



EFFECT OF DEGENERACY ON FRENKEL EXCITONS IN ORDERED AND ORIENTATIONALLY DISORDERED COLUMNAR AGGREGATES

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The effect of the degeneracy of the molecular dipolar transitions on the properties (dispersion curves, oscillator strengths, absorption spectra) of Frenkel excitons in ordered helical and orientationally disordered columnar mesophases, characterized by strong interchromophore interactions and short stacking distance, is investigated through a model based on numerical calculations. It is shown that the degeneracy makes the optical spectra less sensitive to chromophore rotation and maintains the excitons carrying the oscillator strength quite delocalised even in the presence of complete orientational disorder.

Keywords: Frenkel excitons; Columnar aggregates; Exciton degeneracy; Disordered mesophases

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1 INTRODUCTION

The aggregates investigated here are columnar liquid crystals exhibiting either an ordered helical arrangement of the molecules around the column axis or a total orientational disorder when the molecules are freely rotating [1]. According to the symmetry of the chromophores, the dipolar electronic transitions may be either non degenerate or characterised by two orthogonal transitions close in energy. Degeneracy and/or orientational disorder will strongly influence the properties of the Frenkel excitons and the corresponding absorption lineshapes in these columnar phases. In this short communication, an analysis of the Frenkel excitons, based on numerical calculations, is provided and used to calculate the absorption lineshapes in the case of degenerate and non degenerate transitions for an ordered helical aggregate as well as for a fully orientationally disordered (configurationally averaged) structure.

2 FRENKEL EXCITON STATES

We model a columnar aggregate as a linear chain of $N=200$ identical chromophores. The excited states are described as an ensemble of two-level systems (ground and excited state) in the framework of the Frenkel exciton theory. The intermolecular interactions are calculated according to the extended dipole approximation. A doubly degenerate transition is represented by two perpendicular to each other extended dipoles, centred on the column axis. The diagonalisation of the Hamiltonian, H_0 , written in the localised site representation is (i for the site, s for the degeneracy) gives the N eigenstates (or $2N$ in the case of two transitions per chromophore)

$$H_0 = \sum_k E_k |k\rangle \langle k|; |k\rangle = \sum_{i,s} C_{is}^k |is\rangle. \quad (1)$$

The transition moments and oscillator strengths associated with the various eigenstates are

$$\vec{\mu}_k = \sum_{is} C_{is}^k \vec{\mu}_{is}; f_k \propto |\mu_k|^2. \quad (2)$$

The localisation/delocalisation behaviour of these eigenstates are analysed by means of the inverse participation ratios defined as

$$L_k = \sum_{i=1}^N \left[|C_{ix}^k|^2 + |C_{iy}^k|^2 \right]^2, \quad (3)$$

the number of coherently coupled molecules within a given eigenstate being $N_k = 1/L_k$.

In such an analysis, another quantity of interest is the effective number of molecules coupled to the radiation field and that we defined as

$$N_{\text{eff}} = \frac{\sum_k N_k f_k}{\sum_k f_k}. \quad (4)$$

The parameters used in this model are taken from experimental data performed on hexasubstituted triphenylene mesophases [2].

3 ORDERED HELICAL AGGREGATES

From the calculation of the exciton dispersion curves (Eq. (1)), as a function of the helical angle θ , for non degenerate and doubly degenerate transitions, it is shown that the exciton bandwidth is considerably reduced in the degenerate case. It means, in this case, that θ does not influence the position of the absorption peak. Furthermore, from the analysis of the eigenstates oscillator strengths (Eq. (2)) and the inverse participation ratios (Eq. (3)), the oscillator strength is concentrated on very few states located on the upper part of the exciton band. We compare in Figure 1 the calculated absorption spectra in both cases.

4 DISORDERED AGGREGATES

In the case of a random distribution of orientations of the chromophores along the chain, the calculated absorption spectra behave differently for degenerate and non degenerate transitions as depicted in Figure 2. For non degenerate transitions, many configurations of the transition dipoles are sampled, each one having its own energy and oscillator strength, leading, after configuration averaging, to a broad spectrum. The spectrum width obtained for degenerate transitions ($\Delta E = 0$ in Fig. 2) is 5 times smaller. Since, as previously noted, the oscillator strength is mainly born by the

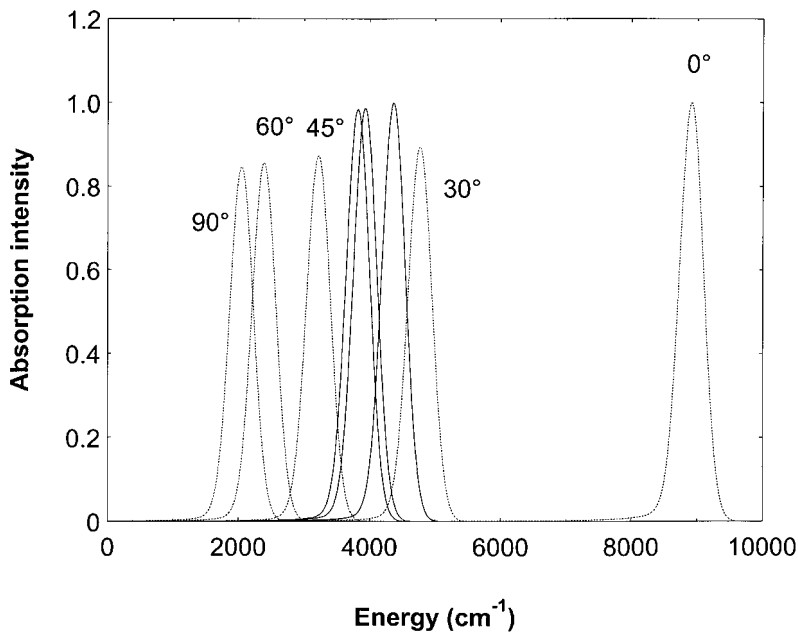


FIGURE 1 Absorption spectra of helical columnar aggregates calculated for various helical angles for single non-degenerate transitions (dotted lines). For doubly degenerate transitions (full lines); the three curves correspond to the following angles (from right to left): $(0, 90^\circ)$; $(30^\circ, 60^\circ)$; 45° .

upper levels of the exciton band, the absorption spectrum is restricted to few eigenstates. When increasing the energy difference between the two components of an initially degenerate transition, the total oscillator strength is distributed over a much larger number of eigenstates thus leading to a broadening of the spectra as it can be seen in Figure 2. This means that the initially extended excitons ($\Delta E = 0$) become more and more localised. An illustration of this effect is given in Figure 3 through the calculation (Eq. (4)) of the effective number of molecules coupled to the radiation field as a function of Δ .

5 CONCLUSIONS

With our simulation model, we have shown that the absorption spectra of columnar aggregates composed of chromophores exhibiting a doubly

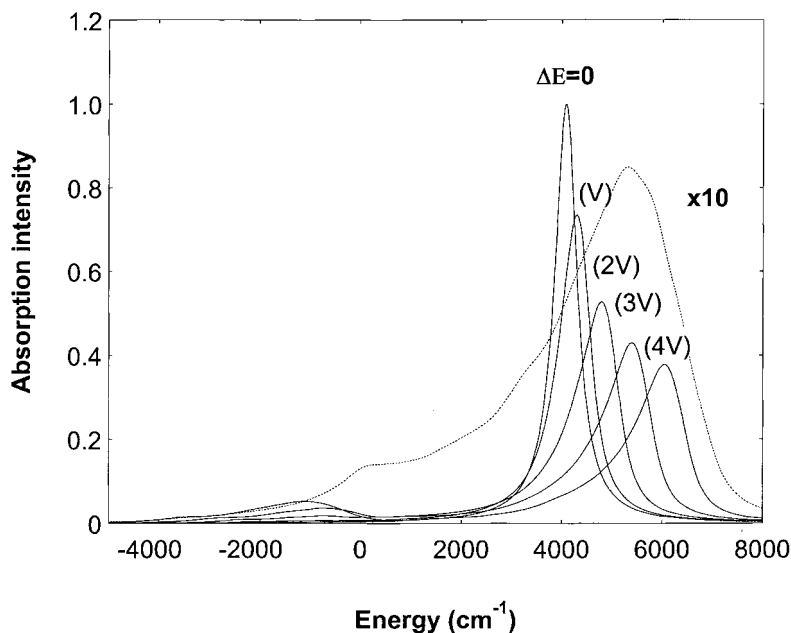


FIGURE 2 Absorption spectra of disordered columnar aggregates (average of 500 configurations) obtained for chromophores characterised by a single dipolar transition (dotted line) or two orthogonal transitions (full lines) with energy difference ΔE expressed in V units. V is the coupling between two parallel transition moments of neighbouring molecules.

degenerate transition are weakly affected by the rotation of the molecular disks around the column axis. Furthermore, we have shown that, for helical aggregates, the maximum of the oscillator strength is always born by the upper eigenstate for doubly degenerate transitions while it depends on the helical angle for singly non degenerate transitions. For disordered aggregates and doubly degenerate transitions the eigenstates are, in average, extended since the eigenstates carrying the maximum of the oscillator strength does not depend on the helical angle while for the non degenerate case, they are localised on very few molecules. This is also illustrated by the dependence of the effective number of molecules coupled with the radiation as a function of the energy separation between the two orthogonal chromophore transitions. This model was compared to experimental data available on triphenylene columnar phases.

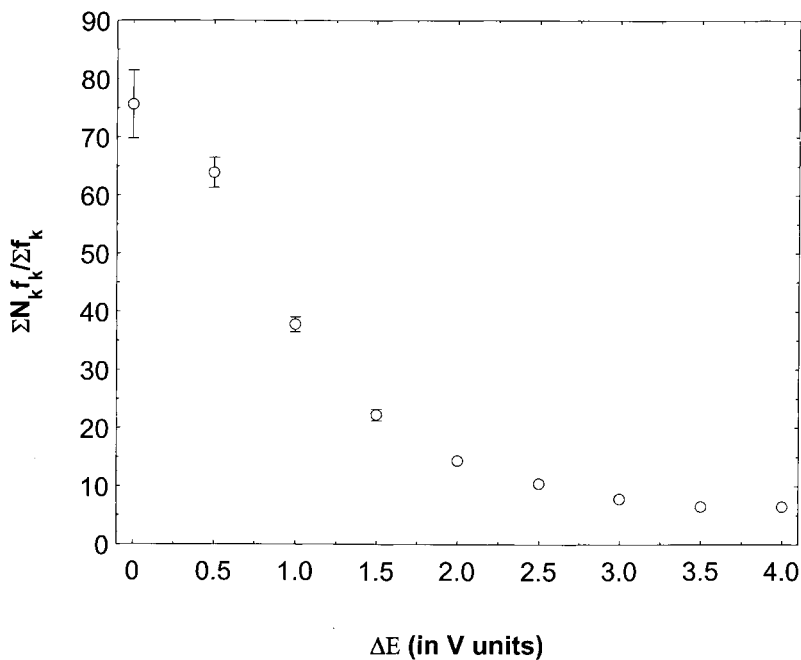


FIGURE 3 Effective number of molecules coupled to the radiation obtained for disordered columnar aggregates with chromophores characterised by two orthogonal transitions with energy difference ΔE expressed in units of V .

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