

Temperature-Dependent Superradiant Decay of Excitons in Small Aggregates

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We investigate the effect of phonons on the cooperative radiative decay of excitons in small aggregates. Our microscopic analysis establishes the existence of a temperature-dependent coherence size, provided the exciton dephasing time scale is much shorter than the fluorescence lifetime τ_n . We calculate the temperature dependence of τ_n and use our results to interpret recent photon-echo and fluorescence experiments in strongly coupled J -aggregates of cyanine dye molecules.

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The optical properties of excitons in geometrically confined systems have been a subject of intense investigations in recent years. Much of this interest was stimulated by experiments on systems with reduced dimensionality, such as molecular J -aggregates,¹⁻³ polysilanes,⁴ and semiconductor quantum wells⁵ and quantum dots,⁶ and the possibility that these materials may exhibit enhanced nonlinear susceptibilities.⁷ General confinement effects include size-dependent spectral shifts in the absorption and emission spectra, and ultrafast radiative decay rates, which are well documented in both semiconductor and molecular systems. When the confinement dimensions are smaller than an optical wavelength, these properties are attributed to the $k=0$ excitonic state; in a molecular aggregate the transition dipole moment from the ground state to the $k=0$ exciton scales as $N^{1/2}$, where N is the aggregate size, leading to a cooperative (superradiant) radiative decay rate which scales linearly with N . When phonons are present, and the $k=0$ exciton is no longer an eigenstate, the situation is more complex; intuitively one expects the nuclear motions to partially or completely destroy the intermolecular cooperativity and therefore the superradiant behavior. The temperature-dependent radiative decay rate of excitons in pseudoisocyanine bromide (PIC-Br) J -aggregates was studied by DeBoer and Wiersma, who showed that the fluorescence lifetime is an increasing function of temperature, indicating a progressive destruction of cooperativity.^{1(a)} Similar conclusions were drawn by Itoh, Ikehara, and Iwabuchi^{6(a)} who studied the fluorescence lifetime of excitons in spherical CuCl microcrystallites and by Feldmann *et al.*⁵ who studied the same effect in GaAlAs quantum wells.

These observations may be explained in terms of a temperature-dependent coherence domain, the size of which is determined by the magnitude of exciton-phonon

scattering.^{1-3,5} The radiative decay rate is then proportional to an effective domain size N_{eff} which is smaller than N and decreases as the temperature is increased. Mobius and Kuhn³ were first to establish the existence of coherence domains based on fluorescence-quenching measurements from acceptor impurities adjacent to a J -aggregate monolayer. A semiempirical relation for the variation of N_{eff} with temperature was derived based on kinetic arguments, $N_{\text{eff}}=3000/T(\text{K})$, which was later confirmed in fluorescence-lifetime experiments,^{1,2} in the high-temperature regime ($T > 20\text{--}50$ K). Grad, Hernandez, and Mukamel⁸ have also calculated N_{eff} using the Haken-Strobl model, where the effect of phonons is modeled via a temperature-dependent coherence dephasing rate Γ . When the dephasing rate is larger than the radiative decay rate, N_{eff} is reduced to 1, i.e., the intermolecular coherence (and therefore superradiance) is destroyed. However, DeBoer and Wiersma have found that the low-temperature superradiative lifetime is 40–50 times shorter than the monomer lifetime, even when the coherence dephasing rate Γ (as measured by an accumulated phonon echo) is an order of magnitude larger than the radiative decay rate. This cannot be explained with the Haken-Strobl model; a more microscopic theory, which incorporates the details of exciton-phonon coupling (for acoustic and optical phonons) is developed in this Letter. For infinite aggregates at sufficiently high temperatures our theory agrees with the pioneering work of Mobius and Kuhn. (The present microscopic treatment is more general, holds over the entire range of temperatures, and includes finite-size effects and microscopic details of the exciton-phonon coupling.)

To this end, consider a linear array of N , electronically coupled two-level systems with periodic boundary conditions. The model Hamiltonian, assuming off-diagonal exciton-phonon coupling,⁹ is

$$H = \hbar \sum_{k=0}^{N-1} \left[\omega(k) + i \frac{N}{2} \gamma \delta_{k,0} \right] \hat{B}_k^\dagger \hat{B}_k + \hbar \sum_s \sum_{q=0}^{N-1} \Omega_s(q) \{ \hat{b}_{q,s}^\dagger \hat{b}_{q,s} + \frac{1}{2} \} + \sum_{s,k,q} \frac{F_s(k,q)}{\sqrt{N}} \hat{B}_{k+q}^\dagger \hat{B}_k (\hat{b}_{q,s} + \hat{b}_{-q,s}^\dagger), \quad (1)$$

where \hat{B}_k^\dagger ($\hat{b}_{q,s}^\dagger$) denotes the creation operator of a Frenkel exciton (phonon) with wave vector k (q), and s differentiates between optical and acoustic phonons. The interaction with the electromagnetic field is derived using the superradiant master equation,¹⁰ which predicts that the $k=0$ exciton undergoes exponential coherence decay with a rate $N\gamma/2$,

with a rate $N\gamma/2$, where γ is the monomer decay rate. $\omega(k) = \omega_0 - 2V \cos(2\pi k/N)$ and $\Omega_s(q)$ are the exciton and phonon dispersion relations, respectively, where V is the nearest-neighbor dipole-dipole interaction energy and $\hbar\omega_0$ is the electronic excited-state energy. The sign of V depends on the angle the transition dipole moment makes with the aggregate axis. In J -aggregates V is positive so that the $k=0$ state is at the bottom of the band. In our calculations we assume V is positive.

Reduced equations of motion for the excitonic popula-

$$\begin{aligned} \frac{dG(k,t)}{dt} = & -N\gamma\delta_{k,0}G(k,t) - \frac{2}{N} \sum_q |F(k,q)|^2 \int_0^t \{(1+n_q)\cos[\Omega_+(k,q)(t-t')] + n_q \cos[\Omega_-(k,q)(t-t')]\} \\ & \times \exp\{-(N\gamma/2)[\delta_{k,0} + \delta_{k+q,0}](t-t')\} G(k,t') dt' \\ & + \frac{2}{N} \sum_q |F(k,q)|^2 (1+n_q) \int_0^t \cos[\Omega_-(k,q)(t-t')] \exp\{-(N\gamma/2)[\delta_{k,0} + \delta_{k+q,0}](t-t')\} G(k+q,t') dt' \\ & + \frac{2}{N} \sum_q |F(k,q)|^2 n_q \int_0^t \cos[\Omega_+(k,q)(t-t')] \exp\{-(N\gamma/2)[\delta_{k,0} + \delta_{k+q,0}](t-t')\} G(k+q,t') dt', \quad (2) \end{aligned}$$

where $\Omega_{\pm}(k,q) \equiv \omega(k+q) - \omega(k) \pm \Omega(q)$. We have solved Eq. (2) numerically for aggregates as large as $N=400$, by evaluating the Fourier-Laplace transform of $G(k,t)$ for a discrete set of frequencies, and transforming back via a fast Fourier transform to obtain the time-dependent functions $G(k,t)$. The calculations were performed on a Cray supercomputer and both acoustic- and optical-phonon effects were studied. For a one-dimensional system with a single molecule per unit cell, acoustic phonons correspond to intermolecular vibrations along the chain while the optical phonons correspond to molecular librations. The dispersion relations are $\Omega_{ac}(q) = \Omega_{ac} |\sin(\pi q/N)|$ and $\Omega_{op}(q) = \Omega_{op}$ and the couplings to excitons are

$$\begin{aligned} F_{ac}(k,q) = & F_{ac} \cos[(2\pi/N)(k+q/2)] \\ & \times \sin(\pi q/N) [|\sin(\pi q/N)|]^{-1/2} \end{aligned}$$

and

$$F_{op}(k,q) = F_{op} \cos[(2\pi/N)(k+q/2)] \cos(\pi q/N),$$

for acoustic and optical phonons, respectively.⁹ F_{ac} and F_{op} are obtained from Eqs. 1.37 and 1.38 in Ref. 9.

The time-dependent fluorescence intensity is equal to $N^2\gamma G(0,t)$. When $G(0,t)$ is numerically evaluated, two types of time scales can be distinguished; long time scales representing the smooth decay of the average value of $G(0,t)$, and short time scales which are associated with the rapid oscillations. We have numerically verified that the short time scales are of the same order as the exciton coherence dephasing time (i.e., the inverse of the absorption linewidth Γ). The fluorescence lifetime is associated with the long time scale, and is the quantity of physical interest (fast oscillations in the $k=0$ population may not be fully resolved due to several factors including a finite instrument response, inhomogeneous

broadening of the exciton frequency, and the aggregate size distribution). The two time scales are well separated when the pure exciton dephasing rate Γ is larger than the cooperative radiative rate $N\gamma$, i.e., $\Gamma \gg N\gamma$. In the opposite limit $\Gamma \ll N\gamma$, the $k=0$ exciton decays superradiantly, faster than any nuclear motion.

tion $G(k,t) \equiv \langle \hat{B}_k^\dagger(t) \hat{B}_k(t) \rangle$ are derived starting from the Heisenberg equation for the operator $\hat{B}_k^\dagger(t) \hat{B}_k(t)$ and subsequent higher-order operators. We average operator quantities and truncate the infinite hierarchy of equations via a factorization approximation at the second level of equations, i.e.,

$\langle \hat{B}_{k+q+q'}^\dagger(t) \hat{B}_k(t) \hat{b}_{-q}^\dagger(t) \hat{b}_{q'}(t) \rangle \cong \langle \hat{B}_k^\dagger(t) \hat{B}_k(t) \rangle n_q \delta_{q,-q'}$, where it is assumed that the phonon bath remains in thermal equilibrium, with $n_q = \{\exp[\hbar\Omega(q)/kT] - 1\}^{-1}$. With these approximations we obtain

When $\Gamma \gg N\gamma$, the coarse-grained average of $G(0,t)$, which contains only the long time scale, can be directly evaluated by writing the solution of Eq. (2) in the Laplace space and expanding the self-energy to the first order in the Laplace variable s . We found that the coarse-grained solution is in excellent agreement with the average of the complete numerical solution when $\Gamma \gg N\gamma$, which is assumed in all subsequent calculations.

Since the coarse-grained solution is generally multiexponential, we have defined the fluorescence lifetime τ_{fl} to be the time in which a fraction $1 - e^{-1}$ of the total fluorescence (or total number of photons) has been emitted. Note that this integral definition is generally unequal to the time when the fluorescence decays to $1/e$ of its initial value. Only when the decay is purely exponential do the two definitions coincide. The effective cooperation number N_{eff} is then defined as $N_{eff} \equiv (\gamma\tau_{fl})^{-1}$, so that in a purely superradiant system [$G(0,t) = \exp(-N\gamma t)$] we have $N_{eff} = N$. In Fig. 1(a) we show N_{eff} as a function of aggregate size and acoustic-phonon coupling strength F_{ac} at $T=0$. For weak coupling the system is superradiant, $N_{eff} = N$. Superradiance is destroyed for sufficiently high exciton-phonon coupling ($N_{eff} = 1$) because the crude adiabatic vibronic states are no longer good eigenstates and consequently the oscillator strength is diluted over $k \neq 0$ exciton states. Alternatively, this effect may be viewed as the destruction of intermolecular coherence by the zero-point motion of nuclear vibrations. Coupling to optical

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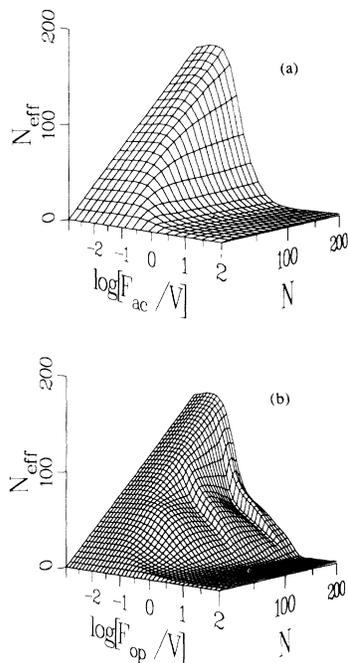


FIG. 1. (a) N_{eff} as a function of N and $\log_{10}(F_{\text{ac}}/V)$, for acoustic phonons with $\Omega_{\text{ac}}=0.01V$. (b) N_{eff} as a function of N and $\log_{10}(F_{\text{op}}/V)$, for optical phonons with $\Omega_{\text{op}}=0.01V$. In both cases $T=0$.

phonons has a similar effect as can be seen in Fig. 1(b). The oscillatory behavior in this figure reflects resonances with the optical-phonon frequency. We should point out that when the Markovian approximation is made in Eq. (2) [$G(0,t)$ is taken out of the integral and the upper time limit is changed to infinity] we obtain an ordinary master equation in k space, which predicts superradiant behavior at $T=0$, independent of the strength of the exciton-phonon coupling. This is because the lowest-energy ($k=0$) exciton is not affected by phonons. The integral (non-Markovian) form of Eq. (2) is therefore essential for the destruction of superradiance at $T=0$.

In Fig. 2(a) we show the dependence of N_{eff} on size and temperature for an aggregate with acoustic phonons. Let us first consider the size dependence at a fixed temperature. The aggregate radiates superradiantly as N increases (e.g., $N_{\text{eff}}=N$) but eventually N_{eff} levels off to a finite value, denoted by $N^*(T)$, which remains constant as N increases. The independence of N_{eff} on size for large aggregates is an important test of our theory. In "infinite" systems such as the monolayers of Ref. 3, the domain size is insensitive to the total number of molecules in the monolayer. We next consider the temperature dependence at a given aggregate size. At low temperatures N_{eff} does not depend on the temperature until a certain threshold temperature is reached, at which point N_{eff} starts to decrease. For very high temperatures, the aggregate lifetime approaches the monomer value ($N_{\text{eff}}=1$), independent of size. The temperature

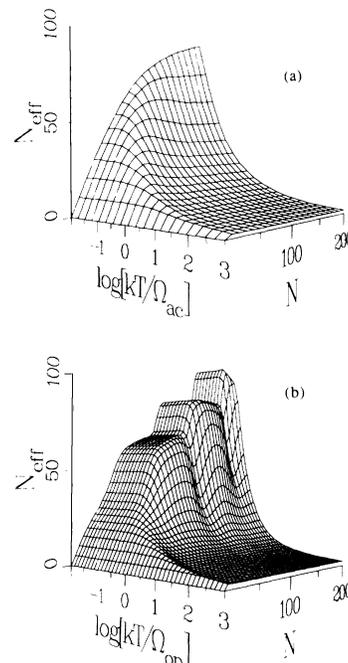


FIG. 2. (a) N_{eff} as a function of N and $\log_{10}(kT/\Omega_{\text{ac}})$, for acoustic phonons with $F_{\text{ac}}=0.05V$ and $\Omega_{\text{ac}}=0.01V$. (b) N_{eff} as a function of N and $\log_{10}(kT/\Omega_{\text{op}})$, for optical phonons with $F_{\text{op}}=0.05V$ and $\Omega_{\text{op}}=0.01V$.

dependence is thermally activated because of the discrete nature of the phonon band structure, and the threshold temperature (and the activation energy) decreases as the aggregate size increases. In large aggregates the acoustic-phonon band structure approaches a continuum with the energy of the lowest level approaching zero. In this size regime, the temperature dependence is therefore governed by a power law.

In Fig. 2(b), N_{eff} is displayed versus size and temperature for an aggregate with a dispersionless optical phonon. The behavior is qualitatively similar to the acoustic case; however, unlike the acoustic-phonon case, the activation temperature persists for all sizes and is approximately given by $T \approx 0.2\Omega_{\text{op}}/k$. Note that N_{eff} has an oscillatory behavior as a function of N and an averaged value N^* should be used to define the temperature-dependent coherence size [the oscillations reflect the exciton-phonon resonances $\Omega_{\pm}(k,q) \cong 0$].

The activated temperature dependence of the fluorescence lifetime induced by optical phonons provides an explanation for the lifetime measurements of PIC-Br made by DeBoer and Wiersma.^{1(a)} They observed a low-temperature superradiant fluorescence lifetime (50–100 times shorter than the monomer value) to be constant in the temperature range 0–50 K. Between 50 and 200 K the lifetime increases roughly linearly with temperature. In addition, the low-temperature dephasing time, as measured by an accumulated photon-echo experiment, is an order of magnitude faster than the

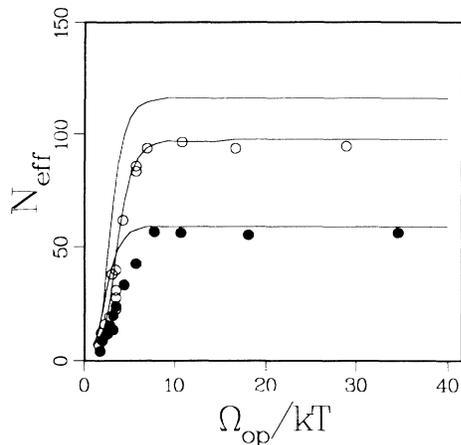


FIG. 3. N_{eff} vs Ω_{op}/kT for aggregates of size $N=75$, 125, and 150 (bottom to top) calculated with the coarse-grain approximation (solid curves). $F_{\text{op}}=0.35V$ and $\Omega_{\text{op}}=0.4V$. The circles represent the experimental measurements of Ref. 1(a); the open circles correspond to the blue site and the solid circles correspond to the red site.

low-temperature superradiative decay rate. In Fig. 3 we show N_{eff} as a function of inverse temperature. The circles represent the experimental results [Fig. 5 in Ref. 1(a)] while the solid curves represent our calculations for various size aggregates with $F_{\text{op}}=0.35V$ and $\Omega_{\text{op}}=0.4V$. The monomer decay rate for PIC-Br, $\gamma=(3.7 \text{ nsec})^{-1}$, and the exciton bandwidth, $4V=2400 \text{ cm}^{-1}$, were used. Our results for the blue (red) site agree quite well with experiment for $N=125$ ($N=75$). Larger values for N and F_{op} also give a satisfactory fit, so that without prior knowledge of one of these parameters we cannot unambiguously determine the other. However, the threshold temperature is relatively stable over a range of N and F_{op} , and this suggests that $\Omega_{\text{op}} \approx 240 \text{ cm}^{-1}$ is the frequency of the optical phonon which is primarily responsible for the destruction of the intermolecular coherence in PIC-Br.

We expect the present results to hold also for Wannier excitons, provided the aggregate size is large compared with the exciton radius. Feldmann *et al.*⁵ have postulated a correlation between the absorption width (Γ) and the radiative lifetime in analyzing the temperature dependence of these quantities for free excitons in quantum wells. Our results support this ansatz since both the phonon contribution to the linewidth and the radiative lifetime increase with temperature.

In summary, we have developed a microscopic theory for the exciton coherence size in small aggregates, valid over the full temperature range. We have found that it is possible to have simultaneously a rapid exciton-phonon scattering rate and a superradiantly enhanced radiative decay rate. In the Haken-Strobl model,⁸ the phonon-

induced coupling between the exciton populations is uniform and proportional to Γ . Therefore, when $\Gamma \gg N\gamma$ the population rapidly becomes uniformly distributed over all N exciton levels and the superradiance is completely destroyed ($N_{\text{eff}}=1$). In our model, the phonon-induced coupling between any two exciton levels depends strongly on the wave vectors of the states involved. A rapid dephasing rate Γ will create an initial, nonuniform, temperature-dependent population distribution where only a subset of the total N levels in k space are significantly populated. The subsequent multiexponential decay of the fluorescence may be interpreted in terms of a time-dependent spatial correlation length, defined as the Fourier transform of the k -space level distribution function $f(k)$. In the limit of high temperature, $f(k)$ is uniform which implies that the spatial correlation length is restricted to a single molecule, yielding the monomer radiation rate. When exciton-phonon coupling is negligible, $f(k)$ is a δ function and the correlation length extends over the entire aggregate, resulting in superradiance.

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