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Exciton dephasing and thermal line broadening in molecular aggregates

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Abstract

Using a model of Frenkel excitons coupled to a bath of acoustic phonons in the host medium, we study the temperature dependence of the dephasing rates and homogeneous line width in linear molecular aggregates. The model includes localization by disorder and predicts a power-law thermal scaling of the effective homogeneous line width. The theory gives excellent agreement with temperature dependent absorption and hole-burning experiments on aggregates of the dye pseudoisocyanine.

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1. Introduction

Molecular *J* aggregates have fascinating optical properties caused by the Frenkel exciton states arising from the strong excitation transfer interactions in these systems. At low temperature, these states give rise to narrow absorption lines (exchange narrowing) [1] and ultra-fast collective spontaneous emission (exciton superradiance) [2]. The temperature dependence of the optical observables of molecular aggregates shows many interesting features as well, and often differs strongly from those of single molecules. For example, the fluorescence lifetime typically increases with growing temperature [2–4], while the fluorescence Stokes shift may exhibit an anomalous (non monotonous) temperature dependence by showing a growth at low temperatures [5,6]. Although the basic physics of these behaviors is often well-understood, a consistent quantitative explanation is mostly missing, due to the fact that the optical dynamics in these systems results from

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the complicated interplay between scattering of the excitons on disorder (localization) as well as vibrations (dephasing). This also holds for the explanation of the experimentally observed thermal growth of the absorption line width and the homogeneous line width as measured in photon echo and hole burning experiments. Several authors have interpreted their measurements of this broadening as an activated process caused by scattering on optical vibrations of the aggregate [3,7,8], while others concluded a powerlaw thermal broadening, possibly arising from excitons scattering on vibrations in the host medium [9]. To add to the uncertainty, the surmised dephasing mechanisms have not been correlated with the temperature dependence of the fluorescence properties.

In this paper, we model the temperature dependent dephasing rates of excitons in linear chains and use the results to analyze the absorption line width and hole width as a function of temperature. Our model includes scattering of the excitons on static disorder as well as on acoustic vibrations in the host medium. The results reveal a good agreement with experiments on aggregates of the dye pseudoisocyanine (PIC). We also comment on the successful application of the model to the fluorescence properties of these aggregates.

The outline of this paper is as follows. In Section 2, we describe the model. The calculation of the scattering rates and dephasing rates are addressed in Section 3, where also the calculation of the absorption spectrum and the hole burning spectra are discussed. In Section 4, we present and discuss our numerical results, while in Section 5 we conclude.

2. Model

Our model consists of a linear Frenkel chain of N two-level molecules ($n = 1, \ldots, N$) with parallel transition dipoles. The Hamiltonian of this system reads

$$H = \sum_{n=1}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{n,m=1}^{N} J_{nm} |n\rangle\langle m|, \tag{1}$$

where $|n\rangle$ denotes the state in which molecule n is excited and all others are in their ground state. The ε_n are the transition energies of the individual chromophores, while the $J_{nm} = -J/|n-m|^3$ denote the intermolecular excitation transfer interactions mediated by the transition dipoles ($J > 0$ is the interaction between nearest neighbors). We account for disorder in the molecular energies, caused by random solvents shifts, by taking the ε_n from uncorrelated Gaussian distributions with standard deviation σ and average ε_0. The exciton eigenstates (labeled ν) follow from diagonalizing the $N \times N$ matrix with the ε_n as diagonal elements and the J_{nm} as off-diagonal ones. They have energy E_ν, and site-amplitudes $\varphi_{\nu n}$, i.e., the eigenstates read

$$|\nu\rangle = \sum_{n=1}^{N} \varphi_{\nu n} |n\rangle. \tag{2}$$

The disorder leads to localization of the exciton states on segments of the chain; the optically dominant states, i.e., those with most oscillator strength, occur in the low-energy tail of the density of states (DOS), near the bottom of the disorder-free exciton band.

The model includes onsite scattering of excitons on harmonic vibrations (phonons) in the host medium through the Hamiltonian [10]

$$V = \sum_{n=1}^{N} \sum_{q} V_{nq} |n\rangle\langle n| a_q + \text{h.c.}, \tag{3}$$

where a_q annihilates a phonon of quantum number (wave vector and branch index) q, with energy ω_q (we set $\hbar = 1$). V_{nq} indicates the strength of the linear exciton–phonon coupling. In most J aggregates, in particular for those of the prototypical PIC aggregates, the exciton–phonon interaction is rather weak. This is evident from the narrowness of the absorption line as well as the absence of a clear fluorescence Stokes shift. As a consequence, the exciton–phonon interaction may be accounted for in a perturbative way. This leads to transfer of population from exciton state ν to state μ with a (scattering) rate $W_{\mu\nu}$ that may be obtained from Fermi's Golden Rule. The calculation of these rates is addressed in the next section.