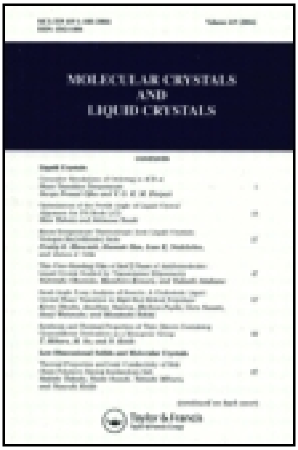

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LASER INDUCED HOLE FILLING OF BACTERIOCHLOROPHYLL *d* MONOMERS OF GREEN SULFUR PHOTOSYNTHETIC BACTERIA ANTENNAE

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Abstract. Spectral hole burning was used to study bacteriochlorophyll *d* (BChl *d*) of green sulphur bacteria *Chlorobium vibriofome*. The zero phonon hole (ZPH) widths (δ_{HB}) burned in the absorption and fluorescence spectra of BChl monomers were small in comparison with the δ_{HB} of BChl oligomers in whole cells. The phenomenon of laser induced hole filling (LIHF) of a primary hole after burning of secondary holes at a different wavelengths is reported for BChl monomers. Relative hole filled area depends mono-exponentialy on the secondary burning exposition. The hole filling coefficient (τ) decreases linearly with the distance between the primary (λ_B) and the secondary burning wavelengths (λ_S) for $\lambda_S < \lambda_B$.

INTRODUCTION

Green sulfur bacteria *Chlorobiaceae* are strictly anaerobic photosynthetic prokaryotes. The main antenna systems (chlorosomes) consist of an enveloping layer containing BChl *a* and of several rod-like elements containing BChl *c*, *d* or *e* together with carotenoids. BChl *c*, *d* and *e* are organized in highly ordered aggregated states where the geometrical arrangement and photophysical properties are rather due to pigment-pigment than pigment-protein interactions. Aggregates of chlorosomes can be converted to monomers and lower-state aggregates. This process is fully reversible.

Spectral hole burning (SHB) technique enables a determination of excited state lifetimes (pure relaxation time, T_1). Using integrated intensities of ZPH and phonon side band hole, Huang-Rhys factor (*S*) characterizing electron-phonon coupling can be estimated. The SHB in absorption and fluorescence spectra was used to study BChl *d* of green sulfur bacterium *Chlorobium vibrioforme*.

The phenomenon of LIHF of a primary hole after burning of secondary holes at a different wavelengths was studied as well. In this contribution we report results of LIHF experiments performed on BChl *d* monomers. Several theoretical models describing the LIHF suggested in literature[1,2,3] are discussed.

MATERIALS AND METHODS

The persistent SHB measurements were performed on BChl *d* prepared by l-hexanol treatment[4] from *Chl. vibrioforme*. At low temperatures (4.2 K), fluorescence was excited in Soret absorption band using 458 nm line of Argon laser. Emitted light was analyzed by double grating monochromator and a cooled photomultiplier. The same monochromator equipped with a tungsten lamp was used to scan absorption spectra.

The persistent holes were burnt by a *cw* dye laser. The typical burning power was ~ 100 - 400 mWcm^{-2}. The burning fluences was ~ 1 Jcm^{-2}. At very low temperatures (~ 1.9 K), a scanning ring dye laser was used both to burn and to scan absorption spectra (typical output power ~ 50 mW, linewidth ~ 10^{-3} cm^{-1}).

RESULTS AND DISCUSSION

Low temperature (4.2 K) absorption and fluorescence spectra of *Chl. vibrioforme* intact cells and BChl *d* monomers and lower-state aggregates are shown on Figure 1.

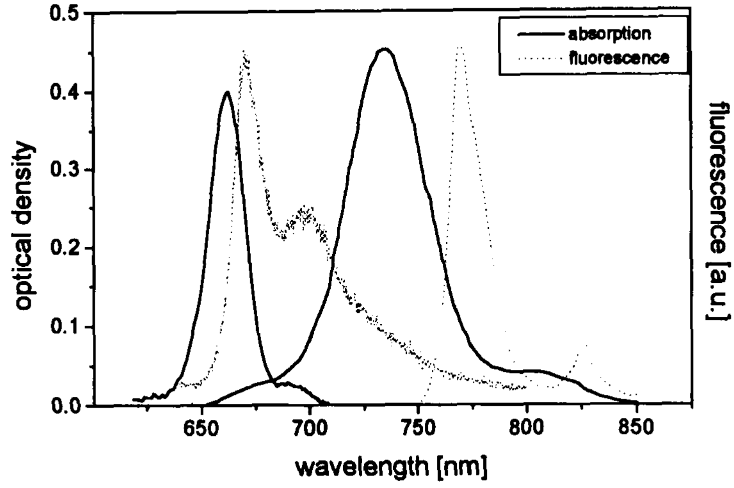

FIGURE 1. Low temperature absorption and fluorescence spectra of whole cells of *Chl. vibrioforme* and BChl *d* monomers and lower-state aggregates.

A chlorosomal BChl *d* band at ~ 730 nm dominates in the absorption spectrum of intact cells, accompanied with a shoulder at ~ 810 nm due to BChl *a*. Absorption spectrum of l-hexanol treated samples consist of a monomeric BChl *d* band at ~ 660 nm and of a BChl *d* lower-state aggregates band at ~ 690 nm. In fluorescence, the chlorosomal BChl *d* band is shifted to ~ 775 nm and it is accompanied with a BChl *a* shoulder at ~ 825 nm. The fluorescence spectrum of l-hexanol treated samples consists of three bands corresponding to BChl *d* monomers (~ 670 nm), lower-state aggregates (band at ~ 700 nm, shoulder at ~ 725 nm).

Excited state lifetimes were estimated from ZPH widths. The excited state lifetimes of BChl *d* monomers, obtained from SHB at very low temperatures (~ 1.9 K), were ~ 30 ns. This lifetime fits well with the results of time-resolved measurements on isolated BChl's, in the absence of energy transfer. On the other hand, broad ZPH's obtained in absorption and emission of systematically studied BChl *c*, *d* and *e* oligomers found in chlorosomes of green sulfur bacteria correspond to ~ 2-5 ps lifetimes. These lifetimes reflect fast energy transfer between BChl *c*, *d* and *e* clusters[5,6].

Electron-phonon coupling strength $S \sim 1$ was estimated from SHB spectra at maximum of the monomeric BChl *d* absorption (~ 661 nm).

Typical spectral behavior and time evolution of LIHF performed on BChl *d* monomers is documented on Figure 2. The 3d-plot shows a bleaching of the primary hole burnt at 660.8 nm during the secondary burning at 659.6 nm.

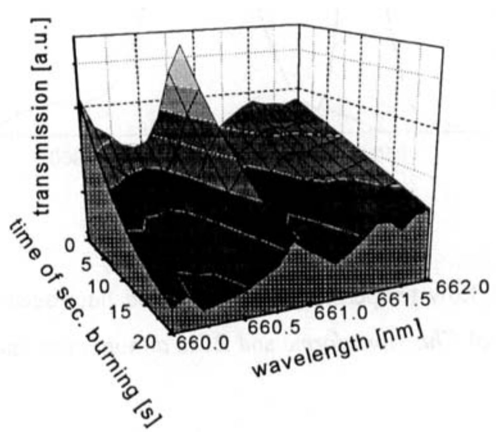

FIGURE 2. Typical behavior of laser induced filled spectra. Primary hole burnt at 660.8 nm (40 s, 225 mW/cm^2), the secondary hole burnt at 659.6 nm (50 mW/cm^2).

Relative area of the primary hole (A) depends mono-exponentialy on the secondary burning exposition $A = A_s + A_0.\exp(-P.t/\tau)$. The constant τ is here referred to as a hole filling coefficient. A_S (A_0) is a non-filled (filled) part of the primary hole after filling saturation. Two typical mono-exponential dependencies of the hole filling are presented on Figure 3. The hole-width remains unchanged during the LIHF experiments. Spontaneous filling was not found in all presented hole filling experiments.

The hole filling coefficient (τ) slightly decreases (i.e. the filling efficiency increases) with the spectral distance between the primary (λ_B) and the secondary (λ_S) burning wavelengths for $\lambda_S < \lambda_B$. The decrease could be approximated by a linear fit in the studied spectral distance range 0 to 9 nm. The parameters of this linear dependence together with declination from it were systematically studied for monomeric BChl. For $\lambda_S > \lambda_B$ the efficiency of LIHF was much smaller and under conditions of our experiments the filling could not be quantitatively characterized.

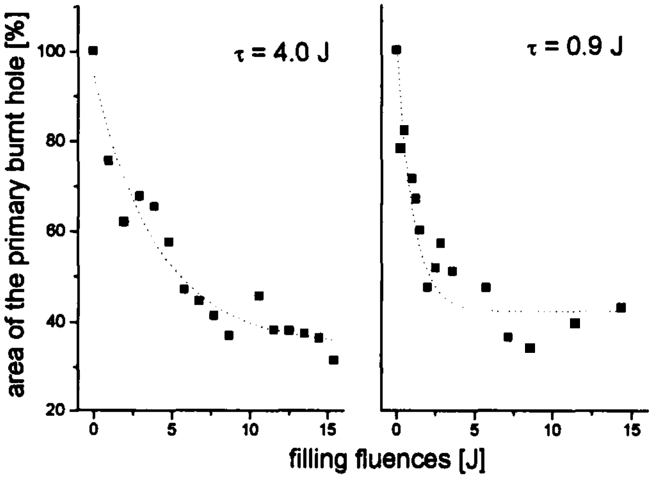

FIGURE 3. Two selected mono-exponential dependencies of the hole filling. Spectral distances between the primary hole and the blue shifted secondary burnings were 1.3 nm (left) and 7.5 nm (right).

The increase of the filling efficiency with an increasing spectral distance between the primary and the secondary burning wavelengths was previously observed[2,3]. In this case the effect was explained by energy transfer. However, such an explanation is excluded in our case. The hole filling is probably caused by excitations of antihole sites via pure electronic and phonon sideband transitions as proposed by Shu and Small[1]. In this explanation, it is assumed that sites not involved in primary burning do not contribute to the bleaching of hole which is filled. As the antihole is dominantly built at the short-wavelength side of the ZPH, the LIHF was significantly more efficient for $\lambda_S < \lambda_B$ than for $\lambda_S > \lambda_B$, in agreement with results of Shu and Small[1]. The integrated intensities of the hole and its antihole should be equal as the overall absorption intensity is conserved during the non-photochemical hole burning, however, being spread over a broad range makes the antihole rather difficult to detect. In contrast with Shu and Small[1], filling of the primary ZPH does not depend linearly on the fluence at λ_B, (filling was mono-exponential) and the filling efficiency was not independent of the λ_B.

We assume that the kinetics in LIHF via antiholes reflects a kinetics of the secondary hole burning. Under widely accepted conditions[7] the solution of kinetic equation of hole burning process could be written in the following form:

$$n(\omega,t)=n(\omega,0)\left(\frac{k_{\rightarrow}(\omega)}{k_{\rightarrow}(\omega)+k_{\leftarrow}}\exp\left[-\left(k_{\rightarrow}(\omega)+k_{\leftarrow}\right)t\right]+\frac{k_{\leftarrow}}{k_{\rightarrow}(\omega)+k_{\leftarrow}}\right)$$

where $n(\omega,t)$ is time dependent inhomogeneous distribution function, $k_{\rightarrow}(\omega)$ and $k_{\leftarrow}$ are rate constants of forward and backward photoreactions. Assuming a weak burning fluence $(k_{\rightarrow}(\omega)+k_{\leftarrow}).t \ll 1$, the exponential function could be approximated linearly as it was described for cresyl violet in PVOH[1]. This condition is not fulfilled in our case (semisaturated regime) of the LIHF experiments on BChl *d*, where the filling kinetics follows an exponential dependence.

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