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edited by

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FLUORESCENCE DECAY AND DEPOLARIZATION KINETICS CALCULATED USING FÖRSTER
INDUCTIVE RESONANCE AND THE MOLECULAR COORDINATES FOR C-PHYCOCYANIN

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1. INTRODUCTION

Excitation energy transfer among photosynthetic antenna pigments is an ubiquitous process in nature for producing efficient photon capture. The transfer of excitation to the photosynthetic reaction centers occurs rapidly, within a few hundred picoseconds, and with minimal loss of energy to fluorescence or heat. It has been proposed that this transfer occurs through a combination of exciton interactions among closely coupled chromophores and inductive resonance interactions among weakly coupled chromophores of pigment protein complexes. Detailed descriptions of the nature of this process have been lacking because, until recently, the molecular structures of the pigment proteins have not been known. The first publications of such structures with sufficient resolution to determine both the positions and orientations of the intrinsic chromophores were presented by Schirmer, *et al.* for C-phycoerythrin (C-PE) from two different organisms (1,2). Examination of the structures supports the conclusion from spectroscopic measurements that exciton interactions probably do not play an important role in C-PE (3).

We have applied the inductive resonance mechanism of Förster to C-PC to calculate the rate constants for successive pairwise excitation transfer steps among the chromophores. Because C-PC consists of two distinct subunits--the α -subunit with one covalently attached phycobilin chromophore and the β -subunit with two, and because these can be prepared in $(\alpha\beta)$ -monomeric, $(\alpha\beta)_3$ -trimeric and $(\alpha\beta)_6$ -hexameric forms (3), the calculations have been carried out for aggregates of different sizes. Experimental data are available for the kinetics of fluorescence intensity decay and for the rate of depolarization of fluorescence on the picosecond to nanosecond time scale for a variety of these preparations (4-9). Comparison of the calculated results with the best time resolved data indicates that the Förster transfer mechanism is sufficient to account for essentially all of the excitation energy transfer in C-PC.

2. PROCEDURE

Details of the method of calculation are described in a related publication (10). Briefly, the molecular structure information for C-PC from *Agmenellum quadruplicatum* was used to specify the interchromophore separations and the transition dipole moment orientations (2). The spectral overlap integrals were determined using absorption and emission spectral components obtained from a deconvolution of the experimental spectra of the α - and β -subunits and of the $\alpha\beta$ -monomer. Values of the extinction coefficients and fluorescence yields were taken from Mimuro *et al.* (11). Fluorescence lifetimes of the chromophores were based on measurements of the α -subunit by Switalski and Sauer (12) and by Hefferle *et al.* (5). Chromophore assignments were α -84 = intermediate (λ_{max} 616 nm), β -84 = fluorescer (λ_{max} 622) and β -155 = sensitizer (λ_{max} 598) (13).

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A set of simultaneous differential equations was formulated to describe the kinetics of excited state populations for each chromophore in the pigment protein. Because of the extensive symmetry of the larger aggregates, the calculational procedure could be appreciably simplified. Where desired, specification of the excitation and emission wavelengths was accounted for in terms of weighting parameters associated with the different chromophores. The differential equations were solved by an iterative (reverse Euler) method using a personal computer. (The authors wish to acknowledge the contribution of Peter Sauer, Carleton College, Northfield, MN in writing most of the programs used in the calculations). Programs were developed to calculate the time evolution of the excited state lifetimes and of the fluorescence emission expected. These results were then analyzed in terms of two or three exponentials, as required by the symmetry of the molecular species.

Depolarization kinetics were calculated using the data describing the time evolution of the excited state population of each chromophore in the complex. Excitation was assumed to initiate on one of the three chromophore types, and fluorescence was assumed to be depolarized by a factor of $(3 \cos^2 \theta - 1)/2$, where θ is the angle between the chromophore initially excited and the fluorescing chromophore (14). The sum of contributions from each chromophore in the complex, normalized by the corresponding excited state population, produced a time-dependent depolarization profile.

3. RESULTS AND DISCUSSION

Relaxation kinetics to compare with experimental fluorescence (isotropic) lifetime measurements were calculated for the separate β -subunit, the $\alpha\beta$ -monomer, the $(\alpha\beta)_3$ -trimer and the $(\alpha\beta)_6$ -hexamer. In the kinetic model the excitation was localized initially on one chromophore in the complex, and the transfer to other chromophores was calculated using the transfer rate constants obtained from the Förster formulation. Radiative plus non-radiative decay processes led to a loss of excited state population with a rate constant $k_F = 0.67 \text{ ns}^{-1}$, corresponding to the experimental longest lifetimes of approximately 1.5 ns. This entire calculation was then repeated for excitation present initially on a chromophore of a second class and, (except for the β -subunit), then on a chromophore of the third class. The results of these two or three calculations were multiplied by weighting parameters appropriate to the particular excitation and emission wavelengths. From these results describing the time evolution of the excited state population of all chromophores present, those for the individual chromophore classes or for the total excited state population were obtained by appropriate summations. The symmetry requires that the calculated decays are the sums of no more than three exponential components (two in the case of the β -subunit), one of which is the excited state decay with a 1.5 ns lifetime (15). The other shorter lifetimes are presented along with some recent results of time-resolved fluorescence relaxation in Table I. Relative amplitudes of the individual decay components are not included; they will depend on the particular excitation and emission wavelengths. Holzwarth (personal communication) has solved the sets of differential equations by inverting the matrix of coefficients (rate constants) and obtained identical values for the lifetimes and amplitudes of the exponential components.

The data are compared to experimental results on C-PC of different aggregate sizes isolated from the cyanobacteria, Synechococcus 6301 (4,15)

and Mastigocladus laminosus (5,7,16). The known structure of the latter PC (1) is similar to that of A. quadruplicatum (2), and a similar arrangement is also believed for the former on the basis of extensive sequence homologies (17). The experimental decay profiles have been resolved into a sum of 2-4 exponentials. General agreement is seen between the calculated and observed lifetimes, especially in the decreasing value of the short lifetime with increasing extent of aggregation. The intermediate decay component is not well matched by the experimental data; however, there is a fourth component resolved experimentally in several studies and that is not predicted by our model. This fourth component may be related to the second one seen for the isolated α -subunit, where only one chromophore is present and only one decay component is expected (5,12). Resolution of these problems must await further study.

Table 1. Comparison of calculated with measured lifetimes. Each calculated relaxation curve is the sum of three exponentials (except, only two for the β -subunit). The slowest ($\tau_F = 1500$ ps) reflects the overall excited state decay. Comparison is with wavelength-resolved experimental measurements. All lifetimes are given in psec.

	These Calculations	<u>Synechococcus</u> 6301 (4,15)	<u>M. laminosus</u> (7)	<u>M. laminosus</u> (16)
β -subunit	48, 1500			
$\alpha\beta$ -	45	47		
Monomer	700	200		
	1500	675, 1320		
$(\alpha\beta)_3$ -	16	20	36	45-61
Trimer	27	122	203	
	1500	600, 1300	807, 1420	1130-1640
$(\alpha\beta)_6$ -	15	10		
Hexamer	18	40-50		
	1500	1800		

The anisotropic fluorescence (depolarization) relaxation kinetics was extracted from the excited state populations by taking into account the relative orientations of the chromophore that initially absorbed the radiation and the one(s) that finally emit it (factorization with $(3 \cos^2\theta - 1)/2$). Again, symmetry may be invoked to decrease the number of initially excited chromophores to one member of each class, but now each emitting chromophore needs to be treated separately with respect to the orientation factor prior to the final summation. It was possible to "resolve" the time dependence of anisotropic fluorescence decay empirically into three exponential components. In this case none of the decays corresponds to the excited state lifetime, and there is no reason to expect that the deconvolution is exact. The results of this analysis are presented in Table II along with the available experimental data. The agreement is less satisfactory than for the isotropic fluorescence decay; however, more extensive experimental results are needed, especially with picosecond time resolution, before definite conclusions can be drawn. It is significant to compare the fastest (5-15 ps) depolarization calculated for the $(\alpha\beta)_6$ -hexamer with the experimental values of 10 ps for phycobilisomes from Synechococcus (8). The fastest depolarization steps were attributed to excitation transfer in C-PC in the phycobilisomes.

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Table II. Comparison of calculated with measured depolarization lifetimes. Each calculated depolarization relaxation curve is resolved into 1 to 3 exponentials. Values obtained assuming (1) equal initial excitation and (2) equal emission intensity for each chromophore class. All values in psec.

	These Calculations	<u>M. laminosus</u> (5)	<u>M. laminosus</u> (16)
β -subunit	50	403	
$\alpha\beta$ -Monomer	46, 1300	580	
$(\alpha\beta)_3$ -Trimer	8, 24, 46	70	36-57, 800-1150
$(\alpha\beta)_6$ -Hexamer	5, 15, 31		

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