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ABSORPTION AND MAGNETIC CIRCULAR DICHROISM OF CHLOROPHYLL *a* AND *b* DIMERS

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The dimerization of chlorophyll *a* to the so-called *special pair*, in which the two monomers are linked together by two nucleophilic molecules (alcohol or water), leads to shifts and splittings of the absorption and magnetic circular dichroism (MCD) spectral bands. The changes in the Q-band region are described starting from a model proposed previously (L.L. Shipman, J.R. Norris and J.J. Katz, J. Phys. Chem. 80 (1976) 877), and which we extended to include the MCD. The parameters α_x and α_y, containing the exciton and environmental parameters (L.L. Shipman, J.R. Norris and J.J. Katz, J. Phys. Chem. 80 (1976) 877) and the relative orientation of the monomers in the dimer, determine the spectral features. Spectral simulation leads to the conclusion that in the special pair α_x and α_y are in the region of 0.6–0.8 and that the dimer has C_2 symmetry. The model was also applied to the case of the pure dimer of chlorophyll *b* where the monomers are bound together directly. With similar values for α_x and α_y the spectra could be reconstructed assuming almost parallel monomers in the dimer. the equilibrium constant for the association $2M \rightleftharpoons M_2$ was determined as $0.8(\pm 0.2)\times 10^6$ mol^{-1}/l. The present choice of compounds was based merely on practical reasons. The model may be applied equally well to other similar cases.

1. Introduction

In solutions of chlorophylls dimerization may take place. Especially the dimers of chlorophyll (Chl) *a* have been investigated quite extensively [3–5]. In dry solvents of CCl_4, octane, etc., the so-called 'pure dimer' forms in which the keto group of molecule I is attached to the magnesium of molecule II. Further aggregation is also possible. In the presence of nucleophilic compounds such as water, alcohol, pyridine, the so-called 'special pair' is present at higher concentrations and lower temperatures. In the dimer the monomer halves are held together by two nucleophilic molecules which play a dual role in that the electron-donating groups are attached to the magnesium and the acceptor parts to the $C=O$ of the chlorophyll [4].

For these dimers several structures have been proposed. In the pure dimers of Chl *a* many relative positions of the two monomers are possible [5], for the special pair of Chl *a* the molecular planes have to be parallel (more or less) and for that case only two possibilities remain, either with or without C_2 symmetry [4].

We have tried to establish a relation between the possible dimer structures and the absorption and magnetic circular dichroism (MCD) spectrum which show splittings and shifts compared to the corresponding monomer spectra. We studied two specific compounds.

Firstly, the special pair of Chl *a*, found at lower temperatures, was studied using high concentrations of Chl *a* in solutions of toluene in the presence of ethanol. The restriction to two possible parallel structures makes the interpretation of the results somewhat simpler than for the other case studied, the pure dimer of Chl *b*. The latter compound was chosen because the spectrum shows considerably more detail than that of the corresponding pure dimer of Chl *a*.

The results were applied for the lower Q bands of the compounds. As a theoretical model we exploited the semi-empirical theory of Shipman et al. [1], which we extended to include the MCD. Inclusion of MCD in the analysis of the spectrum may lead to a better correlation between theory and experiment, due to the additional information provided by the MCD signs. The relative orientations of the transition dipole moments and angular momenta strongly influence the absorption and MCD spectra. Restrictions on these relative orientations, of course, are imposed by the bonds and geometries of the monomers.

In the model one starts from the optical transitions in the monomers. The monomer bands are shifted and split by several effects, expressed by the exciton splitting and the environmental parameters [1].

The monomer (Chl *a* or *b*) exists in a monoligated form with a pentacoordinated magnesium and a diligated form with a hexacoordinated magnesium. Even at low concentrations of an electron-donating molecule the monoligated form is present, preventing the formation of pure dimers. At high concentrations of the nucleophile pyridine, the magnesium binds two pyridine molecules. Diligation with other nucleophiles occurs to a measurable extent only at lower temperatures. The assignments for the spectra of the monoligated form are important for interpretation of the dimer spectra, since at least one of the monomers in the dimer is also pentacoordinated. These assignments are made by comparison of the spectra of the monoligated monomer with those of porphyrins and of diligated monomers.

For the porphyrins, Gouterman [6] in a study of the spectral changes on substitution and following the results of molecular orbital calculations concluded a *y*-polarized lowest absorption band. Despite the fact that chlorophyll has a symmetry which is even more reduced, the strong resemblance of the chlorin and chlorophyll spectra suggests the same assignment for the lowest chlorophyll absorption. A basis for this similarity is the fact that in all these molecular orbital calculations the four-orbital model gives a good description of the Q bands of these compounds [7].

Table 1

Absorption bands of Chl *a* and *b* monomers and dimers in the 550–725 nm region

Chl *a*		
Monomer	580 (*x*)	660 (*y*)
Special pair	592 628 }(*x*)	670 702 }(*y*)
Chl *b*		
Monomer	613 (*x*)	644 (*y*)
Pure dimer	614 634 }(*x*)	646 662 }(*y*)

In table 1 we have listed the wavelengths of monomer and dimer bands of interest. The spectrum of the special pair of Chl *a* (figs. 1 and 2) has *y*-polarized bands at 670 and 702 nm due to the monomer band at about 670 nm [8–10]. The *x*-

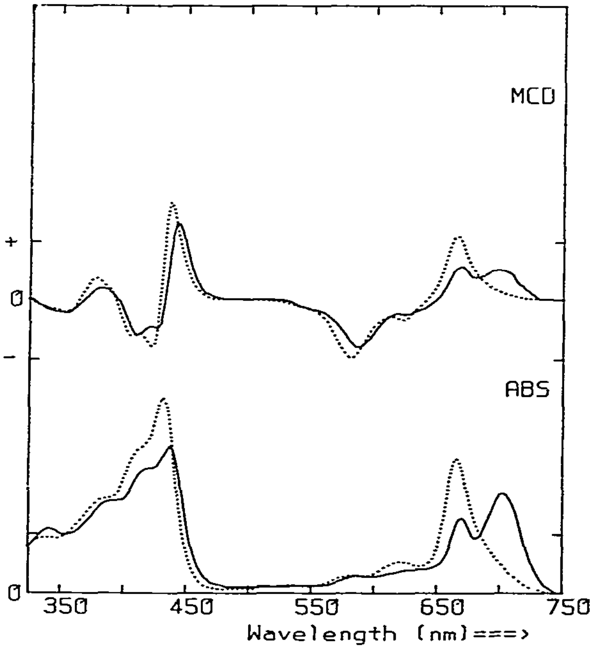

Fig. 1. Absorption and MCD spectrum of Chl *a* in a solution of dry toluene and an equivalent amount of ethanol at 293 K (······) and 130 K (———). Chlorophyll concentration 0.07 mol l^{-1}.

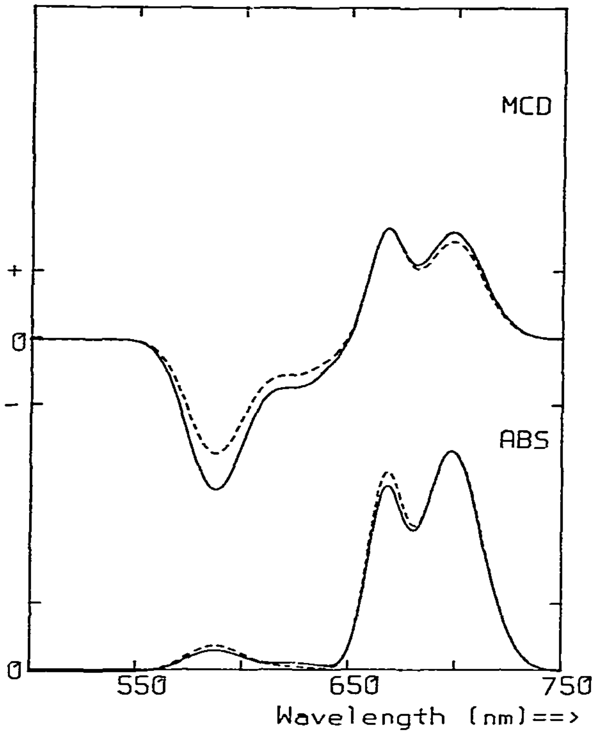

Fig. 2. Experimental (at 130 K) Chl *a* special pair spectrum (———) and the spectrum simulated for $\alpha_x = 0.670$, $\alpha_y = 0.645$ and the angle $\beta = \pi$(------). The low intensities of the 550–650 nm region of the absorption spectrum show a relatively large experimental error and should be considered accordingly (cf. differences with fig. 1).

polarized bands are located at 592 nm and in the region around 630 nm. At 628 nm a small dimer absorption is located which we assumed to be the X-band. The precise location of this band does not influence our calculations to a large extent. On dimerization the absorption in this region does not change significantly. The *x*-polarized monomer band is located around 580 nm.

The pure dimer of Chl *b* (fig. 4) has *y*-polarized bands at 646 and 662 nm due to the splitting of the 644 nm band of the monomer. Similarly, the *x*-polarized bands are located at 614 and 634 nm, with the corresponding 634 nm monomer band. The assignments for the Chl *b* monomer are given in ref. 11. For the dimer the assignment is based

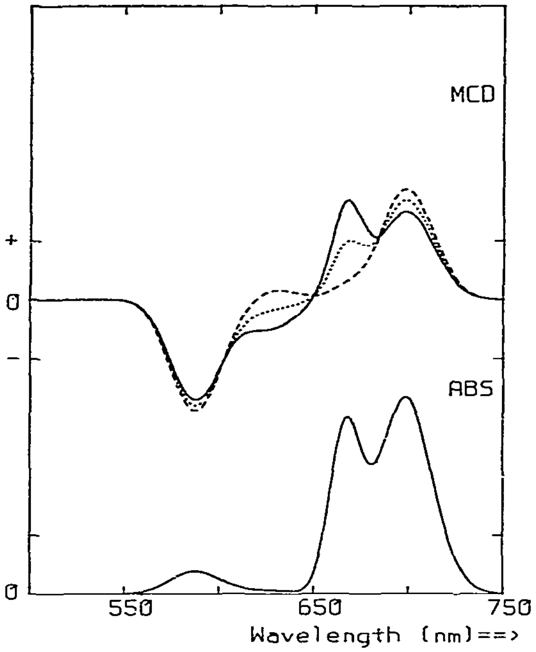

Fig. 3. Simulated Chl *a* spectrum for $\beta = \pi$(———), $\beta = \frac{1}{2}\pi$(······) and $\beta = 0$ (------). In all cases $\alpha_x = 0.670$ and $\alpha_y = 0.645$.

on our absorption and MCD spectra (see below). The strong resemblance of the spectra of Chl *a* and *b*, together with the assignments given for the monomer and dimer of Chl *a* [8,9] further support the present assignments.

2. Experimental

Chl *a* and *b* were obtained commercially from Sigma or prepared from fresh spinach leaves by the procedure described in ref. 13. Samples were kept at low temperatures to prevent possible decomposition.

Water-free solutions could be prepared by dissolving the chlorophyll in a solution of CCl_4 which had been dried over a molecular sieve. Subsequent distillation of part of the solvent then removes traces of water [14]. The special pair of Chl *a* (fig. 1) was formed by adding twice the equivalent of

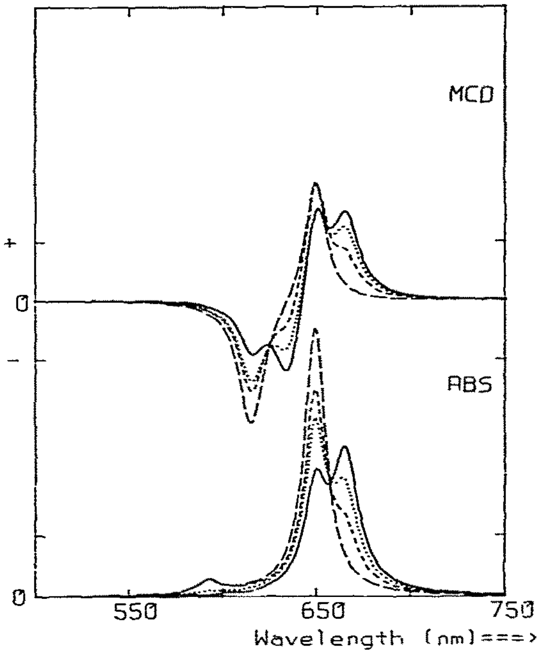

Fig. 4. Absorption and MCD spectrum of Chl *b* in a solution of dry CCl_4. The product of sample thickness and chlorophyll concentration was 2.5×10^{-6} mol l^{-1} cm. The dimer extrapolated spectrum for $C = 2.5 \times 10^{-6}$ (———), the spectrum for $C = 2.5 \times 10^{-5}$ (······), $C = 5 \times 10^{-7}$ (------) and, after addition of ethanol, for $C = 2.5 \times 10^{-6}$ mol l^{-1}; room temperature.

ethanol to a Chl *a* solution at a concentration of 0.07 M in dry toluene. At room temperature no dimerization is visible. A dimer spectrum appears on cooling the solution.

The same compounds were investigated by Shipman et al. [10,16]. At 183 K, for comparable concentrations, the dimer association seems complete, as follows from infrared measurements. Therefore, in our case, at 130 K, one must also assume complete dimerization. The 670 nm band, also present in the monomer, is more intense in our case than in ref. 10.

The spectrum of the pure dimer of Chl *b* in dry solutions of CCl_4 is shown in figs. 4 and 5. The measurements at different concentrations of Chl *b* were made for constant values of the product of concentration and optical path length. The overall monomer concentrations chosen were from 25×10^{-6} (1 mm path) to 5×10^{-7} M (50 mm path).

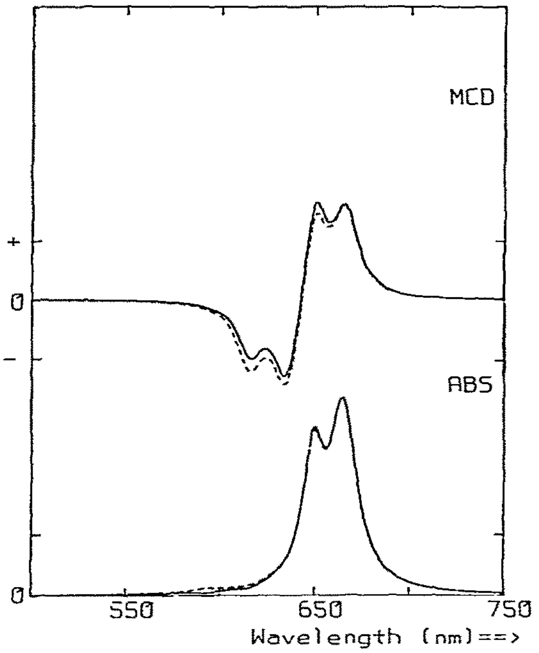

Fig. 5. Experimental extrapolated Chl *b* spectrum (———) and the spectrum simulated for $\alpha_x = \alpha_y = 0.8$ with $\beta = \pi$(------); room temperature.

Unligated monomers can only be obtained in the presence of dimers (at higher concentrations higher polymers are formed). To obtain the monomer spectrum we added a small amount of ethanol to an equilibrium mixture. This leads to the conversion of almost all monomers to the monoligated monomer. We now assumed that the monomer and the monoligated monomer have almost the same spectrum. As indicated by the behavior with respect to the isobestic points on dilution or on adding ethanol, the latter assumption cannot be very far from reality. Also, clearly only two compounds are present in the equilibrium mixture in the solutions.

From the changes of the typical dimer absorption band at 662 nm on dilution we calculated the equilibrium constant for the dimerization reaction $2\text{Chl } b \rightleftharpoons (\text{Chl } b)_2$ as $K = 0.8(\pm 0.2) \times 10^6$ mol^{-1} l.

The contribution of the 662 nm band to the spectrum was determined by deconvolution of the absorption bands.

Subsequently, using the assumption with regard to the monomer spectrum and the value of K, the dimer spectrum could be determined (continuous curve in fig. 4). Again, the spectrum intersections at the isobestic points are as might be expected for a two-component equilibrium.

The measurements were carried out using a home-built apparatus [17]. The absorption spectrum could be measured simultaneously with the MCD. Our instrument had no baseline correction for the absorption. If desired the baseline was corrected by comparison with spectra measured on a Cary 14 instrument. The field strength was generally 5.5 T.

2.1. The dimer spectrum

As can be seen from figs. 1–4 dimerization leads to overall changes of the absorption and MCD spectrum. Especially in the Q-band region from 550- to 700 nm the changes are very obvious (table 1).

2.2. Calculation of dimer absorption and MCD spectra from the monomer contributions

The optical spectrum of both types of Chl *a* dimers has been described in the literature [10,16]. As mentioned above, for the electronic transitions in the dimer the monomer molecular states are a starting point [1]. Charge-transfer effects seem to be small [5,18] and their consideration is beyond our scope. We only look for a correlation between the orientation of the molecular parts and the observed spectra due to the superposition of the absorption and MCD molecular moments.

For the description of the dimer one starts with the ground-state product functions of the two monomers Φ_i^0:

$$\Psi^g = \Phi_1^0 \cdot \Phi_2^0 \tag{1}$$

The lowest excitations are simply the antisymmetrized products in which one of the monomer functions has been excited, i.e., $\Phi_1' \cdot \Phi_2^0$ and $\Phi_1^0 \cdot \Phi_2'$.

The simplest form of the hamiltonian is expressed by the sum of the individual monomer terms H_i and the mutual interaction H_{12}:

$$H = H_1 + H_2 + H_{12} \tag{2}$$

In a calculation one has to diagonalize the interaction matrix ($\boldsymbol{H}$):

$$H\begin{pmatrix} \Delta_1 + \sigma_1 & T \\ T & \Delta_2 + \sigma_2 \end{pmatrix} \tag{3}$$

where $\Delta_i = \langle \Phi_i' | H_i | \Phi_i' \rangle - \langle \Phi_i^0 | H_i | \Phi_i^0 \rangle$ and σ_i expresses the interaction of the molecular part i with the solvent or inequivalence due to changes induced by bonding with the other monomer. In the case where the monomer halves are identical $\sigma_1 = \sigma_2$.

The exciton interaction is expressed by the transition density parameter $T = \langle \Phi_1^0 \cdot \Phi_2' | H_{22} | \Phi_1' \cdot \Phi_2^0 \rangle$.

In this way the lowest excited-state energies are expressed by:

$$E_\pm = \frac{\Delta_1 + \sigma_1 + \Delta_2 + \sigma_2}{2} \pm \tfrac{1}{2}\left[(\Delta_1 - \Delta_2 + \sigma_1 - \sigma_2)^2 + 4T^2 \right]^{1/2} \tag{4}$$

with the eigenstates:

$$\Psi_\pm = \frac{1}{\sqrt{2}}(1 \pm \alpha)^{1/2} \Phi_1' \Phi_2^0 \pm \frac{1}{\sqrt{2}}(1 \mp \alpha)^{1/2} \Phi_1^0 \Phi_2' \tag{5}$$

where the 'interaction parameter' is given by:

$$\alpha = \frac{\Delta_1 - \Delta_2 + \sigma_1 - \sigma_2}{\left((\Delta_1 - \Delta_2 + \sigma_1 - \sigma_2)^2 + 4T^2 \right)^{1/2}} \tag{6}$$

The typical 'exciton only' case is for $\Delta_1 = \Delta_2$, equivalent monomers making up the dimer. and $2T \gg \sigma_1 - \sigma_2$. The difference $\sigma_1 - \sigma_2$ shifts the whole exciton spectrum by that amount.

For an estimate of the quantities in these formulae we use the results of the spectra. First we calculate the absorption and MCD for these dimers.

2.3. Absorption and MCD of dimers

Only B terms contribute to the MCD. The monomer transitions are approximately x- or y-polarized. For the excited state dimer wave function for the Q-band we write:

$$Q_{j_\pm} = \frac{1}{\sqrt{2}}(1 \pm \alpha_j)^{1/2} Q_{j1} \pm \frac{1}{\sqrt{2}}(1 \mp \alpha_j)^{1/2} Q_{j2} \tag{7}$$

where $j = x, y$ and where we have now written for the product functions:

$$\begin{aligned} Q_{j1} &= |\Phi'_{j1} \cdot \Phi^0_2\rangle \\ Q_{j2} &= |\Phi^0_1 \cdot \Phi'_{j2}\rangle \end{aligned} \tag{8}$$

The parameters α_x and α_y do not have to be identical. If we indicate the ground-state product by $G = \Phi^0_1 \cdot \Phi^0_2$ we obtain for the transition $Q_{y_+} \leftarrow G$ the MCD term:

$$\begin{aligned} B_{y_+} = {} & Im\langle Q_{y_+}|\vec{m}|Q_{x_+}\rangle \cdot \langle G|\vec{\mu}|Q_{y_+}\rangle \wedge \langle Q_{x_+}|\vec{\mu}|G\rangle \\ & \cdot \frac{1}{(W_{x_+} - W_{y_+})} \\ & + Im\langle Q_{y_+}|\vec{m}|Q_{x_+}\rangle \cdot \langle G|\vec{\mu}|Q_{y_+}\rangle \wedge \langle Q_{x_-}|\vec{\mu}|G\rangle \\ & \cdot \frac{1}{(W_{x_-} - W_{y_+})} \end{aligned} \tag{9}$$

where the usual notation [19] has been used. The monomer electronic transition dipole moment is denoted by $\vec{\mu}$, the angular momentum operator by $\vec{m}$. The energies of the states in the dimer are given by W_{x_+}, W_{y_+}, etc. Substitution of eq. 7 then leads to:

$$\begin{aligned} B_{y_+} = F\Bigg\{ & \frac{2 + 2\alpha_x\alpha_y + a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} + a_2(1-\alpha_x^2)^{1/2} + a_3(1-\alpha_y^2)^{1/2}}{W_{x_+} - W_{y_+}} \\ & + \frac{2 - 2\alpha_x\alpha_y - a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} - \alpha_2(1-\alpha_x^2)^{1/2} + a_3(1-\alpha_y^2)^{1/2}}{W_{x_-} - W_{y_+}} \Bigg\} \end{aligned} \tag{10}$$

and similarly:

$$\begin{aligned} B_{y_-} = F\Bigg\{ & \frac{2 - 2\alpha_x\alpha_y - a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} + a_2(1-\alpha_x^2)^{1/2} - a_3(1-\alpha_y^2)^{1/2}}{W_{x_+} - W_{y_-}} \\ & + \frac{2 + 2\alpha_x\alpha_y + a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} - a_2(1-\alpha_x^2)^{1/2} - a_3(1-\alpha_y^2)^{1/2}}{W_{x_-} - W_{y_-}} \Bigg\} \end{aligned} \tag{11}$$

$$\begin{aligned} B_{x_+} = -F\Bigg\{ & \frac{2 + 2\alpha_x\alpha_y - a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} + a_2(1-\alpha_x^2)^{1/2} + a_3(1-\alpha_y^2)^{1/2}}{W_{x_+} - W_{y_+}} \\ & + \frac{2 - 2\alpha_x\alpha_y - a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} + a_2(1-\alpha_x^2)^{1/2} - a_3(1-\alpha_y^2)^{1/2}}{W_{x_+} - W_{y_-}} \Bigg\} \end{aligned} \tag{12}$$

$$\begin{aligned} B_{x_-} = -F\Bigg\{ & \frac{2 - 2\alpha_x\alpha_y - a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} - a_2(1-\alpha_x^2)^{1/2} + a_3(1-\alpha_y^2)^{1/2}}{W_{x_-} - W_{y_+}} \\ & + \frac{2 + 2\alpha_x\alpha_y + a_1(1-\alpha_x^2)^{1/2}(1-\alpha_y^2)^{1/2} - a_2(1-\alpha_x^2)^{1/2} - a_3(1-\alpha_y^2)^{1/2}}{W_{x_-} - W_{y_-}} \Bigg\} \end{aligned} \tag{13}$$

In $F = \frac{1}{2} M_{xy} R_{Q_x} R_{Q_y}$, R_{Q_x} and R_{Q_y} are the dipole strengths for the monomer Q_x and Q_y bands, respectively, and M_{xy} the matrix element of the magnetic moment operator connecting the two states.

The dimer absorption and MCD may now be calculated for different sets of the parameters α_x, α_y, a_1, a_2 and a_3. The precise locations and widths of the absorption and MCD bands were determined by deconvolution of the experimental spectra. In a second calculation the B and D values were determined for α_x and α_y between 0.1 and 1.0 for variation of the a values between the extremes of 2.0 and -2.0. The experimental ratios, defined by

$$r_1 = B_{y_+}/B_{y_-},\ r_2 = B_{x_+}/B_{x_-} \text{ and } r_3 = D_{y_+}/D_{y_-}$$

were used to obtain restrictions on the allowed quantities. A rather wide range around these ratios was used in the calculations. From the result of the calculations the set of B and D values closest to the experimental ones was used for the simulated spectral plots with the previously determined band locations and widths.

3. Results and Discussion

3.1. The special pair of Chl a

According to the literature the keto groups are connected through the nucleophile to the magnesium atoms, yielding a structure in which the monomer planes are approximately parallel [1]. The z-axes of the monomer coordinates are either parallel, which corresponds to the Euler angle $\beta = 0$ ($a_1 = 2$), or antiparallel with $\beta = \pi$ ($a_1 = -2$). For these values of a, α_x and α_y were varied between 0.1 and 1.0 for different possible a_2 and a_3. The experimental ratios are $r_1 = 0.69 \pm 0.07$, $r_2 = 3.0 \pm 1.0$ and $r_3 = 0.53 \pm 0.06$. With these restrictions and $a_1 = -2$ one obtains the values $0.61 < \alpha_x < 0.70$ and $0.62 < \alpha_y < 0.68$. Within experimental error the model then yields for α_x and α_y any combination in these ranges. For $r_1 = 0.69$, $r_2 = 4.0$ and $r_3 = 0.53$ one has, for instance, $\alpha_x = 0.670$ and $\alpha_y = 0.645$. For the other possible value of $a_1 = +2$ this procedure does not yield any combination for α_x, α_y. We therefore believe that the Euler angle $\beta = \pi$, which means that the dimer has C_2 symmetry.

If one assumes that the quantities r_1 and r_3 are smaller, as indicated by an earlier publication [10], the same conclusion remains valid, except that α_x and α_y become smaller.

The values of α of about 0.65 in combination with the observed splittings for the y-polarized bands of 680 cm^{-1} may lead to an estimate for the environmental splitting, $\tau_1 - \tau_2$, and the transition density parameter, T. Using the above definitions of these quantities, one obtains $\tau_1 - \tau_2 = 442\ \text{cm}^{-1}$ and $T = 258\ \text{cm}^{-1}$. From the dipolar interaction, $2T = 2\mu^2/R^3$, a rough estimate of the dipolar distance may be made. If the dipole strength of the y-polarized band in the monomer is about 25 debye^2, one has for the distance $R = 8$ Å. Although no particular significance should be attached to these estimated values, some indication as to the correctness of the magnitudes involved is obtained.

Merely to show the behavior of the simulated spectrum on varying the angle β between the z-axis we have given some plots in fig. 3 for the same values of α_x, α_y, a_2 and a_3. In these plots the angle β has the values π, $\frac{1}{2}\pi$ and 0, respectively. Of course, an angle of $\frac{1}{2}\pi$ is impossible for the special pair.

3.2. The pure dimer of Chl b

The ordering of the dimer absorption bands is based on the analogy with Chl a and on the following arguments. By definition, the highest energy band of a pair of x- or y-bands has the subscript + (eq. 4). Also the zero-zero transitions of the x- and y-bands have opposite MCD. We therefore conclude that the ordering, with increasing energy is $y_- y_+ x_- x_+$.

If, for instance, the ordering is $y_- x_- y_+ x_+$, the MCD signs would show the ordering $+ - + -$, contrary to experiment, etc.

The bonding in Chl b dimers is not known. If only one bond exists between the two monomers, as for instance is the case in Chl a pure dimer, all possible orientations seem to be possible. Experiment leads to the ratios $r_1 = 0.82$, $r_2 = 0.60$ and

$r_3 = 0.50$. Contrary to the previous example the value of r_2 could be determined within small limits due to the better resolution of the MCD bands.

If, for instance, it is assumed that $\alpha_x = \alpha_y = 0.8$, a best spectral fit is obtained for $a_1 = -2.0$ to -1.7 (i.e., for $\beta = \pi$ to 0.8π) corresponding to a configuration with approximately parallel monomer planes.

As far as we know, estimates of the interactions for Chl *b* dimers have not been made from other experiments. The symmetry of the MCD spectrum with respect to the splittings indicates that $\alpha_x \approx \alpha_y$.

For smaller values of the interaction parameter the spectrum may be simulated for a larger region of the angle β. For α_x, $\alpha_y < 0.4$ almost any orientation becomes possible.

4. Conclusion

It seems that the absorption and MCD spectrum of dimers may be reconstructed in a simple fashion using the monomer spectrum and the observed band positions and widths of the dimer spectrum. The intensity relations of the absorption and MCD are rather specific for the spectral features. Certain relative positions have to be excluded assuming specific interactions. Unfortunately, precise intensity measurements of the absorption bands could not be made due to possible overlap of the bands. In the case of well defined absorption bands, the quantities α_x and α_y may be determined more precisely and then used in a calculation of the MCD spectrum. We believe, however, that in spite of the limitations this simple model may have a more general application to the description of dimers. In the structural details are more accurately known, estimates of the interaction become more precise and vice versa.

Appendix

The coordinates with respect to the monomers are given by x_1, y_1, z_1 and x_2, y_2, z_2.

For a description of the electric and magnetic vectors a common reference frame is needed for which we take x_1, y_1, z_1.

If the Euler angles which relate the two systems are given by α, β and γ [21], it follows that:

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = A \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \tag{A1}$$

where

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{A2}$$

where the elements a_{ij} are the matrix elements given in ref. 21. One has to calculate expressions of the form

$$\langle Q_{y_\pm}|\vec{m}|Q_{x_\pm}\rangle \cdot \langle G|\vec{\mu}|Q_{y_\pm}\rangle \wedge \langle Q_{x_\pm}|\vec{\mu}|G\rangle$$

which after substitution of the functions leads to:

$$\begin{aligned} &\tfrac{1}{4}(1+\alpha_y)^{1/2}(1+\alpha_x)^{1/2}\langle Q_{y_1}|\vec{m}|Q_{x_1}\rangle \cdot \\ &\quad \Big\{(1+\alpha_y)^{1/2}(1+\alpha_x)^{1/2}\langle G|\vec{\mu}|Q_{y_1}\rangle \wedge \langle Q_{x_1}|\vec{\mu}|G\rangle \\ &\quad + (1+\alpha_y)^{1/2}(1-\alpha_x)^{1/2}\langle G|\vec{\mu}|Q_{y_1}\rangle \wedge \langle Q_{x_2}|\vec{\mu}|G\rangle \\ &\quad + (1-\alpha_y)^{1/2}(1+\alpha_x)^{1/2}\langle G|\vec{\mu}|Q_{y_2}\rangle \wedge \langle Q_{x_1}|\vec{\mu}|G\rangle \\ &\quad + (1-\alpha_y)^{1/2}(1-\alpha_x)^{1/2}\langle G|\vec{\mu}|Q_{y_2}\rangle \wedge \langle Q_{x_2}|\vec{\mu}|G\rangle\Big\} \\ &\quad + \tfrac{1}{4}(1-\alpha_y)^{1/2}(1-\alpha_x)^{1/2}\langle Q_{y_2}|\vec{m}|Q_{x_2}\rangle \cdot \{\text{''}\quad\} \end{aligned}$$

where $Q_{j_i} = \Phi'_{j_i}$ ($j = x, y$ and $i = 1, 2$) are the monomer excited Q states.

For the planar chlorophyll monomers the only magnetic contribution is due to the z-components. Using eq. A1 the elements of m_2 and μ_2 are expressed relative to the reference frame (x_1, y_1, z_1). For instance:

$$\begin{aligned} \langle Q_{x_2}|\vec{\mu}_2|G\rangle_{x_1} &= a_{11}\langle Q_{x_2}|\vec{\mu}_2|G\rangle_{x2} + a_{12}\langle Q_{x_2}|\vec{\mu}_2|G\rangle_{y_2} \\ &\quad + a_{13}\langle Q_{x_2}|\vec{\mu}_2|G\rangle_{z_2} \\ &= a_{11}\langle Q_{x_2}|\vec{\mu}_2|G\rangle_{x_2} = a_{11}R_{Q_x} \end{aligned}$$

since the y_2 and z_2 components of $\langle Q_{x_2}|\vec{\mu}_2|G\rangle$ are zero. It has been assumed that both monomers have the same dipole strengths for the lower Q transitions, thus

$$R_{Q_{x_1}} = R_{Q_{x_2}} = R_{Q_x}$$

and

$$R_{Q_{y_1}} = R_{Q_{y_2}} = R_{Q_y}$$

The same holds for the magnetic moments of the monomer molecules in the dimer.

The expressions of eqs. 10–13 are found with the abbreviations:

$$a_1 = a_{33} + a_{11}a_{22} - a_{12}a_{21} = 2\cos\beta$$

$$a_2 = a_{11} + a_{22}a_{33} - a_{23}a_{32} = 2(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma)$$

$$a_3 = a_{22} + a_{11}a_{33} - a_{13}a_{31} = -2(\sin\alpha\sin\gamma - \cos\alpha\cos\beta\cos\gamma)$$

For the dipole strengths D for these transitions one obtains the expressions:

$$D(a \rightarrow y_+) = R^2_{Q_y}\left\{1 + \tfrac{1}{2}\left(1 - \alpha_y^2\right)^{1/2} a_3\right\}$$

$$D(a \rightarrow y_-) = R^2_{Q_y}\left\{1 - \tfrac{1}{2}\left(1 - \alpha_y^2\right)^{1/2} a_3\right\}$$

$$D(a \rightarrow x_+) = R^2_{Q_y}\left\{1 + \tfrac{1}{2}\left(1 - \alpha_y^2\right)^{1/2} a_2\right\}$$

$$D(a \rightarrow x_-) = R^2_{Q_y}\left\{1 - \tfrac{1}{2}\left(1 - \alpha_y^2\right)^{1/2} a_2\right\} \qquad \text{(A3)}$$

The expressions, eqs. A3 and 10–13, were used for the plots of the absorption and MCD spectra. The best fit was obtained with the experimental positions of the dimer bands and linewidths with a Gaussian or damped oscillator function.

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