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Absorption and dichroism spectra of cylindrical J aggregates and chlorosomes of green bacteria

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Abstract

We study the absorption and linear and circular dichroism spectra of molecular aggregates having the shape of a cylinder. Examples are the chlorosomes of green bacteria and recently synthesized cyanine J aggregates, called amphipipes. We use a Frenkel exciton model and exploit the cylinder symmetry to separate the exciton states into bands with different transverse wavenumbers. Only three of these bands are optically active. The delicate interference between the contributions of these three bands to the CD spectrum, make this spectrum very sensitive to system parameters, such as the cylinder length. This offers a natural explanation for the observed strong variation of the CD spectra of chlorosomes with sample preparation technique.

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Keywords: Molecular aggregates; Chlorosomes; Linear dichroism; Circular dichroism

1. Introduction

Chlorosomes are the light-harvesting complexes in green bacteria [1]. They contain large self-assembled aggregates consisting of bacteriochlorophyll (BChl) molecules, arranged in a cylindrical way. For *Chloroflexus aurantiacus*, these cylinders have a diameter of ~ 5 nm and a length up to hundreds of nm. The proposed structure is helical and may be viewed as strands of molecules that wind around the cylinder [2]. In the traditional language of molecular aggregates, these systems should be referred to as J aggregates, as their absorption band at 740 nm is red-shifted relative to that of a single BChl molecule (675 nm).

Prototype synthetic J aggregates are prepared from polymethine cyanine molecules. Due to their strong transition dipoles, these are among the molecules with the strongest tendency to self-assemble, with the largest absorption strength, and the largest exciton transfer interaction [3]. They would therefore lend themselves well to prepare synthetic light-harvesting systems. Interestingly, it has recently been shown that by adding amphiphilic side groups to the dye 5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolo carbocyanine (TDBC), this molecule forms cylindrical aggregates as well (called “amphipipes”) [4,5], thus mimicking the natural systems. Optical techniques are employed abundantly to unravel the microscopic properties of both natural [6–14] and synthetic [5,15–17] molecular aggregates.

In this paper, we discuss the theory of the linear optical properties of cylindrical molecular

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aggregates, allowing for a helical structure of the cylinders. We will calculate the absorption spectrum and the linear (LD) and circular (CD) dichroism spectra. Using our general results, we address the strong variation observed in the CD spectrum of chlorosomes upon changing sample preparation routes [6,8–12].

The outline of this paper is as follows. In Section 2 we describe the system and separate the two-dimensional Hamiltonian into a set of effective one-dimensional ones. We present the formal results for the various spectra in Section 3. Explicit results are given and discussed in Section 4, while we conclude in Section 5.

2. Model and separation of transverse exciton momenta

The general geometry of a cylindrical molecular aggregate may be generated by rolling a two-dimensional lattice onto a cylinder surface such that the structure has the proper periodicity in the circumferential direction. Assuming that each unit cell is occupied by one molecule, it then follows [18] that the general aggregate structure may be viewed as an equidistant stack of N_1 rings (labeled $n_1 = 1, \dots, N_1$) on each of which N_2 molecules (labeled $n_2 = 1, \dots, N_2$) are placed in an equidistant way (Fig. 1). Each ring has radius R ; adjacent rings are separated by a distance h and are rotated relative to each other over a “helical” angle γ ($0 \leq \gamma < 2\pi/N_2$). Connecting the molecules on neighboring rings that are closest to each other, we see that the structure may also be viewed as a collection of N_2 helices winding around the cylinder (dashed line in Fig. 1). In our labeling of the molecules, we will use the convention that $n_2 = \text{const.}$ refers to a set of molecules on one such helix; $n_1 = \text{const.}$ refers to the molecules on one ring.

We will assume that each molecule has one dominant optical transition, with a transition dipole that is equal in magnitude (μ) and orientation with respect to the local frame of the cylinder. In particular, every dipole makes an angle β with the z -axis (the axis of the cylinder), while its projection on the xy plane makes an angle α with

Fig. 1. The cylindrical aggregate consisting of a stack of N_1 rings that each contain N_2 molecules. The arrows indicate the transition dipoles, which are equal in magnitude (μ) and make an angle β with the cylinder axis. The projection of each dipole on the plane of the rings makes an angle α with the local tangent to the ring. Each ring is rotated with respect to the previous one over an angle γ , so that we may view the aggregate as a collection of N_2 parallel helices (dashed) on the cylinder's surface.

the local tangent to the ring on which the molecule resides.

The electronically excited states of the system are described by a Frenkel exciton Hamiltonian. Setting $\hbar = 1$, we have

$$H = \omega_0 \sum_{\mathbf{n}} b_{\mathbf{n}}^{\dagger} b_{\mathbf{n}} + \sum_{\mathbf{n}, \mathbf{m}} J(\mathbf{n} - \mathbf{m}) b_{\mathbf{n}}^{\dagger} b_{\mathbf{m}}, \quad (1)$$

where $b_{\mathbf{n}}^{\dagger}$ and $b_{\mathbf{n}}$ denote the Pauli operators for creation and annihilation of an excitation on molecule $\mathbf{n}$, respectively. Furthermore, ω_0 is the molecular transition frequency and $J(\mathbf{n} - \mathbf{m})$ is the excitation transfer interaction between molecules $\mathbf{n}$ and $\mathbf{m}$. Due to the symmetry of the system the interaction only depends on the relative positions of the two molecules. The prime on the summation indicates that the term with $\mathbf{n} = \mathbf{m}$ is excluded. We assume that $J(\mathbf{n} - \mathbf{m})$ results from the interactions between the transition dipoles of the two molecules involved and we will in our calculations account for all interactions between all pairs of molecules in the aggregate. This is important in view of the long-range nature of the dipole–dipole interaction.

The one-exciton eigenstates of the Hamiltonian determine the linear optical properties (absorption, LD, CD) of the aggregate. Generally, these states follow from an $N_1 N_2 \times N_1 N_2$ matrix diagonalization, but the situation is simplified, because the cylinder symmetry dictates a Bloch form for the excitons in the circumferential direction. Explicitly we may write the exciton states as

$$|\mathbf{k}\rangle = |k_1, k_2\rangle = \frac{1}{\sqrt{N_2}} \sum_{\mathbf{n}} e^{i2\pi k_2 n_2 / N_2} \times \varphi_{k_1}(n_1; k_2) b_{\mathbf{n}}^{\dagger} |g\rangle \quad (2)$$

with energy $E_{\mathbf{k}} = E_{(k_1, k_2)}$. Here $|g\rangle$ is the overall ground state (with all molecules in their ground state), k_2 is the transverse momentum of the wave function, taking the values $k_2 = 0, \pm 1, \pm 2, \dots, \pm(N_2/2 - 1), N_2/2$ for N_2 even ($k_2 = 0, \pm 1, \pm 2, \dots, \pm(N_2 - 1)/2$ for N_2 odd), and k_1 labels the longitudinal eigenfunctions $\varphi_{k_1}(n_1; k_2)$. They are eigenfunctions (with energy $E_{\mathbf{k}}$) of the effective one-dimensional exciton Hamiltonian with “molecular” frequencies $\omega_0 + J(0; k_2)$ and effective “intermolecular” interaction $J(n_1; k_2) (n_1 \neq 0)$, with

$$J(n_1; k_2) = \sum'_{n_2} J(n_1, n_2) e^{-i2\pi k_2 n_2 / N_2}. \quad (3)$$

The physical meaning of $J(n_1; k_2)$ is the total transfer interaction between all molecules of two rings that are separated by $n_1 h$ and that both reside in their Bloch state with momentum k_2 . The overall inversion symmetry of the cylinder guarantees that each eigenenergy is at least doubly

degenerate. More explicitly, the set of eigenstates of transverse wave number k_2 is degenerate with those of wave number $-k_2$, and the associated longitudinal eigenfunctions are each other's complex conjugates [18].

As we will see below, the linear optical spectra only involve the bands with $k_2 = 0$ and $k_2 = \pm 1$ (degenerate). Hence, calculating those spectra involves the diagonalization of two $N_1 \times N_1$ problems, instead of one big $N_1 N_2 \times N_1 N_2$ diagonalization.

3. Linear optical spectra

We are interested in the absorption spectrum $A(\omega)$ and the linear and circular dichroism spectra ($LD(\omega)$ and $CD(\omega)$, respectively). The CD spectrum is defined as the difference of absorption of left- and right-handed circularly polarized light in an isotropic sample, while the LD spectrum is the difference in the absorption spectrum for light polarized along the cylinder axis in a sample where all cylinders are aligned and the spectrum for light polarized perpendicular to this axis. Using the Fermi golden rule, one may derive the general expressions for these three types spectra. After using the decomposition Eq. (2) and applying the appropriate orientational averaging, we arrive at the following expressions [18].

$$A(\omega) = \frac{\cos^2 \beta}{3} \sum_{k_1} M(k_1, 0) \delta(\omega - E_{k_1, 0}) + \frac{\sin^2 \beta}{3} \sum_{k_1} M(k_1, 1) \delta(\omega - E_{k_1, 1}) \quad (4)$$

with

$$M(k_1, k_2) = N_2 \mu^2 \left| \sum_{n_1} \varphi_{k_1}(n_1; k_2) e^{-in_1 k_2 \gamma} \right|^2. \quad (5)$$

We thus find that the linear absorption spectrum shows two sets of peaks. One set results from states in the $k_2 = 0$ band and is polarized parallel to the axis of the cylinder; the other results from the $k_2 = \pm 1$ bands and are polarized perpendicular to the cylinder axis. The $k_2 = \pm 1$ bands give equal

contributions. For the linear dichroism we find

$$LD(\omega) = \cos^2 \beta \sum_{k_1} M(k_1, 0) \delta(\omega - E_{k_1,0}) - \frac{\sin^2 \beta}{2} \sum_{k_1} M(k_1, 1) \delta(\omega - E_{k_1,1}), \quad (6)$$

which has positive contributions from the states with oscillator strength in the $k_2 = 0$ band and negative ones from the states in the $k_2 = \pm 1$ bands. Finally, for the CD we find

$$CD(\omega) = \frac{\sin 2\beta \cos \alpha \pi R}{3} \frac{\pi R}{2\lambda} \left[\sum_{k_1} M(k_1, 0) \delta(\omega - E_{k_1,0}) - \sum_{k_1} M(k_1, 1) \delta(\omega - E_{k_1,1}) \right] + \frac{\sin^2 \beta \pi h}{3} \frac{\pi h}{2\lambda} \sum_{k_1} W(k_1, 1) \delta(\omega - E_{k_1,1}), \quad (7)$$

where $\lambda = 2\pi c/\omega$ is the wavelength of the exciting light and we defined the real function

$$W(k_1, 1) = \frac{N_2 \mu^2}{i} \sum_{n_1, m_1} [(n_1 - m_1) e^{-i(n_1 - m_1)\gamma} \varphi_{k_1}(n_1; 1) \times \varphi_{k_1}^*(m_1; 1)]. \quad (8)$$

The first two terms in Eq. (7) have opposite signs and equal weights, because $\sum_{k_1} M(k_1, 0) = \sum_{k_1} M(k_1, 1) = N\mu^2$. These two terms together closely resemble the S-shaped CD spectrum of a single ring aggregate and will therefore be referred to as the “ring” contribution. The third term closely resembles the CD spectrum of a single stack (straight line) of molecules with their dipoles winding around the line in helical way and will therefore be referred to as the “helical” contribution.

In general the above expressions for the spectra should be evaluated using numerical diagonalization of the effective one-dimensional problems for the $k_2 = 0$ and the $k_2 = 1$ subspace. In the limit of long cylinders, however, we may impose periodic boundary conditions in the n_1 direction and write the longitudinal wave functions in a Bloch form as well. Then, the label k_1 represents the longitudinal momentum of the exciton. The dispersion relation

is then given by

$$E_{\mathbf{k}} = \omega_0 + \sum_{\mathbf{n}}' J(\mathbf{n}) \cos [2\pi(k_1 n_1 / N_1 + k_2 n_2 / N_2)]. \quad (9)$$

It turns out that in this limit only three super-radiant states contribute to the linear optical spectra, namely the state with zero total momentum and the “helical” ones with momenta $\pm(N_1\gamma/2\pi, 1)$ [18]. The former one is polarized along the cylinder axis, while the latter two (degenerate) are polarized perpendicular to this axis. The energies of these states are denoted $E_0 = \omega_0 + \sum_{\mathbf{n}}' J(\mathbf{n})$ and $E_h = \omega_0 + \sum_{\mathbf{n}}' J(\mathbf{n}) \cos(\gamma n_1 + 2\pi n_2 / N_2)$, respectively. These expressions have been used in Refs. [5,15,16] to estimate N_2 for the cylindrical TDBC aggregates using a short-range approximation to the dipole–dipole interactions and assuming that $\gamma = 0$.

4. Numerical results and discussion

We have used Eqs. (4)–(7) to calculate the three types of spectra for cylinders of varying length N_1 . As example, we have chosen the geometry of the rod elements in the chlorosomes of *Chloroflexus aurantiacus*. The parameters for these BChl *c* aggregates are [2,19]: $R = 2.297$ nm, $N_2 = 6$, $h = 0.216$ nm, $\alpha = 189.6^\circ$ (in Ref. [19] this angle was misplaced by its complement [20]), $\beta = 36.7^\circ$, and $\gamma = 20^\circ$. Furthermore, we have taken ω_0 to agree with a single-molecule absorption peak at 675 nm and we have used $\mu^2 = 20D^2$ for the square of the single-molecule transition dipole. Finally, we have convoluted the delta functions in the stick spectra Eqs. (4)–(7) with a Gaussian lineshape function of full-width at half-maximum $W = 500$ cm^{−1}.

The resulting spectra for five values of N_1 are shown in Fig. 2. We observe that all spectra show a size dependence, but that this dependence is most dramatic for the CD. The absorption spectra always is red-shifted relative to ω_0 , which is due to the fact that the dominant transfer interaction is negative (J aggregate). This dominant interaction occurs between molecules on two neighboring helices and three rings apart: $J_1 \equiv J(n_1 = 3, n_2 = -1) \approx -340$ cm^{−1}. For the absorption spectrum

Fig. 2. Linear absorption (dotted), LD (dashed), and CD (solid) spectra calculated for cylindrical aggregates with a geometry applicable to the rod elements in the chlorosomes of *Chloroflexus aurantiacus* (see text for details). The panels (a)–(e) give the spectra for five different cylinder lengths N_1 . The factor f multiplying the LD is defined by $f = 2/(3[\cos^2 \beta - 1])$ and was introduced to give the absorption and the LD spectrum the same area ($N\mu^2/3$).

and the LD spectrum, the main difference between short and long cylinders is a shift of the spectrum towards higher wavelengths for increasing N_1 . This is due to the long-range nature of the dipole–dipole interactions. The shape of these two spectra converges towards the long-cylinder limit already around $N_1 = 50$. This results from the fact that already for rather small lengths, the separations between the optically dominant transitions in the $k_2 = 0$ and $k_2 = \pm 1$ bands become smaller than the added line width W . This may be estimated by using the dispersion relation E_k obtained for periodic boundary conditions. Two energy scales are of interest: first, the separation between the two different k_2 bands may be estimated to be $\delta_{\perp} = E_h - E_0 \approx 168 \text{ cm}^{-1}$ for the chlorosome geometry. Obviously, this is smaller than W . Second, the separation between the optically dominant states within each subband is due to the quantization of the longitudinal wave functions, and may be estimated to be $\delta_{\parallel} = E_{(1,0)} - E_{(0,0)}$. Keeping only the strongest interaction (J_1), we arrive at $\delta_{\parallel} \approx 4\pi^2 |9J_1|/N_1^2$, which decreases with increasing N_1 , as expected. For $N_1 = 25$ we have $\delta_{\parallel} \approx 195 \text{ cm}^{-1}$, which already is considerably smaller than W . With increasing N_1 the absorption peak position converges to 740 nm, while the line width tends towards 30 nm. Both numbers are in good agreement with experiment [8,9,12]. Generally speaking, the difference between the LD line shape and the absorption line shape in Fig. 2 is bigger than observed experimentally. It may be shown that decreasing β repairs this discrepancy [18]. In fact, no agreement exists about the precise value of this angle [2,7–9].

By contrast to the absorption and LD spectrum, the CD spectra in Fig. 2 show a very strong N_1 dependence. This results from the delicate interference between positive and negative contributions in the CD. For the current geometry, the $k_2 = 0$ band gives negative ring contributions and no helical ones, while the $k_2 = \pm 1$ bands give positive ring contributions and dispersive helical ones. The mutual position of these different contributions is determined by the splittings $\delta_{\perp}$ and $\delta_{\parallel}$. For $\delta_{\perp} \leq \delta_{\parallel}$, all these contributions strongly overlap, giving rise to very strong changes in shape upon changing N_1 , because the latter

gives rise to a change in $\delta_{\parallel}$. When $\delta_{\perp} \gg \delta_{\parallel}$, i.e., for large N_1 the contributions from the two different bands separate and the spectrum converges towards its infinite-length limit, which may be calculated analytically using the solution with periodic boundary conditions [18].

As was first noted by Holzwarth and Prokhorenko [21], the strong variation of the CD with the cylinder length offers an explanation to a well-known problem in the literature on chlorosomes, namely the sensitivity of this spectrum to sample preparation route [6,8–12]. Two types of spectra are typically reported in the experimental literature. The first has a high-wavelength positive peak and a low-wavelength negative dip, much like our spectrum in Fig. 2(c), while the second spectrum has a positive peak, surrounded by two dips, like Fig. 2(d) and (e). As far as we know, spectra resembling Fig. 2(a) and (b) have not been observed, probably because such small cylinder lengths do not occur for chlorosomes. It is important to note that the changes in the CD spectrum observed between $N_1 = 80$ and 140 are not accompanied by any noticeable changes in the absorption spectrum. Indeed, in experimental studies, the big differences observed in the CD spectra upon changing preparation route, only cause very minor changes in the absorption spectrum. We note that for smaller values of β , the cross-over length between the two types of CD spectra is increased [18].

An alternative explanation of the variability of the CD spectrum was given in Ref. [22], where it was suggested that the angle α leads to these changes. Indeed, this would lead to similar shifting of the various CD contributions relative to each other, because the band structure is affected by α . On the other hand, it seems much easier in self-assembled systems with strong hydrogen-bonded networks to change the overall system length than the internal structure. We also point out that some direct experimental evidence exists that different CD line shapes are associated with chlorosomes of different sizes [12].

We note that in the above calculations we used the point-dipole approximation for calculating the interaction $J(\mathbf{n})$. A priori this seems a poor approximation for a tightly bound aggregate. To

Fig. 3. Effect of going from point dipoles (solid) to extended dipoles (dashed and dotted) on the CD spectrum for aggregates of the same geometry as in Fig. 2, with a length of $N_1 = 150$ rings. The dashed and dotted spectra are obtained for a dipole length of 0.3 nm and 0.6 nm, respectively.

check the possible effect, we have also done calculations in which the dipoles were replaced by extended dipoles of length l , adjusting the charges such that the total dipole moment is kept constant. We found that the effect of this extension on the spectra is only a shift; the shapes of the spectra are preserved up to dipole extensions in the order of the size of the chlorophyll molecules. As an example, Fig. 3 shows the CD spectrum for $l = 0, 0.3$ nm, and 0.6 nm for cylinders of $N_1 = 150$ rings. The same shifts are seen for other system sizes, as well as for the absorption and LD spectra. As the exact position of the spectrum depends on parameters (ω_0 and μ^2) that are not accurately known, the spectral shifts do not affect the agreement between theory and experiment and do not change the conclusions regarding the length dependence of the spectra.

5. Concluding remarks

We have presented general expressions for the absorption, LD, and CD spectra of cylindrical molecular aggregates, allowing for a helical structure of the cylinder. We have applied our theory to the case of chlorosomes of green bacteria and, following earlier suggestions [21], shown that the strong variation of the CD spectrum with sample preparation route may result from differences in the chlorosome length. In agreement with

experiment, these changes are not associated with noticeable changes in the absorption and the LD spectrum. Preliminary work on the inclusion of continuous energy disorder on the spectral line shapes, suggests that the above conclusions still hold, although it is an open question how the ratio of exciton localization size and cylinder length affects the spectra, in particular the CD spectra.

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