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Minireview

Excitation energy trapping in anoxygenic photosynthetic bacteria*

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Abstract

Various aspects of excitation energy conversion in anoxygenic photosynthetic bacteria are surveyed. This minireview discusses different models that have been proposed during the past 60 years to describe excitation energy transfer from an antenna molecule to the reaction center. First, a simple one-dimensional model was suggested, but over time the models became more detailed when structural and dynamic information was included. This review focuses mainly on the picture of purple bacteria and green sulfur bacteria developed during the past decades.

Abbreviations: BChl – bacteriochlorophyll; B800, B850 – peripheral antenna of purple bacteria with Q_y absorption peaks near 800 and 850 nm, respectively; Chl – chlorophyll; FMO complex – Fenna–Matthews–Olson complex; LH – light-harvesting; RC – reaction center

Early models

When the concept of the photosynthetic unit had been formulated (R. Emerson and W. Arnold 1932; H. Gaffron and K. Wohl 1936), the question naturally arose how the energy absorbed by a given pigment molecule would be transferred to the reaction center [RC; a term introduced by L.N.M. Duysens in his doctoral thesis (Duysens 1952)]. This point attracted the attention of various researchers already before much experimental evidence was available and before anything was known about the structure of antenna complexes. Even before that, the first to address the issue, more than 60 years ago, were J. Franck and E. Teller (1938). On the basis of a quite unrealistic one-dimensional model, consisting of a string of 1000 chlorophylls (Chls) for the photosynthetic unit, they found that the rate of energy transfer between adjacent molecules should be as fast as $(10\ \text{fs})^{-1}$ in order to obtain a reasonable trapping efficiency.

W. Vredenberg and Duysens (1963) found that in purple bacteria the fluorescence yield shows a hyperbolic dependence on the fraction x, of RCs in the oxidized, 'closed' state:

$$\Phi = \Phi_0 \frac{1}{(1 - px)} \tag{1}$$

where Φ_0 is the fluorescence yield when all RCs are open, and p is a parameter that reflects the difference in the efficiency of fluorescence quenching by open and closed RCs (Figure 2). From this, Vredenberg and Duysens concluded that several RCs must share the same antenna. In other words, the RCs are embedded in a matrix of pigment molecules, and the migration of an optical excitation can be considered as a random walk over this matrix.

Based on this work, more realistic two- and three-dimensional lattice models were proposed by Z. Bay and R. Pearlstein (1963), Pearlstein (1967) and G.

* Sieglinde Neerken dedicates this article to her mentor and co-author Jan Amesz (see Figure 1 for his photograph). Jan passed away on January 29, 2001. His obituary by A.J. Hoff and T.J. Aartsma appears in *Photosynthesis Research* 71: 1–4 (2002).

Figure 1. Jan Amesz, May 1999.

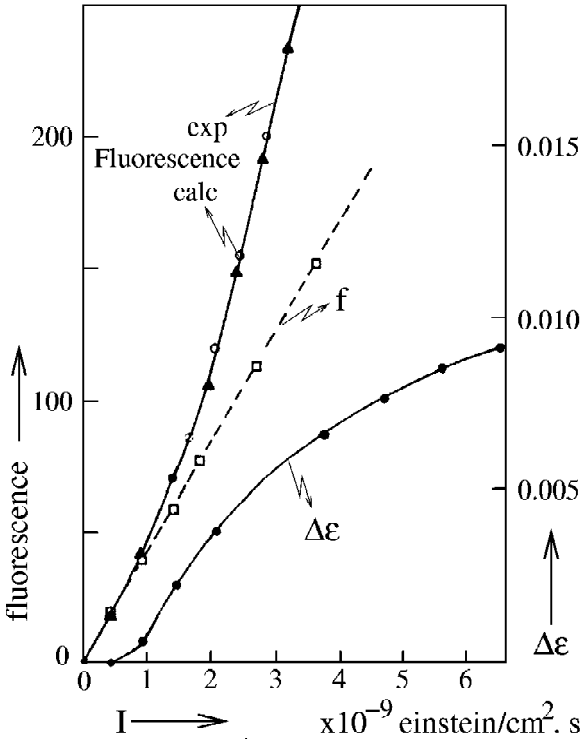

Figure 2. The steady-state absorption difference at 880 nm ($\Delta\varepsilon$), the steady-state level of BChl fluorescence and the initial fluorescence intensity f as a function of the actinic intensity I (λ_{exc} = 500 nm) in *Rhodospirillum rubrum*. Since f is proportional to I, the fluorescence yield at start of the illumination is independent of I. The light-induced decrease in absorption at 880 nm is quantitatively correlated with an increase in fluorescence yield of BChl. From the hyperbolic dependence it was concluded that several RCs share the same antenna; published by W.F.J. Vredenberg and L.N.M. Duysens (1963).

Wilse Robinson (1967), who concluded that efficient trapping would be possible without unreasonably high rates of energy transfer (see Pearlstein, this issue). Both models involved a trap-limited model, which means that the reaction center on the average is visited several times by an excitation before trapping occurs. In Robinson's model, the trapping efficiency for one visit would be as low as 1%. The trap-limited model results automatically from the assumption that the properties of the trap are not basically different from those of the antenna pigments, but it is not an essential feature of the lattice model: by changing the depth of the trap or the lifetime of its excited state, trapping can be made more or less irreversible. With a fully irreversible trap, the model becomes 'diffusion limited', and the rate of trapping equals the rate of diffusion of the excitation energy to the trap. The models have been extended and put on a more rigorous mathematical basis by R.S. Knox (1968) and E.W. Montroll (1969) in the late 1960s. As early as 1948, T. Förster had developed his theory of induced resonance for excitation energy transfer (Förster 1948), which was able to provide a physical basis for observations and calculations.

R.K. Clayton (1967) introduced the concept of domains for excitation energy transfer as the ensemble of antenna molecules among which excitations can be transferred. With multiple excitations within one domain, the non linear process of singlet–singlet annihilation will give rise to a reduction of the fluorescence yield. A general equation was derived by G. Paillotin et al. (1979), who used a master equation approach to describe the shape of the quenching curves (Figure 3). Measured fluorescence quenching curves, as a function of (pulsed) excitation energy, provided information on the rates of energy transfer and trapping, and on the domain size [see the review by R. van Grondelle (1985)]. Extensive discussions on energy transfer in photosynthetic bacteria can also be found in Chapters 16–18 of Clayton and W. Sistrom (1978), and Chapters 15 and 17–20 of R. Blankenship et al. (1995).

As mentioned before, the models had been fully developed when still little or nothing was known about the structures and the optical properties of the an-

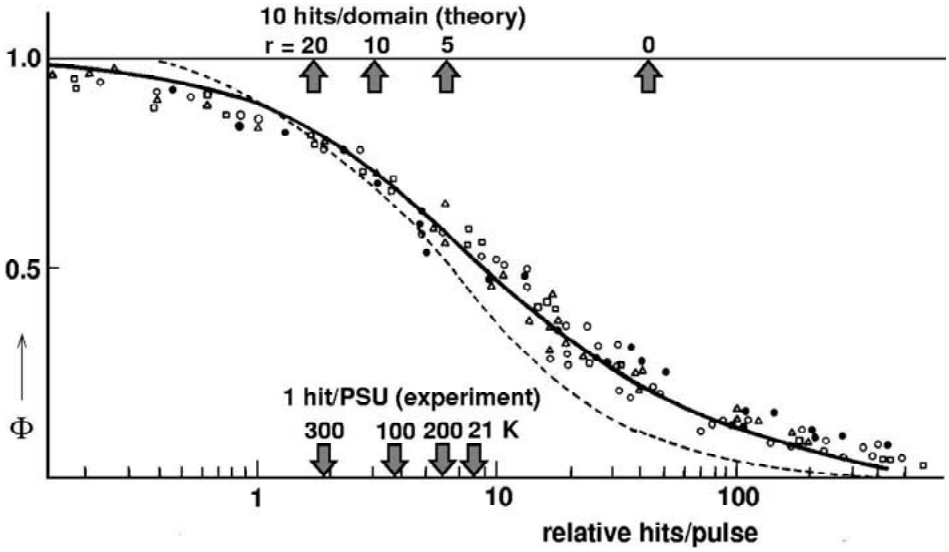

Figure 3. Comparison of calculated and experimental fluorescence quenching curves as a function of the intensity of picosecond laser pulses in photosynthetic membranes at different temperatures (squares: 21 K, closed circles: 100 K, open circles: 200 K, and triangles: 300 K; lines: theoretical curves); reproduced from G. Paillotin et al. (1979). From these data, a minimum size of the photosynthetic domain was estimated to contain more than 2–4 photosynthetic units where each unit was taken to consist of ~300 chlorophylls. For more details, see G. Paillotin et al. (1979).

tenna systems. When such information became available, the models and lattices became more detailed to accommodate the new information (see, e.g., M. Beauregard et al. 1991; O.J.G. Somsen et al. 1994; L. Valkunas et al. 1995; A. Damjanovic et al. 2000 and references therein). Those models can be useful for relatively large antenna reaction center systems with more or less isotropic structures, such as Photosystem I in plants and cyanobacteria. However, in other cases, like the purple bacteria with their ring-shaped antenna complexes, they are less useful. The situation that applies to purple bacteria will be discussed in more detail below; it appears that neither model – trap-limited or diffusion-limited – applies to these bacteria. On the nature of the trapping mechanism in green sulfur, only very limited information is available. A comparison is made with the related heliobacteria.

Trapping mechanisms

The lifetime of an excitation within a photosynthetic antenna reaction center complex is determined by the following processes: (i) the time needed for migration through the antenna, (ii) transfer to the reaction center and (iii) charge separation. As mentioned above, earlier studies of the overall energy trapping by photosynthetic reaction centers have often been discussed in terms of 'diffusion-limited' or 'trap-limited' models. For several photosynthetic pigment–protein systems, fast laser spectroscopy has shown that equilibration of the excitation energy within the antenna is much faster than trapping and therefore the 'diffusion' through the antenna will not be the rate-limiting step.

Purple bacteria

More than 60 years ago, E.C. Wassink and his coworkers (1939) observed the presence of more than one bacteriochlorophyll (BChl) near-infrared absorption band in various species of purple bacteria, including *Chromatium (Chr.) vinosum* and *Rhodopseudomonas (Rps.) palustris*. Ten years later Duysens (1951, 1952) demonstrated the occurrence of energy transfer from short-wavelength to long-wavelength absorbing BChl in *Chr. vinosum*.

It is now known, as Wassink had predicted, that the absorption bands of purple bacteria in the near-infrared are due to different pigment–protein complexes. Most species have two different complexes, called light-harvesting 1 (LH 1) and light-harvesting 2 (LH 2) complexes. LH 1 is closely associated with the reaction center and in fact thought to surround it (S. Karrasch et al. 1995). LH 2 is more peripherally situated. It absorbs shorter wavelengths, has usually two

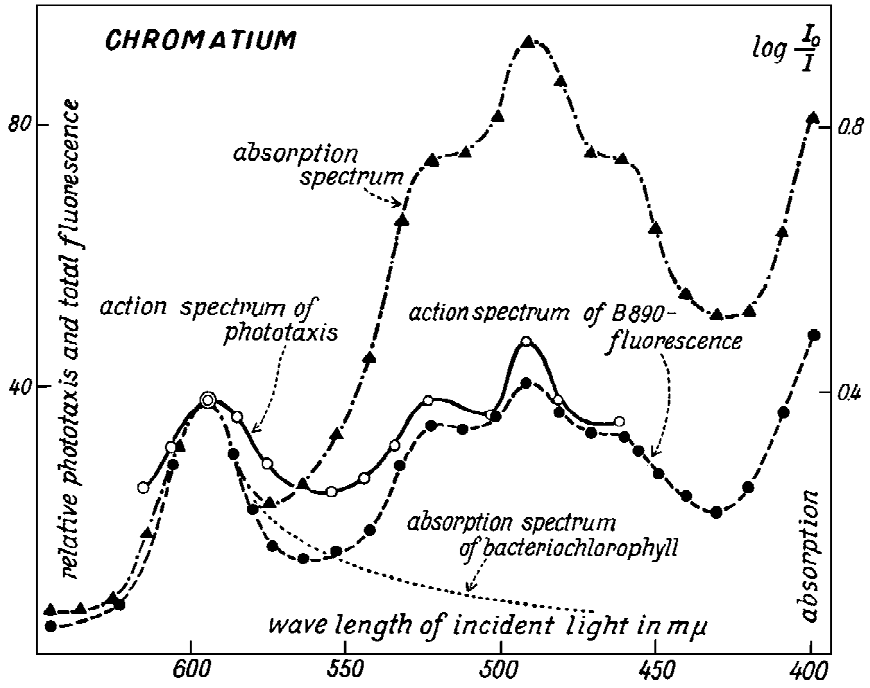

Figure 4. Absorption spectrum and action spectra for phototaxis (photosynthesis) and for B890 fluorescence of *Chromatium vinosum*. The absorption peak at 590 nm is due to BChl, the absorption between 450 and 550 nm mainly to carotenoids. Transfer of light energy from carotenoids to B890 was found to occur with an efficiency of 35–40%; published by L.N.M. Duysens (1951, 1952).

absorption bands, 'B800' and 'B850', and its structure has been resolved at atomic resolution by X-ray analysis (G. McDermott et al. 1995; H. Koepke et al. 1996). A traditional method to study the efficiency of excitation energy transfer between the pigments and antenna complexes is by means of fluorescence excitation spectra. Using this method, Duysens (1951, 1952) determined an efficiency of about 40% for energy transfer from carotenoids (mainly rhodopin in this case) to BChl *a* in *Chr. vinosum* and *Rhodospirillum molischianum* (see Figure 4). These studies were extended to other species in the 1960s and 1970s by, amongst others, J. Amesz and W. Vredenberg (1966), R. Wang and R.K. Clayton (1971) and J.C. Goedheer (1973).

The general picture that emerged from these studies was that of a high efficiency of energy transfer from B800 to B850 and from B850 to LH 1. Recent accurate measurements show efficiencies of more than 95% (H.P. Permentier 2001). Efficiencies of energy transfer from carotenoid to BChl *a* are often lower, but for some carotenoids (spheroidene and okenone) they are more than 80% (Duysens 1952; Goedheer 1959; R.J. Cogdell et al. 1981; P.O. Andersson et al. 1996). A recent extensive study of these efficiencies can be found in Permentier's thesis (Permentier 2001). In the early 1980s, a fairly complete picture had been established of energy transfer in the antenna of purple bacteria, and reasonable estimates could already be made of the rates of energy transfer. An extensive overview of the situation around 1985 can be found in the book by Govindjee et al. (1986). At that time, laser spectroscopic techniques became available, which made the direct measurement of energy transfer rates possible.

Although the long-wavelength emission of cells and membranes of purple bacteria comes from the LH 1 antenna rather than from the reaction center, fluorescence excitation spectra have also yielded important information on the trapping of the excitation energy by the reaction center. The first evidence of this kind was obtained by Clayton and coworkers (R.K. Clayton and W. Sistrom 1966; J. Olson and Clayton 1966; R.T. Wang and Clayton 1971). They showed that excitation of reaction center bands around 800 or 830 nm, now known to be due to the accessory BChls, in species lacking the LH 2 complex, such as *Rhodospirillum (Rsp.) rubrum* and *Rhodopseudomonas (Rps.) viridis* was considerably more efficient in bringing about reaction center photochemistry than in exciting antenna fluorescence. More than 20 years later, F.A.M. Klein-

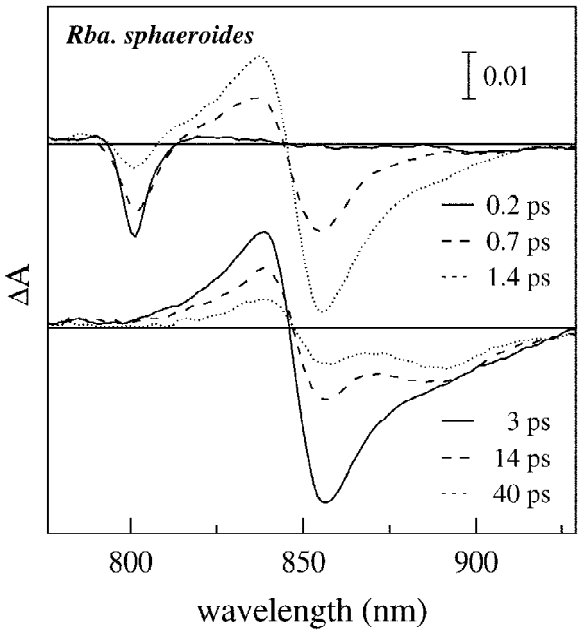

Figure 5. Illustration of energy transfer steps in membrane fragments of purple bacteria. Absorption difference spectra of membrane fragments of *Rba. sphaeroides* at various delays after excitation at 800 nm. Excitation energy transfer: LH 2 (B800 to B850): 0.65 ps; LH 2 (B850) to LH 1: 5.2 ps; LH 1 to RC: 50 ps; reproduced from S. Neerken (2001).

herenbrink et al. (1992) and S.C.M. Otte et al. (1993) confirmed and extended these measurements. Experiments at cryogenic temperatures did not show any contribution of the reaction center bands to the excitation spectra of antenna fluorescence. It was shown that less than 5% of the energy was transferred to the antenna upon excitation of the reaction centers, indicating that the back transfer to the antenna cannot compete with charge separation. At room temperature, the number was less than 10%. Therefore, it was concluded that the rate-limiting step in the overall energy conversion by the reaction center is the transfer from the antenna pigments to the primary electron donor. Similar results were obtained by H. Kramer et al. (1998) and H.P. Permentier (2001) with mutants and with other species. Based on time-resolved picosecond absorption difference and fluorescence measurements at room temperature, the same conclusion was drawn by I.A. Abdourakhmanov et al. (1989) and K. Timpmann et al. (1993, 1995), although in these measurements the back transfer efficiency was somewhat higher (10–25%) than that found by the group at the University of Leiden.

As mentioned already, the rates of energy conversion in purple bacteria have been extensively studied by time-resolved techniques during the recent years (see for reviews R. van Grondelle et al. 1994; A. Freiberg 1995; V. Sundström and R. van Grondelle 1995; R.J. Cogdell et al. 1996, 1999; V. Sundström et al. 1999). Femto- and picosecond measurements have shown that the excitation migration through the light-harvesting antenna complexes LH 2 and LH 1 is essentially completed within the first 10 ps after excitation. The overall trapping in purple bacteria is found to take place with a time constant of about 50 ps (see Figure 5). These data rule out a diffusion-limited model and the mechanism for the trapping process in purple bacteria has been described mostly as 'transfer-to-trap-limited', a term proposed by K. Timpmann and coworkers (Timpmann et al. 1995). In this model, the energy transfer from the antenna to the reaction center is the rate-limiting process. The trapping time of 50 ps in purple bacteria is determined by the transfer of excitation energy from the LH1 antenna to the primary electron donor. This time constant is found to be remarkably similar in different species in spite of widely different positions of the antenna and primary electron donor absorption bands. An overview of this subject can be found in Chapter 1 of the thesis written by S. Neerken (2001).

Green sulfur bacteria

Emission spectra of green sulfur bacteria were first measured by A.A. Krasnovskii et al. (1962) and subsequently by several others (C. Sybesma and J. Olson 1963; J.C. Goedheer 1972; T. Swarthoff 1982). They show two major emission bands. In *Prosthecochloris aestuarii*, the bands are located at 774 and 815 nm at room temperature and at 784 and 830 nm at 4 K (T. Swarthoff et al. 1981). The first band comes from the chlorosomes; its location depends on the BChl species (S.C.M. Otte 1992). The second one is, at least partially, due to the Fenna–Matthews–Olson (FMO) protein and shows the same characteristics as the isolated FMO complex (T. Swarthoff et al. 1981). More recent measurements indicate that part of the fluorescence is due to BChl *a* of the chlorosomal baseplate (S.C.M. Otte 1992). J. Olson and C. Sybesma (1963) were the first to measure the efficiency of energy transfer from the chlorosome to the reaction center by determining the relative efficiencies for cytochrome oxidation upon illumination with light of different wavelengths.

They found an efficiency of 60–70%. In contrast to purple bacteria, fluorescence excitation spectra cannot be used for this purpose because of the very weak and poorly resolved BChl *a* absorption bands, which make a comparison with the excitation spectrum very inaccurate. The method has been applied at 6 K to isolated chlorosomes though, and it was found that at this temperature the efficiencies for energy transfer from BChl *c* to the baseplate BChl *a* is low (R.J. van Dorssen et al. 1986; S.C.M. Otte 1992).

Time-resolved measurements have been performed by picosecond fluorescence and absorbance studies (Z.G. Fetisova and A.Y. Borisov 1980; T. Gillbro et al. 1988; T.P. Causgrove et al. 1992; P.I. van Noort et al. 1994). Decays of excited BChl *c*, *d*, and *e* were multiphasic, components of 30–160 ps being ascribed to energy transfer to the baseplate BChl *a*. Although it is generally believed that the FMO protein is an intermediate in the energy transfer pathway to the reaction center, this has never been proven, and in fact the available evidence (H. Kramer et al. 1996; C. Francke et al. 1996; S. Neerken et al. 1998; H. Oh-oka et al. 1998) all points to a low transfer efficiency from FMO to the reaction center.

Starting with the work of R. Pearlstein and R.P. Hemenger (1978) and based on the three-dimensional structure (R.E. Fenna and B.W. Matthews 1975; D.E. Tronrud et al. 1986), the excitonic properties of the FMO complex have been extensively studied over the years (R. Pearlstein 1992; X. Lu and R. Pearlstein 1993; D. Gülen 1996; R.J.W. Louwe et al. 1997; S.I.E. Vulto et al. 1998a, 1998b; T. Renger and V. May 1998; M. Wendling et al. 2000). These properties are now reasonably well understood on basis of the coordinates of the seven BChls *a* that make up one subunit of the FMO. It was shown that exciton coupling plays a significant role in determining the details of the optical spectrum. Transfer of excitation energy within the FMO was found to occur with time constants of typically 0.1–1 ps, even at low temperature.

C. Francke et al. (1997) have succeeded in preparing core reaction center (RCC) complexes that are completely free from chlorosomes and FMO. These particles contain 16 BChls *a* per reaction center. The pigments have considerable interaction with each other, and energy transfer was studied in the subpicosecond range (S. Neerken et al. 1998, 1999). Rapid equilibration within about 1–2 ps of the excitation energy among the BChl *a* molecules of the core complex was observed and a $\sim$25 ps component for photooxidation of the primary electron donor was measured at 275 K as well as at 10 K. Just as in purple bacteria, equilibration of the excitation energy within the antenna is much faster than trapping and therefore the 'diffusion' through the antenna does not limit the rate of energy conversion. Unfortunately, the present data do not give decisive evidence for one of the trapping mechanisms in the reaction center core complex of green sulfur bacteria. For the related antenna reaction center complex of heliobacteria, however, it was concluded that the trap-limited model, or a similar model, applies at 275 K (S. Lin et al. 1994; U. Liebl et al. 1996; S. Neerken et al. 2000). Analogy with the green sulfur bacteria would suggest the same mechanism in the two groups.

The past decades have shown a spectacular development in the crystallography of large protein structures. The structure of the FMO complex (R.E. Fenna and B.W. Matthews 1975; D.E. Tronrud et al. 1986) and of the reaction center of purple bacteria (J. Deisenhofer et al. 1984, 1995) have been known for some time now, but recent work has revealed the amazingly symmetric structure of the LH 2 antenna complex (G. McDermott et al. 1995; H. Koepke et al. 1996), and most recently the structures of the Photosystem II (A. Zouni et al. 2001) and Photosystem I (P. Jordan et al. 2001) complexes were reported with greatly enhanced resolution. These advances have shifted the focus of research in the field of energy transfer from a more or less phenomenological approach to a detailed molecular description of intermolecular interactions and energy relaxation, where the interaction strength can now be calculated from the structural data. Therefore, this field is still very active, and recent results (S.I.E. Vulto et al. 1998a; V. Sundström et al. 1999; H. van Amerongen et al. 2000; T. Renger et al. 2001) show that detailed pictures will emerge of the energy flow within and between photosynthetic pigment–protein complexes. The challenge will be to integrate this detailed information, mostly based on the structures of isolated systems, with the properties and organization of the photosynthetic membrane as a whole.

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