Biochimica et Biophysica Acta, 725 (1983) 492–507
Elsevier

BBA 41417

TRAPPING, LOSS AND ANNIHILATION OF EXCITATIONS IN A PHOTOSYNTHETIC SYSTEM

I. THEORETICAL ASPECTS

W.T.F. DEN HOLLANDER [a], J.G.C. BAKKER [b] and R. VAN GRONDELLE [b,c]

[a] *Instituut-Lorentz voor Theoretische Natuurkunde, Nieuwsteeg 18, 2311 SB Leiden,* [b] *Vakgroep Biofysica, Huygens Laboratorium, Postbus 9504, 2300 RA Leiden and* [c] *Vakgroep Biofysica, Natuurkundig Laboratorium der Vrije Universiteit, de Boelelaan 1081, 1081 HV Amsterdam (The Netherlands)*

(Received June 7th, 1983)

Key words: Picosecond pulse excitation; Random walk; Fluorescence; Reaction center; Photosynthesis

In this paper are discussed a few theoretical aspects of the transfer, trapping, loss and annihilation of excitations as they occur in a photosynthetic system after a picosecond light pulse. A random-walk model is introduced to describe the dynamical behavior of the excitations in a domain and is used to calculate the parameter that determines the shape of the total fluorescence yield vs. pulse intensity curve in the case in which the reaction centers are all in the closed state (Paillotin, G., Swenberg, C.E., Breton, J. and Geacintov, N.E. (1979) Biophys. J. 25, 513–533). It is shown that this parameter depends critically on the number, λ, of connected photosynthetic units in a domain. A master equation is postulated to describe the decay of the excitations in the case where the transition of the reaction center from the open to the closed state, induced by the capture of an excitation, is included. The trapping and loss of excitation in a mixture of open and closed reaction centers, generated in the course of the transfer process, is assumed to be described by an equation that is the equivalent for a single domain of the Vredenberg–Duysens relation (Vredenberg, W.J. and Duysens, L.N.M. (1963) Nature 197, 355–357). The master equation is used to find the total probability of loss per excitation, $U_\lambda(z)$, and the total fraction of reaction centers closed, $V_\lambda(z)$, as a function of the average number of excitations z created in a domain when the reaction centers are all in the open state before the pulse. It is shown that, for most photosynthetic systems, an increase of $U_\lambda(z)$ with z can occur only if $\lambda \leq 3$. It is further concluded that the combined measurement of $U_\lambda(z)$ and $V_\lambda(z)$ can give detailed information about λ and the parameters involved in the transfer process.

1. Introduction

In photosynthesis, the incident light excites the so-called antenna pigment molecules, e.g., phycobilin, carotenoid or (bacterio)chlorophyll, and the excitations are efficiently transferred to a group of special antenna molecules which absorb at low energy, such as Chl *a* in green plants and algae, absorbing at about 680 nm, or BChl *a*, absorbing around 880 nm in most purple bacteria (B880) [1–4]. The excitations are further transferred through the network formed by these special antenna molecules, until they either reach a reaction center and effective photochemistry is performed (charge separation) or are lost in the course of the transfer process due to fluorescence, triplet formation or internal conversion. The former event is usually referred to as 'trapping', the latter as 'loss'.

The study of energy transfer in photosynthesis, using the (bacterio)chlorophyll fluorescence yield as a monitor for the loss, has been a major theme of research since Duysens' early work [1,5]. Important questions have been, amongst others, the determination of the structure of the network of antenna molecules, the rates of energy transfer and loss on an antenna and the coupling of the reaction center to the antennae. It has been established that for most photosynthetic systems the network of antenna molecules is two-dimensional and the number of antenna molecules per reaction center lies between 40 and 400 [5,6].

The reaction centers can occur in a photochemically active (open) state or a photochemically inactive or less active (closed) state. The capture of an excitation by a reaction center induces its conversion from the open into the closed state, the latter being stable in most experiments. In photosynthetic systems, the fluorescence yield depends on the fraction of reaction centers in the open state. The study of this phenomenon, using low intensities of light, has been a widely applied experimental approach. In purple bacteria, for instance, a 3- to 4-fold increase in the B880 fluorescence yield is observed [7–9] if, by light, the reaction centers are converted into the closed state in which the primary electron donor, a special pair of BChl molecules [10], is oxidized [11]. Similarly, in Photosystem II of green plants the Chl *a* fluorescence yield increases 4- to 5-fold upon reduction of the quinone electron acceptor of the reaction center [12–14]. It was found by Vredenberg and Duysens [7] that in purple bacteria the total fluorescence yield, ϕ_f, depends on the fraction, $\bar{x}$, of closed reaction centers in the system through the relation:

$$\phi_f = \phi_f^o/(1 - p\bar{x}) \tag{1}$$

where ϕ_f^o is the total fluorescence yield observed with all the reaction centers in the open state and p is a constant that depends on the species [15]. From this relation they concluded that in purple bacteria several reaction centers share a common network of antenna molecules (the so-called 'lake model'). This conclusion was confirmed by Clayton [8,16] and later by Monger et al. [17], who studied the quenching of the fluorescence yield by carotenoid triplets, generated by a strong flash, in the purple bacterium *Rhodopseudomonas sphaeroides*. A similar conclusion was drawn for the antenna system of Photosystem II [11,15].

To explain the observed fluorescence data it has been suggested that the reaction center does not act as a perfect trap and that an excitation arriving at a reaction center has a quite large probability of escaping back into the surrounding antenna network and resuming its migration [6,15,18,19]. In the context of the lake model this assumption can explain the hyperbolic dependence of ϕ_f on $\bar{x}$ [15].

For most photosynthetic systems the energy transfer can be adequately described as a random (incoherent) hopping of the excitations through the network of antenna molecules [6]. A random-walk description of the energy transfer was used by Montroll [20,21] to study the average trapping time in a photosynthetic system. His results, in particular those for two dimensions, proved to give a successful description. Recently, Den Hollander and Kasteleyn [22] have extended the model developed by Montroll and calculated the trapping efficiency, introducing a finite probability of loss with each hop of the excitation and a finite probability of escape from a reaction center. A similar extension was given by Kenkre and Wong [23] in the context of a master equation approach (see also Ref. 24 and references mentioned therein).

In the last decade, measurement of fluorescence quenching due to biexcitation phenomena such as singlet–singlet annihilation [25], using high intensity picosecond laser pulses, has become a powerful experimental approach to study the structure and the function of the antenna system. So far, the experiments have suggested that the antenna molecules are arranged in domains of limited size, each of which contains several reaction centers with their associated antennae (photosynthetic units). Within a domain no barriers for energy transfer exist, whereas between the domains cross-over of the excitations is impossible or at least severely restricted. An important goal has been to establish the number of connected photosynthetic units forming a single domain and to determine the bi-excitation annihilation rate constant on an antenna.

Whereas the mono-excitation decay phenomena are easy to describe, the biexcitation decay phenomena are much more difficult to deal with. A rigorous treatment of the annihilation of several excitations in a domain has not yet been given and seems rather ambitious, even more so if trapping and loss are included. On the other hand, a variety of approximative descriptions have been presented [24]. In an extensive study, Paillotin et al. [26], extending earlier work by Mauzerall [27] and Swenberg et al. [28], have shown how the number of connected photosynthetic units can be estimated given the shape of the time-integrated fluorescence yield vs. pulse intensity curve. Their approach is based on the assumption that the energy transfer is sufficiently rapid, compared with the overall decay of the excitations, such that the excitation distribution in a domain is at all times close to random. The decay of the excitations is described by a Pauli master equation that includes both mono- and biexcitation decay terms. The reaction centers are assumed to be in a single fixed state, and therefore the theory is limited in that it describes only those experiments in which the reaction centers are either kept in the closed state, e.g., by applying continuous background illumination [29], or are altogether absent [30].

The outline of this paper is as follows. In section 2 we discuss the results of Paillotin et al. and make a few critical remarks. Using a random-walk description of the energy transfer, we calculate the overall mono- and biexcitation decay rate constants that enter into the master equation describing the decay of the excitations. These rate constants determine the shape of the total fluorescence yield vs. pulse intensity curve and we express them in terms of the rate constants associated with energy transfer, trapping, loss and annihilation on the antenna and of the size and structure of the domain. In the random-walk model, the domain is a simple square lattice and the reaction centers are traps that are arranged periodically in this lattice, so that it can be divided into identical unit cells, each of which contains one trap. The unit cell is to be compared with the photosynthetic unit. All domains are taken as identical. In section 3 we compare the results obtained from the random-walk model and the master equation with those of a Monte-Carlo simulation of the combined decay processes. In section 4 we extend the theory to incorporate the effect of the transition of the reaction center from the open to the closed state, which occurs upon the capture of an excitation. To that end we postulate a Pauli master equation that is an extension of the one used by Paillotin et al. including this transition, and we calculate the total fluorescence yield and the total fraction of reaction centers closed after the light pulse as a function of the pulse intensity. The overall mono- and biexcitation decay rate constants that enter into this master equation are again found from the random-walk model. Section 5 is devoted to a discussion.

This paper is concerned with a few theoretical aspects of energy transfer, loss, trapping and annihilation as it occurs in a photosynthetic system. In a subsequent paper [43], using the results presented here, we analyze and discuss a series of experiments performed with the purple bacteria *Rhodospirillum rubrum* and *Rhodopseudomonas capsulata.* These experiments lead to accurate estimates of the various parameters involved in the energy transfer process in these systems.

2. Trapping, loss and annihilation: a random-walk model

To describe the fluorescence yield of a photosynthetic system with closed reaction centers in a picosecond laser-pulse experiment as a function of the pulse intensity, Paillotin et al. [26] have proposed the following Pauli master equation for the decay of the excitations generated randomly in a domain:

$$\frac{\mathrm{d}p_{mi}(t)}{\mathrm{d}t} = \left\{\gamma_1(i+1)+\tfrac{1}{2}\gamma_2 i(i+1)\right\}p_{m\,i+1}(t) - \left\{\gamma_1 i+\tfrac{1}{2}\gamma_2 i(i-1)\right\}p_{mi}(t) \qquad (2)$$

with $p_{mi}(0)=\delta_{mi}$. Here $p_{mi}(t)$ is the probability that at time t there are i excitations present in the domain given that at $t=0$ there are m $(0 \leqslant i \leqslant m)$, γ_1 is the overall rate of decay due to loss and trapping for a single excitation in the domain and γ_2 is the overall rate of decay for a pair of excitations due to the annihilation which may occur upon their collision. (We mention and consider hereafter the case where only one of the excitations involved disappears.) Annihilation due to simultaneous collision of three or more excitations is neglected. From Eqn. 2 Paillotin et al. have derived the average total fluorescence yield, $\phi_f(z)$, as a function of the average number, z, of excitations generated in the domain. Using the fact that there are many domains in a photosynthetic system and that in an actual experiment the probability that a given domain has m excitations at $t = 0$ is given by a Poisson distribution (with parameter z), they find:

$$\phi_f(z) = \phi_f^c \left(1 + \sum_{k=1}^{\infty} \frac{1}{k+1} \frac{(-z)^k}{(r+1)\ldots(r+k)}\right) \tag{3}$$

where ϕ_f^c is the low-intensity total fluorescence yield observed with all the reaction centers in the closed state (note that the fluorescence represents a fixed fraction of the loss) and $r := 2\gamma_1/\gamma_2$.

In this description no specific assumptions are made concerning the size and the structure of the domain or the details of the decay processes on the antenna. It is, however, assumed that the excitation distribution may at all times be treated as random. As z is proportional to the pulse intensity, the parameter r in Eqn. 3 can be estimated from the shape of the measured ϕ_f vs. pulse intensity curve (in a semilogarithmic plot). From Eqn. 3 the value of z that corresponds to a given pulse intensity can then be found, which determines the number of antenna molecules in a domain. Following this approach Paillotin et al. were able to obtain a lower bound for the number of photosynthetic units in a domain of Photosystem II [26,29]. Similar results were obtained later by Van Grondelle et al. [30] for antenna pigment-protein complexes from several purple bacteria and realistic sizes were found for the various complexes used.

Using a random-walk description of the energy transfer, we shall derive an expression for r in terms of the rate constants of energy transfer, trapping loss and annihilation on the antenna and of the sizes of the domain and the photosynthetic unit. To do so we introduce a random-walk model that describes the dynamical behavior of the excitations in a domain. This model is as follows. The domain is represented by a square lattice, L_D, of $N_D = m_D^2$ lattice points and the reaction centers are represented by traps that are arranged periodically in L_D. For convenience we impose periodic boundary conditions on L_D. The domain is divided into identical unit cells L of $N = m^2$ lattice points with one trap each. The unit cell represents the photosynthetic unit. The excitations are walkers that perform a simple random walk on L_D, in which steps can take place to nearest-neighbor lattice points with probability $\frac{1}{4}$. Further, with each step there is a probability ε, independent of the walk performed, that a walker spontaneously disappears from the lattice. This represents the loss on the antenna. If a walker reaches a trap, there is a probability $1 - \eta_t$ that he is trapped and a probability η_t that he escapes and continues his random walk as prescribed. Finally, if two walkers meet on a lattice point there is a probability $1 - \eta_a$ that one of them annihilates the other and continues his random walk, and a probability η_a that both of them continue without annihilation.

The probabilities ε, η_t and η_a are determined by the rate constants on the antenna. If k_h, k_l, k_t and k_a are the rate constants for excitation transfer between two given neighboring antenna molecules, loss on an antenna molecule, trapping on a reaction center and annihilation in a collision of two excitations, respectively, then it follows that:

$$\varepsilon = \frac{k_l}{4k_h + k_l}, \quad 1 - \eta_t = \frac{k_t}{4k_h + k_l + k_t},$$

$$1 - \eta_a = \frac{k_a}{8k_h + 2k_l + k_a} \tag{4}$$

Using the random-walk model we shall now derive expressions for γ_1 and γ_2 in Eqn. 2 in terms of the rate constants on the antenna and the sizes of the domain and the photosynthetic unit. This will be done by making use of a result of Den Hollander and Kasteleyn [22].

2.1. γ_l

The mono-excitation decay rate constant γ_1 in Eqn. 2 is the overall rate of decay due to loss and trapping for a single excitation in a domain (where it is assumed that the excitation has a random initial position). We have:

$$\gamma_1 = k_l + \bar{k}_t \tag{5}$$

where $\bar{k}_t$ denotes the overall rate of trapping. To find $\bar{k}_t$ we consider the total probability, f_t, that the excitation is trapped, which is given by $f_t = \bar{k}_t/(k_l + \bar{k}_t)$. It follows that:

$$\bar{k}_t = k_l f_t/(1 - f_t) \tag{6}$$

and that we can write:

$$\gamma_1 = k_l/(1-f_t) \tag{7}$$

It therefore remains to find the probability f_t. Because L_D is a repeating structure of unit cells, we may consider the trapping and loss of the excitation on a single unit cell L only, with periodic boundary conditions. The probability f_t then follows from Ref. 22, where it is shown that:

$$f_t = \left\{ N(1-z)\left[G_N(0;z) + \frac{\eta_t}{1-\eta_t} \right] \right\}^{-1} \Bigg|_{z=1-\varepsilon} \tag{8}$$

with $G_N(0;z)$ the Green's function:

$$G_N(0;z) = N^{-1} \sum_{\theta} \left\{ 1 - \tfrac{1}{2} z (\cos\theta_1 + \cos\theta_2) \right\}^{-1}$$

$$=: \{ N(1-z) \}^{-1} + \phi_N(0;z) \tag{9}$$

where the summation runs over $\theta = 2\pi(j_1, j_2)/m$ with $j_i = 0, 1, \ldots, m-1$ $(i = 1, 2)$ and $\frac{1}{2}(\cos\theta_1 + \cos\theta_2)$ is the structure function of the simple random walk.

If $Nk_l \ll k_h$ we can use the following expansion derived in Ref. 22 (see also Ref. 20):

$$\phi_N(0;z) = \phi_N - \phi'_N(1-z) + \mathcal{O}\left(N^2(1-z)^2\right) \tag{10}$$

with:

$$\Phi_N = \pi^{-1} \log N + 0.195 + \mathcal{O}(1/N) \tag{11a}$$

$$\Phi'_N = 0.061N - (2\pi)^{-1} \log N - 0.13 + \mathcal{O}(1/N) \tag{11b}$$

To first order we have:

$$f_t \simeq \left\{ \frac{Nk_l}{4k_h} \left(\phi_N + \frac{4k_h}{k_t} \right) + 1 \right\}^{-1} \tag{12}$$

If $k_h \ll k_t$ and $N \gg 1$, this reduces to $f_t \simeq \{\pi^{-1}(k_l/4k_h) N \log N + 1\}^{-1}$, which is similar to an expression found by Pearlstein [31] and Knox [32]. If $k_t \ll k_h$, on the other hand, and N is not too large we have $f_t \simeq k_t/(Nk_l + k_t)$, which is the expression given by Duysens [15].

Thus, combining Eqns. 7–9, we have an expression for γ_1, the first rate constant in Eqn. 2.

2.2. γ_2

The biexcitation decay rate constant γ_2 in Eqn. 2 is the overall rate of decay due to annihilation for a pair of excitations in a domain (where it is assumed that the excitations have a random initial position). We write $\gamma_2 = \bar{k}_a$. To find this rate constant we consider a pair of excitations in a domain without traps. Let f_a be the probability that in this case annihilation takes place, which is given by $f_a = \bar{k}_a/(2k_l + \bar{k}_a)$. It follows that:

$$\tfrac{1}{2}\gamma_2 = k_l f_a/(1-f_a) \tag{13}$$

It thus remains to find f_a. We can use the results of Ref. 22 again by giving the following simple argument. Let the two excitations be denoted by A and B. Suppose that for each step that A makes we let B make one extra step and, for that extra step, keep A fixed. Because the simple random walk is symmetric this obviously makes no difference if B has a probability $1 - \varepsilon$ of surviving the extra steps. Moreover, the steps of B are well defined, the probability that B makes two steps at once being strictly zero. This excludes the possibility that B passes through A without interacting. The random walk that B now performs relative to A can be treated as if A were a fixed trap with escape probability η_a, except that it proceeds in time twice as quickly. Since we are interested in the total probability of annihilation only, we have:

$$f_a = \left\{ N_D(1-z)\left[G_{N_D}(0;z) + \frac{\eta_a}{1-\eta_a} \right] \right\}^{-1} \Bigg|_{z=1-\varepsilon} \tag{14}$$

an equation similar to Eqn. 8 with N, η_t replaced by N_D, η_a. (The simple argument which leads to this result may easily be more formalized [24].) Thus, combining Eqns. 9, 13 and 14, we have an expression for γ_2, the second rate constant in Eqn. (2).

Combining Eqns. 7–9, 13 and 14, we finally get the desired expression for r, the parameter in Eqn. 3:

$$r = \lambda \frac{\phi_{\lambda N}(0; 4k_h/(4k_h + k_l)) + (8k_h + 2k_l)/k_a}{\phi_N(0; 4k_h/(4k_h + k_l)) + (4k_h + k_l)/k_t}$$

$$\times\left(1+\frac{Nk_l}{4k_h+k_l}\left[\phi_N(0;4k_h/(4k_h+k_l))\right.\right.$$
$$\left.\left.+(4k_h+k_l)/k_t\right]\right) \qquad (15)$$

Here we have introduced the variable $\lambda := N_D/N$, which is the number of photosynthetic units in a domain. In Fig. 1 r is plotted as a function of λ for a few choices of the rate constants on the antenna and the size of the photosynthetic unit. Note that if $Nk_l \ll k_h \ll k_t$, k_a and N not too small, it follows from Eqns. 11a and 15 that $r \simeq \lambda \log \lambda N/\log N$. Note further that the estimate of r obtained from experiments can, with Eqn. 15, yield information about λ without knowledge of z. For instance Paillotin et al. found that for Photosystem II (for various temperatures) $r > 5$ [26]. With $N \approx 300$ and $k_t \lesssim 10^{12}$ s^{-1}, $k_l \lesssim 5\cdot10^8$ s^{-1}, $k_h \gtrsim 10^{12}$ s^{-1}, $k_a \gtrsim 10^2 k_h$ [6,15] this leads to the estimate $\lambda \gtrsim 10$.

Before we conclude this section, we discuss in some detail the assumptions underlying Eqn. 2. This seems appropriate in view of the complexity of the combined decay problem and the need for approximations.

Because of the trapping and annihilation of excitations that takes place in the domain, the excitation distribution, though initially random, is in general not random at positive times. This fact is neglected in Eqn. 2. Paillotin et al. have called this the 'random approximation'. They have indicated that if the transfer of excitations is much faster than their decay, such that the average diffusion length of an excitation is much larger than the average distance between excitations, this approximation makes sense. It may be expected that then after each decay event the spatial arrangement of excitations is sufficiently randomized long before another excitation decays and that the excitation distribution is at all times close to random. We wish to point out, however, that the random approximation also makes sense under much weaker conditions. The reason for this is simple. If indeed the average diffusion length of an excitation is large compared with the average distance between excitations, then not only may it be expected that the excitation distribution is close to random, but also that the decay of excitations at a given instant is to a large extent independent of the excitation distribution as it is present in the domain at that time. If this is the case, the requirement proposed by Paillotin et al. is too strong and there exist conditions under which the excitation distribution is not close to random, but may nevertheless be effectively treated as so. This is important since, due to the presence of traps in the domain, diffusion of excitations is severely limited.

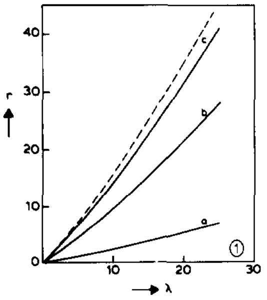


Fig. 1. Plot of r as a function of λ for $N = 7\times7$, $k_h = 2\cdot10^3 k_l$, $k_a = 10^6 k_l$ and (a) $k_t = 10^3 k_l$, (b) $k_t = 10^4 k_l$, (c) $k_t = 10^5 k_l$. The dashed line is the function $r = \lambda \log \lambda N/\log N$.

To illustrate this argument we return to the random-walk model used to describe the dynamical behavior of the excitations in a domain. Consider the simple random walk performed by an excitation on the lattice L_D. Suppose that both the loss on the antenna and the annihilation are excluded and consider the average number of steps of the excitation before it is trapped, as a function of the position of the lattice point it starts from. Rosenstock and Marquardt [33] have shown that, except for lattice points that are close to a trap, this average is nearly the same for all lattice points provided that N, the number of lattice points per trap, is large. A more-or-less equal conclusion was drawn by Knox [6] from Monte-Carlo simulations. In Ref. 22 it is shown that the mean number of steps averaged over all lattice points is equal to $N(\phi_N + \eta_t/(1-\eta_t))$. If $N \lesssim 400$ and $k_t \gtrsim 2k_h$, it follows from Eqns. 4 and 11a that this average is less than approx. $4N = (2m)^2$ and therefore that the average diffusion length of the excitation is of the order of the distance between two traps. Clearly, if the loss on the antenna and the annihilation are included, the average diffusion length will be even smaller. Thus, we see that, at least in the random-walk model, the condition proposed by Paillotin et al. is in general not satisfied, even if the domain consists of a few photosynthetic units only. On the other hand, if N is large, the probability that an excitation is close to a trap is at all times small, and so it may be expected that for example the rate of trapping is to a large extent independent of the excitation distribution as it evolves in time.

It is hard to give the precise conditions under which the random approximation makes sense (let alone to establish these by a rigorous proof). It should nevertheless be clear from the argument given that it does make sense if both the density of the excitations and the density of the reaction centers in the domain are small.

Another approximation in Eqn. 2 is that the overall rates of trapping and loss and the overall rate of annihilation for i excitations in a domain are given by $\gamma_1 i$ and $\frac{1}{2}\gamma_2 i(i-1)$, respectively. It is, however, not at all obvious that the trapping and annihilation of excitations, which are diffusion-limited processes, proceed exponentially in time, i.e., that they can be properly described by rate constants. They may very well not (the reader is referred to Refs. 24 and 34). We, therefore, propose to interpret γ_1 and γ_2 as effective rate constants and to apply Eqn. 2 accordingly, restricting ourselves to time-integrated results only. The derivation of γ_1 and γ_2 given in this section reflects this interpretation.

3. Monte-Carlo simulations

To test the results obtained in section 2 from the random-walk model and the master equation, we have done a computer simulation. First we considered random walks of one or two excitations in the domain with or without traps, then random walks of many excitations subject to trapping, loss and annihilation. The random-walk simulation was performed either with the square lattice L_D with N_D lattice points, that represents the domain, or with one of its unit cells L with N lattice points, that represents the photosynthetic unit. Periodic boundary conditions were imposed on both. In the computer simulation each excitation was generated at a random position and was made to perform a simple random walk on the lattice according to the prescriptions outlined in section 2. The probabilities ε, η_t and η_a were chosen according to Eqn. 4.

The results of the simulation are listed in Table I for $N_D = 28 \times 28$, $N = 7 \times 7$ ($\lambda = 16$) and the following choices of the rate constants on the antenna: $k_l = 5 \cdot 10^8$ s^{-1}, $k_t = 10^{11}$ s^{-1}, $k_a = 2 \cdot 10^{13}$ s^{-1} and several values of k_h ranging from $k_h = 10^{10}$ s^{-1} to 10^{13} s^{-1}. Columns 1 and 3 give the results for the total probability of trapping f_t for one excitation with traps and for the total probability of annihilation f_a for two excitations without traps, respectively. These are compared with the exact values, found from Eqns. 8 and 14, that are listed in columns 2 and 4. It is seen that an excellent agreement exists between theory and simulation in both cases. Columns 5 and 6 display the results for the total probability of annihilation $\gamma_2/(2\gamma_1 + \gamma_2)$ for two excitations with traps, compared with the value found from Eqns. 7 and 13. Finally, columns 7 and 8 give the total probability of loss per excitation for several excitations with traps. Here a varying number of excitations was generated on L_D and the total probability of loss was calculated for each number. Then Poisson statistics were used to obtain the result for an average of $z = 16$ excitations, i.e., one per unit cell. The results are compared with those found from Eqns. 3, 9 and 15. The once again excellent agreement between theory and simulation in all cases

TABLE I

Comparison between computer simulation (odd columns) and theory (even columns) for $N_D = 28 \times 28$, $N = 7 \times 7$ ($\lambda = 16$), $k_t = 2 \cdot 10^2 k_l$, $k_a = 4 \cdot 10^4 k_l$ and (a) $k_h = 2 \cdot 10^1 k_l$, (b) $k_h = 2 \cdot 10^2 k_l$, (c) $k_h = 2 \cdot 10^3 k_l$, (d) $k_h = 2 \cdot 10^4 k_l$. The columns are explained in the text. For each set of parameters $4 \cdot 10^4$ simulations were performed.

	f_t		f_a		$\gamma_2/(2\gamma_1+\gamma_2)$		ϕ_l ($z = 16$)	
a	0.473	0.477	0.049	0.050	0.028	0.027	0.427	0.434
b	0.750	0.751	0.305	0.307	0.103	0.100	0.141	0.147
c	0.797	0.798	0.790	0.790	0.427	0.432	0.048	0.049
d	0.802	0.803	0.941	0.942	0.758	0.762		

considered supports the assumption, formulated in section 2, that Eqn. 2 leads to a correct description of the time-integrated fractions of excitations that are lost, trapped or annihilated, under quite general conditions. We shall therefore continue, and use a similar type of approximate description in the case where we have a mixture of open and closed traps.

4. Trapping, loss and annihilation: inclusion of the transition of the reaction centers

In this section we extend the results obtained in section 2 to include into the description of the combined decay processes the transition of the reaction center from the open to the closed state (i.e., from an active to a less active state), which occurs upon the capture of an excitation. To do so we shall postulate a Pauli master equation that is an extension of Eqn. 2 including this transition. Besides the fact that the thus extended master equation gives a more complete description of the decay of the excitations in a photosynthetic system as it occurs in some experiments, there is at least one other important reason why it is interesting to include the transition of the reaction center. In the previous sections, where we have treated the reaction centers as being in a single fixed state, we have shown that the annihilation between excitations provides a means of determining the number λ of photosynthetic units in a single domain. The reason for this is that the overall rate of annihilation depends on the size of the domain and so does the parameter r in Eqn. 3. If we include the transition of the reaction center we may hope to have a more critical means to determine λ, because also the rate at which the reaction centers are closed depends on the size of the domain. This is important since, as has been pointed out by Paillotin et al. [26], the curves given by Eqn. 3 for different values of r have a nearly identical shape for $r > 5$. Consequently, the value of r cannot always be determined accurately from experiment and in many cases only a lower bound for λ can be obtained. An additional advantage of the inclusion of the transition is that we can calculate the total fraction of reaction centers closed after the pulse, a quantity which is experimentally accessible.

We return to the random-walk model introduced in section 2 and consider the lattice L_D with traps that represents the domain. Now suppose that the traps can occur in two different states, open and closed, with trapping rate constants k_t^o and k_t^c, respectively. Upon capturing an excitation, an open trap changes into a closed trap, whereas a closed trap remains closed. The model is otherwise unchanged. We define the corresponding effective overall trapping rate constants, $\bar{k}_t^o$ and $\bar{k}_t^c$, as in Eqn. 6, together with Eqns. 4 and 8, with k_t replaced by k_t^o and k_t^c. These represent the effective overall rates of trapping for a single excitation in a domain with the traps either all open or all closed.

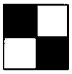
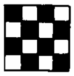
Initially all the traps are in the open state. After the light pulse, in the course of time, traps in the domain are converted into the closed state and mixtures of open and closed traps are generated. The overall rate of trapping of an excitation at a given instant depends on the fractions of open and closed traps present in the domain as well as on the arrangement of the two types of trap in the mixture. By the latter we mean the way in which the two states are arranged on the periodic sublattice of trapping points. In the following we shall make the assumption that the mixtures of open and closed traps are randomly generated. More precisely, we shall make the assumption that, given a mixture of traps, the trap that is closed next is 'selected' randomly from the remaining open traps. This is, of course, an approximation. However, if both the density of excitations and the density of traps in the domain are small we may, for reasons similar to the ones discussed in section 2 with respect to Eqn. 2, expect that this is sensible. In fact, we may expect that in this case the overall rate of trapping is to a large extent independent of the arrangement of the two types of trap in the mixture and that the approximation is harmless. Then, as a simple argument shows, the overall rate of trapping in a domain with a given fraction x of closed traps is an average over the arrangements of the two types of trap. Let $\bar{k}_t(x)$ denote this average. We write $\bar{k}_t(x) := \bar{k}_t^o(x) + \bar{k}_t^c(x)$, where $\bar{k}_t^o(x)$ and $\bar{k}_t^c(x)$ represent the contributions to $\bar{k}_t(x)$ by open and closed traps, respectively. Next, we take:

$$\bar{k}_t^o(x) = (1-x)\bar{k}_t^o \tag{16a}$$

$$\bar{k}_t^c(x) = x\bar{k}_t^c \tag{16b}$$

TABLE II

Computer simulation of a random walk of a single excitation performed to obtain the overall rate of trapping for $N = 7 \times 7$, $\lambda = 16$, $x = \frac{1}{2}$, $k_t^o = 8 \cdot 10^2 k_l$, $k_t^c = 2 \cdot 10^2 k_l$, (a) $k_h = 2 \cdot 10^1 k_l$, (b) $k_h = 2 \cdot 10^2 k_l$, (c) $k_h = 2 \cdot 10^3 k_l$ and several arrangements of open and closed traps. A diagram on top of a pair of columns indicates the arrangement chosen. Listed are the total probability of trapping by open traps (odd columns) and by both open and closed traps (even columns). These are compared in the last two columns with the theoretical average values $f_t^o(\frac{1}{2}) = \bar{k}_t^o(\frac{1}{2})/(k_l + \bar{k}_t(\frac{1}{2}))$ and $f_t(\frac{1}{2}) = \bar{k}_t(\frac{1}{2})/(k_l + \bar{k}_t(\frac{1}{2}))$, which follow from Eqn. 16. For each set of parameters and each arrangement $6 \cdot 10^4$ simulations were performed.

									$f_t^o(\frac{1}{2})$	$f_t(\frac{1}{2})$
a	0.260	0.497	0.267	0.501	0.268	0.501	0.268	0.505	0.273	0.501
b	0.525	0.824	0.541	0.826	0.546	0.826	0.558	0.828	0.573	0.830
c	0.692	0.897	0.698	0.900	0.697	0.900	0.704	0.903	0.706	0.901

or:

$$\bar{k}_t(x) = (1 - x)\bar{k}_t^o + x\bar{k}_t^c \tag{16c}$$

This is another approximation.

Because in the following Eqn. 16 is of vital importance, we shall first discuss some additional arguments in favor of it. First of all, for $\lambda = 1$ Eqn. 16 is obviously ocrrect as x can take the values 0 and 1 only. Furthermore, in Ref. 22 the total probability of trapping for a single excitation is solved for an arbitrary periodic mixture of traps. By making various choices for the unit cell of the periodic pattern, which now is chosen to represent the domain, one can calculate the function $\bar{k}_t(x)$ and assess the validity of Eqn. 16. This is easy to do for small values of λ. For $N = 7 \times 7$, $\lambda = 4$, $x = \frac{1}{2}$, $k_l = 5 \cdot 10^8$ s^{-1}, $k_t^o = 4 \cdot 10^{11}$ s^{-1}, $k_t^c = 10^{11}$ s^{-1} and k_h ranging from $k_h = 10^{10}$ to 10^{13} s^{-1} we find that Eqn. 16 is in error by less than 1%. For intermediate values of λ we have done a computer simulation for several mixtures of open and closed traps and found that the overall rates of trapping that correspond to different mixtures are all within less than 10% equal to the value given by Eqn. 16. For most of the mixtures the agreement is better than 2%. A few results are given in Table II. Finally, for large values of λ Eqn. 16c can be seen to be correct because it leads directly to Eqn. 1, the Vredenberg–Duysens relation. Indeed, from Eqn. 16c it follows that the total probability of loss, $\phi_l(x) = k_l/(k_l + \bar{k}_t(x))$, for a single excitation in a domain depends on x through the relation:

$$\phi_l(x) = \phi_l^o/(1 - px) \tag{17a}$$

with:

$$p = \frac{\bar{k}_t^o - \bar{k}_t^c}{\bar{k}_t^o + k_l} \tag{17b}$$

and $\phi_l^o = k_l/(k_l + \bar{k}_t^o)$. This equation is the equivalent of Eqn. 1 for a single domain, where x, the fraction of closed traps in the domain, replaces $\bar{x}$, the macroscopic fraction of closed traps in the photosynthetic system, i.e., the average of x over all the domains. Since for systems of which the domains have a large number of traps most domains have an equal fraction of traps closed after a light pulse (this is an immediate consequence of the so-called weak law of large numbers, see Ref. 35 and especially pp. 183, 202 and 210, problems 6 and 7), it follows that Eqns. 1 and 17a are equivalent (apart from a trivial factor that gives the fraction of loss that consists of fluorescence). The validity of Eqn. 1 has been established for a number of intact photosynthetic systems. In fact, as stated in the introduction, from Eqn. 1 it was originally concluded that in intact photosynthetic systems the reaction centers share a large common network of antenna chlorophyll molecules [7–9]. The value of p can be found immediately from experiment. It is important to note that p is determined entirely by the parameters of the photosynthetic unit and does not depend on λ. If k_t^o, $k_t^c \ll k_h$ we have, by Eqns. 6 and 8, $\bar{k}_t^o \simeq k_t^o/N$ and $\bar{k}_t^c \simeq k_t^c/N$ and Eqn. 17b reduces to $p \simeq (k_t^o - k_t^c)/(k_t^o + N k_l)$, which is the expression proposed by Duysens [15]. Eqn. 16 is exact in this limit (cf. also Ref. 22).

Having thus motivated Eqn. 16 – and it is particularly important to note that it holds for all values of λ – we turn to the central issue of this section and introduce a Pauli master equation that describes the trapping, loss and annihilation of excitations in a domain with the transition from open to closed traps included. Let $p_{mnij}(t)$ be the probability that at time t there are i excitations and j open traps in the domain, given that at $t = 0$ there are m excitations and n open traps to start with $(0 \leqslant i \leqslant m,\ 0 \leqslant j \leqslant n \leqslant \lambda)$. We postulate that these probabilities satisfy the equation:

$$\begin{aligned}\frac{\mathrm{d}p_{mnij}(t)}{\mathrm{d}t} = {} & \left\{(i+1)\bar{k}_t^o \frac{j+1}{\lambda}\right\} p_{mn\,i+1\,j+1}(t) \\ & + \left\{(i+1)k_l + (i+1)\bar{k}_t^c\left(1 - \frac{j}{\lambda}\right)\right. \\ & \left. + \tfrac{1}{2}\bar{k}_a i(i+1)\right\} p_{mn\,i+1\,j}(t) \\ & - \left\{ik_l + i\bar{k}_t^o \frac{j}{\lambda} + i\bar{k}_t^c\left(1 - \frac{j}{\lambda}\right)\right. \\ & \left. + \tfrac{1}{2}\bar{k}_a i(i-1)\right\} p_{mnij}(t) \end{aligned} \tag{18}$$

with $p_{mnij}(0) = \delta_{mi}\delta_{nj}$. The various terms in Eqn. 18 are easily understood by inspection. We merely remark that, to make the correct distinction between open and closed traps, we have used Eqn. 16a and 16b. Eqn. 18 is an extension of Eqn. 2 and in writing it down we must, of course, assume that the conditions for its approximate validity are fulfilled (see section 2), in other words, we again require that the densities of the excitations and the reaction centers in a domain are sufficiently small.

We have used Eqn. 18 to calculate the average total probability of loss per excitation, $U_n(z)$, and the average total fraction of traps closed, $V_n(z)$, as functions of z, the average number of excitations generated in the domain (with m given by a Poisson distribution with parameter z), and of n, the number of open traps at $t = 0$. The derivation is given in the Appendix. We present the results here.

For the limiting case $k_a = 0$, i.e., with the annihilation between excitations excluded, we find:

$$U_n(z) = \phi_l^c\left(1 - \frac{\mu}{z} f_n\left(\frac{z}{\mu}, \nu\right)\right) \tag{19a}$$

$$V_n(z) = \frac{1}{\lambda} f_n\left(\frac{z}{\mu}, \nu\right) \tag{19b}$$

with $\mu := (\bar{k}_t^o - \bar{k}_t^c)/\bar{k}_t^o$, $\nu := (\bar{k}_t^o - \bar{k}_t^c)/\lambda(k_l + \bar{k}_t^c)$, $\phi_l^c := k_l/(k_l + \bar{k}_t^c)$ (which is the total probability of loss for a single excitation with all the traps closed) and:

$$\begin{aligned} f_n\left(\frac{z}{\mu}, \nu\right) := {} & \sum_{k=1}^{n} \binom{n}{k} (-\nu k)^{k-1} (1 + \nu k)^{n-k} \\ & \times \left\{1 - \exp\left(-\frac{\nu k}{1 + \nu k}\frac{z}{\mu}\right)\right\} \end{aligned} \tag{19c}$$

If initially all the traps are in the open state we take $n = \lambda$. It is easily shown (see the Appendix) that if $k_t^o > k_t^c$ and $k_l > 0$, both $U_\lambda(z)$ and $V_\lambda(z)$ are monotonically increasing functions of z. Furthermore, $V_\lambda(z)$ is concave, whereas $U_\lambda(z)$ is concave if and only if $2p^2 > \lambda(3p - 1)$, where p is given by Eqn. 17b. The latter implies that $U_\lambda(z)$ is

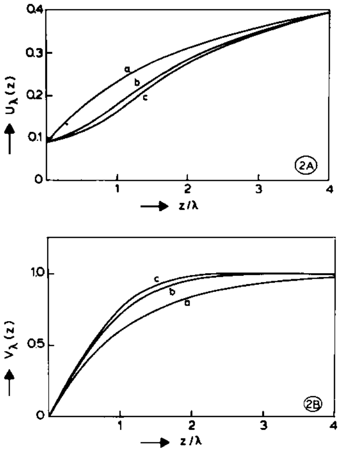


Fig. 2. Plot of (A) $U_\lambda(z)$ and (B) $V_\lambda(z)$ as a function of z/λ for $k_a = 0$, $\bar{k}_t^o = 10k_l$, $\bar{k}_t^c = k_l$ and (a) $\lambda = 1$, (b) $\lambda = 4$, (c) $\lambda = 10$.

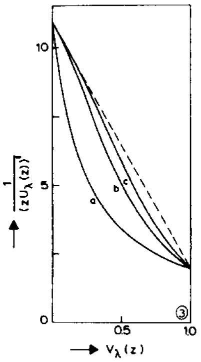


Fig. 3. Sketch of $1/(zU_\lambda(z))'$ vs. $V_\lambda(z)$ for $k_a = 0$, $\bar{k}_t^o = 10k_l$, $\bar{k}_t^c = k_l$ and (a) $\lambda = 1$, (b) $\lambda = 4$, (c) $\lambda = 10$. The dashed line is the theoretical asymptote for $\lambda \to \infty$.

concave if $p \leqslant \frac{1}{3}$ and not concave if $p \geqslant \frac{1}{2}$ (note that $p \leqslant 1$), irrespective of λ. Thus, one should be careful to draw conclusions about λ from the concavity of the experimentally observed total fluorescence yield vs. pulse intensity curve. The limiting behavior of $U_\lambda(z)$ and $V_\lambda(z)$ for $z \rightarrow 0$ and $z \rightarrow \infty$ can be found by using the two identities, for all ν:

$$\sum_{k=1}^{n} \binom{n}{k} (-\nu k)^{k} (1+\nu k)^{n-k-1} = \frac{-n\nu}{1+n\nu}$$

and:

$$\sum_{k=1}^{n} \binom{n}{k} (-\nu k)^{k-1} (1+\nu k)^{n-k} = n$$

It follows that $U_\lambda(z) \simeq \phi_1^{\mathrm{o}}$, $V_\lambda(z) \simeq (1-\phi_1^{\mathrm{o}})z/\lambda$, $z \rightarrow 0$ and $U_\lambda(z) \simeq \phi_1^{\mathrm{c}}(1-(\mu\lambda/z))$, $V_\lambda(z) \simeq 1$, $z \rightarrow \infty$. In Fig. 2 $U_\lambda(z)$ and $V_\lambda(z)$ are plotted for a few values of λ and a particular choice of the parameters $\bar{k}_{\mathrm{t}}^{\mathrm{o}}$ and $\bar{k}_{\mathrm{t}}^{\mathrm{c}}$. It is seen that both functions depend sensitively on λ. In Fig. 3, the inverse of $(zU_\lambda(z))'$ is plotted vs. $V_\lambda(z)$. As λ increases the curves tend to converge to a straight line with slope $1/\phi_1^{\mathrm{c}} - 1/\phi_1^{\mathrm{o}}$. This supports the equivalence of Eqns. 1 and 16c for large domains. It is further interesting to note that there exists the relation:

$$U_\lambda(z) = \phi_1^{\mathrm{c}}\left(1 - \frac{\mu\lambda}{z} V_\lambda(z)\right) \tag{20}$$

(which also follows directly from Eqn. 18).

Next we turn to the case $k_{\mathrm{a}} > 0$. For this case we find that $U_n(z)$ and $V_n(z)$ are given by:

$$U_n(z) = \phi_n \sum_{k=1}^{\infty} \frac{(-z)^{k-1} u_{nk}}{k!} \tag{21a}$$

$$V_n(z) = \psi_n \sum_{k=1}^{\infty} \frac{(-z)^{k-1} z v_{nk}}{k!} \tag{21b}$$

with $\phi_{\mathrm{n}} := k_1/(k_1 + \bar{k}_{\mathrm{t}}(1-n/\lambda))$, $\Psi_{\mathrm{n}} := \bar{k}_{\mathrm{t}}^{\mathrm{o}}/\lambda^2(k_1 + \bar{k}_{\mathrm{t}}(1-n/\lambda))$ and the coefficients u_{nk} satisfying the recurrence relation:

$$u_{n\,k+1} = \frac{k+\alpha_n}{k+\beta_n} u_{nk} - \frac{\alpha_n \beta_n}{\beta_{n-1}(k+\beta_n)} u_{n-1\,k}, \quad k \geqslant 1 \tag{22}$$

with $u_{\mathrm{n1}} = 1$ and with $\alpha_n := 2n\bar{k}_{\mathrm{t}}^{\mathrm{o}}/\lambda\bar{k}_{\mathrm{a}}$, $\beta_n := 2(k_1$

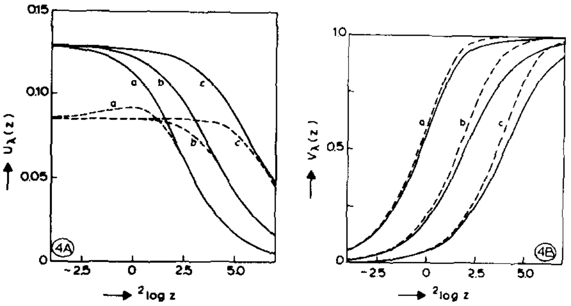


Fig. 4. Plot of (A) $U_\lambda(z)$ and (B) $V_\lambda(z)$ as a function of $^2\log z$ for $N = 7 \times 7$, $k_{\mathrm{h}} = 2 \cdot 10^2 k_1$, (———) $k_{\mathrm{t}}^{\mathrm{o}} = 8 \cdot 10^2 k_1$ and (------) $k_{\mathrm{t}}^{\mathrm{o}} = 8 \cdot 10^3 k_1$, $k_{\mathrm{t}}^{\mathrm{c}} = 2 \cdot 10^2 k_1$, $k_{\mathrm{a}} = 4 \cdot 10^4 k_1$ and (a) $\lambda = 1$, (b) $\lambda = 4$, (c) $\lambda = 16$.

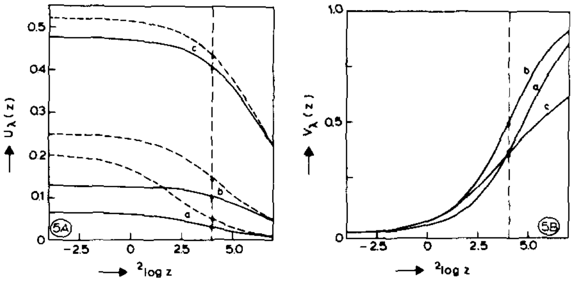


Fig. 5. Plot of (A) $U_\lambda(z)$ and (B) $V_\lambda(z)$ as a function of $^2\log z$ for $N = 7 \times 7$, $\lambda = 16$, $k_{\mathrm{t}}^{\mathrm{o}} = 8 \cdot 10^2 k_1$, $k_{\mathrm{t}}^{\mathrm{c}} = 2 \cdot 10^2 k_1$, $k_{\mathrm{a}} = 4 \cdot 10^4 k_1$ and (a) $k_{\mathrm{h}} = 2 \cdot 10^1 k_1$, (b) $k_{\mathrm{h}} = 2 \cdot 10^2 k_1$, (c) $k_{\mathrm{h}} = 2 \cdot 10^3 k_1$. The dots are the results of a Monte-Carlo simulation for $z = 16$ (see section Monte-Carlo simulation). In (A) the dashed lines represent the function $U_0(z)$, the average total probability of loss per excitation in case initially the reaction centers are all closed.

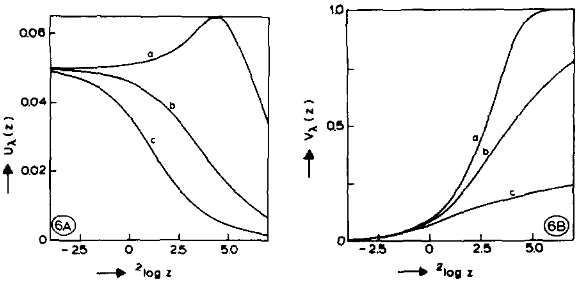


Fig. 6. Plot of (A) $U_\lambda(z)$ and (B) $V_\lambda(z)$ as a function of $^2\log z$ for $\lambda = 10$, $\bar{k}_{\mathrm{t}}^{\mathrm{o}} = 19 k_1$, $\bar{k}_{\mathrm{t}}^{\mathrm{c}} = 5.2 k_1$ and (a) $\bar{k}_{\mathrm{a}} = 1.14 k_1$, (b) $\bar{k}_{\mathrm{a}} = 1.14 \cdot 10^1 k_1$, (c) $\bar{k}_{\mathrm{a}} = 1.14 \cdot 10^2 k_1$.

$+ \bar{k}_t(1 - n/\lambda))/\bar{k}_a$ (for $n = 0$ the second term is to be omitted); the coefficients v_{nk} satisfy an identical recurrence relation, but with $v_{n1} = n$. Thus, the functions $U_n(z)$ and $V_n(z)$ follow recursively for $n = 1,\ldots,\lambda$. We have been unable to find expressions in closed form for $U_\lambda(z)$ and $V_\lambda(z)$. The recurrence relations are, however, easily programmed into a computer to find accurate numerical estimates for $U_\lambda(z)$ and $V_\lambda(z)$, provided that λ and z are not too large. Figs. 4–6 display the dependence of the functions $U_\lambda(z)$ and $V_\lambda(z)$ on λ, k_h and k_a, respectively (for Fig. 4 two values of k_t^o are chosen). In addition, the results of a Monte-Carlo simulation of the combined decay processes, including the transition of the reaction center, are shown in Fig. 5 for $z = 16$ (see section 3).

From the numerical results we draw the following conclusions. First we observe that for very small values of λ (and k_t not too small) $U_\lambda(z)$ shows a characteristic maximum for small z, whereas for larger values it is monotonic. From Eqns. 21 and 22 it follows that $U_\lambda'(0) > 0$ if and only if $\alpha_\lambda > \beta_{\lambda-1}/(\beta_\lambda - \beta_{\lambda-1})$ or $2\bar{k}_t^o/\bar{k}_a > \lambda(k_l + \bar{k}_t^o)/(\bar{k}_t^o - \bar{k}_t^c) - 1$. If $Nk_l \ll k_h \ll k_t^o$, k_a, and for N not too small, we have, by Eqns. 6 and 13, $2\bar{k}_t^o/\bar{k}_a \simeq \lambda \log \lambda N/\log N$. For $\lambda \ll N$ this is close to λ and if $\bar{k}_t^o > \bar{k}_t^c$ it follows that the maximum occurs only if:

$$\lambda \lesssim p/(1 - p) \tag{23}$$

where we have used Eqn. 17b. Note that p does not depend on λ. Thus, for each set of parameters $k_l > 0$, $k_t^o > k_t^c \geqslant 0$ $(0 < p < 1)$ we have an upper bound for λ, beyond which no maximum is possible. The experimental value of p found from Eqn. 1 for a number of photosynthetic systems is about 0.75 [15], so that $\lambda \lesssim 3$ is required. This is presumably too small for a system for which Eqn. 1 is found to hold. If the open reaction centers are weak traps even smaller values of λ are required, whereas if they are very weak traps the maximum cannot occur at all. A maximum for $U_\lambda(z)$ may be observed for larger values of λ, but only if k_a is small [36].

Next we observe that the functions $U_\lambda(z)$ and $V_\lambda(z)$ both vary strongly with λ, k_h and k_a. The balance between trapping, loss and annihilation depends on all the parameters involved. For example, in Fig. 4 it may be observed that for small λ, the number of excitations per reaction center, z/λ, required to close about 90% of the traps is relatively small, whereas for larger λ it is considerable. Furthermore, in Fig. 5 it may be observed that for large values of k_h trapping is very efficient at low intensities and that at high intensities annihilation takes over, resulting in a rather marked dependence of $U_\lambda(z)$ and $V_\lambda(z)$ on z. This in contrast to smaller values of k_h, where much higher intensities are required to shift the balance in favor of annihilation. The 'balance effects' at different pulse intensities are the main reason why measurements of the fluorescence yield and the fraction of traps closed after a light pulse provide a useful tool to study the parameters that are involved in the energy transfer process in a photosynthetic system.

5. Discussion

In this paper we have discussed a few theoretical aspects of trapping, loss and annihilation of excitations as it occurs in a photosynthetic system after an intense picosecond laser pulse. The approach that we have followed to study the total fluorescence yield and the total fraction of reaction centers closed, as a function of the pulse intensity, is based on a Pauli master equation, which describes the decay of the excitations in a domain, and a random-walk model, which describes the dynamical behavior of the excitations. Using the random-walk model we have expressed the overall mono- and biexcitation decay rate constants that enter into the master equation in terms of the rate constants on the antenna.

We have made a number of approximations. These are all related to the degree of randomness of the excitation distribution between successive decay events and the effect that a lack of such randomness has on the decay processes as they evolve in time. Although we have not been able to formulate the exact conditions under which the master equation may be applied, it should be clear from the analysis given that the theory is correct under quite general conditions, provided that the densities of the excitations and the reaction centers in a domain are small. Monte-Carlo simulations support this conclusion and have made it clear that accurate results can be obtained up to relatively large densities. Nevertheless, it would be nice if this could be made into a more precise statement and if a proof could be given for the correctness of some of the most essential approximations made.

At several points the theory is susceptible to refinement. For instance, the trapping of an excitation may proceed via one or more intermediate steps [37,38], each requiring a certain amount of time, or the formation of quenching triplet states at high pulse intensity may not be negligible [17,39,40]. Such additional complications could be accommodated for in Eqns. 2 and 18. Furthermore, in the random-walk model the excitations and the traps are treated as 'point-like objects', that interact on a single lattice point only, and the transfer of excitations is restricted to nearest-neighbor antenna molecules. This is, of course, an idealization. More realistic cases may be investigated. It should be emphasized that the choice of a more sophisticated random-walk model has nothing to do with the master equation. It manifests itself only in the rate constants $\bar{k}_{\rm t}^{\rm o}$, $\bar{k}_{\rm t}^{\rm c}$ and $\bar{k}_{\rm a}$, etc., and Eqns. 2 and 18 are formally not affected.

The latter is true also for Eqn. 20. If in an experiment, instead of a picosecond laser pulse, a light pulse of microsecond duration is used, the average time between the creation of excitations in a domain is much larger than the average decay time of an excitation, even at high pulse intensity, and the annihilation can be neglected. It is easily shown that in this case the results for $k_{\rm a}=0$ derived in section 4 may be used. The parameters $\phi_{\rm l}^{\rm c}$ and $\mu=(\phi_{\rm l}^{\rm c}-\phi_{\rm l}^{\rm o})/\phi_{\rm l}^{\rm c}(1-\phi_{\rm l}^{\rm o})$ in Eqn. 20 follow straight from experiment (as does the fraction of loss that consists of fluorescence [41,42]). From a comparison of the measured total fluorescence yield and the total fraction of traps closed as a function of the pulse intensity the number of antenna molecules per reaction center, N, can then be found. The parameter ν in Eqn. 19 is equal to $(\phi_{\rm l}^{\rm c}-\phi_{\rm l}^{\rm o})/\lambda\phi_{\rm l}^{\rm o}$, so that λ also follows from the measurements. Thus, both N and λ can in principle be obtained without reference to a specific random-walk model. In a picosecond laser-pulse experiment, on the other hand, the annihilation is always present and competes with the closing of the traps. This allows, in general, for a more critical determination of N and λ. In addition, $\bar{k}_{\rm a}$ can be obtained. In this case, however, we have not found a simple relation between $U_\lambda(z)$ and $V_\lambda(z)$.

Once $\bar{k}_{\rm t}^{\rm o}$, $\bar{k}_{\rm t}^{\rm c}$, $\bar{k}_{\rm a}$, etc., are known, the parameters $k_{\rm l}$, $k_{\rm h}$, $k_{\rm t}^{\rm o}$, $k_{\rm t}^{\rm c}$ and $k_{\rm a}$ can be estimated using the random-walk model. It is here that the choice of a particular model, as in this paper, comes into play.

In a subsequent paper we shall apply the formalism discussed in this paper to analyze a series of experiments performed with the purple bacteria *Rhodospirillum rubrum* and *Rhodopseudomonas capsulata*.

Appendix

In this appendix we present the derivation of Eqns. 19, 21 and 22 from Eqn. 18, the Pauli master equation:

$$\begin{aligned}\frac{\mathrm{d}p_{mnij}(t)}{\mathrm{d}t} = {} & \left\{(i+1)\bar{k}_{\rm t}^{\rm o}\frac{j+1}{\lambda}\right\}p_{mn\,i+1\,j+1}(t) \\ & +\left\{(i+1)k_{\rm l}+(i+1)\bar{k}_{\rm t}^{\rm c}\left(1-\frac{j}{\lambda}\right)\right. \\ & \left.+\tfrac{1}{2}\bar{k}_{\rm a}i(i+1)\right\}p_{mn\,i+1\,j}(t) \\ & -\left\{ik_{\rm l}+i\bar{k}_{\rm t}^{\rm o}\frac{j}{\lambda}+i\bar{k}_{\rm t}^{\rm c}\left(1-\frac{j}{\lambda}\right)\right. \\ & \left.+\tfrac{1}{2}\bar{k}_{\rm a}i(i-1)\right\}p_{mnij}(t)\end{aligned}$$

$$\text{for } t\geqslant 0,\ 0\leqslant i\leqslant m,\ 0\leqslant j\leqslant n\leqslant\lambda \tag{A-1}$$

with initial condition:

$$p_{mnij}(0)=\delta_{mi}\delta_{nj} \tag{A-2}$$

Since both i, j and m, n occur as running indices, we find it convenient to define:

$$p_{mnij}(t)\equiv 0,\ i>m \text{ or } j>n \tag{A-3}$$

We introduce the generating function:

$$Z_{mn}(x,y,t):=\sum_{i=0}^{m}\sum_{j=0}^{n}x^iy^jp_{mnij}(t) \tag{A-4}$$

and the Laplace transforms:

$$\hat{p}_{mnij}(s) := \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} p_{mnij}(t) \tag{A-5a}$$

$$\hat{Z}_{mn}(\mathrm{x}, \mathrm{y}, s) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} Z_{mn}(\mathrm{x}, \mathrm{y}, t) \tag{A-5b}$$

with Re $s > 0$. Obviously, by Eqns. A-4 and A-5:

$$\hat{Z}_{mn}(\mathrm{x}, \mathrm{y}, s) = \sum_{i=0}^{m} \sum_{j=0}^{n} \mathrm{x}^i \mathrm{y}^j \hat{p}_{mnij}(s) \tag{A-6}$$

Next we introduce the set of functions $\hat{p}^*_{mnkl}(s)$, $m \gg k \geqslant 0$ and $n \gg l \geqslant 0$, through the relation:

$$\sum_{k=0}^{m} \sum_{l=0}^{n} \hat{p}^*_{mnkl}(s)\, \hat{p}_{klij}(s) = \delta_{mi}\delta_{nj} \tag{A-7}$$

It is easily seen that this relation uniquely determines the set. From Eqns. A-2 and A-7 and the Laplace transform of Eqn. A-1 it follows that:

$$\begin{aligned} \hat{p}^*_{mnkl}(s) &= s\delta_{mk}\delta_{nl} \\ &\quad - (Am + Bmn + Dm(m-1)) \\ &\quad \times (\delta_{m\,k+1}\delta_{nl} - \delta_{mk}\delta_{nl}) \\ &\quad - Cmn(\delta_{m\,k+1}\delta_{n\,l+1} - \delta_{m\,k+1}\delta_{nl}) \end{aligned} \tag{A-8}$$

where we have introduced the constants:

$$\begin{aligned} &A := k_1 + \bar{k}^{\mathrm{c}}_{\mathrm{t}},\ B := (\bar{k}^{\mathrm{o}}_{\mathrm{t}} - \bar{k}^{\mathrm{c}}_{\mathrm{t}})/\lambda \\ &C := \bar{k}^{\mathrm{o}}_{\mathrm{t}}/\lambda,\ D := \tfrac{1}{2}\bar{k}_{\mathrm{a}} \end{aligned} \tag{A-9}$$

From Eqns. A-6–A-8 it follows that $\hat{Z}_{mn}(\mathrm{x}, \mathrm{y}, s)$ satisfies the equation:

$$\begin{aligned} &\mathrm{x}^m \mathrm{y}^n - s\hat{Z}_{mn} \\ &\quad = (Am + Bmn + Dm(m-1))(\hat{Z}_{mn} - \hat{Z}_{m-1\,n}) \\ &\qquad + Cmn(\hat{Z}_{m-1\,n} - \hat{Z}_{m-1\,n-1}) \end{aligned} \tag{A-10}$$

The number m of excitations generated in the domain at $t = 0$ is given by a Poisson distribution. If z is the average number generated, the average of $\hat{Z}_{mn}(\mathrm{x}, \mathrm{y}, s)$ over m is:

$$\hat{Z}_n(\mathrm{x}, \mathrm{y}, s, z) := \sum_{m=0}^{\infty} \frac{z^m \mathrm{e}^{-z}}{m!} \hat{Z}_{mn}(\mathrm{x}, \mathrm{y}, s) \tag{A-11}$$

From Eqns. A-10 and A-11 it now follows that $\hat{Z}_{\mathrm{n}}(\mathrm{x}, \mathrm{y}, s, z)$ satisfies the equation:

$$\begin{aligned} &\mathrm{e}^{-z(1-x)} y^n - s\hat{Z}_n \\ &\quad = Dz^2 \frac{\partial^2}{\partial z^2} \hat{Z}_n + (Dz + A + Bn) z \frac{\partial}{\partial z} \hat{Z}_n + Cnz(\hat{Z}_n - \hat{Z}_{n-1}) \end{aligned} \tag{A-12}$$

Since we are interested in time-integrated results, we shall need this equation only in the limit $s \to 0$.

First we discuss the loss. The average total probability of loss per excitation is equal to $U_n(z) := k_1 z^{-1} u_n(z)$ with:

$$\begin{aligned} u_n(z) &= \int_0^\infty \mathrm{d}t \sum_{m=0}^{\infty} \frac{z^m \mathrm{e}^{-z}}{m!} \sum_{i=0}^{m} \sum_{j=0}^{n} i p_{mnij}(t) \\ &= \lim_{s \to 0} \frac{\partial}{\partial \mathrm{x}} \hat{Z}_n(\mathrm{x}, \mathrm{y}, s, z) \Big|_{\mathrm{x}=\mathrm{y}=1} \end{aligned} \tag{A-13}$$

Using Eqn. A-12 we find that for $u_n(z)$:

$$Dzu_n'' + (Dz + A + Bn)u_n' + Cnu_n = 1 + Cnu_{n-1} \tag{A-14}$$

with initial conditions $u_n(0) = 0$ and $u_n'(0) = 1/(A + Bn)$, corresponding to the total probability of loss for $m = 0$ and $m = 1$, respectively. Eqn. A-14 is a differential–difference equation, from which the $u_n(z)$, $n = 1,\ldots,\lambda$, follow recursively.

First we take $D = 0$. For this case we are able to obtain an expression for $u_n(z)$ in closed form. Eqn. A-14) reduces to:

$$(A + Bn)u_n' + Cnu_n = 1 + Cnu_{n-1} \tag{A-15}$$

from which, with the appropriate boundary conditions, it follows that:

$$\begin{aligned} u_n(z) &= (A + Bn)^{-1} \exp\left(-\frac{Cn}{A + Bn} z\right) \\ &\quad \times \int_0^z \mathrm{d}\xi \exp\left(\frac{Cn}{A + Bn} \xi\right)(1 + Cnu_{n-1}(\xi)) \end{aligned} \tag{A-16}$$

By iteration we find:

$$\begin{aligned} u_n(z) &= \frac{z}{A} - \frac{B}{AC} \sum_{k=1}^{n} \binom{n}{k} \left(-\frac{B}{A}k\right)^{k-1} \left(1 + \frac{B}{A}k\right)^{n-k} \\ &\quad \times \left(1 - \exp\left(-\frac{Ck}{A + Bk} z\right)\right) \end{aligned} \tag{A-17}$$

where we have used the identity $\sum_{k=1}^{n}\binom{n}{k}(-\mathrm{x}k)^{k-1}(1+\mathrm{x}k)^{n-k}=n$, for all x. Substitution of Eqn. A-9 leads to Eqn. 19a with $\mu = B/C$ and $\nu = B/A$.

Next we take $D > 0$. Also for this case Eqn. A-14 can be iterated, but the solution involves hypergeometric functions and is rather unpractical. We have been unable to use it to find an explicit expression for $u_n(z)$. However, if we substitute into Eqn. A-14 the power series:

$$u_n(z) = (A + Bn)^{-1} \sum_{k=1}^{\infty} \frac{(-1)^{k-1} u_{nk}}{k!} z^k \tag{A-18}$$

we find that the coefficients u_{nk} satisfy the recurrence relation (Eqn. 22) with $\alpha_n := Cn/D$ and $\beta_n := (A + Bn)/D$.

Next we discuss the fraction of traps closed. The average total fraction of traps closed is equal to $V_n(z) := \bar{k}_t^{\circ}\lambda^{-2}v_n(z)$ with:

$$\begin{aligned} v_n(z) &= \int_0^{\infty} \sum_{m=0}^{\infty} \frac{z^m e^{-z}}{m!} \sum_{i=0}^{m} \sum_{j=0}^{n} ij p_{mnij}(t) \\ &= \lim_{s \to 0} \frac{\partial^2}{\partial \mathrm{x} \partial \mathrm{y}} \hat{Z}_n(\mathrm{x}, \mathrm{y}, s, z) \Big|_{\mathrm{x}=\mathrm{y}=1} \end{aligned} \tag{A-19}$$

Using Eqn. A-12 we find that for $v_n(z)$:

$$Dzv_n'' + (Dz + A + Bn)v_n' + Cnv_n = n + Cnv_{n-1} \tag{A-20}$$

with initial conditions $v_n(0) = 0$ and $v_n'(0) = n/(A + Bn)$. Note the close resemblance of Eqns. A-14 and A-20. For $D = 0$ we find the explicit expression:

$$\begin{aligned} v_n(z) = \frac{1}{C} \sum_{k=1}^{n} \binom{n}{k} \left(-\frac{B}{A}k\right)^{k-1} \left(1 + \frac{B}{A}k\right)^{n-k} \\ \times \left(1 - \exp\left(-\frac{Ck}{A + Bk} z\right)\right) \end{aligned} \tag{A-21}$$

which is the equivalent of Eqn. A-17. Substitution of Eqn. A-9 leads to Eqn. 19b. For $D > 0$, on the other hand, we can substitute into Eqn. A-20 a power series identical to Eqn. A-18, with u_{nk} replaced by v_{nk}. The coefficients v_{nk} are then found to satisfy a recurrence relation that is the equivalent of Eqn. 22.

Further, there is a number of interesting properties of $U_n(z)$ and $V_n(z)$ that can be proved without much effort. For instance, if $A, C > 0$ and $D = 0$ it follows from Eqn. A-20 that $V_n'(z) > 0$, for $n > 0$, $z \geqslant 0$. The proof is simple. For $n = 0$, $v_0(z) \equiv 0$. For $n > 0$, $v_n'(0) > 0$. Suppose that there exists a $z^* > 0$ such that $v_n'(z^*) = 0$ and $v_n'(z) > 0$, $0 \leqslant z < z^*$. Then clearly $v_n''(z^*) < 0$ and, by Eqn. A-20, $v_{n-1}'(z^*) < 0$. The proof proceeds by induction. In a similar way it can be shown that $v_n''(z) < 0$, for $n > 0$, $z \geqslant 0$, and that $v_n'''(z) > 0$, for $n > 0$, $z > 0$ if $v_n'''(0) > 0$. The latter condition holds for all $n > 0$ if and only if $2p^2 > \lambda(3p - 1)$, by Eqns. 17b, A-9 and A-20. It follows from Eqn. 20 that if $B > 0$, $U_n''(z) < 0$, for $n > 0$, $z \geqslant 0$ under the same condition, and that $U_n'(z) > 0$, for $n > 0$, $z \geqslant 0$ without restriction.

Addendum

While writing this paper the authors have learned that G. Paillotin, N.E. Geacintov and J. Breton have formulated a master equation theory to describe the decay of the excitations in a domain when the transition of the reaction center from the open to the closed state (or the conversion of the antenna from a non-quenching singlet to a quenching triplet state) is taken into account. Their approach does not include the singlet–singlet annihilation. (Geacintov, N.E. and Breton, J., personal communication.)

Acknowledgements

The authors are grateful to Mr. H.N. van der Wal for his help with the computer calculations and simulations used for this work. This research was supported by the Dutch Foundation of Biophysics.

References

1 Duysens, L.N.M. (1952) Thesis, University of Utrecht, The Netherlands

2 Borisov, A.Yu. (1979) in The Photosynthetic Bacteria (Clayton, R.K. and Sistrom, W.R., eds.), pp. 323–331, Plenum Press, New York

3 Van Grondelle, R. and Duysens, L.N.M. (1982) in Handbook of Biosolar Resources (Zaborsky, O.R., ed.), pp. 11–36, CRC Press, Boca Raton

4 Sauer, K. (1975) in Bioenergetics of Photosynthesis (Govindjee, R., ed.), pp. 115–181, Academic Press, New York

5 Duysens, L.N.M. (1964) Prog. Biophys. Mol. Biol. 14, 1–104

6 Knox, R.S. (1977) in Primary Processes of Photosynthesis (Barber, J., ed.), pp. 55–97, Elsevier Scientific Publishing, Amsterdam

7 Vredenberg, W.J. and Duysens, L.N.M. (1963) Nature 197, 355–357

8 Clayton, R.K. (1966) Photochem. Photobiol. 5, 807–821

9 Godik, V.I. and Borisov, A.Yu. (1977) FEBS Lett. 82, 355–358

10 Parson, W.W. (1982) Annu. Rev. Biophys. Bioenerg. 11, 57–80

11 Feher, G. and Okamura, M.Y. (1979) in The Photosynthetic Bacteria (Clayton, R.K. and Sistrom, W.R., eds.), pp. 349–386, Plenum Press, New York

12 Duysens, L.N.M. and Sweers, H.E. (1963) in Studies on Microalgae and Photosynthetic Bacteria, Plant Cell Physiol. (special issue), pp. 353–372, University of Tokyo Press, Tokyo

13 Joliot, P. and Joliot, A. (1964) C.R. Acad. Sci. Paris 258, 4622–4625

14 Van Gorkom, H.J., Pulles, M.P.J. and Etienne, A.L. (1978) in Proceedings of the Symposium on Photosynthetic Oxygen Evolution (Metzner, H., ed.), pp. 135–145, Academic Press, London

15 Duysens, L.N.M. (1979) in Chlorophyll Organization and Energy Transfer in Photosynthesis, CIBA Found. Symp. 61 (new series), pp. 323–340, Elsevier Scientific Publishing Company, Amsterdam

16 Clayton, R.K. (1967) J. Theor. Biol. 14, 173–186

17 Monger, T.G. and Parson, W.W. (1977) Biochim. Biophys. Acta 460, 393–407

18 Hemenger, R.P., Pearlstein, R.M. and Lakatos-Lindenberg, K. (1972) J. Math. Phys. 13, 1056–1063

19 Paillotin, G. (1972) J. Theoret. Biol. 36, 223–235

20 Montroll, E.W. (1969) J. Math. Phys. 10, 753–765

21 Montroll, E.W. (1969) J. Phys. Soc. Japan Suppl. 26, 6–10

22 Den Hollander, W.T.F. and Kasteleyn, P.W. (1982) Physica 112A, 523–543

23 Kenkre, V.M. and Wong, Y.M. (1981) Phys. Rev. B23, 3748–3755

24 Kenkre, V.M. (1982) in Exciton Dynamics in Molecular Crystals and Aggregates (Höhler, G., ed.), pp. 1–109, Springer Tracts in Modern Physics 94, Springer Verlag, Berlin

25 Breton, J. and Geacintov, N.E. (1980) Biochim. Biophys. Acta 594, 1–32

26 Paillotin, G., Swenberg, C.E., Breton, J. and Geacintov, N.E. (1979) Biophys. J. 25, 513–533

27 Mauzerall, D. (1976) J. Phys. Chem. 80, 2306–2309

28 Swenberg, C.E., Geacintov, N.E. and Pope, M. (1976) Biophys. J. 16, 1447–1452

29 Geacintov, N.E., Breton, J., Swenberg, C.E. and Paillotin, G. (1977) Photochem. Photobiol. 26, 619–638

30 Van Grondelle, R., Hunter, C.N., Bakker, J.G.C. and Kramer, H.J.M. (1983) Biochim. Biophys. Acta 723, 30–36

31 Pearlstein, R.M. (1967) Brookhaven Symp. Biol. 19, 8–15

32 Knox, R.S. (1968) J. Theoret. Biol. 21, 244–259

33 Rosenstock, H.B. and Marquardt, C.L. (1980) Phys. Rev. B22, 5797–5809

34 Fastenau, R.H.J. (1982) Thesis, Delft University of Technology, The Netherlands

35 Feller, W. (1950) An Introduction to Probability Theory and Its Applications, Vol. I, Wiley, New York

36 Hirsch, J., Neef, E. and Fink, F. (1982) Biochim. Biophys. Acta 681, 15–20

37 Holten, D., Hoganson, C., Windsor, M.W., Schenck, C.C., Parson, W.W. Migus, A., Fork, R.L. and Shank, C. (1980) Biochim. Biophys. Acta 592, 461–477

38 Schenck, C.C., Parson, W.W., Holten, D. and Windsor, M.W. (1981) Biochim. Biophys. Acta 635, 383–392

39 Den Haan, G.A., Duysens, L.N.M. and Egberts, D.J.N. (1974) Biochim. Biophys. Acta 368, 409–421

40 Breton, J., Geacintov, N.E. and Swenberg, C.E. (1979) Biochim. Biophys. Acta 548, 616–635

41 Connolly, J.S., Janzen, A.F. and Samuel, E.B. (1982) Photochem. Photobiol. 36, 559–563

42 Connolly, J.S., Samuel, E.B. and Janzen, A.F. (1982) Photochem. Photobiol. 36, 565–574

43 Bakker, J.G.C., Van Grondelle, R. and Den Hollander, W.T.F. (1983) Biochim. Biophys. Acta 725, 508–518 (this issue)