

## Radiative decay and energy transfer in molecular aggregates: The role of intermolecular dephasing

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A microscopic theory for radiative lifetimes and energy transfer rates in molecular aggregates is developed. Using an effective Hamiltonian, we show that the radiative decay rate of isolated small aggregates with  $N$  molecules is  $N\gamma$ , where  $\gamma$  is the radiative rate of a single molecule. This linear dependence on  $N$  saturates when the aggregate size becomes comparable with the wavelength of light associated with the optical transition, and for large  $N$  the rate attains a limiting value independent of  $N$ . Intermolecular dephasing processes are incorporated by introducing a thermal bath and solving for the time evolution of the density matrix with use of an effective Liouville operator. Intermolecular dephasing destroys the coherent interaction of the aggregate with the radiation field and the rate changes from  $N\gamma$  to  $\gamma$  as the dephasing rate increases. A coherence length which depends on the strength of intermolecular interactions and on the dephasing rate is defined and calculated.

### I. INTRODUCTION

Spectroscopic studies of molecular aggregates in the gas phase and in condensed phases (solutions, solids, surfaces) provide detailed information regarding intermolecular interactions and dynamical processes. Aggregated dye molecules play an essential role in photography, and extensive studies were conducted on the photophysics of cyanine dyes.<sup>1-8</sup> Other phenomena in which molecular aggregates play an essential role include electron transfer in reaction centers<sup>9</sup> and nonlinear optical processes in organic materials.<sup>10,11</sup> Recent advances in supersonic beam spectroscopy allow a careful study of isolated ultracold molecular aggregates.<sup>12,13</sup>

The calculation of energy transfer and radiative relaxation in molecular aggregates is a fundamental problem which will be addressed in the present article. We consider an aggregate consisting of  $N$  identical two-level molecules. The molecular electronic transition frequency will be denoted  $\omega_0$  and the corresponding wave vector is

$$k_0 = \omega_0/c. \quad (1.1)$$

The radiative decay rate of a single molecule is  $\gamma/\hbar$ , where

$$\gamma = \frac{4k_0^3}{3} |\mu_{eg}|^2. \quad (1.2)$$

Here  $\mu_{eg}$  is the transition dipole matrix element between the ground  $|g\rangle$  and electronically excited  $|e\rangle$  state. For a  $d$ -dimensional aggregate (linear chain, square, or cube for  $d=1,2,3$ , respectively) we define

$$N^* = (k_0 a)^{-d}, \quad (1.3)$$

where  $a$  is the nearest-neighbor intermolecular spacing. When  $N \ll N^*$  we can use the dipole approximation for the entire aggregate since its size is much smaller than

the optical wavelength. A simple back-of-the-envelope calculation shows that the transition dipole in the aggregate will scale as  $N^{1/2}\mu_{eg}$ . The radiative decay rate will thus scale linearly with  $N$  and will be given by  $N\gamma$ . This simple relation is often used to evaluate the aggregate size by measuring its radiative decay rate.<sup>14,15</sup> It is clear that this scaling will not hold as  $N$  becomes comparable with  $N^*$ , since then the aggregate size becomes comparable to the optical wavelength and the dipole approximation no longer holds. This is the reason why the radiative lifetime in a solid ( $N \rightarrow \infty$ ) is not infinitely short. The generalization of this simple scaling for an arbitrary aggregate size is one of the goals of the present article. An important effect which was not incorporated in the above considerations is the role of the other degrees of freedom (e.g., intramolecular vibrations, interaction with the solvent). The  $N\gamma$  radiative rate is a result of a *coherent interaction* of all the molecules in the aggregate with the radiation field. The interaction with a thermal bath will introduce fluctuations which may affect the different molecules in a different way. One possible outcome of such fluctuations is the introduction of *intermolecular dephasing* which will destroy the coherence among different molecules. We expect that due to the dephasing processes, the  $N\gamma$  rate will change into  $N_{\text{eff}}\gamma$  where  $N_{\text{eff}}$  is the effective number of coherently coupled molecules.  $N_{\text{eff}}$  is expected to attain the limiting value  $N_{\text{eff}}=1$  as the dephasing rate becomes sufficiently large to decouple the radiative dynamics of each molecule. We shall further introduce a coherence length  $\xi$  which determines the length scale over which different molecules evolve coherently, i.e.,

$$N_{\text{eff}} \equiv (\xi/a)^d. \quad (1.4)$$

In this article, we develop a general theory for the radiative and nonradiative dynamics of molecular aggregates. In Sec. II we construct an *effective Hamiltonian* which

properly takes the radiative interactions into account. An averaging over the continuum of photons provides a compact way for calculating the radiative rates and energy transfer in isolated aggregates (in the absence of a thermal bath). In order to treat the dephasing processes we need to consider the density matrix in Liouville space and develop an *effective Liouville operator*. This is done in Sec. III. An averaged radiative decay rate  $S$  is defined and a closed-form expression for  $N_{\text{eff}}$  (or the correlation length  $\xi$ ) is derived. In Sec. IV we specialize to  $N=2$  (dimers) and calculate energy transfer and the time evolution following an optical excitation. The radiative decay rate is shown to change from  $2\gamma$  to  $\gamma$  as the intermolecular separation increases. This agrees with the result of Power.<sup>16</sup> In addition, we show how the coherent rate  $2\gamma$  changes to  $\gamma$  for a fixed intermolecular separation as the dephasing rate increases. The energy transfer in the dimer is calculated as well, resulting in a generalization of Forster's rate expression. In Sec. V we consider medium-size aggregates and study the variation of the radiative decay rate with  $N$  and with the dephasing rate. In Sec. VI we repeat these calculations for large (solidlike) aggregates. Finally, in Sec. VII we summarize our results.

## II. THE EFFECTIVE HAMILTONIAN FOR MOLECULAR AGGREGATES

We consider an aggregate consisting of  $N$  identical molecules. We assume that each molecule has two states: a ground state  $|g\rangle$  and an excited state  $|e\rangle$ . In the present article we shall consider only the following zeroth-order states of the aggregate:

$$|g\rangle \equiv \prod_{j=1}^N |g_j\rangle, \quad (2.1a)$$

$$|n\rangle \equiv \prod_{\substack{j=1 \\ (j \neq n)}}^N |g_j\rangle |e_n\rangle, \quad (2.1b)$$

and

$$|u\rangle \equiv \prod_{\substack{j=1 \\ (l \neq j \neq m)}}^N |e_l\rangle |e_m\rangle |g_j\rangle (l \neq m). \quad (2.1c)$$

$|g\rangle$  denotes a state in which all molecules are in the ground state.  $|n\rangle$  denotes a state in which the  $n$ th molecule is excited and all other molecules are in the ground state.  $|u\rangle$  denotes a state in which molecules  $l$  and  $m$  are in the excited state. The total Hamiltonian for the system and the radiation field is given by<sup>16-19</sup>

$$H = H_0 + H_{\text{rad}} + H_{\text{int}} + H_{\text{dd}}, \quad (2.2a)$$

where

$$H_0 = (-\hbar\omega_0) |g\rangle\langle g| + \sum_u (\hbar\omega_0) |u\rangle\langle u|, \quad (2.2b)$$

$$H_{\text{rad}} = \hbar \sum_k \omega_k a_k^\dagger a_k, \quad (2.2c)$$

$$H_{\text{int}} = \sum_\alpha \frac{e_\alpha \mathbf{p}_\alpha \cdot \mathbf{A}(\mathbf{r}_\alpha)}{M_\alpha c} + \frac{e_\alpha^2 A^2(\mathbf{r}_\alpha)}{2M_\alpha c^2}, \quad (2.2d)$$

$$H_{\text{dd}} = \sum_{i,j,n,m} -\mu^{(n)} \cdot \frac{(3\hat{\mathbf{r}}_i \hat{\mathbf{r}}_j - \vec{\mathbf{I}})}{r_{nm}^3} \cdot \mu^{(m)}. \quad (2.2e)$$

The subscript  $\alpha$  runs over all the particles (electrons and nuclei) with charge  $e_\alpha$ , mass  $M_\alpha$ , and position  $\mathbf{r}_\alpha$ .  $i$  and  $j$  label Cartesian coordinates  $(x, y, z)$  and  $\hat{\mathbf{r}}_i$  is a unit vector in the  $i$  direction.  $H_{\text{dd}}$  is the dipole-dipole interaction,  $\mu^{(n)}$  is the dipole operator of the  $n$ th molecule,  $\vec{\mathbf{I}}$  is the unit tensor, the dot in Eq. (2.2e) denotes a tensor product, and  $r_{nm}$  is the intermolecular separation between the  $n$  and  $m$  molecules.  $\omega_0$  is the transition frequency. The zero of energy is taken to be the energy of the  $|n\rangle$  states.  $\mathbf{A}(\mathbf{r})$  is the vector potential of the radiation field at point  $\mathbf{r}$ . It is purely transverse and may be expanded in a Fourier series

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k}, \epsilon} \left[ \frac{2\pi\hbar c}{V k} \right]^{1/2} \epsilon [a_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) + a_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})]. \quad (2.3)$$

$a_{\mathbf{k}}^\dagger$  ( $a_{\mathbf{k}}$ ) is the creation (annihilation) operator for a  $\mathbf{k}$  photon and  $V$  is the quantization volume. The state of the polarization of the electric field is defined by  $\epsilon$  where  $\epsilon$  is a unit vector along the direction of the polarization. Hereafter we neglect the  $A^2$  term in  $H_{\text{int}}$  since it does not contribute to the decay processes under consideration in this article.

We shall be interested in calculating the time evolution following an optical excitation which prepares the system in a superposition of the  $|n\rangle$  states. We consider only the  $|n\rangle$  states and those accessible to the  $|n\rangle$  states by one radiative interaction; hence our choice of states in Eqs. (2.1). The relevant combined states of the aggregate and the radiation field are  $|n, \text{vac}\rangle$  (the aggregate is in the  $|n\rangle$  state and the photon field is in the vacuum state),  $|g, \mathbf{k}\rangle$  (the aggregate is in the ground state  $|g\rangle$  and the radiation field has a single photon  $|\mathbf{k}\rangle$ ), and  $|u, \mathbf{k}\rangle$  (the aggregate is in the excited state  $|u\rangle$  and the radiation field has a single photon  $|\mathbf{k}\rangle$ ). The total wave function of the aggregate and the radiation field at time  $t$  may be expanded in the form

$$|\Psi(t)\rangle = \sum_n c_n(t) |n, \text{vac}\rangle + \sum_k d_k(t) |g, \mathbf{k}\rangle + \sum_k f_{u, \mathbf{k}}(t) |u, \mathbf{k}\rangle, \quad (2.4)$$

where  $d_{\mathbf{k}}(0) = f_{u, \mathbf{k}}(0) = 0$ . In order to solve for the coefficients  $c_n(t)$  it is most convenient to construct an *effective Hamiltonian* which provides a reduced description in which the effects of the continuum states  $|g, \mathbf{k}\rangle$  and  $|u, \mathbf{k}\rangle$  are treated implicitly. This may be done by using projection operators.<sup>20-22</sup> For the present model, the effective Hamiltonian can be calculated exactly. Using the projection operator

$$\hat{P} = \sum_n |n, \text{vac}\rangle\langle n, \text{vac}| \quad (2.5a)$$

and the complementary projection

$$\hat{Q} \equiv 1 - \hat{P} = \sum_{u, k} (|g, k\rangle \langle g, k| + |u, k\rangle \langle u, k|). \quad (2.5b)$$

The projected wave function satisfies the equation

$$\frac{d}{dt} [\hat{P}\Psi(t)] = -i\hat{P}H_0\hat{P}\Psi(t) - \int_0^t \hat{P}R(t-\tau)\hat{P}\Psi(\tau)d\tau. \quad (2.6)$$

Equation (2.6) is a closed equation for the coefficients  $c_n$ , i.e.,

$$\dot{c}_n(t) = - \sum_m \int_0^t d\tau R_{nm}(t-\tau)c_m(\tau), \quad (2.7)$$

where

$$R(t) = \frac{-1}{2\pi i} \int_{-\infty}^{\infty} dE R(E) \exp(-iEt) \quad (2.8)$$

and

$$R(E) = \hat{P}V\hat{P} + \hat{P}V\hat{Q} \frac{1}{E - \hat{Q}H\hat{Q}} \hat{Q}V\hat{P} \quad (2.9)$$

with

$$V = H_{\text{int}} + H_{\text{dd}}. \quad (2.10)$$

The solution of Eq. (2.6) is

$$P\Psi(t) = PU(t)P\Psi(0). \quad (2.11)$$

The time evolution operator  $U$  is related to the Green function

$$\hat{P}U(t)\hat{P} = \frac{-1}{2\pi i} \int_{-\infty}^{\infty} dE \hat{P}G(E)\hat{P} \exp(-iEt), \quad (2.12)$$

and the projected Green function is given by

$$\hat{P}G(E)\hat{P} = \frac{1}{E - H_{\text{eff}}(E)}, \quad (2.13)$$

where we have introduced the effective Hamiltonian<sup>20-22</sup>

$$H_{\text{eff}} = H_0 + R(E). \quad (2.14)$$

The effective Hamiltonian is a complex (non-Hermitian) operator. We shall separate it into its real and imaginary parts [ $\Delta(E)$  and  $\Gamma(E)$ , respectively]

$$R(E) \equiv \Delta(E) - (i/2)\Gamma(E). \quad (2.15)$$

Explicit formulas for the  $\Delta(E)$  and  $\Gamma(E)$  are derived in Appendix A. Since the energy dependence of  $\Delta(E)$  and  $\Gamma(E)$  is weak,<sup>20-22</sup> we can assume that they are independent of  $E$  on the energy shell relevant for the evolution of

$PG(E)P$ . We thus replace  $E$  by  $E_0$  (here  $E_0 = \hbar\omega_0$  is the electronic transition energy) and denote

$$\Delta \equiv \Delta(E_0), \quad (2.16a)$$

$$\Gamma \equiv \Gamma(E_0), \quad (2.16b)$$

and the effective Hamiltonian becomes

$$H_{\text{eff}} = H_0 + \Delta - \frac{1}{2}i\Gamma. \quad (2.17)$$

When Eqs. (2.16) hold, the equation of motion for  $c_n$  [Eq. (2.7)] assumes the form

$$\dot{c}_n = -i \sum_m \Delta_{nm} c_m - \frac{1}{2} \sum_m \Gamma_{nm} c_m. \quad (2.18)$$

The real and imaginary parts of the matrix elements of  $H_{\text{eff}}$  [Eq. (2.16)] are given by<sup>30</sup> (see Appendix A)

$$\Delta_{nn} = 0, \quad (2.19a)$$

$$\Delta_{nm} = \mu_{eg}^{(n)} \cdot \left[ -\vec{\alpha} \frac{k_0^2}{r_{nm}} \cos(k_0 r_{nm}) + \vec{\beta} \frac{k_0}{r_{nm}^2} \sin(r_{nm} k_0) + \frac{\vec{\beta}}{r_m^3} \cos(k_0 r_{nm}) \right] \cdot \mu_{eg}^{(m)}, \quad n \neq m, \quad (2.19b)$$

$$\Gamma_{nn} \equiv \gamma = \frac{4k_0^3}{3} |\mu_{eg}|^2, \quad (2.20a)$$

$$\Gamma_{nm} \equiv 2k_0^3 \mu_{eg}^{(n)} \cdot \vec{\tau}(k_0 r_{nm}) \cdot \mu_{eg}^{(m)} \quad (n \neq m). \quad (2.20b)$$

The  $\vec{\alpha}$  and  $\vec{\beta}$  tensors are given by

$$\alpha_{ij} = \delta_{ij} - \hat{r}_i \hat{r}_j, \quad (2.21)$$

$$\beta_{ij} = \delta_{ij} - 3\hat{r}_i \hat{r}_j, \quad (2.22)$$

where  $i$  and  $j$  denote Cartesian coordinates and

$$\tau_{ij}(x) = \alpha_{ij} \frac{\sin(x)}{x} + \beta_{ij} \left[ \frac{\cos(x)}{x^2} - \frac{\sin(x)}{x^3} \right]. \quad (2.23)$$

We shall now write explicit expressions for  $\Delta_{nm}$  and  $\Gamma_{nm}$ . To that end we consider a pair of molecules. The orientation of the dipole moment of molecule  $n$  ( $m$ ) relative to the intermolecular axis is described by the polar angle  $\varphi_n$  ( $\varphi_m$ ) and the azimuthal angle  $\theta_n$  ( $\theta_m$ ) (Fig. 3). The angle  $\phi_{nm}$  between  $\mu_n$  and  $\mu_m$  is given by the relation

$$\cos(\phi_{nm}) = \sin(\theta_n) \sin(\theta_m) \cos(\varphi_n - \varphi_m) + \cos(\theta_n) \cos(\theta_m). \quad (2.24)$$

Equations (2.19) and (2.20) then assume the form

$$\Delta_{nm} = \frac{3\gamma}{4} \left[ \left[ \frac{-\cos(k_0 r_{nm})}{k_0 r_{nm}} + \frac{\sin(k_0 r_{nm})}{(k_0 r_{nm})^2} + \frac{\cos(k_0 r_{nm})}{(k_0 r_{nm})^3} \right] \cos\phi_{nm} - \left[ \frac{-\cos(k_0 r_{nm})}{k_0 r_{nm}} + \frac{3\sin(k_0 r_{nm})}{(k_0 r_{nm})^2} + \frac{3\cos(k_0 r_{nm})}{(k_0 r_{nm})^3} \right] \cos\theta_n \cos\theta_m \right], \quad (2.25)$$

$$\Gamma_{nm} = \frac{3\gamma}{2} \left[ \left[ \frac{\sin(k_0 r_{nm})}{k_0 r_{nm}} + \frac{\cos(k_0 r_{nm})}{(k_0 r_{nm})^2} - \frac{\sin(k_0 r_{nm})}{(k_0 r_{nm})^3} \right] \cos\phi_{nm} - \left[ \frac{\sin(k_0 r_{nm})}{k_0 r_{nm}} + \frac{3 \cos(k_0 r_{nm})}{(k_0 r_{nm})^2} - \frac{3 \sin(k_0 r_{nm})}{(k_0 r_{nm})^3} \right] \cos\theta_n \cos\theta_m \right]. \quad (2.26)$$

When the intermolecular distance is much smaller than the optical wavelength, i.e.,  $k_0 r_{nm} \ll 1$ ,  $\Gamma_{nm}$  and  $\Delta_{nm}$  assume the following limiting forms:

$$\Gamma_{nm} = \gamma \cos\phi_{nm}, \quad (2.27)$$

$$\Delta_{nm} = \frac{3\gamma}{4(k_0 r_{nm})^3} (\cos\phi_{nm} - 3 \cos\theta_n \cos\theta_m). \quad (2.28)$$

In the other extreme,  $k_0 r_{nm} \gg 1$ , both  $\Gamma_{nm}$  and  $\Delta_{nm}$  vanish as  $r_{nm}^{-1}$ . In Figs. 1 and 2 we display  $\Delta_{12}$  and  $\Gamma_{12}$  for a pair of molecules whose dipole moments are parallel and form a  $90^\circ$  angle with the intermolecular axis ( $\theta_1 = \theta_2 = 90^\circ, \phi_{nm} = 0$ ).

### III. INTERMOLECULAR DEPHASING AND THE EFFECTIVE LIOUVILLE OPERATOR

So far, we have considered the radiative lifetimes of isolated aggregates. Molecular aggregates in condensed phase are usually subject to stochastic perturbations due to the interaction with the surrounding medium (solvent, solid surfaces, etc.). A major effect of these fluctuations is to destroy phase relationships (coherences) between various states. Since the variation of the radiative rate from  $\gamma$  to  $N\gamma$  depends upon the coherent evolution of the entire aggregate, we expect that such fluctuations will reduce the radiative rates. For large fluctuations, each

molecule in the aggregate should behave independently and the radiative rate should become  $\gamma$ . In the present work we assume that the solvent fluctuations introduce dephasing processes which are often dominant in determining spectral line shapes in condensed phases.<sup>11</sup> The dephasing is introduced by assuming that the electronic transition frequency of each molecule is undergoing rapid fluctuations<sup>23,24</sup>

$$\omega_0^{(n)} = \omega_0 + \delta\omega_n(t) \quad (3.1)$$

with

$$\langle \delta\omega_n(t) \rangle = 0 \quad (3.2a)$$

and

$$\langle \delta\omega_n(t) \delta\omega_{n'}(0) \rangle = \hat{\Gamma} \delta(t) \delta_{n,n'}. \quad (3.2b)$$

Here  $\langle \rangle$  denotes an ensemble average over the bath and we assume that the fluctuations of different molecules are uncorrelated.  $\delta\omega_n(t)$  is taken to be a stochastic Gaussian-Markovian process. This model was introduced by Haken and Strobl<sup>23,24</sup> to describe exciton transport in solids. Any experimental observable of this system will require performing an ensemble average over the stochastic fluctuations. To that end we need to write the equation of motion of the density matrix in Liouville space. The ensemble averaged density matrix  $\rho$  evolves

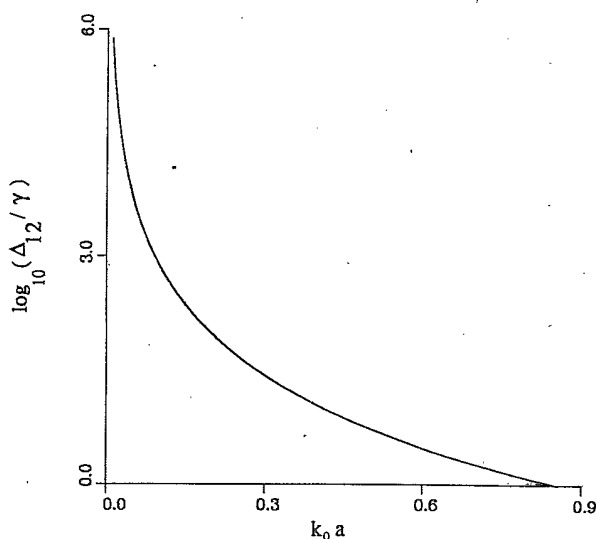


FIG. 1. Real part of the intermolecular coupling in the effective Hamiltonian [Eq. (2.25)] plotted vs  $k_0 a$  on a logarithmic scale (base 10).  $\phi_{12} = 0^\circ$ ,  $\theta_1 = \theta_2 = 90^\circ$ .  $\gamma$  is the radiative lifetime of an isolated molecule [Eq. (1.2)].

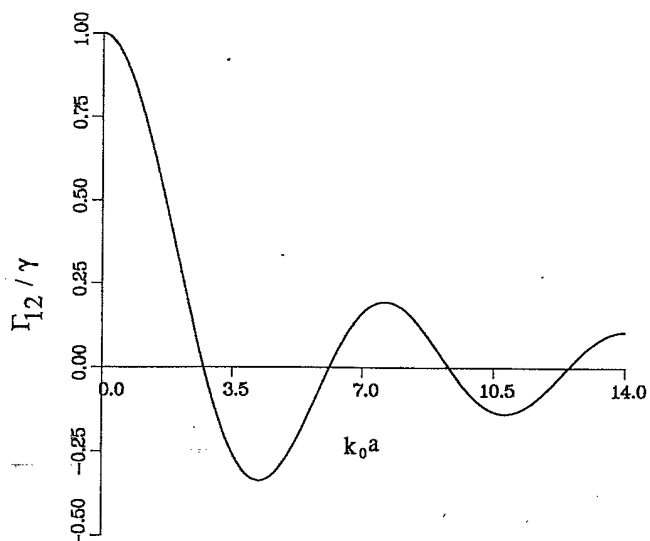


FIG. 2. Imaginary part of the intermolecular coupling in the effective Hamiltonian [Eq. (2.26)] plotted vs  $k_0 a$ .  $\phi_{12} = 0^\circ$ ,  $\theta_1 = \theta_2 = 90^\circ$ .

in time according to the reduced Liouville equation<sup>24,25</sup>

$$\dot{\rho}_{nm} = -i \sum_{n',m'} L_{nm,n'm'} \rho_{n'm'}, \quad (3.3)$$

where

$$L = L_0 + L'. \quad (3.4)$$

$L_0$  is the Liouville operator corresponding to the effective Hamiltonian [Eq. (2.14)], i.e.,

$$L_0 A = H_{\text{eff}} A - A H_{\text{eff}}^\dagger. \quad (3.5a)$$

The tetradic (Liouville space) matrix elements are given by<sup>25</sup>

$$(L_0)_{nm,n'm'} = \delta_{mn'} (H_{\text{eff}})_{nn'} - \delta_{nn'} (H_{\text{eff}}^*)_{mm'}. \quad (3.5b)$$

$L'$  contains the *pure dephasing* resulting from the stochastic modulation and its matrix elements are given by

$$(L')_{nm,n'm'} = -2i(1 - \delta_{n,m}) \hat{\Gamma} \delta_{n,n'} \delta_{m,m'}. \quad (3.6)$$

$\hat{\Gamma}$  induces the decay of intermolecular coherences ( $\rho_{nm}$  where  $n \neq m$ ). Since fluctuations on different sites are uncorrelated [Eq. (3.2b)], the dephasing rate does not depend on  $n$  or  $m$ . The solution of the Liouville equation is

$$\rho_{nm}(t) = \sum_{n',m'} G_{nm,n'm'}(t) \rho_{n'm'}(0), \quad (3.7)$$

where the Liouville-space Green function is given by

$$G(t) = i \int_{-\infty}^{\infty} \exp(-i\omega t) G(\omega) d\omega \quad (3.8)$$

and

$$G(\omega) = (\omega - L_0 - L')^{-1}. \quad (3.9)$$

Equation (3.9) is formally similar to Eq. (2.13). The Liouville-space Green function<sup>25,26</sup> is an  $N^2 \times N^2$  matrix, whereas the Hilbert-space Green function is  $N \times N$ . The effect of the pure dephasing will be explored in detail in the following sections. It will prove useful in our subsequent analysis to consider the total probability of the aggregate to be electronically excited at time  $t$ , i.e.,

$$P_e(t) \equiv \sum_n \rho_{nn}(t) = \sum_{n,n',m'} G_{nn,n'm'}(t) \rho_{n'm'}(0). \quad (3.10)$$

Note that  $P_e(0) = 1$ .  $P_e(t)$  is directly observed in a time-resolved fluorescence experiment, since the total fluorescence is proportional to  $P_e(t)$ . A convenient measure of the radiative decay rate is provided by the quantity  $S$ ,

$$S^{-1} = \int_0^{\infty} dt P_e(t). \quad (3.11)$$

$S^{-1}$  is the average lifetime of an electronic excitation and  $S$  represents an average decay rate.  $S$  depends of course on the initial density matrix  $\rho_{nm}(0)$  which is determined by the nature of the excitation process in a particular experiment. The effective number of radiatively coupled molecules  $N_{\text{eff}}$  and the aggregate coherence length  $\xi$  [Eq. (1.4)] may be defined by

$$N_{\text{eff}} \equiv S/\gamma \equiv (\xi/a)^d. \quad (3.12)$$

#### IV. RADIATIVE PROCESSES IN DIMERS

We shall now analyze the time evolution of a molecular dimer made of two identical molecules separated by a distance  $a$ . The eigenstates of  $H_{\text{eff}}$  [Eq. (2.14)] are, in this case,

$$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle), \quad (4.1a)$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle), \quad (4.1b)$$

with the eigenvalues

$$E_{\pm} = \pm \Delta_{12} + (i/2)(\gamma \pm \Gamma_{12}). \quad (4.2)$$

The  $|+\rangle$  state carries all the oscillator strength, i.e.,

$$|\langle +|\mu|g\rangle|^2 = 2\mu_{eg}^2, \quad (4.3a)$$

$$|\langle -|\mu|g\rangle|^2 = 0. \quad (4.3b)$$

Following a short pulsed excitation, the initial density matrix will then be

$$\rho(0) = |++\rangle = \frac{1}{2}(|11\rangle + |22\rangle + |12\rangle + |21\rangle). \quad (4.4)$$

The Liouville equation [Eq. (3.3)] was solved by using the Dyson equation<sup>22</sup> to get the matrix elements of the  $4 \times 4$  matrix  $G_{nm,n'm'}(\omega)$ . A Fourier transform then yields the time evolution. We have calculated  $P_e(t)$  [Eq. (3.10)] with the initial condition [Eq. (4.4)] resulting in

$$P_e(t) = \frac{1}{2} \left[ 1 + \frac{(\hat{\Gamma} - \Gamma_{12})}{\kappa} \right] \exp[(-\gamma - \hat{\Gamma} + \kappa)t] + \frac{1}{2} \left[ 1 - \frac{(\hat{\Gamma} - \Gamma_{12})}{\kappa} \right] \exp[(-\gamma - \hat{\Gamma} - \kappa)t], \quad (4.5)$$

where

$$\kappa = (\hat{\Gamma}^2 + \Gamma_{12}^2)^{1/2}. \quad (4.6)$$

Note that  $P_e(t)$  does not depend on the real part of the intermolecular coupling  $\Delta_{12}$ . Let us consider the limiting cases of Eq. (4.5). For  $\hat{\Gamma} \ll \Gamma_{12}$ ,  $\kappa \cong \Gamma_{12}$  and

$$P_e(t) \cong \exp[-(\gamma + \Gamma_{12})t]. \quad (4.7a)$$

Typically, for molecular aggregates  $k_0 a \ll 1$  (for example, taking  $a = 2 \text{ \AA}$  and an optical wavelength of  $6000 \text{ \AA}$  we have  $k_0 a = 0.002$ ). In this case  $\Gamma_{12}$  is given by Eq. (2.27). For a parallel configuration  $\phi_{12} = 0$  we have  $\Gamma_{12} \cong \gamma$  and Eq. (4.7a) results in

$$P_e(t) \cong \exp(-2\gamma t). \quad (4.7b)$$

In this limit the radiative time evolution is coherent and the rate is  $2\gamma$ . In the other extreme of fast dephasing  $\hat{\Gamma} \gg \Gamma_{12}$  we have  $\kappa \cong \hat{\Gamma}$  and Eq. (4.5) yields

$$P_e(t) \cong \exp(-\gamma t). \quad (4.8)$$

In this limit, the two molecules are decoupled and the radiative decay is identical to that of a single molecule. Using Eqs. [(4.5)-(4.6)] we get for the average decay rate

$$S = \left[ \frac{\eta}{1+\eta} \right] \Gamma_{12} + \gamma, \quad (4.9a)$$

where

$$\eta \equiv \frac{\gamma - \Gamma_{12}}{2\hat{\Gamma}} \quad (4.9b)$$

In the physically realistic limit whereby  $k_0 a \ll 1$ , we have, using Eqs. (4.9b) and (2.27),

$$\eta \approx \frac{\gamma}{2\hat{\Gamma}} \left[ (1 - \cos\phi_{nm}) + (k_0 r_{nm})^2 \left[ \frac{2 \cos\phi_{nm} - \cos\theta_n \cos\theta_m}{10} \right] \right] \quad (4.10)$$

$$P_0(t) = \frac{\exp[-(\hat{\Gamma} + \gamma)t]}{4} \left[ \frac{\kappa - \hat{\Gamma}}{\kappa} \exp(-\kappa t) + \frac{\kappa + \hat{\Gamma}}{\kappa} \exp(\kappa t) + \frac{\alpha + i\hat{\Gamma}}{\alpha} \exp(-i\alpha t) + \frac{\alpha - i\hat{\Gamma}}{\alpha} \exp(i\alpha t) \right], \quad (4.12)$$

where

$$\alpha = (4\Delta_{12}^2 - \hat{\Gamma}^2)^{1/2} \quad (4.13)$$

and  $\kappa$  is given in Eq. (4.6). In the absence of dephasing  $\hat{\Gamma} = 0$ ,  $\kappa = \Gamma_{12}$ , and  $\alpha = 2\Delta_{12}$ , we get

$$P_0(t) = \frac{\exp(-\gamma t)}{2} [\cos(2\Delta_{12}t) + \cosh(\Gamma_{12}t)]. \quad (4.14)$$

The time evolution is oscillatory and shows quantum beats<sup>20,22</sup> with frequency  $\Delta_{12}$ . In the other extreme  $\hat{\Gamma} \gg \Gamma_{12}$ ,  $\Delta_{12}$  we have  $\kappa = \hat{\Gamma}$ ,  $\alpha = i\hat{\Gamma}$ , and

$$P_0(t) = \frac{\exp(-\gamma t)}{2} \left[ \exp\left[\frac{\Gamma_{12}^2}{2\hat{\Gamma}} t\right] + \exp\left[-\frac{2\Delta_{12}^2}{\hat{\Gamma}} t\right] \right] \quad (4.15)$$

If we neglect the imaginary part of the intermolecular coupling and set  $\Gamma_{12} = 0$ , Eq. (4.15) represents an incoherent energy transfer described by a Pauli master equation with an energy transfer rate  $2\Delta_{12}^2/\hat{\Gamma}$ . This corresponds to the Forster limit. Since typically  $\Gamma_{12} \ll \Delta_{12}$  (see Figs. 1 and 2), neglecting  $\Gamma_{12}^2/\hat{\Gamma}$  compared to  $\Delta_{12}^2/\hat{\Gamma}$  may usually be justified. Power and Thirunamachandran<sup>17</sup> have evaluated  $P_0(t)$  in the absence of dephasing ( $\hat{\Gamma} = 0$ ) using the Fermi golden rule and assuming that  $P_0(t)$  decays exponentially with time. The present results are at variance with their analysis. In general, the time evolution of  $P_0(t)$  as given by Eq. (4.12) is oscillatory and shows quantum beats.<sup>20,22</sup> Only when  $\hat{\Gamma}$  is much larger than  $\Delta_{12}$  and  $\gamma$ , will the time evolution of  $P_0(t)$  become exponential and the Fermi golden rule hold. A similar behavior was found by Kenkre and Knox.<sup>29</sup>

It is interesting to note that both the radiative decay [as reflected in  $P_e(t)$ ] and the energy transfer [as reflected in  $P_0(t)$ ] are incoherent when  $\hat{\Gamma}$  is sufficiently large. A relatively small dephasing which is large compared with  $\gamma$  is sufficient to destroy the radiative coherence and make the radiative decay rate incoherent. However, in order to obtain incoherent energy transfer  $\hat{\Gamma}$  has to be large compared with the intermolecular coupling  $\Delta_{12}$ .

As expected, for the limit  $k_0 a \ll 1$ ,  $S$  varies between the value  $\gamma[1 + \cos\phi_{nm}]$  for  $\eta \gg 1$  and  $\gamma$  for  $\eta \ll 1$ .

Energy transfer in molecular aggregates may be studied by exciting a molecule and following the probability of the excitation to remain on the initially excited molecule:

$$P_0(t) \equiv G_{11,11}(t). \quad (4.11)$$

This is the Forster energy transfer problem.<sup>27-29</sup> Using the same Green function used in the calculation of  $P_e(t)$ , we have derived the following expression for  $P_0(t)$ :

Since typically  $\Delta_{12} \gg \gamma$  (for example, taking  $\varphi_{12} = 0^\circ$ ,  $\theta_1 = \theta_2 = 90^\circ$ , and  $a = 2 \text{ \AA}$ , we have  $\Delta_{12}/\gamma = 8 \times 10^7$ , see Figs. 1 and 2) the incoherence in the lifetime is achieved much earlier than for the energy transfer. It is therefore conceivable that in the same aggregate the radiative decay will be incoherent with a rate  $\gamma$  while at the same time the energy-transfer process will be coherent.

## V. RADIATIVE PROCESSES IN MEDIUM SIZE AGGREGATES

We are now in a position to study the variation of the radiative lifetime with aggregate size. We consider a linear chain of  $N$  identical molecules separated by a distance  $a$  (Fig. 3). We further assume  $\varphi_{nm} = 0^\circ$  and  $\theta_n = 90^\circ$ , i.e., the dipole moments of the molecules are parallel to each other and are perpendicular to the intermolecular axis. We first consider the eigenvalues and eigenstates of  $H_{\text{eff}}$  which determine the time evolution in the absence of dephasing  $\hat{\Gamma} = 0$

$$H_{\text{eff}} |j\rangle = (E_j - \frac{1}{2}i\gamma_j) |j\rangle. \quad (5.1)$$

These eigenvalues and eigenvectors may be calculated numerically. Unlike for the dimer, the state  $|+\rangle$  is no longer an eigenstate of  $H_{\text{eff}}$ . However, one eigenstate will still be dominant in the optical transition and will carry most of the oscillator strength. This is illustrated in Fig. 4 where we display  $E_j$  and  $\gamma_j$  for an aggregate with

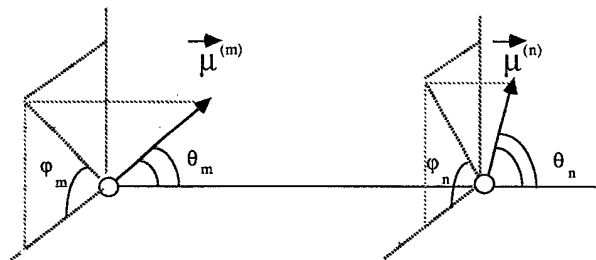


FIG. 3. Geometry of a molecular aggregate.

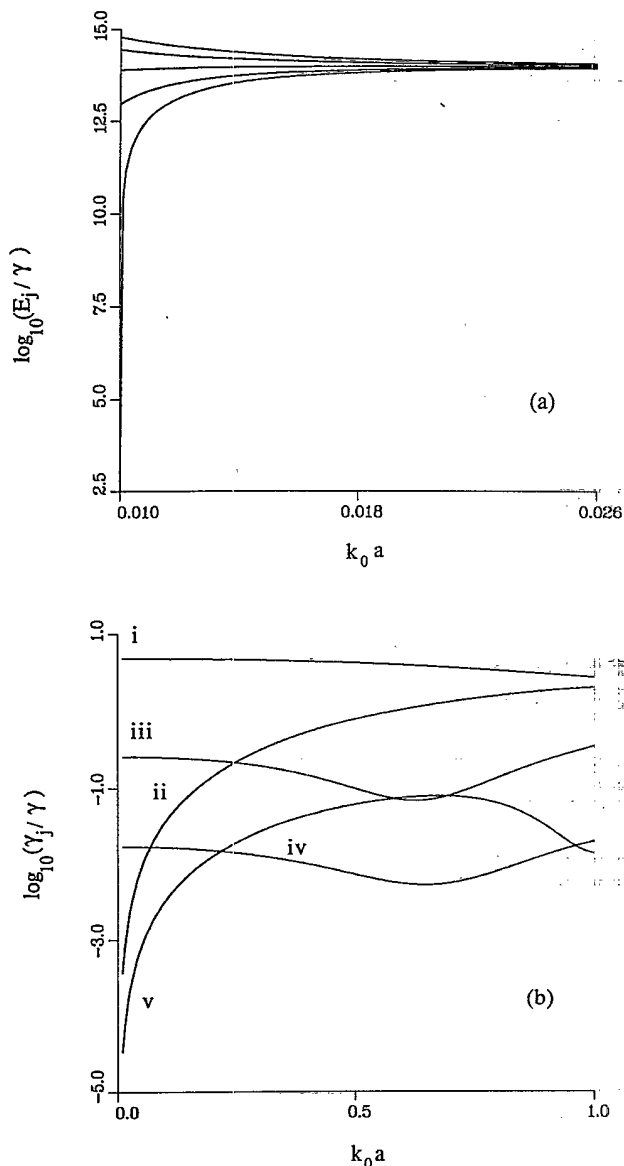


FIG. 4. Eigenvalues of the effective Hamiltonian for a one-dimensional aggregate with five molecules ( $N=5$ ) plotted vs  $k_0 a$ . The eigenvalues are labeled in order of decreasing energy (i), ..., (v), respectively.  $\phi_{ij}=0^\circ$ ,  $\theta_i=90^\circ$  ( $i, j=1, N$ ), and the dephasing rate  $\hat{\Gamma}=0$ . (a) The real part of the eigenvalues. (b) The imaginary part of the eigenvalues.

$N=5$ . The dominant eigenstate has  $\gamma_j \sim 5$  and the other eigenstates have much smaller values of  $\gamma_j$ . We shall denote this state as  $|d\rangle$ . When the various eigenvalues  $E_j$  are sufficiently far apart (compared with their widths) it may be possible to excite the aggregate to the state  $|d\rangle$  using a short pulse. Numerical calculations of  $P_e(t)$  and  $S$  were performed assuming that the system is initially prepared in the state with the highest oscillator strength

$$\rho(0) = |dd\rangle. \quad (5.2)$$

In Figs. 5 and 6 we present our calculations for the di-

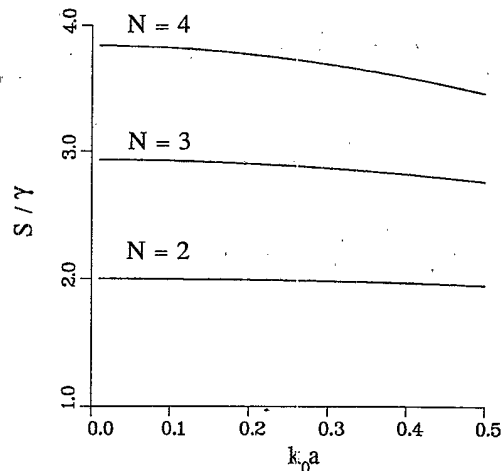


FIG. 5. Effective radiative decay rate  $S$  for a linear chain with 2, 3, and 4 molecules ( $N=2, 3, 4$ ) vs  $k_0 a$ . The initial state is taken to be the state with the largest oscillator strength  $|d\rangle$  (see text). The geometry is shown in Fig. 3.  $\phi_{ij}=0^\circ$ ,  $\theta_i=90^\circ$  ( $i, j=1, N$ ), and the dephasing rate  $\hat{\Gamma}=0$ .

mer, trimer, and tetramer. In Fig. 5 we set  $\hat{\Gamma}=0$  and varied the intermolecular separation, whereas in Fig. 6 we used a fixed intermolecular separation and varied  $\hat{\Gamma}$ . In Fig. 7 we specialize to the trimer and display the variation of  $S$  with  $\hat{\Gamma}$  for different intermolecular separations  $a$ . In Fig. 8 we show the variation of  $S$  with  $N$  for various values of  $\hat{\Gamma}$ . These figures clearly demonstrate how  $S$  changes from  $\sim N\gamma$  to  $\gamma$  as  $a$  or  $\hat{\Gamma}$  are increased and the coherent radiative dynamics is destroyed.

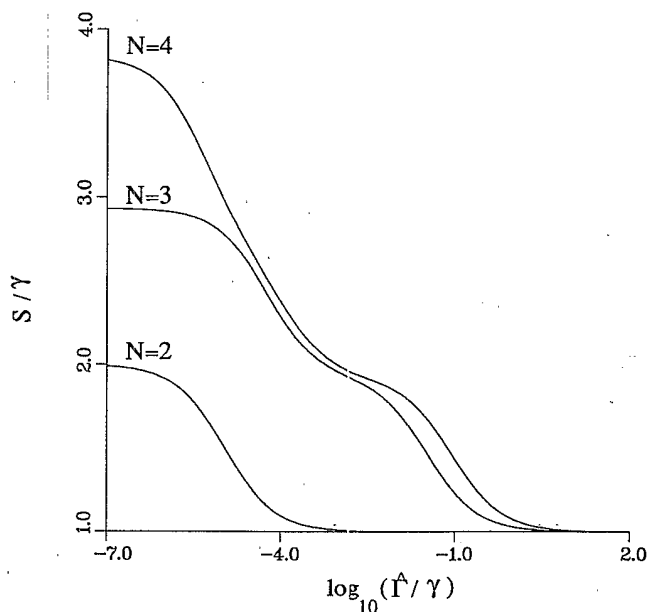


FIG. 6. Effective radiative rate  $S$  for a linear chain with 2, 3, and 4 molecules ( $N=2, 3, 4$ ) vs  $\hat{\Gamma}$ . The initial state is taken to be the state with the largest oscillator strength  $|d\rangle$  (see text). The geometry is shown in Fig. 3.  $\phi_{ij}=0^\circ$ ,  $\theta_i=90^\circ$  ( $i, j=1, N$ ), and  $k_0 a=0.01$ .

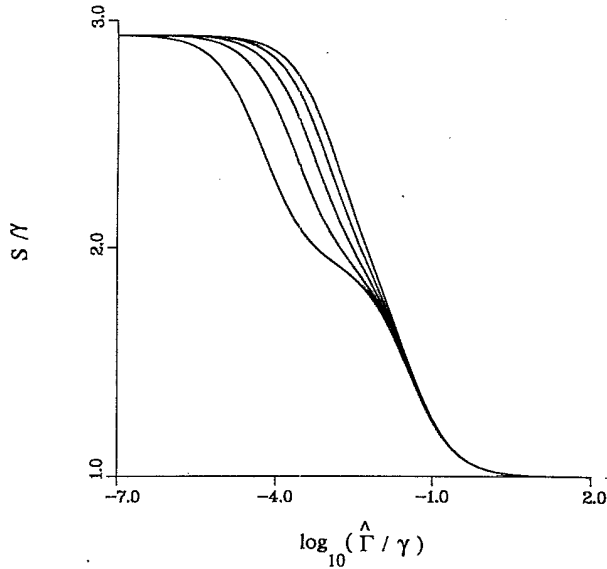


FIG. 7. Effective radiative decay rate  $S$  for a linear chain of three molecules vs  $\hat{\Gamma}$ . The various curves correspond to different intermolecular separations. From the bottom to the top,  $k_0 a = 0.01, 0.02, 0.03, 0.04,$  and  $0.05$ . The initial state is taken to be the state with the largest oscillator strength  $|d\rangle$  (see text). The geometry is shown in Fig. 3.  $\phi_{ij} = 0^\circ$ ,  $\theta_i = 90^\circ$  ( $i, j = 1, 3$ ), and the dephasing rate  $\hat{\Gamma} = 0$ .

## VI. RADIATIVE PROCESSES IN LARGE AGGREGATES

We shall now analyze aggregates whose size is much larger than the optical wavelength, i.e.,  $N \gg N^*$ . In this case we can calculate the time evolution analytically. We consider a linear chain, a two-dimensional lattice, or a

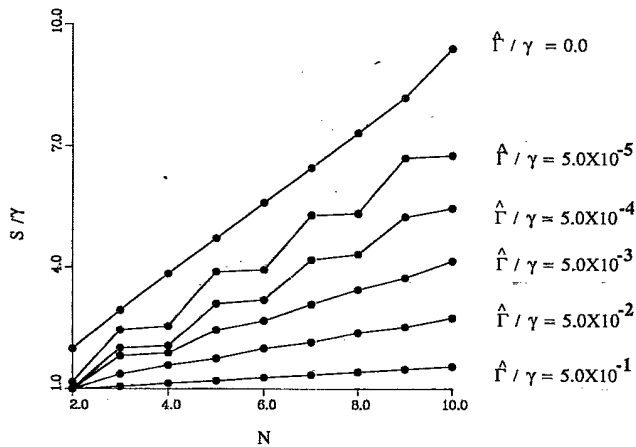


FIG. 8. Effective radiative decay rate  $S$  for linear aggregates of various sizes.  $k_0 a = 0.01$ , the geometry is shown in Fig. 3.  $\phi_{ij} = 0^\circ$ ,  $\theta_i = 90^\circ$  ( $i, j = 1, N$ ). The initial state is taken to be the state with the largest oscillator strength  $|d\rangle$  (see text). The various curves correspond to different values of the dephasing rate  $\hat{\Gamma}$  as indicated. As  $\hat{\Gamma}$  becomes large, the coherent evolution is destroyed and  $S/\gamma \rightarrow 1$ .

cubic lattice of  $N$  identical molecules separated by a distance  $a$ . The dipole moments of the molecules are parallel to each other and form an angle  $\theta$  with the intermolecular axis. When  $N$  is very large, the boundary effects for the eigenstates of  $H_{\text{eff}}$  become irrelevant, and the eigenstates are simply given by the Bloch states.<sup>30</sup> We denote the state which carries all the oscillator strength by

$$|+\rangle \equiv \frac{1}{\sqrt{N}} \sum_{n=1}^N |n\rangle. \quad (6.1)$$

We wish to calculate the effective radiative decay rate  $S$ , using the initial condition  $\rho(0) = |+\rangle\langle+|$ , i.e.,

$$S^{-1} = i \sum_n G_{nn,++}(\omega=0). \quad (6.2)$$

The Liouville-space Green function is calculated in Appendix B using the method developed by Loring and Mukamel.<sup>26</sup> This results in the following expression for  $S$ :

$$S = \frac{\hat{\Gamma} + F(0)}{N} \sum_{\mathbf{q}} F(\mathbf{q}) [\hat{\Gamma} + F(\mathbf{q})]^{-1}, \quad (6.3a)$$

where  $\mathbf{q}$  is a  $d$ -dimensional vector with components

$$q_i = \frac{2\pi n_i}{Na}, \quad n_i = 0, 1, \dots, N-1, \quad i = x, y, z \quad (6.3b)$$

and

$$F(\mathbf{q}) = \frac{1}{N} \sum_{n,m} \Gamma_{nm} \exp[i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)]. \quad (6.4)$$

The following limits are clear from Eq. (6.3). When  $\hat{\Gamma} = 0$ , we have

$$S = F(0) = \frac{1}{N} \sum_{n,m} \Gamma_{nm}. \quad (6.5)$$

For large dephasing  $\hat{\Gamma} \gg \gamma$ , Eq. (6.3) yields

$$S = \Gamma_{nn} = \gamma. \quad (6.6)$$

The lattice sums in Eqs. (6.3)–(6.5) can be evaluated approximately by converting the sums to integrals, as shown in Appendix B. For a one-dimensional aggregate we then get

$$S = \left[ \frac{ak_0}{\pi} \right] [\hat{\Gamma} + F'(0)] \times \int_0^{2\pi/ak_0} F'(q') [\hat{\Gamma} + F'(q')]^{-1} dq', \quad (6.7)$$

where

$$F'(q') = ak_0 \int_{-\infty}^{\infty} \Gamma(x) \exp(iq'x) dx \quad (6.8a)$$

and

$$q' \equiv \frac{q}{k_0}. \quad (6.8b)$$

For large  $\hat{\Gamma}$  Eq. (6.7) reduces to Eq. (6.6). For small  $\hat{\Gamma}$  we have expanded Eq. (6.7) in a Taylor series in  $\hat{\Gamma}$ . For  $\phi_{nm} = 0$  and  $\theta_n = \theta_m = 90^\circ$  (i.e., all the dipole moments parallel to each other and perpendicular to the inter-



molecular axis) we get<sup>31</sup>

$$\frac{S}{\gamma} = \frac{3\pi}{2ak_0} + \left[ \frac{1}{ak_0} - \frac{1}{8} \right] \chi + \left[ \frac{1}{12\pi} - \frac{1}{6\pi^2} \right] \chi^2 + \left[ \frac{1}{36\pi^2} \right] \chi^3 + \dots, \quad (6.9)$$

where

$$\chi \equiv \frac{2ak_0 \hat{\Gamma}}{\gamma}. \quad (6.10)$$

In the limit of no dephasing ( $\hat{\Gamma}=0$ ),  $S/\gamma$  assumes the following form, for  $\phi_{nm}=0$  and  $\theta_n=\theta_m=\theta$ :

$$S/\gamma = \frac{3\pi\gamma}{2k_0 a} (1 + \cos^2\theta). \quad (6.11)$$

In  $d$  dimensions,  $S/\gamma$  in the limit of small dephasing  $\hat{\Gamma} \rightarrow 0$  [i.e., the leading term in the expansion (6.9)] will be of the order of  $(ak_0)^{-d}$ .

## VII. DISCUSSION

In this article we develop a theoretical framework for calculating radiative lifetimes and energy transfer in molecular aggregates. An effective Hamiltonian allows us to treat isolated aggregates. We further develop an effective Liouville operator which determines the time evolution in the presence of a thermal bath which induces dephasing. The competition between the intermolecular interactions and the dephasing processes results in a finite coherence length. Molecules closer than the coherence length evolve in time in phase. As the dephasing rate increases, the coherence length vanishes and the radiative decay rate attains the limiting value of an isolated molecule.

The present theory unifies and generalizes several earlier treatments.<sup>32-36</sup> The dimer problem with dephasing was considered previously by Rahman, Knox, and Kenkre<sup>32</sup> who calculated the fluorescence depolarization. The equations of Sec. III are in agreement with their work. Our present results with  $\hat{\Gamma}=0$  agree with the results of Philpott,<sup>33</sup> Hopfield,<sup>34</sup> Silbey,<sup>35</sup> and Nienhuis and Schuller<sup>36</sup> in their treatments of the polariton problem found, on the other hand, that the radiative damping vanishes. This may be understood as follows. By considering an infinite crystal and quantizing the radiation field with the same boundary conditions of the matter and with the inclusion of only the first Brillouin zone, there is exactly the same number of polarization (matter) and radiation modes. These modes combine to form the polariton waves which are polarization waves dressed by the electromagnetic field. These waves constitute elementary excitations of the crystal and propagate without decay. If we consider a finite crystal and quantize the radiation field in a bigger box we increase the density of field modes without changing the density of matter modes. The field modes thus form a true dissipative continuum which is a necessary condition to have radiative damping.<sup>20,21</sup> This

is actually what is done in the present article (and by Philpott) since we are integrating over all  $k$  (rather than summing over the first Brillouin zone). These considerations may also explain the observation of Agranovich and Dubovskii<sup>37</sup> who noted that the cancellation of spontaneous emission as found by Hopfield<sup>34</sup> does not occur in one- and two-dimensional crystals when the radiation field is quantized in three dimensions. In this case there are many more radiation modes than matter modes and the radiation field forms a dissipative continuum which induces spontaneous emission. Our effective Liouville operator allows us to study these effects for finite-size systems and to include dephasing processes. Extensions to include random geometries and internal degrees of freedom (vibrations and rotations) are straightforward and will be made in the future.

Finally, it should be noted that an enhancement of oscillator strength analogous to that found in molecular aggregates may result in interesting nonlinear optical properties. This was found in quantum well structures and small semiconductor particles.<sup>33</sup> The present formulation may be extended to treat nonlinear optical line shapes as well.

## ACKNOWLEDGMENTS

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## APPENDIX A:

### DERIVATION OF THE EFFECTIVE HAMILTONIAN

In this appendix we derive explicit formulas for the matrix elements of  $H_{\text{eff}}$  [Eqs. (2.19) and (2.20)] to second order in  $V$ . Using Eqs. (2.9) and (2.15) and converting the summation over photon  $k$  states to an integration we get for the diagonal elements of  $H_{\text{eff}}$

$$\Delta_{nn}(E) = \frac{2k_0^2}{3\pi} \mu_{eg}^{(n)} \cdot \mu_{eg}^{(n)} \mathbf{P} \int \hbar c k \left[ \frac{1}{E + \hbar\omega_0 - \hbar ck} + \frac{1}{E - \hbar\omega_0 - \hbar ck} \right] dk, \quad (A1a)$$

$$\Gamma_{nn}(E) = \frac{4k_0^2}{3} \mu_{eg}^{(n)} \cdot \vec{\Psi}(E) \cdot \mu_{eg}^{(n)}, \quad (A1b)$$

where we are adopting tensor notation,  $i$  and  $j$  denote Cartesian components, and  $\mathbf{P}$  denotes the Cauchy principal part of the integral. The tensor  $\vec{\Psi}$  is given by

$$\Psi_{ij}(E) = \begin{cases} \delta_{ij} \left[ \frac{E + \hbar\omega_0}{\hbar c} + \frac{E - \hbar\omega_0}{\hbar c} \right], & E > \hbar\omega_0 \\ \delta_{ij} \frac{E + \hbar\omega_0}{\hbar c}, & -\hbar\omega_0 < E < \hbar\omega_0 \\ 0, & E < -\hbar\omega_0. \end{cases} \quad (\text{A2})$$

The off-diagonal elements of  $H_{\text{eff}}$  are given by

$$\Delta_{nm}(E) \equiv \text{Re}[R_{nm}(E)] = \frac{k_0^2}{\pi} \mu_{eg}^{(n)} \cdot \left[ \text{P} \int \hbar c k \tilde{\tau}(kr_{nm}) \left[ \frac{1}{E + \hbar\omega_0 - \hbar c k} + \frac{1}{E - \hbar\omega_0 - \hbar c k} \right] dk \right] \cdot \mu_{eg}^{(m)} + \frac{1}{r_{nm}^3} \mu_{eg}^{(n)} \cdot \vec{\alpha} \cdot \mu_{eg}^{(m)}, \quad (\text{A3a})$$

and

$$\Gamma_{nm}(E) \equiv -2 \text{Im}[R_{nm}(E)] = -2k_0^2 \mu_{eg}^{(n)} \cdot \vec{\Phi}(E) \cdot \mu_{eg}^{(m)}, \quad (\text{A3b})$$

$$\Phi_{ij}(E) = \begin{cases} \frac{E + \hbar\omega_0}{\hbar c} \tau_{ij} \left[ \frac{(E + \hbar\omega_0)r_{nm}}{\hbar c} \right] + \frac{E - \hbar\omega_0}{\hbar c} \tau_{ij} \left[ \frac{(E - \hbar\omega_0)r_{nm}}{\hbar c} \right], & E > \hbar\omega_0 \\ \frac{E + \hbar\omega_0}{\hbar c} \tau_{ij} \left[ \frac{(E + \hbar\omega_0)r_{nm}}{\hbar c} \right], & -\hbar\omega_0 < E < \hbar\omega_0 \\ 0, & E < -\hbar\omega_0 \end{cases} \quad (\text{A4})$$

and

$$\tau_{ij}(x) = \alpha_{ij} \frac{\sin(x)}{x} + \beta_{ij} \left[ \frac{\cos x}{(x)^2} - \frac{\sin x}{(x)^3} \right], \quad (\text{A5})$$

with

$$\alpha_{ij} = \delta_{ij} - \hat{r}_i \hat{r}_j, \quad (\text{A6})$$

$$\beta_{ij} = \delta_{ij} - 3\hat{r}_i \hat{r}_j. \quad (\text{A7})$$

$\Delta_{nm}$  is related to the Lamb shift. We shall assume that it is already included in  $\omega_0$  and set it to zero.

#### APPENDIX B: THE LIOUVILLE-SPACE GREEN FUNCTION AND THE RADIATIVE DECAY RATE OF LARGE AGGREGATES

In this appendix, we derive an expression for the Liouville-space Green function and the radiative decay rate of infinite-size aggregates. The derivation follows the procedure developed earlier.<sup>26</sup> In Liouville space, an ordinary operator  $A$  is represented by the ket  $|A\rangle\rangle$ , while  $A^\dagger$  is represented by the bra  $\langle\langle A|$ . An inner product can be defined as

$$\langle\langle A|B\rangle\rangle \equiv \text{Tr}(A^\dagger B). \quad (\text{B1})$$

Similarly, the "matrix element" of a tetradic operator  $L$  is defined by

$$\langle\langle A|L|B\rangle\rangle \equiv \text{Tr}(A^\dagger L B). \quad (\text{B2})$$

We define a basis set of Liouville vectors of the form

$$|A(\mathbf{s}, \mathbf{k})\rangle\rangle = N^{-1/2} \sum_{\mathbf{r}} \exp(-i\mathbf{k} \cdot \mathbf{r}) \times |\mathbf{r} - (\mathbf{s}/2)\rangle\rangle \langle\mathbf{r} + (\mathbf{s}/2)|. \quad (\text{B3})$$

In Eq. (B3),  $\mathbf{r}$  is the position vector of a lattice site, and  $N$  is the number of lattice sites. Substitution of Eq. (B3) into Eq. (B1) shows that the  $|A(\mathbf{s}, \mathbf{k})\rangle\rangle$  vectors form an orthonormal set

$$\langle\langle A(\mathbf{s}', \mathbf{k}')|A(\mathbf{s}, \mathbf{k})\rangle\rangle = \delta_{\mathbf{s}, \mathbf{s}'} \delta_{\mathbf{k}, \mathbf{k}'}. \quad (\text{B4})$$

The matrix element of the Liouvillian in this basis set is defined by

$$L(\mathbf{s}, \mathbf{k}; \mathbf{s}' \mathbf{k}') \equiv \langle\langle A(\mathbf{s}, \mathbf{k})|L|A(\mathbf{s}', \mathbf{k}')\rangle\rangle. \quad (\text{B5})$$

Substitution of the Liouvillian defined in Eqs. (3.4)–(3.6) into Eq. (B5) yields

$$L(\mathbf{s}, \mathbf{k}; \mathbf{s}' \mathbf{k}') \equiv \delta_{\mathbf{k}, \mathbf{k}'} [L_1(\mathbf{s}, \mathbf{s}'; \mathbf{k}) + L_2(\mathbf{s}, \mathbf{s}')] \quad (\text{B6})$$

with

$$L_1(\mathbf{s}, \mathbf{s}'; \mathbf{k}) = \{ 2i\Delta(s - s') \sin[\mathbf{k} \cdot (\mathbf{s} - \mathbf{s}')/2] - i\Gamma(s - s') \cos[\mathbf{k} \cdot (\mathbf{s} - \mathbf{s}')/2] - i\delta_{s, s'} \hat{\Gamma} \}, \quad (\text{B7})$$

$$L_2(s, s') = i\delta_{s,s'}\delta_{s,0}\hat{\Gamma} \quad (\text{B8})$$

In Eq. (B8)  $\mathbf{0}$  is the vector of length zero. From Eq. (B6), we see that  $L$  is diagonal in the index  $\mathbf{k}$ .  $L(s, \mathbf{k}; s', \mathbf{k}')$  is composed of  $L_1(s, s'; \mathbf{k})$ , which depends on  $s-s'$  and  $\mathbf{k}$  and of  $L_2(s, s')$ , which depends only on the magnitude of  $s$ .  $\Delta(s-s')$  stands for  $\Delta_{n+s, n+s'}$  where  $\Delta_{n,m}$  is given in Eq. (2.19).

We are interested in calculating the average radiative lifetime [Eq. (6.2)]

$$\begin{aligned} S^{-1} &\equiv i \sum_{n, n'm'} G_{nn', n'm'}(\omega=0) \\ &= i\sqrt{N} \sum_s \langle\langle A(\mathbf{0}, \mathbf{0}) | G(\omega=0) | A(s, \mathbf{0}) \rangle\rangle \\ &\quad \times \langle\langle A(s, \mathbf{0}) | ++ \rangle\rangle. \end{aligned} \quad (\text{B9})$$

We define a zero-order Green function  $G^0(\omega)$  as

$$G^0(\omega) = (\omega - L_1)^{-1}. \quad (\text{B10})$$

Its matrix elements are

$$\begin{aligned} \langle\langle A(s, \mathbf{k}) | G^0(\omega) | A(s', \mathbf{k}') \rangle\rangle &= \frac{1}{N} \sum_{\mathbf{q}} \exp[-i\mathbf{q}\cdot(\mathbf{s}-\mathbf{s}')] \left[ \omega + i\hat{\Gamma} + \sum_{\mathbf{r}} \exp(i\mathbf{q}\cdot\mathbf{r}) [-2i\Delta(r) \sin(\mathbf{k}\mathbf{r}/2) \right. \\ &\quad \left. + i\Gamma(r) \cos(\mathbf{k}\mathbf{r}/2)]^{-1} \right] \delta_{\mathbf{k}, \mathbf{k}'}. \end{aligned} \quad (\text{B11})$$

$G(\omega)$  is then given by

$$G(\omega) = G^0(\omega) + G^0(\omega)T(\omega)G^0(\omega), \quad (\text{B12})$$

where the  $T$  matrix is<sup>26</sup>

$$\langle\langle A(s, \mathbf{k}) | T(\omega) | A(s', \mathbf{k}') \rangle\rangle = \delta_{\mathbf{k}, \mathbf{k}'} \delta_{s, s'} \delta_{s, 0} \{ i\hat{\Gamma} / [1 - i\hat{\Gamma}Z(\omega)] \} \quad (\text{B13})$$

and

$$\begin{aligned} Z(\omega) &= \langle\langle A(\mathbf{0}, \mathbf{k}) | G^0(\omega) | A(\mathbf{0}, \mathbf{k}) \rangle\rangle \\ &= N^{-1} \sum_{\mathbf{q}} \left[ \omega + i\hat{\Gamma} - \sum_{\mathbf{r}} \exp(i\mathbf{q}\cdot\mathbf{r}) [2i\Delta(r) \sin(\mathbf{k}\mathbf{r}/2) - i\Gamma(r) \cos(\mathbf{k}\mathbf{r}/2)] \right]^{-1}. \end{aligned} \quad (\text{B14})$$

When Eqs. (B10)–(B14) are substituted in Eq. (B9), we finally get

$$S = \frac{\hat{\Gamma} + F(\mathbf{0})}{N} \sum_{\mathbf{q}} F(\mathbf{q}) [\hat{\Gamma} + F(\mathbf{q})]^{-1}, \quad (\text{B15a})$$

where  $q$  is a  $d$ -dimensional vector with components

$$q_i = \frac{2\pi n_i}{Na}, \quad n_i = 0, 1, \dots, N-1, \quad i = x, y, z \quad (\text{B15b})$$

and

$$F(\mathbf{q}) = \frac{1}{N} \sum_{n, m} \Gamma_{nm} \exp[i\mathbf{q}\cdot(\mathbf{r}_n - \mathbf{r}_m)]. \quad (\text{B16})$$

Equation (B15) is identical to Eq. (6.3). The summation over  $n$  and  $m$  in Eq. (B16) goes over all the lattice sites of

an infinite chain, square lattice, or cubic lattice in 1, 2, and 3 dimensions, respectively. It may be approximated by an integration using the substitution

$$\sum_{n, m} \rightarrow \frac{2}{(k_0 a)^d} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} dx_1 \dots dx_d. \quad (\text{B17})$$

The summation over  $q$  in Eq. (B15) may be converted into an integral over the first Brillouin zone,

$$\frac{1}{N} \sum_{\mathbf{q}} \rightarrow \left[ \frac{ak_0}{2\pi} \right]^d \int_0^{2\pi/k_0 a} d\mathbf{q}. \quad (\text{B18})$$

We further define

$$\Gamma(r_{nm}) \equiv \Gamma_{nm}.$$

These relations are used in the derivation of Eq. (6.4).

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