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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

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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

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 v) 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_v, and site-amplitudes φ_{vn}, i.e., the eigenstates read

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

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 v to state μ with a (scattering) rate $W_{\mu v}$ that may be obtained from Fermi's Golden Rule. The calculation of these rates is addressed in the next section.

3. Scattering rates and spectra

Applying Fermi's Golden Rule to the exciton–phonon scattering problem is straightforward. The result becomes particularly simple for a disordered host (appropriate in most experimental situations), in which the V_{nq} are stochastic variables uncorrelated for the various sites n. Referring to Refs. [6,11] for details, we simply quote the result

$$W_{\mu v} = \mathscr{F}(|\omega_{\mu v}|)G(\omega_{\mu v}) \sum_{n=1}^{N} \varphi_{\mu n}^2 \varphi_{v n}^2. \qquad (4)$$

Here, $\omega_{\mu v} = E_\mu - E_v$ and $\mathscr{F}(\omega) = 2\pi \sum_q |V_q|^2 \delta(\omega - \omega_q)$, the one-phonon spectral density (V_q characterizes the coupling of this mode to the excitons). Furthermore, $G(\omega) = n(\omega)$ if $\omega > 0$ and $G(\omega) = 1 + n(-\omega)$ if $\omega < 0$, with $n(\omega) = [\exp(\omega/k_B T) - 1]^{-1}$, the mean thermal occupation number of a phonon mode of energy ω.

The $W_{\mu v}$ may be used to study the intraband relaxation of excitons after photo-excitation by using them to set up a Pauli master equation for the occupation probabilities of the exciton states [6,12]. In addition, however, the $W_{\mu v}$ govern the temperature dependent dephasing of the excitons, and hence their homogeneous line widths. Specifically, the thermal dephasing rate of the vth exciton state is given by $\Gamma_v \equiv \frac{1}{2} \sum_\mu W_{\mu v}$ and depends on temperature through the $n(\omega)$. The temperature behavior of the dephasing rates depends sensitively on the form of the spectral density. Here, we will assume that acoustic phonons in the host medium dominate the scattering process. This leads to $\mathscr{F}(\omega) = W_0(\omega/J)^3$, where the ω^3 scaling derives from the fact that the phonon density of states scales as ω^2 (Debye behavior) and the $|V_q|^2$ scales like ω for acoustic phonons. The remaining factor W_0 is a free parameter in the model, which together with the disorder strength σ, may be used to fit experimental data.

The above dephasing rates determine the absorption width of the individual exciton states. As a consequence, the total absorption spectrum reads

$$A(E) = \frac{1}{N} \left\langle \sum_v \frac{F_v}{\pi} \frac{\Gamma_v + \gamma_v/2}{(E - E_v)^2 + (\Gamma_v + \gamma_v/2)^2} \right\rangle, \qquad (5)$$

where $F_v = (\sum_n \varphi_{vn})^2$ is the dimensionless oscillator strength of the vth exciton state, $\gamma_v = \gamma_0 F_v$ is its radiative rate (γ_0 is the emission rate of a single chromophore), and the angular brackets denote averaging over the static disorder in the ε_n. In the next section we will report on numerical simulations of Eq. (5). In addition, the above dephasing rates may be used to calculate the shape and width of holes in hole burning experiments. To do this, one restricts the summation over v in Eq. (5) to those states that fall within the spectral interval covered by the laser used to burn the hole. We will address examples of this application in Section 4.

4. Results

It is useful to briefly consider the situation in the absence of disorder ($\sigma = 0$) with only nearest-neighbor interactions, where the exciton states can be obtained analytically. The lowest ($v = 1$) state in the band then carries more than 80% of the oscillator strength and it can be shown analytically that its phonon-induced homogeneous width Γ_1 then scales with temperature according to $T^{7/2}$. This power law directly results from the ω^3 dependence of the spectral density and the $\omega^{1/2}$ dependence of the integrated DOS close to the band bottom of one-dimensional systems. Inclusion of long-range dipolar interactions slightly modifies the power law to $T^{3.85}$, as follows from numerical calculations [13].

In the presence of disorder, the dephasing rates of individual exciton states vary considerably from one state to the other [14], due to stochastic fluctuations in the energy differences and wave function overlap summations that feature in Eq. (4). Especially at low temperature, the width of the distribution of these rates may be of the same order as their mean [13]. This makes it hard to identify a typical homogeneous width. Instead, it is more useful to directly simulate experimental observables.

For chains of 250–1000 molecules, we simulated the linear absorption spectrum according to Eq. (5) and extracted from it the full width at half maximum $\Delta(T)$ as a function of temperature. We have found that over an appreciable range of σ

and W_0 values, $\Delta(T)$ follows an almost universal power law given by

$$\Delta(T) = \Delta(0) + aW_0(k_B T/J)^p, \qquad (6)$$

where a and p depend only weakly on the parameters σ and W_0. As an example, Fig. 1 displays the calculated $\Delta(T)$ values (symbols) for two sets of parameters, together with the power-law fits. The (fit) parameters are given in the caption. More generally, we have found that for $0.05J < \sigma < 0.5J$, $p = 4.2 \pm 0.2$, while $a = 1.2 \pm 0.1$. The scaling Eq. (6) implies that the total width may be interpreted as the sum of an inhomogeneous width $\Delta(0)$ and a dynamic contribution. We note that the power p lies rather close to the value of 3.85 obtained in the absence of disorder. The reason is that the states to which most of the population is scattered lie higher in the exciton band, where the DOS is not affected much by disorder.

Interestingly, Renge and Wild [9] found that the total J-bandwidth $\Delta(T)$ of aggregates of PIC, with counter ions chloride as well as fluoride, over a wide temperature range (from 10 to 300 K) follows a power-law scaling as in Eq. (6). Although the power reported by these authors ($p = 3.4$) is smaller than the ones we obtained above, from direct comparison to the experimental data we have found that our model yields excellent fits to the experimental data over the entire temperature range, both for the shape and the width of the J-band. This also holds for the J-bandwidth of PIC-Br (bromide), measured between 1.5 and 180 K [3]. Details will be published elsewhere [15].

We have also calculated hole-burning spectra, according to the method described at the end of Section 3. We present here a fit to the results reported by Hirschmann and Friedrich [7]. Using the hole-burning technique, they measured the homogeneous width of the exciton states in the center of the J-band for PIC-I (iodide) over the temperature range 350 mK–80 K. Their data for the holewidth Γ are reproduced as triangles in Fig. 2. The solid line shows our fit to these data, obtained by simulating disordered chains of $N = 250$ molecules. The resonant interaction strength and the monomer radiative rate were chosen at the accepted values of $J = 600\,\text{cm}^{-1}$ and $\gamma_0 = 1.5 \times 10^{-5}J = 2.7 \times 10^8\,\text{s}^{-1}$, respectively. Thus, the only free parameters were the disorder strength σ and scattering strength W_0. First, we fixed the value of σ by fitting the low-temperature (4 K) absorption spectrum, where the homogeneous broadening may be neglected. This yielded $\sigma = 0.21J$. Next, W_0 was adjusted such that the measured growth of the hole width was reproduced in an optimal way. Thus, we found $W_0 = 180J$.

We observe from Fig. 2 that our model yields a good fit to the measurements. We have also tried
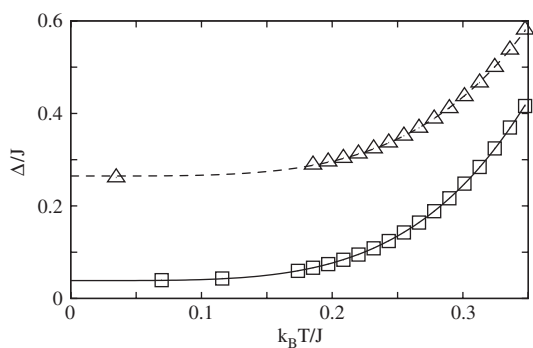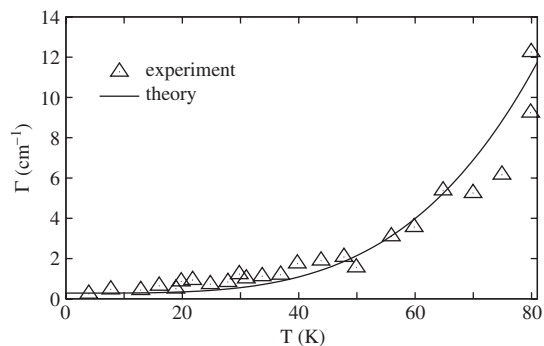

Fig. 1. Calculated temperature dependence of the width of the absorption spectrum (symbols) and corresponding fits to Eq. (6) (lines) for two values of the disorder strength: $\sigma = 0.1J$ (solid) and $\sigma = 0.4J$ (dashed). The fit parameters (a, p) take the values $(1.2, 4.2)$ and $(1.2, 4.3)$, respectively. $W_0 = 25J$ and $\gamma_0 = 1.5 \times 10^{-5}J$.

Fig. 2. Hole width Γ as a function of temperature measured for aggregates of PIC-I after pumping in the center of the J-band (triangles) [7]. The solid line is our fit; model parameters are discussed in the text.

to fit the absorption and holeburning data using a spectral density that (on average) scales with ω according to a power different from three and found that is not possible to obtain a good fit. This suggests that scattering on acoustic phonons of the host dominates the dynamics of excitons in PIC aggregates. This conclusion differs markedly from previous interpretations, where the optical vibrations of the aggregate itself were considered the dominant scattering agents, leading to sums of activated temperature dependencies [7,8,16]. In order to describe the strong increase of the line width for large temperatures, such a fit requires both a high activation energy (several hundreds of cm^{-1}) and a large pre-exponential factor. The prefactor is directly related to the exciton–vibration coupling constant. A simple perturbative treatment shows that the thus estimated coupling constant should be so large (few thousand $cm^{-1}s$) that a strong polaron effect is to be expected. This is inconsistent with the generally accepted excitonic nature of the optical excitations in cyanine aggregates.

Using the same parameters as for the fit to the PIC-I holeburning data in Fig. 2, we have also calculated the temperature dependence of the hole width after burning in the red and blue wings of the absorption line, respectively. Specifically, we used burning frequencies taken $\Delta(T)$ to the red of the peak of the absorption band and $\Delta(T)$ to the blue of the peak. The results are given in Fig. 3, together with the results when burning at the peak position. It is clearly seen that the hole width increases with increasing burning frequency. At low temperatures, this is to be expected: the dephasing of the excitons in the red wing (curve a in Fig. 3) is determined solely by radiative decay, whereas for the states at higher energy (curves b and c in Fig. 3) also relaxation to lower-energy exciton states contributes to the dephasing rate. The latter contribution grows for growing exciton energy. With increasing temperature, the hole width increases for all three burning frequencies, because downward as well as upward scattering on phonons becomes more prominent. It turns out that for all cases, the hole width scales with temperature according to a power law like Eq. (6), where the power p depends on the burning
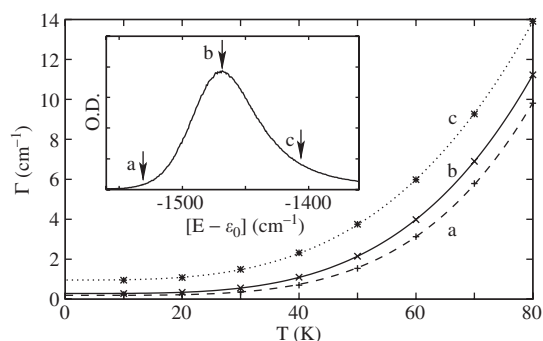

Fig. 3. Theoretical hole widths Γ as a function of temperature for burning frequencies in the red wing (dashed, a), the center (solid, b) and the blue wing (dotted, c) of the absorption spectrum. In the inset the arrows indicate the burning frequencies in the absorption spectrum of the aggregate at a temperature of 30 K. Model parameters as in Fig. 2.

frequency (4.1 for the red side, 3.8 for the peak, and 3.3 for the blue side). At high temperatures, the hole widths for the three burning frequencies tend towards each other, because upward scattering in the exciton band then totally dominates the dephasing rates. We note that the frequency dependence of the dephasing rate within the J-band has also been observed using photon-echo experiments, see, e.g., Ref. [17].

5. Concluding remarks

In summary, we have studied the temperature dependent dephasing rate of exciton states in disordered Frenkel chains, caused by scattering on acoustic phonons that are characterized by a Debye-like ($\propto \omega^3$) spectral density. We have found a power-law temperature dependence for the absorption line width as well as the hole width obtained through hole burning. The model yields good quantitative explanations to absorption and hole-burning experiments on aggregates of the dye PIC with various counter-ions. In Ref. [15] we show that our model also explains the temperature dependence of the fluorescence lifetime of PIC aggregates.

We finally note that our model does not account for two-phonon scattering processes; in particular we neglected pure dephasing. We have investigated such processes and found that for acoustic

phonons their contribution to the dynamic linewidth of the excitons scales according to T^s, with s in the range 7–8.5 [13], which does not agree with the experimental findings. Apparently the contribution of such processes is not noticeable in aggregates of PIC. This may partly result from the fact that the pure-dephasing rate is suppressed by a factor that is equal to the delocalization size of the exciton states [13], i.e., typically by a factor of 50 for the case of PIC.

Acknowledgement

References

[1] E.W. Knapp, Chem. Phys. 85 (1984) 73.
[2] S. de Boer, D.A. Wiersma, Chem. Phys. Lett. 165 (1990) 45.
[3] H. Fidder, J. Knoester, D.A. Wiersma, Chem. Phys. Lett. 171 (1990) 529.
[4] E.O. Potma, D.A. Wiersma, J. Chem. Phys. 108 (1998) 4894.
[5] I.G. Scheblykin, O.Yu. Sliusarenko, L.S. Lepnev, A.G. Vitukhnovsky, M. Van der Auweraer, J. Phys. Chem. B 105 (2001) 4636.
[6] M. Bednarz, V.A. Malyshev, J. Knoester, Phys. Rev. Lett. 91 (2003) 217401;
M. Bednarz, V.A. Malyshev, J. Knoester, J. Chem. Phys. 120 (2004) 3827.
[7] R. Hirschmann, J. Friedrich, J. Chem. Phys. 91 (1989) 7988.
[8] H. Fidder, D.A. Wiersma, Phys. Status Solidi B 188 (1995) 285.
[9] I. Renge, U.P. Wild, J. Phys. Chem. A 101 (1997) 7977.
[10] A.S. Davydov, Theory of Molecular Excitons, Plenum, New York, 1971.
[11] M. Bednarz, V.A. Malyshev, J. Knoester, J. Chem. Phys. 117 (2002) 6200.
[12] M. Shimizu, S. Suto, T. Goto, J. Chem. Phys. 114 (2001) 2775.
[13] D.J. Heijs, V.A. Malyshev, J. Knoester, J. Chem. Phys. 123 (2005) 144507.
[14] A.V. Malyshev, V.A. Malyshev, Phys. Rev. B 63 (2001) 196111;
A.V. Malyshev, V.A. Malyshev, J. Lumin. 94–95 (2001) 369.
[15] D.J. Heijs, V.A. Malyshev, J. Knoester, Phys. Rev. Lett. 95 (2005) 177402.
[16] F.C. Spano, J.R. Kuklinski, S. Mukamel, Phys. Rev. Lett. 65 (1990) 211.
[17] S.S. Lampoura, C. Spitz, S. Dähne, J. Knoester, K. Duppen, J. Phys. Chem. B 106 (2002) 3103.