Resonance-Light-Scattering Study and Line-Shape Simulation of the *J* Band

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Line-shape simulations and resonance-light-scattering experiments of the *J* band in aggregates of pseudoisocyanine are reported. It is concluded that the *J* band can be described as a disordered Frenkel-exciton band with states that are pseudolocalized on segments of the aggregate chain. The resonance-light-scattering experiments show that the *homogeneous* dephasing of the excitonic states is dominated by phonon scattering to thermally accessible band states and that excitonic dephasing occurs in the *fast modulation* limit.

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The optical dynamics of excitonic systems with reduced dimensions such as quantum-well structures, one-dimensional polymers, and molecular aggregates has attracted much attention. The prediction[1] that such systems have size-dependent and possibly large optical nonlinearities due to cooperative effects stimulated new research in the area. Recently, it was shown that the low-temperature *radiative* lifetime of "excitons" in both quantum-well structures[2] and molecular aggregates[3,4] can be extremely short because of emission from a dipole-allowed delocalized state. The lifetime of this superradiant emission becomes longer at higher temperature and shows a strong correlation with the homogeneous linewidth of the excitonic transition. This effect can be understood as arising from a decrease of the population of the dipole-allowed state by exciton-phonon scattering.[2,5] While in the case of GaAs/GaAlAs multiple-quantum-well structures the radiative dynamics could be understood on basis of a thermalized excitonic population,[2] for the *J*-aggregate of pseudoisocyanine (PIC) such a description fails.[6] Recently, Spano, Kuklinski, and Mukamel[5] showed that for the *J*-aggregate exciton-phonon coupling needs to be taken into account explicitly, to simulate the observed temperature dependence of the fluorescence decay. Furthermore, for a proper description of the exciton's radiative dynamics use of a non-Markovian master equation was found to be essential. An important prediction of this theory is that for strong electron-phonon coupling, the *effective* number of coupled molecules at $T=0$ saturates for large aggregates. However, the theory does not account for inhomogeneity of the *J* band, which is known to destroy superradiance, even in the absence of phonons.[7] The theory of Spano, Kuklinski, and Mukamel predicts also that phonon-induced scattering produces a *nonthermal* distribution over band states by *k*-selective scattering. These predictions motivated us to begin a thorough investigation of the low-temperature exciton dynamics and analysis of the effect of inhomogeneity on the band structure and radiative decay of the *J*-aggregate.

In this Letter we report results of a line-shape simulation and resonance-light-scattering study of the *J* band. The important conclusions from this work are (1) the *J* band in PIC is best described as a disordered exciton band, (2) superradiance at low temperature is limited by inhomogeneity, (3) exciton dynamics occurs in the *fast modulation* limit, and (4) exciton-phonon scattering proceeds via *all* thermally accessible band states.

The aggregate samples were made as described in Ref. 3, while the resonance-light-scattering (RLS) experiments were performed as reported in Ref. 6. Excitation powers used varied from 2 mW on resonance to 60 mW off resonance focused to a spot size of 0.03 mm^2. Eigenvalue and eigenvector calculations of real symmetrical matrices with Gaussian disorder on the diagonal were performed on a Vax 11/750 computer. The basic programs were taken from Ref. 8. The diagonalization program conserves the oscillator strength and the trace of the matrix to better than 0.01%.

Figure 1 shows the absorption spectrum of the *J*-aggregate at 1.5 K. It has been shown[3] that the two absorption lines at 570.2 and 576.1 nm correspond to the zero-phonon transitions of two structurally different *J*-aggregates, which show similar behavior regarding their optical dynamics.[3,4,6] The RLS experiments were performed on the 576.1-nm transition.

We begin with a discussion of the line-shape simulation of the *J* band. The effective Hamiltonian for a disordered Frenkel-exciton system in the absence of phonons has the following form:[9]

$$H_{\mathrm{ex}}=\sum_n(\langle\varepsilon\rangle+D_n)a_n^\dagger a_n+\sum_{m,n}J_{mn}a_m^\dagger a_n\,. \tag{1}$$

Here the Pauli operator $a^\dagger$ (a) creates (annihilates) an electronic excitation of energy $\langle\varepsilon\rangle+D_n$ at site n. D_n represents the inhomogeneous shift from the average molecular excitation energy $\langle\varepsilon\rangle$; it is assumed to be randomly distributed according to a Gaussian distribution, $P(D_n)\propto\exp(-D_n^2/2D^2)$. J_{mn} stands for the dipolar coupling energy between sites m and n and is scaled to the

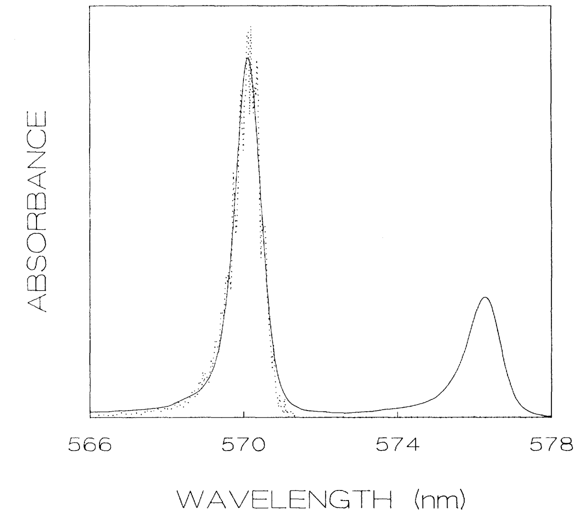

FIG. 1. Absorption spectrum of PIC Br at 1.5 K (——) and the calculated line shape (····) for $D/J_{12}=0.11$, with $J_{12}=-600\ \mathrm{cm}^{-1}$.

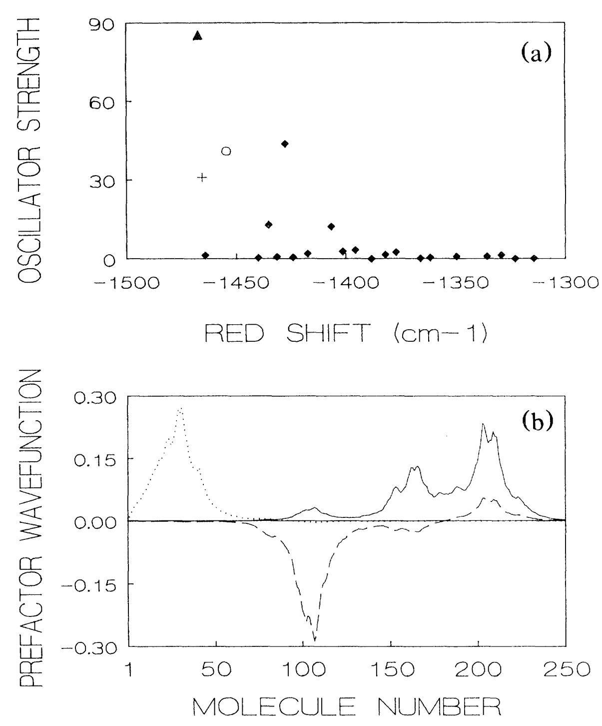

FIG. 2. (a) Eigenvalues and corresponding oscillator strengths at the lower band edge for one chain of 250 molecules with diagonal disorder. (b) Eigenvectors corresponding to states marked in (a): ▲→ ——, ○→ ····, and +→ ---.

nearest-neighbor coupling energy J_{12}, which for PIC has been determined[10] to be about $-600\ \mathrm{cm}^{-1}$. The transition dipole of each eigenstate was calculated from the eigenvectors, whereby the site transition dipole was taken to be parallel to the chain axis. We present here the results of a calculation on aggregates of 250 molecules, taking account of all dipolar couplings on the chain. The dotted curve in Fig. 1 portrays the line shape for $D/J_{12}=0.11$ obtained by adding the frequency-dependent oscillator strengths from 500 chains. Figure 2 shows the oscillator strength and site amplitudes of eigenstates near the bottom of the band from one of the 500 matrices that were diagonalized. The figure shows that only a few states close to the band edge contain appreciable oscillator strength and that these states are *pseudolocalized* on segments of the chain. The localized nature of these excitonic states is further demonstrated by the fact that removal of fifty molecules from either end of the chain or a change in the inhomogeneity of these segments hardly affects the wave functions of the states that are localized at other segments of the chain. Moreover, calculations for $D/J_{12}=0.11$ show that changing the number of molecules from 250 to 100 only slightly affects the results. The conclusion therefore is that the *effective number* of coupled molecules saturates for chain lengths longer than about 100 molecules. Our findings also explain why holes can be burned in the J band. Excitation of pseudolocalized states in the band most likely changes the local disorder. This results in new eigenstates at other frequencies in the J band. The calculations further show that the average oscillator strength per state in the low-energy region is 49 times that of a monomer. The low-temperature fluorescence lifetime in this band is thus predicted to be a factor of 49 shorter than the monomer's radiative lifetime. This prediction is in good agreement with the fluorescence lifetime obtained for the red site but about a factor of 2 too low for the blue site. However, in both cases the line shape of the J bands can be described with about the same D/J_{12} value. This fact demonstrates that the absorption line shape is not sensitive to details of the band structure, which may be crucial to the size of the coherence volume.

We proceed now with a discussion of the RLS spectra of the aggregate. Prior to showing the results we first wish to present some theoretical background. It can be shown that when the optical Bloch equations are used to describe a system's dynamics, the ratio R between the yields of the vibrational fluorescence and Raman scattering equals $2T_1/T_2^*$, independent of frequency detuning.[11] T_1 presents the population relaxation time and T_2^* the pure dephasing time constant of the system. However, experimentally R always decreases when the excitation is moved off resonance. When a non-Markovian master equation is used, which takes into account the finite memory time of the frequency fluctuations, R becomes frequency dependent. If the so-called COP (chronological ordering prescription) non-Markovian master equation is employed for the description of the dynamics, R

becomes[12]

$$R_{\mathrm{nM}}^{\mathrm{COP}} = \frac{2T_1\Delta^2\tau_c}{1+(2\pi\delta)^2\tau_c^2}, \tag{2}$$

where Δ and τ_c are parameters that characterize the correlation function of frequency fluctuations $A(\tau)=\Delta^2\times\exp(-\tau/\tau_c)$, and δ is the frequency detuning from resonance. In the impact limit where $\delta\tau_c \ll 1$, $R_{\mathrm{nM}}^{\mathrm{COP}}$ reduces to R_{M}.

While Eq. (2) was derived for a two-level model, we may also apply it to the aggregate, because a typical Rabi frequency in the experiments is less than the average spacing in the multilevel aggregate system.

Alternatively, one can use the POP (partial ordering prescription) master equation[13] to describe the dynamics. In the limit $\Delta\tau_c \ll 1$ (*vide infra*) use of $R_{\mathrm{nM}}^{\mathrm{POP}}$ for analysis of the RLS spectra yields the same results.

Figure 3 shows the dephasing-induced fluorescence profiles obtained at different temperatures when the J band is excited with a narrow-band laser tuned 30 cm^{-1} below the absorption maximum. The profiles shown have been scaled to the red side of the absorption line shape and do not present actual intensities. First note that the fluorescence observed is at the *blue* side of the excitation wavelength. This emission is not observed at 1.5 K which implies that at this temperature *pure* dephasing processes do not occur. Therefore, the earlier noted discrepancy between the fluorescence and photon-echo lifetime cannot be ascribed to remnant dephasing processes.[4] It can be shown[14] that this "discrepancy" is partially caused by a variation of the oscillator at every position in the J band. Also note in Fig. 3 that with increasing temperature the emission profile embodies a larger fraction of the band. We interpret these results by assuming that the initially excited state is scattered by phonons to other states in the band. When the ratio of a hot-fluorescence profile at temperature T and the one at 77 K is taken, we find that, for every temperature down to 8 K, this ratio is fitted by the Boltzmann expression $\exp[(\omega-\omega_l)(1/77-1/T)/k_B]$. Here $\omega-\omega_l$ is the distance to the laser frequency and k_B is Boltzmann's constant. From this finding we conclude that the emission comes from a *thermalized* excitonic population. Because at 8 K the exciton-phonon scattering time constant is about 150 ps,[3] and much longer than the fluorescence lifetime of 70 ps, we conclude that the cross section for exciton-phonon scattering from the initial state to all

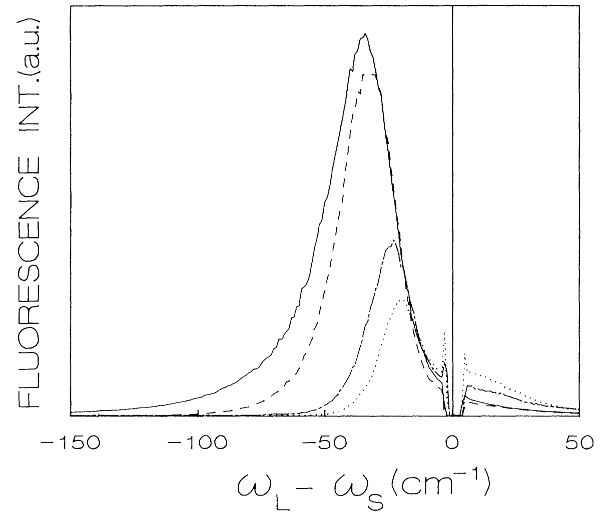

FIG. 3. Dephasing-induced fluorescence profiles of the 576.1-nm transition at 77.5 K (——), 24.4 K (---), 11.4 K (-·-·), and 8.26 K (····). The laser frequency is 30 cm^{-1} below the absorption maximum, at all temperatures.

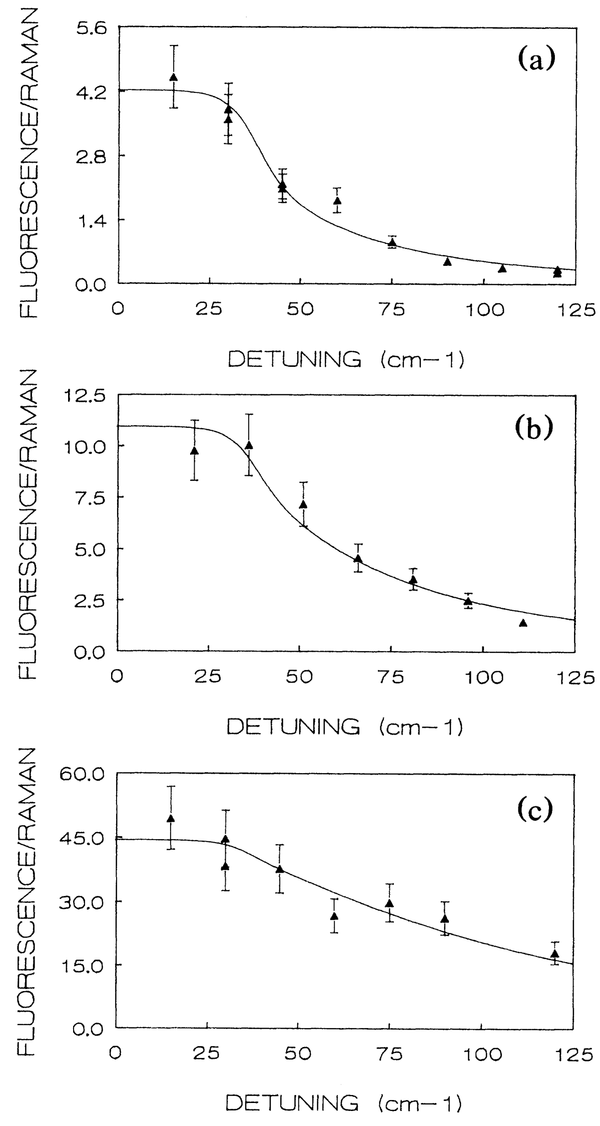

FIG. 4. Detuning dependence of the fluorescence/Raman ratio at (a) 24.4 K, (b) 39.4 K, and (c) 77.5 K. Parameters of the fits are listed in Table I.

other band states is equal. In these circumstances, the population of the final state is determined only by the phonon population at the relevant frequency gap. We therefore conclude that all thermally accessible band states participate in the dephasing process and that a low-frequency doorway state may not exist.[3]

Figure 4 presents the frequency dependence of R at three different temperatures. Qualitatively, the weaker frequency dependence of R at higher temperature is caused by a shorter correlation time of frequency fluctuations. The solid lines through the data points of Fig. 4 are based on Eq. (2) with a T_1 of 70 ps,[4] and best-fit values for Δ and τ_c. The effect of inhomogeneous broadening on the RLS spectra was taken into account by convoluting the product of $R_{\mathrm{nM}}^{\mathrm{POP}}$ and the homogeneous line-shape function, derived from photon-echo experiments, with a Gaussian of 25 cm^{-1} FWHM width. To normalize this quantity the convoluted product was divided by the convolution of the Gaussian and the homogeneous (Lorentzian) line shape. The parameters obtained from the fits to the data are given in Table I.

The first thing to note from Table I is that at all temperatures $\Delta\tau_c \ll 1$, which means that optical dephasing occurs in the fast modulation limit. Table I further shows that Δ is approximately linear with temperature, which suggests that Δ is determined by the population of low-frequency phonons active in the scattering process. It is tempting to interpret τ_c as the average "lifetime" of the exciton-phonon collision complex and Δ as a measure for the coupling strength of this compound state.

In summary, we have shown that the J band in aggregates of pseudoisocyanine can be described as a disordered Frenkel-exciton band. The superradiant states are close to the bottom of the band and delocalized over about 100 molecules. This localization effect is caused by inhomogeneities. It is concluded also that exciton-phonon scattering involves all thermally accessible band states and that the dephasing-induced fluorescence comes from a Boltzmann population of band states. Furthermore, it was found that exciton dephasing occurs in the *fast modulation* limit and that at $T = 0$ no *pure* dephasing processes exist. We conclude that recent theories concerning the temperature dependence of superradiance in aggregates[5,6] are incomplete because they take no account of the system's inhomogeneity, which is crucial to the creation of localized superradiant states in the system.

TABLE I. Parameters of the frequency fluctuation correlation function.

T (K)	τ_c (fs)	Δ (cm^{-1})	$\Delta\tau_c$	Δ/k_BT
24.4	151^{+40}_{-25}	2.7 ± 0.5	0.08 ± 0.02	0.16 ± 0.03
39.4	106 ± 15	4.4 ± 0.9	0.09 ± 0.02	0.16 ± 0.03
77.5	59 ± 10	9.8 ± 2.0	0.11 ± 0.03	0.18 ± 0.04

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