Decoherence of Excitons in Multichromophore Systems: Thermal Line Broadening and Destruction of Superradiant Emission

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We study the temperature-dependent dephasing rate of excitons in chains of chromophores, accounting for scattering on static disorder as well as acoustic phonons in the host matrix. From this we find a power-law temperature dependence of the absorption linewidth, in excellent quantitative agreement with experiments on dye aggregates. We also propose a relation between the linewidth and the exciton coherence length imposed by the phonons. The results indicate that the much debated steep rise of the fluorescence lifetime of pseudoisocyanine aggregates above 40 K results from the fact that this coherence length drops below the localization length imposed by static disorder.

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A wide variety of materials consisting of interacting chromophores exists. Some examples are molecular aggregates, conjugated polymers, natural light-harvesting systems, and arrays of quantum dots. Lately, such multichromophore systems have received much attention for their collective optical properties [1–4], efficient and controlled energy transport processes [5], the occurrence of strong quantum entanglement of collective chromophore states [6,7], and their possible application in schemes for quantum computation [6,8]. All these properties sensitively depend on the temporal and spatial energy and phase relaxation of the chromophores' collective excitations, which make such relaxation processes a topic of broad interest and importance. The nature of the collective excitations and their dynamics are governed by the complicated interplay of their scattering on static disorder (e.g., inhomogeneity in the excitation energy of the individual chromophores) and on dynamic degrees of freedom (vibrations). A variety of experimental techniques are used to investigate the resulting intricate dynamics. The theoretical study of the combined effects of static disorder and a heat bath on exciton decoherence and optical response remains relatively unexplored [9].

Recently, a model of weakly localized Frenkel excitons coupled to acoustic phonons in the host medium proved to yield an excellent description of the nonmonotonous temperature dependence of the fluorescence Stokes shift as well as the linear temperature scaling of the radiative lifetime of aggregates of the dye 3, 3′-disulfopropyl-5, 5′-dichloro-9-ethylthiacarbocyanine (THIATS) measured between 0 and 100 K [4]. More direct insight into the interplay of static disorder and homogeneous dephasing, and thus a more stringent test for the model, is provided by temperature-dependent absorption, photon echo, and hole burning measurements. Such measurements, over the interval 0–300 K, have been performed for the prototypical J aggregates of the dye pseudoisocyanine (PIC) [10–14]. No unique interpretation of the thermal dephasing and line broadening in multichromophore systems has emerged from these studies: activated processes involving several optical phonons of the aggregate have been suggested as mechanism [11–13], but also power-law broadening due to host vibrations [14]. Another unsolved issue is the temperature dependence of the fluorescence lifetime at elevated temperatures. For aggregates of PIC-Br, its steep rise above 40 K has been only explained using a two-dimensional aggregate model [15], which contradicts the generally accepted chainlike geometry of these systems in solution [16].

In this Letter, we revisit the model of excitons in a linear chain with static energy disorder, coupled to acoustic phonons in the host. We show that the dephasing rates calculated within this model give an excellent explanation of the temperature-dependent absorption measurements for PIC aggregates. Furthermore, for the strong-scattering regime we introduce a relation between the exciton coherence length and the dephasing rates and demonstrate that this explains the steep rise of the fluorescence lifetime.

Our model consists of a linear Frenkel chain of N two-level chromophores ($n = 1, \dots, N$), with uncorrelated Gaussian disorder of standard deviation σ in the chromophore energies ε_n and resonant dipole-dipole interactions between chromophores n and m given by $J_{nm} = -J/|n-m|^3$, $J > 0$ being the nearest-neighbor interaction. All transition dipoles are parallel. 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 $\varphi_{\nu n}$; the disorder leads to their localization on segments of the chain. The model includes on-site scattering of excitons on a phonon bath. If the exciton-phonon interaction is not too strong, it induces scattering from exciton state ν to state μ with a rate that may be obtained from Fermi's golden rule [see, e.g., Ref. [4]]:

$$W_{\mu\nu} = \mathcal{F}(|\omega_{\mu\nu}|)G(\omega_{\mu\nu})\sum_{n=1}^{N}\varphi_{\mu n}^2\varphi_{\nu n}^2. \quad (1)$$

Here, $\omega_{\mu\nu} = E_\mu - E_\nu$ and $\mathcal{F}(\omega) = 2\pi\sum_q |V_q|^2\delta(\omega - \omega_q)$, the one-phonon spectral density (ω_q is the energy of a phonon in mode q and V_q characterizes the coupling of this mode to the excitons; we set $\hbar = 1$). Furthermore, $G(\omega) = n(\omega)$ if $\omega > 0$ and $G(\omega) = 1 + n(-\omega)$ if $\omega < 0$, with $n(\omega) = [\exp(\omega/k_BT) - 1]^{-1}$, the mean thermal occupation number of a phonon mode of energy ω.

While in Ref. [4] the $W_{\mu\nu}$ were only used to study the intraband exciton relaxation and the resulting fluorescence kinetics, they also govern the temperature-dependent dephasing of the excitons, and hence their homogeneous linewidths. Specifically, the thermal dephasing rate of the νth exciton state is given by $\Gamma_\nu \equiv \frac{1}{2}\sum_\mu W_{\mu\nu}$ and depends on temperature through the $n(\omega)$. In contrast to the fluorescence kinetics, the temperature dependence of the dephasing rates and absorption linewidth sensitively depends on the form assumed for the spectral density. Here, we will assume that $\mathcal{F}(\omega) = W_0(\omega/J)^3$. This form is appropriate for acoustic phonons, for which the density of states (DOS) scales as ω^2 (Debye behavior) and $|V_q|^2$ scales like ω; the remaining factor W_0 is a free parameter in the model. As we will see, the ω^3 scaling gives a natural explanation for the linewidth measurements on linear dye aggregates. Similar good agreement between theory and experiment is found if we allow for fluctuations of $\mathcal{F}(\omega)$ around an average ω^3 scaling, but the agreement is lost by changing to a power different from 3 [17].

Using the above model, we simulated the absorption spectrum for an ensemble of chains. The expression for this spectrum reads:

$$A(E) = \frac{1}{N}\left\langle\sum_\nu \frac{F_\nu}{\pi}\frac{\Gamma_\nu + \gamma_\nu/2}{(E - E_\nu)^2 + (\Gamma_\nu + \gamma_\nu/2)^2}\right\rangle, \quad (2)$$

where $F_\nu = (\sum_n \varphi_{\nu n})^2$ is the dimensionless oscillator strength of the νth exciton state, $\gamma_\nu = \gamma_0 F_\nu$ 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. The resulting linewidth $\Delta(T)$ is determined as the full width at half maximum (FWHM) of the simulated spectrum. We used chain lengths of 250–1000 chromophores and averaged over 1000–400 000 disorder realizations, depending on parameter choices.

In the absence of disorder and for long chains with nearest-neighbor interactions only, we found that $\Delta(T) \propto T^{3.5}$ (neglecting the radiative contribution, which is allowed unless T is very low). The explanation is simple: for $\sigma = 0$, the lowest ($\nu = 1$) exciton state dominates the spectrum. The above scaling then simply results from summing the $W_{\mu,\nu=1}$ over all higher lying states μ. The ω^3 dependence of $\mathcal{F}(\omega)$, combined with the $\omega^{-1/2}$ dependence of the exciton DOS near the bottom of the one-dimensional band, upon integration, yields the $T^{3.5}$ behavior. It turns out that the long-range dipolar interactions slightly change the power from 3.5 to 3.85 [17].

If we include disorder, the spectral width at zero temperature, $\Delta(0)$, is dominated by the inhomogeneous width, which for linear aggregates scales like $\sigma^{4/3}$ [18]. From extensive simulations we have found that in the presence of disorder the thermal broadening follows a power law:

$$\Delta(T) = \Delta(0) + aW_0(k_BT/J)^p, \quad (3)$$

where a and p depend only weakly on the parameters σ and W_0. The scaling relation Eq. (3) implies that, although the spectrum results from a distribution of exciton states with different dephasing rates, the total width may be interpreted as the sum of an inhomogeneous width, $\Delta(0)$, and a dynamic contribution. For six σ/J values in the interval $[0.05, 0.5]$ (taking $W_0/J = 25$), our simulated data are presented as symbols in Fig. 1(a), together with

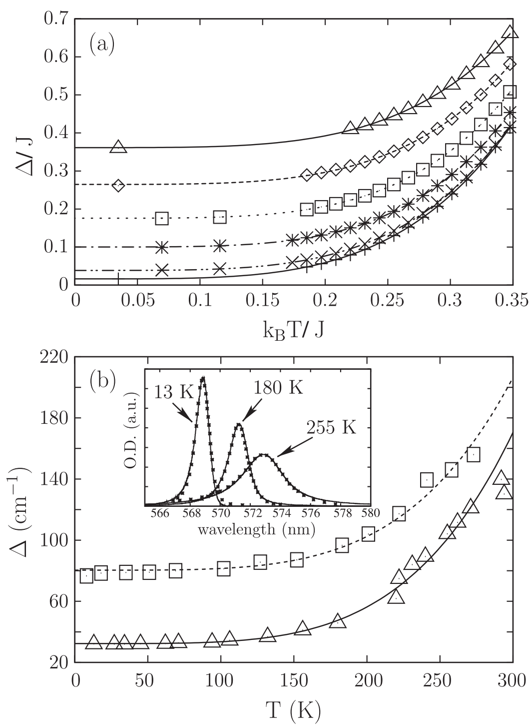

FIG. 1. (a) Calculated temperature-dependent width of the absorption spectrum (symbols) and corresponding fits to Eq. (3) (lines) for six values of the degree of disorder $\sigma/J = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$ (bottom to top). The fit parameters (a, p) take the values (1.1, 4.0), (1.2, 4.2), (1.3, 4.3), (1.2, 4.3), (1.2, 4.3), and (1.0, 4.1), respectively. $W_0/J = 25$ and $\gamma_0/J = 1.5 \times 10^{-5}$. (b) Comparison of theory (curves) and experiment (symbols) for the absorption linewidth as a function of temperature for aggregates of PIC-Cl (triangles) and PIC-F (squares). The model parameters are given in the text. The inset compares the line shape calculated for PIC-Cl aggregates (curves) to experiment (symbols) for three temperatures. We note that the thermal shift of the absorption band is not accounted for in our theory; the calculated spectra were shifted by hand to facilitate comparison of the line shape. Experimental data were taken from Ref. [14].

fits to Eq. (3). The fit parameters are given in the caption. The power p is seen to lie in a narrow range, $p = 4.2 \pm 0.2$, which is close to the disorder-free value 3.85. The reason for this small effect of disorder is that the dynamic width is governed by scattering from the optically dominant DOS tail states to high-lying intraband states, whose DOS is modified only slightly by disorder. The small increase of p primarily results from the possibility to scatter further downward in the tail of the disordered exciton band.

A scaling relation like Eq. (3) was also found experimentally by Renge and Wild [14] for aggregates of PIC with counter ions Cl^- and F^-. Fits of their data, presented in Fig. 1(b), demonstrate good agreement between theory and experiment. These fits were obtained using the accepted values of $J = 600$ cm^{-1} and $\gamma_0 = 2.7 \times 10^8$ s^{-1} ($= 1.5 \times 10^{-5} J$) for PIC and taking the fit parameters $\sigma/J = 0.128$ and $W_0/J = 16.0$ for PIC-Cl and $\sigma/J = 0.249$ and $W_0/J = 15.9$ for PIC-F. In the inset we show (for PIC-Cl) that not only the width, but also the experimental line shape as a function of temperature is recovered very well by our model.

We next address PIC-Br aggregates, for which the absorption linewidth as well as the fluorescence lifetime were measured up to 190 K (triangles and squares, respectively, in Fig. 2). We first discuss the width, for which it turned out that our model also for this counterion gives a very good fit to experiment (solid line in Fig. 2, fit parameters $\sigma/J = 0.135$, $W_0/J = 32.5$). It should be noted that the same data have previously been fitted assuming activated behavior, supposedly resulting from scattering on optical phonons of the aggregate [13]. In order to describe the strong increase of the linewidth for large temperatures, such a fit requires both a high activation energy (several hundreds of cm^{-1}) and a large preexponential 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.

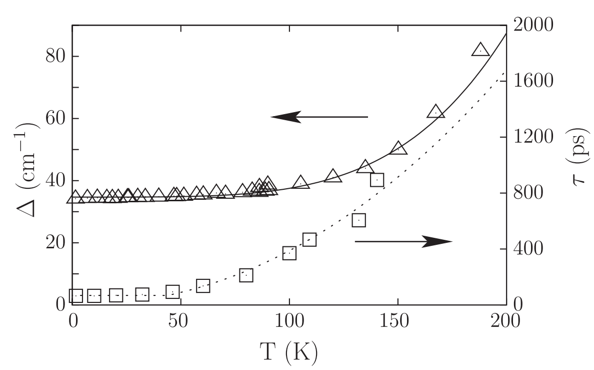

FIG. 2. Calculated and measured linewidth and fluorescence lifetime for aggregates of PIC-Br as a function of temperature. Linewidth: triangles [measured [12]] and solid (calculated); lifetime: squares [measured [13]] and dashed (calculated).

This is inconsistent with the generally accepted excitonic nature of the optical excitations in cyanine aggregates.

At low temperature, the fluorescence lifetime is determined by a competition between spontaneous emission and intraband relaxation of the weakly localized excitons, and may be analyzed using a master equation for their populations [4]. While successful for THIATS aggregates up to 100 K, this approach turns out not to explain the steep rise of the measured lifetime for PIC-Br above about 40 K (cf. Fig. 2). In fact, using the above fit parameters, the model only yields a doubling of the lifetime from 0 to 150 K, which is an order of magnitude too small. Other approaches have seen similar problems in explaining the measurements [12,19]; the closest (far from perfect) agreement has been found using a two-dimensional aggregate model [15]. Here we argue that the problem arises from phonon-induced decoherence of the excitons inside their localization segments.

If we consider weak exciton-phonon scattering in homogeneous chains ($\sigma = 0$), the exciton coherence length (or mean-free path), $N_\mu^{\rm coh}$, is much larger than its wavelength. In other words, the uncertainty in the exciton's quasimomentum, $\delta K \sim 1/N_\mu^{\rm coh}$, is much smaller than the quasimomentum itself. Because of the quadratic dispersion relation near the band bottom, $E_\mu = 2J - JK^2$, δK results in an energy uncertainty $\delta E_\mu = 2JK\delta K \sim JK/N_\mu^{\rm coh}$. Identifying δE_μ with the exciton's homogeneous width Γ_μ, we thus obtain an estimate for the coherence length: $N_\mu^{\rm coh} \sim JK/\Gamma_\mu$. In the strong-scattering regime, $N_\mu^{\rm coh}$ becomes smaller than the exciton wavelength and the quasimomentum is not a good quantum number anymore: $\delta K \sim K$. Hence $\delta E_\mu \sim J(\delta K)^2 \sim J/(N_\mu^{\rm coh})^2$, leading to the estimate $N_\mu^{\rm coh} \sim (J/\Gamma_\mu)^{1/2}$.

We now address this issue for the localized band edge states in the presence of disorder. At low temperature [$k_B T \ll \Delta(0)$], the coherence length $N_\mu^{\rm coh}$ associated with the exciton-phonon scattering is much larger than the localization length $N_\mu^{\rm loc}$; hence the latter plays the role of the coherence length and determines the optical dynamics. The main consequence of the exciton-phonon scattering in this regime is the intraband relaxation (equilibration) described above already [4]. Upon increasing T, $N_\mu^{\rm coh}$ decreases and at some temperature T_0 becomes comparable with $N_\mu^{\rm loc}$. In other words, excitons start to scatter *within* localization segments. For $T > T_0$, the coherence length $N_\mu^{\rm coh}$, rather than the localization length, governs the optical dynamics. It is to be stressed that when T surpasses T_0, the optically dominant states immediately fall in the strong-scattering regime, because they resemble standing waves without nodes with a typical "wavelength" on the order of $N_\mu^{\rm loc}$ [20].

The crossover temperature T_0 separates two different regimes for the fluorescence lifetime as a function of temperature. This lifetime is inversely proportional to the number of coherently emitting chromophores. At low temperature, this number should be identified with the typical localization length of the optically dominant exciton states, N^*; at high temperatures, it is to be identified with the T-dependent coherence length, $N^{\rm coh}(T)$. Denoting $\tau_0 = 1/\gamma_0$ as the single-chromophore lifetime, the essential behavior of the lifetime is thus given by:

$$\tau(T) = \begin{cases} \tau_0/N^*, & T < T_0, \\ \tau_0/N^{\rm coh}(T) = \tau_0 b\sqrt{\Gamma(T)/J}, & T > T_0, \end{cases} \qquad (4)$$

where in the estimate for the coherence length we used for the typical dephasing rate the effective homogeneous width $2\Gamma(T) \equiv \Delta(T) - \Delta(0)$ and b is a parameter of order unity. Here, the value of T_0 is determined from the condition $b\sqrt{\Gamma(T_0)/J} = 1/N^*$.

We used this approach to analyze the fluorescence data for PIC-Br. We took $N^* = 54$, as follows from the low-temperature lifetime $\tau(0) = 68$ ps in combination with $\tau_0 = 3.7$ ns, [12,13], and which also is consistent with the participation ratio [18] of 58 calculated for $\sigma/J = 0.135$. The resulting very good fit, using the $\Delta(T)$ calculated above, is seen as dashed line in Fig. 2. Here we used $b = 2.2$ as only fit parameter, which gave $T_0 = 44$ K.

Two comments are in place. First, in the low-temperature regime our fit does not account for population relaxation, which for growing T increases the lifetime from the value τ_0/N^* due to thermal population of dark states. Using the master-equation approach of Ref. [4], we found that this effect for PIC-Br leads to a small ($\sim$20 ps) linear growth of the lifetime between $T = 0$ and $T = T_0$. Second, a scaling of the lifetime with the linewidth was also suggested by Feldmann *et al.* [21] for quantum wells. Translating their arguments to a one-dimensional system, one obtains $\tau(T) = (\tau_0/\pi)\sqrt{\Delta(T)/J}$, which in the high-temperature limit agrees with our result, except that the prefactor b is reduced considerably. The reason for this difference is that the argument of Ref. [21], based on counting the number of states within the absorption width, does not relate to the coherence length, but rather to population redistribution.

In conclusion, a model that considers weakly localized excitons which scatter on acoustic host phonons yields power-law thermal line broadening that is in excellent agreement with experiments on dye aggregates. In addition, a new method to relate the exciton coherence length within the strong-scattering regime to the homogeneous linewidth gives good agreement with temperature-dependent fluorescence lifetime data. Our work shows that, in contrast to earlier claims, a one-dimensional model for PIC aggregates suffices to explain all experimental data. We believe that both the on-site (diagonal) disorder and the one-phonon scattering on host vibrations with a Debye-like spectral density ($\propto \omega^3$) are the essential and physically sound ingredients to reach this conclusion. It is known that off-diagonal disorder yields a symmetric low-temperature absorption profile [22], while two-phonon scattering (including pure dephasing) results in power-law broadening with a power that is about twice as large as the values of p obtained for one-phonon scattering [17]. Both facts are inconsistent with experimental data. Finally, off-site scattering on acoustic phonons is also characterized by a spectral density proportional to ω^3 [see, e.g., the work cited in Ref. [19]]; therefore, its inclusion would not change the power $p = 4.2$, but only alter the microscopic meaning of the phenomenological scattering parameter W_0 to a sum of two (on-site and off-site) scattering parameters.

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