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DEPHASING-INDUCED DAMPING OF SUPERRADIANT EMISSION IN J-AGGREGATES

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Results of temperature-dependent accumulated photon echo, fluorescence lifetime and fluorescence quantum yield measurements are reported on aggregates of the dye pseudoisocyanine bromide in an ethylene glycol/water glass. The results show that the lowest excited state of the J-aggregate can be described as a superradiative exciton, whose radiative and optical coherence lifetime are determined by dephasing processes. The results further indicate that the phonon-induced fluctuations of the site energies must be highly correlated. The observed discrepancy between the low-temperature photon echo decay time of 16 ps and fluorescence lifetime of 70 ps is ascribed to observation of dephasing of an excitonic wave packet in the echo and incoherent relaxation of the same *k*-states in the fluorescence.

1. Introduction

Molecular aggregates are abundantly found in biological systems where they function as energy funnels for sunlight to be used in photochemical reactions [1]. Aggregates of dyes have also found technological application as sensitizers in the photographic industry [2]; recently they have shown great promise for use in the field of opto-electronics [3]. Studies of clusters in supersonic beams [4] and the condensed phase [5] have therefore attracted many spectroscopists of late. Directly related to the investigation of aggregates is the study of "optical" polymers [6] and small semiconductor particles [7]. Dramatic size effects have been observed in the latter case, which suggests that synthetic control of the size of clusters with interesting (non-linear) optical properties [8] could lead to new applications in the opto-electronics industry. From a scientific point of view, understanding of the physical properties of clusters of molecules or semiconductor particles presents a great challenge in itself, as these species bridge the gap between a single "molecule" and a crystal. While in the past much of the work on aggregates was aimed at understanding the spectroscopy in terms of an excitonic model [9-11], recently the focus has changed to comprehend the dynamical properties of

aggregates. Recently, Mukamel and co-workers showed [12,13] that the exciton radiative and transport dynamics are determined by the imaginary and real parts of the intermolecular dipole–dipole coupling, respectively, and that dephasing processes may easily quench the superradiant emission of the aggregate. The effect of local inhomogeneity on the superradiant emission and excitation delocalization was also studied.

In this Letter we focus our attention on the optical dynamics of aggregates of the molecule pseudoisocyanine bromide (PIC-Br); specifically we report on the temperature dependence of the *radiative* and *coherence* lifetime of the energetically lowest excitonic transition of the aggregate.

Spectroscopic studies on aggregates of PIC date back to the mid thirties when Scheibe [14] and Jelly [15] independently discovered that concentrated solutions of PIC develop a sharp red-shifted absorption band. This band, now commonly referred to as J-band, was interpreted by them as arising from an aggregate of the PIC molecule. Following this observation much work has been done to obtain a fundamental understanding of the spectroscopy and dynamics of this transition [16]. Scheibe was the first one to show [17] that in streaming solutions of these aggregates the J-band was polarized parallel to the

streaming direction. This experiment clearly indicates that these aggregates are thread-like in shape and that the J-band is polarized parallel to the long axis of the aggregate. Using an excitonic model including moderate vibronic coupling, Scherer and Fischer [10,18] succeeded in reconstructing the complete aggregate spectrum assuming the aggregate to be a linear chain with two molecules per unit cell. In this analysis the J-band was assigned to a transition from the ground state to the $k=1$ state at the lower band edge. Knapp [11] showed that the unusual sharpness of the J-band in solution (180 cm^{-1}) can be understood in terms of an optical excitation moving fast along a chain thereby averaging out the local inhomogenities.

Understanding of the optical dynamics of the J-band has progressed at a much slower pace. Lifetime measurements involving the J-band have given extremely controversial results [19–24]. Sundström et al. [25] recently showed that much of the controversy can be traced back to use of too high excitation intensities in many of the earlier experiments. In this case exciton annihilation dominates the observed fluorescence decay. From intensity-dependent pump–probe experiments on the J-band, Sundström et al. [25] concluded that the energy transfer process in solution proceeds via hopping and that the physical length of the aggregate may encompass 50000 dye molecules. Recently we reported on the optical dynamics of the J-band in the condensed phase using the photon-echo and hole-burning technique [26,27] as probes. Friedrich's group [28] also reported results of hole-burning experiments on aggregates of PIC, confirming a fast decay of the exciton's coherence at low temperature. Most noteworthy in our experiments was the observation of a fast photon-echo decay (14 ps) at low temperature under low intensity excitation conditions. With reference to earlier lifetime measurements [19] this ultrafast decay was interpreted as the exciton fluorescence lifetime. The recent work of Sundström et al. [25], however, raises the question of how to reconcile a room-temperature fluorescence lifetime of 400 ps with a 14 ps lifetime at 1.5 K. More specifically: is this difference due to a change in fluorescence quantum yield with temperature or does the excitation delocalize over a greater number of molecules at lower temperature? With these questions in mind we decided to under-

take temperature-dependent fluorescence lifetime and quantum yield measurements on J-aggregates in the condensed phase. From these measurements radiative rate constants as a function of temperature can be obtained.

The experiments reported here clearly show that the *radiative* lifetime of the aggregates is strongly dependent on temperature. Feldmann et al. [29] recently reported a similar observation for free excitons in GaAs/AlGaAs quantum wells. They interpreted this effect as arising from a dephasing-induced localization of the excitation process: the effective number of coherently coupled molecules (unit cells) decreases at higher temperature. Möbius and Kuhn earlier [30,31] concluded that the radiative lifetime of aggregates is temperature dependent because of excitation localization with increasing temperature. They arrived at this conclusion by performing a series of elegant energy-transfer measurements on doped monolayer assemblies of aggregates. Dorn and Müller [24] performed lifetime measurements on these aggregates and found a marked lengthening of the lifetime with increase in temperature. Following Möbius and Kuhn [30,31] they interpreted their finding as compelling evidence for a temperature-dependent localization of the excitation. However, Dorn and Müller used an excitation intensity more than three orders of magnitude larger than employed in our lifetime measurements, which almost certainly means that their decays are dominated by exciton annihilation rather than radiative decay [25]. Mukamel and coworkers recently showed [12,13] that a temperature-dependent radiative lifetime does not necessarily imply a change in localization of the excitation on the aggregate. They showed that while the superradiant emission is easily quenched by intermolecular dephasing, the energy delocalization is much less sensitive to this process. The reason for this difference is that the cooperative emission is governed by the imaginary part of the dipole–dipole coupling, while the energy delocalization is determined by the real part of this interaction that may be six to eight orders of magnitude larger.

2. Experimental

Pseudoisocyanine bromide (PIC-Br) was obtained from Exciton Chemical Company and used without further purification. Samples were made by dissolving PIC-Br to a concentration of 5×10^{-3} in a mixture of triply distilled water and ethylene glycol (Merck Pro Analysis grade) (50/50 vol%). Drops of such solutions were pressed between flat glass slides such that the final sample thickness was about 10 μm. These samples were cooled down to 77 K in a few minutes yielding perfectly transparent samples. The optical densities obtained at the zero-phonon lines of the aggregates could be varied between 0.05 and 1.0 OD by slightly changing the PIC-Br concentration and/or the imposed pressure on the glass slides. In the fluorescence lifetime measurements samples were used with an OD of less than 0.1.

The accumulated photon echo [32,33] experiments were done as earlier described [26,27]. Single-shot two-pulse photon-echo experiments were performed by placing a travelling wave acousto-optic modulator directly behind the standing wave acousto-optic modulator in order to randomize the phase relationship between consecutive pulse pairs [32]. These experiments gave the same decay times as the ones obtained from the accumulated photon echo. However, the signal to noise ratio achieved in the accumulated echo was much higher for the same average laser power. Fluorescence lifetimes were measured with a time-resolved single-photon-counting system. Optical excitation of the aggregates took place with a cavity-dumped, synchronously pumped dye laser operating at a wavelength of 545 nm. The cavity dump rate employed was 80 kHz and a typical excitation density used was 3×10^{9} photons cm^{-2} $pulse^{-1}$. The fluorescence was passed through a 0.5 m Jarrell–Ash monochromator and detected with a Hamamatsu 1534-U01 microchannel plate detector. The electrical pulses of the detector were amplified using two chained GHz amplifiers (Minicircuits ZFM 2000) and fed into a Tennelec 455 discriminator. The discriminator was modified according to the description given by the manufacturer. The output pulse of the discriminator was used to start an ORTEC 457 time-to-amplitude converter. The stop pulses were obtained from the laser pulse using a fast photodiode (risetime < 200 ps), which were also

passed through a Tennelec discriminator. The overall system response, optical plus electrical, was 75 ps (fwhm), which was obtained by masking the grating of the spectrometer. The system response without the spectrometer is about 60 ps. A microcomputer is used to store the data and fit the fluorescence decays by an iterative deconvolution process. In obtaining fluorescence decays, care was taken to prevent electrical pulse pile-up distortions.

3. Results

When a sample of PIC-Br in an ethylene glycol/ water glass is cooled rapidly, the origin region contains two sharp zero-phonon transitions located at 568.6 and 575.5 nm at 1.5 K, as shown in the upper panel of fig. 1. We first note that with rising temperature both lines experience a considerable red-shift and that near the glass transition temperature the red site transforms into the blue site. The linewidths of these J-transitions at 1.5 K are only 24 and 34 cm^{-1} for the blue and red site respectively, which is exceptionally sharp for an optical transition in a glass.
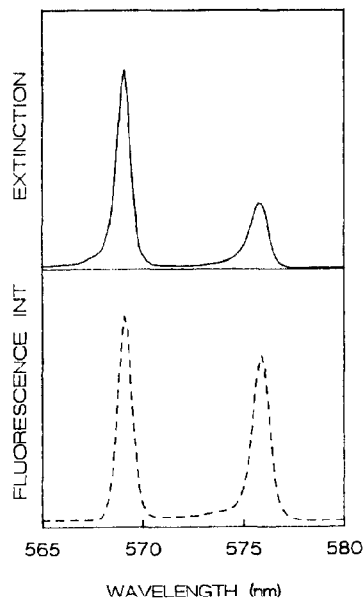

Fig. 1. Zero-phonon lines in absorption (lower panel) and emission (upper panel) of structurally different aggregates of PIC-Br in an ethylene glycol/water glass at 1.5 K.

Hirschmann et al. [28] showed that for PIC-Cl and PIC-I also two sites are observed with comparable splittings. As the relative intensities of these sites depends on the type of anion (Cl, Br or I) used and cooling speed of the dye solution, it was earlier argued [26,28,34] that these absorptions belong to structurally different aggregates. This suggestion was confirmed in the present work by showing that the excitation spectra of the two sites at 1.5 K, shown in fig. 2, are virtually identical except for a shift of about 150 cm^{-1} with respect to one another. However, when the excitation spectrum of the red site was taken, we also observed a peak at the origin of the blue site. We interpret this finding as evidence for the occurrence of energy transfer between the blue and red site (vide infra). Regarding the structural difference between the two sites we can only speculate at this point. An attractive possibility is that the two aggregates only differ by the orientation of the end-ring on the chain [35]. In that case a transition from one type aggregate to the other would just involve rotation of this ring across a barrier. Using this model our experiments imply that the blue site is energetically more stable in the ground state, while the red site is energetically more stable in the excited
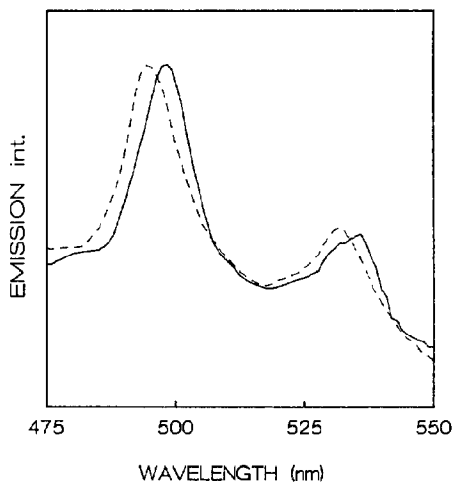

Fig. 2. Fluorescence excitation spectra of the structurally different aggregates of PIC-Br in an ethylene glycol/water glass at 1.5 K. The solid line is the excitation spectrum obtained by detection of the emission at the wavelength of the red site (575.5 nm), the dotted line is obtained by detection of the emission at the wavelength of the blue site (568.6 nm).

state. This model would explain the appearance of the blue site in the excitation spectrum of the red site as caused by a barrier crossing process on the excited state potential energy surface. Obviously, more experiments need to be done to explore the consequences of this model to the observed (excitation) spectra.

The fluorescence spectra of J-aggregates at 1.5 K are presented in the lower panel of fig. 1. This figure clearly shows that the emission consists of only a single sharp line resonant with the absorption. The absence of a Stokes shift in emission indicates that the final state in absorption and the initial state in emission are the same: namely the $k=1$ exciton state at the bottom of the band. Further it is to be noted that the atomic-like behaviour of the J-aggregate in emission is unique and points at negligible distortion of the nuclear framework on excitation, in agreement with the marked absence of a Stokes shift. To probe the dynamic behaviour of this excitation on the aggregate we performed photon echo and fluorescence lifetime measurements on both sites, for sample temperatures between 1.5 and 100 K for the echo and up to 220 K for fluorescence. Above 220 K the glass starts to melt; at this point it becomes uncertain whether the *physical* length of the aggregate remains constant. Fig. 3 shows the low-temperature (1.5 K), stochastically excited accumulated photon-echo decays of the red (upper trace) and blue (lower trace) sites of the aggregate, under low-intensity excitation conditions. Both decays are non-exponential and can be fitted to a double exponential decay curve with time constants of 9 ps (0.7 weight) and 33 ps (0.3 weight) for the red site and 6 ps (0.8 weight) and 20 ps (0.2 weight) for the blue site, respectively. When these decays are fitted to a single-exponential time constant, we obtain a 16 ps (compared to 14 ps reported in ref. [26]) lifetime for the red and an 8 ps lifetime for the blue site. Using transform limited 3 ps excitation pulses, the decays are also found to be non-exponential throughout both bands with the amplitude of the fast component increasing to higher energy. We further note that when the two-pulse photon echo is used as a probe, the decays observed can be fitted with the same decay components. This implies that spectral diffusion, involving glass dynamics [36], does not affect the observed decay of the accumulated photon echo. The temperature de-
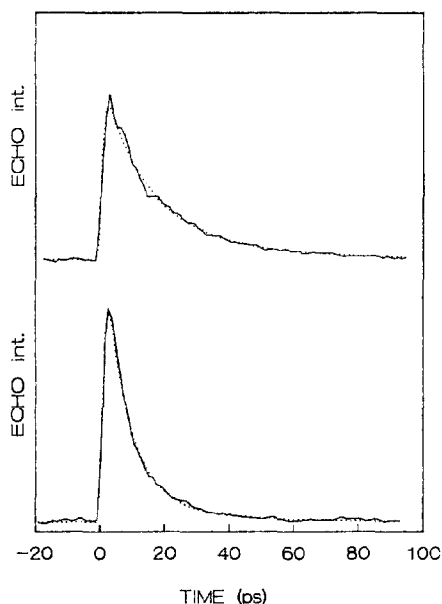
Fig. 3. Decays of the accumulated photon echo obtained by stochastic excitation of the origins of aggregates of PIC-Br; the sample temperature is 1.5 K. The upper trace is obtained from the red site, the lower from the blue site. The dotted lines are fits to a double-exponential decay with parameters given in the text.
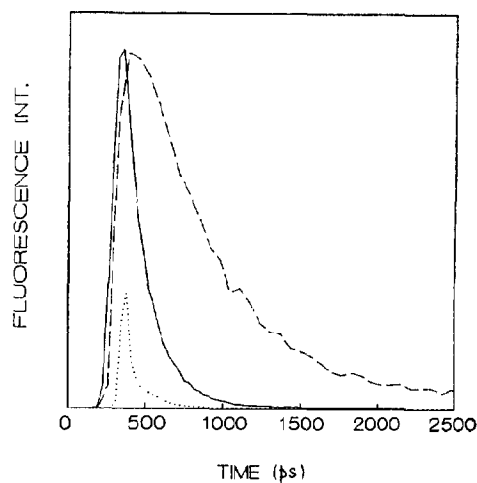

Fig. 4. Fluorescence decays obtained on the "red" J-aggregate of PIC-Br in an ethylene glycol/water glass using a time-resolved single-photon-counting system. The dotted curve presents the systems response function. The solid line is the fluorescence decay obtained at 1.5 K with a lifetime of 70 ps, the dashed curve presents the fluorescence decay obtained at 180 K with a lifetime of 450 ps.

pendence of the photon-echo decay was reported earlier [26] and we only recall here that the temperature dependence of the pure dephasing time constant (T_2^*) for both sites was found to be indistinguishable.

Fig. 4 shows typical traces of the fluorescence decay at 1.5 and 180 K of the red site along with the system response function. Similar traces were obtained for the blue site but somewhat faster than for the red site at the same temperatures. The main result of this paper is presented in fig. 5. This figure shows a plot of the measured *radiative* rates for both sites as a function of the inverse temperature. This plot was obtained by measurement of the temperature-dependent fluorescence lifetime and the relative quantum yield of emission. Furthermore, the absolute fluorescence quantum yields ($\phi_{\mathrm{fl}}(0)$) for both sites were taken to be 1 at 1.5 K. In case $\phi_{\mathrm{fl}}(0) < 1$, the vertical scale needs to be multiplied by $\phi_{\mathrm{fl}}(0)$ (vide infra). The relative quantum yield of emission for the red site was found to decrease by 25% and for the blue site to increase by about the same amount
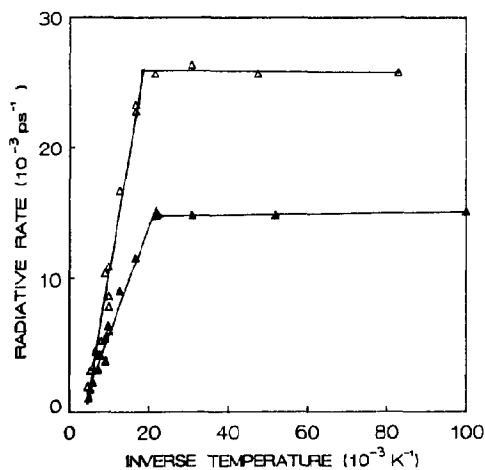

Fig. 5. Plots of the radiative rate constants as a function of the inverse temperature for aggregates of PIC-Br in an ethylene glycol/water glass. For both sites we have taken the low-temperature fluorescence quantum yield to be 1 (see text). The solid straight lines are meant as guide for the eye, not theoretical fits. The closed triangles (▲) are data points for the red site, the open triangles (△) are data points for the blue site. Note that these data were obtained from fluorescence lifetime and relative fluorescence quantum yield measurements.

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for temperatures between 80 and 220 K. We note that the fluorescence lifetimes for the red and blue sites change from 70 and 40 ps at 50 K to 600 and 500 ps at 200 K, respectively. Below 50 K the fluorescence lifetimes were found to be independent of temperature, as can be also inferred from fig. 5.

4. Discussion

In this Letter we restrict ourselves to a discussion of the following two points: (1) the temperature dependence of the radiative lifetime, and (2) the discrepancy between the low temperature photon echo and fluorescence lifetimes for both sites. Discussion of the observed temperature-dependent line shifts and fluorescence quantum yields of the two sites will be reserved for a future paper.

To describe the radiative dynamics of the aggregate, Mukamel and coworkers [12,13] used the superradiance master equation [37] which incorporates the effect of the imaginary and real part of the dipole–dipole coupling on the time-dependent density matrix of the system. For aggregates in a glass, the presence of a substantial local inhomogeneity must also be taken into account. This effect counteracts the real part of the dipole–dipole coupling that delocalizes the optical excitation over the aggregate. At elevated temperatures an additional complication arises from dephasing that competes with the imaginary part of the dipolar coupling. This imaginary part leads to cooperative emission of many molecules on the aggregate. From Spano and Mukamel's paper [13], one can infer that in the absence of inhomogeneous broadening, the incoherently excited fluorescence intensity of a linear aggregate at low temperature at a distance r can be expressed as follows:

$$I_n(r, t) = Ms(r) \sum_{k=1}^{N} \left(\frac{2}{N+1}\right)^2 \cot^4\left(\frac{k\pi}{2(N+1)}\right)$$
$$\times \exp(-\epsilon_k^L/kT) \exp(-2\Gamma_k^L t), \quad (1)$$

with

$$\epsilon_k^L = 2V\cos\left(\frac{k\pi}{N+1}\right), \quad k=1,...,N, \quad (2)$$

$$\Gamma_k^L = \frac{\gamma}{2}\frac{8}{(k\pi)^2}(N+1), \quad k=\text{odd}, \quad (3a)$$

$$\Gamma_k^L = 0, \quad k=\text{even}. \quad (3b)$$

Here V is the intermolecular dipolar coupling energy, γ the radiative rate constant of a single dye molecule, M a constant and $s(r)$ a directional factor [13]. Note that in the derivation of eq. (1) vibronic coupling has not been taken into account, which is allowed for k-states near the bottom of the band [10]. In the case of PIC, V has been determined to be -630 cm^{-1} [38]. Eq. (2) shows that for a negative value of V, the $k=1$ state is indeed at the bottom of the band and the $k=N$ state at the top. The splitting between the different k-states depends on the number of coherently coupled molecules N_c, as eq. (2) also shows. Eqs. (1) and (3a) show that for large N, the $k=1$ excitonic state attains the superradiant lifetime of $(0.81N\gamma)^{-1}$. In our previous Letter on this subject [26] we used an enhancement factor N, which is only obtained for a cyclic aggregate. Eq. (1) shows that the fluorescence decay of a linear aggregate is dominated by the decay of the $k=1$ state, but also may contain contributions of other k-states. The low temperature fluorescence decays were exponential, which suggests that the emission comes only from the $k=1$ state. With this assumption one can easily calculate the number of *coherently* coupled molecules (N_c) from the equation

$$N_c = 2\tau_n\phi_n\Gamma_{k=1}^L(\cos^2\alpha)^{-1}, \quad (4)$$

where τ_n is the monomer's 3.7 ns radiative lifetime [39], ϕ_n the quantum yield of emission and $\cos^2\alpha$ a geometrical factor, which is about $1/2$ [18]. For the red site we take ϕ_n to be ≈ 1 at low temperature [40]; for the blue site ϕ_n must be close to 0.5 [41]. With these numbers we calculate N_c to be 130 and 115 for the red and blue site, respectively. Using another result of Spano and Mukamel's paper [13], one can estimate that in the inhomogeneous broadening case, with $\sigma/V=1/4$, N_c is a factor of 5 larger; therefore about 650 for the red and 575 for the blue site. σ is defined here by the Gaussian distribution function of homogeneous line centers:

$$g(\omega-\omega_0)^2 = (\pi^{1/2}\sigma)\exp[-((\omega-\omega_0)/\sigma)^2].$$

Note that N_c calculated from the radiative lifetime is much smaller than N_c derived by Sundström et al. [25] from intensity-dependent pump–probe experiments at room temperature. We suggest that the number reported by Sundström et al. pertains to the *physical* and our number to the *coherence* length of the aggregate. Another consequence of the presence of local inhomogeneity is that the higher k-states become more radiative than expressed by eq. (3a); in fact for the conditions appropriate for PIC ($V \approx 4\sigma$), the $k = 2$ and $k = 3$ levels may attain about the same radiative rate as the $k = 1$ state [13]. It therefore seems quite likely that in all coherent optical experiments pertaining to these aggregates, the initial excited state is a wave packet composed of k-states from all segments of the aggregate.

We now turn to a discussion of the observed temperature dependence of the radiative rate constant of these aggregates. An appealing interpretation of our results is based on the idea that a change in radiative lifetime reflects a change in N_c. With this assumption one calculates N_c to change by a factor of 12 between 40 and 220 K, being independent of temperature below 40 K. Fig. 5 further shows that between 40 and 220 K the radiative lifetime is directly proportional to the temperature, a result earlier obtained by Möbius and Kuhn for a different aggregate [30,31]. In their case, this functional dependence held down to 20 K. Along the same lines one can interpret the temperature *in*dependence of the radiative rate below 40 K as being because of the fact that the aggregate's coherence length is limited by kinks in the chain. However, Grad et al. [12] have shown that the radiative lifetime of the aggregate only connects with the excitation's coherence length in the absence of pure dephasing. At elevated temperatures, the number of coherently coupled molecules calculated from the radiative lifetime is the *effective* rather than the real number of molecules over which the excitation is delocalized. The decrease in radiative lifetime in their formalism is due to intermolecular dephasing processes which reduce the effective transition dipole of the $k = 1$ state on the chain. We therefore conclude that the measured temperature dependence of the aggregate radiative lifetime is because of a phonon-induced modulation process of the frequency difference of transitions at neighbouring molecules. This dephasing process will be characterized by the rate constant Γ_{im} that equals the pure dephasing constant of the exciton $\Gamma_2^* (= (T_2^*)^{-1})$, in the case that the frequency modulation process at different sites is uncorrelated. Grad et al. [12] showed that in case Γ_{im} exceeds $N_c\gamma$, the superradiant emission becomes quenched. This implies that an alternative interpretation of the measured temperature *in*dependence of the radiative lifetime below 40 K is that in this temperature regime, $\Gamma_{im} \ll N_c\gamma$. Here N_c is the number of coherently coupled molecules calculated in the absence of inhomogeneous broadening (eq. (4)). From photon-echo measurements we derive that at 40 K, the pure dephasing time constant (T_2^*) for the excitonic transition is 10 ps [26] compared to 70 ps for the superradiant lifetime ($N_c\gamma$) at the same temperature. In the case of uncorrelated frequency modulation the aggregate superradiant emission would have been severely affected at this temperature. From the fact that at 40 K optical dephasing begins to influence the superradiant decay time, we infer that at this temperature $\Gamma_{im} \approx N_c\gamma \approx 1.4 \times 10^{10}$ s^{-1}. This implies that $\Gamma_2^*/\Gamma_{im} \approx 7$ at 40 K.

Continuing now with a discussion of the observed linear temperature dependence of the radiative lifetime above 40 K, we first note that the same functional relationship was inferred by Möbius and Kuhn from energy transfer experiments [29,30], and that the same linear temperature dependence was reported by Feldmann et al. [29] for the radiative lifetime of free excitons in GaAs/AlGaAs quantum well structures. In order to explain their data and ours in terms of a dephasing-induced quenching of the superradiance [12], one must know how the superradiant emission lifetime is affected by dephasing processes. For the case of a dimer this problem has been dealt with by Grad et al. [12]. At this point we can only speculate on what will happen in the case of an exciton.

Finally we wish to discuss the observed discrepancy between the low temperature (accumulated) photon-echo lifetime, $\frac{1}{2}T_2$, and the fluorescence lifetime, T_1. On basis of the results of Spano and Mukamel [13] we expect the photon-echo intensity (I_{2PE}) from a homogeneous aggregate to have the following decay function:

$$I_{2PE}(r,t) = M^2 s(r) \sum_{k=1}^{N} \sum_{k'=1}^{N\dagger} \left(\frac{2}{N+1}\right)^2$$

$$\times \cot^2\left(\frac{k\pi}{2(N+1)}\right) \cot^2\left(\frac{k'\pi}{2(N+1)}\right)$$

$$\times \exp\{[i(\epsilon_k^L - \epsilon_{k'}^L) - 2(\Gamma_{2k}^L + \Gamma_{2k'}^L)]t\}, \qquad (5)$$

where $\Gamma_{2k}^L = \Gamma_{2k}^{*L} + \frac{1}{2}\Gamma_k^L$ is the optical dephasing time of the excitonic transition involving level k. Γ_{2k}^{*L} is the pure dephasing time and Γ_k^L the population relaxation time of a two-level system: the ground state and a particular k-level. t is the time between the excitation pulses and the dagger in the summation of eq. (5) indicates that only odd values of k are counted.

Eq. (5) shows that in the photon echo, in contrast to fluorescence (eq. (1)), one probes the interference in emission of different k-states that have been coherently excited. As mentioned earlier, the situation is more complex than described by eqs. (1) and (5), because we must account for the fact that the physical length exceeds by far the *coherence* length (N_c molecules) of an aggregate. Including this effect into the decay functions one must add another summation (over all segments on an aggregate) to both eqs. (1) and (5). If the coherent band width of the excitation spans all optically allowed states on the aggregate, as with stochastic excitation, then the photon echo measures the microscopic dephasing and relaxation of this wave packet onto the segment with lowest energy. It is this combined effect that causes the photon-echo decay to be non-exponential. At this point it is tempting to interpret the fast component in the photon-echo decay as arising from the microscopic dephasing of the excited wave packet. Eq. (1) shows that the fluorescence observed in our experiments arises from the *incoherent* decay of the lowest energy k-state or states on the chain that are populated by relaxation after excitation of vibronic states at 545 nm.

Additional experiments and further theoretical work need to be done to fully understand the connection between superradiant emission excitation localization and dephasing of aggregates. Fluorescence depolarization experiments and quantum yield experiments on doped aggregates may be particu-larly useful to obtain additional information.

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