Superradiance in molecular aggregates

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Using a reduced equation of motion for the density matrix which accounts for spontaneous emission and superradiance, we analyze the fluorescence and transient grating (TG) decays from a dilute, optically thin distribution of molecular aggregates. We find that the fluorescence is a limited form of superradiance, where cooperativity is restricted to the number N of two level systems which make up the aggregate. The dependence of the linear aggregate decay rate on the amount of inhomogeneous broadening, which is randomly distributed according to Gaussian line shape of width $(1/e)2\sigma$, is calculated. It is shown that σ must be comparable in magnitude to the nearest neighbor dipole–dipole coupling V and not the superradiant decay rate, in order to quench the superradiance.

I. INTRODUCTION

The study of various types of mesoscopic structures, from small semiconductor "quantum dots" to molecular clusters is an area of intense current interest. From a practical viewpoint, these structures, which have highly size-dependent electronic properties, offer an additional degree of freedom and control in the synthesis of novel electronic devices. They are also of great scientific concern, as entities exhibiting properties which are between those of an isolated molecule and the bulk crystal. In simple molecular aggregates the electron and hole formed upon optical excitation are tightly bound on the same molecule and form a Frenkel exciton. In typical semiconductor aggregates the electron and hole are more loosely bound and form a Wannier exciton with a large radius (50–100 Å). It has been shown recently that systems with spatially confined excitations such as quantum well structures or microcrystallites may show interesting nonlinear optical properties.[1–5] Dramatic size effects have been observed in semiconductor quantum dots such as 100 Å CdS particles and it has been argued that molecular and semiconductor aggregates may exhibit enhanced giant nonlinear optical susceptibilities due to the cooperativity in the radiation–matter interaction.[3]

The optical properties of molecular aggregates have been studied in molecular beams,[6] in solution[7] and on metal or semiconductor surfaces.[7,8] In this paper, we are specifically concerned with the optical properties of small J aggregates of dye molecules.[9] These are formed when certain dye molecules, such as pseudoisocyanine (PIC), are cooled in solution at a sufficiently high concentration. The appearance of a red-shifted, narrow band (the "J" band) in the absorption spectrum, first observed by Scheibe[10] and Jelly,[11] indicates the existence of dye aggregates. Wiersma and co-workers[12] have recently conducted nonlinear optical studies (hole burning and accumulated photon echo) on several dye aggregates. They found evidence that in strongly coupled J aggregates the electronic excitation is delocalized, whereas weakly coupled aggregates did not show J aggregation and have the signature of excitation trapping and polaron formation. Other evidence for strong electron-phonon coupling in

these systems comes from the analysis of the temperature dependence of the absorption line shape. Most theoretical treatments of the aggregate optical properties have dealt with details of the J-band line shape and have included molecular electronic interactions as well as phonons.[13–18] Here, we develop a theory describing time-resolved fluorescence and transient grating (TG) experiments at low temperature, neglecting the influence of phonons, but retaining a static distribution of inhomogeneous broadening. Knapp[19] has presented a theory for the J-aggregate absorption spectrum from such a system (electronic coupling and static inhomogeneous broadening only) but did not consider spontaneous emission and superradiant effects. We consider a system of interacting two-level systems (TLS) using the Lehmberg density matrix master equation,[20] which describes general superradiance. We show that both the fluorescence and TG decay resulting from low power excitation pulses can be described by the linearized Lehmberg equation. In this level of approximation our approach is similar to that of Devoe[21] and more recently of Grad et al.[18] using an effective Hamiltonian method, and Keller and Bustamante[22] which treats each molecule as a linear harmonic dipole oscillator interacting with its neighbors through the classical dipole electric field. However, the Lehmberg equation, allows us to treat higher nonlinear phenomena and calculate, for example, nonlinear susceptibilities. Unlike the above mentioned theories it also accounts for intermolecular correlations which arise, for example, in superfluorescence.[23–28] We demonstrate that the fluorescence (observed at right angles from the excitation pulse) from M aggregates of N coupled monomers is, indeed, a superradiant process, since the initial intensity is proportional to N^2 and the subsequent decay is N times faster than the single monomer radiative decay. This differs from the conventional definition of superradiance which is a result of full cooperation of *all* (MN) molecules in the sample. We refer to the former example as *microscopic* superradiance and the latter as *macroscopic* superradiance. In general both types of superradiance are operative in an optically dense collection of molecular aggregates. In a sample which is many wavelengths long in the direction of the exciting laser pulse (z axis), the macroscopic superradiance will be restricted to a narrow emission cone in the forward direction centered along the z axis.[24] However, the micro-

scopic superradiance, since it originates from the coopera-
tion of molecules over the length scale of a single aggregate,
is not highly directional and can be observed at right angles
to the z axis. More importantly, the macroscopic superra-
diance directly competes with dephasing caused by an inho-
mogeneous distribution of molecular transition frequencies,
and can be quenched if the inhomogeneous dephasing time,
T_2^* is much smaller than the macroscopic superradiant time
τ_R. This condition was shown by Hartmann[25] to imply an
optically thin sample. Conversely, the microscopic superra-
diance (aggregate fluorescence) can still be fully operative
in an optically thin sample; in a one dimensional aggregate
we show that the necessary condition is that the nearest
neighbor intermolecular coupling V be much larger than 1/
T_2^*.

To date, an accurate experimental determination of the
approximate J-aggregate size is lacking. Several attempts
based on absorption spectroscopy[19,29] and excited state life-
time measurements[12,30-32] have produced estimates of N
ranging from about ten to tens of thousands. Based on the
results of our analysis, we suggest the transient grating ex-
periment as a more accurate method for determining N.
When interaggregate interactions are neglected, the TG de-
cay is directly related to the decay of the overall excited state
population,[33] which at low temperature, we show to be a
result of (microscopic) superradiance. This differs from the
situation in a pure crystal where excitation transfer due to
dipole–dipole coupling also contributes to the grating de-
cay.[33-35] The TG experiment is superior to a fluorescence
measurement because the TG signal is coherent and direc-
tional, making its detection easier.

The paper is divided into six sections. In Sec. II the den-
sity matrix equation of motion is presented and in Sec. III,
both the fluorescence and TG observables are calculated
based on a second order solution (in excitation pulse area).
In Sec. IV we discuss small aggregate fluorescence and TG
response, trying to remain as general as possible. In the fol-
lowing section we specifically deal with one dimensional ag-
gregates and calculate the effect of inhomogeneous broaden-
ing on the lifetimes using second order perturbation theory.
For higher degrees of broadening we resort to numerical
computations. An approximate "universal" curve is ob-
tained which allows us to predict the fluorescence or TG
lifetime given the aggregate size *and* the amount of inhomo-
geneous broadening. Recent estimates of the size of PIC ag-
gregates (from lifetime measurements) do not consider in-
homogeneous broadening.[12] When this broadening is
included we find that the actual size may be substantially
larger. Finally, we summarize our findings in the last sec-
tion.

II. REDUCED EQUATIONS OF MOTION

Our model consists of a low temperature macroscopic
"solution" (glass) of M molecular aggregates, each com-
posed of N molecules having two electronic states—a ground
state and the first excited state. There are thus MN total
molecules. The two states are assumed to possess no perma-
nent electric dipole, but transitions between them are electric
dipole allowed. Since the system is at low temperature,
phonon interactions will not be important; however, we do
allow for a static inhomogeneous distribution of two-level
transition frequencies. The system we are describing most
closely resembles one investigated by De Boer et al.[12] con-
sisting of PIC Br in a glycol/water glass at 1.5 K.

Molecular interaction in the above picture is restricted
to electromagnetic coupling, including dipole–dipole cou-
pling and radiative coupling, which is strongest between
molecules on a common aggregate. We are essentially in the
realm of superradiance,[20,23-28] which can be described by a
reduced Heisenberg equation of motion for a general molec-
ular operator Q first derived by Lehmberg.[20] The analogous
interaction picture equation of motion for the molecular
density matrix in the rotating frame at the line center fre-
quency ω_0 is

$$
\begin{aligned}
\frac{d\rho(t)}{dt} = &\sum_{n=1}^{MN} i\Delta_n \left[\rho(t), B_n^+ B_n\right] + \sum_{m,n=1}^{MN} i\Omega_{mn} \left[\rho(t), B_m^+ B_n\right] \\
&+ \sum_{m,n=1}^{MN} \gamma_{mn}\left[B_m \rho(t) B_n^+ - \frac{1}{2}(B_m^+ B_n \rho(t) \right.\\
&+ \rho(t) B_m^+ B_n) \bigg] \\
&+ i\frac{\mu}{2\hbar} E_0(t) \sum_{n=1}^{MN} \left\{ [\rho(t), B_n^+] e^{i\mathbf{k}\cdot\mathbf{r}_n} \right. \\
&+ [\rho(t), B_n] e^{-i\mathbf{k}\cdot\mathbf{r}_n} \bigg\},
\end{aligned}
\tag{1}
$$

where B_m^+ and B_m are two-level fermion creation and anni-
hilation operators, respectively (identical to the spin-1/2
raising and lowering operators in NMR), obeying the fol-
lowing anticommutation rule,

$$
\{B_m^+, B_n\} = \delta_{mn} + 2B_m^+ B_n(1 - \delta_{mn}).
\tag{2}
$$

The resonant offset for molecule "m" is given by,
$\Delta_m = \omega_m - \omega_0$, and Ω_{mn} and γ_{mn} are the real and imagi-
nary parts of the intermolecular coupling, respectively, and
are responsible for excitation transfer and damping. The γ_{mn}
are solely responsible for the overall radiative damping, in-
cluding spontaneous emission and superradiance. The ex-
plicit forms are[20,28]

$$
\Omega_{mn} = \frac{3\gamma}{4}\left\{ [\cos^2\theta_{mn} - 1]\frac{\cos(kr_{mn})}{kr_{mn}} + [1 - 3\cos^2\theta_{mn}]\left[\frac{\sin(kr_{mn})}{(kr_{mn})^2} + \frac{\cos(kr_{mn})}{(kr_{mn})^3}\right]\right\} \quad m \neq n,
$$

$$
\Omega_{mn} = 0 \quad m = n,
\tag{3a}
$$

and

$$
\gamma_{mn} = \frac{3\gamma}{2}\left\{ [1 - \cos^2\theta_{mn}]\frac{\sin(kr_{mn})}{kr_{mn}} + [1 - 3\cos^2\theta_{mn}]\left[\frac{\cos(kr_{mn})}{(kr_{mn})^2} - \frac{\sin(kr_{mn})}{(kr_{mn})^3}\right]\right\},
\tag{3b}
$$

where $k = \omega_0/c$, r_{mn} is the distance between molecule m and molecule n and the transition dipole moment is $\mathbf{p} = \mu\mathbf{i}$. θ_{mn} is the angle between $\mathbf{r}_{mn}$ and $\mathbf{p}$. We assume that $\mathbf{p}$ is the same for all molecules, i.e., all transition moments are parallel. In the small aggregate limit, the condition $kr_{mn} \approx 0$ results in $\gamma_{mn} \approx \gamma$, independent of θ_{mn} and $\Omega_{mn} \approx V_{mn}$ (for $3\cos^2\theta - 1 \neq 0$) for m,n on a single aggregate. The Lamb shift Ω_{mm} is set equal to zero since the actual value, which is identical for all molecules, can be absorbed into the definition of ω_0.

The last term in Eq. (1) contains the classical external electric field of the pulse or pulses in the experiment and is given by

$$E(\mathbf{r},t) = E_0(t)e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_0 t)} + C.C, \tag{4}$$

where $E_0(t)$ is the pulse envelope, $\mathbf{k}$ is the wave vector, and we assume the central frequency is tuned to the molecular transition frequency ω_0.

Equation (1) is the general equation of motion or master equation for the molecular density matrix. We should point out that the derivation of Eq. (1) is based on a Markovian approximation which is valid when the distance between two cooperating molecules r_{mn} is not greater than a certain maximum distance $L = \Delta t/c$, where Δt is the time scale over which significant molecular de-excitation occurs. In other words, any two molecules must be close enough to "see" each other well within the time scale of the decay. In order to describe the response of a molecular system to a pulse sequence (a single pulse for fluorescence and three pulses for the transient grating experiment) we need to solve Eq. (1) in two regimes (I) during the pulsed electric field and (II) subsequent evolution in the absence of the pulse(s). For simplicity we assume a square pulse envelope:

$$\begin{aligned} E_0(t) &= E_0 \quad 0 < t < t_p \\ &= 0 \quad \text{all other times,} \end{aligned} \tag{5}$$

where t_p is the pulse width. We also assume the electric field is sufficiently large so that the remaining terms in Eq. (1) can be ignored during the short time of interaction t_p. Specifically, the electric field satisfies

$$(\mu E_0/\hbar) \gg \Omega_{mn}, \gamma_{mn}, \Delta\omega_m \tag{6}$$

and its duration t_p obeys

$$t_p \ll \Delta\omega_m^{-1}, \Omega_{mn}^{-1}, (N\gamma_{mn})^{-1}. \tag{7}$$

Under these conditions Eq. (1) reduces to the usual on-resonant Bloch equations without damping, i.e.,

$$\frac{d\rho(t)}{dt} = -i\frac{\mu}{2\hbar}E_0 \sum_{n=1}^{MN} [B_n^+ + B_n, \rho(t)], \tag{8}$$

where we have redefined B_n^+ and B_n to include the phase factors e^{ikz_n} and e^{-ikz_n} respectively ($\mathbf{k}\cdot\mathbf{r}_n = kz_n$). Equation (8) has the well-known solution

$$\rho(t_p) \equiv \rho(0) = e^{-i\theta\Sigma_{n=1}^{MN}(B_n^+ + B_n)}\rho(-\infty)e^{i\theta\Sigma_{n=1}^{MN}(B_n^+ + B_n)}, \tag{9}$$

where $\theta = (\mu E_0/2\hbar)t_p$ is the pulse area and $\rho(-\infty)$ is the steady-state equilibrium density matrix existing prior to the arrival of the pulse. Notice that the form of the solution preserves the factorability property of the density matrix,

i.e., if $\rho(-\infty) = \rho_1(-\infty)\rho_2(-\infty)\cdots\rho_{MN}(-\infty)$ then the same is true of $\rho(0)$.

In region II the external electric field has gone to zero and we retain all terms in Eq. (1) but the last one. Unlike in region I the solution is now a very formidable problem. Consider, for example, the equation of motion for the expectation values of the polarization at site m, $\mu\langle B_m^+\rangle = \mu \, \mathrm{Tr}[\rho(t)B_m^+]$. Using Eq. (1) this is

$$\begin{aligned} \frac{d\langle B_m^+\rangle}{dt} &= -i\Delta\omega_m \langle B_m^+\rangle \\ &+ \sum_{n=1}^{MN} (i\Omega_{mn} + \gamma_{mn}/2)\langle B_n^+ B_m^+ B_m \\ &- B_n^+ B_m B_m^+ \rangle \exp[ik(z_m - z_n)]. \end{aligned} \tag{10}$$

The evolution of the single body operator depends on two-body operators: in general, a whole hierarchy of equations, ultimately involving the MN-body operators, must be solved to obtain $\langle B_m^+\rangle$. The number of such equations is equal to $2^{MN} \times 2^{MN}$—the total number of reduced density matrix elements. Unlike the solution in region I, molecular correlations do develop and the density matrix is not factorable. However, if the pulse area is small, Eq. (1) will preserve the factorization property. This semiclassical approximation, which will be described in the following section, allows the many body expectation values to be factored into the product of single body expectation values, truncating the hierarchy and reducing the number of equations to N.

III. THE SEMICLASSICAL APPROXIMATION

In this section we develop a closed set of equations of motion which are valid to third order in the excitation pulse area and allows us to calculate the expectation values of the operators B_m^+, and $B_m^+ B_n$. These are needed to evaluate the absorption, system energy, and fluorescence intensity (as we shall see). We show that $\langle B_m^+ B_n\rangle = \langle B_m^+\rangle\langle B_n\rangle + O(\theta^4)$. This is done by first demonstrating that this relation is exact immediately after excitation when $m \neq n$ and correct to fourth order in θ when $m = n$, and then by showing that $\langle B_m^+ B_n\rangle$ and $\langle B_m^+\rangle\langle B_n\rangle$ satisfy the same evolution equation. In this approximation $\langle B_m^+\rangle$ and $\langle B_m\rangle$ are the only relevant dynamical variables. The system is thus equivalent to a set of coupled Drude oscillators, which provides a simple semiclassical interpretation for its radiative dynamics.

In what follows, we are concerned with the dynamics of MN interacting molecules (a system of M, N-mer aggregates). In the fluorescence experiment we expand the density matrix in powers of $\theta = \theta_p$, the excitation pulse area. In the transient grating experiment, two time-coincident but noncollinear pulses with areas θ_1 and θ_2, create a spatial grating in the effective pulse area so that an aggregate at site m (and center of mass $\mathbf{r}_m$) "sees" a pulse with area $\theta = 2\cos[(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}]\theta_p$ (if $\theta_1 = \theta_2 \equiv \theta_p$; $\mathbf{k}_1$ and $\mathbf{k}_2$ are the pulse wave vectors). We therefore start by expanding the density matrix immediately after interaction with an on resonant pump pulse of area θ. Before arrival of the pulse, all molecules are in the ground state. The initial density matrix is

$$\rho_0 = \rho(-\infty) = \prod_{m=1}^{MN} B_m B_m^+ \equiv |0\rangle\langle 0|, \qquad (11)$$

where the *ket* $|0\rangle$ denotes the ground state, $|0\rangle \equiv |0_1 0_2 \cdots 0_{MN}\rangle$. The effect of the short excitation pulse is given by Eq. (9), which gives for the density matrix immediately after the pulse $\rho(0)$

$$\rho(0) = \prod_{m=1}^{MN} \left\{ \cos^2\frac{\theta}{2} B_m B_m^+ + \sin^2\frac{\theta}{2} B_m^+ B_m \right.$$
$$\left. + (i/2)\sin\theta(B_m^+ - B_m) \right\}. \qquad (12)$$

Expanding Eq. (12) in powers of θ gives

$$\rho(0) = (1 - \theta^2/2)\rho_0 + i\theta/2 \left\{ \sum_{m=1}^{MN} B_m^+ \rho_0 - \sum_{m=1}^{MN} \rho_0 B_m \right\}$$
$$+ \theta^2/4 \left\{ \sum_{mn=1}^{MN} B_m^+ \rho_0 B_n \right.$$
$$\left. - \sum_{mn=1}^{MN} B_m^+ B_n^+ \rho_0 - \sum_{mn=1}^{MN} \rho_0 B_m B_n \right\} + O(\theta^3). \qquad (13)$$

The density matrix at *any* time can be represented to second order in θ by

$$\rho(t) = c_0\rho_0 + \sum_{i=1}^{5} \sum_{m,n=1}^{MN} c_i^{mn} A_i^{mn}, \qquad (14)$$

where

$$A_0 = \rho_0, \qquad (15)$$
$$A_1^{mn} = \delta_{mn} B_m^+ \rho_0,$$
$$A_2^{mn} = \delta_{mn}\rho_0 B_m,$$
$$A_3^{mn} = B_m^+ \rho_0 B_n,$$
$$A_4^{mn} = B_m^+ B_n^+ \rho_0,$$
$$A_5^{mn} = \rho_0 B_m B_n.$$

Altogether expansion (14) consists of $3(MN)^2 + 2MN + 1$ operators and an equal number of coefficients c. The coefficients can be obtained from a knowledge of the expectation values of $3(MN)^2 + 2MN + 1$ independent operators, which we choose to be the unit operator and all linear and bilinear products of B_m^+, B_n^+ and their Hermitian conjugates. We therefore have

$$c_0(t) = 1 - \sum_{n=1}^{MN} \langle B_n^+(t)B_n(t) \rangle, \qquad (16)$$
$$c_1^{mm}(t) = \langle B_m(t) \rangle,$$
$$c_2^{mm}(t) = \langle B_m^+(t) \rangle,$$
$$c_3^{mn}(t) = \langle B_m^+ B_n(t) \rangle,$$
$$c_4^{mn}(t) = \langle B_m(t)B_n(t) \rangle,$$
$$c_5^{mn}(t) = \langle B_m^+(t)B_n^+(t) \rangle,$$

where the expectation value of operator O is given by,

$$\langle O(t) \rangle = \mathrm{Tr}[O\rho(t)] \qquad (17)$$

using $\rho(t)$ from Eq. (14). The evolution equations for $\langle B_m^+(t) \rangle$ and $\langle B_m^+(t)B_n(t) \rangle$ are found by multiplying Eq. (1) by B_m^+ and $B_m^+ B_n$ and taking the trace [using $\rho(t)$ from Eq. (14)]

$$\frac{d\langle B_m^+(t) \rangle}{dt} = i\Delta_m \langle B_m^+(t) \rangle + \sum_{n=1}^{MN}(i\Omega_{mn} - \gamma_{mn}/2)$$
$$\times \langle B_n^+(t) \rangle e^{ik(z_m - z_n)}, \qquad (18a)$$

$$\frac{d\langle B_m^+(t)B_n(t) \rangle}{dt}$$
$$= i(\Delta_m - \Delta_n)\langle B_m^+(t)B_n(t) \rangle$$
$$+ \sum_{m'=1}^{MN}(i\Omega_{mm'} - \gamma_{mm'}/2)\langle B_{m'}^+(t)B_n(t) \rangle$$
$$\times e^{ik(z_m - z_{m'})}$$
$$+ \sum_{n'=1}^{MN}(-i\Omega_{nn'} - \gamma_{nn'}/2)\langle B_m^+(t)B_{n'}(t) \rangle$$
$$\times e^{-ik(z_n - z_{n'})} \qquad (18b)$$

with $\langle B_m(t) \rangle = \langle B_m^+(t) \rangle^*$. [If the exact density matrix instead of Eq. (14) was used Eq. (18a) and (18b) would contain third and fourth order corrections in θ, respectively.] From the initial conditions in Eq. (12) we have

$$\langle B_m^+(0) \rangle = -i(\theta/2), \qquad (19a)$$
$$\langle B_m(0) \rangle = i(\theta/2), \qquad (19b)$$
$$\langle B_m^+(0)B_n(0) \rangle = \theta^2/4, \qquad (19c)$$

so that immediately after excitation,

$$\langle B_m^+(0)B_n(0) \rangle = \langle B_m^+(0) \rangle\langle B_n(0) \rangle. \qquad (20)$$

By comparing with Eq. (18b) it is seen that the product $\langle B_m^+(t) \rangle\langle B_n(t) \rangle$ obeys exactly the same equation of motion as $\langle B_m^+(t)B_n(t) \rangle$

$$\frac{d\langle B_m^+(t) \rangle\langle B_n(t) \rangle}{dt}$$
$$= i(\Delta_m - \Delta_n)\langle B_m^+(t) \rangle\langle B_n(t) \rangle$$
$$+ \sum_{m'=1}^{MN}(i\Omega_{mm'} - \gamma_{mm'}/2)\langle B_{m'}^+(t) \rangle\langle B_n(t) \rangle$$
$$\times e^{ik(z_m - z_{m'})}$$
$$+ \sum_{n'=1}^{MN}(-i\Omega_{nn'} - \gamma_{nn'}/2)\langle B_m^+(t) \rangle\langle B_{n'}(t) \rangle$$
$$\times e^{-ik(z_n - z_{n'})}. \qquad (21)$$

Therefore, we finally arrive at

$$\langle B_m^+(t)B_n(t) \rangle = \langle B_m^+(t) \rangle\langle B_n(t) \rangle. \qquad (22)$$

Using the complete density matrix instead of Eq. (14) reveals a fourth order correction, $O(\theta^4)$, to the last expression. An immediate consequence of this relation is that the excited state population at site m is given by $\langle B_m^+(t)B_m(t) \rangle$ which is equal to $|\langle B_m^+(t) \rangle|^2$ so that only the polarization expectation value, which can be solved directly from Eq. (18a), need be calculated.

We now present the fluorescence and transient grating observables from a general distribution of MN interacting two-level systems. The quantum mechanical intensity as measured by a detector placed at a distance $R \gg r_{mn}$ for the radiation in unit direction $\mathbf{R}$ is given by[20,36]

$$I(\mathbf{R},t)$$
$$= w(\mathbf{R}) \sum_{m,n=1}^{MN} \langle B_m^+(t)B_n(t) \rangle\exp[-ik(z_m - z_n)]$$
$$\times \exp[ik\,\mathbf{R}\cdot(\mathbf{r}_m - \mathbf{r}_n)]$$

$$= w(\mathbf{R}) \sum_{m,n=1}^{MN} \langle B_m^+ (t) \rangle \langle B_n (t) \rangle \exp[-ik(z_m - z_n)]$$

$$\times \exp[ik\mathbf{R}\cdot(\mathbf{r}_m - \mathbf{r}_n)], \qquad (23)$$

where $w(\mathbf{R}) = (3\gamma/8\pi)(1 - (\hat{\mathbf{R}}\cdot\hat{\mathbf{p}})^2]$ is the number of photons/s per unit sterradian emitted in the unit direction $\hat{\mathbf{R}}$ for an oscillating dipole of magnitude μ (we continue to assume parallel dipole moments) and unit direction $\hat{\mathbf{p}}$. Equation (23) is basically the far-field solution of the Maxwell equations for a system of point dipole oscillators.[37] The second equality follows from the semiclassical approximation.

We assume the excitation pulse has a $\mathbf{k}$ vector in the direction $\hat{\mathbf{z}}$. When $\hat{\mathbf{R}} = \hat{\mathbf{y}}$ the system fluorescence is measured. For a *uniform* and dilute distribution of absorbers (with dipole m orginally excited with the phase $\exp[ikz_m]$) the terms in Eq. (23) with $m \neq n$ will destructively interfere and contribute a negligible amount to the fluorescence.[40] The MN terms with $m = n$ do not have a phase factor and therefore are the main contributors to the fluorescence intensity. In this case the fluorescence directly probes the excited state population. However, for a dilute, uniform distribution of small aggregates the same arguments reveal that the main contribution to the signal comes from terms with m and n belonging to a common aggregate. Cross terms with $m \neq n$ can now contribute; for an aggregate consisting of N absorbers these terms outnumber the population terms $(m = n)$ by N^2: N. Therefore, for a distribution of aggregates, the fluorescence does not directly measure the excited state population.

When $\hat{\mathbf{R}} = \hat{\mathbf{z}}$ the free induction decay or (macroscopic) superradiant pulse is measured. The $(MN)^2$ terms with $m \neq n$ will be the main contributors since the inherent phase factor created by the initial pulse, $\exp[-ik(z_m - z_n)]$ now exactly cancels the second phase factor in the observable. If the subsequent evolution is dominated by inhomogeneous dephasing the emission is referred to as a free induction decay (FID); if it is dominated by cooperative radiative damping it is referred to as (macroscopic) superradiance.[27]

It is convenient to divide the total emitted intensity $I(\mathbf{R},t)$ into two portions; the fluorescence intensity and the macroscopic superradiant intensity,

$$I(\mathbf{R},t) \equiv I_{FL}(\mathbf{R},t) + I_{MS}(\mathbf{R},t) \qquad (24)$$

The fluorescence observable, which is our main concern, is given by

$$I_{FL}(\mathbf{R},t) = w(\mathbf{R}) \sum_{m,n=1}^{MN} \langle B_m^+ (t) \rangle \langle B_n (t) \rangle \zeta_{mn}, \qquad (25)$$

where $\zeta_{mn} = 1$ if m,n belong to the same aggregate and $\zeta_{mn} = 0$ otherwise. The phase factor is no longer necessary since the aggregates are much smaller than a wavelength of the emitted light. The highly directional macroscopic superradiance $I_{MS}(\mathbf{R},t)$, defined in Eq. (24), consists of the remaining, more numerous interaggregate terms. In Appendix A we show that radiative decay is mainly channeled through the fluorescence and not the macroscopic superradiance if the optical density is much smaller than unity.

In a transient grating experiment the system is excited with a pair of simultaneous pulses with wave vectors, $\mathbf{k}_1$ and $\mathbf{k}_2$ which create an excitation grating of the form

$\cos[(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}]$. After a variable delay, a probe pulse with wave vector $\mathbf{k}_3$ is scattered off the grating, in the direction $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$, and its intensity is measured as a function of the delay. It can be shown that in the absence of excitation transfer, the decay is a direct measure of the square of the excited state population[33]

$$I_{TG}(\mathbf{R},t) = S(\mathbf{R}) \left| \sum_{n=1}^{MN} \langle B_n^+ B_n (t) \rangle \right|^2$$

$$= S(\mathbf{R}) \left| \sum_{n=1}^{MN} \langle B_n^+ (t) \rangle \langle B_n (t) \rangle \right|^2, \qquad (26)$$

where $S(\mathbf{R})$ is a spatially dependent factor which peaks in a direction $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$ and the second equality is a result of the semiclassical approximation. The mechanism for the decay of this signal is therefore inherently different from the decay in a pure crystal[34,35] which is largely dependent on excitation transfer. The transient grating decay can be simply related to the spatially integrated intensity [Eq. (24)]. From Eq. (A10) in Appendix A we have the relation

$$W(t) = W(0) - \int_0^t dt \int \int d^2\mathbf{R}\, I(\mathbf{R},t), \qquad (27)$$

where $W(t)$ is the total excited state population in units of photon number, given by Eq. (A8). The transient grating is then

$$I_{TG}(\mathbf{R},t) = S(\mathbf{R}) \left| W(0) - \int_0^t dt \int \int d^2\mathbf{R}\, I(\mathbf{R},t) \right|^2. \qquad (28)$$

For an optically thin distribution of small aggregates we show in Appendix A that $I(\mathbf{R},t)$ can be replaced by $I_{FL}(\mathbf{R},t)$ yielding a simple relationship between I_{TG} and I_{FL}.

IV. THE FLUORESCENCE AND TG SIGNALS

In this section we discuss some general properties of small aggregates based on the solution of Eq. (18a). We begin by evaluating the polarization eigenmodes of aggregates satisfying $kr_{mn} \ll 1$ for which the imaginary part of the coupling Γ can be treated as a small perturbation. We are then in a position to write down general expressions for the fluorescence decay and the transient grating signal decay which we specifically evaluate in the next section for one dimensional aggregates.

We begin by writing Eq. (18a) for a single aggregate in matrix notation

$$\frac{d\mathbf{P}(t)}{dt} = i(\boldsymbol{\epsilon} + i\boldsymbol{\Gamma})\mathbf{P} \qquad (29)$$

where $\mathbf{P}$ is a vector with elements P_n defined through the relation $\langle B_n^+ (t) \rangle = i(\theta_p/2)P_n (t)$ so that $P_n (t)$ is a dimensionless variable ranging from 0 to 1. The real part of $\mathbf{P}$ measures the in-phase (dispersive) polarization (relative to the exciting electric field) and the imaginary part gives the out-of-phase (absorptive) component. $\boldsymbol{\epsilon}$ is the real part of the coupling matrix given by $\boldsymbol{\epsilon} = \boldsymbol{\Omega} + \boldsymbol{\Delta}$. The electromagnetic coupling matrices are $\boldsymbol{\Omega}$ and $\boldsymbol{\Gamma}$ with elements, $\Omega_{mn} = \Omega_{mn}(1 - \delta_{mn})$ and $\Gamma_{mn} = \gamma_{mn}/2$, with $n = 1,2...N$. The matrix $\boldsymbol{\Delta}$ represents the effect of inhomogeneous broadening, which is diagonal in the molecular basis set, $|n\rangle$; $\Delta_{mn} = \delta_{mn}\Delta_n$. Δ_n is the (static) transition frequency shift

(from the average frequency ω_0) of the molecule at site n and has a probability distribution given by a normalized Gaussian function

$$p(\Delta) = \frac{1}{\pi^{1/2}\sigma}\exp[-(\Delta/\sigma)^2].\tag{30}$$

Equation (29) is linear and can be solved by finding the eigenvalues and eigenvectors of the complex matrix, $\epsilon + i\Gamma$. This is, in general, possible with an orthogonal but nonunitary transformation of the form,[38]

$$[\mathbf{U}(\epsilon + i\Gamma)\mathbf{U}^{-1}]_{kk'} = (\epsilon_k + i\Gamma_k)\delta_{kk'}\tag{31}$$

ϵ_k is the frequency and Γ_k is the inverse lifetime for state $|k\rangle$. The nonunitary property of $\mathbf{U}$ necessitates the definition of the right and left eigenvectors of $\epsilon + i\Gamma$

$$(\epsilon + i\Gamma)|k\rangle = (\epsilon_k + i\Gamma_k)|k\rangle\tag{32a}$$

$$\langle \bar{k}|(\epsilon + i\Gamma) = \langle \bar{k}|(\epsilon_k + i\Gamma_k),\tag{32b}$$

where $|\bar{k}\rangle = |k\rangle^*$ if $U^{-1} = U^T$. $|\bar{k}\rangle$ and $|k\rangle$ are orthogonal ($\langle\bar{k}|k\rangle = \delta_{kk'}$) and form a complete basis set,

$$\sum_k |k\rangle\langle\bar{k}| = 1.\tag{33}$$

The matrix elements of $\epsilon + i\Gamma$ are therefore

$$\langle\bar{k}|\epsilon + i\Gamma|k'\rangle = (\epsilon_k + i\Gamma_k)\delta_{kk'}.\tag{34}$$

The complimentary basis will be used later when we apply perturbation theory.

At this time we introduce two additional transformations which will be used later

$$[\mathbf{U}_0(\epsilon + i\Gamma)\mathbf{U}_0^{-1}]_{kk'}$$
$$= (\bar{\epsilon}_k + i\overline{\Gamma}_k)\delta_{kk'} + i\overline{\Gamma}_{kk'}(1 - \delta_{kk'})\tag{35a}$$

and,

$$[\mathbf{U}_1(\epsilon + i\Gamma)\mathbf{U}_1^{-1}]_{kk'}$$
$$= (\hat{\epsilon}_k + \Delta_k + i\hat{\Gamma}_k)\delta_{kk'} + \Delta_{kk'}(1 - \delta_{kk'}).\tag{35b}$$

The unitary matrix, $\mathbf{U}_0$ diagonalizes the real part of the coupling matrix ϵ whereas the orthogonal (but nonunitary) matrix, $\mathbf{U}_1$ diagonalizes the matrix, $\Omega + i\Gamma$. The transformation $\mathbf{U}_0$ is useful for performing a perturbation calculation with respect to the imaginary part, Γ whereas $\mathbf{U}_1$ is useful when the inhomogeneous broadening is small and can be treated perturbatively.

The orthogonality of the transformation (31) together with the cyclic properties of the trace, leads to the important sum rule

$$\sum_{k=1}^N (\epsilon_k + i\Gamma_k) = \sum_{n=1}^N (\Delta_n + i\Gamma_n) = N\overline{\Delta} + i\frac{N\gamma}{2},\tag{36}$$

where $\overline{\Delta}$ is the average inhomogeneous offset for a particular aggregate and the rhs is the sum over the complex eigenvalues of the coupling matrix. Thus, the sum of the damping rates from each eigenstate is equal to $N(\gamma/2)$ while the sum of the real energies is equal to N times the average inhomogeneous offset.

In this paper we are concerned with aggregates which are small compared to an optical wavelength; therefore the real couplings dominate the interaction. If we first diagona-

lize ϵ with a unitary transformation (since $\epsilon = \Omega + \Delta$ is a real, symmetric matrix) according to Eq. (35a), we can then use perturbation theory to correct for the smaller off diagonal parts arising only from the damping matrix Γ. The zero order basis set is given by the eigenvectors $|k\rangle$ (which are the exciton basis vectors if inhomogeneous broadening is neglected), and the zero-order complex eigenvalues are $\bar{\epsilon}_k + i\overline{\Gamma}_k$. In the limit $kr_{mn} \ll 1$ Eq. (3b) shows that $\Gamma_{mn} = \gamma/2$, independent of m or n. Therefore:

$$\overline{\Gamma}_{kk'} = \sum_{n=1}^N \sum_{n'=1}^N [U_0]_{kn}[U_0^\dagger]_{n'k'}\Gamma_{nn'}$$

$$= (\gamma/2)\sum_{n=1}^N \sum_{n'=1}^N [U_0]_{kn}[U_0]_{k'n'}^*.\tag{37}$$

Using second order perturbation theory, the energy of state $|k\rangle$, ϵ_k is given by

$$\epsilon_k = \bar{\epsilon}_k + \sum_{k'(\neq k)}^N \frac{(i\overline{\Gamma}_{kk'})^2}{\bar{\epsilon}_k - \bar{\epsilon}_{k'}} + O(\overline{\Gamma}_{kk'}^4).\tag{38a}$$

The third order term is imaginary due to the $(i\overline{\Gamma}_{kk'})^3$ factor and is therefore absent. The imaginary part of the eigenvalue Γ_k, the damping rate, is given simply by the first order term

$$\Gamma_k = \overline{\Gamma}_k + O(\overline{\Gamma}_{kk'}^3).\tag{38b}$$

From Eq. (38) it follows that the perturbative solution is accurate whenever the minimum energy difference between states $|k\rangle$, is much larger than the coupling matrix element, i.e.,

$$\text{MIN}[\bar{\epsilon}_k - \bar{\epsilon}_{k'}] \gg \overline{\Gamma}_{kk'}\,(< N\gamma/2).\tag{39}$$

Under this condition the basis vectors $|k\rangle$ closely approximate the exact eigenbasis and the eigenvalues of $\epsilon + i\Gamma$ are given by $\bar{\epsilon}_k + i\overline{\Gamma}_k$. As we will see in the next section, condition (39) is well satisfied when inhomogeneous broadening is absent and the dipole–dipole splitting is sufficient to overcome the off-diagonal $\overline{\Gamma}_{kk'}$ elements by several orders of magnitude. When inhomogeneous broadening is included (as high as $\sigma = 10$ V in our numerical calculations) the levels are still sufficiently separated so that Eqs. (38) retain their accuracy. This is due to the noncrossing property of the energy levels as the inhomogeneous broadening is increased.

Finally, when condition (39) holds, we can define the transition dipole moment to the state k (the zero-order state) as

$$\mu_{0k} = \langle 0|\mu|k\rangle = \langle 0|\sum_{n=1}^N \mu\{|0\rangle\langle n| + |n\rangle\langle 0|\}|k\rangle$$

$$= \mu\sum_{n=1}^N [U_0]_{kn}\tag{40}$$

yielding

$$|\mu_{0k}|^2 = \mu^2\sum_{n=1}^N \sum_{n'=1}^N [U_0]_{kn}[U_0]_{kn'}^*.\tag{41}$$

From Eqs. (37) and (41) we obtain the ubiquitous relationship, $\overline{\Gamma}_k \propto |\mu_{0k}|^2$; the radiative decay rate from the eigenstate $|k\rangle$ is proportional to the square of the transition dipole matrix element to that state. The validity of this result depends on condition (39).

We are now ready to consider the fluorescence from a

macroscopic collection of noninteracting aggregates. Appendix A shows that for a dilute, optically thin sample the interaggregate interactions may be neglected, and the directional emission is given by

$$I_{FL}(\mathbf{R},t) = \sum_{n=1}^{MN} \sum_{n'=1}^{MN} w^{(n)}(\mathbf{R})\cos^2\theta_n P_n^*(t)P_{n'}(t)\zeta_{nn'},$$
(42)

where we have generalized the expression to include randomly oriented aggregates by assigning each aggregate a spatial emission factor $w^{(n)}(\mathbf{R})$ defined as $w^{(n)}(\mathbf{R}) = (\theta_p/2)^2(3\gamma/8\pi)\{1 - (\widehat{\mathbf{R}}\cdot\hat{\mathbf{p}}_n)^2\}$, and equal to the number of photons/s emitted per unit solid angle in the direction $\mathbf{R}$ by an oscillating dipole of magnitude $(\theta_p/2\mu)$. θ_n is the angle between the unit dipole moment vector of molecule n, $\hat{\mathbf{p}}_n$, and the electric field polarization vector, $\hat{\mathbf{x}}$; $\cos\theta_n = \hat{\mathbf{p}}_n\cdot\hat{\mathbf{x}}$, (all molecules within an aggregate have parallel dipole moments). Equation (42) can be interpreted as an "average aggregate" response, where the averaging is over the aggregate axis direction (or, equivalently, the direction of the molecular transition dipole moment, $\hat{\mathbf{p}}_n$) and the configuration of inhomogeneous frequency offsets, Δ_n. If we perform the directional average (which is independent of the inhomogeneous frequency average) we get

$$I_{FL}(\mathbf{R},t) = Ms(\mathbf{R})\left\langle \sum_{n,n'=1}^{N} P_n^*(t)P_{n'}(t) \right\rangle,$$
(43)

where $s(\mathbf{R})$ is a directional factor, which, for an isotropic distribution of aggregate axis directions is given by

$$s(\mathbf{R}) = \left(\frac{\theta_p}{2}\right)^2\left[\frac{3\gamma}{8\pi}\right]\frac{4 - 2(\widehat{\mathbf{R}}\cdot\hat{\mathbf{x}})^2}{15}.$$
(44)

In Eq. (43) M is the number of aggregates and $\langle\cdots\rangle$ denotes the average over Δ_n. Applying the results of the previous section we obtain

$$I_{FL}(\mathbf{R},t) = Ms(\mathbf{R})\left\langle \sum_{k=1}^{N}\sum_{k'=1}^{N} I_k^* I_{k'} \exp[i(\epsilon_{k'} - \epsilon_k)t - (\Gamma_k + \Gamma_{k'})t] \right\rangle,$$
(45)

where the weighting factor I_k is defined by

$$I_k = \sum_{n=1}^{N}\sum_{n'=1}^{N} [U^{-1}]_{nk}[U]_{kn'}.$$
(46)

Expression (46) is completely general; replacing U by U_0 and the eigenvalues $\epsilon_k + i\Gamma_k$ by their perturbation approximations, $\bar{\epsilon}_k + i\bar{\Gamma}_k$, gives highly accurate solutions in the small aggregate limit for systems where Eq. (39) applies. In this limit we also have

$$I_k = 2\bar{\Gamma}_k/\gamma.$$
(47)

In the limit of extreme inhomogeneous broadening ($\sigma \gg V$) the eigenstates are the localized states with $\epsilon_k \approx \Delta_n$ and $\Gamma_k \approx \gamma/2$. U reduces to the identity matrix so that $I_k \approx 1$, independent of k. In this case the initial fast decay (arising from the average over terms with $k \neq k'$) is analogous to an incoherent optical free induction decay. From Eq. (45) we get

$$I_{FL}(\mathbf{R},t) \approx MN(N-1)s(\mathbf{R})\frac{1}{\pi^{1/2}\sigma}\int_{-\infty}^{\infty}\exp\left[-\frac{\Delta^2}{2\sigma^2}\right]$$
$$\times \exp[i\Delta t]d\Delta$$
$$= 2^{1/2}MN(N-1)s(\mathbf{R})\exp\left[\frac{\sigma^2 t^2}{2}\right]$$
(48)

which is a Gaussian decay with a time constant ($1/e$ point) $T_2^* = 2^{1/2}/\sigma$. After the $k \neq k'$ terms have dephased, the remaining decay is due to terms with $k = k'$. This is exponential with a time constant equal to the isolated molecular relaxation time, $1/\gamma$

$$I_{FL}(\mathbf{R},t) = MNs(\mathbf{R})\exp[-\gamma t].$$
(49)

The superradiance is completely quenched by the inhomogeneous broadening. The intensity is proportional to the total number of molecules MN in the sample, unlike the initial decay, Eq. (48), which is proportional to $MN(N-1)$. The N^2 enhancement in intensity is only operative during the brief Gaussian inhomogeneous decay T_2^* which does not depend on N. The initial decay is therefore not referred to as superradiance.

In the opposite limit ($V \gg \sigma$) the inhomogeneous broadening is a small perturbation on the zero order states, $|k\rangle$ (with complex energy $\hat{\epsilon}_k + i\widehat{\Gamma}_k$), obtained by diagonalizing the coupling matrix, $\Omega + i\Gamma$ [transformation (35b)]. To first order, the exact complex eigenvalue is

$$\epsilon_k + i\Gamma_k = \hat{\epsilon}_k + \text{Re}\,\Delta_k + i(\widehat{\Gamma}_k + \text{Im}\,\Delta_k) + O(\Delta_{kk'}^2),$$
(50)

where,

$$\Delta_k = \sum_{n=1}^{N}\langle\bar{k}|n\rangle\langle n|k\rangle\Delta_n$$
(51)

and $|\bar{k}\rangle = |k\rangle^*$ is the complementary basis set. The first order effect of the inhomogeneous broadening (after averaging over Δ_k) is twofold. The real part creates a Gaussian distribution of energy levels centered around each $\hat{\epsilon}_k$. The effect of this is to cause the $k \neq k'$ "beating" terms in the fluorescence to dephase relative to each other on some timescale so that subsequent evolution is dictated entirely by the $k = k'$ terms. This timescale is actually longer than $T_2^* = (2^{1/2}/\sigma)$ because of motional narrowing (as we will see). The imaginary part of the first order term, $\text{Im}\,\Delta_k$, causes a small change in the lifetime, $\widehat{\Gamma}_k$ of state $|k\rangle$ [and by relation (47), a small change in I_k as well]. However this change (as we later show for linear aggregates) depends on the quantity $\Delta_{kk'}/(\epsilon_k - \epsilon_{k'})$ where k and k' refer to eigenstates of Ω, and not $\Omega + i\Gamma$. As long as σ is much smaller than the energy level spacing this term can be neglected. We therefore consider only the real part of the first order term.

In order to calculate the initial dephasing we need to know the distribution of $\text{Re}\,\Delta_k$, given the Gaussian distribution (30) for Δ_n. To this end we use the property that the variance, σ_x^2, of a normal random variable X which is equal to the sum of normal random variables, $X = a_1X_1 + a_2X_2 + \cdots + a_nX_n$, is given by, $\sigma_x^2 = a_1^2\sigma_{x_1}^2 + a_2^2\sigma_{x_2}^2 + \cdots + a_n^2\sigma_{x_n}^2$. Therefore,

$$P(\text{Re}\,\Delta_k) = \frac{1}{\pi^{1/2}\sigma}\exp\left[-\frac{\Delta_k^2}{\sigma_k^2}\right]$$
(52)

with σ_k^2 defined by

$$\sigma_k^2 = \sigma^2 \sum_{n=1}^{N} \{ \mathrm{Re}[\langle \bar{k} | n \rangle \langle n | k \rangle] \}^2. \tag{53}$$

In strongly delocalized systems where $\langle \bar{k} | n \rangle \approx N^{-1/2}$ the sum in the last expression goes as N^{-1}, and the width of the energy distribution, $\mathrm{Re}\, \Delta_k$, for a delocalized state $| k \rangle$ is $\sigma_k^2 \approx \sigma^2/N$. This narrowing leads to a longer $k \neq k'$ dephasing time, $\bar{T}_2 > T_2^*$ where $\bar{T}_2$ is the dephasing time in the motional narrowing regime. In this limit, the fluorescence intensity using Eq. (45) is

$$I_{\mathrm{FL}}(\mathbf{R},t) = M s(\mathbf{R}) \sum_{k=1}^{N} \sum_{k'(\neq k)}^{N} I_k^* I_{k'} \, \exp[\, i(\hat{\epsilon}_k - \hat{\epsilon}_{k'})t$$
$$- (\hat{\Gamma}_k + \hat{\Gamma}_{k'})t \,] \exp\left[-\frac{t^2}{4}(\sigma_k^2 + \sigma_{k'}^2) \right]. \tag{54}$$

Whenever the $k \neq k'$ dephasing is accomplished in a time much shorter than the superradiant lifetime, we can ignore the initial dephasing and write the subsequent fluorescence decay as

$$I_{\mathrm{FL}}(t) = M s(\mathbf{R}) \sum_{k=1}^{N} |I_k|^2 \exp[\, -2\hat{\Gamma}_k t \,], \tag{55}$$

where only $k = k'$ terms are retained. This expression represents, in general, superradiant decay since the sum rule (36) dictates that some $\hat{\Gamma}_k$ must be larger than $\gamma/2$ (and also some are smaller so that the sum is constant). Since $\hat{\Gamma}_k$ is proportional to I_k [Eq. (47)], the faster decays also have the larger weighting factors. The effect is most pronounced in cyclic aggregates [see Eq. (85)], in which case the intensity is proportional to N^2 and the decay is enhanced by a factor of N. This is what we refer to as microscopic superradiance.

In the intermediate regime where σ and the energy level spacing are comparable, the motional narrowing will be only partially complete so that the initial fast decay will take place over an interval of time somewhere in between T_2^* and $\bar{T}_2$.

The transient grating (TG) signal in Eq. (24) can also be readily evaluated for a system of small aggregates which do not interact. Because the excitation cannot be transferred between aggregates and each aggregate is much smaller than a wavelength of the excitation light, the transient grating signal is independent of the distance between nulls which is determined by the angle between the two pump beams and is always greater than $\lambda/2$. Because the diffracted beam is coherent and directional, the transient grating experiment is a better probe of small aggregate superradiance than is the time-resolved fluorescence experiment.

The transient grating experiment directly probes the excited state population relaxation. From Eq. (A10) and Eq. (43) we have

$$W(t) = W(0) - \frac{1}{3} \frac{\gamma}{s(\mathbf{R})} \left(\frac{\theta_p}{2}\right)^2 \int_0^t I_{\mathrm{FL}}(\mathbf{R},t) dt. \tag{56}$$

Substitution of expression (45) for the fluorescence into this equation gives

$$W(t) = \frac{M}{3} \left(\frac{\theta_p}{2}\right)^2 \left\langle \sum_{k=1}^{N} I_k \exp[\, -2\Gamma_k t \,] \right\rangle, \tag{57}$$

where we have neglected the terms of order $\Gamma_{kk'}/(\epsilon_k - \epsilon_{k'})$, and we have used Eq. (47). The TG decay is propor-

tional to the square of the excited state population,

$$I_{\mathrm{TG}}(\mathbf{R},t) = M^2 S(\mathbf{R}) \left\langle \sum_{k=1}^{N} I_k \exp[\, -2\Gamma_k t \,] \right\rangle^2 \tag{58}$$

which follows from Eq. (57). The grating signal is highly directional and coherent, and much larger than the fluorescence intensity in the peak direction. This arises because I_{TG} is proportional to the square of the sum of the emitted electric fields from *all* molecules in the sample (hence the factor M^2) while I_{FL} is proportional to the sum of the individual intensities (hence the factor of M). Also, the grating signal contains no oscillating terms, which are a result of excitation transfer between the various k states. Hence, there is no fast component of the decay due to inhomogeneous dephasing; the effect of the inhomogeneous broadening is included implicitly in the values of Γ_k and in the averaging thereof. The (time) integrated TG decay is not σ independent as is the integrated fluorescence [see Eq. (A11)].

In the limit where $\sigma \gg V$, using parallel arguments from the last section, we get a simple exponential grating decay

$$I_{\mathrm{TG}}(\mathbf{R},t) = S(\mathbf{R})(MN)^2 \exp[\, -2\gamma t \,] \tag{59}$$

which shows a macroscopic superradiant signal strength but an independent molecule emission rate. In the motional narrowing limit ($V \gg \sigma$), to first order in the inhomogeneous perturbation, we get

$$I_{\mathrm{TG}}(\mathbf{R},t)$$
$$= S(\mathbf{R})M^2 \sum_{k=1}^{N} \sum_{k'=1}^{N} I_k I_{k'} \, \exp[\, -2(\bar{\Gamma}_k + \bar{\Gamma}_{k'})t \,] \tag{60}$$

which is a direct measure of superradiant damping. The fluorescence signals corresponding to the TG decays in Eqs. (59) and (60) are (49) and (55) respectively, after the $k \neq k'$ dephasing is over.

In the next section we will apply our results to a specific model—small linear and cyclic aggregates. Analytical results in the motional narrowing regime will be presented to second order in the inhomogeneous broadening, with numerical results for the intermediate regime.

V. SUPERRADIANCE IN ONE DIMENSIONAL AGGREGATES

The results of the previous section are now used to calculate the time-resolved fluorescence and TG decay from a collection of small, one dimensional aggregates. This is a common model for J aggregates, which have been shown experimentally to fluoresce at a rate much larger than the rate for an individual dye molecule.[12,30–32] Previous theories[13–19] have adequately explained the qualitative features of the enhancement: an N-dependent transition dipole moment ($N^{1/2}\mu$) to the exciton state with the greatest oscillator strength leads to a factor of N increase in the radiative rate [see Eq. (41)]. In this section we present analytical expressions for the fluorescence and TG signal from an optically thin and dilute distribution of one dimensional aggregates, and consider the destructive effect of inhomogeneous broadening. The analytical expressions are valid for a dimer and a general N-mer in the motional narrowing limit ($V \gg \sigma$); be-

yond that limit we resort to numerical computations. We begin our analysis of the role of inhomogeneous broadening in superradiance with a distribution of dimers, which is exactly soluble.

A. Superradiance in dimers

For the case of two coupled molecules, denoted a and b, with a distribution of transition frequencies given by Eq. (30), the fluorescence decay can be calculated exactly. The coupling matrix, $\mathbf{\Omega} + \mathbf{\Delta} + i\mathbf{\Gamma}$ is given by

$$\mathbf{\Omega} + \mathbf{\Delta} + i\mathbf{\Gamma} = \begin{bmatrix} \Delta_a + i\gamma/2 & V + i\gamma/2 \\ V + i\gamma/2 & \Delta_b + i\gamma/2 \end{bmatrix}, \qquad (61)$$

where the assumption $r_{ab} \ll \lambda$ leads to $\Gamma_{ab} = \gamma/2$, and $\Omega_{ab} = V$. Solving Eq. (29) for the symmetric part of the polarization, $P_a(t) + P_b(t)$, by standard matrix methods, and using the symmetric initial condition, $P_a(0) = P_b(0) = 1$ gives

$$P_a(t) + P_b(t) = \{ I_1 \exp[-i\omega_1 t]$$
$$+ I_2 \exp[-i\omega_2 t] \} \exp[i\Delta_+ t] \quad (62)$$

with the following definitions:

$$\omega_1 = (-i\gamma/2) \pm i\left[\left(\frac{\gamma}{2} - iV \right)^2 - \Delta_-^2 \right]^{1/2}, \qquad (63a)$$

$$\Delta_\pm = \frac{\Delta_a \pm \Delta_b}{2}, \qquad (63b)$$

$$I_1 = \frac{2(\omega_1 - V)}{\omega_1 - \omega_2} \text{ and } I_2 = \frac{2(\omega_2 - V)}{\omega_2 - \omega_1}. \qquad (63c)$$

The coefficients I_k are easily seen to obey the sum rule, $I_1 + I_2 = 2$, which follows directly from Eq. (46). Using Eq. (43) the fluorescence decay, which is proportional to the square magnitude of Eq. (62) is then

$$I_{\mathrm{FL}}(t) = Ms(\mathbf{R}) \left(\frac{1}{\pi^{1/2}\sigma_-} \right) \int_{-\infty}^{\infty} d\Delta_- \exp\left[-\frac{\Delta_-^2}{\sigma_-^2} \right]$$

$$\times \sum_{k,k'=1}^{2} I_k^* I_{k'} \exp[-i(\omega_{k'} - \omega_k^*)t]. \qquad (64)$$

The integration is over the Gaussian inhomogeneous distribution of Δ_- with $\sigma_-^2 = (1/2)\sigma^2$. [The average over Δ_+ yields unity since the integrand in Eq. (64) does not contain Δ_+.]

In the motional narrowing limit $V \gg \Delta_-$ the two eigenvalues are, to second order in Δ_-/V

$$\omega_1 = V\left(1 + \frac{\Delta_-^2}{2V^2} \right) - i\frac{\gamma}{2}\left(\frac{\Delta_-^2}{2V^2} \right), \qquad (65a)$$

$$\omega_2 = -V\left(1 + \frac{\Delta_-^2}{2V^2} \right) - i\frac{\gamma}{2}\left(2 - \frac{\Delta_-^2}{2V^2} \right), \qquad (65b)$$

and the weighting coefficients are

$$I_1 = \frac{\Delta_-^2}{2V^2}, \qquad (66a)$$

$$I_2 = 2 - \frac{\Delta_-^2}{2V^2}. \qquad (66b)$$

The superradiant decay rate (imaginary part of ω_2) decreases with $(\Delta_-/V)^2$ consistent with the notion that inho-

mogeneous broadening "quenches" superradiance. Notice also that the change in the weighting factors obey $\Gamma_k = \mathrm{Im}\,\omega_k = (\gamma/2)I_k$. If the small second order change is neglected we obtain the pure superradiant solution, that is, a single exponential decay at twice the rate of the independent molecule decay and an initial intensity which is four times the independent molecule initial intensity.

$$I_{\mathrm{FL}}(\mathbf{R},t) = 4Ms(\mathbf{R})\exp[-2\gamma t] \qquad (67)$$

We should point out that the absorption spectrum, unlike the time-resolved fluorescence decay, is highly sensitive to the inhomogeneous distribution, even when $V \gg \sigma$. This is because the distribution of transition frequencies (and hence the absorption line shape) for each dimer is $p(\Delta_+)$, a Gaussian distribution of reduced width, $\sigma_+^2 = (1/2)\sigma^2$. Motional narrowing was studied in detail by Knapp,[19] who showed that the absorption linewidth upon aggregation is inversely proportional to $N^{1/2}$.

When $\sigma \gg V$ the coefficients I_k approach unity for most configurations and $\omega_{1/2}$ approaches $\pm \Delta_- - i(\gamma/2)$. In this case the fluorescence is given by

$$I_{\mathrm{FL}}(\mathbf{R},t) = 2Ms(\mathbf{R})\{ 1 + \exp[-(t/T_2^*)^2] \}\exp[-\gamma t], \qquad (68)$$

where the inhomogeneous decay time ($1/e$ point) is $T_2^* = 1/\sigma_-$. The two molecules of the dimer can communicate coherently for only a short time T_2^* during which the intensity is superradiant but the lifetime dependence is not (it is determined by dephasing, not damping). Afterwards, the emission is that of two independent molecules.

The transient grating decay for a distribution of dimers in the two regimes is easily found to be

$$I_{\mathrm{TG}}(\mathbf{R},t) = 4M^2 S(\mathbf{R})\exp[-2\gamma t], \quad \sigma \gg V \qquad (69)$$

and

$$I_{\mathrm{TG}}(\mathbf{R},t) = 4M^2 S(\mathbf{R})\exp[-4\gamma t], \quad \sigma \ll V. \qquad (70)$$

B. Superradiance in $N > 2$, 1D aggregates

We now consider larger linear and cyclic aggregates consisting of N molecules. Unlike the dimer case, an analytic solution for a general configuration of inhomogeneous broadening is not possible. However, if we neglect the broadening, analytic solutions are attainable. The unitary matrices which diagonalize only the real part of the electromagnetic coupling $\mathbf{\Omega}$ are given by[19]:

$$U_{kn}^L = \left(\frac{2}{N+1} \right)^{1/2} \sin\left[\frac{\pi kn}{N+1} \right] \qquad (71)$$

for a linear aggregate and

$$U_{kn}^C = N^{-1/2} \exp[2\pi i(k-1)(n-1)/N] \qquad (72)$$

for a cyclic aggregate, where only nearest neighbor dipole–dipole coupling is included. $\mathbf{U}^C$ completely diagonalizes the matrix, $\mathbf{\Omega} + i\mathbf{\Gamma}$ and is a transformation like Eq. (31) [or Eq. (35b), since the inhomogeneous broadening is zero], while $\mathbf{U}^L$ fails to diagonalize $\mathbf{\Gamma}$; it is therefore a transformation like Eq. (35a). Using Eq. (71), we get for the energy of the linear aggregate exciton state $|k\rangle$:

$$\epsilon_k^L = 2V\cos\left[\frac{k\pi}{N+1}\right], \tag{73a}$$

where V is the nearest neighbor dipole–dipole coupling, and the inverse lifetime

$$\Gamma_{kk'}^L = \left(\frac{\gamma}{N+1}\right)\cot\left[\frac{\pi k}{2(N+1)}\right]\cot\left[\frac{\pi k'}{2(N+1)}\right]$$

for k,k' odd

$$\Gamma_{kk'}^L = 0 \quad \text{for } k \text{ even or } k' \text{ even} \tag{73b}$$

($\Gamma_{kk}^L \equiv \Gamma_k^L$). [We will ignore the bar over ϵ and Γ since the superscript "L" implies the use of transformation (35a)]. In the limit of large N ($N \gg k$) the linear aggregate decay rate Γ_k^L reduces to

$$\Gamma_k^L = \frac{\gamma}{2}\frac{8}{(k\pi)^2}(N+1), \quad k \text{ odd} \tag{74}$$

showing that the $k = 1$ exciton has a superradiant lifetime which approaches a value $[0.81N]$ times shorter than the single molecule lifetime.

Using Eq. (73) the condition (39) becomes

$$V\frac{16\pi^2}{(N+1)^2} \gg N\gamma/2, \tag{75}$$

where we have taken the energy difference between the $k = 1$ and $k = 3$ states since this is the minimum separation in the limit $N \gg k$, and have used $N\gamma/2 = \text{Max}(\Gamma_{ij})$ on the right-hand side. As N increases, condition (39) is harder to satisfy because the energy difference between the $k = 1$ and $k = 3$ states becomes smaller. When condition (39) is not satisfied, there will be a second order frequency shift, according to Eq. (38a). Higher order terms contain corrections to the radiative rate as well. Typical experimental parameters for PIC (at low temperatures) are $V = 600$ cm^{-1} and $N\gamma/2 \approx 0.3$ cm^{-1} (using $N = 100$ and $(1/\gamma) = 4$ ns[12]). Condition (39) is well satisfied for these parameters, so we expect exciton-like eigenstates when inhomogeneous broadening is absent.

For the cyclic aggregate we have

$$\epsilon_k^C = 2V\cos\left[\frac{2\pi(k-1)}{N}\right], \tag{76a}$$

$$\Gamma_k^C = N(\gamma/2)\delta_{k1}. \tag{76b}$$

It is easy to see the N fold enhancement in the decay rate from the $k = 1$ state.

When the inhomogeneous broadening is absent Eq. (46) and Eq. (71) lead to the following weighting factors I_k^L for a linear aggregate:

$$I_k^L = 2(N+1)^{-1}\cot^2[\pi k/(2(N+1))] \quad \text{for } k \text{ odd}$$
$$I_k^L = 0 \quad \text{for } k \text{ even} \tag{77}$$

Equation (45) with Eqs. (73) and (77) then yield the fluorescence decay for a linear aggregate

$$I_{\text{FL}}^L(\mathbf{R},t) = Ms(\mathbf{R})\sum_{k=1}^{N}\sum_{k'=1}^{N}{}'\left(\frac{2}{N+1}\right)^2\cot^2\left[\frac{\pi k}{2(N+1)}\right]$$

$$\times \cot^2\left[\frac{\pi k'}{2(N+1)}\right]\exp\left[\{i(\epsilon_k^L - \epsilon_{k'}^L)\right.$$

$$\left. - (\Gamma_k^L + \Gamma_{k'}^L)\}t\right]. \tag{78}$$

The prime on the summation indicates that only odd values of k are counted. The fluorescence decay, as already mentioned in the previous section contains oscillating components. The weighting factor, I_k^L, is a rapidly decreasing function of k, therefore only the first few k states contribute significantly to the fluorescence. (For $N \gg k$, I_k^L goes as k^{-2}, $k = 1,3,5\cdots$.) The second largest term is the $k = 1$, $k' = 3$ term which oscillates at $\Omega_{33} - \Omega_{11} = 2V\{\cos[3\pi/(N+1)] - \cos[\pi/(N+1)]\}$. The total decay is dominated by cross polarization terms $[P_n^*(t)P_m(t); m \neq n]$ and not exclusively by population terms $[P_n^*(t)P_n(t)]$ which is usually associated with a fluorescence decay. The "beat" term arises not from oscillations in the total population but from the interference of photons with different k-dependent frequencies. The quantum beats in Eq. (78) will be observable as long as T_2^* is not much smaller than $(N\gamma)^{-1}$ and provided the excitation pulse satisfies Eqs. (6) and (7). Furthermore, the result is independent of the temporal coherence properties of the short pulse, since a temporally incoherent pulse will only affect the amount of energy absorbed by a given aggregate and hence the initial polarization magnitude, but not the initial phase relationship between the molecular polarizations. This, of course, assumes the spatial coherence length of the pulse is much larger than the aggregate dimensions (which is easily satisfied since $kr_{mn} \ll 1$). Figure 1(a) shows the oscillatory fluorescence decay from a distribution of $N = 10$ aggregates with no inhomogeneous broadening using Eq. (78).

The cyclic aggregate contains equivalent molecules (when the inhomogeneous broadening is absent) and there are no oscillations since only the $k = 1$ state is involved. Equations (46) and (72) give

$$I_k^C = N\delta_{k1}. \tag{79}$$

The fluorescence, from Eqs. (45), (76), and (79) is

$$I_{\text{FL}}^C(\mathbf{R},t) = MN^2s(\mathbf{R})\exp[-N\gamma t]. \tag{80}$$

The full superradiant enhancement of the decay rate and the emitted density is clearly evident.

In the motion narrowing limit ($V \gg \sigma$) only the linear aggregate is significantly affected by the inhomogeneous distribution of transition frequencies, which causes an initial dephasing of the odd numbered k states according to Eq. (54). The resulting distribution of energy levels centered about the unperturbed k levels ϵ_k^L has a width which is found from Eq. (53) and Eq. (71). With the definition $\sigma_k^2 \equiv \sigma_{\text{LA}}^2$ we get

$$\sigma_{\text{LA}}^2 = \frac{3}{2(N+1)}\sigma^2 \tag{81}$$

which is independent of k. From Eq. (81) we see that the distribution of the kth energy level is narrowed by a factor inversely proportional to the number of molecules in the aggregate. The fluorescence decay using Eq. (54) is (with $\hat{\epsilon}_k \approx \epsilon_k^L$, and $\hat{\Gamma}_k \approx \Gamma_k^L$):
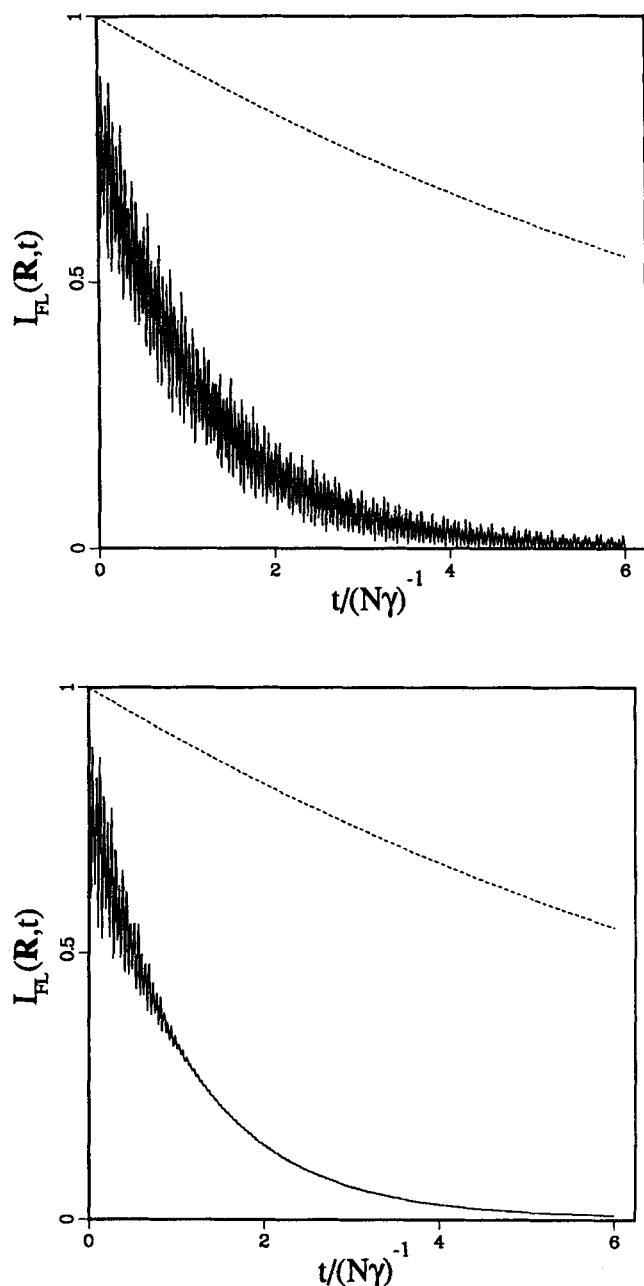
which still contains the oscillating terms, but within a Gaussian envelope with dephasing time, $\overline{T}_2$ which is longer than $T_2^*(= 2^{1/2}/\sigma)$, i.e.,

$$\overline{T}_2 = [2(N+1)/3]^{1/2} T_2^*. \tag{83}$$

After the $k \neq k'$ oscillations have dephased, the decay is given by

$$I_{FL}(\mathbf{R},t) = Ms(\mathbf{R})\gamma \sum_{k=1}^{N} \left(\frac{2}{N+1} \right)^2$$

$$\times \cot^4 \left[\frac{\pi k}{2(N+1)} \right] \exp[-2\Gamma_k^L t] \tag{84}$$

where we continue to use $\hat{e}_k \approx e_k^L$ and $\hat{\Gamma}_k \approx \Gamma_k^L$. Figure 1(b) demonstrates the dephasing of the oscillations for $N = 10$. The decay is obtained numerically by diagonalizing the coupling matrix, $\Omega + \Delta + i\Gamma$ to obtain the complex eigenfrequencies and the weighting factors for each of several thousand configurations of inhomogeneous broadening distributed according to Eq. (30) with $\sigma = 100\gamma$. For a cyclic aggregate, there is no initial fast dephasing since only a single k level participates. The decay for all time is therefore given by Eq. (80), where, the small influence of inhomogeneous broadening on the decay rate has been neglected.

In contrast to the fluorescence decay, the transient grating experiment directly measures the decay of the total population. Using Eqs. (58), (73), and (77) we get for a linear aggregate with no inhomogeneous broadening

$$I_{TG}^L(\mathbf{R},t) = S(\mathbf{R})M^2 \sum_{k=1}^{N} \sum_{k'=1}^{N} \left(\frac{2}{N+1} \right)^2$$

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

$$\times \exp[-2(\Gamma_k^L + \Gamma_{k'}^L)t]. \tag{85}$$

As indicated earlier, this signal, unlike the fluorescence decay, contains no oscillations. Figure 2 shows this decay for

FIG. 1. The fluorescence decay from a linear aggregate with $N = 10$. The dashed curve is the single molecule ($N = 1$) decay. In (a) there is no inhomogeneous broadening [Eq. (78)]. Note the very rapid initial decay due to dipole–dipole dephasing. The curve in (b) is obtained numerically by averaging together 5000 individual aggregate decays each with a unique configuration of transitions frequencies which are normally distributed [Eq. (30)] with $\sigma = 100\gamma$. $V = 10^6\gamma$ so that individual oscillations are not resolvable on the time scale of the figure. However, it is easily seen that the envelope of the oscillations decays with a $1/e$ point in excellent agreement with $\overline{T}_2 \approx 0.4/(N\gamma)^{-1}$ from Eq. (83).

$$I_{FL}(\mathbf{R},t) = Ms(\mathbf{R})e^{- [(\sigma_{LA}^2 t^2/2)]} \sum_{k=1}^{N} \sum_{k'=1}^{N} \left(\frac{2}{N+1} \right)^2$$

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

$$\times \exp[\{(e_k^L - e_{k'}^L) - (\Gamma_k^L + \Gamma_{k'}^L)\}t] \tag{82}$$
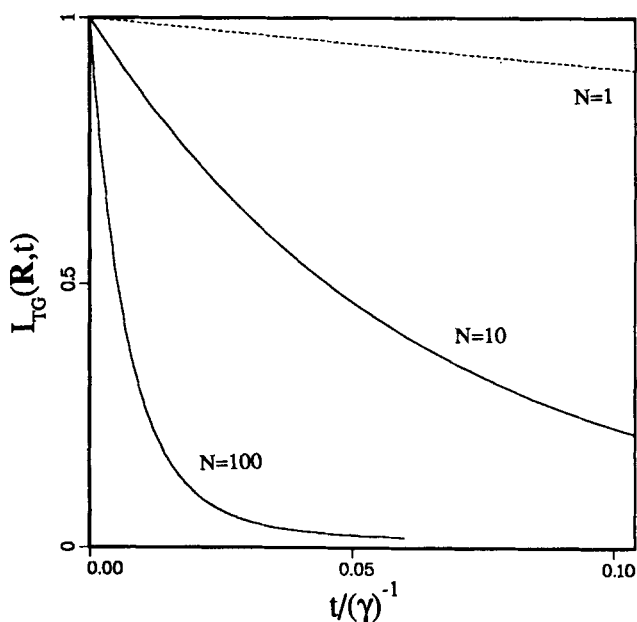
FIG. 2. The transient grating decay for $N = 1$, $N = 10$ and $N = 100$ linear aggregates with no inhomogeneous broadening using Eq. (85). $V = 10^6\gamma$.

several size aggregates using Eq. (85). In this motional narrowing limit, $V \gg \sigma$, the decays are multiexponential, but are dominated by the $k = 1, k' = 1$ component. This component displays the full superradiant enhancement, so that the TG decay curves are approximately exponential decays with decay rates equal to $4\Gamma_k^L \approx 1.6N\gamma$ for $N \gg 1$. Unlike the fluorescence decay after the $k \neq k'$ terms have dephased, the TG decay does contain contributions from the $k \neq k'$ terms, so that the multiexponential behavior is more pronounced. Therefore, the next largest component is the $k = 1$, $k' = 3$ (and not the $k = 3$, $k' = 3$ component as is the case with the fluorescence decay), with a lifetime of $2(\Gamma_1^L + \Gamma_3^L) \approx (1 + 1/9)N\gamma$ [see Eq. (73(b))] and a weighting factor one ninth as large as the primary component, $I_1^L I_3^L \approx 1/9 I_1^L I_1^L$. (Remember, $I_k = (2/\gamma)\Gamma_k$).

For a homogeneous cyclic aggregate, using Eqs. (58), (76b), and (79) we get a single, exponential superradiant decay

$$I_{TG}^C (\mathbf{R},t) = S(\mathbf{R})(MN)^2 \exp[-2N\gamma t] \qquad (86)$$

We now proceed to determine the influence of inhomogeneous broadening on the decay rates, Γ_k^L for a linear aggregate using second order perturbation theory. This is one step beyond the results we have obtained so far in the motional narrowing regime since there we included only the first order correction to the *real* energy of the states which causes the $k \neq k'$ dephasing. If we assume that $\bar{T}_2 \ll MAX[\Gamma_k^{L-1}]$ then this early dephasing is unimportant (see Fig. 5); according to Eq. (45) the subsequent decay is then determined by an inhomogeneous average over terms like $(I_k^L)^2 \exp[-2\Gamma_k^L]$. For the transient grating decay the averaging is slightly different. From Eq. (58) one must evaluate the average of the sum of terms $\Sigma_k I_k^L \exp[-2\Gamma_k^L]$ and then square the result. For both signals the important quantities are $\Gamma_k(\Delta_1\Delta_2 \times \cdots \Delta_N)$ and $I_k(\Delta_1\Delta_2 \cdots \Delta_N)$ which we calculate to second order in the inhomogeneous broadening. Fortunately, by relation (47), the two are trivially related so we need only to calculate Γ_k. The second order expressions are then simplified by averaging over the distribution of transition frequencies [Eq. (30)]. We have shown numerically that for small values of $N^{3/2}\sigma/V$ the decays obtained by using the average decay rates and weighting factors accurately reproduce the correct decays from Eqs. (45) and (58), i.e., $\langle I_k^2 \times \exp[-2\Gamma_k]\rangle \approx \langle I_k\rangle^2 \times \exp[-2\langle\Gamma_k\rangle]$ for the fluorescence decay, for example. We now proceed to evaluate $\langle \Gamma_k \rangle$ to second order in σ/V.

The zero-order states we start with [the basis set in transformation Eq. (35b)] are the exciton-like states but with a complex first order correction

$$|k_s\rangle = |k\rangle + i\sum_{k'(\neq k)}^{N} \frac{\Gamma_{kk'}^L}{\epsilon_k^L - \epsilon_{k'}^L} |k'\rangle \qquad (87)$$

where $|k\rangle$ denotes the exciton basis set associated with the transformation U^L and $|k_s\rangle$ is the basis set of a transforma-

tion (35b), with the complimentary basis set $\langle \bar{k}_s|$. According to our notation the zero-order eigenvalues are now $\hat{\epsilon}_{k_s} + i\hat{\Gamma}_{k_s}$ which we approximate according to Eq. (38) by $\epsilon_k^L + i\Gamma_k^L$. The introduction of inhomogeneous broadening will mix these states. Our goal is to find the second order correction to the complex eigenvalues and weighting factors I_k. The first order correction is simply given by

$$E_{k_s}^{(1)} = \langle k_s|\Delta|k_s\rangle = \Delta_k + 2i\sum_{k'(\neq k)}^{N} \frac{\Gamma_{kk'}^L}{\epsilon_k^L - \epsilon_{k'}^L} \Delta_{kk'}, \qquad (88)$$

where $\Delta_{kk'}$ is given by

$$\Delta_{kk'} = \sum_{n=1}^{N} \langle k|n\rangle\langle n|k'\rangle\Delta_n$$

$$= \frac{2}{N+1}\sum_{n=1}^{N} \sin\left[\frac{k\pi n}{N+1}\right]\sin\left[\frac{k'\pi n}{N+1}\right]\Delta_n. \qquad (89)$$

From Eq. (88) the first order change in the zero order complex energy, $E_{ks}^{(1)} = \epsilon_{k_s}^{(1)} + i\Gamma_{k_s}^{(1)}$, has both a real and imaginary part. Because Δ_n assumes positive and negative values with equal probability so does $\Delta_{kk'}$ and the first order change in radiative lifetime given by the second term in Eq. (88) can be positive or negative (with equal probability). *An inhomogeneous distribution of transition frequencies can actually enhance the radiative decay rate of a single aggregate*; this result is counterintuitive from previous notions of superradiance which views inhomogeneous broadening as an exclusively destructive mechanism. However, the fluorescence signal from a large collection of aggregates depends on the appropriate averaging over Δ_n and therefore this first order term does not contribute. We must turn to the second order term to determine the lowest order contribution.

$$E_{k_s}^{(2)} = \sum_{k_s'(\neq k_s)}^{N} \frac{\Delta_{k_s k_s'}\Delta_{k_s' k_s}}{(\epsilon_{k_s} + i\Gamma_{k_s}) - (\epsilon_{k_s'} + i\Gamma_{k_s'})} \qquad (90)$$

where the complex, zero order energies must be used in the denominator ($\epsilon_{k_s} = \epsilon_k^L, \Gamma_{k_s} = \Gamma_k^L$). When this expression is rewritten in terms of the k(exciton) basis set we obtain

$$E_{k_s}^{(2)} = \sum_{k'\neq k}^{N} \frac{1}{(\epsilon_k^L + i\Gamma_k^L) - (\epsilon_{k'}^L + i\Gamma_{k'}^L)}$$

$$\times \left\{ (\Delta_{kk'})^2 + 2i\sum_{k''\neq k'}^{N} \frac{\Gamma_{k'k''}^L \Delta_{kk'}\Delta_{k''k}}{\epsilon_{k'}^L - \epsilon_{k''}^L} \right.$$

$$\left. + 2i\sum_{k''\neq k}^{N} \frac{\Gamma_{kk''}^L \Delta_{kk'}\Delta_{k'k''}}{\epsilon_k^L - \epsilon_{k''}^L} \right\}. \qquad (91)$$

Equation (91) contains the second order correction to the energy and lifetime of the complex energy, $\epsilon_{k_s}^{(2)} + i\Gamma_{k_s}^{(2)}$. We are only interested in the second order change in the radiative decay rate which is the imaginary part of Eq. (91).

$$\Gamma_{k_s}^{(2)} = \sum_{k'\neq k}^{N}\sum_{n,m=1}^{N} \left\{ U_{kn}U_{k'n}U_{km}U_{k'm} \frac{\Delta_n\Delta_m}{(\epsilon_k^L - \epsilon_{k'}^L)^2}(\Gamma_{kk}^L - \Gamma_{k'k'}^L) \right.$$

$$+ 2 \sum_{k''\neq k'}^{N} U_{kn} U_{k'n} U_{km} U_{k''m} \frac{\Delta_n \Delta_m}{(\epsilon_{k'}^L - \epsilon_{k''}^L)(\epsilon_k^L - \epsilon_{k'}^L)} \Gamma_{k'k''}^L$$

$$+ 2 \sum_{k''\neq k}^{N} U_{kn} U_{k'n} U_{k'm} U_{k''m} \frac{\Delta_n \Delta_m}{(\epsilon_k^L - \epsilon_{k''}^L)(\epsilon_k^L - \epsilon_{k'}^L)} \Gamma_{kk''}^L \Bigg\}, \qquad (92)$$

where $U_{kn} \equiv U_{kn}^L$. The imaginary part of Eq. (88) along with Eq. (92) constitute the first and second order corrections, respectively, to the zero order radiative rate, Γ_{k_s} of the exciton state $|k\rangle$ due to inhomogeneous broadening, $\Gamma_{k_s} = \Gamma_k^L + \Gamma_{k_s}^{(1)} + \Gamma_{k_s}^{(2)}$.

The average decay rate, defined by averaging the second order decay rate over the Gaussian distribution of inhomogeneous broadening in Eq. (30), is an accurate measure of the fluorescence decay rate (as we will see shortly). Fortunately, its calculation provides some simplification over expressions (88) and (92). As stated earlier the first order correction averages to zero, while the second order correction becomes

$$\langle \Gamma_{k_s}^{(2)} \rangle = - \left(\frac{2}{N+1} \right)^2 \left(\frac{N+1}{4} \right) \sum_{k'\neq k}^{N} \frac{\langle \Delta^2 \rangle}{(\epsilon_k^L - \epsilon_{k'}^L)^2} (\Gamma_k^L - \Gamma_{k'}^L) + \left(\frac{2}{N+1} \right)^2 \left(\frac{N+(-1)^b}{4} \right)$$

$$\times \sum_{k'\neq k}^{N} \sum_{k''\neq k'}^{N} \frac{\langle \Delta^2 \rangle}{(\epsilon_{k'}^L - \epsilon_{k''}^L)(\epsilon_k^L - \epsilon_{k'}^L)} \Gamma_{k'k''}^L \{\delta_{2k,k'+k''} - \delta_{2k,k'-k''} - \delta_{2k,k''-k}$$

$$+ \left(\frac{2}{N+1} \right)^2 \left(\frac{N+(-1)^b}{4} \right) \sum_{k'\neq k}^{N} \sum_{k''\neq k}^{N} \frac{\langle \Delta^2 \rangle}{(\epsilon_k^L - \epsilon_{k''}^L)(\epsilon_k^L - \epsilon_{k'}^L)}$$

$$\times \Gamma_{kk''}^L \{\delta_{2k',k+k''} - \delta_{2k',k-k''} - \delta_{2k',k''-k}\}, \qquad (93)$$

where $b = 0$ if a positive delta function in Eq. (93) is satisfied and $b = 1$ if a negative delta function is satisfied. In deriving Eq. (93) we have assumed a site to site uncorrelated inhomogeneous distribution, i.e., $\langle \Delta_n \Delta_m \rangle = \langle \Delta^2 \rangle \delta_{mn}$. We have also taken advantage of the following identities

$$\sum_{n=1}^{N} \sin^2 \left[\frac{k\pi n}{N+1} \right] \sin \left[\frac{k'\pi n}{N+1} \right] \sin \left[\frac{k''\pi n}{N+1} \right]$$

$$= \left(\frac{N+(-1)^b}{8} \right) \{\delta_{2k,-k'-k''} + \delta_{2k,k'+k''}$$

$$- \delta_{2k,k'-k''} - \delta_{2k,k''-k'}\} \qquad (94a)$$

for $k' \neq k''$ and

$$\sum_{n=1}^{N} \sin^2 \left[\frac{k\pi n}{N+1} \right] \sin^2 \left[\frac{k'\pi n}{N+1} \right] = \frac{N+1}{4} \qquad (94b)$$

for $k \neq k'$.

In Fig. 3 we have plotted the second order decay rate vs σ/V (dashed curve) for the states $k = 1, 2,$ and 3 in an $N = 10$ aggregate. We also show numerical results, obtained by diagonalizing the full coupling matrix for 10 000 configurations of inhomogeneous offset frequencies, Δ_n $\{n = 1 \cdots 10\}$, which are distributed according to the normalized Gaussian function, and then averaging the eigenvalues. The analytical results are in agreement with the numerical results for values of $\sigma/V < 0.3$, which represents a relatively large amount of inhomogeneous broadening. A better approximation can be obtained using a Padé approximant, where the σ dependence of the $k = 1$ state, for example, is represented by $\Gamma_1/(N\gamma/2) = [A + B(\sigma/V)^2]/ [1 + C(\sigma/V)^2]$. The three parameters, A, B, and C can be determined from the known values of $\Gamma_k (\sigma = 0)$ and $\Gamma_{k_s}^{(2)}$ [from Eqs. (73b) and (93), respectively] and the asymptotic result $\lim_{\sigma \to \infty} \Gamma_k = \gamma/2$, giving $A = 0.88$, $B = 0.1$, and $C = 1$. For the $k = 1$ state the decay rates obtained by this

procedure are within 10% of the numerical values for $\sigma/V < 2$.

The aggregate size dependence of the second order solution can be simply calculated in the limit $N \gg k$. The normalized second order change in the average lifetime [Eq. (93)/ $N\gamma/2$] in this limit is given by
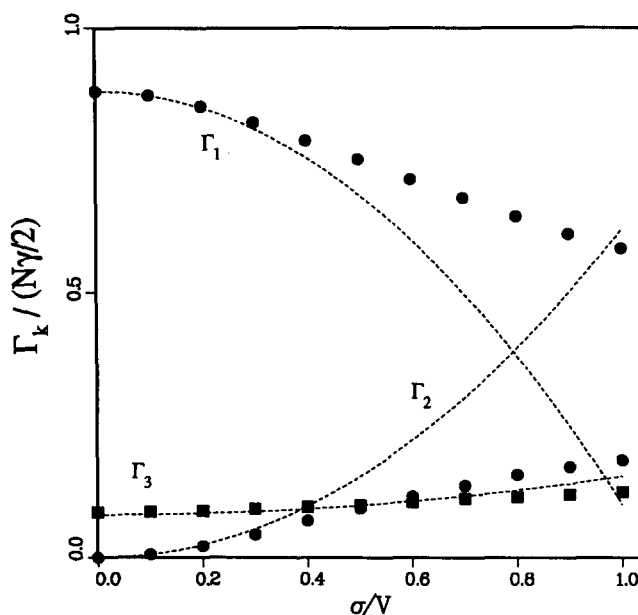

FIG. 3. Radiative decay rates of the $k = 1, 2,$ and 3 states vs σ/V for an $N = 10$ linear aggregate, calculated by numerically diagonalizing the coupling matrix [Eq. (29)] and averaging over several thousand configurations of Δ_n. The dashed curves are the second order results from Eq. (93) which are accurate when $[N^{3/2}(\sigma/V)]$ is small. $V = 10^6 \gamma$.

$$\left(\frac{2}{N\gamma}\right)\langle\Gamma^{(2)}_{k_s}\rangle = \frac{N^3\sigma^2}{2\pi^6 V^2}F(k), \quad N \gg k, \tag{95}$$

where the limiting forms of ϵ^L_k and Γ^L_k were used. ($\epsilon^L_k \approx 2V[1 - \pi^2 k^2/(2N^2)]$ and Γ^L_k is approximated by Eq. (74)). $F(k)$ is the remaining convergent sum over k' and k''. $F(k) = -0.93, 0.77$, and 0.08 for $k = 1, 2$, and 3, respectively. The magnitude of the right-hand side of Eq. (95) must be small compared to unity in order to remain within the limits of second order perturbation theory

$$N^3\frac{\sigma^2}{V^2} \ll 2\pi^6 F(1) \approx 2 \times 10^3. \tag{96}$$

For $N = 10$, this expression becomes $\sigma/V \ll 2^{1/2}$; however, for larger values of N the lifetime of the aggregate becomes more sensitive to the relative amount of inhomogeneous broadening, σ/V. This is expected since, for large N, the exciton cannot travel quickly enough to efficiently average over all sites.

Equation (93) is actually valid to third order in the inhomogeneous broadening and contains only even order terms because $\langle\Delta_i\Delta_j\cdots\Delta_m\rangle$ is zero when the number of Δ's is odd for a Gaussian random variable. If we assume that the $2n$th term has a size dependence given by $[N^3\sigma^2/V^2]^n$ then the lifetime of an aggregate is a function of the scaled variable $N^{3/2}\sigma/V$

$$\Gamma_k(\sigma) = \Gamma_k\left[N^{3/2}\frac{\sigma}{V}\right]. \tag{97}$$

In Fig. 4 we test our assertion by showing the lifetimes for the $k = 1,2,3$ states for $N = 10$ and $N = 40$, calculated numerically, vs the scaled variable, $N^{3/2}\sigma/V$. The curves are very close to coincidence, which is somewhat surprising since $\sigma/$

V is an order of magnitude larger in the $N = 10$ case. Figure 4 acts as a convenient "ruler" for determining the approximate radiative lifetime for an aggregate of size N and inhomogeneous broadening σ/V such that the scaled variable (97) is less than about 300.

Figure 5 shows the fluorescence decays for $N = 10$ for several values of inhomogeneous broadening. The curves were obtained by averaging the decay curves for several thousand aggregates. As is evident, the area of each curve is constant according to conservation of energy arguments [see Eq. (A11)]. The details of the very rapid initial decay or inhomogeneous dephasing cannot be resolved on the time scale of the figure, even for the smallest value of $\sigma/V = 0.1$, because σ is still much larger than $N\gamma$. In order to more clearly demonstrate the effect of inhomogeneous broadening on the lifetime, we show in Fig. 6 normalized decay curves for $N = 10$ and values of σ/V up to $\sigma/V = 10$.

The decay curves obtained by using the average lifetimes from Figs. 3 or 4 are not, in general, the same as the average *decay* curves (Figs. 5 and 6), which represent the correct fluorescence decay from Eq. (45). However, we have numerically verified out to $\sigma/V = 10$ for $N = 10$ that the difference is negligible for $\sigma/V < 0.5$ and slowly increases to about 15% for $\sigma/V = 10$. Therefore, the fluorescence decay constructed by using the average lifetimes is approximately valid.

Figure 7 demonstrates the destructive influence of inhomogeneous broadening on the TG decay. Numerically calculated TG signal decay curves are shown for several values of σ/V, and $N = 10$. As in the fluorescence case the curves

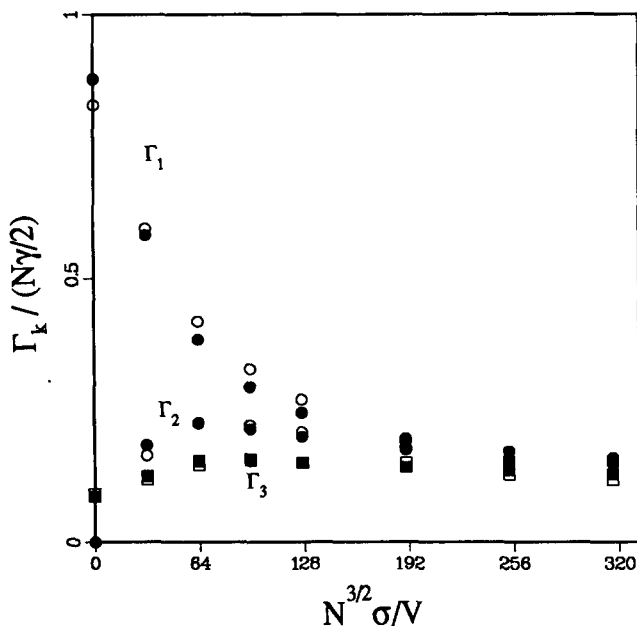FIG. 4. The normalized (to $N\gamma/2$) decay rates of the $k = 1,2$, and 3 states vs $N^{3/2}\sigma/V$ for linear aggregates with $N = 10$ (solid symbols) and $N = 40$ (open symbols) obtained by numerically diagonalizing the coupling matrix, Eq. (29). Note that both curves corresponding to a given k state are nearly identical, independent of N. $V = 10^6\gamma$.
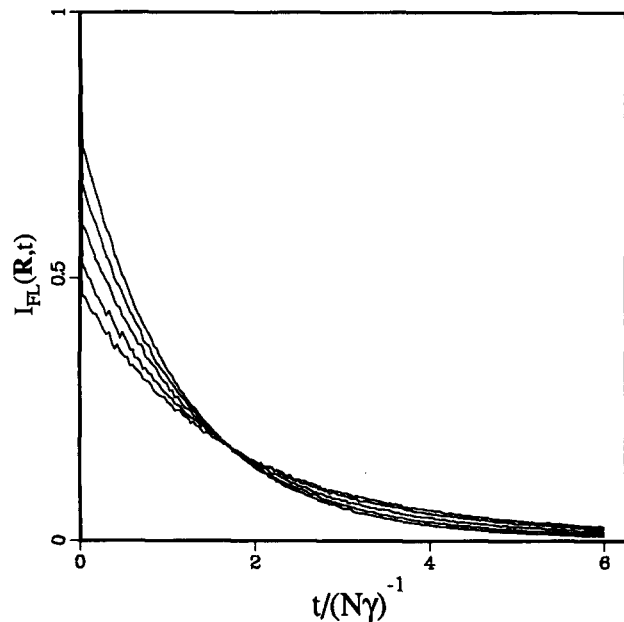

FIG. 5. Numerical fluorescence decays for $N = 10$ linear aggregates for several values of σ/V. The curves are a result of averaging together several thousand numerically calculated decay curves, each corresponding to a separate configuration of Δ_n, according to Eq. (45). The values of σ/V are 0.1, 0.3, 0.5, 0.7, and 0.9, corresponding to the curves with the highest to lowest initial values. The integrated area for each curve is independent of σ/V according to Eq. (A11). $V = 10^6\gamma$.
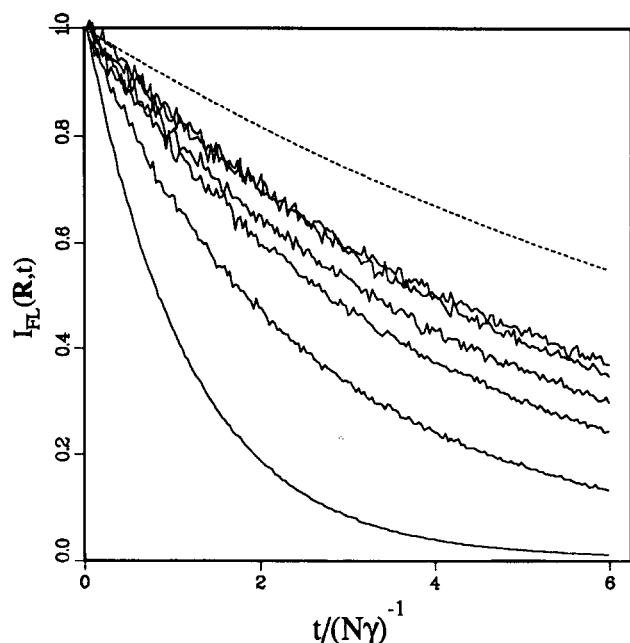
FIG. 6. Numerical fluorescence decays for $N = 10$ linear aggregates and several values of σ/V. The curves are normalized to the value immediately after the initial $k \neq k'$ dephasing and are calculated in the same way as the previous figure [Eq. (45)]. The values of σ/V are 10, 8, 6, 4, 2, and 1, corresponding to the curves with the slowest to fastest decay rates. The dashed curve represents the single molecule decay. $V = 10^6 \gamma$.
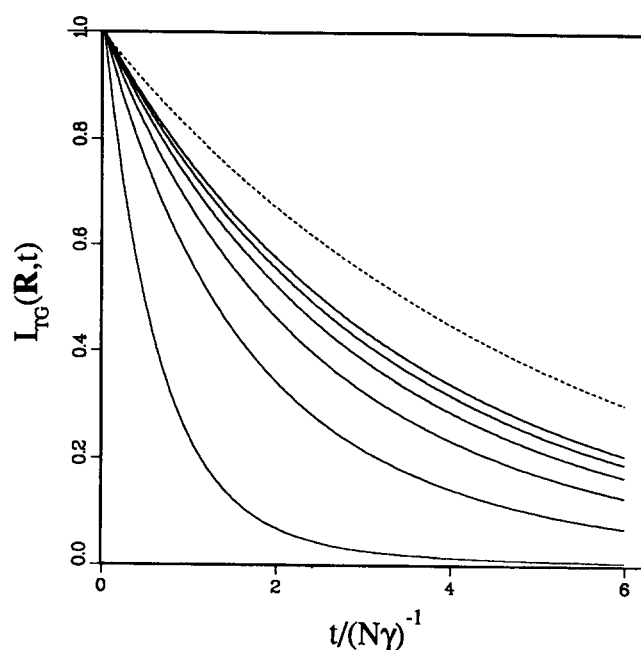
FIG. 7. Numerical transient grating decays for $N = 10$ linear aggregates and several values of σ/V. The curves are found by averaging together several thousand numerically calculated decay curves, each corresponding to a separate configuration of Δ_n according to Eq. (58). The values of σ/V are 10, 8, 6, 4, 2, and 1, corresponding to the curves with the slowest to fastest decay rates. The dashed curve represents the single molecule decay. $V = 10^6 \gamma$.

can be adequately described as multiexponential decays using the average decay constants, calculated numerically, or, for small inhomogeneous broadening, by the second order formula, Eq. (93). By comparison with Fig. 6 it appears that the TG decay might simply be the square of the fluorescence decay (after the initial $k \neq k'$ dephasing). For homogeneous cyclic aggregates this is indeed the case to within a normalization factor [compare Eqs. (86) and (80)]. However, for homogeneous linear aggregates or general inhomogeneously broadened aggregates the relationship is not valid. For example the square of Eq. (55) for the fluorescence contains the terms $I_k^2 I_{k'}^2 \cdot \exp[- 2(\Gamma_k + \Gamma_{k'})]$ compared to the TG decay which contains $I_k I_{k'} \cdot \exp[- 2(\Gamma_k + \Gamma_{k'})]$. The TG decay has a more pronounced multiexponential character because $I_k I_{k'}$ does not decrease with increasing k,k' as fast as $I_k^2 I_{k'}^2$.

VI. CONCLUSIONS

In this paper we have studied in detail the time-resolved fluorescence and TG decay from a low temperature solution (glass) of noninteracting molecular aggregates. After demonstrating that the time resolved fluorescence is equivalent to a limited form of superradiance, the destructive effect of inhomogeneous broadening was worked out. The universal curve, shown in Fig. 4 allows one to approximately determine the reduced lifetime for a linear aggregate, given the size N and the relative inhomogeneous broadening, σ/V. The approximations arise from: (1) the difference between the decay curve obtained using the average lifetimes and the (correct) curve obtained by averaging over the individual aggregate decays, (2) the validity of the scaling law in Eq.

(97), and (3) the nearest neighbor coupling approximation. We have tested the last approximation numerically, by calculating the full coupling fluorescence decays for $N = 10$ and for several values of σ/V up to 4. In all cases the full coupling decays were faster by at most 20% for a given value of σ/V. This is understandable, since in the full coupling case the excitation transfer rate is greater allowing a more effective motional narrowing. Using the available parameters of PIC ($\sigma = 300$ cm^{-1} and $V = 600$ cm^{-1}) and the radiative enhancement factor of about 500 measured in Ref. 12 gives a scaled variable [Eq. (97)] of approximately 2800 if $N = 500$. This is far off the scale of Fig. 4; however we can safely say that $N = 500$ is far too low to yield a radiative enhancement of 500 when the inhomogeneous broadening is randomly distributed with $\sigma/V = 0.50$. We therefore suspect a much larger aggregate size, or, a correlated distribution of inhomogeneous broadening. For example, the 500 fold enhancement factor could be reached if each aggregate of $N = 500$ is homogeneous with a constant transition offset Δ_m which is distributed for each aggregate according to a Gaussian distribution of width σ. Knapp[19] has considered the effect of intersite correlation on the absorption line shape.

The nature of the effect of the inhomogeneous broadening on the lifetime can be studied exactly for the case of a dimer. From expression (65) the lifetime depends on the relative magnitude of Δ and V, Δ/V, and not on Δ/γ as might be expected. This feature is present in our numerical results for larger aggregates as well, and leads to the important conclusion that the microscopic superradiant decay does *not* depend on the condition $T_2^* \gg (N\gamma)^{-1}$ which *is* true

for macroscopic superradiance. In other words, having a rapid inhomogeneous dephasing destroys the MN cooperativity of the entire sample but not the N cooperativety on a single aggregate as long as $V \gg \sigma$. A different situation arises in the case of homogeneous dephasing such as phonon assisted dephasing in the Haken–Strobl model. This is represented in our model by an additional term in Eq. (29) for P_n, given by $-\Gamma_{ph} P_n$. It is easy to show that this term will destroy superradiance in a dimer when the ratio Γ_{ph}/γ is comparable to one. Therefore, unlike inhomogeneous dephasing, homogeneous dephasing competes directly with superradiance and is more effective in destroying it. Mathematically this is due to the fact that both homogeneous dephasing and superradiant damping terms are real in the equation of motion for P_n, while the homogeneous dephasing and dipole–dipole coupling terms are complex.

Although we have restricted the analysis to optically thin samples, the fluorescence decay in an optically thick sample should still display the microscopic N-body superradiance. This is because in such samples the macroscopic superradiant decay (emitted in the forward direction) is faster than the inhomogeneous dephasing. Therefore, this will affect only the (unimportant) initial fluorescence decay, which is then temporally well separated from the subsequent microscopic N-body superradiant decay. However, the majority of photons will be emitted in the forward direction, leaving a smaller number to be emitted at right angles through fluorescence. The transient grating experiment, however, offers a significant advantage since it is coherent and highly directional. In addition, the TG decay is free of the real part of the dipole–dipole coupling, V.

Finally, we suggest that the low-temperature molecular aggregate system may yield interesting new information about the process of N-body superfluorescence, a special type of superradiance which arises from a system of perfectly inverted populations. It is already well known that the fluorescence decay from J aggregates is highly sensitive to the power of the excitation pulse.[30–32] Under low temperature conditions, and with strong enough excitation pulse energies to completely invert the transition, superfluorescence may be observed from these systems.

ACKNOWLEDGMENTS

APPENDIX A: CONDITIONS FOR THE NEGLECT OF INTERAGGREGATE INTERACTIONS

In this Appendix we derive through qualitative arguments, the conditions under which interaggregate interactions can be neglected in a macroscopic solution of aggregates. Our plan is to evaluate the maximum effect of the electric field produced by all other aggregates on a given aggregate, and require that this effect be small.

We start with a system of M, N-mer aggregates distributed uniformly (but randomly) in a solution or glass with inhomogeneous broadening given by the Gaussian distribution function Eq. (30). At $t = 0$ the aggregates are excited by an external pulse. We wish to calculate the electric field at a representative aggregate (denoted as aggregate n) at $t = 0$. For simplicity we assume each aggregate to be a linear oscillator with transition dipole moment of magnitude $\mu_N = N^{1/2}\mu$, frequency Δ_m and lifetime $(N\gamma)^{-1}$ (this is an excellent approximation for a cyclic aggregate with $\sigma \ll V$). The initial polarization of an aggregate at z_n is $P_A(0) = (\theta/2)N^{1/2}\mu_N \exp[ikz_n] = \mu_N P_0 \exp[ikz_n]$, where $P_0 = (i\theta/2)N^{1/2}$. The initial electric field at the site of aggregate "n" (in the rotating frame at ω_0) is given by

$$E(x_n, y_n, z_n, t = 0) = \left(\frac{\hbar}{\mu_N}\right) P_0 \sum_{m(\neq n)}^{M} (\Omega_{mn}^N - i\gamma_{mn}^N/2)$$
$$\times \exp[-ikz_m], \qquad (A1)$$

where we have used the fact that the electric field of an oscillating dipole of magnitude, $P_0\mu_N$, at r evaluated at a point r' is given by the classical formula $(\hbar/\mu_N)\{\Omega^N(r - r') - i\gamma^N(r - r')/2\}P_0$ for the component along the polarization vector direction (we assume all dipole moments are parallel).[37] Also, since the real and complex coupling coefficients, Ω_{mn} and γ_{mn} are proportional to γ for a monomer [see Eq. (3b)], Ω_{mn}^N and γ_{mn}^N are proportional to $N\gamma$ for the aggregate. In order to approximately evaluate (A1) we go to the continuum limit and rewrite it as

$$E(0,0,z,t=0)$$
$$= (\frac{\hbar}{\mu_N})P_0 \int_0^L dz' \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy'\{\Omega^N(r'-r)$$
$$- i\gamma^N(r'-r)/2\}\exp[ik(z'-z)] \qquad (A2)$$

where $r = (0,0,z)$ is now the coordinate of aggregate n and we have assumed a slab of infinite transverse geometry and thickness L. The electric field has also been redefined by multiplying it by a phase factor $\exp(-ikz)$ so that the real and imaginary parts of E now refer to the in-phase and out-of-phase components (with respect to the polarization at r) respectively. The transverse part of the integral has been evaluated in Ref. 39, and is simply given by

$$\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy'\{\Omega^N(r'-r) - i\gamma^N(r'-r)/2\}$$
$$= i(3\pi N\gamma/2k^2)\eta \exp(ik|z-z'|), \qquad (A3)$$

where η is the number of aggregates per unit area. With this relation we can now write the initial electric field at r as

$$E(0,0,z,t=0)$$
$$= i\frac{3\hbar\pi N\gamma\eta}{2\mu_N k^2}P_0\left\{\int_0^z dz' \exp[ik(z'-z)]\exp[ik(z-z')]\right.$$
$$\left. + \int_z^L dz' \exp[ik(z'-z)]\exp[ik(z'-z)]\right\} \qquad (A4)$$

and

$$E(0,0,z,t=0) = P_0(3\hbar\pi N\gamma/2\mu_N k^2)\rho\{iz + (2k)^{-1}$$
$$\times [1 - \exp(2ik(z-L))]\}, \qquad (A5)$$

where ρ is the aggregate concentration. For sufficiently large

$z(\gg\lambda)$ the out-of-phase component (first term) is dominant. Aggregates at $z = L$ experience the largest electric field, which, because of its $\pi/2$ phase relationship to the polarization at $z = L$, will act to drive the aggregate to its ground state with the simultaneous (stimulated) emission of photons. This is the mechanism of superradiance. The real part of Eq. (A5) is responsible for a frequency shift of the aggregate polarization at r and is a manifestation of excitation transfer between aggregates without photon emission.

There are then two requirements for the neglect of these interaggregate interactions. Both the in-phase and out-of-phase electric field at the site of a particular aggregate must perturb the aggregate polarization only slightly. The maximum influence is estimated by multiplying the Rabi frequency $\mu_N E/\hbar$ by the time during which all dipoles remain approximately in phase T_2^*—or the maximum time for which the electric field is large due to constructive interference. We require that $\mathrm{Re}(\mu_N E/\hbar)T_2^*, \mathrm{Im}(\mu_N E/\hbar)T_2^* \ll P_0$. The imaginary part gives the inequality

$$\frac{3\pi\gamma\rho NT_2^*}{2k^2} L \ll 1 \text{ or } \alpha L \ll 1, \qquad (A6)$$

where the inverse Beer's length is defined as $\alpha = (3N\pi\gamma\rho T_2^*/2k^2)$. The optical density is equal to $\alpha L / 2.3$, therefore Eq. (A6) requires the sample to be optically thin. The second requirement comes from the real part of E

$$\frac{3\pi\gamma\rho NT_2^*}{4k^3} \ll 1 \text{ or } \rho \ll M_c/\lambda^3, \qquad (A7)$$

where $M_c = (32/3)\pi^2/(N\gamma T_2^*)$. For aggregates which rapidly dephase relative to each other before they get a chance to de-excite and emit photons, $N\gamma T_2^*$ is a small number so the concentration of aggregates for which interaggregate excitation transfer can be safely neglected can be correspondingly larger. On the other hand if they emit their photons while they remain roughly in phase then $N\gamma T_2^*$ is large and the concentration must be lower in order to neglect the interactions.

Although we did not consider the more general problem of a uniform distribution of isotropically, randomly oriented aggregates, we can approximately include this feature by replacing N by $N/3$ in the above expressions. The factor of $1/3$ arises from an averaging over all orientations, assuming now that the initial polarization contains a factor of $\cos\theta_m$ for aggregate m. (θ_m is the angle between the aggregate dipole moment and the external electric field polarization vector).

When both requirements (A6) and (A7) are satisfied we can ignore interactions between aggregates. One further implication is that under condition (A6) the rate of photon emission is due almost entirely to the spatially integrated fluorescence rather than the spatially integrated and highly directional, macroscopic superradiance. The total excited state population for a distribution of randomly oriented aggregates is given by

$$W(t) = \frac{1}{3}\left(\frac{\theta_P}{2}\right)^2 \sum_{n=1}^{MN} P_n^*(t)P_n(t). \qquad (A8)$$

Taking the first time derivative and using Eq. (29) yields

$$\frac{dW(t)}{dt} = \frac{1}{3}\left(\frac{\theta_P}{2}\right)^2 \gamma \sum_{n=1}^{MN} \sum_{m=1}^{MN} P_n^*(t)P_m(t)$$

$$\times \exp[ik(z_m - z_n)]$$

$$\approx \frac{M}{3}(\frac{\theta_P}{2})^2\gamma\left\langle \sum_{n=1}^{N} \sum_{m=1}^{N} P_n^*(t)P_m(t)\right\rangle, \qquad (A9)$$

where the brackets denote an average over the inhomogeneous broadening. The second equality follows when one neglects inter-aggregate interactions in Eq. (29). Using this and the expression for $I_{FL}(\mathbf{R},t)$ [Eq. (43)] we get

$$\frac{dW(t)}{dt} = \iint d^2\mathbf{R}\, I(\mathbf{R},t) \approx \iint d^2\mathbf{R}\, I_{FL}(\mathbf{R},t) \quad (A10)$$

which means that the rate of photon emission is due almost entirely to fluorescence when the optical density is low.

Integrating (A9) from $t = 0$ to $t = \infty$ and using Eqs. (43) and (44) gives

$$\int_0^\infty I_{FL}(\mathbf{R},t)dt = \frac{s(\mathbf{R})}{\gamma} MN, \qquad (A11)$$

where we have also used $W(0) = (1/3)MN(\theta_p^2/4)$. Equation (A11) says that the integrated fluorescence is independent of the width of the inhomogeneous broadening σ and is a statement of the conservation of energy. This can be seen in the fluorescence decays in Fig. 5.

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