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AN ASYMMETRIC DIMER EXCITON MODEL

APPLICATION TO THE PRIMARY ELECTRON DONOR OF BACTERIAL PHOTOREACTION CENTER

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An asymmetric dimer exciton theory is developed that takes into account both environmental and vibronic effects on the electronic transition energies. Explicit equations are presented for the transition energies, the dipole moments, the angle between the dipole moments and the dipole and rotational strengths for the electronic transitions in this asymmetric dimer. This model is proposed to describe the structure of the special pair of bacteriochlorophyll *a* molecules believed to constitute the primary electron donor of bacterial photoreaction center. The model is found to be consistent with most of the spectroscopic properties of the photoreaction center. We used the equations derived from the asymmetric model along with absorption and circular dichroism spectroscopy data to predict a geometrical structure for the primary electron donor.

Introduction

The primary act of energy conversion in photosynthesis involves the transfer of an electron from a primary donor to a primary acceptor molecule. This process occurs in a chromoprotein called the photoreaction center which, in purple photosynthetic bacteria, contains four molecules of bacteriochlorophyll (BChl) and two molecules of bacteriopheophytin [1,2]. These pigment molecules play a crucial role in the primary photochemistry [3] which, therefore, cannot be fully understood before we know their geometrical arrangement and the nature of their interactions.

Since the most direct experimental approach, X-ray diffraction, has not yet borne its fruits, most of our present information on this point is based on spectroscopic evidence. On the basis of circular dichroism spectroscopy (CD), Sauer et al. [4] suggested that the Q_y absorption spectrum of BChl in the photoreaction center is due to a coupled set of all the BChl molecules. On photooxidation, the exciton band would disappear and be replaced by a new band due to monomeric BChl. On the other hand, electron paramagnetic resonance and electron and nuclear double resonance spectra of the oxidized primary donor are generally interpreted as an equal sharing of the unpaired electron among two BChl molecules, the 'special pair' [5,6]. The model of Sauer et al. [4] would not predict any identifiable absorption spectrum for the special pair. However, Vermeglio and Clayton [7] have deduced by linear photodichroism spectroscopy of oriented chromatophores that two components are bleached on photooxidation, a main component with a peak wavelength at 870 nm and a small component with a peak at 812 nm. They suggested that these bands are the results of an excitonic interaction (of the type formulated by Tinoco [8]

Abbreviation: BChl, bacteriochlorophyll.

and McRae and Kasha [9]) between the two Q_y transitions of the BChl molecules in the special pair. The photoreaction center pigment interaction has been recently reviewed [10,11].

Recently, we have studied the CD spectra of oriented photoreaction center. We found that the biphasic bands at 870 and 810 nm and at 630 and 600 nm decrease drastically when measured along a particular axis of the oriented sample. Since the rotational strengths of exciton bands disappear when measured along an axis of symmetry [12], the best explanation of our results is that the two biphasic bands are Q_y and Q_x BChl dimer exciton bands. If the exciton interaction between the two BChl molecules of the special pair is of the type formulated by Tinoco [8] and McRae and Kasha [9], then the two resultant transition dipoles of the exciton bands should be orthogonal to each other and give rise to absorption and CD bands of equal widths. However, contrary to predictions, the two transition dipoles are found not to be orthogonal in strain G9 of *Rhodospirillum rubrum* (Mar, T. and Gingras, G., unpublished data) and the two CD bands have very different bandwidths [4,13–15]. Hence, we are left with an apparent paradox.

The underlying assumption of the exciton model of Tinoco [8] and of McRae and Kasha [9] is that the molecular components of the dimer are identical and are bound by strong interaction. The fact that this model ignores any possible distortions in the symmetry of the molecular transition energies makes it ideally applicable to the spectral behavior of dimers in solution. However, if the two component molecules of the dimer were subjected to an asymmetric environmental field such as might be found in a protein, then situations might arise where the environmental and excitonic interaction energies would be comparable. In such situations, the symmetric model would not hold [16]. This would be also true of its main consequence, that the single transition of the monomer is split into two transitions of equal bandwidths and of perpendicular dipole moments. The aim of the present article is to develop a dimer model of exciton coupling that removes the symmetry condition and to examine the predictions of this model for the structure of the primary donor. We find that such a model is in agreement with most optical properties of the photoreaction center. Using these optical properties, the model allows us to predict a geometry of the primary electron donor which is amenable to future confrontation with experiment.

Exciton theory for an asymmetric dimer

In this section, we present the electronic spectral properties of an asymmetric dimer. For simplicity, we will assume that there is no overlap of the electronic wavefunctions and that the Born-Oppenheimer approximation holds in all cases [17].

Consider two identical molecules A and B embedded in a large aggregate. The distance between the two molecules is such that the interaction is large enough to allow the excited states to be delocalized over the two molecules. We assume that the relative orientation and the relative motions of their center of mass are fixed. Using the Born-Oppenheimer approximation, ψ_G, the ground electronic state of the dimer, can be represented by the simple product of the wave functions

$$\psi_G = \phi_A(q_A, Q_A)\phi_B(q_B, Q_B) \tag{1}$$

where ϕ_A is the electronic wave function for the A molecule when its nucleus is at rest, q_A and Q_A are respectively the electronic and nuclear coordinates of A. The Hamiltonian of the system is

$$\mathscr{H} = \mathscr{H}_A + \mathscr{H}_B + \mathscr{H}_{AB} \tag{2}$$

where $\mathscr{H}_A$ is the electronic Hamiltonian of A and satisfies the eigenvalue equation

$$\mathscr{H}_A\phi_A(q_A, Q_A) = E_A\phi_A(q_A, Q_A) \tag{3a}$$

with

$$E_A = w_A^0 + \tfrac{1}{2}kQ_A^2 \tag{3b}$$

w_A^0 is the ground-state energy of the A molecule and $\frac{1}{2}kQ_A^2$ is the potential energy for nuclear vibration written in harmonic approximation [18]. k is the force constant. We assume that the nuclear vibrations can be adequately described by a one-dimensional potential surface. In Eqn. 2, $\mathscr{H}_{AB}$ denotes the interaction between A and B. In the absence of resonance interaction between the two chromophores, if either one of the chromophores is excited, we have two nonstationary states with energies $E_{A'B}$ and $E_{AB'}$. The two excited-state energies, $E_{A'B}$ and $E_{A'B}$, are different if the environmental shift of the ground to first excited singlet state transition energies of molecules A and B are not the same [16] and if the nuclear configurations of the two states have unequal nuclear coordinates Q_A and Q_B [19]. For the treatment of resonance interaction with two molecules of dissimilar energy, we will follow the calculation of Förster [19]. He showed that the first excited state of the dimer can be described by a linear combination of two stationary states, ψ_I and ψ_{II}, where

$$\psi_I = \left(\cos\frac{\alpha}{2}\right)\phi_A^+\phi_B + \left(\sin\frac{\alpha}{2}\right)\phi_A\phi_B^+$$

$$\psi_{II} = \left(\sin\frac{\alpha}{2}\right)\phi_A^+\phi_B - \left(\cos\frac{\alpha}{2}\right)\phi_A\phi_B^+ \qquad (4)$$

with corresponding energies

$$E_I = \frac{E_{A'B} + E_{AB'}}{2} + \frac{U}{\sin\alpha}$$

$$E_{II} = \frac{E_{A'B} + E_{AB'}}{2} - \frac{U}{\sin\alpha} \qquad (5)$$

where U is the resonance integral between the two configurations with A and then with B excited. U is defined as

$$U = \langle \phi_A^+\phi_B | \mathscr{H}_{AB} | \phi_A\phi_B^+ \rangle \qquad (6)$$

The angle α in Eqns. 4 and 5 is defined by the equation

$$\tan\alpha = \frac{2U}{E_{A'B} - E_{AB'}} \quad \text{for } 0 \leqslant \alpha \leqslant \pi \qquad (7)$$

The transition dipole moments $\boldsymbol{\mu}_I$ and $\boldsymbol{\mu}_{II}$ can now be calculated from the wave functions given in equation 4:

$$\boldsymbol{\mu}_I = \cos\frac{\alpha}{2}\boldsymbol{\mu}_A + \sin\frac{\alpha}{2}\boldsymbol{\mu}_B$$

$$\boldsymbol{\mu}_{II} = \sin\frac{\alpha}{2}\boldsymbol{\mu}_A - \cos\frac{\alpha}{2}\boldsymbol{\mu}_B \qquad (8)$$

we see from Eqns. 4, 5, 7 and 8 that if $E_{A'B}$ is equal to $E_{AB'}$, then the wave functions ψ_I and ψ_{II}, the corresponding energies E_I and E_{II} and transition dipole moments $\boldsymbol{\mu}_I$ and $\boldsymbol{\mu}_{II}$ reduce to values obtained from the exciton theory for two symmetric molecules [9].

Although the theory of resonance interaction of two molecules of different energies has been developed [19], very little work has been done to describe the consequences of the theory on the absorption and CD spectra of the dimer. On the other hand, the consequences of the exciton theory for a symmetric dimer have been well formulated for the absorption and CD spectra [8,9]. A summary of the formulae obtained for the transition energies, the dipole moments, the angle between the dipole moments, the dipole strength and the rotational strength is presented in Table I. Using the electronic wave functions given in Eqn. 4 and the transition dipole moments in Eqn. 8, we have derived expressions for: the dipole strength, D ($D = \boldsymbol{\mu} \cdot \boldsymbol{\mu}$), the rotational strength, R, the angle between the dipole moments and the ratio and sum of the dipole strengths and rotational strengths of the two transitions for the asymmetric dimer. Table I also shows how the spectral properties will be affected by a different interaction of molecules A and B with their environment. Here are the main differences in the spectral properties of the dimer predicted by the asymmetric exciton model as compared to the predictions of the symmetric model. (1) The two exciton bands are no longer equally split on either side of the monomer absorption band. This is shown in Eqn. Ib (equation b of Table I). (2) The energy difference between the two exciton bands is no longer equal to $2U$ but to $2U/\sin\alpha$ (Eqn. Ib). (3) The angle between the two chromophores can no longer be calculated from the ratio of the dipole strengths. A factor $\sin\alpha$ must now be included to take into account the added interactions of the two chromophores (Eqn. Ie). (4) The transition dipole moments of the ground state to the two excited stationary states are no longer orthogonal to each other. As can be seen from Eqn. Ig, the asymmetric exciton model predicts that $\boldsymbol{\mu}_A$ is orthogonal to $\boldsymbol{\mu}_B$. Cos α will be equal to zero only if $E_{A'B}$ equals $E_{AB'}$. (5) The rotational strengths of both transitions will be affected equally by environmental and vibronic interactions (Eqn. Ih). (6) The sums of the dipole strengths and of the rotational strengths remain the same regardless of environmental and vibronic interactions (Eqns. If and Ii).

TABLE I

EXPLICIT EQUATIONS FROM EXCITON THEORY OF DIMERS

θ denotes the angle between the transition dipole moment of the two monomer. R_A and R_B denote the rotational strength of the two monomers A and B, respectively. $\boldsymbol{R}_{12}$ denotes the intermolecular distance between the two monomers. λ denotes the wavelength of the absorption transition between the ground state and the first excited state of the unperturbed monomer. α is defined in Eqn. 11 of text. U is the transition dipole-transition dipole interaction energy. $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are the electric transition dipole moments of the two unperturbed monomers. $\boldsymbol{m}_A$ and $\boldsymbol{m}_B$ are the magnetic transition dipole moments of the two unperturbed monomers.

Properties	Dimer with molecules of different energies	Dimer with molecules of identical energies	
Electronic wave functions	$\psi_I = \cos\frac{\alpha}{2}\phi_A^+\phi_B + \sin\frac{\alpha}{2}\phi_A\phi_B^+$ $\psi_{II} = \sin\frac{\alpha}{2}\phi_A^+\phi_B - \cos\frac{\alpha}{2}\phi_A\phi_B^+$	$\psi_I = \frac{1}{\sqrt{2}}(\phi_A^+\phi_B + \phi_A\phi_B^+)$ $\psi_{II} = \frac{1}{\sqrt{2}}(\phi_A^+\phi_B - \phi_A\phi_B^+)$	(a)
Transition energies	$E_I = \frac{E_{A'B} + E_{AB'}}{2} + \frac{U}{\sin\alpha}$ $E_{II} = \frac{E_{A'B} + E_{AB'}}{2} - \frac{U}{\sin\alpha}$	$E_I = E_{\text{monomer}} + U$ $E_{II} = E_{\text{monomer}} - U$	(b)
Dipole moments	$\boldsymbol{\mu}_I = \cos\frac{\alpha}{2}\boldsymbol{\mu}_A + \sin\frac{\alpha}{2}\boldsymbol{\mu}_B$ $\boldsymbol{\mu}_{II} = \sin\frac{\alpha}{2}\boldsymbol{\mu}_A - \cos\frac{\alpha}{2}\boldsymbol{\mu}_B$	$\boldsymbol{\mu}_I = \frac{1}{\sqrt{2}}(\boldsymbol{\mu}_A + \boldsymbol{\mu}_B)$ $\boldsymbol{\mu}_{II} = \frac{1}{\sqrt{2}}(\boldsymbol{\mu}_A - \boldsymbol{\mu}_B)$	(c)
Dipole strengths	$D_I = D_{\text{monomer}}(1 + \sin\alpha\cos\theta)$ $D_{II} = D_{\text{monomer}}(1 - \sin\alpha\cos\theta)$	$D_I = D_{\text{monomer}}(1 + \cos\theta)$ $D_{II} = D_{\text{monomer}}(1 - \cos\theta)$	(d)
Ratio of dipole strengths	$\frac{D_I}{D_{II}} = \frac{1 + \sin\alpha\cos\theta}{1 - \sin\alpha\cos\theta}$	$\frac{D_I}{D_{II}} = \frac{1 + \cos\theta}{1 - \cos\theta}$	(e)
Sum of dipole strengths	$D_I + D_{II} = 2D_{\text{monomer}}$	$D_I + D_{II} = 2D_{\text{monomer}}$	(f)
Angle between dipole moments	$\boldsymbol{\mu}_I \cdot \boldsymbol{\mu}_{II} = -D_{\text{monomer}}\cos\alpha\cos\theta$	$\boldsymbol{\mu}_I \cdot \boldsymbol{\mu}_{II} = 0$	(g)
Rotational strengths	$R_I = \cos^2\frac{\alpha}{2}R_A + \sin^2\frac{\alpha}{2}R_B$ $+\frac{1}{2}\sin\alpha \cdot \mathrm{i}(\boldsymbol{\mu}_A \cdot \boldsymbol{m}_B + \boldsymbol{\mu}_B \cdot \boldsymbol{m}_A)$ $+\frac{\Pi\sin\alpha}{2\lambda}\boldsymbol{R}_{12} \cdot \boldsymbol{\mu}_B \times \boldsymbol{\mu}_A$ $R_{II} = \sin^2\frac{\alpha}{2}\boldsymbol{R}_A + \cos^2\frac{\alpha}{2}R_B$ $-\frac{1}{2}\sin\alpha \cdot \mathrm{i}(\boldsymbol{\mu}_A \cdot \boldsymbol{m}_B + \boldsymbol{\mu}_B \cdot \boldsymbol{m}_A)$ $-\frac{\Pi\sin\alpha}{2\lambda}\boldsymbol{R}_{12} \cdot \boldsymbol{\mu}_B \times \boldsymbol{\mu}_A$	$R_I = \frac{1}{2}(R_A + R_B)$ $+\frac{1}{2}\mathrm{i}(\boldsymbol{\mu}_A \cdot \boldsymbol{m}_B + \boldsymbol{\mu}_B \cdot \boldsymbol{m}_A)$ $+\frac{\Pi}{2\lambda}\boldsymbol{R}_{12} \cdot \boldsymbol{\mu}_B \times \boldsymbol{\mu}_A$ $R_{II} = \frac{1}{2}(R_A + R_B)$ $-\frac{1}{2}\mathrm{i}(\boldsymbol{\mu}_A \cdot \boldsymbol{m}_B + \boldsymbol{\mu}_B \cdot \boldsymbol{m}_A)$ $-\frac{\Pi}{2\lambda}\boldsymbol{R}_{12} \cdot \boldsymbol{\mu}_B \times \boldsymbol{\mu}_A$	(h)
Ratio of rotational strengths	$\frac{R_I}{R_{II}} = -1 \text{ if } R_A + R_B \cong 0$	$\frac{R_I}{R_{II}} = -1 \text{ if } R_A + R_B \cong 0$	(i)

The asymmetric exciton model also predicts unequal widths at half-maximum (hereafter called bandwidths) for the two exciton absorption bands. Using an oversimplified model system consisting of nuclear potential surfaces, we show how the asymmetric environmental interaction changes unequally the distance between the equilibrium configurations of the ground state and of the two excited states (Appendix I). This results in unequal bandwidths of the two individual exciton bands. As the asymmetric interaction energy decreases to zero, the bandwidths of the two bands become equal, as predicted by the symmetric exciton theory [20].

Application of the asymmetric exciton model to the BChl special pair

Circular dichroism spectroscopy recently performed on oriented photoreaction center preparations from *Rsp. rubrum* has provided good evidence that the CD bands at 870, 810, 630 and 600 nm are exciton bands and that the CD band at 795 nm is due to monomeric BChl [12]. Since previous CD spectroscopy [4,14,15] has shown that it is the former (exciton) bands that are bleached on oxidation, they can safely be attributed to the two BChl molecules of the special pair deduced from EPR and ENDOR spectroscopy [5,6]. Consequently, the exciton bands should have all the characteristics found in dimers. In the lines that follow, we will compare some of the observed characteristics with theoretical expectations.

The 600 and the 630 nm CD bands resemble exciton dimer bands [15], the high- and the low-energy bands being respectively of positive and negative signs with conserved rotatory strength. The 810 and the 870 nm CD bands also resemble exciton dimer bands with the high- and low-energy bands being respectively of negative and positive signs. In the latter case, the rotatory strengths are nearly but not strictly conserved. The slight discrepancy with strict conservation may be due to the monomer BChl molecules having non-negligible rotatory strength in their protein environment (Eqn. Ih).

One pecularity of the CD bands is that the bandwidth of the 870 nm band is not only somewhat greater than that of monomer BChl in solution but also more than 2-times that of the 810 nm band [13–15]. This is very different from the values of $(1/\sqrt{2})$-times the bandwidth of the monomer that are predicted for the bandwidths of a dimer in a homogeneous environment (Appendix I and Ref. 20). However, this discrepancy may be due to the erroneous assumption that the BChl molecules are in identical environments. If these environments were different, the conservative biphasic CD spectra characteristic of symmetric dimers would still be observed (Eqn. Ih) but with decreased rotatory strengths and with different bandwidths of the two exciton transitions. The difference in bandwidth is due to the fact that, in an asymmetric environment, the nuclear vibrations of the two exciton states have their equilibrium positions separated from each other and no longer halfway between those of the ground and excited states of the monomer (Appendix I).

That the BChl molecules of the special pair may be in different environments is also indicated by the observation that, on cooling, the maximum of the 810 nm CD band remains approximately at the same position while the maximum of the 870 nm CD band shifts to the red [15,10]. In the symmetric exciton theory, the increased splitting of the two exciton bands is difficult to reconcile with the red shift of their center of gravity (midpoint between the two maxima). However, according to the asymmetric exciton theory, an increased splitting could result from an induced shift of the absorption maximum of one of the two BChl molecules. If asymmetry was due, for instance, to the proximity of an ionized acid in the protein to one BChl molecule, causing a red shift of its absorption band [21], then lowering the temperature might decrease the distance between that negative charge and the BChl molecule. The induced red shift of the corresponding monomer band would entail both an increased splitting of the exciton bands and a red shift of their center of gravity (Eqns. Ib and Ic). This would tend to shift one exciton band to the red much more than the other. A large red shift of one of the monomer bands associated with a slight blue shift of the other monomer band due to different environmental interactions could produce the observed band shifts without any change in the exciton interaction (Appendix II). As first pointed out by Shipman et al. [15], differences in the environmental interactions tend to reduce the amount of mixing of the excited states localized on single molecules. This tends to allow the exciton bands some monomer properties and qualitatively explains why the red shift of the 870 nm band observed on cooling has monomer characteristics.

The large rotatory strengths of the 870 nm and 810 nm CD bands imply that the Q_y absorption dipoles of the BChl monomers are not parallel to each other (Eqn. Ih). Exciton theory would predict that the corresponding dipole strengths are non-negligible (Eqn. Id) and therefore that absorption bands should be found at these two wavelengths. Linear dichroism [7,22] has shown that the 870 nm band is indeed a single band. The 810 nm band is more difficult to ascertain because it is obscured by the absorption bands of the other BChl molecules. Indeed, temperature dependency of energy transfer [23] and detailed polarization studies (Mar, T. and Gingras, G., unpublished data) showed that the 800 nm absorption band must be composed of at least three differently oriented transition dipoles. Vermeglio and Clayton [7] have shown that their data on linear dichroism of light-induced absorbance changes in oriented photoreaction center can be explained by postulating a bleaching of the 810 nm band. If the 810 nm and the 870 nm bands were indeed exciton bands the symmetric exciton theory would predict that these transition dipoles should be orthogonal (Eqn. Ig). However, contrary to expectations, we found that, in photoreaction center from *Rsp. rubrum* G9, the angle between the two transition dipoles cannot be greater than 70° [12]. This discrepancy was explained by postulating that the two BChl molecules are in different environments. A consequence of such asymmetric interaction between the two special BChl molecules is that orthogonality of the two dimer dipoles is no longer predicted (Eqn. Ig).

In principle (Eqn. IIa), the amount of asymmetric interaction of the special pair BChl molecules could be calculated from the ratio of the oscillator strengths of the two absorption bands at 810 and at 870 nm and the angle between these two transition dipoles (Eqn. IIa). Unfortunately, only the

TABLE II

MOLECULAR PARAMETERS OF THE SPECIAL PAIR BChl CALCULATED BY THE ASYMMETRIC EXCITON THEORY

θ' denotes the angle between the 810 nm transition dipole and the 870 nm transition dipole. θ denotes the angle between the Q_y transition dipole moments of the two BChl monomers forming the special pair. α, U, E_{I}, E_{II}, $E_{\mathrm{A'B}}$, $E_{\mathrm{AB'}}$, D_{I}, D_{II} are defined in the text. $D_{\mathrm{I}}/D_{\mathrm{II}} = 1/6$ was used in the calculations.

Parameters	Values calculated	Formula used	Derivation from equations:
θ'	$70° > \theta' > 36°$		
α	$73° > \alpha > 51°$	(a) $\alpha = \tan^{-1}\left[\frac{1 - D_{\mathrm{I}}/D_{\mathrm{II}}}{2[D_{\mathrm{I}}/D_{\mathrm{II}}]^{1/2}\cos\theta'}\right]$	Id,f,g
U	$376 > U > 306$ cm^{-1} cm^{-1}	(b) $U = \left[\frac{E_{\mathrm{I}} - E_{\mathrm{II}}}{2}\right]\sin\alpha$	Ib
$E_{\mathrm{A'B}} - E_{\mathrm{AB'}}$	$252 < E_{\mathrm{A'B}} - E_{\mathrm{AB'}} < 489$ cm^{-1} cm^{-1}	(c) $E_{\mathrm{A'B}} - E_{\mathrm{AB'}} = \frac{2U}{\tan\alpha}$	11
$E_{\mathrm{A'B}} + E_{\mathrm{AB'}}$	23906 cm^{-1}	(d) $E_{\mathrm{A'B}} + E_{\mathrm{AB'}} = E_{\mathrm{I}} + E_{\mathrm{II}}$	Ib
$E_{\mathrm{A'B}}$	$12079 < E_{\mathrm{A'B}} < 12198$ cm^{-1} cm^{-1}		IIc,d
$E_{\mathrm{AB'}}$	$11827 < E_{\mathrm{AB'}} < 11708$ cm^{-1} cm^{-1}		IIc,d
θ	$138° < \theta < 156°$	(e) $\theta = \cos^{-1}\left[\frac{-1}{\sin\alpha}\left[\frac{1-(D_{\mathrm{I}}/D_{\mathrm{II}})}{1+(D_{\mathrm{I}}/D_{\mathrm{II}})}\right]\right]$	Ie

oscillator strength of the 870 nm band is known. However, an estimate of the oscillator strength of the 810 nm band can be obtained by comparing the areas of the absorption bands at 800 nm and at 870 nm. Reed and Peters [24] found a ratoi of 4 : 3 in *Rps. sphaeroides* photoreaction center, and we find the same ratio in *Rsp. rubrum* photoreaction center. Since the oscillator strengths of chlorophyll molecules in vitro are virtually the same in different solvents [25], we will assume that the BChl monomers in the photoreaction center protein have approximately the same oscillator strength. Using this assumption and the fact that the oscillator strengths are conserved in exciton interaction (Eqn. IId), we see that 1/8 of the oscillator strength of the 800 nm band belongs to the 810 nm band of the special pair BChl. The oscillator strength of the 810 nm band must then be approx. 1/6 that of the 870 nm band. The angle between the 810 nm transition dipole and the 870 nm transition dipole has been found to be less than 70° in strain G9 of *Rsp. rubrum.* We will assume this to be the maximum possible angle for all *Rps. sphaeroides* and *Rsp. rubrum* photoreaction center. As will be later shown, the smallest possible angle between the two exciton transition dipoles is estimated to be 36° from the calculation of the rotatory strength of the 870 nm CD band. Using these values and the formulae given in Table II, we calculated the approximate values of the transition dipole-dipole interaction energy and the asymmetry ($E_{\mathrm{A'B}} - E_{\mathrm{AB'}}$). These values are also listed in Table II. The transition dipole-dipole interaction energy, estimated to be between 375 cm^{-1} and 300 cm^{-1}, is slightly higher than the value of 245 cm^{-1} that was found for BChl dimers in carbon tetrachloride [26]. The asymmetry ($E_{\mathrm{A'B}} - E_{\mathrm{AB'}}$) has a value between 250 cm^{-1} and 490 cm^{-1} depending on the angle between the two exciton transition dipoles. The asymmetry is then found to be as large as the transition dipole-dipole interaction energy.

The asymmetric exciton model can provide information concerning the molecular configuration of the special pair BChl. Using the point dipole approximation, Tinoco [8] has shown that the dimer dipole strength, the sign and magnitude of the rotational strength and the interaction energy depend on the geometry of the dimer. Modifying his equations to include the asymmetric interaction energy, it is possible to calculate a geometry of the two BChl molecules that will satisfy the observed rotational strengths and dipole strengths:

$$D_{\pm} = \mu^2(1 \pm \sin\alpha \sin\theta_2 \cos(\phi_1 - \phi_2)) \tag{9}$$

$$R_{\pm} = \pm\left(\frac{\Pi\nu_0}{2c}\right) R_{12}\mu^2 \sin\phi_1 \cos\theta_2 \sin\alpha \tag{10}$$

$$U = \frac{\mu^2}{R_{12}^2}(\sin\theta_2 \cos(\phi_1 - \phi_2) - 3\sin\theta_1 \sin\theta_2 \cos\phi_1 \cos\phi_2) \tag{11}$$

In the above equations the axes of the right-handed coordinate system are chosen with the *x* axes along the intermolecular distance vector $\boldsymbol{R}_{12}$ and with the dipole moment μ_1 along the *xy* plane (see Fig. 1). The angles θ_1, θ_2, ϕ_1, ϕ_2 are defined with this coordinate system (Fig. 1).

CD studies of oriented photoreaction center indicate that the two BChl molecules of the special pair may have C_2 symmetry [12]. C_2 symmetry

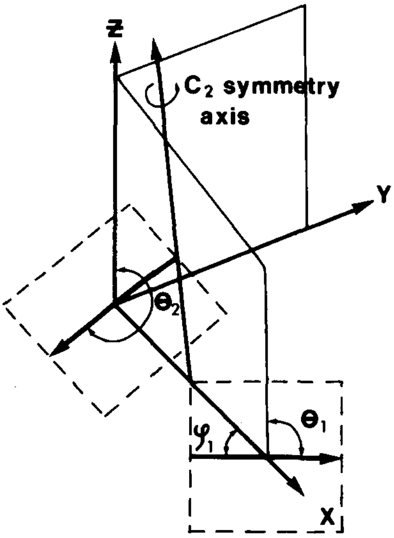

Fig. 1. The reference system of a dimer with two identical chromophores. The *x* axis is defined along the intermolecular distance vector. The transition dipole of the first molecule is defined to be in the *x*-*y* plane. The *z* axis is defined along the molecular planes of the first molecule. *θ* is defined as the angle between the *z* axis and the transition dipole. *φ* is defined as the angle between the *x* axis and the transition dipole along the *x*-*y* plane.

implies the equivalence of the two BChl molecules with respect to one another on rotating 180° about the axis of symmetry. This symmetry condition implies that the planes of the two molecules are parallel to each other. In this case, the angles ϕ_1 and ϕ_2 in Eqns. 9–11 would be identical. Qualitatively for $\phi_1 = \phi_2$, one can see that, since the dipole moments of the higher energy Q_y exciton band (D_+) is much smaller than that of the lower energy Q_y exciton band (D_-) and since the rotational strength of the higher energy band (R_+) and that of the lower energy band (R_-) have negative and positive values respectively, the angle θ_2 in Eqns. 9 and 10 must have values which are such that $\sin\theta_2$ and $\cos\theta_2$ are both negative. θ_2 must then have values between 270° and 180°. This implies that the Q_y transition dipoles (directed along the I and III nitrogen atoms of the pyrrole rings [27]) of the BChl molecules are directed in opposite directions from each other. For the Q_x transition dipole which is oriented perpendicular to the Q_y transition dipole [27], on the other hand, D_+ is much larger than D_- and R_+ and R_- have positive and negative values, respectively. θ_2 in this case must have values between 0° and 90°, which implies that the Q_x transition dipoles of the two BChl molecules are oriented in the same direction. The two BChl molecular planes must then be oriented so that they are face to face with each other and with the C_2 symmetry axis in the direction of the Q_x transition dipole.

From the CD spectra of Boucher et al. [13] and Sauer and Austin [28], we estimate the rotational strength of the 870 nm CD band in photoreaction centers of *Rsp. rubrum* and *Rps. sphaeroides* to be approx. 2.6 debye magneton. Results of detailed calculations using different geometries and intermolecular distances which satisfy a rotational strength of 2.6 debye magneton for the 870 nm CD band and a dipole moment ratio of 1/6 between the 810 nm and 870 nm bands are shown in Table III. The large rotational strength of the 870 nm band puts a limit on the angle between the two BChl molecules. We find the largest possible angle between the two Q_y transition dipoles to be 154° (see Table III). Larger angles predict smaller rotational strengths. The smallest angle is found to be 136° in the case where there is no asymmetric interaction. Detailed calculations also show that the angle ϕ_1 is less than 90°, implying that the planes of the two BChl molecules are not directly on top of one another but slightly displaced to one side of each other. The distance between the two molecular planes is calculated to be between 5.3 and 10.7 Å depending on the amount of asymmetric interaction. This structure of the bacterial photoreaction center is very similar to the model proposed by Shipman et al. [29] for the chlorophyll special pair of green plants.

The asymmetric exciton interaction model pre-

TABLE III

POSSIBLE CONFIGURATIONS OF THE BChl SPECIAL PAIR FROM ROTATIONAL STRENGTH CALCULATIONS OF THE Q_y TRANSITION BANDS ($\mu_1(Q_y) = \mu_2(Q_y) = 37.6^{a}$ debye^2; $\phi_1 = \phi_2 = \phi$; $\theta_1 = 90°$)

R_{pp} is the interplanar distance. θ' and α are defined in Table II. θ_1, θ_2, ϕ, R_{12} are defined in Fig. 1. U is calculated by Eqn. IIb. R_{12}, $R_\pm$, $D_\pm$ are calculated by Eqns. 13, 14 and 15.

θ' (deg.)	α (deg.)	θ_2 (deg.)	ϕ (deg.)	R_{12} (Å)	R_{pp} (Å)	U (cm^{-1})	$D_\pm$ (debye^2)	$R_\pm$ (debye magneton)
90	90	226	78.3	5.0	4.9	392	$37.5(1 \mp 0.714)$	∓ 2.6
90	90	226	20.7	13.7	4.9	392	$37.6(1 \mp 0.714)$	∓ 2.6
70	73	228	78	5.5	5.3	376	$37.6(1 \mp 0.714)$	∓ 2.6
70	73	228	22.3	14.0	5.3	376	$37.6(1 \mp 0.714)$	∓ 2.6
54	60	236	75.6	7.2	6.9	340	$37.6(1 \mp 0.714)$	∓ 2.6
54	60	236	28.0	14.8	6.9	340	$37.6(1 \mp 0.714)$	∓ 2.6
36	51	246	55.0	13.1	10.7	306	$37.6(1 \mp 0.714)$	∓ 2.6
30	50	250	55.0	13.3	10.9	299	$37.6(1 \mp 0.714)$	∓ 2.2

[a] Values obtained from Ref. 4.

sented in this article is based on a semi-classical approach. A more quantitative description of the exciton interaction between molecules in different environments can be conducted at a higher level of sophistication. However, a virtue of our approach is that it allowed the development of a simple model that is qualitatively consistent with a large number of spectroscopic observations. The main ones are the existence of CD and absorption change bands at 600, 630, 810 and 870 nm, their bandwidths, their relative oscillatory and rotatory strengths and the peculiar temperature-dependency of their wavelength maxima. This model is also consistent with linear polarization data and with photodichroic studies which indicate that the 810 nm and 870 nm transition dipoles may not be orthogonal. Furthermore, it is compatible with recent oriented CD work which indicates that the 600 and 630 nm bands, on the one hand, and the 810 and 870 nm bands, on the other hand, are the result of exciton interaction between two BChl molecules and that the BChl dimer may have C_2 symmetry. The model also has predictive value that is best illustrated by Fig. 2. These predictions will probably have to await X-ray crystallography before they can be verified.

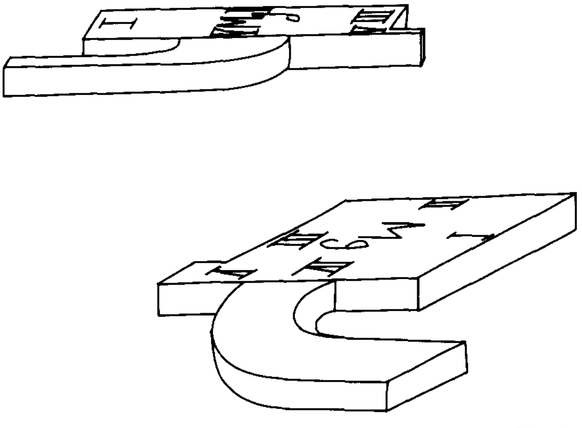

Fig. 2. Schematic representation of the special pair BChl deduced from CD and absorption spectroscopy. The two BChl molecules are in separate parallel planes which are roughly 5–11 Å apart. The axes that join the nitrogen atoms of the pyrrole rings I and III in the two molecules form an angle of between 138 and 156 degrees with each other, whereas the axes that connect the pyrrole rings II and IV form an angle of between 24 and 44 degrees with each other. The two molecules are oriented face to face so that there exists a C_2 symmetric axis. The two faces are slightly eccentric with respect to one another so that the line joining the centers of the molecules forms an angle of between 23 and 78 degrees with the planes of the molecules.

Finally, it should be pointed out, as a caveat, that our model leaves some questions unanswered. For instance, why is the rotational strength of the 795 nm band so high [4] if this is a monomer band and, more importantly, why is no bleaching of the 800 nm band observed on formation of state P^R [30,31]? Another possible difficulty with our model is that it does not consider possible charge-transfer contribution. Warshel's calculations [32] indicate that the contribution of the charge transfer state is small when the two molecular planes are more than 5 Å apart. Our model predicts a distance of between 5 and 11 Å and therefore would lead us to assume that charge-transfer contribution is small. However, while our model is self-consistent, it provides us with no means of assessing the amount of charge-transfer contribution because it does not take this possibility into account. It is our hope that this model may stimulate more experimental and theoretical work that will uncover the wealth of information contained in optical spectroscopy of the photoreaction center.

Appendix I

Bandwidths of the two exciton absorption bands as calculated by the asymmetric exciton model

We assume that the nuclear vibrational modes of the whole system can be adequately described by nuclear potential surfaces. Klick and Schulman [33] have shown that the width of the absorption band at half-maximum is proportional to the displacment along the nuclear coordinates of the minimum of the excited and ground state potential surfaces. Accordingly, for a single molecule, the energies of the ground (W_G) and excited (W_E) state are equal to

$$W_G = w_G^0 + \frac{k}{2}(Q - Q_0)^2$$

$$W_E = w_E^0 + \frac{k}{2}(Q - Q_0')^2 \tag{A1}$$

where w_G^0 and w_E^0 are the energies of the lowest ground and excited states, respectively; Q is the nuclear coordinate and Q_0 and Q_0' are the respective equilibrium positions for the ground and excited states; k is the force constant. The displacement of the minimum of the excited and ground state potential surfaces is equal to $Q_0 - Q'_0$. Hence the width of the absorption band of the monomer at half-maximum is proportional to $Q_0 - Q'_0$.

For a dimer consisting of two molecules (A and B) of the same kind embedded in the same environment, the potential energy of the ground state (W_G^s) and the first excited singlet states ($W_\pm^s$) can be taken as (following the derivation of Förster [19])

$$W_G^s = 2w_G^0 + V + \frac{k}{2}\left[(Q_A - Q_0)^2 + (Q_B - Q_0)^2\right]$$

$$\begin{aligned} W_\pm^s = w_G^0 + w_E^0 + V' + \frac{k}{4}\Big[&(Q_0 - Q'_0)^2 \\ &+ (Q_A + Q_B - Q_0 - Q'_0)^2 + (Q_A - Q_B)^2\Big] \\ &\pm \left[(k(Q_A - Q_B)(Q_0 - Q'_0))^2 + 4U^2\right]^{1/2} \end{aligned} \quad \text{(A2)}$$

where Q_A and Q_B are nuclear coordinates, V is the interaction energy between the two ground states, V' is the interaction energy between the excited molecule and the unexcited one, U is the resonance energy. We assume that both molecules have the same Q_0, Q'_0 and k. For the condition that $2U \geq k(Q_0 - Q'_0)^2$, the potential energy surfaces $W_\pm^s$ have a minimum at

$$Q_A^{\min} = Q_B^{\min} = \tfrac{1}{2}(Q_0 + Q'_0) \quad \text{(A3)}$$

The displacement of the minimum of the excited and ground-state potential energy surfaces is equal to $(1/\sqrt{2})(Q_0 - Q'_0)$ (Fig. 3A), which is less than that of the monomer by a factor of $1/\sqrt{2}$. This implies that the bandwidth of the individual band of the dimer should be smaller than that of the monomer. A more exact calculation by Hemenger [20] showed that the bandwidth of the inidvidual exciton band is $1/\sqrt{2}$ that of the monomer.

For a dimer consisting of two molecules of the

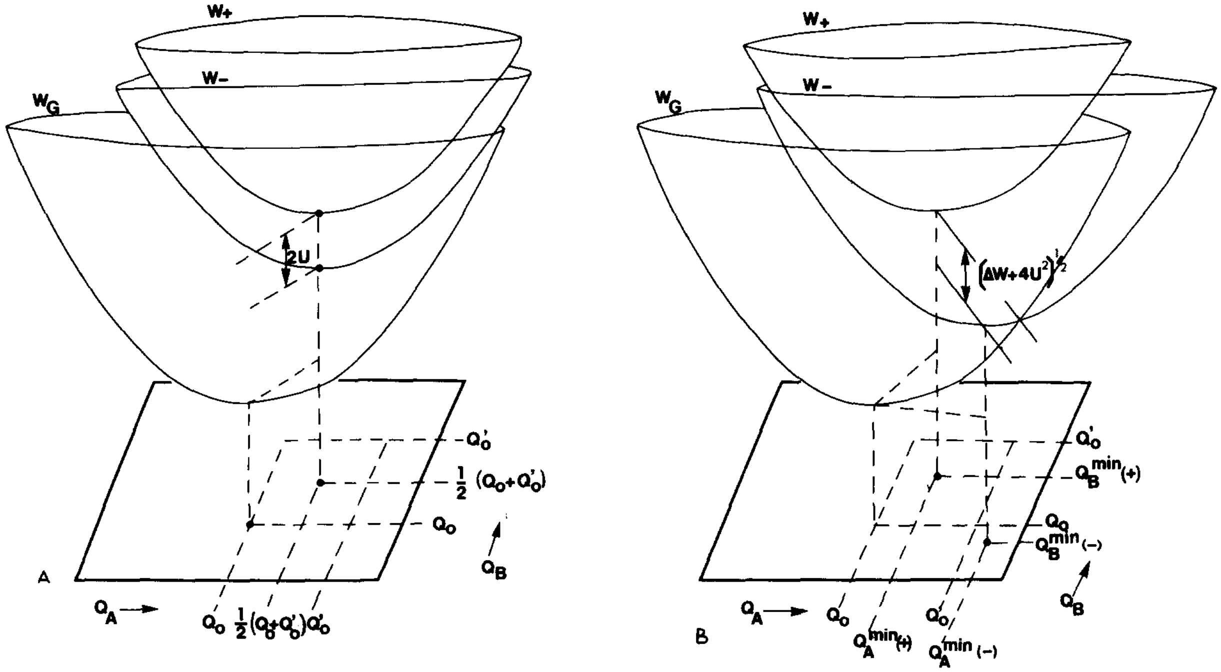

Fig. 3. (A) A schematic two-dimensional nuclear configurational diagram for a symmetric dimer. W_C, W_+ and W_- are potential surfaces for the ground state, the higher energy excited state and the lower energy excited state, respectively. The potential surfaces are drawn along two nuclear coordinates Q_A and Q_B. Q_0 and Q'_0 are the equilibrium coordinates for the ground state and excited states, respectively. U is the resonance energy. (B) A schematic two-dimensional nuclear configurational diagram for an asymmetric dimer. The asymmetric interaction energy (Δw) changes the difference in energy in W_+ and W_- and shifts the potential surfaces to new equilibrium positions which are not equidistant to Q_0. $Q_A^{\min}(\pm)$ and $Q_B^{\min}(\pm)$ are defined in Eqns. 5A and 6A of the text.

same kind but embedded in different environments, the potential energy surfaces of the ground state (W_G) and the first excited singlet states ($W_\pm$) can be taken as (following the derivation of Föster [19] and taking the difference of environment interaction (Δw) into account)

$$W_G = 2w_G^0 + V - \frac{k}{2}\left[(Q_A\text{-}Q_0)^2 + (Q_B - Q_0)^2\right]$$

$$\begin{aligned} W_\pm = w_G^0 + w_E^0 + V' + \frac{k}{4}\Big[&(Q_0 - Q_0')^2 \\ &+ (Q_A + Q_B - Q_0 - Q_0')^2 + (Q_A - Q_B)^2\Big] \\ &+ \tfrac{1}{2}\left[\left(\Delta w + k(Q_A - Q_B)(Q_0 - Q_0')\right)^2 + 4U^2\right]^{1/2} \end{aligned} \quad \text{(A4)}$$

As before, we assume that both molecules have the same Q_0 and Q_0' and that the force constant k is the same for both the ground and excited states. For the condition that $2U + \Delta w > k(Q_A - Q_B) \times (Q_0 - Q_0')$

$$\begin{aligned} W_\pm = w_G^0 + w_E^0 + V' + \frac{k}{4}\Big[&(Q_0 - Q_0')^2 + (Q_A + Q_B - Q_0 - Q_0')^2 \\ &+ (Q_A - Q_B)^2(1 \pm S) \pm T(Q_A - Q_B)\Big] \\ &\pm \tfrac{1}{2}(4U^2 + \Delta w^2)^{1/2} \end{aligned} \quad \text{(A5)}$$

where

$$S = \frac{k(Q_0 - Q_0')^2}{(4U^2 + \Delta w^2)^{1/2}}$$

$$T = \frac{2\Delta w(Q_0 - Q_0')}{(4U^2 + \Delta w^2)^{1/2}}$$

For the condition that $(4U^2 + \Delta w^2)^{1/2} \geqslant \frac{1}{2}k(Q_0 - Q_0')^2$, the potential energy surfaces $W_\pm$ have minimums at

$$Q_A^{\min}(\pm) = \frac{Q_0 + Q_0'}{2} \mp \frac{T}{4(1 \pm S)}$$

$$Q_B^{\min}(\pm) = \frac{Q_0 + Q_0'}{2} \pm \frac{T}{4(1 \pm S)} \quad \text{(A6)}$$

Consequently the distance between the equilibrium configurations of the ground and the higher energy excited state ($\Delta +$) is different from that of the ground and the lower energy excited state ($\Delta -$) (Fig. 3B). Their ratio is equal to

$$\frac{\Delta +}{\Delta -} = \frac{\left(\dfrac{1}{2} + \dfrac{1}{2}\left(\dfrac{\Delta w}{(\Delta w^2 + 4U^2)^{1/2} + k(Q_0 - Q_0')^2}\right)^2\right)^{1/2}}{\left(\dfrac{1}{2} + \dfrac{1}{2}\left(\dfrac{\Delta w}{(\Delta w^2 + 4U^2)^{1/2} - k(Q_0 - Q_0')^2}\right)^2\right)^{1/2}} \quad \text{(A7)}$$

This implies that the bandwidths of the individual exciton band would no longer be equal to each other when there is asymmetric interaction. As the asymmetric interaction decreases to zero, the bandwidths of the two bands become equal, as predicted by the symmetric exciton theory [20].

Appendix II

Spectral shifts of the CD band of the special pair BChl on cooling

On cooling the photoreaction center, the splitting between the 810 nm and 865 nm exciton bands ($E_I - E_{II}$) increases and the center of the two bands $\frac{1}{2}(E_I + E_{II})$ shifts to the red [15]. From Eqns. IIb, c and d.

$$E_I - E_{II} = \left((E_{A'B} - E_{AB'})^2 + 4U^2\right)^{1/2}$$

$$\frac{E_I + E_{II}}{2} = \frac{E_{A'B} + E_{AB}'}{2}$$

Assuming that the resonance energy, U, remains constant with temperature, assuming moreover, that on cooling the decrease in $E_{AB'}$ is greater than the increase in $E_{A'B}$, it follows that $E_I - E_{II}$ will increase and $(E_I + \mathrm{E}_{II})/2$ will decrease. On the basis of these assumptions, one can calculate the relative shift (ΔE) in $E_{A'B}$ and in $E_{AB'}$ necessary to satisfy the experimental observation that the 810 nm band (E_I) remains constant as the 865 nm band (E_{II}) shifts to the red. Using Eqns. IIb, c and d:

$$\Delta E_{A'B} = -\frac{(E_I - E_{II})}{2} + U\left[1 + \frac{1}{\tan\left(\sin^{-1}\dfrac{2U}{E_I - E_{II}}\right)}\right]$$

$$\Delta E_{\mathrm{AB'}} = -\frac{(E_{\mathrm{I}} - E_{\mathrm{II}})}{2} + U\left[1 - \frac{1}{\tan\left(\sin^{-1}\dfrac{2U}{E_{\mathrm{I}} - E_{\mathrm{II}}}\right)}\right]$$

At low temperatures, when the exciton splitting (1100 cm^{-1}) is about 3-times the resonance energy, U, (340 cm^{-1}, Table I), we find from the above equations that $-\Delta E_{\mathrm{AB'}} \sim 4\Delta E_{\mathrm{A'B}}$.

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