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4. PHOTOSYSTEM I

EXCITED STATE PROPERTIES OF A MODIFIED PIGMENT OF BACTERIAL PHOTOSYNTHESIS

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1. INTRODUCTION

Due to the central role of bacteriochlorophyll a (BChla) in the process of bacterial photosynthesis the properties of its excited electronic states are of particular interest. In order to understand several non-linear effects in bacterial photosynthetic systems such as singlet-singlet annihilation (1, 2), it is necessary to know the excited singlet state absorption cross sections and lifetimes of the pigments. Given the possibility to exchange BChla in reaction centers of *Rhodobacter sphaeroides* against modified BChl`s (3) it is also important to know these properties for such modified pigments. One such pigment, from which important information on the function and electronic structure has been gained, is [3-vinyl]-BChla. Its only difference is the presence of a vinyl- instead of the acetyl-group at (-3), which is conjugated to the macrocyclclic π-system.

To characterize the photophysics of [3-vinyl]-BChla in diethylether we have investigated its first and higher excited states properties in comparison with those of BChla and Chla.

2. MATERIALS AND METHODS

2.1 Preparation

BChla and [3-vinyl]-BChla were prepared as described in (3). The solvent diethylether was of UVASOL grade.

2.2 Fluorescence

Spectra, emission cross sections, quantum yields, decay times and ISC rates were determined according to (4,5).

For determination of the quantum yield of [3-vinyl]-BChla, BChla in diethylether was used as a reference (ϕ = 0.19, (6)).

2.3 Nonlinear absorption

The apparatus is described in (7). Excitation was performed by a nitrogen laser pumped dye laser (spectral region: 700 - 800 nm, pulse duration: 1.4 ns, pulse energy: 6 -12 μJ). For further details cf. (4).

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2.4 Lasing

Lasing properties were investigated in a nonselective resonator (0.5 cm cell) with transverse pumping by single pulses of a nitrogen laser (850 kW, λ = 337 nm, 0.5 ns), focused by a 2.5 cm cylindrical lens.

3. RESULTS AND DISCUSSION

3.1 Fluorescence and intersystem crossing

The fluorescence quantum yields, lifetimes and ISC-rates of both compounds are listed in comparison with those of Chla in Table 1.

TABLE 1. Excited-singlet-state deactivation channels of Chla, [3-vinyl]-BChla and BChla in diethylether

compound	τ_τ [ns]	ϕ_F	k_{ic} [10^7 s^{-1}]	k_{isc} [10^8 s^{-1}]	k_{rad} [10^7 s^{-1}]
Chla	6.0	0.32	1.7	1.0	5.3
[3-vinyl]-BChla	3.1	0.22	2.5	2.3	7.1
BChla	3.0	0.19	1.7	2.5	6.3

3.2 Non-linear absorption and lasing

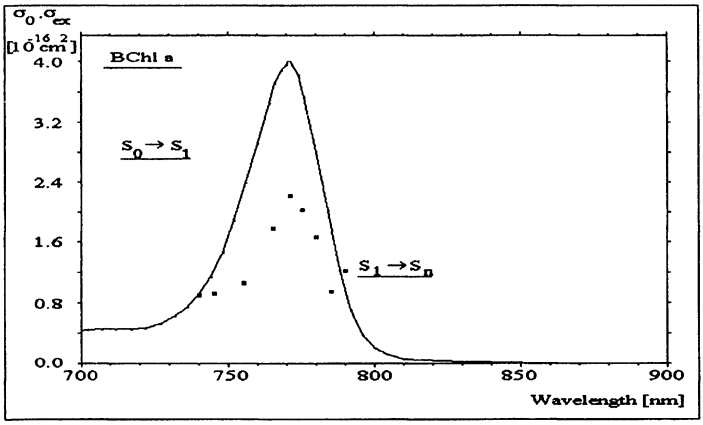
The results of the lasing experiments are summarized in Table 2.

TABLE 2. Lasing properties of Chla, [3-vinyl]-BChla and BChla in diethylether (N = 10^{17} cm^{-3})

compound	laser threshold [nm]	expected self-tuned laser threshold [nm] with σ_{ex}	[nm] without σ_{ex}
Chla [+])	671.5	671.5	679.0
[3-vinyl]-BChla	760.2	762.0	766.5
BChla	786.5	788.0	795.0

[+]) pulse duration: 1.7 ns, no lasing for 0.5 ns pulse duration (3)

From the bleaching curves, the excited singlet state spectra were calculated for both compounds by means of curve simulation (cf. Fig.1). For the required determination of excited state absorption cross sections and lifetimes [8] we used an energy level scheme with two absorption steps in the singlet and one absorption step in the triplet band system (cf. Fig. 2).



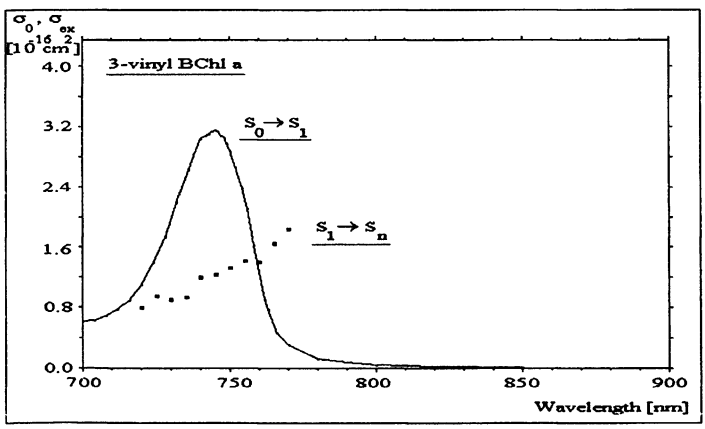


FIGURE 1. Excited state absorptions: top) BChla, bottom) [3-vinyl]- BChla in diethylether

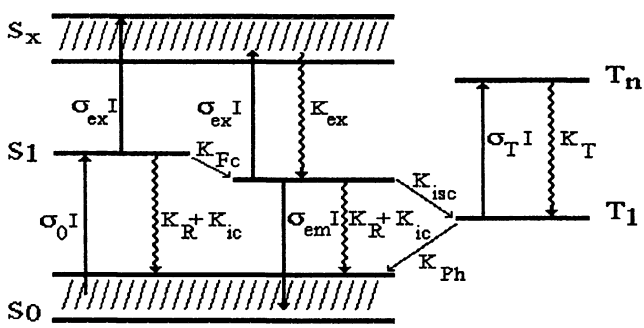


FIGURE 2. Energy level scheme used for curve simulation

4. CONCLUSIONS

The parameters of the excited states deactivation channels change continously in the order Chla → [3-vinyl]-BChla → BChla. The fluorescence lifetime decreases and intersystem crossing increases.
For all compounds strong excited state absorptions within the $S_0 \rightarrow S_1$ band could be found. This was confirmed by the observed lasing wavelengths. BChla has a $S_1 \rightarrow S_x$ spectrum very similar to its $S_0 \rightarrow S_1$ spectrum, wereas for [3-vinyl]-BChla the $S_1 \rightarrow S_x$ spectrum is red shifted relative to the $S_0 \rightarrow S_1$ band.
Because of the very strong excited state absorptions these processes should be necessarily considered in exciton annihilation experiments (1) and non-linear polarization spectroscopy (9).

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