Cooperative Nonlinear Optical Response of Molecular Aggregates: Crossover to Bulk Behavior

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Equations of motion for the nonlinear optical response of arbitrary-size molecular aggregates are derived. The relative role of intramolecular and intermolecular (two-exciton) nonlinearities and the cooperative enhancement induced by the latter are analyzed. A crossover from $\sim N^2$ to $\sim N$ scaling of the nonlinear polarizability is predicted as the aggregate dimension becomes comparable to the optical wavelength, N being the aggregate size. The limitations of the local-field approximation are demonstrated.

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Currently, the optical properties of molecular aggregates are receiving a great deal of attention. Spectral shifts, broadening, and cooperative radiative decay rates have been measured.[1-3] Interest in the nonlinear optical properties of Frenkel excitons in molecular aggregates and monolayers[4-6] is rapidly approaching that of their semiconductor counterparts: Wannier excitons in quantum dots and wells.[7]

In this Letter, we derive equations of motion for the nonlinear polarization of molecular aggregates, which lead to an expression for the third-order aggregate hyperpolarizability, $\gamma(-\omega;\omega,-\omega,\omega)$, the behavior of which is investigated over the entire range of aggregate sizes; from small to large compared with the optical wavelength. We explore the roles of intramolecular and intermolecular nonlinearities, show the limitations of the local-field approximation, and discuss the factors affecting cooperative enhancement.

Consider a linear aggregate consisting of N-coupled two-level molecules with transition frequency ω_0, and nearest-neighbor-only dipole-dipole coupling V.[4] We neglect intermolecular vibrations and librations. Within this model, weak optical excitation produces Frenkel excitons. If we assume the aggregate axis to be normal to the external field wave vector, then the excitons have a zero wave vector and the superradiative damping rate γ_N is given by $\gamma_N=\sum_{n=1}^{N}\gamma(\mathbf{r}_n-\mathbf{r}_1)$, where $\gamma(\mathbf{r}_n-\mathbf{r}_1)$ is the imaginary (retarded) part of the dipole-dipole interaction responsible for spontaneous emission ($n=1$) and superradiance ($n\neq 1$). Here, the nth molecule is located at $\mathbf{r}_n=n\mathbf{a}$, where $\mathbf{a}$ is the lattice vector and $\mathbf{r}_{N+1}=\mathbf{r}_1$ (periodic boundary conditions). We further assume that the molecular transition dipole moments are aligned along the aggregate axis so that[8] $V=-\frac{3}{2}\gamma(\cos x+x\sin x)/x^3$ and $\gamma(\mathbf{r})=-3\gamma(y\cos y-\sin y)/y^3$ with $x\equiv\omega_0 a/c$ and $y\equiv\omega_0 r/c$. When the aggregate is much smaller than an optical wavelength, γ_N is simply equal to $N\gamma$.

For a proper description of nonlinear excited-state dynamics, Frenkel two excitons and coherences between excitons and two excitons must also be considered. The two-exciton wave function is a delocalized state of two interacting excitons (to be distinguished from biexcitons which are bound states). The two-level nature of the individual molecules leads to an *intramolecular* optical nonlinearity. In addition, an *intermolecular* nonlinearity is caused by exciton-exciton scattering which arises because two excitons cannot reside on the same molecule (Pauli exclusion principle). As a result, the two-exciton wave functions are not simply products of two exciton wave functions with energies equal to the sum of the two exciton energies. The $\mathbf{k}=0$ two-exciton states (where $\mathbf{k}$ is the momentum conjugate to the center of mass) form a manifold of $(N-1)/2$ delocalized states (for N odd) of bandwidth 8 V (for N infinite), twice the exciton bandwidth.[4] The deviation of the band-edge two-exciton energy from twice the $\mathbf{k}=0$ exciton energy, leads to enhanced nonlinear susceptibilities.[4-6]

Uniform excitation by an external electric field with wave vector oriented normal to the aggregate axis results in a spatially symmetric aggregate polarization operator equal to $\mu\hat{B}_0^\dagger+\mu\hat{B}_0$ which is related to the individual molecular polarizations by $\mu\hat{B}_0^\dagger\equiv\mu\sum_{n=1}^{N}\hat{B}_n^\dagger$, where $\hat{B}_n^\dagger$ is the Pauli raising operator for the two-level molecule at site n. A general analysis for $\mathbf{k}\neq 0$ excitons excited when the aggregate axis is not normal to the laser beam wave vector is straightforward. However, all of the essential physics is contained in the $\mathbf{k}=0$ exciton analysis. The superradiant master equation[8] yields an infinite hierarchy of equations of motion for molecular operators in the Heisenberg representation. To third order in the external field $E(\mathbf{r},t)$, the hierarchy may be truncated, resulting in the following equations:

$$\frac{d}{dt}\langle\hat{B}_0^\dagger\rangle = i[\omega_e + i\gamma_N/2]\langle\hat{B}_0^\dagger\rangle + \sum_{q=1,3,\ldots}^{N-2} K(q)\langle\hat{C}_q^\dagger\rangle\langle\hat{B}_0\rangle + i\frac{\mu}{\hbar}E(r,t)\left[N - \frac{2}{N}\langle\hat{B}_0^\dagger\rangle\langle\hat{B}_0\rangle\right], \tag{1a}$$

$$\frac{d}{dt}\langle C_q^\dagger\rangle = i\Omega(q)\langle C_q^\dagger\rangle - \sum_{q'}\Gamma_{q,q'}\langle C_{q'}^\dagger\rangle + 2i\frac{\mu}{\hbar}E(r,t)\cot\left(\frac{\pi q}{2N}\right)\langle B_0^\dagger\rangle. \tag{1b}$$

$\hat{B}_0^\dagger$ represents delocalized single-photon coherences, which, to lowest order in the external electric field, oscillate at the exciton frequency, $\omega_e = \omega_0 + 2V$. For simplicity, we have considered in Eq. (1) only odd values of N. The analysis for even values can be made along the same lines.[5] The $(N-1)/2$ two-exciton operators $C_q^\dagger$ represent delocalized two-photon coherences and are defined as

$$\hat{C}_q^\dagger \equiv \sum_R \sum_s \sin\left(\frac{\pi q s}{N}\right)\hat{B}_{R-s/2}^\dagger \hat{B}_{R+s/2}^\dagger$$

with $q = 1,3,\ldots,N-2$. These operators, when acting on the ground state, create two-exciton coherences with relative momentum $2\pi q/Na$ and zero center-of-mass momentum. The two-exciton frequencies in Eq. (1b) are $\Omega(q) = 2\omega_e + 4V\cos(\pi q/N) - 4V$. The two-exciton superradiant decay matrix is nondiagonal:

$$\Gamma_{q,q'} = \frac{4}{N}\sum_{s,s'=1}^{(N-1)/2} \sin\left(\frac{\pi q s}{N}\right)\sin\left(\frac{\pi q' s'}{N}\right)[\gamma((s-s')\mathbf{a}) + \gamma((s+s')\mathbf{a})].$$

The exciton and two-exciton variables are coupled through the kernel $K(q)$, which is given by

$$K(q) = \frac{2i}{N^2}\sum_{q'=1,3,\ldots}^{N-2} \cot\left(\frac{\pi q'}{2N}\right)F_{q',q},$$

where

$$F_{q,q'} \equiv [\Omega(q) - 2\omega_e]\delta_{q,q'} + i[\Gamma_{q,q'} - \gamma_N\delta_{q,q'}].$$

We shall demonstrate below that the coupling of the polarization to the $\hat{C}_q^\dagger$ variables by $K(q)$ represent *intermolecular nonlinearities* which are responsible for enhanced (cooperative) nonlinearities in molecular aggregates.

Rewriting Eq. (1) in the frequency domain, and iterating to third order in the external field, yields the third-order hyperpolarizability $\gamma(-\omega;\omega_1,\omega_2,\omega_3)$. In this Letter we calculate the nonlinear absorption of a single cw laser beam with frequency ω and amplitude E. The total absorption coefficient for an optically thin and dilute distribution of aggregates is equal to $-\rho\,\mathrm{Im}[\alpha(\omega) + \gamma(-\omega;\omega,-\omega,\omega)|E|^2]$, where α is the linear polarizability and ρ is the density of aggregates.

Invoking the rotating-wave approximation (RWA) in Eq. (1), we obtain the third-order hyperpolarizability for a molecular aggregate with N molecules:

$$\gamma(-\omega;\omega,-\omega,\omega) = \frac{N\mu^4}{4\hbar^3}A\frac{1}{-\Delta\omega + i\gamma_N/2}\times\left(\frac{1}{\Delta\omega + i\gamma_N/2}\right)^2, \tag{2}$$

where the cooperative enhancement factor A is given by

$$A \equiv N - (N-1)\mathbf{D}^T\frac{2\Delta\omega + i\gamma_N}{2\Delta\omega + i\gamma_N - \mathbf{F}^*}\mathbf{D}, \tag{3}$$

$\Delta\omega \equiv \omega - \omega_0$ is the laser detuning, and $\mathbf{D}$ is a normalized vector with

$$D_q \equiv [2/N(N-1)]^{1/2}\cot(\pi q/2N)$$

for $q = 1,3,\ldots,N-2$.

The scaling of A with aggregate size is determined by the relative magnitude of the norm of F and $|2\Delta\omega + i\gamma_N|$. Denoting the amplitude of the maximum eigenvalue of F by $f_{\max}$, then when $f_{\max} \ll |2\Delta\omega + i\gamma_N|$ we obtain the following expansion:

$$A = 1 + \frac{4V - i(\gamma_N - \gamma)}{2\Delta\omega + i\gamma_N} + O\left(\frac{f_{\max}^2}{(2\Delta\omega + i\gamma_N)^2}\right). \tag{4a}$$

In the opposite limit, when the minimum eigenvalue $f_{\min} \gg |2\Delta\omega + i\gamma_N|$, A is given by

$$A = N + (N-1)\mathbf{D}^T[(2\Delta\omega + i\gamma_N)/\mathbf{F}^*]\mathbf{D} + O([(\Delta\omega + i\gamma_N)/f_{\min}]^2). \tag{4b}$$

In the first case [Eq. (4a)], the optical nonlinearity is essentially that of a single molecule with minor corrections. In the second case [Eq. (4b)], the nonlinearity is cooperative and $A \sim N$ which implies an N^2 dependence of $\gamma(-\omega;\omega,-\omega,\omega)$.

Before considering the limiting cases any further, it is instructive to introduce the equation of motion for the polarization within the local-field approximation, which is commonly used in the calculation of nonlinear susceptibilities.[9] This is obtained by writing the Heisenberg equations [Eq. (1)] in the site basis and factoring all n-body expectation values into single-body expectation values:[10]

$$\frac{d}{dt}\langle B_0^\dagger\rangle = i[\omega_0 + i\gamma/2]\langle B_0^\dagger\rangle + i\frac{\mu}{\hbar}E_L(r,t)[-2\langle B_0^z\rangle]\,, \quad (5)$$

where $\langle B_0^z\rangle \equiv (1/N)\langle B_0^+\rangle\langle B_0^-\rangle - N/2$ is the expectation value of the total aggregate population difference (excited-state population minus ground-state population) and the local field is given by $E_L = E + E_M$, with the electric field radiated by the medium, E_M (at any $\mathbf{r}_n$), expressed as

$$E_M = (\hbar/N\mu)[2V - i(\gamma_N - \gamma)/2]\langle B_0^\dagger\rangle\,.$$

Equation (5) is simply the optical Bloch equation for the total aggregate polarization and population difference, which is driven by the *local* electric field. When Eq. (5) is used to calculate $\gamma(-\omega;\omega,-\omega,\omega)$, we obtain an expression like Eq. (2), with A given by the first two terms in the expansion (4a). The local-field approximation is therefore correct to first order in $V\Delta\omega^{-1}$ and $\gamma_N\Delta\omega^{-1}$ and it improves for large detunings and low density. Note that when $\Delta\omega \gg |V|$, $A=1$ in Eq. (2), and the N monomer result is recovered, i.e., the hyperpolarizability of a single off-resonant two-level molecule multiplied by N. This limit is attained for *all* $\Delta\omega$ when the molecular density approaches zero, in which case when $V \approx 0$, $\Gamma_{q,q'} \approx \gamma\delta_{q,q'}$, and $\gamma_N \approx \gamma$ so that $F \approx 0$.

Generally when ω is close to the exciton resonance ($\Delta\omega \approx 0$), the local-field approximation is inadequate, completely missing the intermolecular nonlinearities. In particular, when the aggregate dimensions are smaller than λ, the region of "enhanced" nonlinear susceptibilities (which is absent in the local-field approximation) is obtained. Here, the second limiting case [Eq. (4b)] pertains since $f_{\min} \approx |\Omega(q=1) - 2\omega_e|$, and

$$\gamma_N \ll |\Omega(q=1) - 2\omega_e| = 8|V|\sin^2(\pi/2N) \quad (6)$$

is satisfied along with an identical relation with $|\Delta\omega|$ on the left-hand side. If we assume an aggregate density $\eta \gg 1$, and a sufficiently large N so that $\sin(\pi/2N) \approx \pi/2N$, this condition becomes $Na \ll \lambda$. Therefore, only aggregates smaller than the optical wavelength λ allow expansion (4b). Here, A is proportional to N in the frequency interval $|\Delta\omega| \ll |\Omega(q=1) - 2\omega_e|$ so that $\gamma(-\omega;\omega,-\omega,\omega)$ in Eq. (2) contains an N^2 prefactor.

We have defined a dimensionless reduced third-order nonlinear absorption coefficient

$$\alpha_{\rm NL}(\Delta\omega) \equiv -\mathrm{Im}[(4\hbar^3\gamma^3/N\mu^4)\gamma(-\omega;\omega,-\omega,\omega)]\,.$$

$\alpha_{\rm NL}$ is proportional to the susceptibility *per molecule* in the aggregate because of the division by N. In Fig. 1, $\log[-\alpha_{\rm NL}(0)]$ is displayed as a function of N for three different molecular densities ($\eta = 20,40,60$) where $\eta \equiv \lambda/a$. In the small-aggregate limit, the nonlinear absorption actually decreases with increasing N, despite the N^2 prefactor, because of the presence of $\gamma_N \approx N\gamma$ in the three-frequency denominators. Equation (2) therefore

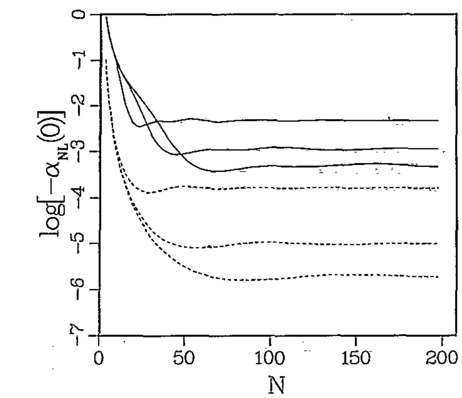

FIG. 1. The resonant nonlinear absorption $\log[-\alpha_{\rm NL}(0)]$ as a function of aggregate size N. Solid curves are evaluated numerically from Eqs. (2) and (3). Dashed curves correspond to the local-field approximation Eqs. (2) and (4a) with $\eta = 20,40,60$ from the top to bottom.

shows that the peak value of $\gamma(-\omega;\omega,-\omega,\omega) \sim N^{-1}$. For larger sizes, a crossover from small aggregate to bulklike behavior is clearly observed and the nonlinear absorption becomes independent of size. This behavior is clearly illustrated in Fig. 1. We can define the approximate crossover aggregate size N_c as that which makes condition (6) an equality, i.e., $N_c \equiv (1/2\pi)^{1/2}\eta$, where $\gamma_N \approx 3\eta\gamma/4$ for an infinite aggregate has been used. Therefore the crossover region is proportional to the molecular density, as is evident from Fig. 1. When $N \gg N_c$, $\alpha_{\rm NL}(0)$ is a constant, independent of N, reflecting bulklike behavior, where $\gamma(-\omega;\omega,-\omega,\omega)$ is simply proportional to the aggregate size N (or A is independent of N). Using contour integration, we have shown this limiting behavior analytically. Ishihara and Cho[5] have done likewise, but without incorporating the radiative decay. The local-field approximation (dashed curves) reproduces the correct qualitative behavior but not the absolute magnitude of the nonlinearity.

In Fig. 2 we show $-\alpha_{\rm NL}(\Delta\omega)$ as a function of $\Delta\omega$ for several size aggregates with $\eta = 40$ (solid curves), together with the local-field approximation reduced by a factor of 10 (dashed curves). In the small-aggregate region where condition (6) holds, $\gamma(-\omega;\omega,-\omega,\omega)$ [Eq. (2)] reduces near resonance $[|\Delta\omega| \ll 4|V\cos(\pi/N) - 4V|]$ to that of a single excitonic two-level system with a transition dipole $N^{1/2}\mu$. This leads to the superradiant decay rate $\gamma_N = N\gamma$ and an N^2 prefactor in $\gamma(-\omega;\omega,-\omega,\omega)$ (or $A = N$). As the aggregate size increases [Figs. 2(a) and 2(b)], but remains in the small-aggregate regime ($N < N_c = 15$), the enhanced excitonic line broadens and decreases in amplitude because of $\gamma_N = N\gamma$ in the three-frequency denominators. Note the additional two-photon resonance at $\Delta\omega = \frac{1}{2}[4V\cos(\pi q/N) - 4V]$ with $q=1$ on the blue side of the spectrum ($V<0$). The negative sign associated with the two-photon absorption reflects increased absorption, as opposed to the bleaching

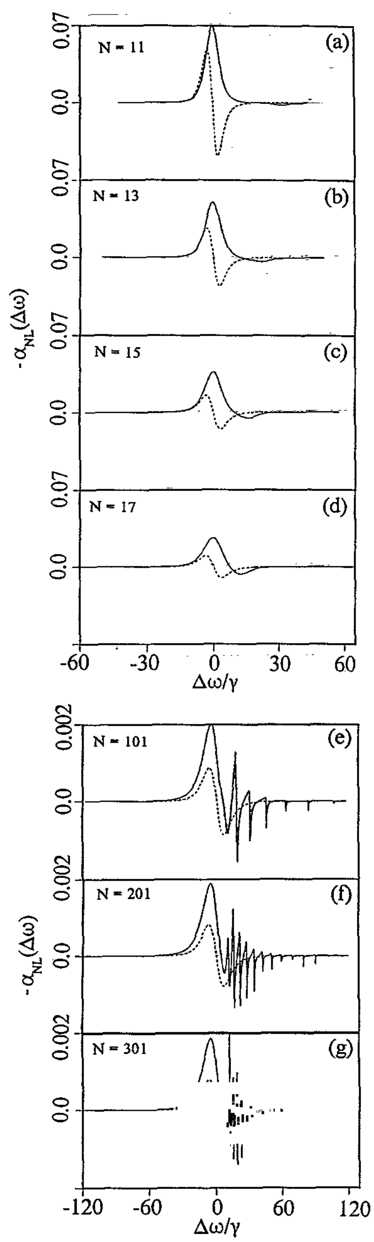

FIG. 2. The nonlinear absorption $-\alpha_{NL}(\Delta\omega)$ as a function of $\Delta\omega$, for a succession of aggregate sizes, evaluated numerically from Eqs. (2) and (3) (solid curves), with $\eta=40$. Panels (a)–(d) show the small-aggregate and crossover regions ($N_c=15$) and panels (e)–(g) show the bulk behavior. The dashed curves show the local-field approximation and have been reduced by a factor of 10. The two-photon resonances are absent in this case. Note the reduction of the two-exciton blueshift as the aggregate size is increased.

of the exciton line. As the aggregate size increases, the $q=1$ resonance moves towards the exciton line and eventually interferes destructively with it, when $N \sim N_c$ [Figs. 2(c)–2(g)]. In Figs. 2(e)–2(g) the bulk limit behavior is demonstrated, where the destructive interference is complete, resulting in the complete cancellation of the $\sim N^2$ prefactor in $\gamma(-\omega;\omega,-\omega,\omega)$ or, equivalently, the $\sim N$ dependence in A. At this point $\alpha_{NL}(\Delta\omega)$ is independent of N; the red side of the spectrum has converged completely, while the blue side still shows resolved two-photon resonances. These, however, become more congested as N increases and eventually the laser beam linewidth will exceed the line spacing, making the blue side a smooth function of $\Delta\omega$, with no N dependence. The local-field approximation (dashed curves) does not reproduce the correct magnitude of the hyperpolarizability. In addition, within this approximation, the small-aggregate region is completely missed, the N^2 prefactor never arises, and the two-photon resonances are completely absent.

In conclusion, the present theory provides a unified framework for interpreting the nonlinear optical response of aggregates and demonstrates the crossover from the small aggregate to the bulk limit. We expect the failure of the local-field approximation demonstrated here to be a general phenomenon, which will show up in other $\chi^{(2)}$ and $\chi^{(3)}$ measurements. Enhanced optical nonlinearities ($A \sim N$) are only possible in small aggregates with $Na \ll \lambda$, where the two-level excitonic resonance is spectrally well separated from the two-photon resonances. In larger aggregates, the intermolecular nonlinearities due to exciton-exciton scattering are diminished so that the hyperpolarizability is simply proportional to size. This reduction is due to interference between excitonic nonlinearities and two-photon nonlinearities, and is more effective when the two-photon resonance approaches twice the exciton resonance. Were it not for this interference, the nonlinear susceptibility would scale as N^2 for any size aggregate because the radiation rate γ_N converges for large N, leaving all the N dependence to A.

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