Theories for kinetics and yields of fluorescence and photochemistry: how, if at all, can different models of antenna organization be distinguished experimentally?

Karen Bernhardt, Hans-Wilhelm Trissl *

Fachbereich Biologie/Chemie, Abteilung Biophysik, Universität Osnabrück, Barbarastraße 11, D-49069 Osnabrück, Germany

Abstract

The models most commonly used to describe the antenna organization of the photosynthetic membrane are the connected units model and the domain model. The theoretical descriptions of the exciton dynamics according to these models are reviewed with emphasis on a common nomenclature. Based on this nomenclature we compare for the two models the kinetics and yields of photochemistry and fluorescence under non-annihilation and annihilation conditions both under continuous light and under flash excitation. The general case is considered, that all initially open reaction centers become gradually closed and that exciton transfer between photosynthetic units (PSUs) is possible. Then, calculated kinetics and yields depend on the model assumptions made to account for the exciton transfer between PSUs. Here we extend the connected units model to flash excitation including exciton-exciton annihilation, and present a new simple mathematical formalism of the domain model under continuous light and flash excitation without annihilation. Product and fluorescence yields predicted by the connected units model for different degrees of connectivity are compared with those predicted by the domain model using the same sets of rate constants. From these calculations we conclude that it is hardly possible to distinguish experimentally between different models by any current method. If at all, classical fluorescence induction measurements are more suited for assessing the excitonic connectivity between PSUs than ps experiments. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A most common experimental assay for studying photosynthetic exciton and electron transport processes is the excitation by light, either constant light (cw light) which is suddenly switched on (electrome- chanically with a shutter or electronically with light-emitting diodes) or flashes of various durations. On the one hand, measurements of fluorescence yield changes upon cw excitation (fluorescence induction) give information on the electron transport (e.g. in photosystem II (PS II)) and on the antenna organization of photosynthetic systems. A recent review on fluorescence induction has been published by Dau [1]. On the other hand, measurements of fluorescence kinetics and yields upon flash excitation give information on the trapping kinetics, exciton dynamics and antenna organization [2]. The various aspects

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Abbreviations: ODE, ordinary differential equation; P, primary donor; PS II, photosystem II; PSU, photosynthetic unit; RC, reaction center

* Corresponding author. Fax: +49 (541) 969-2870;
E-mail: trissl@biologie.uni-osnabrueck.de

of exciton dynamics and trapping in photosynthetic systems have been reviewed by van Grondelle et al. [3,4]. The term antenna organization shall be used here for the structural and functional assembly of a photosynthetic unit (PSU) including the excitonic communication between the PSUs (inter-unit exciton transfer). For some photosynthetic systems it has been established that PSUs can be so close to each other that the excited state (exciton) created by light absorption in one PSU diffuses to a vast number of neighboring PSUs. In other systems like isolated reaction centers (RCs) an exciton remains restricted to just one PSU. Still for other systems a limited inter-unit exciton transfer is possible.

Since the early 1960s various approaches to describe exciton dynamics in photosynthetic membranes have been developed [5–7]. For example, the exciton dynamics has been described by random walk of excitons between individual pigments and RCs in the membrane. Theories based on this approach shall not be discussed here. Another possibility is the grouping of individual pigments around one RC into a PSU for which the structural details are disregarded. This view, which is adopted here, corresponds to the 'pebble-mosaic' model introduced by Sauer [8].

Some current models for the antenna organization in the photosynthetic membrane are shown in Fig. 1. For the exciton exchange between PSUs two extreme cases can be distinguished, namely separate units (or puddle) with excitons completely restricted to one PSU (Fig. 1d) or a lake (or matrix) with excitons completely free to visit all RCs in the membrane (Fig. 1c) before they get trapped [9].
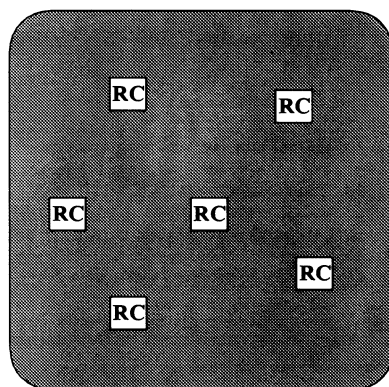
a) connected units model:
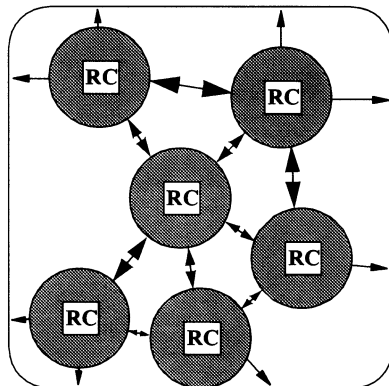
b) domain model ($\lambda = 2$):
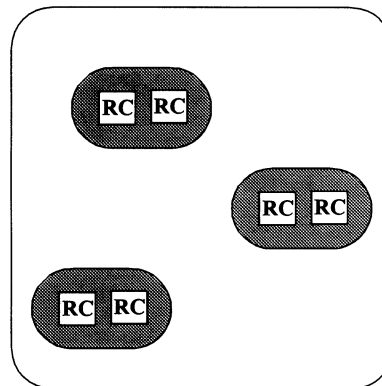
c) lake model:
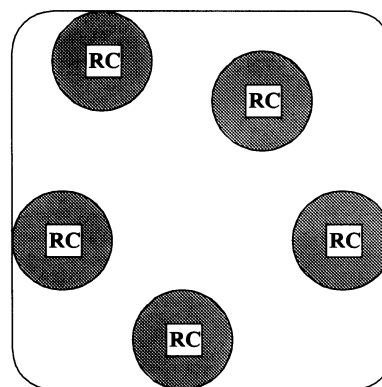
d) separate units model:

Fig. 1. Different models to describe the photosynthetic units in a photosynthetic membrane. For explanations, see Section 1.

For the intermediate case – where excitons can be exchanged between PSUs to a certain degree – two additional, conceptionally different models have been developed: the connected units model introduced by Joliot and Joliot [10] and the domain model [11,12]. The first model accounts for limited exciton transfer between PSUs by treating them as a continuum with partial connectivity (absence of strict boundaries). Here – in contrast to the domain model – no special assumptions about structural details of the antenna organization are required.

On the simplest level of the continuum theory (Fig. 1a) the PSUs in a given fluorescent (i.e. redox) state are quantified by normalized concentrations. The exciton exchange between PSUs, called connectivity, is described by a variety of quantities like an empirical parameter (p or J) [10,13–15], a transition probability [16–18] or a rate constant [19–22]. Product yields (the term 'product yield' is used here generically for the first irreversibly formed photochemical product or secondary products formed with 1:1 stoichiometry) and fluorescence yields have been predicted only for cw excitation. In the present article the connected units theory will be extended to flash excitation.

An alternative way to account for limited exciton transfer is to divide the photosynthetic membrane into domains (Fig. 1b). The term domain was introduced by Clayton [23] to define a region of light harvesting pigments that can be probed by an exciton during its lifetime. Hence it may comprise a cluster of PSUs (mostly assumed as an integer number [11]). Unrestricted exciton motion within a domain (i.e. mini-lake) and absence of exciton exchange between the domains (i.e. separate units) are postulated. Several groups have worked out the domain theory to calculate product and fluorescence yields for cw as well as for flash excitation [11,12]. However, no analytical solutions are available for the time courses of product formation or fluorescence decay when short flashes are applied *and* the transition from open to closed RCs is considered. Mathematical solutions of the domain theory for fluorescence decay kinetics have been published for the case of closed RCs, but this analysis has not been extended to the transition from the open to the closed state of the RC [11].

If the flashes are much shorter than the mean exciton lifetime (δ-function approach) and if they are strong enough to excite a considerable fraction of PSUs, excitons can interact with each other and get lost by mutual annihilation. Annihilation competes significantly with the primary photochemistry [24,25,37] and leads to complex kinetics of product formation and fluorescence decay. The extent of this effect depends quadratically on the exciton density and, therefore, can have a considerable impact on the interpretation of results obtained with fs laser pulses where high excitation energies are common. We shall inspect here whether careful analysis of the annihilation process can contribute useful information on the topology of antenna pigment beds in photosynthetic systems as has been assumed in the past [2,26].

We focus here on the general case of a mixture of open and closed RCs coexisting at a given time in the photosynthetic membrane. With this restriction there are three key references, out of a large number, which we summarize with respect to their different model assumptions for the antenna organization as well as to the type of excitation source to which they were adapted (Table 1). The theory by Deprez et al. [24] has been specifically designed for the kinetics and yields due to δ-function excitation in a lake system, whereas the domain theory [12] describes the yields due to either cw or flash excitation, accounting for the different degrees of connectivity by the introduction of different domain sizes. It should be mentioned that the practical application of the latter theory is hampered by the intricate mathematical formalism. Kinetics have been published for cw but not for flash excitation. One can extract from Table 1 that only the connected units model [19] and its extension in the present work ((3)+(4) in Table 1) accounts for gradual connectivity, for all excitation conditions and describes both, kinetics and yields.

The present article serves four purposes. First, we give a synopsis of the basic principles and their solutions for the yields of photochemistry and fluorescence as they follow from the different theories. Second, we derive a set of starting equations for the connected units model which is suited for flash excitation and show graphs of their solutions. Third, we give a simplified mathematical treatment of the domain model for fluorescence induction, which is based on a set of ordinary differential equations

Table 1
Survey of the capabilities of the main theoretical approaches to describe antenna organizations in photosynthetic membranes[a]

| | Domain theory | | | Lake theory | | | cu theory | | |
| | (1) | | | (2) | | | (3) | (4) | |
	cw, Y and K	flash, Y	flash, K	cw, Y and K	flash, Y	flash, K	cw, Y and K	flash, Y	flash, K
su	+	+	−	−	−	−	+	+	+
Lake	+	+	−	−	+	+	+	+	+
cu	−	−	−	−	−	−	+	+	+
Domains	+	+	+	−	−	−	−	−	−

[a]The following key references are used: (1) domain theory [12]; (2) lake theory [24]; (3) connected units theory [19]; (4) connected units theory (this work). The symbols Y and K indicate solutions by a given theory for yields and kinetics, respectively. Excitation with continuous light or flashes is labeled by 'cw' or 'flash'. A reference is marked by '+' if it accounts for a given model as a special case. A reference is marked by '−' if it does not account for or when it is not explicitly designed for a given type of antenna organization (see Fig. 1, su = separate units, cu = connected units).

(ODE). Fourth, the results predicted by the different approaches are critically compared with respect to distinguishing experimentally between the models.

In order to make the symbolisms comparable we had to use a consistent nomenclature for the rate constants and to redefine several rate constants. We also prove the convergence of the equations of the connected units model with those of other available formalisms for limiting cases of antenna organization.

2. Materials and methods

The equations of the connected units model (Eqs. 16a and b) were solved numerically using the Runge-Kutta formalism with constant stepwidth with 35 000 points in 2 ns and assuming $k_\ell = (1 \text{ ns})^{-1}$ throughout. Only PSUs with up to 40 excitons were considered, because higher maximal exciton numbers did not influence the results. Concentrations of PSUs with negative exciton numbers were set zero.

The infinite sums needed to calculate the yields for the domain theory (Eqs. 31a and b) were calculated up to the index 160. This allowed to calculate results with sufficient accuracy up to a maximum domain size of $\lambda = 12$ and a maximal energy of $z_0 = 7$. For smaller domain sizes higher energy values (up to $z_0 = 76$) are treatable. The combination of larger values for both quantities, however, requires sophisticated and unconventional programming.

3. Theories

3.1. General definitions

The photosynthetic membrane generally consists of hundreds of reaction centers and of ten thousands of antenna pigments. It is convenient to divide it into PSUs which are formally defined as one RC together with a number of antenna pigments given by the stoichiometric ratio of the total number of antenna pigments to the total number of RCs in the photosynthetic membrane. From the two possibilities to model the membrane (i) by treating all pigments individually (e.g. by random walk) or (ii) by grouping them into pools (PSUs or domains), we discuss here only the latter. Then, within a PSU thermal equilibration of the excitons over the antenna pigments is assumed, i.e. the PSU itself forms a lake with one trap (mini-lake). This condition is well established for PS II and for PS I [27–29] and reasonable for the antenna system of purple bacteria. A domain is defined as a group of PSUs (containing a distinct number of RCs) in which all the pigments are thermally equilibrated (i.e. a domain also forms a lake, but including several RCs).

Two pathways shall be distinguished for the decay of a single exciton in a PSU, namely losses occurring in the antenna system, rate constant k_ℓ, and losses occurring at the open or closed RC with the rate constants k_o and k_c, respectively. This definition of k_o and k_c does not require to specify the trapping mechanism, e.g. RC-controlled or transfer-to-the-

trap-limited. Losses in the antenna comprise losses by fluorescence (rate constant, k_{rad}), internal conversion and intersystem crossing. To achieve generality, a closed RC may be one with a reduced acceptor (like PS II) or with an oxidized donor (like in purple bacteria). The PSUs in the photosynthetic membrane are characterized by one of the two redox states of their RCs and quantified by normalized concentrations.

Single turn-over conditions are assumed throughout this work.

3.2. The connected units model

3.2.1. Subcase: low intensity excitation

To introduce the nomenclature used in this work we recapitulate the connected units model [19]. If the normalized concentration of open RCs is q (concentration of closed ones, $1-q$), this model can be depicted as:
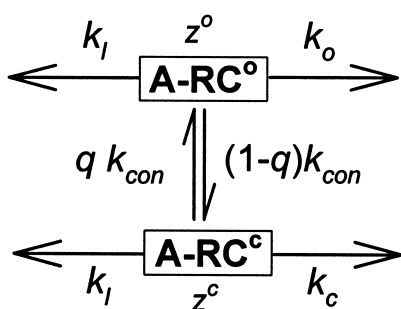
A-RC^o and A-RC^c stand for the two different populations of the PSUs (open or closed), and k_{con} is the overall molecular rate constant for inter-unit exciton transfer. The scheme implies a mono-exponential exciton decay with the rate constant $k_o + k_\ell$ or $k_c + k_\ell$ if the PSUs are isolated or all in the same state. Such a reaction scheme is well adopted for purple bacteria, but not for PS II where the proposed exciton-radical pair equilibrium mechanism predicts biphasic kinetics [30–32]. However, for low light excitation, the rate constants k_o and k_c may be expressed by the molecular rate constants of the exciton-radical pair equilibrium model ($k_o = \alpha_p + \alpha_d$ and $k_c = \beta$ in Lavergne and Trissl [19]). (Note: this identification yields approximate product yields and identical fluorescence yields in the two models (irreversible vs. reversible trapping). However, for $\alpha_d = 0$ also the product yields are identical.)

To account for the general case, that the photochemical product is different from the initially formed closed RC, we introduce the product yield, $Y(q) = 1-q$, which leaves open the chemical nature of consecutively formed products.

For low intensity excitation the product yield, $Y(q)$ and fluorescence quantum yield, $\Phi_f(q)$, when all RCs are open or closed, follow directly from this scheme interpreting the rate constants as probabilities:

$$Y(q = 1) = \frac{k_o}{k_o + k_\ell}, \tag{1}$$

$$\Phi_f(q = 1) = \frac{k_{rad}}{k_o + k_\ell} \sim F_o, \tag{2}$$

$$\Phi_f(q = 0) = \frac{k_{rad}}{k_c + k_\ell} \sim F_m, \tag{3}$$

and the ratio of the fluorescence yields of the two quenching states is:

$$\frac{F_m}{F_o} = \frac{\Phi_f(q = 0)}{\Phi_f(q = 1)} = \frac{k_o + k_\ell}{k_c + k_\ell}. \tag{4}$$

The symbols F_m and F_o stand for measured fluorescence amplitudes, which are proportional to the quantum yields. These former quantities can easily be determined experimentally. For this reason, we use these quantities whenever possible. (Note: the fluorescence yield, Φ_f, is a quantum yield, whereas the product yield, Y, is an integral measure for the product after a given light exposure.)

The above scheme of the connected units model leads to the following ODEs, in which z^o and z^c stand for the exciton concentrations in PSUs with open or closed RCs respectively:

$$\frac{dz^o}{dt} = -[k_o + k_\ell + k_{con}(1-q)]z^o + k_{con}qz^c, \tag{5a}$$

$$\frac{dz^c}{dt} = -[k_c + k_\ell + k_{con}q]z^c + k_{con}(1-q)z^o, \tag{5b}$$

$$\frac{dq}{dt} = -k_oqz^o. \tag{5c}$$

For *cw excitation*, which creates no more than one exciton within a large number of PSUs during the lifetime of an exciton, these ODEs can be solved analytically. For the exciton creation rate z (hits per PSU and time), the product and fluorescence

yields as a function of open RCs can be expressed in terms of rate constants [19]:

$$\Phi_p(q) = k_o \frac{(k_c + k_\ell + k_{con})q}{(k_c + k_\ell)(k_o + k_\ell + k_{con}) + k_{con}(k_o - k_c)q},$$
(6a)

$$\Phi_f(q) = k_{rad} \frac{k_o + k_\ell + k_{con} + (k_c - k_o)q}{(k_c + k_\ell)(k_o + k_\ell + k_{con}) + k_{con}(k_o - k_c)q},$$
(6b)

and the time dependence of the open RCs obeys the law:

$$z \cdot t \Phi_p(1)(J + 1) = J(1 - q) - \ln(q).$$
(7a)

The parameter J can be expressed by F_m/F_o and rate constants:

$$J = \left(\frac{F_m}{F_o} - 1\right) \frac{k_{con}}{k_o + k_\ell + k_{con}}.$$
(8a)

J has been called sigmoidicity parameter because it controls the sigmoidicity of the resulting fluorescence induction curve [19].

The time courses of the closed RCs or the product yield, $Y(t)$, and of the instantaneous fluorescence yield, $\Phi_f(t)$, are obtained by substituting q by t in Eq. 6a or Eq. 6b by means of Eq. 7a. The time course of the product yield is then calculated by:

$$Y(t) = 1 - q(t),$$
(9a)

and the normalized instantaneous fluorescence yield (classical fluorescence induction curve) by:

$$F_n(t) = \frac{\Phi_f(t)}{\Phi_f(t = 0)} = \frac{F_m/F_o - (F_m/F_o - 1 - J)q(t)}{1 + Jq(t)}.$$
(9b)

As mentioned, in PS II the reversible molecular mechanism of charge separation, described by the exciton-radical pair equilibrium model, predicts a biphasic exciton decay kinetics. The incorporation of this model into the connected units model for fluorescence induction has been described by Lavergne and Trissl [19]. However, measurements at low light intensity excitation, with always less than one exciton in the photosynthetic membrane, do not contain information on the detailed molecular deactivation mechanism. Therefore, the more simple formalism

using k_o and k_c is sufficient for classical fluorescence induction.

In the absence of connectivity (separate units with $k_{con} = 0$) the sigmoidicity parameter is simply:

$$J^{su} = 0,$$
(8b)

and for perfect connectivity (lake with $k_{con} \to \infty$) the expression for J (Eq. 8a) simplifies to:

$$J^{lake} = \frac{F_m}{F_o} - 1.$$
(8c)

The total number of excitons created by cw light in a PSU is proportional to time. This means that product and fluorescence yields can be expressed either as a function of time, t, or of the accumulated number of excitons created during this time, $z \cdot t$. When a flash does not allow for exciton-exciton annihilation the yields are independent of the time course and the duration of the excitation.

3.2.2. Subcase: flashes without annihilation

For *flash excitation* of arbitrary duration, the flash energy z_0 (hits per PSU and flash) can be obtained formally by integrating over the time course of the excitons created in the PSU, $\tilde{z}(t)$, $z_0 = \int_0^\infty \tilde{z}(t)\, dt$. If exciton-exciton interactions can be neglected, the product yield due to a flash of energy z_0 is simply obtained from Eq. 7a:

$$z_0 \Phi_p(1)(J + 1) = JY(z_0) - \ln[1 - Y(z_0)].$$
(7b)

The equivalence of Eqs. 7a and b implies that the product yield does not depend on the shape of the flash, but only on the number of absorbed photons provided that only two fluorescent states are involved. The fluorescence yield, normalized to $\Phi_f(q = 1)$ and the flash energy, is given by:

$$F_n(z_0) = \frac{1}{\Phi_f(q = 1)z_0} \int_0^\infty \Phi_f(t)\, dt.$$
(10)

Next we want to derive the equations for limiting cases of antenna organization, since the results obtained for those cases must converge for the different theoretical approaches. For the *lake model* ($k_{con} \to \infty$) the product yield (Eq. 7b) simplifies with the use of Eq. 8c to:

$$z_0 \Phi_p(1)\frac{F_m}{F_o} = \left(\frac{F_m}{F_o} - 1\right) Y(z_0) - \ln(1 - Y(z_0))$$
(7c)

and for the normalized fluorescence yield an analytical solution of Eq. 10 can be given:

$$F_n^{\text{lake}}(z_0) = \frac{F_m/F_o}{1 + (F_m/F_o - 1)(1 - Y(z_0))}. \tag{11}$$

For the product yield in the *separate units model* one obtains from Eq. 7b, setting $J = 0$ (Eq. 8b):

$$Y(z_0) = 1 - e^{-\Phi_p(1)z_0}. \tag{12}$$

This equation can also be derived by means of hit theory [33,34]. For the normalized fluorescence yield Eq. 10 yields with $k_{\text{con}} \to 0$ also an analytical solution:

$$F_n^{\text{su}}(z_0) = \frac{F_m}{F_o} - \left(\frac{F_m}{F_o} - 1\right)e^{-\Phi_p(1)z_0}. \tag{13}$$

3.2.3. Subcase: flashes with annihilation

The connected units model has so far not been elaborated for short and intense flashes in which exciton-exciton annihilation can occur. We introduce the rate constant for annihilation, k_a, which accounts for the mutual annihilation of two excitons into one

$$^1S + {}^1S \xrightarrow{k_a} {}^1S + {}^0S. \tag{14}$$

This annihilation reaction may occur on any pigment of the antenna system.

To treat excitation with short flashes (e.g. δ-function excitation) one has to leave the concept of considering average exciton concentrations ($z^{o/c}$) but has to regard the distribution of excitons over all PSUs which is initially given by a Poisson distribution [33]. The concentrations of PSUs accommodating an integer number of excitons, i, and RCs in one of the two redox states shall be denoted by $U_i^{o/c}$. These concentrations are related to the concentration of excitons in PSUs with open or closed RCs by $z^{o/c} = \sum_i i U_i^{o/c}$. For δ-function flashes of energy z_0 the initial condition is a Poisson distribution of excitons over the PSUs with initially all open RCs:

$$U_i^o = \frac{(z_0)^i}{i!}e^{-z_0} \text{ and } U_i^c = 0. \tag{15a}$$

The rate equations for the concentrations of PSUs with open or closed reaction centers accommodating i excitons read:

$$\frac{dU_i^o}{dt} = -i(k_o + k_\ell + k_{\text{con}})U_i^o - \frac{1}{2}k_a i(i-1)U_i^o + k_{\text{con}}$$

$$\left[\sum_{l=1}^{\infty} l(U_l^o + U_l^c)\right](U_{i-1}^o - U_i^o) + (i+1)(k_\ell + k_{\text{con}})$$

$$U_{i+1}^o + \frac{1}{2}k_a(i+1)iU_{i+1}^o, \tag{16a}$$

$$\frac{dU_i^c}{dt} = -i(k_c + k_\ell + k_{\text{con}})U_i^c - \frac{1}{2}k_a i(i-1)U_i^c + k_{\text{con}}$$

$$\left[\sum_{l=1}^{\infty} l(U_l^o + U_l^c)\right](U_{i-1}^c - U_i^c) + (i+1)$$

$$[k_o U_{i+1}^o + (k_c + k_\ell + k_{\text{con}})U_{i+1}^c] + \frac{1}{2}k_a(i+1)iU_{i+1}^c. \tag{16b}$$

The summation terms in each of the two equations account in differential manner for the following processes:

1. Depopulation of a PSU accommodating i excitons by quenching by open/closed RCs, losses in the antenna system, and transfer to neighboring PSUs (inter-unit exciton transfer).
2. Loss of one exciton due to bimolecular annihilation (Eq. 14).
3. De- and repopulation by inter-unit exciton transfer, considering that each PSU with $i-1$ excitons can receive excitons from all other PSUs – closed or open – that accommodate one or more excitons, and considering that each PSU with i excitons can transfer excitons to all other PSUs, which again may be closed or open.
4. Repopulation of a PSU accommodating i excitons from PSUs in the same redox state containing one more exciton. Both, in open and in closed RCs this occurs by losses in the antenna as well as by inter-unit transfer, whereas in closed RCs an additional term is needed which accounts for quenching by P^+ and for trapping by PSUs with open RCs and $i+1$ excitons.
5. Repopulation due to annihilation in PSUs of the same redox state containing one more exciton.

These two coupled equations (Eqs. 16a and b) have to be solved numerically (see Section 2).

The product yield is obtained as

$$Y_0 = Y(t \to \infty) = U_0^c(t \to \infty) \tag{17a}$$

and the normalized fluorescence yield as

$$F_n(z_0) = \frac{1}{\Phi_f(q=1)z_0} \sum_{i=1}^{\infty} i k_{rad}$$

$$\left(\int_0^{\infty} U_i^o(t) \, dt + \int_0^{\infty} U_i^c(t) \, dt \right). \tag{17b}$$

If the flash cannot be approximated by a δ-function, but has the time course $\tilde{z}(t)$ one has to add the following exciton generation terms in Eqs. 16a and b:

$$\frac{dU_i^o}{dt} = \cdots + \tilde{z}(t)(U_{i-1}^o - U_i^o) + \cdots, \tag{18a}$$

$$\frac{dU_i^c}{dt} = \cdots + \tilde{z}(t)(U_{i-1}^c - U_i^c) + \cdots, \tag{18b}$$

under the initial condition (all RCs open) $U_0^o = 1$, $U_i^c = 0$ for $i > 0$ and $U_i^c = 0$ for all i.

In the limiting case of low light excitation where the concentrations of the PSUs with more than one exciton are negligible, the ODEs (Eqs. 16a and b) converge to Eqs. 5a, b and c as shown in Appendix A.

The results for the *separate units model* ($k_{con} \to 0$) follow directly by omitting all terms containing k_{con} in Eqs. 16a and b whereas for the *lake model* analytical solutions exist, which have been published by Deprez et al. [24]. They are recapitulated in Section 3.3.

3.3. The lake theory for flash excitation

In the lake model all PSUs, may they contain open or closed RCs, share a common thermally equilibrated antenna system and the excitons are no longer associated with particular PSUs. Therefore, only one rate equation for the exciton decay and one for the product formation is needed:

$$\frac{dz}{dt} = \tilde{z}(t) - [k_o(1-Y) + k_c Y + k_\ell] z - \tfrac{1}{2} k_a z^2, \tag{19a}$$

$$\frac{dY}{dt} = k_o(1-Y)z. \tag{19b}$$

(Note: the symbols for the rate constants $k_{o/c}$, which in our nomenclature refer to quenching by open or closed RCs, have been used by Deprez et al. [24] for $k_{o/c} + k_\ell$.) For δ-function excitation analytical solutions for the product and normalized fluorescence yields have been derived [24]. Translating those for F_m/F_o these are:

$$[1 - Y(z_0)]^\alpha \left[z_0 \Phi_p(1) \frac{F_m}{F_o} + \frac{F_m/F_o - 1}{\alpha - 1} + \frac{1}{\alpha} \right]$$

$$= [1 - Y(z_0)] \frac{F_m/F_o - 1}{\alpha - 1} + \frac{1}{\alpha}, \tag{20a}$$

$$F_n(z_0) = \frac{-1}{\Phi_p(1)z_0} \ln[1 - Y(z_0)], \tag{20b}$$

with $\alpha = k_a/2k_o$, which is identical to the so-called competition parameter in the original paper. Without annihilation ($\alpha \to 0$) Eq. 20a simplifies, as expected, to Eq. 7c [24].

Next, we want to comment briefly on the consequences of incorporating the exciton-radical pair equilibrium model valid for PS II, as this model predicts biphasic kinetics in contrast to the monophasic decay implied by the above formalism. For the lake model and δ-function excitation we inspected the differences due to these two trapping mechanisms (irreversible vs. reversible) by choosing the numerical values of the parameters such that the same low energy limit yields resulted. It turned out that the integral fluorescence yields differed by $< 10\%$ for medium values of z_0 ($5 < z_0 < 15$). For larger and smaller values of z_0 the differences were on the order of 1% and less. The differences in the kinetics of the fluorescence decay for increasing z_0 became progressively smaller and were negligible for $z_0 > 1$ (data not shown). From these model calculations (with $\alpha = 2$) it can be concluded that under annihilation conditions the detailed molecular mechanism of trapping is irrelevant and that it suffices to apply a simplified formalism based on the two rate constants, k_o and k_c.

3.4. The domain theory for cw excitation

3.4.1. Published formalism

As defined above a domain contains an integer number λ of PSUs assuming a lake approximation

within the domain. To adapt the original nomenclature used by Den Hollander et al. [12] to the one used here, we identify their 'overall' trapping rate constants $\overline{k_t^o} = k_o$ and $\overline{k_t^c} = k_c$. The master equations of the domain model are much more complex than those of the connected units formalism, because the state of a domain is characterized by its initial, m, and actual, i, number of excitons and the initial, n, and actual, j, number of open traps. Against this background the time-dependent changes of the probabilities for domains in a defined state, p_{mnij}, have to be quantified. The probabilities p_{mnij} correspond – in principle – to our $U_i^{o/c}$. However, for the conversion of these probabilities into our $U_i^{o/c}$ we would have to divide the domain into λ PSUs which may be open or closed, containing i excitons, and to consider all possible permutations of excitons in order to calculate the concentrations of the different states of the PSUs in a domain. Because such a reformulation would not simplify the matter, we skip the original master equations and refer to Den Hollander et al. [12]. Only for separate units the identification of the $U_i^{o/c}$ with domains is straightforward (see below).

The solutions of the master equations yield the time dependence of the overall probability of losing one exciton within a domain, $P(t)$, and the closure of open RCs, $q(t)$.

$$P(t) = \frac{k_\ell}{k_\ell + k_c}\left(1 - \frac{\mu}{\lambda\nu}f(t,\mu,\nu)\right) \tag{21a}$$

and

$$q(t) = 1 - \frac{1}{\lambda}f(t,\mu,\nu), \tag{21b}$$

with

$$f(t,\mu,\nu) = \sum_{j=1}^{\lambda}$$

$$\left\{\frac{\lambda!}{j!(\lambda-k)!}(\nu \cdot j)^{j-1}(1 + \nu \cdot j)^{\lambda-j}\left[1 - \exp\left(\frac{-\nu \cdot j \; \lambda \cdot t}{1 + \nu \cdot j \cdot \mu}\right)\right]\right\} \tag{22}$$

and

$$\mu = \frac{k_o - k_c}{k_o} \quad \text{and} \quad \nu = \frac{k_o - k_c}{\lambda(k_\ell + k_c)}. \tag{23}$$

The time dependence of the product yield and the

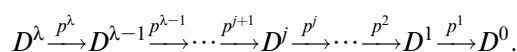instantaneous fluorescence yields are then given by Eq. 9a and by

$$F_n(t) = \frac{1}{P(0)}\left(t \cdot \frac{d}{dt}P(t) + P(t)\right). \tag{24}$$

In the case of separate units the domain consists of only one PSU and the domain treatment must converge with the connected units treatment. This can be proven by identifying $P_{m1i1} = U_i^o$ and $p_{m1i0} = U_i^c$ (compare Eqs. 16a and b).

3.4.2. Treatment of domains by ODEs

We next give an alternative, simplified treatment for low excitation energies where exciton-exciton annihilation can be neglected and all RCs are initially open. In this case the state of a domain is characterized solely by the number of open RCs contained in it. Product and instantaneous fluorescence yield can be derived from the time courses of the concentrations of these states.

The concentrations of domains with j open RCs shall be denoted by D^j with $j \leq \lambda$. These are populated from D^{j+1} with the probability p^{j+1} per exciton and are depopulated with the probability p^j per exciton, according to the consecutive reaction scheme

$$D^\lambda \xrightarrow{p^\lambda} D^{\lambda-1} \xrightarrow{p^{\lambda-1}} \cdots \xrightarrow{p^{j+1}} D^j \xrightarrow{p^j} \cdots \xrightarrow{p^2} D^1 \xrightarrow{p^1} D^0.$$

The conversion of hits per domain into hits per PSUs requires the multiplication of the former by the domain size λ. The above reaction scheme is described by a system of $\lambda+1$ ODEs:

$$\frac{d}{dt}D^j(t) = z\lambda p^{j+1}D^{j+1}(t) - z\lambda p^j D^j(t) \tag{25a}$$

with

$$p^j = \frac{k_o j/\lambda}{k_o j/\lambda + k_c(\lambda-j)/\lambda + k_\ell}. \tag{25b}$$

The ODEs can be solved by standard mathematical procedures – either numerical or analytical (see below) – for the time dependence of the individual domain types $D^j(t)$.

The time dependence of the product yield follows from the concentrations of domains containing one or more closed RC. In order to maintain our nomenclature based on PSUs, one has to form the average of the closed RCs per PSU in a domain. The average PSU in a domain with $\lambda - j$ closed RC results in a

product yield of $(\lambda - j)/\lambda$. The time dependence of the over all product yield is then given by the sum of these PSU-product yields multiplied by their concentrations:

$$Y(t) = \sum_{j=0}^{\lambda-1} \frac{\lambda - j}{\lambda} D^j(t). \qquad (26)$$

The overall instantaneous fluorescence yield follows from the fluorescence yield of the domains containing $\lambda - j$ closed RCs (pre-factors in the following equation) according to:

$$\Phi_f(t) = \sum_{j=0}^{\lambda} \frac{k_{rad}/\lambda}{k_o j/\lambda + k_c(\lambda-j)/\lambda + k_\ell} \cdot D^j(t), \qquad (27a)$$

and the normalized instantaneous fluorescence yield reads:

$$F_n(t) = \frac{\Phi_f(t)}{\Phi_f(t=0)}. \qquad (27b)$$

This treatment allows a much easier calculation of fluorescence induction curves for domains of any size than the original formalism of Den Hollander et al. [12].

3.4.3. Analytical equations for dimers (domains with $\lambda = 2$)

Particularly simple equations follow for the domain size $\lambda = 2$. As this dimer case has recently been proposed for PS II of cyanobacteria and higher plants [35,36], we shall derive the explicit solutions here.

Analytical solution of the above set of ODEs (Eqs. 25a and b) for $\lambda = 2$ yields for the time dependences of the states:

$$D^2(t) = 1 - D^0(t) - D^1(t), \qquad (28a)$$

$$D^1(t) = \frac{k_\alpha}{k_\beta - k_\alpha}(e^{-k_\alpha t} - e^{-k_\beta t}), \qquad (28b)$$

$$D^0(t) = \frac{k_\alpha k_\beta}{k_\beta - k_\alpha}\left(\frac{1}{k_\beta}e^{-k_\beta t} - \frac{1}{k_\alpha}e^{-k_\alpha t}\right) + 1, \qquad (28c)$$

with

$$k_\alpha = \frac{z2k_o}{k_o + k_\ell} \text{ and } k_\beta = \frac{z2k_o}{k_o + k_c + 2k_\ell}.$$

According to Eq. 26 the product yield is given by

$$Y(t) = \frac{1}{2}D^1(t) + D^2(t) =$$

$$1 + \frac{k_o - k_c}{2(k_c + k_\ell)}e^{-k_\alpha t} - \frac{k_o + k_c + 2k_\ell}{2(k_c + k_\ell)}e^{-k_\beta t}, \qquad (29)$$

and the overall instantaneous fluorescence yield follows from Eqs. 27a and b:

$$\Phi_f(t) = \frac{k_{rad}}{2k_o + 2k_\ell}D^2(t) + \frac{2k_{rad}}{k_o + k_c + 2k_\ell}D^1(t) +$$

$$\frac{k_{rad}}{2k_c + 2k_\ell}D^0(t). \qquad (30a)$$

The normalized instantaneous fluorescence yield is

$$F_n(t) = \frac{\Phi_f(t)}{\Phi_f(t=0)}. \qquad (30b)$$

Thus, for dimers the fluorescence induction kinetics can be described conveniently by an explicit analytical expression.

3.5. The domain theory for flash excitation

Exciton-exciton annihilation in domains is described in Den Hollander et al. [12] by the rate constant, $\overline{k}_a = k_a/\lambda$. The following solution for the product yield as a function of z_0 has been derived from a master equation analogous to that used for fluorescence induction, but extended for annihilation of excitons [12]:

$$Y(z_0) = \frac{k_o}{\lambda^2(k_\ell + k_o + k_c)}\sum_{k=1}^{\infty}\frac{(-\lambda z_0)^{k-1}z_0 \nu_{\lambda,k}}{k!} \qquad (31a)$$

with the recurrent coefficients

$$\nu_{n,k+1} = \frac{k + \alpha_n}{k + \beta_n}\nu_{n,k} - \frac{\alpha_n \beta_n}{\beta_{n-1}(k + \beta_n)}\nu_{n-1,k}$$

and $\nu_{n,1} = n$ where $n = 0, 1, ..., \lambda$ denotes the open traps per domain at $t = 0$. The summation index runs from one to infinity, $k = 1, 2, ..., \infty$. The parameters α_n and β_n are given by:

$$\alpha_n = \frac{2nk_o}{k_a} \text{ and } \beta_n = \frac{2\lambda\left[k_\ell + \frac{n}{\lambda}k_o + \left(1 - \frac{n}{\lambda}\right)k_c\right]}{k_a}.$$

For δ-flash excitation the initial condition is again a Poisson distribution of the excitons over the domains (analog to Eq. 15). The fluorescence yield as a function of z_0, normalized to the fluorescence yield in the low energy limit, results as an infinite sum:

$$F_n(z_0) = \sum_{k=1}^{\infty} \frac{(-\lambda z_0)^{k-1} u_{\lambda,k}}{k!} \tag{31b}$$

with the recurrent coefficients

$$u_{n,k+1} = \frac{k + \alpha_n}{k + \beta_n} u_{n,k} - \frac{\alpha_n \beta_n}{\beta_{n-1}(k + \beta_n)} u_{n-1,k}$$

and $u_{n,1} = 1$.

The kinetics of the product and the fluorescence yield can be derived by solving the master equations numerically.

4. Results

4.1. Predictions for experimental tests

4.1.1. Kinetics

In this section we inspect, in the framework of the connected units model, the influence of the connectivity on the kinetics of product formation and exciton decay upon δ-function flashes. Annihilation is accounted for by choosing for the competition parameter $\alpha = 2$; for the quotient of the different quenching powers of open and closed RCs we choose $k_o/k_c = 3$, which simulates the situation in purple bacteria (Trissl [21] and references therein). In Fig. 2 we compare the kinetics for different excitation energies and different antenna organizations. The kinetics of product formation and exciton decay for the *lake model* are shown in Fig. 2a,b. In agreement with previous results [25,37,38] a significant fraction of RCs cannot be closed even with highest intensity flashes ($z_0 = 10$), and the trapping kinetics (initial slopes) are strongly accelerated with increasing excitation energy. A similar strong acceleration is predicted for the exciton decay as demonstrated in the inset of Fig. 2b which presents the data in a normalized manner.

The kinetics of product formation and exciton decay for the *connected units model* were calculated for three different values of k_{con} (∞, $(50 \text{ ps})^{-1}$, 0) as

shown in Fig. 2. The three sets of traces look very similar, the most notable difference being an increase of the final product yields Y_0 with decreasing connectivity.

As expected, the differences between the corresponding kinetics calculated from the domain theory with $\lambda = 1$ and 3 were similarly small (data not shown).

4.1.2. Yields

The final product yields and the normalized fluorescence yields as a function of the energy of δ-function flashes are shown in Fig. 3. To illustrate the influence of the connectivity and the model (domain vs. connected units) we varied k_{con} in the connected units model (for $k_o/k_c = 1$ as well as $k_o/k_c = 3$) and compared the results for $k_o/k_c = 3$ with the ones from the domain theory. The special case $k_o = k_c$ is equivalent to the experimental situation in which fluorescence quenching curves are measured with closed RCs only, a case that has been theoretically treated for domains by Paillotin et al. [11]. In both theories an increase in connectivity leads to a decrease in product yields (Fig. 3a,c,e) and also to diminished fluorescence yields (Fig. 3b,d,f). A notable effect of k_{con} is on the slope of the curves at half quenching in all examples considered. The influence of different quenching power between open and closed RCs ($k_o/k_c = 1$ vs. $k_o/k_c = 3$) on the product yield is small but recognizable (Fig. 3a,c). The same holds true for the normalized fluorescence yields (Fig. 3b,d).

4.1.3. Comparison of the models

To check whether the connected units model and the domain model can be distinguished experimentally, we used the results for the fluorescence yield with a given set of rate constants from the domain theory assuming $\lambda = 4$ and fitted these data with the connected units theory, using k_{con} as a fit parameter. All other rate constants as well as the z_0 ordinate were kept identical. (The assumption of the same z_0-scale presumes that it is possible to assess it experimentally with high precision which is difficult in practice.) We did the fitting for two different values of k_o/k_c ($k_o/k_c = 1$ and $k_o/k_c = 3$) to simulate the photosystems of higher plants and purple bacteria. As a general result we notice that all deviations are below the 2% level (Fig. 4). In the case of equal quenching
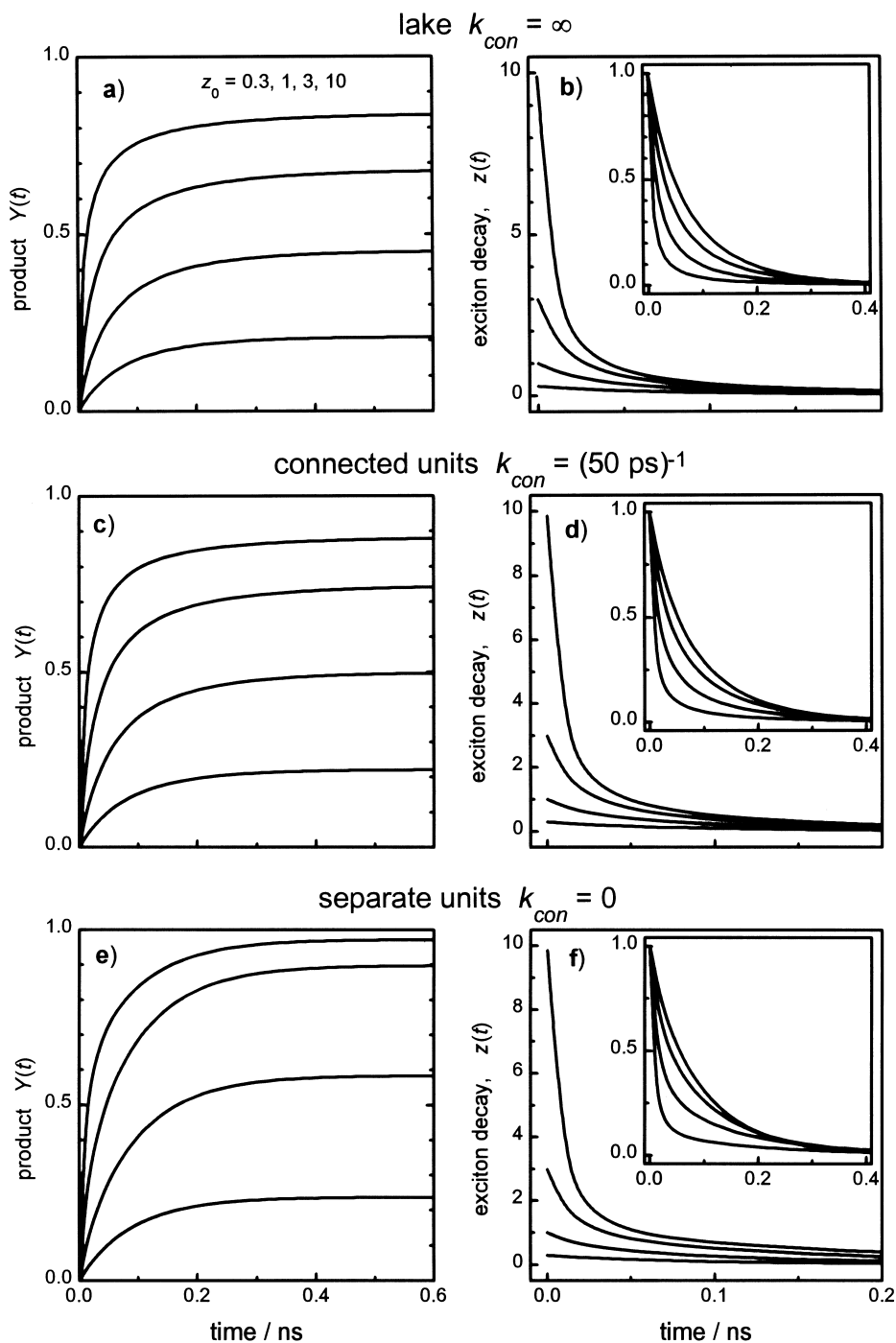
Fig. 2. Kinetics of product formation and excited state decay calculated for the connected units model. (a) Kinetics of product formation for a lake-like case: $k_{con} = (5\ ps)^{-1}$, $k_o = (100\ ps)^{-1}$, $k_c = (300\ ps)^{-1}$, $k_a = (40\ ps)^{-1}$, $\alpha = 2$, $z_0 = 0.3$, 1, 3, 10. (b) Kinetics of exciton decay for the same parameters as in (a). Inset: kinetics normalized to the fluorescence at $t = 0$. (c) Kinetics of product formation for a connected unit case: $k_{con} = (50\ ps)^{-1}$, $k_o = (100\ ps)^{-1}$, $k_c = (300\ ps)^{-1}$, $k_a = (40\ ps)^{-1}$, $\alpha = 2$, $z_0 = 0.3$, 1, 3, 10. (d) Kinetics of exciton decay for the same parameters as in (c). Inset: kinetics normalized to the fluorescence at $t = 0$. (e) Kinetics of product formation for a separate units case: $k_{con} = 0$, $k_o = (100\ ps)^{-1}$, $k_c = (300\ ps)^{-1}$, $k_a = (40\ ps)^{-1}$, $\alpha = 2$, $z_0 = 0.3$, 1, 3, 10. (f) Kinetics of exciton decay for the same parameters as in (e). Inset: kinetics normalized to the fluorescence at $t = 0$.
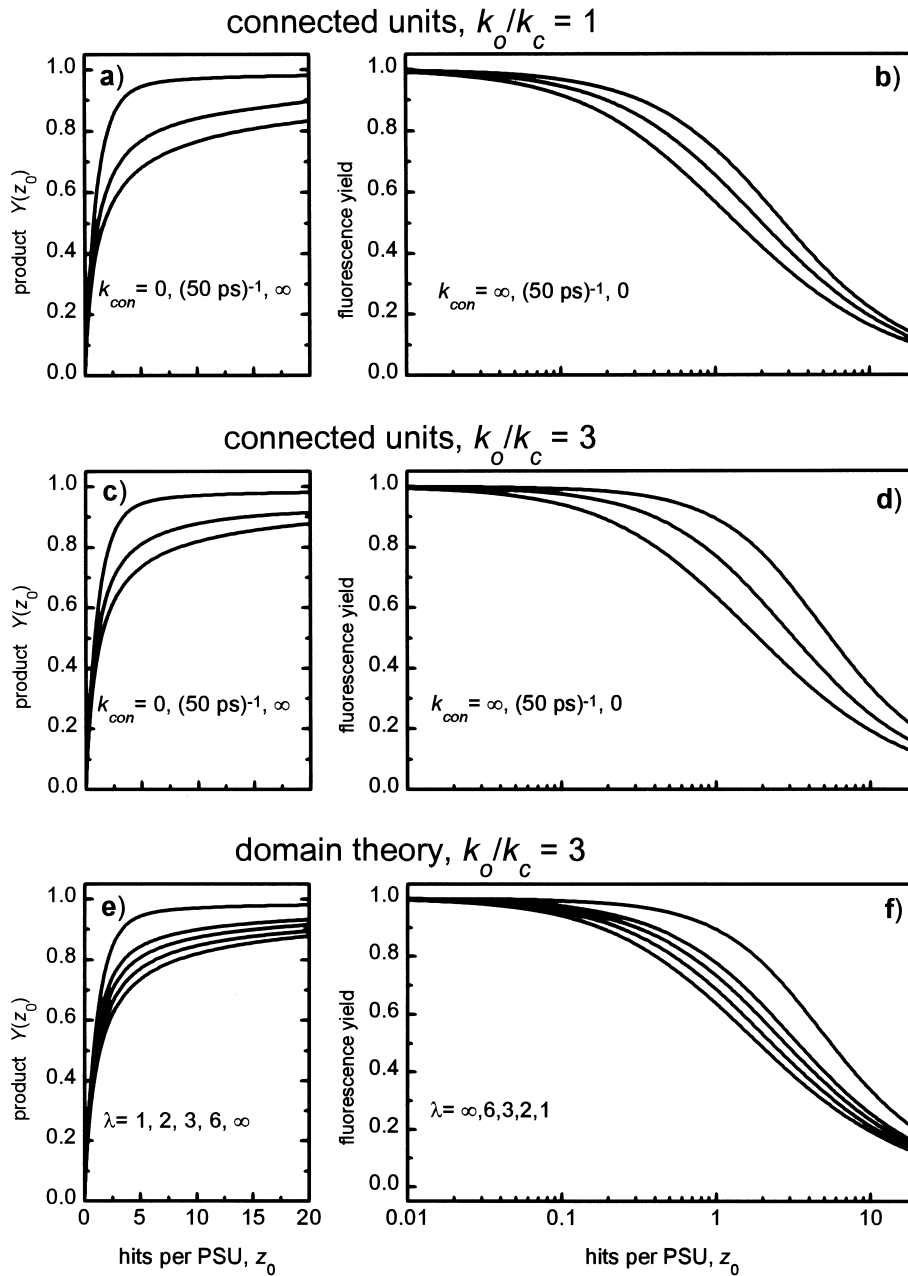
Fig. 3. Influence of the quotient k_o/k_c at different degrees of connectivity and comparison of the connected units model and the domain model. (a, b) Saturation curves for lake, connected units ($k_{con} = (50$ ps$)^{-1}$) and separate units (domain size $\lambda = 1$) for parameters as in Fig. 2, except $k_o = k_c = (100$ ps$)^{-1}$. (c, d) Saturation curves for lake, connected units ($k_{con} = (50$ ps$)^{-1}$) and separate units (domain size $\lambda = 1$) for parameters as in Fig. 1. (e, f) Saturation curves for domain theory with parameters as in Fig. 1 and the domain sizes $\lambda = 1, 2, 3, 6, \infty$.

powers the residuals of the fit are even below 0.5% (Fig. 4d).

The above model calculations show that excitation with ps flashes is hardly suited to distinguish between the different theoretical approaches. A corresponding model calculation by Trissl and Lavergne [20] shows that classical fluorescence induction with cw light may be a better option: specifically, the residuals resulting from a fit of fluorescence induction curves calculated by the *domain model* for $\lambda = 2$ and 5 with
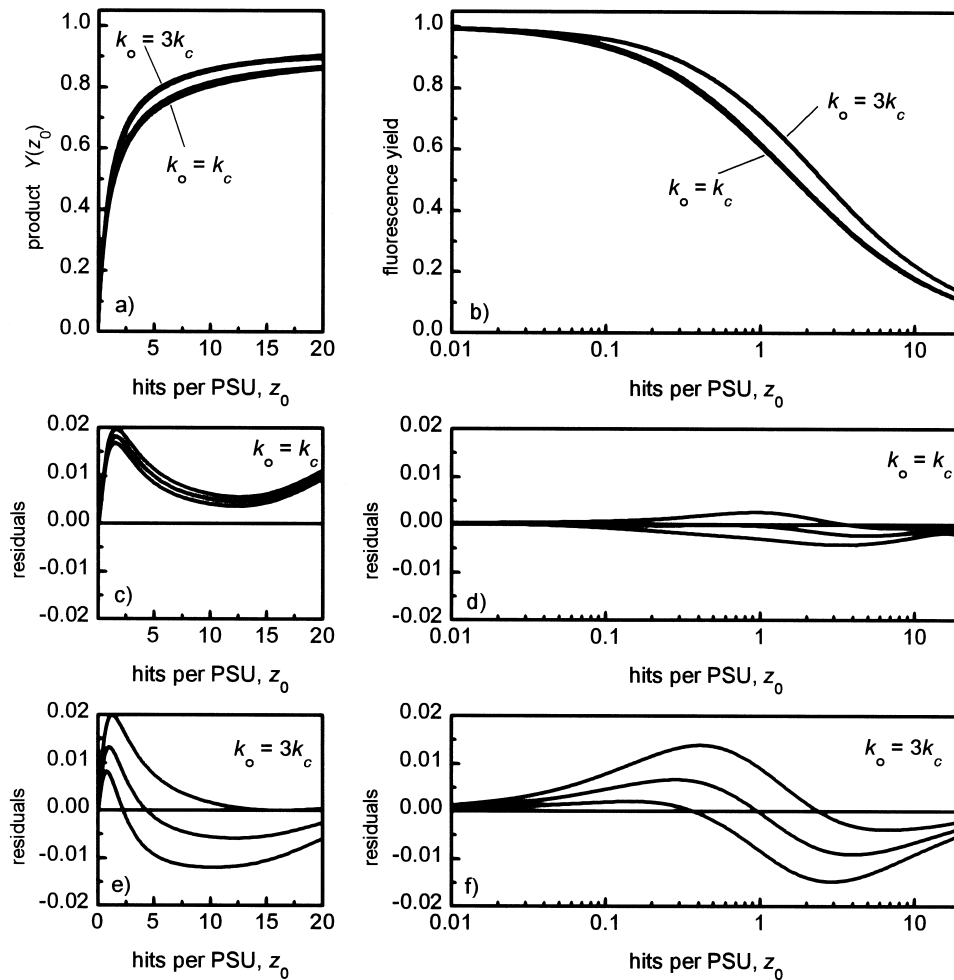
Fig. 4. Comparison of the domain and connected units theory. Parameters: upper curves and upper residuals: $k_o = (100 \text{ ps})^{-1}$, $k_c = (300 \text{ ps})^{-1}$, $k_a = (40 \text{ ps})^{-1}$, $\alpha = 2$, $\lambda = 4$, connected units-model: $k_{con} = (18, 19, 20 \text{ ps})^{-1}$. Lower curves and lower residuals: $k_o = (100 \text{ ps})^{-1}$, $k_c = (100 \text{ ps})^{-1}$, $k_a = (40 \text{ ps})^{-1}$, $\alpha = 2$, $\lambda = 4$, connected units model: $k_{con} = (15, 20, 25 \text{ ps})^{-1}$.

theoretical curves from the *connected units model* are on the order of 10–30%. This shows clearly that for assaying the antenna organization, fluorescence induction measurements with cw light are superior to measurements of kinetics and yields with ps flashes.

4.1.4. Comparison of cw and flash excitation for different connectivities

Next we want to check which one of the two excitation sources (cw light vs. flash) is better suited to distinguish between different degrees of connectivity in the absence of annihilation. The main difference between the two types of excitation is that in the case of cw light the instantaneous fluorescence yield is measured, whereas in the case of flashes the integral fluorescence yield is measured. (Note: the flash

curves follow from the cw light curves by integrating the latter, $F_n(z0) = 1/[\Phi_F(q = 1)] \int_0^{z_0} [\Phi_F(z)]/z \, dz$.) The corresponding induction curves for cw and flash excitation in the separate units and lake case using the semi-logarithmic z_0 scale are shown in Fig. 5a and b, respectively. The differences between the separate units and lake case are shown in Fig. 5c for cw excitation and in Fig. 5d for flash excitation. It is obvious that the connectivity (separate units vs. lake) has more influence on the shape of the curve for cw light than for flash excitation. Therefore, classical fluorescence induction curves obtained by cw excitation are the preferable experimental assay.

In contrast to the fluorescence yields, the product yields for cw light and flashes *without annihilation* are identical and the curves are indistinguishable.
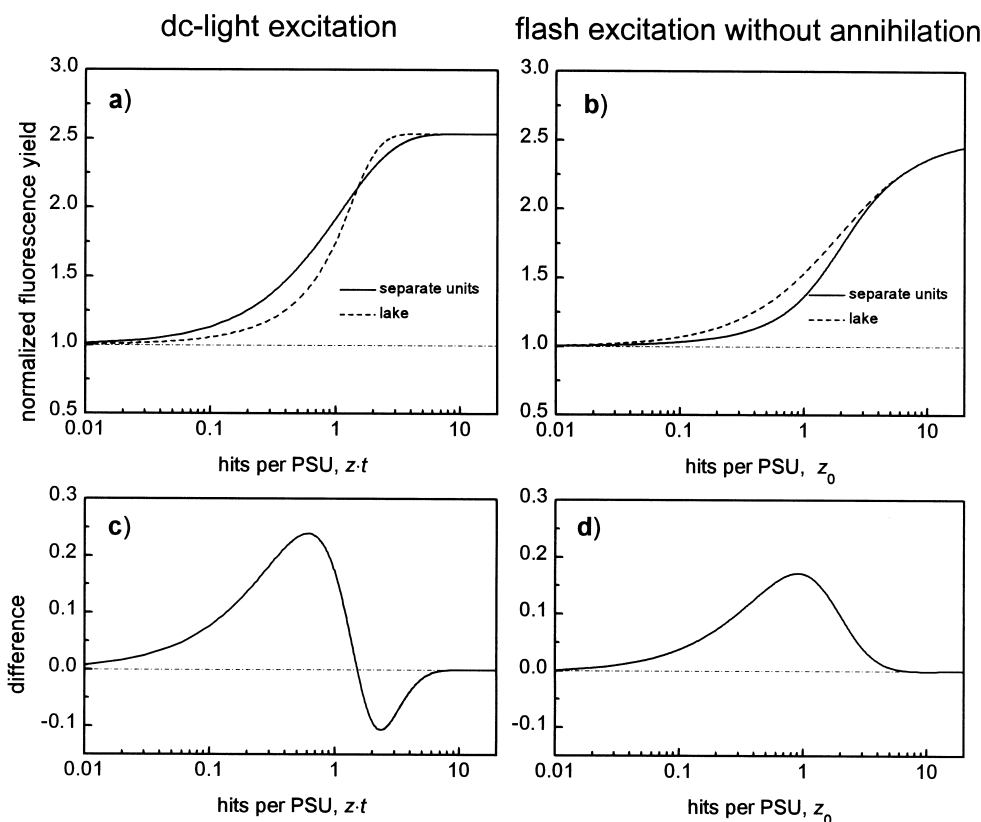
Fig. 5. Comparison between classical fluorescence induction curves (cw light) and fluorescence yield increase due to flash excitation under non-annihilation conditions for the extreme cases of separate units (a) and lake (b). Parameters: $k_o = (100 \text{ ps})^{-1}$, $k_c = (300 \text{ ps})^{-1}$, $k_\ell = (1 \text{ ns})^{-1}$, $\alpha = 0$. (c, d) The differences between the limiting cases for the two different excitation conditions.

At this occasion we want to briefly discuss pump-probe experiments, which are often used for the fluorescence yield assay. If the flashes exclude exciton-exciton interactions the fluorescence yield due to the probe flash is determined by the product yield of the pump-flash and is therefore given by the fluorescence yield of the corresponding cw excitation (with same energy $z{\cdot}t$ as the pump flash, z_0; Fig. 5a). This means that the fluorescence yield due to the probe flash as a function of the pump-flash energy necessarily displays the same sigmoidicity as classical fluorescence induction curves, provided that there are really only two fluorescent states involved. This condition may experimentally not always be met [39,40], in particular when using microsecond pump flashes [41]. Depending on the duration of the pump flash and the kinetics of the electron transport processes additional interactions of an incoming exciton with triplet states or intermediate redox states of the RC (like S states in the case of PS II etc.) that quench differently may

be the cause for more than two fluorescent states and require more detailed treatments.

4.1.5. Fluorescence decay kinetics in the low energy limit with mixed RCs

The high repetition rate in single photon timing measurements often produces a steady-state mixture of open and closed RCs. This leads to multiphasic decays for two reasons: first, two different fluorescent states are involved, and second, exciton transfer from closed to open RCs influences the detailed kinetics. To inspect the influence of the connectivity on the decay kinetics we took the connected units model and calculated in Fig. 6 the normalized exciton decay for different degrees of connectivity ($k_{con} = 0$, $k_{con} = (200 \text{ ps})^{-1}$, $k_{con} = (50 \text{ ps})^{-1}$, $k_{con} \rightarrow \infty$), setting q at 0.5 (50% of the RCs are closed). For comparison, the all open and all closed cases – which are invariant of the connectivity – are also shown. These latter curves are monophasic. Obviously, for a mix-
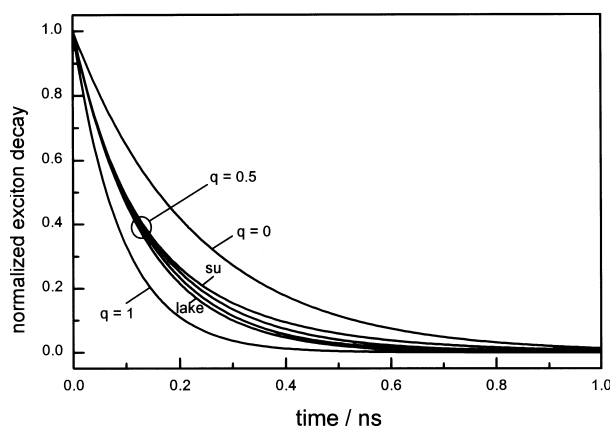
Fig. 6. Normalized exciton decay kinetics for different values of q and weak δ-function flash excitation ($z_0 = 0.001$) and various connectivities. In the cases of all open or all closed RCs ($q = 1$ or $q = 0$) the kinetics are identical and do not depend on the connectivity. For $q = 0.5$ four traces were calculated with the parameter set: $k_o = (100 \text{ ps})^{-1}$, $k_c = (300 \text{ ps})^{-1}$, $k_\ell = (1 \text{ ns})^{-1}$, $k_{con} = 0$ (su: separate units), $k_{con} = (200, 50, 1 \text{ ps})^{-1}$.

ture of open and closed RCs the kinetics are also monophasic for the lake model but biphasic for the separate units model. However, for intermediate values of connectivity the kinetics cannot be described as a finite sum of exponential functions. Nevertheless it may be hard to experimentally distinguish between our mathematical curve and an exponential approximation: we attempted to fit a decay curve calculated with $q = 0.33$ and $k_{con} = (200 \text{ ps})^{-1}$ with two, three and four exponentials. The maximal deviations occurred at short times and amounted to only 5×10^{-5} for two exponentials and 2×10^{-5} for three and four exponentials.

4.2. Limiting cases and convergences

Above we have outlined a unified mathematical description of different models of antenna organization. Clearly, results calculated for limiting forms of antenna organizations with the different theoretical approaches must converge. For instance, (i) the separate units case can both be described by the connected units theory ($k_{con} = 0$) and by the domain theory ($\lambda = 1$). It can easily be shown that for this case, Eqs. 16a and b and the master equations of the domain theory are identical. (ii) Also the lake case can be described both by the connected units theory ($k_{con} \to \infty$) and by the domain theory ($\lambda \to \infty$). We

checked numerically that the results of both treatments agree with the analytical solutions given by Eqs. 20a and b. (iii) In the early literature [11,42] the extreme case of total annihilation in separate units has been considered. If all excitons in a separate units model, except the last one, get lost by annihilation before performing photochemistry, the normalized fluorescence yield is given by [11,42]:

$$F_n(z_0) = \frac{1}{z_0} \sum_{i=1}^{\infty} \frac{z_0^{i-1}}{i!} e^{-z_0} = \frac{1}{z_0}(1 - e^{-z_0}). \qquad (32)$$

Both the connected units theory and the domain theory converge to this limiting case when choosing $k_a \to \infty$. The same mathematical relation has been derived by Mauzerall, who assumed the annihilation process to occur only at the RC [42,43] rather than anywhere in a PSU, as we did. However, this does not influence kinetics as the description of exciton-exciton annihilation in a PSU by a rate constant k_a leaves open where the process occurs.

5. Summary and conclusions

- In this paper we have introduced a consistent nomenclature to describe gradual connectivity of photosynthetic units in the photosynthetic membrane for two theoretical approaches, namely the connected units model and the domain model.
- The formalism for the connected units model – which has been applied to classical fluorescence induction curves – is extended to flash excitation without and with annihilation.
- A new, simple mathematical formalism of the domain model for cw and flash excitation without annihilation is given.
- We show that the different theoretical approaches converge for various limiting cases.
- We used our unified formalism to calculate curves of product saturation and fluorescence quenching for the various models. From these curves we conclude that – if at all – cw excitation is better suited than flash excitation to distinguish between the models.
- The calculations also show that the parameters of exciton-radical pair equilibrium model can only be determined from flash experiments in the low en-

ergy limit. They cannot be extracted from classical fluorescence induction measurements and can only be grossly estimated from experiments with intense flashes.

6. List of symbols

k_{I}	rate constant for losses in the antenna
k_{con}	rate constant for inter-unit exciton transfer
k_{o}	rate constant for trapping by open RCs
k_{c}	rate constant for trapping by closed RCs
k_{rad}	rate constant for fluorescence
k_{a}	rate constant for singlet-singlet annihilation
z	excitons created per PSU and time
$z^{\mathrm{o}}, z^{\mathrm{c}}$	exciton concentration per PSU with open/closed RC
z_0	flash energy described as excitons per PSU
$\tilde{z}(t)$	time dependent exciton generation
$F_{\mathrm{o}}, F_{\mathrm{m}}$	measured fluorescence for all RCs open or closed
F_{n}	normalized fluorescence yield
x_{p}	product quantum yield
x_{f}	instantaneous fluorescence yield
t	time
K	competition parameter
Y	product yield
$U_i^{\mathrm{o/cu}}$	concentration of PSUs with open/closed RCs and i excitons
q	normalized concentration of open RCs
i, l, j	number of excitons in a PSU or domain
n, m	number of open traps in a domain
K_n, L_n	coefficients in the domain theory
$u_{n,k}, X_{n,k}$	coefficients in the domain theory
$P(t)$	overall probability for the loss of one exciton in a domain
W, X	coefficients in domain theory
D^j	concentration of domains with j excitons
k_K, k_L	rate constants in the ODE treatment of domains without annihilation
p^j	probability of exciton decay by closing one RC in a domain with j RCs open

Acknowledgements

Appendix A

In the following we show that for low light excitation, where the concentration of PSUs with more than one exciton are negligible, the ODEs of the connected units model with annihilation (Eqs. 16a and b) converge to the connected units model without annihilation (Eqs. 5a, b and c). For low light excitation conditions one can equate $U_1^{\mathrm{o}} = z^{\mathrm{o}}$, $U_1^{\mathrm{c}} = z^{\mathrm{c}}$, $q = U_0^{\mathrm{o}} + U_1^{\mathrm{o}} = U_0^{\mathrm{o}} + z^{\mathrm{o}}$ and $1-q = U_0^{\mathrm{c}} + U_1^{\mathrm{c}} = U_0^{\mathrm{c}} + z^{\mathrm{c}}$ and $U_i^{\mathrm{o/c}} = 0$ for $i > 1$. Then Eqs. 16a and b simplify to:

$$\frac{dU_1^{\mathrm{o}}}{dt} = \frac{dz^{\mathrm{o}}}{dt} =$$

$$-(k_\ell + k_{\mathrm{o}} + k_{\mathrm{con}})z^{\mathrm{o}} + k_{\mathrm{con}}(z^{\mathrm{o}} + z^{\mathrm{c}})(U_0^{\mathrm{o}} - z^{\mathrm{o}})$$

$$= -(k_\ell + k_{\mathrm{o}})z^{\mathrm{o}} + k_{\mathrm{con}}[(z^{\mathrm{o}} + z^{\mathrm{c}})(q - 2z^{\mathrm{o}}) - z^{\mathrm{o}}],$$
$$(A1a)$$

$$\frac{dU_1^{\mathrm{c}}}{dt} = \frac{dz^{\mathrm{c}}}{dt} =$$

$$-(k_\ell + k_{\mathrm{c}} + k_{\mathrm{con}})z^{\mathrm{c}} + k_{\mathrm{con}}(z^{\mathrm{o}} + z^{\mathrm{c}})(U_0^{\mathrm{c}} - z^{\mathrm{c}})$$

$$= -(k_\ell + k_{\mathrm{c}})z^{\mathrm{o}} + k_{\mathrm{con}}[(z^{\mathrm{o}} + z^{\mathrm{c}})(1 - q - 2z^{\mathrm{c}}) - z^{\mathrm{c}}].$$
$$(A1b)$$

For the low energy limit the quadratic terms in z can be neglected and one obtains Eqs. 5a and b, which demonstrates the consistency of our formalism.

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