

THEORY OF EXCITATION ENERGY TRANSFER IN THE PRIMARY PROCESSES OF PHOTOSYNTHESIS I. GENERAL RESULTS

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A general theory of the excitation energy transfer in the primary processes of photosynthesis based on the generalized master equation is formulated. The work provides a general theoretical description of four different regimes of the excitation energy transfer, analyzes the contribution of these regimes to the quantum yield characterizing the total efficiency of the transfer processes, presents a general analysis of mutual relations of nine experimental observables, takes into consideration limitations following from a finite experimental resolution and clarifies question what information on the excitation energy transfer processes can be obtained from experimental observables.

1. Introduction

The excitation energy transfer in the primary processes of photosynthesis, i.e. the excitation energy transfer from the antenna system (A) to the reaction center (RC), is very fast (transfer time to the RC is less than 1 ns) and very efficient (the corresponding quantum yield is higher than 0.9) [1-5]. These features of the transfer have been investigated in a number of works [1-25], however, all the so far investigated theoretical models have only a limited range of applicability (assumption of the coherent or incoherent exciton motion, finiteness of the experimental resolution is not usually taken into account, numerical solution of the problem does not allow to find an explicit dependence of the experimental observables on the model parameters, etc.).

Many experimental papers have been devoted to standard optical methods (fluorescence, phosphorescence, CD and LD spectroscopy, ...) with the belief that detailed information on the intermolecular energy transfer can be obtained from the experimental results. One of our aims is to clarify this question.

For these reasons, we decided to develop a theoretical description of the excitation energy transfer which is quite general as far as the most interesting step of the transfer, i.e. the intermolecular one it is con-

cerned. Discussing this model and using arguments as general as possible we make an attempt to find the *first principle* answers to the following fundamental problems.

(1) What are physical reasons of the high value of the quantum yield η_{CT} of the excitation energy transfer to the charge transfer state (CT) of the RC? We would also like to know on what parameters this quantum yield depends. An interesting question is the dependence of the yield on the geometry and structure of the photosynthetic unit (PSU).

(2) What information on the intermolecular transfer may be obtained from the experimental observables?

(3) What is the effect of a finite experimental resolution and other usual experimental conditions on the attainability of this information?

(4) What is the mutual relation of the experimental observables?

(5) What is the importance of different transfer regimes – coherent (short times), intermediate and incoherent (long times) – from the point of view of the efficiency of the excitation energy transfer to the RC? In other words, we want to know what is the contribution of these regimes to η_{CT} .

Keeping generality of the discussion throughout part I of this work on a high level we arrive at conclusions that should apply to any photosynthetic system.

In part II [26], we make use of the recent information on the geometry of the PSU in the bacterial photosynthesis [27] and discuss the most important incoherent stage of the transfer in more detail.

The structure of sections 2–9 of part I is as follows. In section 2, we describe the model consisting of N antenna Chl molecules with S_0 , S_1 and T_1 energy levels and the RC special Chl pair which has besides of these levels also the charge transfer state CT. The geometrical arrangement of the Chl molecules may be arbitrary. The excitation moves from the antenna system to the CT level which acts as a trap representing subsequent electron transfer and photochemical and chemical processes. Sections 3–6 are devoted to a general discussion in which no concrete assumptions about the mechanism of the excitation energy transfer of a limited applicability are made. After the definition of nine experimental observables (section 3) equations of motion in the form of the generalized master equation (GME) are formulated (section 4). Using generally valid results for the GME we show in section 5 that only one of the observables is independent. The following discussion in sections 6–9 concerns the intensity of the antenna fluorescence as the independent observable. The effect of the experi-

mental resolution on the measured observables is discussed in section 6. In sections 7 and 8 we use the Pauli master equation (PME), Schrödinger equation and interpolation formula to get more information on the possible form of the observables in the incoherent, coherent and intermediate regime. Concluding remarks are given in section 9. In the appendix, the most important results regarding the Liouville equation, GME and PME for a non-Hermitian Hamiltonian are presented.

2. Model and description of intramolecular processes

Our model (see fig. 1) takes into consideration only the parts of the PSU important from the point of view of the excitation energy transfer. The detailed structure of the antenna and RC complexes (see e.g. ref. [28]) is not considered explicitly here and the influence of the other parts of the PSU is taken into account only indirectly. This should not lead to any significant changes of the results since the intermolecular transfer among the S_1 states is described generally. The antenna system is represented by the Chl molecules having S_0 , S_1 and T_1 levels which may in general

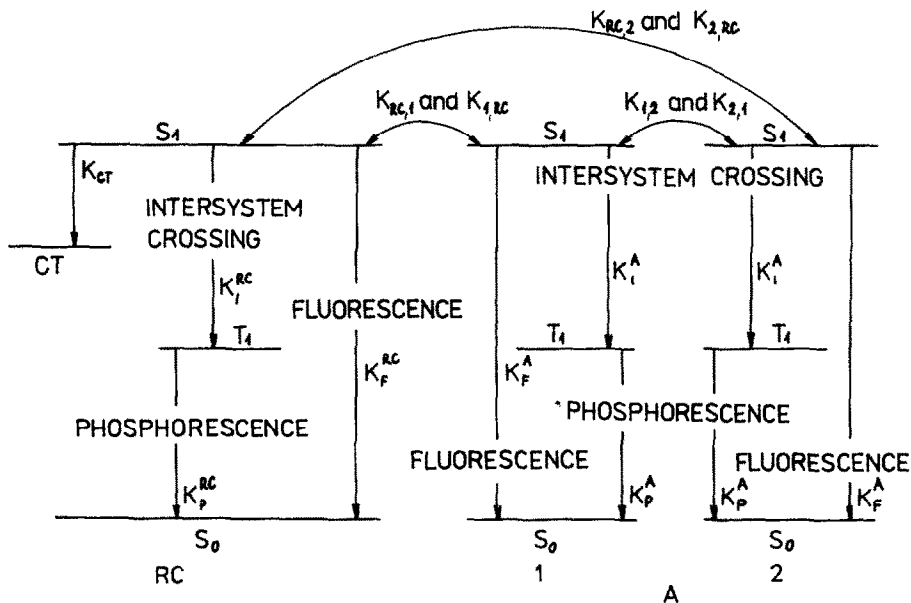


Fig. 1. Model of the excitation energy transfer processes in the PSU. Two antenna Chl molecules (S_0 , S_1 and T_1 levels) and the RC special pair (S_0 , S_1 , T_1 and CT levels) together with the corresponding intramolecular and intermolecular transfer processes are shown (arrows).

be different in different molecules. The RC is represented by the special pair of the two Chl molecules and has the same S_0 , S_1 , T_1 levels and the CT level. The CT state is a trap representing processes leading to the creation of the electron–hole pair. The geometrical arrangement of the antenna Chl molecules and the special pair as well as the orientation of their dipole moments can be arbitrary, including the globule structure [25].

The intramolecular processes (fluorescence, phosphorescence, transfer to the CT state and intersystem crossing) are described by means of usual kinetic equations,

$$\frac{dP_{CT}}{dt} = k_{CT}P_{RC}, \quad (2.1)$$

$$\frac{dP_{RC}^{T_1}}{dt} = k_1^{RC}P_{RC} - k_P^{RC}P_{RC}^{T_1}, \quad (2.2)$$

$$\frac{dP_{RC}^{S_0}}{dt} = k_P^{RC}P_{RC}^{T_1} + k_F^{RC}P_{RC}, \quad (2.3)$$

$$\frac{dP_m^{T_1}}{dt} = k_1^\wedge P_m - k_P^\wedge P_m^{T_1}, \quad m \in A, \quad (2.4)$$

$$\frac{dP_m^{S_0}}{dt} = k_P^\wedge P_m^{T_1} + k_F^\wedge P_m, \quad m \in A. \quad (2.5)$$

Here, $P_{RC}^{T_1}$ and $P_{RC}^{S_0}$ denote probabilities of finding the RC at the T_1 and S_0 state, respectively. Analogously, $P_m^{T_1}$ and $P_m^{S_0}$ are probabilities of finding the m th antenna Chl molecule in the T_1 and S_0 state. P_{RC} and P_m (no superscript) are probabilities of finding the RC and the m th antenna at the S_1 state mediating the intermolecular excitation transfer. The kinetic equations for P_{RC} and P_m are given in section 4. The intermolecular transfer among the T_1 levels is not considered in our model. We assume also a low light intensity so that any mutual interaction of the excitons or their annihilation is not considered. The non-radiative de-excitation processes, except for the intersystem crossing, are not considered in the model. If necessary they can be included into eqs. (2.1)–(2.5) as additional terms. A denotes the Chl molecules in the antenna system.

The values of the intramolecular rate constants used throughout this work were obtained from a critical

survey of the literature on the bacterial photosynthesis: $k_F^\wedge = 6.7 \times 10^7 \text{ s}^{-1}$ (the $S_1 \rightarrow S_0$ antenna fluorescence rate constant), $k_F^{RC} = 1.34 \times 10^8 \text{ s}^{-1}$ (the $S_1 \rightarrow S_0$ RC fluorescence), $k_1^\wedge = k_1^{RC} = 1.34 \times 10^8 \text{ s}^{-1}$ (the $S_1 \rightarrow T_1$ antenna and RC intersystem crossing), $k_P^\wedge = k_P^{RC} = 5.9 \times 10^2 \text{ s}^{-1}$ (the $T_1 \rightarrow S_0$ antenna and RC phosphorescence), $k_{CT} = 3.3 \times 10^{11} \text{ s}^{-1}$ (the $S_1 \rightarrow CT$ reaction center rate constant) [8,29–32]. We use these rate constants for estimates rather than for exact calculations so that their values are not critical.

3. Definition of observables

Assuming that only a single photon is absorbed at $t=0$ the RC and antenna fluorescence intensities I_F^{RC} and I_F^\wedge (the $S_1 \rightarrow S_0$ transitions) are proportional to the probability of finding the exciton at the S_1 reaction center and antenna levels, respectively,

$$I_F^{RC}(t) = k_F^{RC}P_{RC}(t), \quad (3.1)$$

$$I_F^\wedge(t) = k_F^\wedge \sum_{m \in A} P_m(t). \quad (3.2)$$

If several different spectral forms of the antenna pigment–protein complexes were introduced $I_F^\wedge(t)$ would represent the total fluorescence intensity of all the forms. The time-dependent quantum yields of the corresponding fluorescences may be defined as

$$\eta_F^{RC}(t) = \int_0^t I_F^{RC}(\tau) d\tau, \quad (3.3)$$

$$\eta_F^\wedge(t) = \int_0^t I_F^\wedge(\tau) d\tau. \quad (3.4)$$

The usual quantum yields are obtained for $t \rightarrow \infty$. Analogous quantities for the phosphorescence ($T_1 \rightarrow S_0$ transitions) equal

$$I_P^{RC}(t) = k_P^{RC}P_{RC}^{T_1}(t), \quad (3.5)$$

$$I_P^\wedge(t) = k_P^\wedge \sum_{m \in A} P_m^{T_1}, \quad (3.6)$$

$$\eta_P^{RC}(t) = \int_0^t I_P^{RC}(\tau) d\tau, \quad (3.7)$$

$$\eta_{\hat{P}}^{\hat{A}}(t) = \int_0^t I_{\hat{P}}^{\hat{A}}(\tau) d\tau. \quad (3.8)$$

A quantity characterizing the total efficiency of the primary processes of photosynthesis is the quantum yield of the excitation energy transfer to the reaction center CT level,

$$\eta_{CT}(t) = P_{CT}(t). \quad (3.9)$$

The time-dependent definition of the quantum yield $\eta_{CT}(t)$ makes possible to calculate the contribution of the transfer processes on a given time interval $(0, t)$ to the total yield $\eta_{CT}(t \rightarrow \infty)$. The quantum yield (3.9) and the fluorescence intensities $I_{\hat{P}}^{\hat{A}}$ and $I_{\hat{P}}^{\text{RC}}$ are the most important observables discussed in the following sections.

4. Kinetic equations for observables

The kinetic equations for $I_{\hat{P}}^{\text{RC}}$ and $I_{\hat{P}}^{\hat{A}}$ describing the intersystem crossing and phosphorescence (see fig. 1 and eqs. (2.2), (3.1), (3.5), (2.4), (3.2) and (3.6)) are

$$\frac{dI_{\hat{P}}^{\text{RC}}}{dt} = k_{\hat{P}}^{\text{RC}} k_{\hat{I}}^{\text{RC}} / k_{\hat{F}}^{\text{RC}} I_{\hat{F}}^{\text{RC}} - k_{\hat{P}}^{\text{RC}} I_{\hat{P}}^{\text{RC}}, \quad (4.1)$$

$$\frac{dI_{\hat{P}}^{\hat{A}}}{dt} = k_{\hat{P}}^{\hat{A}} k_{\hat{I}}^{\hat{A}} / k_{\hat{F}}^{\hat{A}} I_{\hat{F}}^{\hat{A}} - k_{\hat{P}}^{\hat{A}} I_{\hat{P}}^{\hat{A}}. \quad (4.2)$$

To describe the intermolecular transfer among the S_1 antenna and RC levels we use a general formalism based on the generalized master equation (GME) (see e.g. refs. [33–35] and appendix). Most of the theoretical works assume the incoherent (diffusion like) character of the exciton motion [10,12–14,17, 19,21–25] leading to a relatively easily solvable Pauli master equation (PME) [36]. The relaxation time t_{rel} of the transition from the coherent to incoherent exciton motion depends on the radiative losses and the interaction of the electronic system with other degrees of freedom of the PSU. It should obviously be larger than the period of the characteristic vibrations of the Chl molecules, $t_{\text{rel}} > 10^{-14} - 2 \times 10^{-13}$ s [37]. The condition of the applicability of the incoherent description of the excitation energy transfer in the PSU is $t \gg t_{\text{rel}}$. On the other hand, the coherent (wave-like) formulation of the excitation transfer theory

neglecting the dephasing processes can be used for very short times $t \ll t_{\text{rel}}$. According to ref. [38] the time of the decay of the memory functions for the bacteriochlorophyll which characterizes the transition from the coherent to incoherent character of the exciton motion amounts $t_{\text{rel}} \approx 3 \times 10^{-14}$ s. Ref. [15] using the Haken–Strobl model as well as the investigation of some general features of electronic systems interacting with the thermodynamical bath [39] indicates much longer validity of the coherent regime (over 1 ps). These two last investigations however, are based on the idea of one electronic system interacting with one vibrational thermodynamic bath while the situation in the PSU is different. It is rather a complex system of electronic, vibrational and rotational states of individual chlorophyll molecules mutually interacting relatively weakly. The approach used in these works does not seem therefore adequate to photosynthesis. We note, however, that a largely coherent character of the excitation motion would lead to such effects as the dependence of the luminescence quantum yield on initial conditions [40,41].

The description of the excitation energy transfer in the PSU on a quite general level can be achieved by means of the Liouville equation (see e.g. ref. [34]). The corresponding density matrix ρ , however, carries complete information on the system so that its projection to a physically relevant partial information is usually made. As a result, the GME for the relevant part is obtained (see e.g. refs. [33–35,43–45] and appendix).

The GME allows to consider the general character of the exciton motion (coherent, incoherent or intermediate), however, it has to be supplemented by the life time and trapping terms in agreement with the supposed intramolecular transitions from the S_1 levels,

$$\begin{aligned} \frac{dP_{RC}}{dt} = & \int_0^t \sum_m K_{RC,m}(t-\tau) P_m(\tau) d\tau \\ & + I_{RC} - (k_{\hat{F}}^{\text{RC}} + k_{\hat{I}}^{\text{RC}} + k_{CT}) P_{RC}, \end{aligned} \quad (4.3)$$

$$\begin{aligned} \frac{dP_n}{dt} = & \int_0^t \sum_m K_{n,m}(t-\tau) P_m(\tau) d\tau \\ & + I_n - (k_{\hat{F}}^{\hat{A}} + k_{\hat{I}}^{\hat{A}}) P_n, \quad n \in A. \end{aligned} \quad (4.4)$$

The derivation of this GME based on the use of the

non-Hermitian Hamiltonian with imaginary terms describing the losses in the PSU is given in the appendix. K_{mn} are memory functions, I_n are initial terms (see appendix) and the last terms on the right-hand side of eqs. (4.3) and (4.4) represent the intramolecular transitions from the S_1 levels (the fluorescence, intersystem crossing and transfer to the CT state; see fig. 1, eqs. (2.1)–(2.5) and appendix). The summation in eqs. (4.3) and (4.4) runs over all the RC and antenna S_1 levels.

Using the definitions of I_{F}^{RC} and I_{F}^{A} (eqs. (3.1) and (3.2)) we get from eqs. (4.3) and (4.4) the following kinetic equations:

$$\frac{1}{k_{\text{F}}^{\text{RC}}} \frac{dI_{\text{F}}^{\text{RC}}}{dt} = \int_0^t \sum_m K_{\text{RC},m}(t-\tau) P_m(\tau) d\tau + I_{\text{RC}} - \frac{k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}} + k_{\text{CT}}}{k_{\text{F}}^{\text{RC}}} I_{\text{F}}^{\text{RC}}, \quad (4.5)$$

$$\frac{1}{k_{\text{F}}^{\text{A}}} \frac{dI_{\text{F}}^{\text{A}}}{dt} = \sum_{n \in \text{A}} \int_0^t \sum_m K_{n,m}(t-\tau) P_m(\tau) d\tau + \sum_{n \in \text{A}} I_n - \frac{k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}}{k_{\text{F}}^{\text{A}}} I_{\text{F}}^{\text{A}}. \quad (4.6)$$

In general, the time dependence of the observables I_{F}^{RC} and I_{F}^{A} may be very complex and depends also on the initial conditions (via I_n). Fortunately, summation rules (A.10) and (A.11) for K_{mn} and I_n allow to derive from eqs. (4.5) and (4.6) a relatively simple relation not containing K_{mn} and I_n .

5. Relations among observables

It follows from eqs. (4.1) and (4.2) that the phosphorescence intensities can be calculated assuming the fluorescence intensities are known,

$$I_{\text{P}}^{\text{RC}}(t) = \exp(-k_{\text{P}}^{\text{RC}} t) I_{\text{P}}^{\text{RC}}(0) + \frac{k_{\text{P}}^{\text{RC}} k_{\text{I}}^{\text{RC}}}{k_{\text{F}}^{\text{RC}}} \int_0^t \exp[-k_{\text{P}}^{\text{RC}}(t-\tau)] I_{\text{F}}^{\text{RC}}(\tau) d\tau, \quad (5.1)$$

$$I_{\text{P}}^{\text{A}}(t) = \exp(-k_{\text{P}}^{\text{A}} t) I_{\text{P}}^{\text{A}}(0) + \frac{k_{\text{P}}^{\text{A}} k_{\text{I}}^{\text{A}}}{k_{\text{F}}^{\text{A}}} \int_0^t \exp[-k_{\text{P}}^{\text{A}}(t-\tau)] I_{\text{F}}^{\text{A}}(\tau) d\tau. \quad (5.2)$$

Eqs. (2.1), (3.1) and (3.9) lead to a similar relation between $\eta_{\text{CT}}(t)$ and $I_{\text{F}}^{\text{RC}}(t)$,

$$P_{\text{CT}}(t) = \eta_{\text{CT}}(t) = \frac{k_{\text{CT}}}{k_{\text{F}}^{\text{RC}}} \int_0^t I_{\text{F}}^{\text{RC}}(\tau) d\tau + P_{\text{CT}}(0). \quad (5.3)$$

Adding eqs. (4.5) and (4.6) and using generally valid summation rules (A.10) and (A.11) for the memory functions and initial terms we get the following relation between I_{F}^{RC} and I_{F}^{A} :

$$\frac{1}{k_{\text{F}}^{\text{A}}} \frac{dI_{\text{F}}^{\text{A}}}{dt} + \frac{k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}}{k_{\text{F}}^{\text{A}}} I_{\text{F}}^{\text{A}} + \frac{1}{k_{\text{F}}^{\text{RC}}} \frac{dI_{\text{F}}^{\text{RC}}}{dt} + \frac{k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}} + k_{\text{CT}}}{k_{\text{F}}^{\text{RC}}} I_{\text{F}}^{\text{RC}} = 0. \quad (5.4)$$

This simple equation is a generally valid relation between the antenna and RC fluorescence showing that these quantities are not independent. This equation does not explicitly contain any information on the intermolecular transfer included in K_{mn} and I_m . All the rate constants appearing in eq. (5.4) describe the intramolecular processes. Eq. (5.4) is valid for arbitrary time and arbitrary degree of the transport coherence. If we assume that I_{F}^{A} is known we solve eq. (5.4) for I_{F}^{RC} ,

$$I_{\text{F}}^{\text{RC}}(t) = \exp[-(k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}} + k_{\text{CT}})t] I_{\text{F}}^{\text{RC}}(0) - \frac{k_{\text{F}}^{\text{RC}}}{k_{\text{F}}^{\text{A}}} \int_0^t \exp[-(k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}} + k_{\text{CT}})(t-\tau)] \times \left(\frac{dI_{\text{F}}^{\text{A}}(\tau)}{d\tau} + (k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) I_{\text{F}}^{\text{A}}(\tau) \right) d\tau. \quad (5.5)$$

It is known that the excitation into higher Chl levels (S_2, \dots) relaxes very fast and the molecules transfer to the S_1 state. Assuming further that originally all the Chl molecules are in the ground state S_0 and that the photon absorption at $t=0$ excites the molecules into the S_1 state we can write $I_{\text{F}}^{\text{A}}(0) = I_{\text{F}}^{\text{RC}}(0) = P_{\text{CT}}(0) = 0$.

Now we can formulate the answer to problem (4) given in section 1. Eqs. (5.3), (5.1), (5.2), (3.1), (3.2), (3.7), (3.8), (3.3) and (3.4) show that the observables η_{CT} , I_{P}^{RC} , I_{P}^{A} , I_{F}^{RC} , I_{F}^{A} , $\eta_{\text{F}}^{\text{RC}}$, $\eta_{\text{F}}^{\text{A}}$, $\eta_{\text{F}}^{\text{RC}}$ and $\eta_{\text{F}}^{\text{A}}$ are not independent. If we assume that I_{F}^{A} and the intramolecular rate constants are known the other observables can be determined from the above equations. This result is valid for arbitrary time and does

not depend on the character of the motion (coherent, incoherent, intermediate), structure of the PSU (the Chl–Chl distances, orientation of their dipole moments, existence of globules) and other properties of the PSU. It follows from an integral (global) character of the observables regarding the antenna system or RC as a whole and the law of conservation of the excitation energy flowing through different channels in the PSU (the CT level, fluorescence and phosphorescence of the antenna system and RC).

Let us discuss eq. (5.2) in greater detail. Assuming for simplicity a single-exponential form of $I_{\hat{F}}^{\wedge}$,

$$I_{\hat{F}}^{\wedge}(t) = I_{\hat{F}}^{\wedge}(0) \exp(-kt), \quad (5.6)$$

where $k \approx 0.5$ ns [46] it follows from eq. (5.2) that

$$I_{\hat{F}}^{\wedge}(t) = \left(I_{\hat{F}}^{\wedge}(0) - \frac{k_{\hat{F}} k_{\hat{F}}^{\wedge} I_{\hat{F}}^{\wedge}(0)}{k_{\hat{F}}^{\wedge} (k_{\hat{F}}^{\wedge} - k)} \right) \exp(-k_{\hat{F}}^{\wedge} t) + \frac{k_{\hat{F}} k_{\hat{F}}^{\wedge} I_{\hat{F}}^{\wedge}(0)}{k_{\hat{F}}^{\wedge} (k_{\hat{F}}^{\wedge} - k)} \exp(-kt). \quad (5.7)$$

The first term goes down slowly ($k_{\hat{F}}^{\wedge} \approx 10^2$ s⁻¹) while the second one decays to small values for $t > 1$ ns. We see that starting from $t \approx 1$ ns the form of the phosphorescence intensity is determined by $k_{\hat{F}}^{\wedge}$ only and is not influenced by the intermolecular transfer. The same conclusion applies for $I_{\hat{P}}^{\text{RC}}$ and the corresponding quantum yield $\eta_{\hat{P}}^{\text{RC}}$. Because of this reason and the possibility to express all the other observables in terms of $I_{\hat{F}}^{\wedge}$ we confine our attention to the discussion of the antenna fluorescence $I_{\hat{F}}^{\wedge}$.

6. Experimental resolution and observables

The antenna fluorescence $I_{\hat{F}}^{\wedge}$ has generally a complex form depending on the values of the intramolecular rate constants, conformation of the PSU, character of the intermolecular transfer and initial conditions (see eqs. (4.5) and (4.6)). Unfortunately, a lot of this information may be lost during measurements. In order to estimate the limitations following from the usual experimental conditions we investigate in this paragraph factors playing the most important role in this respect.

(1) A finite time resolution t_{res} leads to an averaging over the corresponding time interval

$$\overline{I_{\hat{F}}^{\wedge}}(t) = \frac{1}{t_{\text{res}}} \int_t^{t+t_{\text{res}}} I_{\hat{F}}^{\wedge}(\tau) d\tau, \quad (6.1)$$

where $\overline{I_{\hat{F}}^{\wedge}}$ denotes the measured intensity of fluorescence.

(2) The effect of the form, intensity and length of the excitation light pulse $G(\tau)$ may be described as

$$\overline{I_{\hat{F}}^{\wedge}}(t) = \int_0^t G(\tau) I_{\hat{F}}^{\wedge}(t-\tau) d\tau. \quad (6.2)$$

(3) The effect of the size of a sample, following from different optical paths for different PSUs, leads to a similar effect as in eq. (6.1) (see fig. 2). Taking into consideration the velocity of light the difference of the optical paths ≈ 1 mm in vacuum leads to an effective time resolution ≈ 3 ps.

(4) The configurational averaging over different conformations of the PSUs which can differ by the number and geometrical configuration of the Chl molecules as well as in other respects can significantly influence measured quantities. If we assume for simplicity the $1/R^6$ dependence of the intermolecular rate constants as in the Förster theory [47] the change of the Chl–Chl distance R by 1 Å for $12 \leq R \leq 35$ Å leads to the change of the rate constant by 20–60%. Assuming the dipole–dipole interaction in the Hamiltonian describing the interaction of the Chl molecules, i.e. the $1/R^3$ dependence we get the analogous change of the interaction as 10–30%. It is obvious that such changes can influence the resulting form of the observables very significantly. At the same time, the resulting effect is difficult to evaluate. The above estimates are applicable namely to the mea-

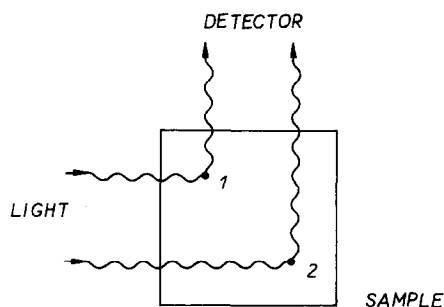


Fig. 2. Different optical paths for different PSUs (dots).

surements in vivo where significant irregularities of the conformation of the PSUs can be expected. For model systems with a more regular structure this effect may be less significant.

In order to illustrate the effect of the configurational averaging we show in fig. 3 the probability of finding the excitation at one of the molecules in the Chl *a* dimer without and with configurational averaging over an ensemble of dimers with the Gaussian distribution of the Chl *a*–Chl *a* distance R (a mixed statistical ensemble). It is obvious that for the considered averaging the probabilities $P_m(t)$ in the coherent case and, consequently, also the observables can change their form significantly. This averaging namely influences the characteristic quantum beats which disappear for $t > 0.1$ ps. The influence of averaging in the incoherent case is small. Fig. 3 corresponds to the Chl *a* dimer. It can be shown that the configurational averaging of $P_m(t)$ for the PSU with N Chl molecules can be reduced to a sum of similar functions as shown in fig. 3 so that our conclusions have general validity.

All the effects (1)–(4) and the effect of a nonzero temperature have to be taken into consideration simultaneously. As a result, most of important details of the observables on the time scale shorter than a few picoseconds may be lost during measurements.

The answer to the problem (3) may be therefore formulated as follows. The first loss of information follows from the integral character of the observable $I_{\hat{A}}$ (summation in eq. (3.2), see also ref. [19]). Further loss of information follows from a finite time resolution and averaging over the form, intensity and length of the excitation light pulse. The effect of the size of a sample for the usual experimental arrangement leads to a similar loss of information as in the case of the finite time resolution. The configurational averaging and temperature effects may be significant factors further reducing the attainable information. The resulting effective time resolution for usual experimental conditions can hardly be better than 0.1–1 ps.

7. Long time fluorescence

Assuming the relaxation time $t_{rel} \leq 0.1$ ps which is comparable with the effective time resolution men-

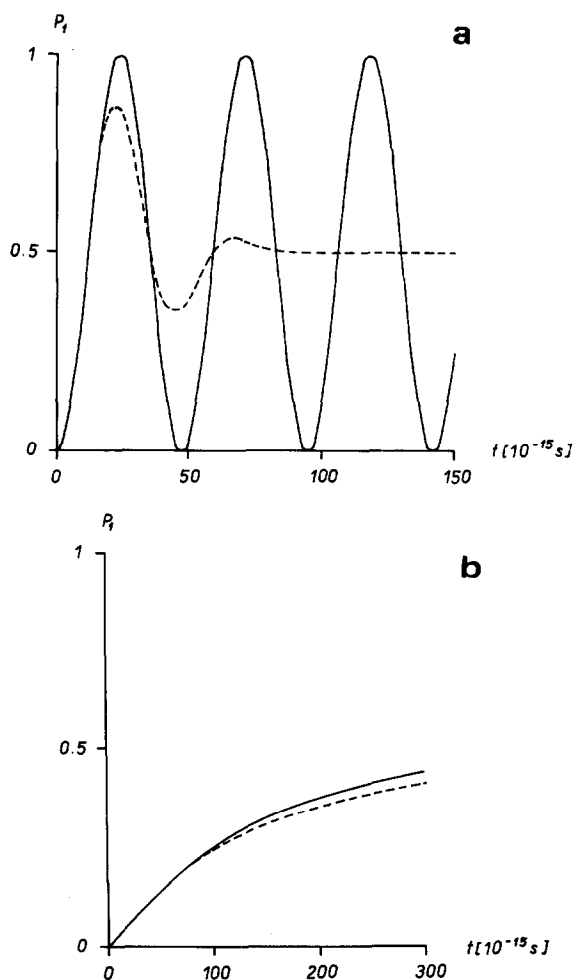


Fig. 3. The illustration of the effect of the configurational averaging on the probabilities $P_m(t)$. The calculations were done for the Chl *a* dimer for the most favorable orientation of their dipole moments giving the largest value of H_{mn} and F_{mn} , $R = 35$ Å. The initial excitation is assumed at the second Chl *a* molecule $P_1(0) = 0, P_2(0) = 1$. Case (a) corresponds to the solution of the Schrödinger equation (8.8) (coherent motion) while case (b) follows from the solution of the PME (7.1) (incoherent motion). The full lines are the probabilities $P_1(t)$ with no configurational averaging. The dashed lines show $P_1(t)$ for an ensemble of dimers with Gaussian distribution of the intermolecular distance R . The average distance is $R = 35$ Å, the half-width of the Gaussian distribution being 3 Å. The rate constants are given in section 2, $R_0 = 64$ Å.

tioned above we see that investigating the above mentioned observables we can observe experimentally mainly the incoherent stage of the excitation

transfer which can be described by means of the PME.

The PME can be obtained from the GME (4.3) and (4.4) by neglecting the initial terms I_n and the memory effects of the memory functions K_{mn} (see eq. (A.13) and refs. [34,35,48–50])

$$\frac{dP_m}{dt} = \sum_{n \in \text{RC,A}} F_{mn} P_n - (k_F^A + k_I^A) P_m, \quad m \in \text{A}, \quad (7.1)$$

$$\frac{dP_{\text{RC}}}{dt} = \sum_{n \in \text{RC,A}} F_{\text{RC},n} P_n - (k_F^{\text{RC}} + k_I^{\text{RC}} + k_{\text{CT}}) P_{\text{RC}}. \quad (7.2)$$

The values of the intermolecular rate constants F_{mn} may be estimated from the Förster formula [47]

$$F_{mn} = \frac{3}{2} \frac{[\mathbf{u}_m \cdot \mathbf{u}_n - 3(\mathbf{u}_m \cdot \mathbf{r})(\mathbf{u}_n \cdot \mathbf{r})]^2}{\tau_F} \left(\frac{R_0}{R} \right)^6, \quad m \neq n, \quad (7.3)$$

$$F_{mm} = - \sum_{n (\neq m)} F_{nm}, \quad m \in \text{RC,A}, \quad (7.4)$$

where \mathbf{u}_m and \mathbf{u}_n are unit vectors giving the directions of the transition dipole moments of the $S_0 \rightarrow S_1$ transitions of the m th and n th Chl molecule, respectively. The unit vector along the direction connecting the molecules is \mathbf{r} , R denotes their distance, τ_F is the fluorescence life time and R_0 is the Förster radius. If $m = \text{RC}$ or $n = \text{RC}$, $m \neq n$, the rate constant according to eq. (7.3) has to be multiplied by two because the special pair consists of the two Chl molecules.

The applicability of the Förster model as well as the value of R_0 which is critical for the values of the rate constants has been questioned many times (see e.g. ref. [51]). For this reason, we use it rather for estimates than for a systematic discussion. Most of the conclusions of this section are independent of the use of the Förster prescription.

For two Chl **a** molecules with the transition dipole moments oriented perpendicularly to \mathbf{r} , $\tau_F = 5$ ns and $R_0 = 64$ Å [22] we get $F_{mn} \approx 10^{10} \text{ s}^{-1}$ for $R = 35$ Å. The corrections to F_{mn} following from the spatial distribution of the charge in the Chl **a** molecules are less than 100% for $R > 10$ Å [51]. Such changes are from the point of view of the following discussion insignificant.

Now we shall discuss some general properties of the kinetic equations (7.1) and (7.2) which are independent of a concrete form of the PSU.

The PME (7.1) and (7.2) is a system of linear differential equations of the first order so that its general solution has the form

$$P_m(t) = \sum_{\lambda} c_{\lambda} \exp(\lambda t) h_m(\lambda), \quad m \in \text{RC,A}, \quad (7.5)$$

where c_{λ} are coefficients given by the initial conditions and λ and $h_m(\lambda)$ satisfy the eigenvalue problem

$$\sum_n F'_{mn} h_n(\lambda) = \lambda h_m(\lambda), \quad (7.6)$$

$$F'_{mn} = F_{mn} \quad \text{for } m \neq n, \quad (7.7)$$

$$F'_{mm} = F_{mm} - (k_F^A + k_I^A), \quad m \in \text{A}, \quad (7.8)$$

$$F'_{mm} = F_{mm} - (k_F^{\text{RC}} + k_I^{\text{RC}} + k_{\text{CT}}), \quad m = \text{RC}. \quad (7.9)$$

The probabilities $P_m(t)$ must be finite for $t \rightarrow \infty$ so that all the eigenvalues λ for arbitrary values of the intramolecular rate constants must be less than or equal to zero. Eq. (7.5) shows that the antenna and RC fluorescence can be written for $t \gg t_{\text{rel}}$ as a sum of $N+1$ decaying exponentials, where N is the number of the antenna Chl molecules. Therefore, these observables are in general rather complex functions and contain a lot of information on the intermolecular transfer. It is obvious, however, that starting from a certain time t_0 all the exponentials in eq. (7.5) may be neglected except for that one with the eigenvalue λ_1 having the smallest absolute value. It leads to a particularly simple single-exponential form of the probabilities $P_m(t)$ and related observables which we now discuss in detail. As we show below t_0 is of the order 10 ps and the excitation energy transfer for $t > t_0$ contributes to $\eta_{\text{CT}}(t \rightarrow \infty)$ substantially.

It follows from the single-exponential form of $P_m(t)$ that the ratio of the probability of finding the exciton in the antenna system and RC, respectively, is a time-independent constant,

$$\sum_{m \in \text{A}} P_m(t) / P_{\text{RC}}(t) = \nu. \quad (7.10)$$

From eqs. (3.1) and (3.2) we get for $t > t_0$

$$I_{\text{F}}^{\text{RC}}(t) = \frac{1}{\nu} \frac{k_{\text{F}}^{\text{RC}}}{k_{\text{F}}^{\text{A}}} I_{\text{F}}^{\text{A}}(t) \quad (7.11)$$

so that eq. (5.4) may be integrated and an *analytic* expression for I_{F}^{A} is obtained,

$$I_{\text{F}}^{\text{A}}(t) = I_{\text{F}}^{\text{A}}(t_0) \times \exp\left(-\frac{k_{\text{CT}} + \nu(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}}}{\nu + 1}\right) \times (t - t_0). \quad (7.12)$$

Eq. (7.5) gives an analytic expression for λ_1 ,

$$\lambda_1 = -\frac{k_{\text{CT}} + \nu(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}}}{\nu + 1}. \quad (7.13)$$

We see that $I_{\text{F}}^{\text{A}}(t)$ and $I_{\text{F}}^{\text{RC}}(t)$ are for $t > t_0$ single decaying exponentials. The other observables can also be calculated analytically (see also ref. [12]).

Assuming quite generally and for arbitrary time that ν is not a constant but a function of time, it follows from eq. (A.12) independently of the degree of the coherence of the exciton motion,

$$\begin{aligned} \frac{d\nu}{dt} P_{\text{RC}} + (\nu + 1) \frac{dP_{\text{RC}}}{dt} &= -[k_{\text{CT}} + \nu(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}}] P_{\text{RC}}, \quad (7.14\text{a}) \\ -\frac{1}{\nu} \frac{d\nu}{dt} \sum_{m \in \text{A}} P_m + (\nu + 1) \frac{d}{dt} \sum_{m \in \text{A}} P_m &= -[k_{\text{CT}} + \nu(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}}] \sum_{m \in \text{A}} P_m. \quad (7.14\text{b}) \end{aligned}$$

According to these equations, the time dependence of $I_{\text{F}}^{\text{RC}} = k_{\text{F}}^{\text{RC}} P_{\text{RC}}$ and $I_{\text{F}}^{\text{A}} = k_{\text{F}}^{\text{A}} \sum_{m \in \text{A}} P_m$ is given by k_{CT} , k_{F}^{A} , k_{I}^{A} , k_{F}^{RC} , k_{I}^{RC} and $\nu(t)$. The investigated observables do not depend on the excitation distribution in the antenna system P_m , $m \in \text{A}$ and their measurement cannot give any information in this respect. Only the function $\nu(t)$ describing the distribution of the excitation between the antenna system and RC can be determined in this way (problem (2)). Eqs. (7.11)–(7.13) are a special consequence of eqs. (7.14) if the time dependence of $\nu(t)$ may be neglected.

The time-resolved measurements of $I_{\text{F}}^{\text{A}}(t)$ and $I_{\text{F}}^{\text{RC}}(t)$ for $t > t_0$ can be used for the experimental determination of ν . To estimate ν theoretically we use the first-order perturbation theory to calculate λ_1 and, consequently, ν .

If we assume $k_{\text{F}}^{\text{A}} = k_{\text{F}}^{\text{RC}} = k_{\text{I}}^{\text{A}} = k_{\text{I}}^{\text{RC}} = k_{\text{CT}} = 0$ and use the summation rule $\sum_n F_{mn} = 0$ (see eqs. (A.10), (A.13) and (7.4)) we see that the matrix F has in this case the zero eigenvalue $\lambda_1 = 0$ with the eigenvector

$$h_m(\lambda_1) = 1/(N+1)^{1/2}, \quad m \in \text{RC, A}. \quad (7.15)$$

Considering the problem (7.6) with $k_{\text{CT}} = 0$, $k_{\text{F}}^{\text{A}} = k_{\text{F}}^{\text{RC}}$, $k_{\text{I}}^{\text{A}} = k_{\text{I}}^{\text{RC}}$ we see that the eigenvector (7.15) fulfills eq. (7.6) with

$$\lambda_1 = -(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}). \quad (7.16)$$

This is the zero-order solution of eq. (7.6).

If we assume now $k_{\text{CT}} \neq 0$, $k_{\text{F}}^{\text{A}} \neq k_{\text{F}}^{\text{RC}}$, $k_{\text{I}}^{\text{A}} \neq k_{\text{I}}^{\text{RC}}$ and use first-order perturbation theory [52] for the ‘‘potential’’

$$V_{mn} = (k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}} - k_{\text{F}}^{\text{RC}} - k_{\text{I}}^{\text{RC}} - k_{\text{CT}}) \delta_{mn} \delta_{m,\text{RC}}, \quad (7.17)$$

we get λ_1 calculated in the first order,

$$\begin{aligned} \lambda_1 &= -(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + \sum_{m,n} h_m(\lambda_1) V_{mn} h_n(\lambda_1) \\ &= -\frac{k_{\text{CT}} + N(k_{\text{F}}^{\text{A}} + k_{\text{I}}^{\text{A}}) + k_{\text{F}}^{\text{RC}} + k_{\text{I}}^{\text{RC}}}{N+1}. \quad (7.18) \end{aligned}$$

Comparing eqs. (7.13) and (7.18) we see that the first-order perturbation theory gives

$$\nu = N, \quad (7.19)$$

i.e. the distribution of the excitation between the antenna system and RC is proportional to the number of the Chl antenna molecules (respectively special pairs in the case of RC) in these systems. The eigenvector corresponding to λ_1 is given by the corresponding first-order perturbation formula [52] and will not be given explicitly here.

For the values of the rate constants given in section 2 and $\nu = N = 100$ we may write with good accuracy $\lambda_1 = -k_{\text{CT}}/(\nu + 1) = -3.3 \times 10^9 \text{ s}^{-1}$. It means that $|\lambda_1|$ is in first approximation proportional to k_{CT} and decreases with increasing ν similarly to conclusions of refs. [12,19]. If there are no eigenvalues λ close to λ_1 we may find the upper estimate to t_0 from $t_0 \approx 1/|\lambda_1| = 3 \times 10^{-10} \text{ s}$.

In summary, these results show that for $t > t_0$

(1) I_{F}^{A} , I_{F}^{RC} and η_{CT} have the single exponential form

$$I_{\text{F}}^{\text{A}}(t) = I_{\text{F}}^{\text{A}}(t_0) \exp[\lambda_1(t - t_0)], \quad (7.20)$$

$$I_{\text{F}}^{\text{RC}}(t) = \frac{k_{\text{F}}^{\text{RC}}}{\nu k_{\text{F}}^{\text{A}}} I_{\text{F}}^{\text{A}}(t), \quad (7.21)$$

$$\eta_{\text{CT}}(t) = \frac{k_{\text{CT}}}{\nu k_{\text{F}}^{\text{A}} \lambda_1} [I_{\text{F}}^{\text{A}}(t) - I_{\text{F}}^{\text{A}}(t_0)] + \eta_{\text{CT}}(t_0). \quad (7.22)$$

We call this regime of the excitation energy transfer a *single exponential* one.

(2) The time development of the observables (7.20)–(7.22) is given by the intramolecular rate constants k_F^A , k_F^{RC} , k_I^A , k_I^{RC} , k_{CT} and the constant ν . No information on the intermolecular transfer within the antenna system can be obtained from the measurement of the investigated observables for $t > t_0$ as well as for shorter times. The initial conditions have, with the exception of $\eta_{CT}(t_0)$, no influence on the observables in this time range.

(3) If the conditions for the use of the first-order perturbation theory are satisfied the ratio ν equals the number of the antenna Chl molecules N .

(4) The zero-order expression (7.15) for the eigenvector $h_m(\lambda_1)$ and eq. (7.5) show that the probability $P_m(t)$ of finding the excitation at the S_1 antenna or RC levels equals

$$P_m(t) = [c_{\lambda_1} / (N+1)^{1/2}] \exp[\lambda_1(t-t_0)], \quad m \in RC, A, \quad t > t_0. \quad (7.23)$$

We see that the zero-order probability of finding the excitation at different sites m is the same for all the antenna Chl molecules and RC. If the losses and trap did not exist the state of the PSU in the single-exponential regime would be similar to the equilibrium state, $P_m(t) = \text{const}$, $m \in RC, A$. (If the conditions for the use of the perturbation theory are not fulfilled const depends on m .) The time dependence of all the probabilities is the same ($\exp(-|\lambda_1|t)$ decay). We see that no interesting dynamics of the intermolecular transfer can be observed for $t > t_0$.

Depending on the values of the rate constants and N the conditions for the use of perturbation theory may be more or less well satisfied and eqs. (7.19) and (7.23) may be more or less approximate. In the following, we discuss this problem in detail.

The condition for the use of perturbation theory is fulfilled if the distance of the levels close to λ_1 in the zero-order problem is large in comparison with the perturbation correction. Assuming for simplicity $k_F^A = k_F^{RC}$ and $k_I^A = k_I^{RC}$ the perturbation correction equals $-k_{CT}/(N+1)$. The distance of the levels increases with the values of the rate constants F so that the necessary condition may be formulated as

$$|F_{mn}| \gg k_{CT}/(N+1), \quad m \neq n, \quad (7.24)$$

i.e. the intermolecular transfer must be fast in comparison with the trapping rate of the CT state. Using the Förster formula (7.3) with the above given constants, k_{CT} from section 2 and $N=100$, the relation (7.24) is fulfilled for $R \leq 20$ Å. Numerical calculations show that for $R > 20$ Å the first-order and higher-order corrections become significant and eqs. (7.19) and (7.23) are not fulfilled. However, eqs. (7.10)–(7.13), (7.20)–(7.22) remain valid.

If the antenna system as a whole has some symmetry (as it seems for example to be the case of bacterial photosynthesis [27]) then the antenna fluorescence cannot depend on the symmetry operation (rotation, reflection, etc.) transforming the antenna system into itself. It means according to the group theory [53] that I_F^A must transform according to the totally symmetric representation A_1 of the antenna symmetry group. It follows then from eqs. (3.2) and (7.5) that only the states corresponding to the A_1 representation can appear in I_F^A ,

$$I_F^A(t) = k_F^A \sum_{\lambda \in A_1} c_\lambda \exp(\lambda t) \sum_{m \in A_1} h_m(\lambda), \quad (7.25)$$

where $\sum_{\lambda \in A_1}$ denotes the summation over the states corresponding to the unit representation ($\sum_{m \in A} h_m(\lambda) = 0$ for other representations). In such a case, I_F^A is a linear combination of a smaller number of exponentials and the single-exponential decay of I_F^A can appear for considerably shorter times (see ref. [26]). Numerical calculations show that the eigenvalues λ_i close to λ_1 belong to other than to the A_1 representation and the eigenvalues λ_i corresponding to the A_1 representation are well separated. Therefore, the single-exponential regime appears at considerably shorter times than $t \approx 1/|\lambda_1|$ [26]. Taking into account mutual relations of the observables discussed above (for I_F^{RC} see eq. (5.4)) we see that the symmetry of the antenna system reduces the number of exponentials also in other observables similarly to eq. (7.25).

According to our calculations [12,13] for the average nearest-neighbor distance $R = 12$ Å in a regular two-dimensional lattice of the Chl molecules the time t_0 lies in the range ≈ 1 –10 ps. It follows from the $1/R^6$ dependence in eq. (7.3) that the value of t_0 for larger R should increase roughly as $(R/12 \text{ Å})^6$ in agreement with our numerical calculations. Calculations based on the recently obtained experimental ge-

ometry of the PSU in the bacterial photosynthesis [27] give $t_0=4-25$ ps [26].

Now we show that the single-exponential regime can contribute very significantly to the value of the quantum yield $\eta_{CT}(t \rightarrow \infty)$, i.e. it can be very important from the point of view of the efficiency of the primary processes of photosynthesis as a whole. The contribution of the single-exponential regime to the value of the quantum yield η_{CT} can be estimated as follows. According to eqs. (2.1) and (3.9)

$$\eta_{CT}(t \rightarrow \infty) = k_{CT} \int_0^{\infty} P_{RC}(\tau) d\tau. \quad (7.26)$$

The contribution of the single-exponential regime equals

$$\begin{aligned} \eta_{CT}^{se}(t \rightarrow \infty) &= \eta_{CT}(t \rightarrow \infty) - \eta_{CT}(t_0) \\ &= \frac{k_{CT}}{\nu k_F^A |\lambda_1|} I_F^A(t_0). \end{aligned} \quad (7.27)$$

If we assume the validity of eq. (7.19) and neglect the losses in the PSU for small t_0 we may write approximately

$$I_F^A(t_0) = k_F^A \frac{N}{N+1}. \quad (7.28)$$

From eqs. (7.27), (7.28) and (7.19) we have

$$\begin{aligned} \eta_{CT}^{se}(t \rightarrow \infty) &= \frac{k_{CT}}{(N+1)|\lambda_1|} \\ &= \frac{k_{CT}}{k_{CT} + N(k_F^A + k_I^A) + k_F^{RC} + k_I^{RC}}. \end{aligned} \quad (7.29)$$

Using the rate constants given in section 2 and $N=100$ we get $\eta_{CT}^{se}(t \rightarrow \infty) = 0.94$. This is the estimate of the maximum value of $\eta_{CT}^{se}(t \rightarrow \infty)$.

For large t_0 we must take into account the losses in the PSU. Assuming for simplicity the single-exponential decay of $I_F^A(t)$ following from eq. (7.14b) for $\nu=N$,

$$I_F^A(t_0) = k_F^A \frac{N}{N+1} \exp(\lambda_1 t_0), \quad (7.30)$$

we get from eq. (7.27)

$$\eta_{CT}^{se}(t \rightarrow \infty) = \frac{k_{CT}}{(N+1)|\lambda_1|} \exp(\lambda_1 t_0). \quad (7.31)$$

This gives for $\lambda_1 = -3.3 \times 10^9 \text{ s}^{-1}$ and $t_0 = 3 \times 10^{-10} \text{ s}$ $\eta_{CT}^{se}(t \rightarrow \infty) = 0.35$. The estimated lower and upper bounds to $\eta_{CT}^{se}(t \rightarrow \infty)$ are therefore

$$0.35 \leq \eta_{CT}^{se}(t \rightarrow \infty) \leq 0.94. \quad (7.32)$$

The value of $\eta_{CT}^{se}(t \rightarrow \infty)$ corresponding to the largest calculated $t_0 = 25$ ps [26] is $\eta_{CT}^{se}(t \rightarrow \infty) = 0.87$.

The answer to problem (1) and partially to (2) and (5) may be therefore formulated as follows. Obvious conditions for a high value of $\eta_{CT}(t \rightarrow \infty)$ are that the intermolecular transfer is fast ($|F_{mn}| \gg k_F^A, k_I^A, k_F^{RC}, k_I^{RC}$) and the trapping rate k_{CT} is large in comparison with the fluorescence and intersystem crossing rate constants ($k_{CT} \gg k_F^A, k_F^{RC}, k_I^A, k_I^{RC}$). Under such conditions which are fulfilled for the photosynthetic system under consideration the excitation energy transfers fast to the reaction center CT state where it is exploited for the charge separation. The radiative losses are small during the transfer. The ratio $\nu(t) = \sum_{m \in A} P_m(t) / P_{RC}(t)$ is a function of time, however, becomes constant in the single-exponential regime ($t > t_0$). The calculated values $t_0 \approx 4-25$ ps [26] lead to the conclusion that the contribution $\eta_{CT}^{se}(t \rightarrow \infty)$ of the single-exponential regime to $\eta_{CT}(t \rightarrow \infty)$ is close to 0.9. From this point of view, the single-exponential regime is the most significant stage of the energy transfer to RC. The intermolecular transfer within the antenna system has in the single-exponential regime no effect on $\eta_{CT}(t \rightarrow \infty)$ as well as on other investigated observables. The dependence of $\eta_{CT}^{se}(t \rightarrow \infty)$ on the geometry of the PSU is given only by ν , i.e. the distribution of the excitation energy between the antenna system and RC. Therefore, the quantum yield $\eta_{CT}(t \rightarrow \infty)$ depends only very little on the details of the geometrical arrangement of the PSU.

8. Short time fluorescence

The exciton trap, i.e. the reaction center CT state, and the radiative losses destroy the phase relations of the density matrix by damping its off-diagonal matrix elements (see eq. (A.4)). Using the rate constants from section 2 we see that they are damped at $t \approx 10^{-11} - 10^{-9}$ s. We see that considering only one of the dephasing processes the coherent regime can play

an important role only for times considerably shorter than this estimate.

Before going into more detailed discussion we first estimate the contribution of the short time transfer processes to $\eta_{CT}(t \rightarrow \infty)$. Assuming the maximum possible value of P_{RC} , $P_{RC}=1$, we obtain from eqs. (3.9) and (2.1) the following upper bound:

$$\eta_{CT}(t) = k_{CT} \int_0^t P_{RC}(\tau) d\tau \leq k_{CT} t. \quad (8.1)$$

For $k_{CT} = 3.3 \times 10^{11} \text{ s}^{-1}$ and $t = 10^{-13} \text{ s}$ we get

$$\eta_{CT}(10^{-13} \text{ s}) \leq 0.033. \quad (8.2)$$

The wavelength of the visible light is large in comparison with the dimensions of the PSU so that a more or less delocalized initial excitation of the PSU at $t=0$ can be expected. Therefore, taking $P_{RC} = (N+1)^{-1}$ instead of $P_{RC}=1$ as a more probable value we get approximately

$$\eta_{CT}(t) = k_{CT} t / (N+1). \quad (8.3)$$

This yields for $t = 10^{-11} \text{ s}$ and $N = 100$

$$\eta_{CT}(10^{-11} \text{ s}) = 0.033. \quad (8.4)$$

We see that the short time processes ($t \leq 10 \text{ ps}$) can contribute to $\eta_{CT}(t \rightarrow \infty)$ only a few per cent (problem (5)). From this point of view, they are practically insignificant.

On the other hand, it has been shown above that the single-exponential regime can yield only very limited information on the intermolecular excitation energy transfer between the antenna system and RC ($\nu = \text{const}$). In order to gain more information in this respect times $t \leq t_0$ have to be considered. Therefore, we discuss in this section the form of $I_{\hat{F}}$ in the coherent and intermediate case.

The excitation energy transfer for very short times $t \ll t_{rel}$ may be described by means of the Schrödinger equation

$$i\hbar \partial\psi / \partial t = H\psi, \quad (8.5)$$

where

$$\psi = \sum_n c_n \psi_n, \quad (8.6)$$

$c_n(t)$ is a probability amplitude of finding the excitation at the S_1 level of the n th antenna or RC mole-

cule and ψ_n describes the state in which all the Chl molecules are in the S_0 state (φ^0) except for the n th one which is in the S_1 state (φ^{exc}). The probability $P_m(t)$ equals

$$P_m(t) = |c_m(t)|^2. \quad (8.7)$$

The Schrödinger equation (8.5) reads in matrix representation

$$i\hbar dc_m/dt = \sum_n H_{mn} c_n, \quad (8.8)$$

where the values of the matrix elements H_{mn} may be estimated from the dipole-dipole interaction of the Chl molecules,

$$H_{mn} = \langle \psi_m | \sum_{i < j} V_{ij} | \psi_n \rangle, \quad (8.9)$$

$$V_{ij} = [\mathbf{d}_i \cdot \mathbf{d}_j - 3(\mathbf{d}_i \cdot \mathbf{r})(\mathbf{d}_j \cdot \mathbf{r})] / R^3, \quad (8.10)$$

where \mathbf{r} is the unit vector along the direction connecting the molecules, R denotes their distance and \mathbf{d}_i is the dipole moment operator corresponding to the electron in the i th molecule. Assuming only small overlap of φ_m^0 and φ_n^{exc} functions ($m \neq n$) we get

$$H_{mn} = [\mathbf{t}_m \cdot \mathbf{t}_n - 3(\mathbf{t}_m \cdot \mathbf{r})(\mathbf{t}_n \cdot \mathbf{r})] / R^3, \quad (8.11)$$

where

$$\mathbf{t}_m = \langle \varphi_m^0 | \mathbf{d}_m | \varphi_m^{exc} \rangle \quad (8.12)$$

is the transition dipole moment of the m th molecule.

The matrix elements H_{mn} may be estimated from the experimentally known value of the Chl a dipole moment. For the Chl a in diethyl ether $|t| = 4.3 \text{ D}$ [54]. Assuming that t_m and t_n are parallel and at the same time perpendicular to \mathbf{r} we get $H_{mn}/\hbar = 6.67 \times 10^{13} \text{ s}^{-1}$ for $R = 12 \text{ \AA}$ and $H_{mn}/\hbar = 2.7 \times 10^{12} \text{ s}^{-1}$ for $R = 35 \text{ \AA}$.

In order to include the radiative and non-radiative losses it is necessary to modify the Hamiltonian H into a non-Hermitian form H' [42] corresponding to the loss terms on the right-hand side of the GME (4.3) and (4.4) (see appendix),

$$H'_{mn} = H_{mn}, \quad m \neq n, \quad (8.13)$$

$$H'_{mm} = H_{mm} - \frac{1}{2} i\hbar (k_F^A + k_I^A), \quad m \in A, \quad (8.14)$$

$$H'_{mm} = H_{mm} - \frac{1}{2} i\hbar (k_F^{RC} + k_I^{RC} + k_{CT}), \quad m = RC. \quad (8.15)$$

A general solution of the Schrödinger equation

(8.5) with the Hamiltonian H' has the form

$$c_m(t) = \sum_E a_E \exp(Et/i\hbar) h_m(E), \quad m \in \text{RC, A}, \quad (8.16)$$

where E and $h_m(E)$ satisfy the stationary problem

$$\sum_n H'_{mn} h_n(E) = E h_m(E) \quad (8.17)$$

and a_E are constants given by the initial conditions. The Hamiltonian H' is complex and non-Hermitian so that both its eigenvalues E and eigenvectors $h_m(E)$ are also complex. At the same time, all the imaginary parts of E have to be less than or equal to zero

$$\text{Im } E \leq 0 \quad (8.18)$$

since the radiative and non-radiative losses from the S_1 levels lead to a decay of the probabilities $P_m(t)$. The real part of the frequencies E/\hbar can be expected of the order H_{mn}/\hbar , i.e. 10^{12} – 10^{14} s $^{-1}$. The imaginary parts of E/\hbar are given above all by the values of the intramolecular rate constants k_F^\wedge , k_F^{RC} , k_I^\wedge , k_I^{RC} and k_{CT} . The lower bound to the imaginary part of the complex eigenvalues E can be found from the Gershgorin theorems [55] for the perturbation matrix formed by the imaginary part of H' ,

$$\text{Im}(E/\hbar) \geq -\frac{1}{2}(k_F^{\text{RC}} + k_I^{\text{RC}} + k_{\text{CT}}). \quad (8.19)$$

As the imaginary part of H' is small in comparison with the real part first-order perturbation theory can be used to estimate $\text{Im}(E/\hbar)$. Assuming for example the existence of a state close to a uniform distribution of the probabilities $P_m(t)$ which can result from the delocalized initial excitation (the wavelength of the light is large in comparison with the dimensions of the PSU),

$$h_m(E_1) = 1/(N+1)^{1/2}, \quad (8.20)$$

we get

$$\text{Im}(E_1/\hbar) = \frac{1}{2}\lambda_1, \quad (8.21)$$

where λ_1 is given by eq. (7.18). Therefore, $\text{Im}(E/\hbar) = -1.65 \times 10^9$ s $^{-1}$ so that the quantum beats of such a state would be damped at $t \approx 200$ ps. Using the expression $\lambda_1 \approx -k_{\text{CT}}/(N+1)$ we see that the reaction center CT state plays an important role in reducing the coherence of the excitation transfer in the PSU. We note also that other dephasing processes are

not included in this estimate so that real dephasing time should be considerably shorter.

The initial conditions, i.e. the values of a_E determining $c_m(t=0)$ in eq. (8.16), are given by the wavelength, direction and polarization of the exciting light. We note that the influence of the initial conditions can to a considerable extent be reduced by the configurational averaging.

We see from eqs. (8.16), (8.7) and (3.2) that the antenna fluorescence I_F^\wedge is given for very short times $t \ll t_{\text{rel}}$ by a linear combination of $(N+1)^2$ exponentially damped functions depending on the eigenvalues and eigenvectors of the Hamiltonian H' and initial conditions. For the symmetric antenna system the number of the functions in the linear combination may be reduced analogously to our discussion of eq. (7.25). Therefore, I_F^\wedge carries a lot of information on the antenna system–RC transfer. If we take into consideration the complexity of eqs. (8.16) and (8.7), the integral character of I_F^\wedge and the effect of the experimental resolution we see, however, that it is very difficult to obtain this information experimentally.

Till now we have assumed very short times $t \ll t_{\text{rel}}$ for which the Schrödinger equation may be used. In the intermediate time range $t \approx t_{\text{rel}}$ the GME has to be solved. The GME (4.3) and (4.4) is a complex system of integro-differential equations. It can be transformed into a simpler algebraic form by means of Bessel functions [56–58], however, the resulting problem is still too complex for the PSU. For this reason we suggested a simple interpolation formula for constructing approximate solutions to the GME from known solutions in the coherent and incoherent limits [59]. This approach which is practical even for systems like the PSU may be formulated as follows.

The probabilities $P_m(t)$ in the intermediate regime may be approximately described by means of the interpolation formula [59]

$$P_m(t) = P_m^{\text{PME}}(t) + \exp(-\zeta t) [P_m^{\text{SCHE}}(t) - P_m^{\text{PME}}(t)]. \quad (8.22)$$

Here, P_m^{PME} and P_m^{SCHE} denote the solutions of the PME and Schrödinger equation given above and ζ is a parameter describing an average rate of the transition from the coherent to incoherent regime. It can be estimated from $\zeta \approx 1/t_{\text{rel}}$, where $10^{-13} \leq t_{\text{rel}} \ll 3$

$\times 10^{-10}$ s. Because of the meaning of t_{rel} and t_0 the relation $t_{\text{rel}} < t_0$ must be fulfilled.

The decay of the fluorescence intensity I_F^A in the intermediate regime is influenced by the relaxation processes and is even more complex than for $t \ll t_{\text{rel}}$. Therefore, our comment on the difficulty of obtaining the information on the excitation transfer from the observables is valid also here.

9. Concluding remarks

In this work, a general theory of the excitation energy transfer in the primary processes of photosynthesis has been formulated. Using general arguments independent of the concrete form of the photosynthetic system and details of the model calculations we have given answers to a few important problems formulated in the introduction. Most of conclusions are formulated generally and, where possible, numerical estimates and the lower and upper bound to the quantities of interest are given. More detailed and concrete calculation devoted mainly to the incoherent and especially the single-exponential regime is given in ref. [26].

The above discussed results (the integral character of the observables and their mutual relation, insignificant role of the coherent transfer, decisive role of the single-exponential regime, impossibility of direct determination of the parameters of the intermolecular transfer from the observables, consequences of a finite experimental resolution and experimental conditions, ...) show difficulties in getting any detailed information on the intermolecular transfer by means of standard optical methods. The importance of the single exponential regime of the transfer leads to the value of $\eta_{\text{CT}}(t \rightarrow \infty)$ about 0.9 which is to a great extent independent of the structure and geometry of the PSU and initial conditions. It seems that just these properties of the photosynthetic unit guarantee high efficiency of the light conversion under diverse condition.

Our model is certainly far from being a complete picture of the primary processes in the PSU and can be improved in many respects. However, generality of the arguments used in this work seems to justify our belief that most of the conclusions of this work have general validity.

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Appendix

In this work, the GME has been used for the first time for the discussion of the excitation energy transfer in the PSU. For this reason, we show here how the usual GME has to be modified to include the loss processes in the PSU.

The Hamiltonian H in standard quantum mechanics is Hermitian ($H^+ = H$). This property of the Hamiltonian leads to the conservation of the normalization of the wave function and density matrix ρ ($\text{Tr} \rho = 1$) as well as to real eigenvalues of the Hamiltonian. In order to include phenomenologically radiative and non-radiative losses in the PSU we modify the diagonal elements of H so that it becomes non-Hermitian, eqs. (8.14) and (8.15). This leads to a decay of the probabilities respectively observables with increasing time (see eqs. (8.7) and (8.16)). Necessary modifications of the GME and PME are summarized as below.

The Liouville operator [42] for a non-Hermitian Hamiltonian corresponding to eqs. (8.14) and (8.15)

$$H' = H - i \begin{pmatrix} \alpha_1 & & & \\ & \alpha_2 & 0 & \\ & & \ddots & \\ 0 & & & \alpha_N \end{pmatrix}, \quad (\text{A.1})$$

$H^+ = H$, α_j real numbers, $\alpha_j > 0$, has the form

$$L\rho = (1/i\hbar)[H'\rho - \rho(H')^+], \quad (\text{A.2})$$

i.e. it is also non-Hermitian. It follows from the Liouville equation

$$\partial\rho/\partial t = L\rho \quad (\text{A.3})$$

and eqs. (A.1) and (A.2) that in the matrix representation

$$\partial \rho_{mn} / \partial t = (1/i\hbar) [H, \rho]_{mn}$$

$$- \frac{1}{\hbar} \begin{pmatrix} 2\alpha_1 \rho_{11} & (\alpha_1 + \alpha_2) \rho_{12} \dots & & \\ (\alpha_2 + \alpha_1) \rho_{21} & 2\alpha_2 \rho_{22} & \dots & \\ \dots & & & 2\alpha_N \rho_{NN} \end{pmatrix}_{mm} \quad (\text{A.4})$$

We see that the diagonal elements $\rho_{mm} = P_m$ of the density matrix are destroyed at the rate $2\alpha_m/\hbar$ corresponding to the loss terms on the right-hand side of eqs. (4.3), (4.4), (7.1) and (7.2).

The GME, i.e. the equation for the diagonal part of the density matrix $D\rho$, can be obtained by means of a projection operator technique [33],

$$\frac{d(D\rho)}{dt} = \int_0^t K(t-\tau) D\rho(\tau) d\tau + I(t) - G D\rho, \quad (\text{A.5})$$

where D is a projection operator,

$$(D\rho)_{mn} = \rho_{mm} \delta_{mn}, \quad (\text{A.6})$$

$K = \{K_{mn}\}$ is a matrix of the memory functions,

$$K(t) = -(D/\hbar)L \times \exp[-(i/\hbar)t(1-D)L](1-D)L D, \quad (\text{A.7})$$

$I = \{I_m\}$ denotes initial (or inhomogeneous) terms,

$$I(t) = -(i/\hbar)DL \times \exp[-(i/h)t(1-D)L](1-D)\rho(0) \quad (\text{A.8})$$

and

$$G = -DL D \quad (\text{A.9})$$

gives the damping of the diagonal elements of ρ in eq. (A.4). The memory functions are symmetric $K_{mn} = K_{nm}$. The GME (A.5) has a finite memory, i.e. the memory functions and initial terms go to zero for $t \rightarrow \infty$. We note that the loss terms from eq. (A.4) are included in the definition of the memory functions and initial terms in contrast with the so-called sink model [34].

The damping of the density matrix described by eqs. (A.4) and (A.5) follows from the loss processes considered in our model. Additional damping resulting from the interaction of the considered system with the rest of the PSU is in these equations not explicitly taken into consideration. It can approximately be

taken into account by the $\exp(-\zeta t)$ term in the interpolation formula (8.22).

Writing the exponentials in eqs. (A.7) and (A.8) as a power series it can be shown that generally valid summation rules

$$\sum_m K_{mn}(t) = 0 \quad (\text{A.10})$$

and

$$\sum_m I_m(t) = 0 \quad (\text{A.11})$$

are valid for the non-Hermitian Hamiltonian H' as well as for the original one H . It follows from eqs. (A.5), (A.9), (A.10) and (A.11) that

$$\frac{d}{dt} \sum_m P_m = -\frac{2}{\hbar} \sum_m \alpha_m P_m. \quad (\text{A.12})$$

The right-hand side of eq. (A.12) describes all the losses of the excitation energy from the S_1 levels so that eqs. (A.10) and (A.11) give the law of the conservation of the excitation energy.

The incoherent limit to the GME, i.e. the PME, may be derived assuming infinitely short memories [34,35]

$$K_{mn}(t) = F_{mn} \delta(t), \quad I_m = 0. \quad (\text{A.13})$$

Eq. (A.5) then becomes

$$\frac{dP_m}{dt} = \sum_n F'_{mn} P_n \quad (\text{A.14})$$

in agreement with eqs. (7.1), (7.2) and (7.7)–(7.9). The summation rule $\sum_n F_{mn} = 0$ follows from eqs. (A.10) and (A.13) and the relation $K_{mn} = K_{nm}$.

We note that no assumptions about the density matrix ρ are made here. It can include for example the configurational averaging or it can describe the PSU at non-zero temperature $T \neq 0$. Most of the results are therefore valid also in such cases.

Note added in proof

Approximate equation for the fluorescence life time $\tau = -1/\lambda_1 = (N+1)/k_{CT}$ in the single exponential regime (see eq. (7.20)) is in good agreement with the experimental results published in ref. [60].

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