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Hypothesis

Excitonic interactions in the light-harvesting antenna of photosynthetic purple bacteria and their influence on picosecond absorbance difference spectra

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A new model of the light-harvesting antenna (core complex) of purple photosynthetic bacteria is proposed based on excitonic interactions in circular aggregates of bacteriochlorophyll molecules. The calculated absorbance difference spectra of circular aggregates demonstrate all special features observed in the experimental spectra of purple bacteria In particular, the absorption changes with high amplitude of bleaching at the long-wavelength side of the absorption band at different excitation energy are predicted.

Excitonic interaction; Picosecond absorbance difference spectrum; Bacterial photosynthesis; Light-harvesting antenna

1. INTRODUCTION

According to investigations of the light-harvesting antenna of photosynthetic purple bacteria the absorption bands of bacteriochlorophyll (BChl) molecules in the near infrared range are inhomogeneous. For the B880 complex from *Rhodospirillum rubrum* and the B890 complex from *Chromatium minutissimum* the increase in exciting pulse energy is followed by shape changes and a shift of the bleaching band to the short-wavelength side in picosecond absorbance difference spectra [1–4]. In the case of a short-wavelength excitation ($\lambda < 880$ nm) the absorption changes are characterized by a low degree of anisotrophy ($r < 0.1$). In the case of a long-wavelength excitation ($\lambda > 890$ nm) they display a high degree of anisotropy ($r = 0.25$). A low degree of anisotropy at the short-wavelength side of the absorption band was observed even at short time intervals (of the order of 1 ps) after excitation; a high degree of anisotrophy at the long-wavelength side did not decrease with time [5,6]. The value of absorption changes at the long-wavelength bleaching peak per absorbed light quantum corresponded to complete bleaching of at least four BChl molecules [7].

All these facts cannot readily be explained by application of a model assuming the presence of the long-wavelength minor form of BChl molecules [1,2,5,8,9] or using a model of inhomogeneous broadening of pigment bands [10,11].

In [12,13], the antenna core complex was suggested to be a circular aggregate, having two dipole allowed excitonic states with different absorption anisotropy. Such a model not only provides an explanation for the two spectral forms ('minor' and 'major') but is also in agreement with the concept of cyclic structures due to association of α,β-pairs [14,15].

In this work we have shown that excitonic interactions in circular aggregates may account for the shape of the picosecond absorbance difference spectra of antenna of purple bacteria and for its dependence on the excitation energy. The high value of bleaching per absorbed quantum has been explained as well.

2. MODEL

Assume that light-harvesting complexes are in the form of a circular aggregate with the C_N-symmetry, where N is the number of BChl molecules. The electronically excited energy level of the aggregate is split into N sublevels with energies E_k [16]:

$$E_k = \Delta E + 2M \cos\vartheta k, \ \vartheta = 2\pi/N \qquad (1)$$

where ΔE is the excitation energy of an isolated molecule; M is the matrix element of excitation transfer be-

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tween nearest-neighbor molecules (let everywhere $M < 0$); k takes N integer values (0, ± 1, ± 2,...).

The transition dipole moment of the n^{th} molecule is:

$$\vec{d}_n = d_\parallel \vec{x} \cos\vartheta n + d_\parallel \vec{y} \sin\vartheta n + d_\perp \vec{z} \qquad (2)$$

where $\vec{x}$, $\vec{y}$ are the unit length vectors lying in the circle plane and $\vec{z}$ is the unit vector perpendicular to the circle plane.

The dipole moments of transitions from ground state $|g>$ to one-exciton states $|k>$

$$<k\,|\hat{d}|\,g> = N^{1/2}(d_\parallel/2\,(\vec{x} \pm i\vec{y})\delta_{k,\pm 1} + d_\perp \vec{z}\,\delta_{k,0}) \qquad (3)$$

are non-zero only for the two lowest exciton components, $k = 0$ and $k = \pm 1$. The level, $k = 0$, corresponds to absorption of an incident electromagnetic wave $\vec{E} = \vec{e}E \cdot \exp(i\omega t)$ with linear polarization ($\vec{e} = \vec{z}$ and has high absorption anisotropy. The twofold degenerated level, $k = \pm 1$, corresponds to absorption of circularly polarized light ($\vec{e} = (\vec{x} \pm i\vec{y})/\sqrt{2}$) and has low absorption anisotropy.

The dipole moments of transitions from the one-exciton state $|k>$ to the two-exciton states $|k_1k_2>$ are equal to

$$<k_2k_1\,|\hat{d}|\,k> =$$
$$N^{1/2}(d_\parallel/2(\vec{x} \pm i\vec{y})F_{\pm 1}\delta_{k1+k2,\,k\pm 1} + d_\perp \vec{z}\,F_0\delta_{k1+k2,k})$$

$$F_\varepsilon = (i\vartheta/2\pi)\,[\text{ctg}((k_2 - \varepsilon)\,\vartheta/2) - \text{ctg}(\,(k_1 - \varepsilon)\vartheta/2)],\ \varepsilon = $$
$$= 0,\ \pm 1 \qquad (4)$$

In this formula k_1, k_2 take N half-integer values (± 1/ 2, ± 3/2,...) [16] whereas k takes N integer values. The transition energy between levels $|k>$ and $|k_1k_2>$ is equal to $E_{k1,k2} = E_{k1}+E_{k2}-E_k$.

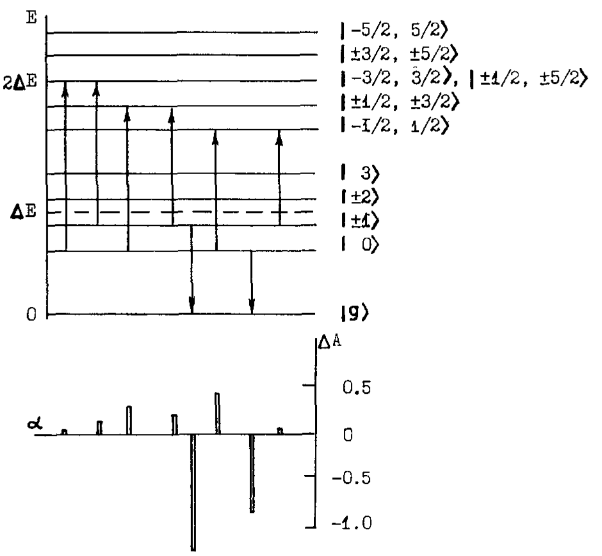

Fig. 1. The scheme of excitonic levels for $N = 6$ and the arrangement of spectral lines for transitions from one-exciton states for ($2d_\perp/d_\parallel = 7/9$.)

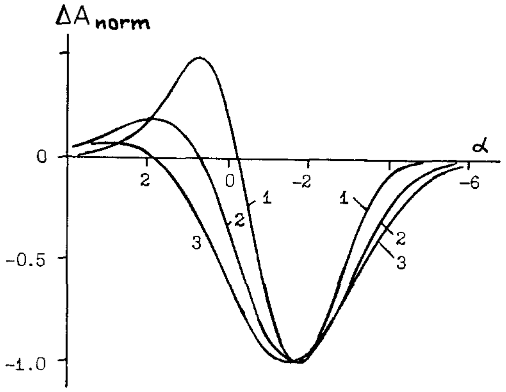

Fig. 2. The normalized calculated picosecond absorbance difference spectra $\Delta A(\alpha)$ at low (curve 1), room (curve 2) and high (curve 3) temperature for ($2d_\perp/d_\parallel = 7/9$ All spectra were calculated without correction for temperature line shifts. The relative line bandwiths 1.3, 2 and 2 5 were assumed for curves 1, 2 and 3, respectively

3. CALCULATIONS OF DIFFERENCE ABSORBANCE SPECTRA FOR $N = 6$

When calculating the difference absorbance spectra it was assumed that: (a) the pump and probe pulses had the same linear polarization; (b) the pump wavelength was chosen at the long-wavelength side of the absorption band; (c) laser pulses were much longer than the time constant of population equilibration between exciton levels; (d) the sample was not oriented.

These assumptions are adequate to the experimental conditions under which the picosecond absorbance difference spectra were measured earlier [1,2,4,7].

Let the difference spectra for the circular aggregate of six BChl molecules be a simple example. The energy level diagram for this aggregate and the transitions from one-exciton states are shown in Fig. 1. It is convenient to characterize the position of spectral lines, corresponding to these transitions, by the parameter α, which is equal to the energy measured from ΔE and normalized on $|M|$. The ΔA values for these lines are shown at room temperature (the corresponding populations: 1/2 ($k = 0$), 1/4 ($k = 1$), 1/4 ($k = -1$), 0 ($k = \pm 2,3$). Here $\Delta A = \Delta A_N/|\Delta A_1|$, where ΔA_N and ΔA_1 are the induced absorption changes for the aggregate of N molecules and for the monomer, respectively. The overall difference spectrum has a long-wavelength negative branch due to the transition between ground and one-exciton states, and a broad short-wavelength positive branch, corresponding to the transition from one-exciton states to two-exciton states (Fig. 2).

The spectra of absorption changes for low temperatures, when only the $k = 0$ state is populated, and for

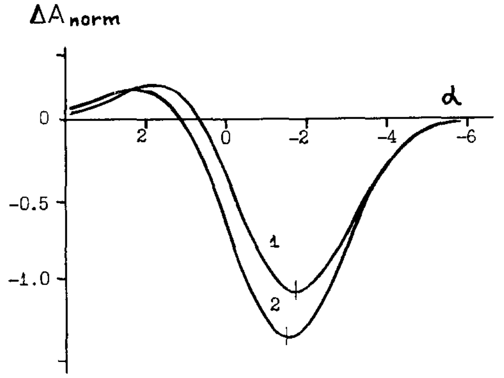

Fig. 3. The normalized picosecond absorbance difference spectra $\Delta A(\alpha)$ for low (curve 1) and high (curve 2) energy of exciting pulses for $(2d_1/d_0)^2 = 7/9$.

a hypothetical high temperature, when all states are equally populated, are shown in Fig. 2 as well.

All the preceding is related to low-energy exciting pulses when each complex absorbs no more than one quantum. At high-energy exciting pulses each complex may absorb two or more quanta. After absorption of two quanta the system would be at one of the two-exciton levels $|k_1k_2\rangle$. The transitions from this level to levels $|k\rangle$ (with quantum emission) and to levels $|k'k''k'''\rangle$ (with quantum absorption) are available. Here k', k'', k''' take integer values [16]).

Fig. 3 shows the difference spectra at room temperature for low and high excitation energies. The shape of the spectrum for high excitation energy is approximately the same as for low energy but blue-shifted. Similar changes of experimental picosecond absorbance difference spectra were found in [1–4].

4. CALCULATIONS OF DIFFERENCE ABSORBANCE SPECTRA FOR ARBITRARY *N*

The shape of spectra does not exhibit significant changes with the N increase (and decrease as well). However, the absolute magnitude of induced absorption changes may undergo a large increase with the N increase. In particular, approximate estimates of the absolute magnitude of the long-wavelength bleaching peak can be obtained:

$$\Delta A = \Delta A_N/|\Delta A_1| = N/12(-4 + (2/N)^2 \operatorname{ctg}^2(\pi/2N)) \qquad (5)$$

It was shown in [7] that ΔA at the long-wavelength bleaching peak is equal to 4.2 ± 0.3 for the monocentral B890 complex from *Chromatium minutissimum*. Then it would give $N = 21.2 \pm 1.5$. That rough estimate causes us to anticipate that $N = 24$ as it is expected from the model of B875(890) complex comprising twelve α,β-pairs [14,15].

5. CONCLUSIONS

The circular aggregate of strongly coupled BChl molecules as a model of the light-harvesting core complex allows us to explain several characteristics of antenna optical spectra, namely existence of two lines with different anisotropy corresponding to different excitonic levels, the form of picosecond absorbance difference spectra at low and high energies of exciting pulses and the large value of bleaching at the long-wavelength side of the near-infrared absorption band.

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