



Disorder, intraband relaxation and dephasing of Frenkel excitons in molecular aggregates

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Abstract

A theoretical model, based on numerical simulations, is provided to analyze the properties of Frenkel excitons of strongly coupled aggregates such as columnar phases of liquid crystals or linear chains of J-aggregates. The effects of the degeneracy of the molecular transitions and of the orientational disorder in columnar phases on the delocalization behaviour and on the optical lineshapes of excitons are investigated. Considering the dynamic disorder in J-aggregate, it is shown that the intraband scattering and dephasing processes contribute, with increasing temperature, to the decrease of the number of coherently coupled molecules and to the lengthening of the exciton fluorescence lifetime.

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Many experimental and theoretical studies are currently investigated to analyze the exciton dynamics in molecular aggregates like columnar mesophases [1–3] or J-aggregates [4–10]. Columnar aggregates can be represented as ensembles of finite linear chains of parallel molecules. For some of them, the molecules exhibit a helical arrangement of their transition dipoles in a well-ordered structure or they can rotate freely around the column axis resulting in an orientational disorder.

Furthermore, for an ordered or disordered configuration, the electronic transition of the monomer can be nondegenerate or degenerate according to the symmetry of the molecule. J-aggregates can also be described as ensembles of finite linear chains of strongly coupled parallel molecules. Contrary to the columnar phases for which the upper states of the quasiexciton band carry the maximum of the oscillator strength (H-aggregates), the electronic intermolecular interaction is negative. This means that in J-aggregates, the optically allowed state is located at the bottom of the quasiexciton band.

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A general formalism, based on the Frenkel exciton theory, is presented to analyze the properties of the eigenstates of such systems. The dynamic disorder induced by the stochastic coupling of excitons to the phonons creates an intraband scattering (incoherent energy transfer) among the states of the quasiexciton band. The scattering rates are calculated and used in a master equation to get the time evolution of the exciton populations and the luminescence lineshapes.

At high temperatures, the dephasing of the exciton states by the molecular vibrations (homogeneous broadening) is assumed to become the dominant mechanism. Increasing the temperature destroys the phase coherence among the sites and correspondingly decreases the number of coherently coupled molecules. At low temperature, the homogeneous width arises from the pure dephasing mechanism involving a low-frequency phonon mode with an energy close to the energy separation of the two lowest exciton states. At higher temperature, we suggest that the dephasing originates from the coupling of excitons to a vibrational mode [10].

Let us consider a linear chain of N identical two-level molecules. In the localized site representation the electronic Hamiltonian is written as

$$H_0 = \sum_i E_i |i\rangle \langle i| + \sum_{ij} V_{ij} |i\rangle \langle j|. \quad (1)$$

The E_i are the molecular site excitation energies and the V_{ij} describe the electronic interactions among the sites expressed in the simplest approach of the point dipole model as

$$V_{ij} = V_0 / |i - j|^3. \quad (2)$$

V_0 denotes the nearest neighbor interaction and $|i - j|$ is the distance between molecules i and j with a unity lattice spacing. In the delocalized representation of the Hamiltonian

$$H_0 = \sum_k E_k |k\rangle \langle k|. \quad (3)$$

$|k\rangle$ denotes the N eigenstates with energies E_k and eigenvectors $|k\rangle = \sum_i C_i^k |i\rangle$.

The transition moments, oscillator strengths and inverse participation ratios of the exciton

eigenstates are respectively given by

$$\begin{aligned} \mu_k &= \sum_i C_i^k \mu_i, \quad F_k \propto E_k |\mu_k|^2 \text{ and} \\ L_k &= \sum_i |C_i^k|^4. \end{aligned} \quad (4)$$

In columnar aggregates, the photophysical properties are greatly influenced by the geometry (helical structure or orientational disorder) and by the degeneracy [3]. In the case of two orthogonal transitions per chromophore the matrix elements of the dipolar interactions are easily calculated [3].

The simulations are performed by considering first a helical ordered column of $N=200$ molecules with a stacking distance $d=0.36$ nm and a dipole moment $\mu=10$ D. From the calculation of the eigenstates, it is shown that, for nondegenerate transitions, the exciton energy dispersion strongly depends on the helical angle θ . For doubly degenerate states, the exciton bandwidth slightly depends on θ and is considerably reduced compared to that of the nondegenerate case. This means that the angle θ between the dipole moments of nearest neighbor molecules does not influence the position of the absorption peak. The normalized participation ratio of the eigenstate bearing the maximum of the oscillator strength is given, for a doubly degenerate transition, by [3]

$$r_k = 1/N L_k = \sum_i \left| C_{ix}^k \right|^2 + \left| C_{iy}^k \right|^2, \quad (5)$$

and depicted in Fig. 1 as a function of the angle θ . It is shown that for doubly degenerate transitions, r_k is always born by the upper eigenstate with a constant value equals to 0.7. In the case of nondegenerate transitions, r_k depends on the helical angle and also on the dipole length used in the extended dipole calculation.

In the case of random distribution of orientations of the molecules along the column, the calculated absorption spectra, depicted in Fig. 2 behave differently for degenerate and non-degenerate dipolar transitions. The simulation of the absorption spectra of orientationally disordered aggregates is performed by averaging many configurations of the transitions dipoles. For non-degenerate transitions the absorption exhibits the density of states of a linear chain. For doubly

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