenna BChls of several purple bacteria ([5–7], see also Refs. [1,2]), while the rate constants k_e for the primary charge separation in RCs were measured to be about $(3\ \mathrm{ps})^{-1}$ [1,2,8]. The latter process was widely recognized to play the role of excitation trapping. Until the middle of the 1980s, such a scheme could reconcile all experimental data available in purple bacteria provided one assumes the trapping-limited model of photosynthetic units (PSUs) (see, e.g., Refs. [9,10]). This concept requires large rate constants $k_{i,j}$ from each donor molecule i to at least one neighboring acceptor molecule j, especially those between the RC special pair and its closest neighbors, the core antenna BChl. It also requires that $k_{i,j} \gg k_e \cong (3\ \mathrm{ps})^{-1}$.

Progress in crystallization of pigment–protein complexes and their X-ray structural analysis enabled precise measurements of intermolecular distances both in reaction centers [11,12] and in antenna particles [13–15]. Many intermo-

Abbreviations: RC, reaction center; PSU, photosynthetic unit; BChl, bacteriochlorophyll; P_2, BChl special pair in RC; BChl-*a** and P_2*, BChl-*a* and RC special pair in singlet excited state, respectively; $[P_2^+X^-]$, RC state after completion of the primary electron transfer; X^-, reduced primary electron accepter; EE, electronic excitation in the first singlet state.

* Corresponding author. All-Russia Research Institute for Agricultural Microbiology, Podbelsky Chaussee 3, St. Petersburg-Pushkin 8, 189620 Russia. Tel.: +7-812-470-5100; fax: +7-812-470-4360.
E-mail address: borissov@genebee.msu.su (A.Y. Borisov).
† Y.M. Sidorin (Deceased).

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lecular distances are as short as about 10 Å, thus, suggesting that in such molecular ensembles, singlet excitations may exist as delocalized excitons. These works have laid the basis for the revision of the migration mechanism in antenna complexes (see Refs. [1,2] for details). However, the distances between closest BChl chromophores belonging to different antenna complexes may be as long as about 20 Å or even more [14], and here, excitation transfer remains amenable to the Foerster theory. Note that these very "bottle necks" determine the magnitude of the overall rate of excitation fluxes from antenna BChls to the RC special pair.

Here, we demonstrated that, in the light of recent findings, the currently accepted model requires a reevaluation. Two physical mechanisms are considered and discussed which may help to solve the problems encountered with the currently accepted model of excitation energy transfer.

2. Modeling method

A modeling method was suggested [16] which enables one to check the fit of models of limited pigment ensembles to their sets of experimental data. It may be applied not only to "pure Foerster systems" but also to condensed dye ensembles or associates such as dimers in the role of electronic excitation (EE) quenchers and, in particular, to photosynthetic units (PSUs) with RCs acting as EE quenchers.

Assume some arbitrary pigment ensemble with neighboring molecules close enough to exchange EE (see Fig. 1A). The method implies the construction of some idealized model consisting of the same molecules and quenchers, but with optimal intermolecular migration rates. This is demonstrated in Fig. 1B in which all molecules of Fig. 1A are arranged such (which is always possible mathematically) that they all have direct contacts with all quenching centers present with equal rate constants of high values. Such a construction serves two evident purposes: (i) it reduces maximally the length of migration routes thus making the ensemble of the trapping-limited type, and (ii) it drastically reduces the number of differential equations which describe the system.

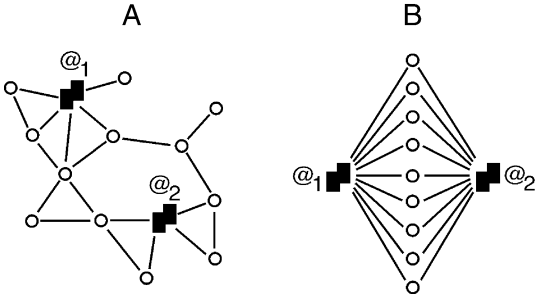

Fig. 1. (A) Arbitrary model of an ensemble of spectrally homogeneous molecules with n excitation deactivation centers. In the particular case $n=2$ with deactivation centers labeled by $@_1$ and $@_2$. (B) The ideal (mathematical) version of the model in (A), constructed as described in the text. Every molecule has direct access to both deactivation centers and all rate constants are equal.

This procedure can be generalized for a heterogeneous ensemble. In this case, all molecules of spectral fraction "i" must have direct contacts with all of their "j" quenchers, the spectral inhomogeneity being taken into account by the ratios of the corresponding rate constants. Here, also the rate constants $k_{i,j}$ must be so large that the lifetime calculated for such a model becomes only moderately sensitive to their values, i.e., the model to be analyzed is close to the trapping-limited one. In our model, the largest migration rate constants were equal to 10^{12} s^{-1} and their reduction to 0.5×10^{12} s^{-1} hardly caused noticeable changes.

The abovementioned simplifications evidently cause the value of EE lifetime calculated for such an ideal model to be smaller than the experimental one for the real ensemble. If it is not the case, it inevitably follows that the model representation of the molecular ensemble is incorrect and that some additional factors are involved. This criterion will be applied below to the currently accepted model of PSUs in purple bacteria.

3. Modeling and discussion

The following idealized model for a typical PSU of purple bacteria is suggested for the analysis (see Fig. 2).

(1) One PSU contains 30 core "antenna" BChls ($N_a=30$) which are considered as 15 dimers and one RC ($n_{rc}=2$, one P_2 dimer).
(2) EEs in core-BChls and in P_2 have equal energies.
(3) Core-BChls have the sum of trivial intramolecular losses (EE conversion into triplet, oscillations, fluorescence and quenching in wasteful centers) equal to $k_\Sigma=1.5\times10^9$ s^{-1} (weak EE quencher) [1,17].
(4) The value of the rate constant for primary e-transfer ($P_2^*\rightarrow P_2^+X^-$) is equal to $k_e=(3\text{ ps})^{-1}=3.33\times10^{11}$ s^{-1} (main EE quencher).
(5) In accord with our method, each core-BChl dimer can exchange EE with the P_2 dimer with the pairwise constant $k_{i,rc}=k_m$ equal to that for the core-BChl dimer which is in the best mutual orientation relative to the P_2 special pair, and vice versa. As to the reversed EE migration from the P_2 dimer to all antenna dimers, it evidently amounts to $k_{rc,a}=\Sigma_{Na}k_{i,rc}=\Sigma_{Na}k_m=N_ak_m$.

This basic scheme of the model can be represented by a set of three differential equations. For a long time, the available experimental data did not contradict such a model, provided the distance between the P_2 pairs and their closest core-BChls was assumed to be rather short, and correspondingly, the pairwise rate constants for EE migration between them were assumed to range between 10^{11} s^{-1} and 10^{13} s^{-1}. Such an ideal trapping-limited model yields the quantum yield of primary charge separation within 90–95% and

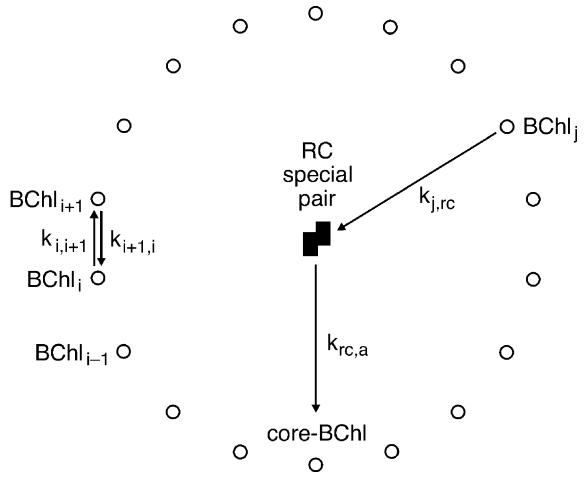

Fig. 2. An ideal model of the photosynthetic unit of purple bacteria-type. The core-BChls form a circle around the special pair. Each excited core-BChl molecule has the same rate constant for EE migration to the P_2 pair ($k_{j,rc}=k_m$) and similar rate constants for EE migration to its two neighbors ($k_{i,i+1}$, $k_{i,i-1}$). EE back migration from the excited special pair to the core-BChl ensemble is represented by an overall rate constant $k_{rc,a}$. For further explanation, see text.

an extreme excitation lifetime in core-BChl, t_a^{mod}, of about 40 ps [9,10], in good agreement with the experimentally determined lifetime t_a for many purple bacteria, $t_a^{mod} < t_a =$ 50–60 ps [1,2]. However, data were later obtained [18–20] which confirmed first measurements by Zankel et al. [21] and indicate that only a minor portion of EE can return from excited P_2 pairs back to antenna core-BChl. It will be demonstrated by means of our method that a computation with the model presented above, using the data given in Refs. [18–21], yields a value for t_a^{mod} which is considerably larger than the t_a values measured in real purple bacteria.

Let us analyze the model in Fig. 2 using points 1–5 mentioned above, and with the further simplification of one P_2 dimer being surrounded by 15 antenna BChl dimers (instead of 30 monomers), as proposed by Scherz and Rosenbach-Belkin [22]. There is a good reason for such a view because the close parts of the π-electronic circuits of the chromophores of the BChl special pairs are characterized by a spacing of about 5 Å [11,12], therefore, EEs are most likely delocalized in the special pairs. The specificity of exciton approaches to the core-BChl antennae (chromophore spacing ~ 9.3 Å [15,22]) will be discussed in more detail below. In accord with our method, all core-BChl dimers have equal rate constants for EE migration to the P_2-RC dimer, $k_{i,rc}=k_m$, where $i=1, 2,\ldots,15$ is the number of the separate core-BChl dimers, and $k_m \approx 10^{12}\ s^{-1}$.

According to points 1–5 above, the rate constant $k_{rc,a}$ for reversed EE migration from the excited P_2 dimer to the whole ensemble of core-BChl dimers becomes

$$k_{rc,a} \approx \sum_{i=1}^{Na} k_{i,rc} = k_m N_a/2 = 15K_m \quad (1)$$

The local dielectric permeability and mutual orientations of molecules are similar in both directions. Therefore, in accord with the principle of detailed balance, the ratio of rate constants in both directions will approximate to

$$k_{i,rc}/k_{rc,a} = 0.5 n_{rc} k_m/(k_m N_a/2) = 1/15 \quad (2)$$

Now assume in accord with the data in Refs. [18–21] that no more than 15% of EEs migrate from excited P_2 pairs back to the core-BChl (except for the BChl-*b* containing *Rhodopseudomonas viridis* antennae whose migration model is not yet clear). Within the framework of the model of Fig. 2, this means that

$$k_{rc,a} \cong 0.15 k_{e1} = 0.15 \cdot 3.3 \times 10^{11} s^{-1} \cong 5 \times 10^{10} s^{-1} \quad (3)$$

and, by means of Eq. (2),

$$k_{i,rc} = k_{rc,a}/15 \cong (330\ ps)^{-1} \quad (4)$$

It is evident that EE migration along core-BChl molecules ($k_{i,i+1}$ in Fig. 2) does not affect the probability of EE transfer to P_2 and thus cannot affect the EE lifetime. Moreover, the quantum yield of EE trapping is proved to reach 0.90 in purple bacteria [23–25]. Then it is easy to calculate the lifetime of EEs for the model in Fig. 2 as

$$t_a^{mod} \cong [k_{i,rc}(1 + k_{i,rc}/k_{rc,a})^{-1} + k_\Sigma]^{-1} \cong (k_{i,rc})^{-1} \cong 300\ ps \quad (5)$$

However, according to our method, the t_a^{mod} value should be at least 30% smaller than the values measured with purple bacteria, i.e., about 40–45 ps in view of $t_a \approx$ 50–60 ps [1,2]. This is clearly in contradiction to $t_a^{mod} \cong 300$ ps calculated with the ideal model. Hence, the current EE transfer model should be reconsidered.

First, it should be mentioned that the model in Fig. 2 was constructed with several approximations. More realistic data should be used for modeling, in particular, the following points should be considered:

- The secondary electron transfer, $P_2^+X^-Q_A \rightarrow P_2^+XQ_A^-$ and the back reactions, i.e., $P_2^+X^- \rightarrow P_2{}^*X$ and $P_2^+XQ_A^- \rightarrow P_2^+X^-Q_A$ should be included. According to Ref. [26], the energy gap between the states $P_2{}^*X$ and $P_2^+X^-$ is about 350–550 cm^{-1}, and hence, the back electron transfer cannot be neglected.
- According to recent work (see Refs. [1,15]), the distance between the P_2 pairs and their closest core-BChls is much larger than that between the neighboring antenna molecules so that the corresponding PSU approaches the migration-limited case.
- A number of additional B(800–850) BChls may be present in some bacteria which exchange EEs with the core-BChl.
- Some transition dipoles of the core-BChls may have an unfavorable mutual orientation with respect to those of the RC special pairs [15,21].

Taking these points into account causes a decrease of the quantum yield of EE trapping and a substantial increase in t_a^{mod} (at least up to 450 ps), i.e., these points augment instead of remove the discrepancy mentioned above.

At first sight, it may appear that shifting P_2 from the core-BChl center could improve the situation. A shift by $\Delta R = R_c/8$, where R_c is the radius of antenna circle, was tested. In accord with the Foerster theory [4] the following proportionality was assumed for the pairwise rate constant $k_{i,rc}$,

$$k_{i,rc} = k_m[R_c/(R_c + \gamma \Delta R)]^6 \; with \; -1 \le \gamma \le 1 \qquad (6)$$

With $k_m = 10^{12}\ s^{-1}$ for EE migration along the core-BChl ring, the shift did increase the magnitude of the overall rate constant for EE migration from the core-BChls to P_2. But it simultaneously increased the fraction of EEs migrating back from P_2, and thus, the total effect of shifting P_2 turned out to be negligible. Moreover, the values of the parameters k_m and k_{e1} were varied in the ranges $2 \times 10^{11}\ s^{-1} < k_m < 10^{13}\ s^{-1}$ and $2.5 \times 10^{11}\ s^{-1} < k_{e1} < 4 \times 10^{11}\ s^{-1}$, respectively, but this had hardly any effect on the value of t_a^{mod}.

4. Revision of the PSU model with the aim to eliminate the inconsistency

All the parameters used above were reliably established for purple bacteria by many independent researchers and can hardly be subjected to doubt. Therefore, in order to overcome the above contradiction it seems only possible to analyze whether there exist:

(A) some alternative trapping mechanism in RCs, or
(B) some objective reasons which cause a substantial increase in the crucial ratio of rate constant magnitudes $k_{i,rc}/k_{rc,a}$.

Both approaches were investigated. One of type A was first suggested by Fok and Borisov [27] and then analyzed in detail [16,28]. It was shown that, contrary to the previous model, the EE trapping in P_2 and the primary e-transfer reaction occur in two different stages. EE trapping is a separate process which precedes primary e-transfer and occurs in a time span of about 100–300 fs. The idea of the relevant physical mechanism was also developed [16,27,28]. Briefly, it is known that the excited state of P_2 is converted into a strong charge–transfer complex (CT) with about one third of the electron charge being transferred from P_B to P_A [29,30]. The electric field of such a dipole must induce dielectric polarization in the vicinity of P_2. In addition to universal polarization of electrons in fixed bonds, which is the source for the decrement of dielectric polarization in terms of the refraction index n at optical frequencies $\nu \cong 10^{15}\ s^{-1}$, there appears to be another potential source of rapid polarization in the time domain of about 10^{-13} s. From all particles known, only H-atom have a sufficiently small mass to be shifted in about 100 fs [31–33]. H-atoms with a substantial electron deficit may be present in water molecules weakly bound near or to the RC special pair. In the field of a constant electric dipole of the P_2* CT state, mobile H-atoms can reorient in about 100–300 fs due to the system's tendency to minimize its potential energy ("water latch" mechanism). It is worth noting that CT complexes are more potent in electron donation than monomer molecules [32] because in these complexes, charge separation partially proceeds in the CT state and the reverse process is substantially hampered by rapid polarization of the surrounding media. This rapid H-polarization consumes up to 40–50 meV of the P_2* electronic energy [16,28] which thus creates an "energy hole" and decreases the back electron transfer about four to five times (according to the Boltzman equation, a 57-meV barrier gives rise to 10-fold decrease at room temperature). Correspondingly, t_a^{mod} is expected to decrease from about 450 to about 110–75 ps, which is still insufficient to completely eliminate the inconsistency outlined above (it requires $t_a^{mod} \cong 40$–45 ps). References to experimental data, which are in line with the proposed H-reorientation model, can be found in Refs. [16,28].

It is instructive to compare this process with exciton localization in aromatic crystals [34] where delocalized excitons rapidly turn into so-called charge–transfer excitons, with electron and hole being separated and localized in two adjacent molecules. This conversion leads to a local deformation of the crystal lattice and to a self-trapping of such a CT exciton in a pair of molecules. As a result of a strong coupling with phonons, the absorption spectra of such CT excitons adopt the form of a broad band resembling those observed for the P_2 pairs in RCs. An energy gap of about 30 meV was estimated for such self-trapped excitons [34], which is in reasonable agreement with the estimation presented above for the RC special pairs in purple bacteria.

A mechanism of type B was first proposed by Novoderezkin and Razjivin [35] and further developed by these [36,37] and several other authors (reviewed in Ref. [38], and in more detail in Ref. [39]). The authors have analyzed the situation when EE migration to and from the P_2 pairs proceeds via exciton states in the core-BChls of purple bacteria. The pronounced red shifts and sometimes widening of the absorption bands are evident indications of delocalized exciton states in vivo. In the present context, it seems reasonable to discuss two important points pertaining to the delocalized exciton approach.

(1) The cumulative "transition dipole" of an exciton expands over several core BChl molecules and is thus substantially increased, which causes the increase of $k_{a,rc}$, and correspondingly, of the crucial ratio $k_{a,rc}/k_{rc,a}$. This quality of excitons should be specially considered and analyzed in general form in relation to the fundamental physical problem, i.e., excitons as promoters of EE in separate molecules or small subsets. This problem is impor-

tant not only for photosynthesis; such processes (if they exist) could lead, in the near future, to important applications for the design of microchips in information transfer, and in general, for micromolecular centers in nanotechnology.

(2) How much can the ratio $k_{a,rc}/k_{rc,a}$ be increased in favor of the minor molecular fraction due to the presence of excitons in P_2 and in the core-BChl fractions? The number of core-BChls sharing an exciton, p, was treated theoretically for values of p from 2–4 up to all BChls which form a circle around a RC [35–38]. It was shown that just after photon absorption, practically all BChl molecules of LH-1 may share an exciton, but the number of these molecules decays rapidly in the sub- and picosecond time range and soon levels off at $p=2–4$ [40]. Recent experiments also yielded similar numbers (between 4 and 6 BChls, see review in Ref. [38]). In early works, authors have admitted that the square of the "transition moment" of an exciton delocalized over n molecules is about n times larger than that of a monomer. Sundström [41] stated that instead of $t_a^{mod} \approx 400$ ps in the monomer or dimer model, one should obtain about 65 ps, providing an exciton that extends over 6 core-BChls. According to our view, such a gain may be obtained only in the limiting case of collinear molecules. If one deals with strongly interacting molecules, which form a circle like that described by Karrasch et al. [15], this decrease must be smaller. For example, the oscillator strength of the P870 band of the RC special pair is only about 1.7 of that for monomeric BChl due to a 12° angle between the transition moments of the P_2 molecules, in excellent agreement with Davydov's theory [42]. The remaining 0.3 fraction of this oscillator strength can be allocated to the minor excitonic band at around 800 nm which is unlikely to contribute to EE migration from the core-BChl. If core-BChl dimers do form a ring and excitons do expand over it, the square of summed "transition dipole" would increase, but no more than 4–4.5 times, bearing in mind the progresssively increasing angles between different core-BChl transition dipoles and the energy dispersion due to splitting into n excitonic levels. Exciton delocalization over many molecules requires a high regularity of the core-BChls. This causes difficulties for a theoretical construction of absorption spectra, which are similar to those registered in vivo. Novoderezhkin et al. [37] have estimated n as 4–6 core-BChls, i.e., 2–3 dimers. We believe that the crucial ratio $k_{a,rc}/k_{rc,a}$ may increase up to 2.4 times in the limiting case of excitons extending over 6 core-BChls (instead of 3.0 for BChls with collinear transition dipoles) but this also depends on the symmetry of the system. Within our method, it would reduce the value of t_a^{mod} to 400 ps/2.4 = 167 ps, which is still larger than the about 40–45 ps according to the condition $t_a^{mod} < t_a = 50–60$ ps. Thus, as in the case of the water latch model, exciton delocalization over several core-BChl pairs can substantially diminish but not remove the above-formulated discrepancy. Fiedor et al. [40] have estimated that one artificial quenching center can efficiently deactivate about 10 LH-1 BChl molecules, but this does not mean that 10 BChls share an exciton during about 100 ps or more, as required for the exciton model.

Another mechanism of type B was later developed by several authors (e.g., Refs. [42–46], reviewed in Ref. [38]). Quantum-mechanical Hamiltonians were constructed which include all nonnegligible interaction energies in circular aggregates of core-BChl and carotenoids in LH-2 and LH-1 [43–45]. Several experimentally undetermined parameters were varied and chosen such that available spectral data could be reproduced. The conclusions reached by Meier et al. [43] offer an alternative to those discussed above [35–38]; they write "the accessory BChls of the photosynthetic RC are found to be crucial for the LH-1 → RC transfer, which would take several hundred picoseconds [!] without these bacteriochlorophylls". Damjanovic et al. [45] estimated this time to be as long as 600 ps. If we assume that the minimal value of this lifetime is about 150–200 ps, it would be in accord with our concept of exciton delocalization being involved in the core-BChl* → P_2^* route, but the ratio $k_{i,rc}/k_{rc,a}$ would increase only 2- to 2.5-fold which is not sufficient. Although modern quantum-mechanical methods can evidently cope with such complex systems as RC particles even with a circular arrangement of BChl in LH-1, it should be kept in mind that these methods depend on several factors, such as the influence of local uncompensated charges or the static and dynamic disorder of BChl transition moments, which have to be adjusted in order to obtain reasonable results. It seems that these adjustments are not unique but may be done in different ways; as a consequence, the estimated value of t_a ranges between 15 and 105 ps [44]. The concepts discussed above should then be considered as hypothetical because they have not yet been confirmed by experimental data.

Finally, we should mention that the models with 32 core-BChl molecules forming a circle appear to us somewhat doubtful. With a distance of 9.3 Å between neighboring BChls [15], the radius of the circle becomes 47 Å. This is too long a distance for an efficient EE transfer to the RC pair located in the center of the antenna circle.

5. Conclusions

1. An inconsistency is revealed within the widely accepted model of excitation migration and trapping, at least for purple bacteria but possibly also for plant photosystems. It is shown that this model cannot accommodate all experimental data presently available.
2. Using an estimation method we can calculate to what extent "water latch" [16,27,28] and delocalized exciton [35–38,43–45] mechanisms can reduce the revealed discrepancy.
3. Our analysis demonstrates that neither "water latch" nor delocalized exciton mechanisms alone are sufficient. The cumulative action of both mechanisms (or some other yet

unknown mechanism) appears to be necessary in order to reconcile this model for purple bacteria with all experimental data so far available.

Notes

Recently, a paper [A. Yakovlev, A. Shkuropatov, V. Shuvalov, Nuclear wave packet motion between RC potential surfaces, Biochemistry 41 (2002) 14019–14027] was published in which a water molecule (HOH-302) near the RC special pair of *Rhodobacter sphaeroides* R-26 is described. This water molecule performs several oscillations just after the RC is excited. In our view, this fact proves that (i) H_2O is connected with the RC special pair, and (ii) that these oscillations reflect an H_2O rotation. Irrespective of the nature or mechanism which enable H_2O to rotate we believe that, providing H_2O does rotate, it can change the direction of its electric dipole, just what is needed for the water latch mechanism [see Refs. [16,27], and the further developed version in A.Y. Borisov, S.A. Kuznetsova, On the involvement of the water-polaron mechanism in energy trapping, Biochemia-Moscow 67 (2002) 1483-1489].

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References

[1] R. van Grondelle, J.P. Dekker, T. Gilbro, V. Sundström, Energy transfer and trapping in photosynthesis, Biochim. Biophys. Acta 187 (1994) 1–65.
[2] R. van Grondelle, O.J. Somsen, Excitation energy transfer in photosynthesis, in: D.L. Andrews, A.A Demidov (Eds.), Resonance Energy Transfer, Wiley, Chichester, 1999, pp. 366–391.
[3] L.N.M. Duysens, Transfer of excitation energy in photosynthesis, Nature 8 (1951) 548–552.
[4] T.H. Foerster, Excitation transfer, in: J.S. Kirby-Smith, J.L. Magee (Eds.), Comparative Effects of Radiation, Wiley, New York, 1960, pp. 300–319.
[5] A.Y. Borisov, V. Godik, Fluorescence lifetime of BChl and RC photooxidation in photosynthetic bacterium, Biochim. Biophys. Acta 223 (1970) 441–443.
[6] A.Y. Borisov, V.I. Godik, Energy transfer to the reaction centers in bacterial photosynthesis, Bioenergetics 3 (1972) 515–523.
[7] A.J. Campillo, R.C. Hyer, T.G. Monger, W.W. Parson, S.L. Shapiro, Light collection and harvesting processes in photosynthesis in picosecond time scale, Proc. Natl. Acad. Sci. U. S. A. 74 (1977) 1997–2001.
[8] M.G. Rockley, M.W. Windzor, R.J. Cogdell, W.W. Parson, Picosecond detection of an intermediate in the photosynthetic photoelectric conversion, Proc. Natl. Acad. Sci. U. S. A. 72 (1975) 2251–2256.
[9] R.M. Pearlstein, Excitation migration and trapping in photosynthesis, Photochem. Photobiol. 35 (1982) 835–844.
[10] A.Y. Borisov, Transfer of excitation energy in photosynthesis, Photosynth. Res. 20 (1989) 35–58.
[11] U. Ermler, G. Fritzsch, S.K. Buchanan, H. Michel, The structure of the photosynthetic reaction center from *Rb. sphaeroides*, Structure 2 (1994) 925–936.
[12] J.P. Allen, G. Feher, T.O. Yeates, H. Komiya, D.C. Rees, Structure of the reaction center from *Rb. sphaeroides*, Proc. Natl. Acad. Sci. U. S. A. 84 (1987) 5730–5734.
[13] R.J. Cogdell, R.K. Fyfe, S.J. Barrett, S. Prince, A.A. Freer, N.W, Isaaks, C.N. Hunter, The purple bacteria photosynthetic units, Photosynth. Res. 48 (1996) 55–63.
[14] R.E. Fenna, B.W. Mattews, Chlorophyll arrangement in a bacteriochlorophyll-protein from *Chlorobium limicola*, Nature 258 (1975) 573–577.
[15] S. Karrasch, P.A. Bullough, R. Ghosh, The 8.5Å projection map of the light-harvesting complex 1 from *Rhodospirillum rubrum* reveals a ring composed of 16 subunits, EMBO J. 14 (1995) 631–638.
[16] A.Y. Borisov, The widely accepted model of primary photosynthesis events in purple bacteria must be revised, Biochemia-Moscow 65 (2000) 1266–1271.
[17] V.I. Godik, A.Y. Borisov, Excitation trapping by different states of reaction centers, FEBS Lett. 82 (1973) 355–358.
[18] I.A. Abdourakhmanov, R.V. Danielius, A.P. Razjivin, Efficiency of excitation trapping by reaction centers of complex B890 from *Chromatium minutissimum*, FEBS Lett. 245 (1989) 47–50.
[19] K.N. Timpmann, F.G. Zhang, A.M. Freiberg, V. Sundström, Detrapping of the energy from the reaction center in photosynthetic bacterium *Rs. rubrum*, Biochim. Biophys. Acta 1183 (1993) 185–193.
[20] S.C. Otte, F.A. Kleinherenbrink, J. Amesz, Energy transfer between reaction center and antenna in bacterial photosynthesis, Biochim. Biophys. Acta 1143 (1993) 84–90.
[21] K.L. Zankel, D.W. Reed, R.K. Clayton, Fluorescence and photochemical quenching in photosynthetic reaction centers, Proc. Natl. Acad. Sci. U. S. A. 61 (1968) 1243–1247.
[22] A. Scherz, V. Rosenbach-Belkin, Comparative study of optical absorption and circular dichroism of bacteriochlorophyll oligomers in the antenna pigment B850, Proc. Natl. Acad. Sci. U. S. A. 86 (1989) 1505–1509.
[23] P.A. Loach, D.A. Secura, The quantum yield of the primary photoreaction in purple bacteria, Photochem. Photobiol. 7 (1968) 2642–2649.
[24] E. Barski, A.Y. Borisov, Determination of the quantum yield of the primary photosynthesis events in purple bacteria, J. Bioenerg. 2 (1971) 275–281.
[25] W.W. Parson, The role of P870 in acterial photosynthesis, Biochim. Biophys. Acta 153 (1967) 251–269.
[26] A.G. Yakovlev, V.A. Shuvalov, Charge separation in reaction centers of photosynthesis at femtosecond excitation, Biochemia-Moscow 66 (2001) 261–272.
[27] M.V. Fok, A.Y. Borisov, Water and energy conversion in photosynthesis, Stud. Biophys. 84 (1981) 115–124.
[28] A.Y. Borisov, M.V. Fok, The polarization model in bacterial photosynthesis, Biochem. Mol. Biol. Int. 47 (1999) 117–125.
[29] M.A. Steffen, K. Lao, S.G. Boxer, Dielectric asymmetry in the photosynthetic reaction centers, Science 264 (1994) 810–815.
[30] L.J. Moore, H. Zhou, S.G. Boxer, Excited state electronic asymmetry of the special pair in photosynthetic RC mutants, Biochemistry 38 (1999) 11949–11960.
[31] W.W. Parson, Z.T. Chu, A. Warshel, Reorganization energy of the initial electron transfer step in photosynthetic RCs, Biophys. J. 74 (1998) 182–191.
[32] A.N. Terenin, in: N.A. Kruglikova (Ed.), Molecular Photonics, Nauka, Leningrad, 1967, pp. 345–349.
[33] A. Nitzan, Ultrafast relaxation in water, Nature 402 (1999) 472–475.
[34] V.M. Agranovich, A.A. Zakhidov, Interaction of charge transfer ex-

citons with phonons in molecular crystals, Chem. Phys. Lett. 50 (1977) 278–281.
[35] V.I. Novoderezkin, A.P. Razjivin, Excitonic interactions in the light-harvesting antenna of photosynthetic purple bacteria and their influence on picosecond absorbance difference spectra, FEBS Lett. 333 (1993) 9–13.
[36] V.I. Novoderezkin, A.P. Razjivin, Exciton dinamics in circular aggregates: application to antenna of purple bacteria, Biophys. J. 68 (1995) 1089–1100.
[37] V.I. Novoderezhkin, R. Monshouwer, R. van Grondelle, Disordered exciton model for the core antenna of *Rhodopseudomonas viridis*, Biophys. J. 77 (1999) 666–681.
[38] R. Van Grondelle, V.I. Novoderezhkin, Dynamics of excitation energy transfer in the LH-1 and LH-2 light-harvesting complexes of photosynthetic bacteria, Biochemistry 40 (2001) 15057–15068.
[39] T. Renger, V. May, O. Kuhn, Ultrafast excitation energy transfer dynamics in photosynthetic pigment–protein complexes, Phys. Rep. 343 (2001) 137–254.
[40] L. Fiedor, H. Scheer, C.N. Hunter, F. Tschirschwiz, B. Voigt, J. Ehlert, E. Nibbering, D. Leupold, T. Elsaesser, Introduction of a 60-fs deactivation channel in the photosynthetic antenna LH-1 by Ni-bacteriochlorophyll *a*, Chem. Phys. Lett. 319 (2000) 145–152.
[41] V. Sundström, personal Communication, December 26, 2000.
[42] A.S. Davydov, in: V.L. Levshin (Ed.), The Theory of Molecular Excitons, Nauka, Moscow, 1968, pp. 296–298.
[43] T. Meier, Y. Zhao, V. Chernyak, S. Mukamel, Bacteriochlorophyll and carotenoid excitonic coupling in purple bacteria, Chem. Phys. Lett. 107 (1997) 7763–7774.
[44] X. Hu, T. Ritz, A. Damjanovic, K. Schulten, Pigment organization and transfer of electronic excitations in the photosynthetic unit of purple bacteria, J. Phys. Chem., B 101 (1997) 3854–3871.
[45] A. Damjanovic, T. Ritz, K. Schulten, Excitation energy trapping by the reaction center of *Rhodobacter sphaeroides*, Int. J. Quant. Chem. 77 (2000) 139–151.
[46] X. Hu, A. Damjanovic, T. Ritz, K. Schulten, Architecture and mechanism of the light-harvesting apparatus of purple bacteria, Proc. Natl. Acad. Sci. U. S. A. 95 (1998) 5935–5941.