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DAMPING OF SUPERRADIANT EXCITONS IN MOLECULAR AGGREGATES

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Results of temperature dependent accumulated photon echo, fluorescence lifetime and fluorescence quantum yield measurements are reported on the zero-phonon transitions of structurally different aggregates of the dye molecule pseudoisocyanine. In each case a substantial discrepancy is found between the low temperature ps decay of the exciton's coherence and its population lifetime, with the former being much faster and non exponential. The difference is attributed to the fact that the excitonic wave packet excited in the photon echo is composed of different k -states that interfere in its decay. In the fluorescence lifetime measurements the incoherent relaxation of these levels is observed. The radiative rate constant of the aggregates at low temperature is found to be extremely large and interpreted as arising from the cooperative emission of hundreds of molecules. The temperature dependence of the radiative rate constant above 50 K may be understood as resulting from phonon induced quenching of the superradiant emission of the aggregate.

1. Introduction

Ever since the discovery by Scheibe [1] and Jelly [2] that concentrated solutions of pseudoisocyanine (PIC) molecules possess a sharp red-shifted optical transition, spectroscopists have been trying to obtain a basic grasp of the dynamics of this J -transition. Understanding the dynamics of clusters of molecules or semiconductor particles generally has become an urgent matter as these entities are expected to exhibit giant nonlinear optical susceptibilities [3]. In the case of the J -transition of PIC it was shown by Scherer and Fischer [4] that an excitonic model involving moderate vibronic coupling satisfactorily explains the static features of the optical spectrum of the aggregate. With respect to the dynamics of the transition, the situation has been less clear. Sundström et al. [5] showed that much of the earlier controversy regarding the fluorescence lifetime of the aggregate can be traced back to use of too high light intensities [6–11], in which case exciton annihilation dominates the observed excited state decay. We have recently started an investigation of the dynamics of the PIC aggregate in the condensed phase [12,13], using nonlinear optical techniques such as the photon echo and holeburning as a probe. Hirschmann et al. have also reported results of holeburning experiments on this system [14]. From our experiments we concluded that the low temperature fast photon echo decay was caused by the cooperative emission of a few hundred molecules. Following the publication of Sundström et al. [5], however, the question was how to explain the discrepancy between the measured lifetime of 400 ps at room temperature and the reported photon echo lifetime of 14 ps at 1.5 K. In view of this we decided to

measure the fluorescence lifetime of the aggregate in the condensed phase. Relative fluorescence quantum yield measurements were also performed as a function of temperature. The results of these experiments are reported in this paper and show that the aggregates' radiative lifetime is highly dependent on the temperature. This can be interpreted as a phonon induced localization of the excitation; the effective number of coherently coupled molecules decreases at higher temperature. Möbius and Kuhn earlier [15,16] arrived at the same result, indirectly, for a different aggregate, by performing a series of elegant energy transfer measurements on doped monolayer assemblies. However, Mukamel and coworkers have recently shown [17,18] that a temperature dependent radiative lifetime need not necessarily imply a change in localization of the excitation on the aggregate. They showed that while the cooperativity in 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 which is typically 6 to 8 orders of magnitude larger.

2. Experimental

Pseudo isocyanine-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} M in a mixture of triply distilled water and analytical grade ethylene

glycol (50/50 vol.%). Drops of this solution were pressed between flat glass slides such that the final sample thickness was around 10 μm . These samples were cooled in a few minutes down to 77 K, yielding perfectly transparent samples. The optical densities at the zero phonon lines of the aggregates could be varied up to 1.0, by slightly changing the PIC-Br concentration or the imposed pressure on the glass slides. In the fluorescence lifetime measurements samples were used with an optical density of less than 0.1.

The accumulated photon echo experiments were performed as earlier described [13]. Single shot two pulse photon echo experiments were also performed, by placing an acousto-optic modulator directly behind the standing wave modulator in order to randomize the phase relationship between consecutive pairs, yielding the same decay data.

The time resolved single photon counting experiments were performed according to the scheme reported by Bebelaar [19], using a 0.5 m Jarrell-Ash monochromator to select the emission and a Hamamatsu 1534 U-01 PMT as a detector. The time resolution of this setup is typically 15 ps. The decays were fitted by an iterative deconvolution process using a microcomputer. A cavity-dumped synchronously pumped dye laser, operating at 545 nm, was used to excite the aggregate's emission. Typical excitation intensities used were 3×10^9 photons cm^{-2} pulse $^{-1}$.

3. Results

The upper panel of fig. 1 shows the absorption spectrum of a quickly cooled sample of PIC-Br in the ethylene glycol/water glass at 1.5 K. The sharp lines at 570.2 and 576.1 nm represent the zero phonon transitions of structurally different *J*-aggregates. The linewidths in this case are only 24 and 34 cm^{-1} for the blue and red site, respectively. We note that the line positions of the blue and red sites undergo a substantial red shift with rising temperature [20]. The lower panel of fig. 1 shows that the fluorescence spectrum of the aggregates is extremely simple, just a single sharp line resonant with the zero phonon absorption line of the aggregate. This shows that absorption and emission come from the same lowest excitonic type transition at the PIC aggregate. Photon echo and fluorescence lifetime measurements were performed 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. Note that the *physical* length of the aggregate may exceed by far the *coherence* length, the number of molecules over which the excitation is delocalized (see earlier).

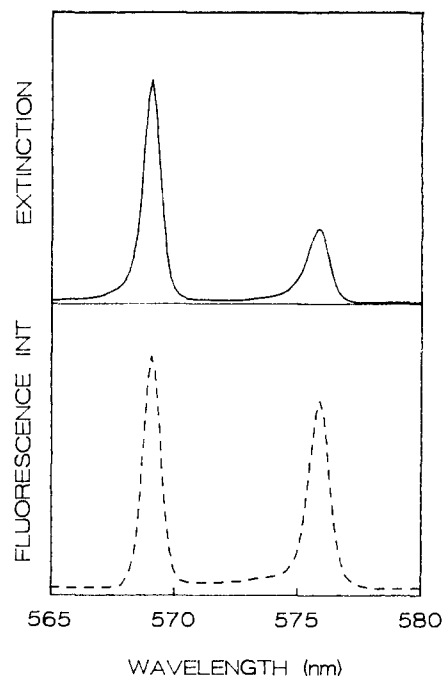


Fig. 1. Zero phonon lines in absorption (upper panel) and emission (lower panel) of different aggregates of pseudoisocyanine-bromide in an ethylene glycol/water glass at 1.5 K.

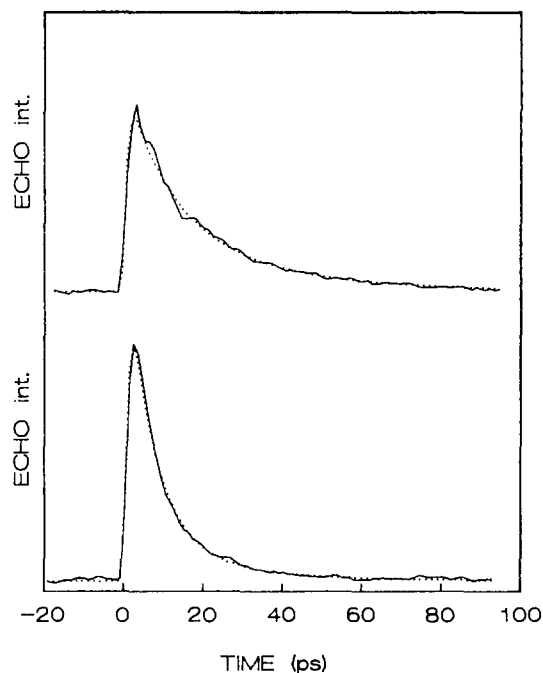


Fig. 2. Decays of the accumulated photon echo obtained by stochastic excitation of the origins of aggregates of pseudoisocyanine-bromide; the sample temperature is 1.5 K. The upper trace is obtained from the red site, the lower from the blue site. The dotted lines are fits to a biexponential decay with parameters given in the text.

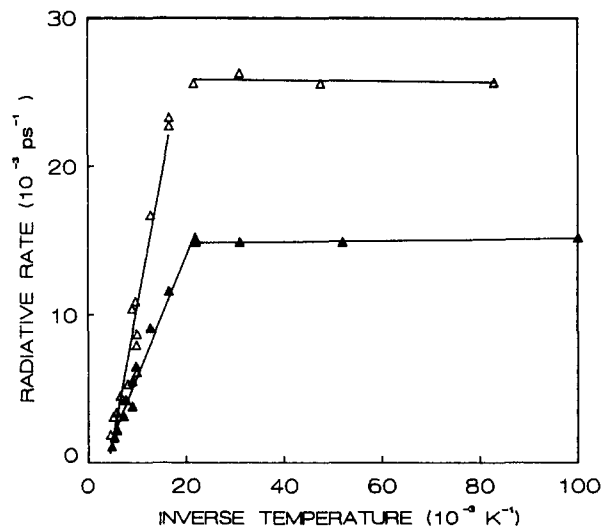


Fig. 3. Plots of the radiative rate constants as a function of the inverse temperature for aggregates of pseudoisocyanine-bromide. For both sites the low temperature fluorescence quantum yield is taken to be 1 (see text). The solid straight lines are a guide to the eye, not theoretical fits. The closed triangles (\blacktriangle) are data points for the red site, the open triangles (\triangle) are data points for the blue site. Note that these data were obtained from fluorescence lifetime and relative fluorescence quantum yield measurements.

Fig. 2 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. 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 transform limited 3 ps excitation pulses are used the decays are also non exponential throughout both bands with the amplitude of the fast component increasing to higher energy. We also note that the same decays are found when the two pulse photon echo is used as a probe. This implies that spectral diffusion does not affect the observed decay of the accumulated photon echo. Fig. 3 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 ($\phi_{\text{fl}}(0)$) for both sites were taken to be 1 at 1.5 K. For $\phi_{\text{fl}}(0) < 1$, the vertical scale needs to be multiplied by $\phi_{\text{fl}}(0)$. 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 for temperatures between 80 and 220 K. The fluorescence lifetimes for the red and blue site at 1.5 K were measured to be 70 and 45 ps, respectively.

4. Discussion

In this presentation we will focus our attention on 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.

To describe the radiative dynamics of the aggregate, Mukamel and coworkers [17,18] employed the superradiance master equation [21] which incorporates the effect of the imaginary and real part of the dipole-dipole coupling on the time dependent operators. 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 processes that compete with the imaginary part of the dipolar coupling that leads to cooperative emission of many molecules on the aggregate. From Spano and Mukamel's paper [18], one may conclude that the incoherently excited fluorescence intensity of a linear aggregate at low temperature, and in the absence of inhomogeneous broadening, at a distance r can be expressed as follows:

$$I_{\text{fl}}(r, t) = Ms(\mathbf{r}) \sum_{k=1}^N \left[\frac{2}{N+1} \right]^2 \cot^4 \left[\frac{\pi k}{2(N+1)} \right] \times \exp[-\epsilon_k^L/k_{\text{B}}T] \exp[-2\Gamma_k^L t], \quad (1)$$

with

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

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

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

where V is the intermolecular dipolar coupling energy, γ the radiative rate constant of a single dye molecule, M a constant and $s(\mathbf{r})$ a directional factor [18].

Eqs. (1) and (3a) show that the $k = 1$ excitonic state attains, for large N , the superradiant lifetime of $(0.81N\gamma)^{-1}$. In our previous article on this subject [12] we have used an enhancement factor N , which is only obtained in the case of 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 found to be perfectly exponential which suggests that emission only arises from the $k = 1$ state. In this case one can easily calculate the number of coherently coupled molecules (N_c) from the equation:

$$N_c = 2\tau_{\text{fl}}\phi_{\text{fl}}\Gamma_{k=1}^L (\cos^2 \alpha)^{-1}, \quad (4)$$

where τ_n is the monomers radiative lifetime, ϕ_n the quantum yield of emission and $\cos^2 \alpha$ a geometrical factor. For the red site we assume ϕ_n to be ≈ 1 [22]; for the blue site it must be closer to 0.5 [23]. With these numbers we calculate N_c to be 130 and 100 for the red and blue site, respectively. Using another result of Spano and Mukamel's paper [18] one can estimate that in the case when the inhomogeneous broadening is taken into account (with $\sigma/V \approx \frac{1}{4}$), N_c can be estimated to be a factor of 5 larger; therefore of the order of 650 for the red and 500 for the blue site. 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, the $k=2$ and $k=3$ may attain about the same radiative rate as the $k=1$ state [18].

We now turn to a discussion of the temperature dependence of the radiative rate of these aggregates. The most appealing interpretation of our results is based on the assumption that the change of radiative lifetime is directly connected to N_c . With this assumption one calculates N_c to change by a factor of 12 between 50 and 220 K, being independent of temperature below 50 K. Fig. 3 further shows that between 50 and 220 K the radiative rate is directly proportional to the inverse temperature, a result obtained earlier by Möbius and Kuhn for a different aggregate [15,16]. In their case, this functional dependence held down to 20 K. The temperature independence of the radiative rate below 50 K can be interpreted as caused by the fact that the aggregates coherence length is limited by off diagonal disorder in the chain. Grad et al. [17] have shown that 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's radiative lifetime is due to a phonon induced modulation process of the frequency difference of transitions at neighbouring molecules on the aggregate. Grad et al. [17] show that in the case when the rate constant associated with this effect ($1/T_2'$) exceeds γ , the superradiant emission becomes quenched. This implies that an alternative interpretation of the measured temperature independence of the radiative lifetime below 50 K, is that in this temperature regime $T_2' \ll \gamma^{-1}$. Currently, however, no theory explicitly accounts for the observed inverse temperature dependence of this dephasing process. Additional experiments need to be performed to probe the extent of excitation delocalization on the aggregate.

Finally we wish to comment upon the measured discrepancy between T_2 and $2T_1$ at low temperature.

We suggest that in the photon echo one coherently excites a number of different k -states on the aggregate. The microscopic dephasing of these states is monitored as a fast non exponential decay in the photon echo. The fluorescence observed, after incoherent excitation, arises from the incoherent decay of the populated k -states.

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