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Degeneracy, orientational disorder and chromophore size effects on Frenkel excitons in columnar mesophases

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Abstract

The properties of Frenkel excitons in columnar mesophases are analysed using numerical calculations with a particular emphasis on the off-diagonal disorder induced by rotation of the molecular disks around the column axis. The influence of degeneracy of the molecular electronic transitions and the effect of the chromophore size are illustrated by means of the extended dipole model. The localisation/delocalisation behaviour of the exciton states is characterised by calculation of the participation ratio. It is shown that the existence of two orthogonal dipolar transitions per chromophore makes the optical spectra less sensitive to chromophore rotation and maintains the eigenstates bearing the oscillator strength quite delocalised, even in the presence of complete orientational disorder. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Columnar liquid crystals are usually formed by molecules composed of a disk-like, flat and rigid core, surrounded by flexible chains [1]. The disks stack yielding segregated columns (Fig. 1). As the stacking distance is short (3–4 Å) compared to the intercolumnar distance (typically 20–40 Å), electronic interactions within the same column are much stronger than interactions between chromophores in neighbouring columns. Due to their highly anisotropic constitution, these materials are quite promising for applications in the field of molecular electronics and optoelectronics and as such, they have been the object of numerous studies dealing with photoinduced energy [2–9] and charge [10–13] transport. The first step of any photoinduced process is the formation of a collective excited state whose properties (energy, oscillator strength, degree of delocalisation, etc.) depend on the structure of the constitutive molecules. The latter determines not only the molecular excited states but also the various degrees of freedom in the system and, therefore, the type of disorder which will mainly affect its behaviour. It is thus important to predict this behaviour in a quantitative way and design the appropriate molecules accordingly.

In some discotic columnar phases a helical arrangement of the molecules around the column axis is encountered [14,15] whereas, in most of

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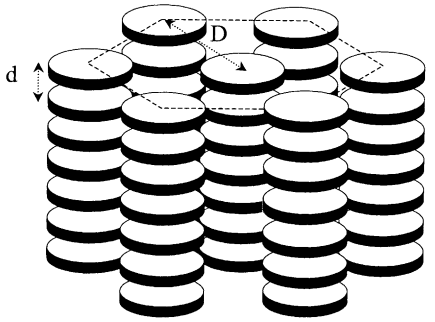

Fig. 1. Schematic representation of a typical discotic columnar mesophase. *D* and *d* denote the intercolumnar and the stacking distance, respectively.

them, molecules can rotate freely around the column axis [16] resulting in orientational disorder. As the absorption maximum in the visible or the near UV spectral domain corresponds to $\pi \rightarrow \pi^*$ electronic transitions polarised within the molecular plane, such a structural disorder may lead to important modifications in the dipolar coupling. Due to the particular characteristics of the columnar liquid crystals, two factors play a crucial role in the way that the off-diagonal disorder will affect the properties of the Frenkel excitons [17–19]: the number of the molecular electronic states involved in the collective states and the chromophore size.

Frenkel excitons may be built on one or more electronic states of the individual chromophores depending on whether the coupling between the corresponding transition moments is larger or smaller than the excited state separation. The disk-like part of the molecules forming columnar liquid crystals typically possesses a C_3 (i.e. triphenylenes [7]), C_4 (i.e. metal phthalocyanines [3,4]) or C_6 (i.e. benzenes [20], coronenes [21]) symmetry axis. As a result, the electronic transitions corresponding to the absorption maximum are doubly degenerate. Other discotic chromophores (i.e. metal free phthalocyanines [3], triarylpyrylium cations [22–24]) are characterised by two orthogonal transitions close in energy. Finally, others (i.e bent-rod hexacatenar mesogens [25]), have a well separated in energy non-degenerate dipolar transition. The above patterns of dipolar transitions affect in a different manner the behaviour of the corresponding exciton states in the presence of orientational disorder. In particular, orientational disorder is expected to have only a weak effect in the case of degenerate molecular transitions. Indeed, it was shown [26] that the absorption spectra of silicon phthalocyanine dimers change only slightly upon rotation of one monomer with respect to the other around the fourfold symmetry axis. A similar effect was observed for larger columnar triphenylene aggregates [27]. In contrast, large fluctuations are observed for rod-like aromatic cores characterised by single dipolar transitions [25].

The chromophore size in columnar phases is always larger than the stacking distance. Therefore, the point dipole approximation for the calculation of the dipolar coupling is quite inadequate. In this case, the atomic charge distribution model gives a correct determination of the coupling as revealed from a comparison between experimental and calculated absorption spectra of triphenylene aggregates [27]. Alternatively, the extended dipole approximation [28] can be used, provided that, for a given chromophore, the extended dipole length has been correctly adjusted [27]. The practical issue is that, for a given transition moment, when the chromophore size increases the dipolar coupling between neighbouring chromophores becomes weaker. Consequently, we expect the absorption spectra to shift towards lower energies. The effect of the extended dipole length on the absorption spectra has not been examined so far. In contrast, such an effect was recently simulated for the fluorescence spectra of rod-like aromatic cores [25].

Although it is possible to predict in a qualitative way how the degeneracy of the molecular electronic transitions and the chromophore size will influence the properties of Frenkel excitons in columnar phases, it is important to study their role in a systematic way. With this in mind, we have undertaken a numerical investigation focused on the effect generated by rotation of the chromophores around the column axis. We deal only with off-diagonal disorder and we examine the position of the eigenstates within the exciton band, their degree of delocalisation and the absorption spectra.

In the present communication, first we describe the characteristics of the studied systems (Section 2) and the formalism we use in our calculations (Section 3). Then, we present and discuss our results obtained for ordered aggregates with helical structure, followed by those found for disordered aggregates (Section 4). Finally, our conclusions are drawn in Section 5.

2. Description of the system

The geometric and electronic parameters of the systems examined in the simulations are inspired from the properties of columnar liquid crystals whose photophysical properties are experimentally studied. The aromatic cores are centred to the column axis perpendicular to it. The stacking distance d is 3.6 Å. The angle θ formed between two neighbouring chromophores either has a constant value, corresponding to a helical arrangement, or it varies randomly, yielding orientationally disordered aggregates.

We consider single aggregates with aggregation number $N = 200$. We have verified that the computed quantities remain practically unaltered upon further increase of N or upon adding additional columns at distances equal or larger than 20 Å. The properties of orientationally disordered aggregates correspond to the average of 500 random configurations.

The properties of electronic transitions of non-coupled molecules roughly correspond to the experimental absorption maximum of hexasubstituted triphenylenes ($S_0 \rightarrow S_4$ transition) [27]. The latter absorption band can be represented by a non-degenerate transition with a dipole moment of 10 D or by a doubly degenerate transition, each component of which has a dipole moment equal to 7 D. All chromophores characterised by either a single non-degenerate transition or by a doubly degenerate transition have the same excitation energy $E_0 = 30\,000\ \mathrm{cm}^{-1}$ which is chosen as origin energy. For chromophores characterised by two non-degenerate orthogonal transitions, we consider that each one has a transition moment of 7 D; their energies are symmetrically located with respect to E_0 ($E_0 + \Delta E/2$, $E_0 - \Delta E/2$). The energy difference between them ΔE varies from 0 to $4V_{\|}$, where $V_{\|}$ is the dipolar coupling between two parallel transition moments of neighbouring molecules.

We consider that only dipolar coupling is acting. The dipolar coupling is calculated according to the extended dipole approximation (Section 3). Since the important factor is the chromophore size with respect to the stacking distance d, the relevant quantity is l/d, where l is the extended dipole length; l/d is given the values 0, 1, 2 and 3. The extended dipoles are centred on the column axes. A non-degenerate electronic transition is represented by a single extended dipole. When there are two transitions (degenerate or not) per chromophore, they are represented by two perpendicular to each other extended dipoles (x and y polarisations).

3. The Frenkel exciton states

Let us consider a linear chain of N identical chromophores featuring a columnar aggregate. The excited states of such an aggregate can be described as an ensemble of two-level systems (ground and excited states) in the framework of the Frenkel exciton theory since the electronic intermolecular interactions are weak compared to the molecular energies. In the localised site representation the total Hamiltonian is written as

$$H_0 = \sum_{i,s} E_{is}|is\rangle\langle is| + \sum_{i\neq j,s,t} V_{is,jt}|is\rangle\langle jt|. \qquad (1)$$

E_{is} are the molecular site energies ($i, j = 1, n$), and ($s, t = x, y$) denote the polarisations of the molecular transitions in the case of two transitions per chromophore. The term $V_{is,jt}$ describes the dipolar interaction between transition moments of chromophores at the sites i and j. As emphasised in Section 1, for the columnar mesophases investigated, the simplest approach of point dipoles to describe the dipolar interactions is not valid. Thus, we use the extended dipole approximation according to which an electronic transition is represented by two opposite charges $+q$ and $-q$ at a distance l, so that $\mu = ql$, where μ is the transition

moment of the isolated molecule. The dipolar coupling between two non-degenerate transitions V_{ij} is then given by

$$V_{ij} = \frac{2\mu^2}{l^2 R_{ij}} \left[\left(1 + \frac{l^2}{2R_{ij}^2}(1 - \cos\theta_{ij}) \right)^{-1/2} - \left(1 + \frac{l^2}{2R_{ij}^2}(1 + \cos\theta_{ij}) \right)^{-1/2} \right], \tag{2}$$

where R_{ij} represents the distance between the centres of the corresponding extended dipoles and θ_{ij} is the angle formed between them.

In the case of two orthogonal transitions per chromophore with x and y polarisations, the matrix representation of the electronic interaction between the i and j chromophores is

	$\lvert ix\rangle$	$\lvert iy\rangle$	$\lvert jx\rangle$	$\lvert jy\rangle$
$\langle ix\rvert$	$-\Delta E/2$	0	V_{ij}^{xx}	V_{ij}^{xy}
$\langle iy\rvert$	0	$\Delta E/2$	V_{ij}^{yx}	V_{ij}^{yy}
$\langle jx\rvert$	V_{ij}^{xx}	V_{ij}^{xy}	$-\Delta E/2$	0
$\langle jy\rvert$	V_{ij}^{yx}	V_{ij}^{yy}	0	$\Delta E/2$

(3)

with

$$V_{ij}^{xx} = V_{ij}^{yy} = V_{ij}(\cos(\theta_{ij}));$$
$$V_{ij}^{xy} = V_{ij}(\cos(\theta_{ij} + \pi/2));$$
$$V_{ij}^{yx} = V_{ij}(\cos(\theta_{ij} + 3\pi/2));$$

ΔE is the energy separation between the two transitions.

If $R_{ij} \gg l$, we recover the well-known expression for dipolar interactions in the point dipole approximation

$$V_{ij} = 5.04 \frac{\mu^2}{R_{ij}^3} \cos(\theta_{ij}), \tag{4}$$

in which the numerical constant is introduced in order to express V_{ij} in wave numbers, μ in Debye and R_{ij} in nanometers.

Diagonalisation of the Hamiltonian H_0 gives the N eigenenergies and eigenvectors (or $2N$ in the case of two transitions per chromophore):

$$H_0 = \sum_k E_k |k\rangle\langle k|, \tag{5}$$

$$|k\rangle = \sum_{i,s} C_{is}^k |is\rangle. \tag{6}$$

The transition moments associated with the various eigenstates are easily obtained

$$\vec{\mu}_k = \sum_{is} C_{is}^k \vec{\mu}_{is}, \tag{7}$$

as well as the oscillator strengths

$$f_k = C(E + E_k)|\vec{\mu}_k|^2, \tag{8}$$

where $C = 4.68 \times 10^{-7}$ and E is the energy of non-coupled transitions.

For the simulation of the absorption spectra each transition is represented by a gaussian curve centred at E_k, with a standard deviation $\sigma = 200$ cm^{-1} (Boltzmann factor at room temperature) and a maximum height proportional to the oscillator strength per chromophore f_k/N.

When there is one transition per chromophore, the localised or delocalised behaviour of the eigenstates is generally analysed by means of the inverse participation ratio defined as [29,30]

$$L_k = \sum_{i=1}^{N} |C_i^k|^4, \tag{9a}$$

in which $|C_i^k|^2$ represents the square amplitude of the site i on a given eigenstate k. L_k equals unity for states localised on a single molecule, whereas it goes to zero as $1/N$ for states evenly delocalised over N molecules. The participation ratio, defined as $N_k = 1/L_k$, gives for each eigenstate the number of coherently coupled molecules. When there are two transitions per chromophore, the inverse participation ratio given by Eq. (9a) becomes [27]

$$L_k = \sum_{i=1}^{N} \left[|C_{ix}^k|^2 + |C_{iy}^k|^2 \right]^2. \tag{9b}$$

We shall use in what follows the normalised participation ratio $r_k = N_k/N$. Another quantity of interest is the effective number of molecules coupled to the electromagnetic radiation which can be defined as

$$N_{\text{eff}} = \frac{\sum_k N_k f_k}{\sum_k f_k} \tag{10}$$

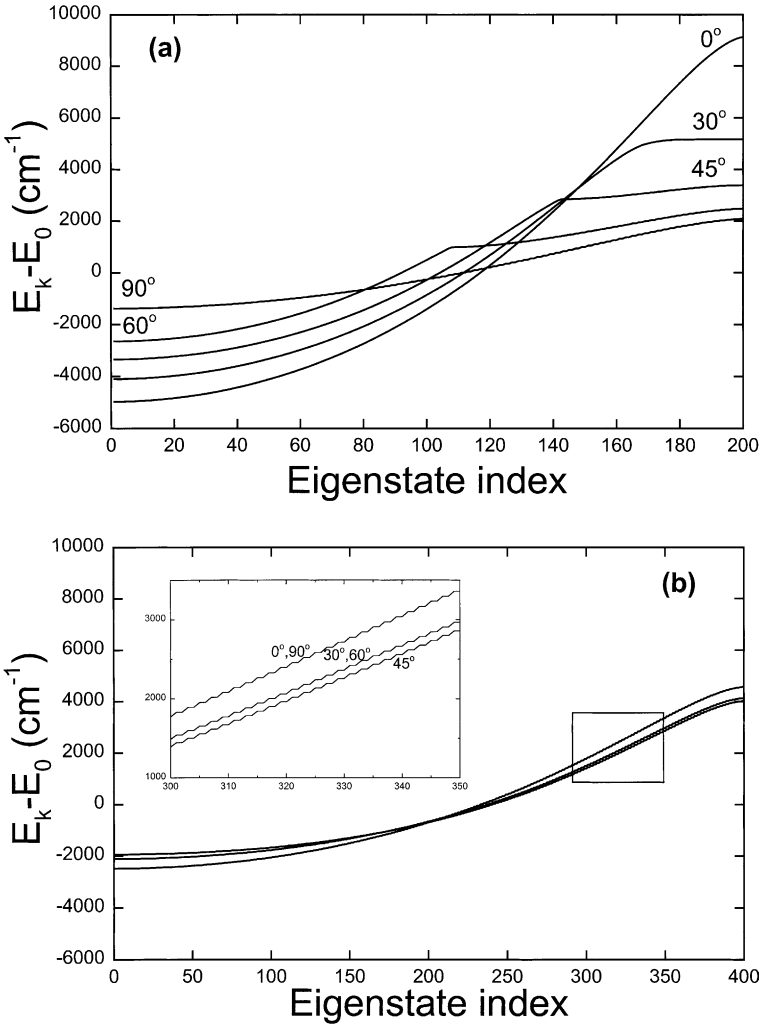

Fig. 2. Energy ($E_k - E_0$) dispersion curves for columnar helical aggregates as a function of the helical angle θ in the case of (a) a single non-degenerate transition and (b) a doubly degenerate transition; $l/d = 2$.

and represents the average number of molecules calculated over the distribution of the oscillator strength.

4. Results and discussion

4.1. Ordered helical aggregates

First, we consider helical aggregates with several typical helical angles θ (0°, 30°, 45°, 60° and 90°) and we address the question how the helical angle affects the structure of the exciton band. Our results are shown in Fig. 2, where the eigenstate energy is plotted as a function of the eigenstate index. If we consider a single non-degenerate transition per chromophore, we observe large variations as a function of θ. Upon increasing θ, the bandwidth, defined as the energy difference between the upper (E_{top}) and lower (E_{bottom}) eigenstates, decreases considerably; it is 14 000 cm^{-1} when $\theta = 0°$ and it becomes only 3500 cm^{-1} for $\theta = 90°$. The upper and lower eigenstates are not symmetrically located with respect to E_0, even for

parallel transition moments. Such an asymmetry of the exciton band is due to the existence of long range interactions. When only nearest neighbour interactions are considered all the curves are symmetrically distributed around E_0 and they cross at the middle of the band. This asymmetry has been largely discussed in the case of J aggregates where the transition moments are parallel [31]. Our results show that the asymmetry of the band, defined as $E_{\text{top}}/(E_{\text{top}} - E_{\text{bottom}})$, diminishes when θ increases up to 60° but it increases again for $\theta = 90°$. Another important feature in the energy dispersion curves is the existence of a large number of eigenstates lying in a narrow energy domain, as it appears from the almost horizontal rightmost part of the plots obtained for $\theta = 30°$, 45° and 60°. This feature is also related to the existence of long range interactions but it also depends on the chromophore size. As a matter of fact, as the chromophore size increases (i.e. l/d increases) the position of the inflection points moves to lower eigenstates.

When the molecular transitions are doubly degenerate, all the eigenstates are also doubly degenerate, which gives a step-like aspect to the energy dispersion curves (Fig. 2b). In this case, in spite of the fact that long range interactions are considered, all the curves cross at a common point at the middle of the band, for all l/d values. However, they are still asymmetric and a larger density of states is found at the lower part of the exciton band. As expected, the helical angle θ has only a small effect on the dispersion curves. This happens because, in the case of degenerate transitions, there are four interactions for each molecular pair; when the angle θ changes, two of them decrease while the other two increase, compensating each other.

According to whether the molecular transitions are degenerate or not, the index of the eigenstate bearing the maximum oscillator strength k_{fmax} shows a different pattern as a function of the helical angle. In the former case, the oscillator strength is concentrated on very few eigenstates located on the upper part of the exciton band and its maximum corresponds always to the upper eigenstate. For non-degenerate transitions, a more complex picture appears (Fig. 3). Upon increasing the angle θ up to a certain value θ_0, the maximum oscillator strength is born by continually lower eigenstates. Then, the opposite trend is observed. Finally, at 90°, k_{fmax} coincides again with the upper eigenstate. The magnitude of this variation depends on the size of the chromophores: the smaller

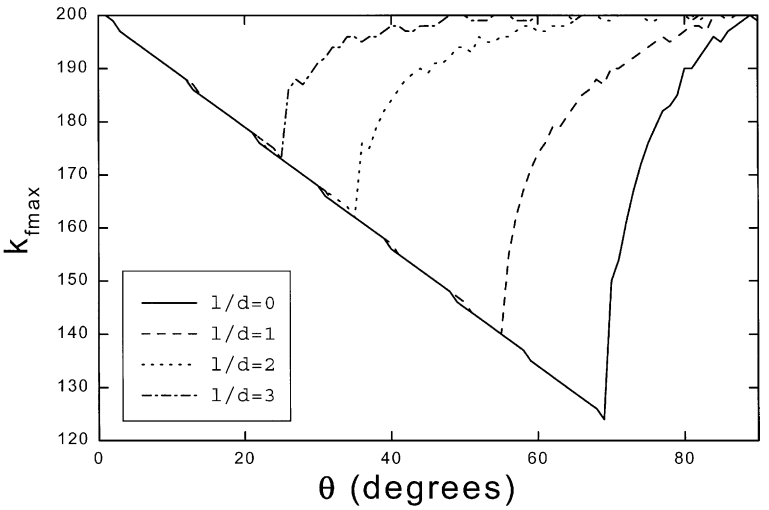

Fig. 3. Columnar helical aggregates with single non-degenerate molecular transitions: index of the eigenstate bearing the highest oscillator strength (k_{fmax}) as a function of the helical angle θ for different l/d values. For degenerate transitions the highest oscillator strength is always born by the upper eigenstate.

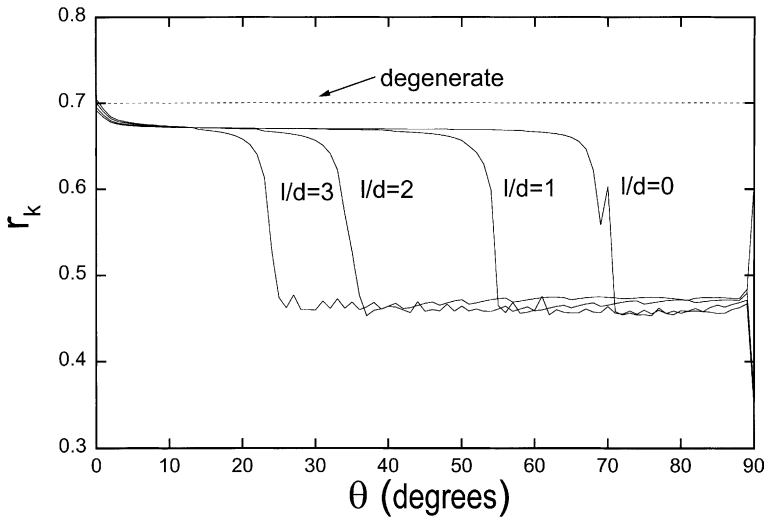

Fig. 4. Normalised participation ratio r_k of the eigenstate bearing the maximum oscillator strength as a function of the helical angle obtained for columnar helical aggregates with single non-degenerate molecular transitions (—) or doubly degenerate transitions (- - -).

the l/d value, the lower the θ_0 value. For $l = 0$ (i.e. point dipole approximation), the k_{fmax} state is rather close to the middle eigenstate.

Another interesting quantity to examine is the participation ratio of the eigenstate bearing the maximum oscillator strength because this state can be reached directly by light absorption. We can see in Fig. 4 that when the molecular transitions are degenerate, for any value of the helical angle θ, the normalised participation ratio of k_{fmax} is always high and equal to 0.7. For single non-degenerate transitions, the normalised participation ratio of k_{fmax} as a function of the helical angle shows the following behaviour. For $\theta = 0°$, it is equal to 0.7 and it decreases slightly reaching very rapidly a plateau at the value of 0.68. Then, following an abrupt transition, a second plateau at 0.48 is observed. The two plateaux values do not depend on the chromophore size. In contrast, the chromophore size does affect the angle at which the abrupt transition between the two appears; as l/d increases this transition appears at smaller angles. If we compare Figs. 3 and 4, we remark that both the index of the eigenstate bearing the maximum oscillator strength and its participation ratio show a change in their behaviour at the same angle θ_0. This happens because the profile of the wave function of k_{fmax} undergoes a drastic modification at θ_0. For helical angles smaller than θ_0 the wave functions are roughly represented by a sinusoidal curve of constant amplitude, whereas for $\theta > \theta_0$ large variations in the amplitude are observed.

Next, we compare the spectra of helical aggregates calculated for non-degenerate and degenerate transitions (Fig. 5). All spectra consist of one main peak which is quite structureless and a tail situated at the red part of the spectrum. This tail is related to the existence of lower energy eigenstates bearing a non-zero oscillator strength. For non-degenerate transitions, upon increasing θ, the main peak is red-shifted and its intensity decreases slightly. The absorption maximum corresponding to $\theta = 0°$ (parallel transition dipoles) is located at 9000 cm^{-1}, whereas when the consecutive transition dipoles in a column are perpendicular to each other ($\theta = 90°$) it appears at energies lower than 2000 cm^{-1}. The spectra obtained for degenerate transitions are less sensitive to the variation of the angle.

The above trends are illustrated in a more systematic way in Fig. 6, where we have plotted the absorption maximum (E_{max}) as a function of the helical angle θ. For non-degenerate transitions a variation of θ from 0° to 90° induces a decrease of E_{max} by 7000 cm^{-1}. In contrast, fluctuations smaller by more than one order of magnitude

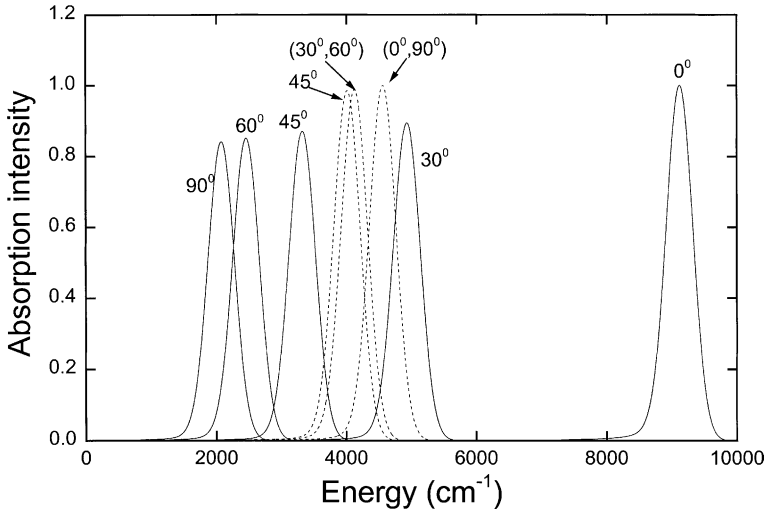

Fig. 5. Absorption spectra of helical columnar aggregates calculated for various helical angles for single non-degenerate (—) and doubly degenerate (···) transitions; $l/d = 2$. Origin energy: $E_0 = 30000$ cm^{-1}.

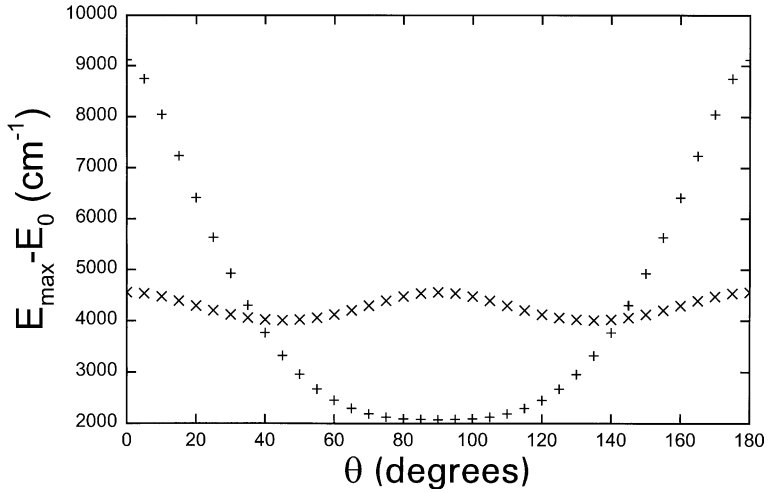

Fig. 6. Absorption maxima ($E_{max} - E_0$) of helical columnar aggregates as a function of θ, for single non-degenerate (+) and doubly degenerate (×) molecular transitions; $l/d = 2$.

(~400 cm^{-1}) are found for degenerate transitions. In the latter case, the E_{max} has a minimum value at $\theta = 45°$. The difference in symmetry observed in the two curves is understandable since doubly degenerate dipolar transitions present a C_4 symmetry axis, while non-degenerate ones are characterised by a C_2 symmetry axis.

The plots in Fig. 6 were calculated using an l/d value equal to 2. Quite similar patterns are reproduced for other l/d values but the magnitude of fluctuations observed as a function of θ decreases with increasing l/d. For example, the E_{max} variation corresponding to a single non-degenerate transition is 22 500 cm^{-1} when $l/d = 0$, but it is only 4500 cm^{-1} when $l/d = 3$. This is understandable because as the chromophores become larger while their transition moments remain constant, the coupling decreases. For example, when

the transition moment is 10 D and $\theta = 0$, the dipolar interaction between nearest neighbours is 10 800, 6300, 3000 and 1600 cm^{-1}, respectively for l/d equal to 0, 1, 2 and 3.

The variation of the total oscillator strength, i.e. the sum of the oscillator strengths $\sum f_k$ corresponding to the transitions towards all the eigenstates k of a given aggregate, with the helical angle exhibits the same pattern as that shown in Fig. 6. Such a similarity can be demonstrated analytically with the nearest neighbour approximation, [1] but it is not so straightforward for the systems studied here. It is worth noticing that such a change of the total oscillator strength was invoked to explain the hypochromism (decrease in the absorption intensity) observed upon pairing two DNA single strands and formation of a double helix [32].

4.2. Disordered aggregates

In Fig. 7 we compare the absorption spectra of disordered columnar aggregates obtained for chromophores characterised by a single dipolar transition with those having two orthogonal transitions differing in energy by ΔE. We observe that non-degenerate transitions yield extremely broad spectra, with noticeable structure. Such a spectrum width is derived from the fact that, when the angles are random, there are many different configurations of the transition dipoles sampled, and each configuration has its own characteristic energies. The combination of all these energies results in a broad spectrum. We also remark a smaller peak at E_0 which corresponds to eigenstates localised on single chromophores.

The spectrum width found for disordered aggregates with degenerate transitions ($\Delta E = 0$) is five times smaller (500 cm^{-1} instead of 2500 cm^{-1}) and quite similar to that found for the corresponding helical aggregates. If the difference in energy of the two components of the initially degenerate transition increases, the spectra of disordered aggregates shift to higher energies, and also they become broader and less intense. At the same time the tail at the red side of the spectrum becomes more and more pronounced and a weak intensity band appears at negative energy values. We remark that even when the energy difference equals $4V_{\|}$, which is roughly the exciton bandwidth, the eigenstates are still built on both molecular transitions. We stress that when only nearest interactions are acting, two independent exciton bands appear for $\Delta E = 4V_{\|}$.

In Fig. 8 we plot the average values over 500 configurations of the normalised participation ratio $\langle r_k \rangle$ determined for all the eigenstates of disordered aggregates. In the case of single non-degenerate molecular transitions, all the exciton states have a participation ratio close to zero. This means that all the eigenstates are localised on a small number of molecules only. For chromophores presenting doubly degenerate transitions, a non-uniform behaviour is observed. Eigenstates located at the upper half of the exciton band remain largely delocalised in spite of the disorder, whereas those located on the lower part become gradually localised. It is worth noticing that the most delocalised eigenstate is not the one bearing the maximum oscillator strength which is located at the top of the band. Such a profile of the participation ratio will affect energy transport via intraband scattering in columnar aggregates [33]. Although the photon energy is initially distributed over a certain number of molecules, it will be rapidly spread over a much longer distance since the system will relax going through eigenstates with larger participation ratio.

When the energy difference between the two components of the initially degenerate transition increases, although the profile of $\langle r_k \rangle$ as a function of the eigenstate index remains similar, all eigenstates have continuously lower $\langle r_k \rangle$ values (Fig. 8). For those systems, although the maximum value of the oscillator strength is born by an eigenstate at the top of the exciton band, the total oscillator strength is distributed over a large number of other

[1] This is understandable because the total oscillator strength is obtained by summing over all the eigenstates the squared transition moments multiplied by the corresponding eigenenergy. As the oscillator strength mainly arises from eigenstates located at a spectral region around E_{max}, which is small compared to the energy of the exciton, $\sum f_k$ can be approximated by a constant multiplied by E_{max}.

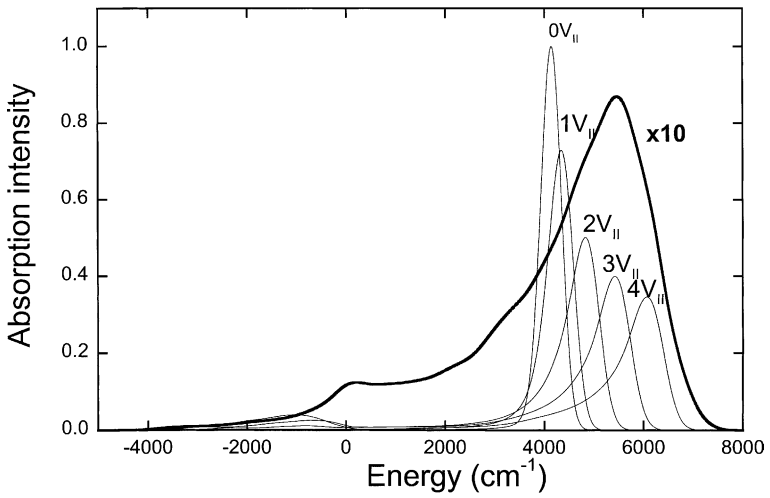

Fig. 7. Absorption spectra of disordered columnar aggregates obtained for chromophores characterised by a single dipolar transition (thick line) or two orthogonal transitions (thin lines) with energy difference ΔE expressed in $V_{\parallel}$ units. $V_{\parallel}$ is the coupling between two parallel transition moments of neighbouring chromophores; $l/d = 2$ and $V_{\parallel} = 1500\ \mathrm{cm}^{-1}$. Origin energy: $E_0 = 30000\ \mathrm{cm}^{-1}$.

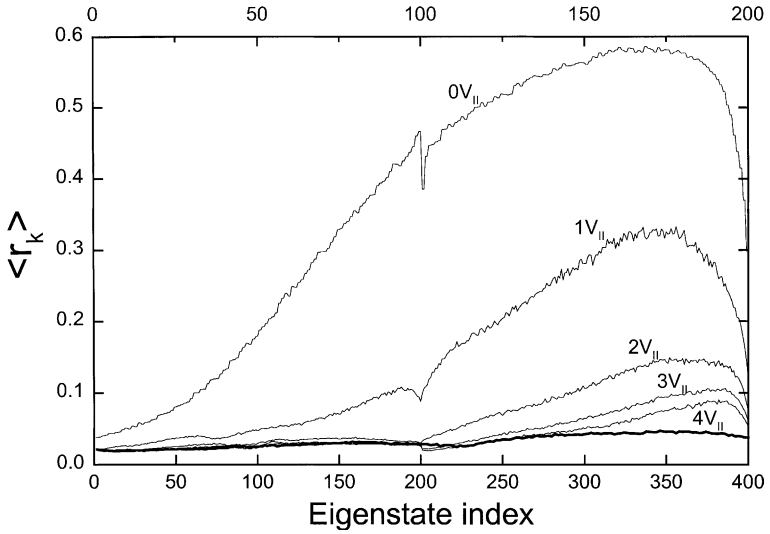

Fig. 8. Average values over 500 configurations of the normalised participation ratio $\langle r_k \rangle$ obtained for the eigenstates of disordered columnar aggregates for chromophores characterised by a single dipolar transition (thick line, 200 eigenstates) or two orthogonal transitions (thin lines, 400 eigenstates) with energy difference ΔE. $V_{\parallel}$ is the coupling between two parallel transition moments of neighbouring chromophores.

eigenstates, as shown by the increasing width of the absorption spectra. Therefore, the degree of delocalisation of the eigenstates formed directly by photon absorption is better illustrated by considering the effective number of molecules coupled to the radiation $N_{\mathrm{eff}} = \sum N_k f_k / \sum f_k$. Upon increasing ΔE, we observe a narrowing in the dispersion of the N_{eff} values which become smaller (Fig. 9).

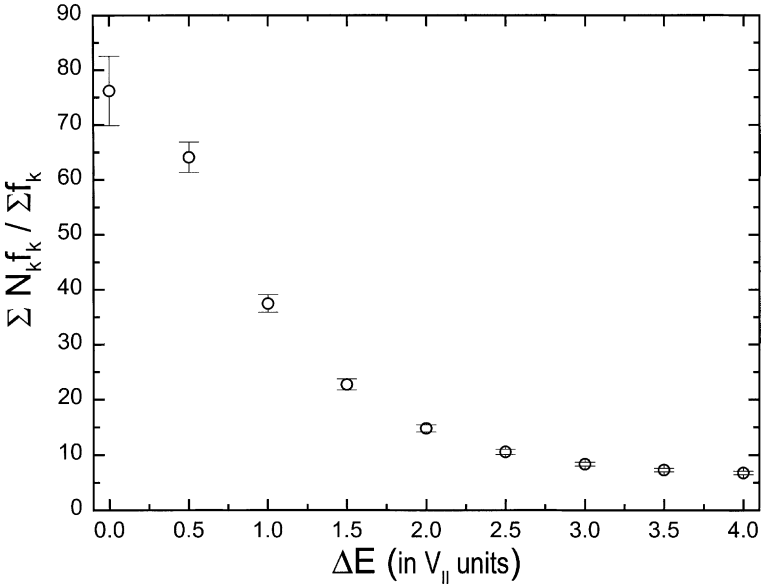

Fig. 9. Effective number of molecules coupled with the radiation $N_{\text{eff}} = \sum N_k f_k / \sum f_k$ obtained for disordered columnar aggregates with chromophores characterised by two orthogonal transitions with energy difference ΔE. $V_{\|}$ is the coupling between two parallel transition moments of neighbouring chromophores. Average values over 500 configurations with $l/d = 2$ and $V_{\|} = 1500$ cm^{-1}.

We stress that, although the participation ratio of $k_{\max}$ depends on the l/d value (circles in Fig. 8), N_{eff} is not affected by the chromophore size.

5. Conclusions

The main conclusions of our numerical calculations are summarised as follows. With the present simulation model we found that Frenkel excitons in columnar phases can be well approximated by excitons in single columnar aggregates with an accuracy of 200 cm^{-1}.

As expected, the absorption spectra of columnar aggregates composed of chromophores with a doubly degenerate transition are only weakly affected by rotation of the molecular disks around the column axis. In contrast, large variations are observed in the case of chromophores with a single dipolar transition and the magnitude of those variations increases upon decreasing the chromophore size.

For helical aggregates with doubly degenerate molecular transitions, the maximum oscillator strength is always born by the upper eigenstate and its extent does not depend on the chromophore size. For single non-degenerate molecular transitions the properties of the eigenstate bearing the maximum oscillator strength are different according to whether the helical angle is larger or smaller than a limiting value determined by the chromophore size.

All the eigenstates of disordered aggregates with a single dipolar transitions per chromophore are, on the average, localised on very few molecules. For doubly degenerate transitions, the eigenstate bearing the maximum oscillator strength is, on the average, quite extended; as the system evolves to lower eigenstates via intraband scattering, the excitation energy can be spread over longer distances.

When the energy difference between the initially doubly degenerate molecular transitions increases, the absorption maxima of disordered aggregates are shifted to higher energies. For an energy difference as large as four times the maximum value of dipolar coupling, the two molecular transitions are still coupled within the same exciton band.

Finally, we illustrated the degree of delocalisation by the effective number of molecules coupled to the radiation and we have found that this number does not depend on the chromophore size.

The model used in our calculations has been compared successfully with experimental data in the specific case of triphenylene columnar phases for which a quantitative agreement between simulated and experimental absorption spectra was found [27]. The conclusions drawn in the present work could provide a guideline to experimentalists working with these molecular materials and inspire new experiments. For example, a comparison of the excitation transfer efficiency for chromophores characterised by single and doubly degenerate electronic transitions seems quite appealing. Moreover, they could suggest the appropriate design of new discotic chromophores aiming to minimise the perturbation of the photophysical properties by the orientational disorder.

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References

[1] S. Chandrasekhar, G.S. Ranganath, Rep. Prog. Phys. 53 (1990) 57.
[2] D. Markovitsi, F. Rigaut, M. Mouallem, J. Malthête, Chem. Phys. Lett. 135 (1987) 236.
[3] B. Blanzat, C. Bartou, N. Tercier, J.J. Andrée, J. Simon, J. Am. Chem. Soc. 109 (1987) 6193.
[4] G. Blasse, G.J. Dirksen, A. Meijerink, J.F. Van der Pol, E. Neelman, W. Drenth, Chem. Phys. Lett. 154 (1989) 420.
[5] B.A. Gregg, M.A. Fox, A.J. Bard, J. Phys. Chem. 93 (1989) 4227.
[6] D. Markovitsi, I. Lécuyer, J. Simon, J. Phys. Chem. 95 (1991) 3620.
[7] D. Markovitsi, A. Germain, P. Millié, P. Lécuyer, L. Gallos, P. Argyrakis, H. Bengs, H. Ringsdorf, J. Phys. Chem. 99 (1995) 1005.
[8] D. Markovitsi, S. Marguet, L.K. Gallos, H. Sigal, P. Argyrakis, H. Ringsdorf, S. Kumar, Chem. Phys. Lett. 306 (1999) 163.
[9] D. Markovitsi, S. Marguet, J. Bondkowski, S. Kumar, J. Phys. Chem. B 105 (2001) 1299.
[10] N. Boden, R.J. Bushby, J. Clements, J. Chem. Phys. 98 (1993) 5920.
[11] J. Warman, P.G. Schouten, J. Phys. Chem. 99 (1995) 17181.
[12] D. Adam, P. Schumacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, D. Haarer, Nature 371 (1994) 141.
[13] T. Christ, B. Glüsen, A. Greiner, A. Kettner, V. Stümpflen, V. Tsukruk, J. Wendorff, Adv. Mat. 9 (1997) 48.
[14] E. Fontes, P.A. Heiney, W.H. de Jeu, Phys. Rev. Lett. 61 (1988) 1202.
[15] A.M. Levelut, J. Chim. Phys. 80 (1983) 149.
[16] R.Y. Dong, D. Goldfarb, M.E. Moseley, Z. Luz, H. Zimmermann, J. Chem. Phys. 88 (1984) 3148.
[17] J. Frenkel, Phys. Rev. 37 (1931) 1276.
[18] A.S. Davydov, Theory of Molecular Excitons, Plenum Press, New York, 1971.
[19] E.I. Rashba, M.D. Sturge, Excitons, North-Holland, Amsterdam, 1982.
[20] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, Pramana 9 (1977) 471.
[21] A.M. Van der Craats, J.M. Warman, K. Müllen, Y. Geerts, J.D. Brand, Adv. Mater. 10 (1998) 36.
[22] C. Ecoffet, D. Markovitsi, C. Jallabert, H. Strzelecka, M. Veber, Thin Solid Films 282 (1994) 83.
[23] C. Ecoffet, D. Markovitsi, P. Millié, M. Veber, C. Jallabert, H. Strzelecka, J. Chem. Soc., Faraday Trans. 89 (1993) 457.
[24] C. Ecoffet, D. Markovitsi, P. Millié, J.P. Lemaistre, Chem. Phys. 177 (1993) 629.
[25] I. Levitsky, K. Kishikawa, S.H. Eichhorn, T.M. Swager, J. Am. Chem. Soc. 122 (2000) 2474.
[26] L. Oddos-Marcel, F. Madeore, A. Bock, D. Neher, A. Ferencz, H. Rengel, G. Wegner, C. Kryschi, H.P. Trommsdorff, J. Phys. Chem. 100 (1996) 11850.
[27] S. Marguet, D. Markovitsi, P. Millié, H. Sigal, S. Kumar, J. Phys. Chem. B 102 (1998) 4697.
[28] V. Czikkleky, H.D. Fösterling, H. Kuhn, Chem. Phys. Lett. 6 (1970) 207.
[29] P. Dean, Rev. Mod. Phys. 44 (1972) 127.
[30] M. Schreiber, Y. Toyozawa, J. Phys. Soc. Jpn. 51 (1982) 1537.
[31] H. Fidder, J. Knoester, D.A. Wiersma, J. Chem. Phys. 95 (1991) 7880.
[32] I. Tinoco Jr., R.W. Woody, D.F. Bradley, J. Chem. Phys. 38 (1963) 1317.
[33] J.P. Lemaistre, Chem. Phys. 246 (1999) 283.