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PHASE CONJUGATE DEGENERATE FOUR-WAVE MIXING IN MOLECULAR AGGREGATES

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We investigate phase conjugate degenerate four-wave mixing (DFWM) in molecular aggregates consisting of N interacting, homogeneously broadened two-level systems in a cyclic configuration with a dimension much smaller than an optical wavelength. The interaction includes both the static dipole–dipole coupling and superradiant coupling. We show that, in general the size dependence of $\chi^{(3)}$ is determined by the relative magnitudes of the homogeneous dephasing rate and the superradiant decay rate. We predict the existence of a narrow dephasing-induced resonance superposed on the broader superradiant exciton lineshape.

1. Introduction

The optical properties of molecular aggregates and semiconductor microstructures have received a great deal of attention recently since they exhibit properties between those of the isolated molecule and the bulk crystal. Of particular interest are J-aggregates [1] consisting of a regular arrangement of dye molecules. Upon aggregation, the absorption spectrum of a dye solution dramatically narrows and shifts to the red. These aggregates also display interesting excited state dynamics [2], in particular, an enhanced radiative decay rate (superradiance) which depends on aggregate size. Semiconductor quantum wells [3] and quantum dots [4] display size dependent blue shifted absorption spectra (compared to the bulk). As with the J-aggregate Frenkel exciton, there is evidence that the semiconductor Wannier exciton is also superradiant [5]. Futhermore, it has been theorized that these microstructures should exhibit giant third order nonlinear susceptibilities [6] although experimental confirmation is thus far lacking. Materials with large values for $\chi^{(3)}$ for frequencies far from the absorption maxima are ideal for fast switching optical modulators needed in optical communications and computing.

The present paper deals with the third order nonlinear optical properties of Frenkel excitons in molecular aggregates. We calculate the phase conjugate degenerate four-wave mixing (DFWM) signal from a system of homogeneously broadened, one dimensional cyclic aggregates composed of N coupled two-level systems with an aggregate dimension much smaller than an optical wavelength. The homogeneous dephasing is described by the well known Haken Strobl model [7]. The analysis is based on the superradiant density matrix equation of motion [8], the details of which can be found in ref. [9], where a completely quantum mechanical expression for $\chi^{(3)}$ is derived including the effects of biexcitons. We use this expression to evaluate the phase conjugate DFWM spectrum and consider two cases: when the pump beams are tuned to the exciton absorption and when they are far from resonance. Within these limits the combined effects of homogeneous dephasing and superradiance on the DFWM spectrum is determined. We predict the existence of a narrow resonance which results from a dephasing induced population transfer from the $k = 0$ superradiant exciton state to the $N - 1$ subradiant exciton states. Such narrow resonances have recently been observed in quantum wells [10].

2. Model

We consider cyclic, one dimensional aggregates (N equally spaced molecules on a circle) with N odd. Each molecule is modelled as a two level system with transition frequency, ω_0. The calculation of $\chi^{(3)}$ is greatly simplified in this configuration. We believe, however, that our analysis and general conclusions regarding the cooperativity are not restricted to this special case.The equation of motion which describes the electromagnetic interactions between the N molecular polarizations within the aggregate and between the aggregate polarization and the applied electromagnetic field is the superradiant master equation [8]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \sum_{n=1}^{N} \mathrm{i}\omega_0 [\rho, b_n^+ b_n] + \sum_{mn\neq}^{N} \mathrm{i}\Omega_{mn} [\rho, b_m^+ b_n]$$

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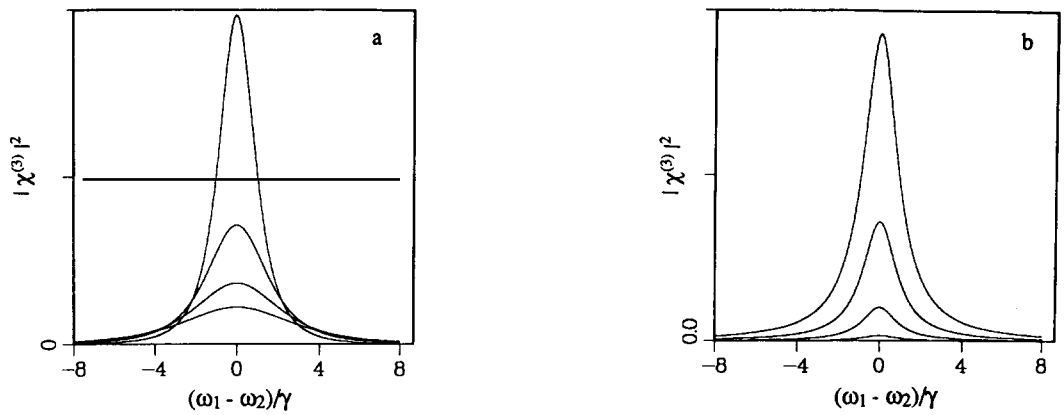

Fig. 1. Phase conjugate DFWM spectra $|\chi^{(3)}(-2\omega_1+\omega_2;\ \omega_1,-\omega_2,\omega_1)|^2$ versus $\omega_1-\omega_2$ for several aggregates sizes $N=3$, 5, 7 and 9 with the pump beam tuned to the exciton absorption peak resonance. (a) $\hat{\Gamma}=0$ and spectra with the larger peak values of $|\chi^{(3)}|^2$ correspond to the smaller aggregate sizes. (b) $\hat{\Gamma}=10^4\ \gamma$, and the size progression is reversed. $N=9$ now has the largest values of $|\chi^{(3)}|^2$.

$$+\sum_{mn=1}^{N}\gamma_{mn}\left[b_m\rho b_n^{+}-\tfrac{1}{2}\left(b_m^{+}b_n\rho+\rho b_m^{+}b_n\right)\right]$$
$$+\frac{i\mu}{2\hbar}\sum_{n=1}^{N}E(\boldsymbol{r}_n,t)\left[\rho(t),\,b_n^{+}+b_n\right]-iL'\rho(t), \tag{1}$$

where $b_m^{+}(b_m)$ are creation and anilhation operators for the excitation at site m, Ω_{mn} (γ_{mm}) is the real (imaginary) part of the electromagnetic coupling, and $E(\boldsymbol{r},t)$ is the component of the external electric field along the molecular transition dipole moment $\boldsymbol{\mu}$. In this article we assume that the aggregate is small compared to an optical wavelength $k_0 r_{mn}\ll 1$, so that all $E(\boldsymbol{r}_n,t)$ can be replaced by $E(\boldsymbol{r},t)$. In this limit we further have:

$$\Omega_{mn}=\frac{3\gamma}{4}\frac{\left(1-3\cos^2\theta_{mn}\right)}{\left(k_0 r_{mn}\right)^3}\equiv V_{mn} \tag{2a}$$

and

$$\gamma_{mn}=\gamma, \tag{2b}$$

where V_{mn} is the static dipole–dipole coupling, γ is the single molecule spontaneous emission rate, and $k_0=\omega_0/c$. For simplicity we shall include only the nearest neighbor coupling in the real part of the interaction V_{mn} and define $V\equiv V_{12}$.

Homogeneous dephasing is represented by the last term in eq. (1) and is introduced by assuming that each molecular electronic frequency is undergoing rapid fluctuations:

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

with

$$\langle\delta\omega_n(t)\rangle=0$$

and

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

Here $\langle\ldots\rangle$ denotes an ensemble average over the bath, and it is assumed that fluctuations on different molecules are uncorrelated. $\delta\omega(t)$ is taken to be a stochastic Gaussian–Markov process. This model was introduced by Haken and Strobl to describe exciton transport in solids [7]. Accordingly, $\rho(t)$ in eq. (1) is the *ensemble averaged* density matrix. The general form of L' is quite complicated and is given in ref. [9].

Starting with eq. (1) we have derived in ref. [9] a complete expression for $\chi^{(3)}$ using time dependent perturbation theory within a Liouville formalism. For the exact calculation it is sufficient to work in a reduced operator space which includes only exciton and biexciton coherences and populations.

3. Phase conjugate four wave mixing

In phase conjugate DFWM, two pump beams with frequency ω_1 counterpropagate in a nonlinear medium ($\boldsymbol{k}_3=-\boldsymbol{k}_1$), with the probe beam (frequency ω_2, wavevector $\boldsymbol{k}_2$) entering at some arbitrary angle. A phase conjugate signal with an intensity proportional to $|\chi^{(3)}(-2\omega_1+\omega_2;\ \omega_1,-\omega_2,\omega_1)|^2$ is generated in the $\boldsymbol{k}_s=\boldsymbol{k}_1+\boldsymbol{k}_3-\boldsymbol{k}_2=-\boldsymbol{k}_2$ direction with a frequency equal to $2\omega_1-\omega_2$. In DFWM, the pump frequency ω_1 is held fixed while the probe beam frequency is scanned over a narrow frequency interval centered at ω_1. In this section we treat two cases. In the first case the pump beams are tuned to the exciton absorption maximum $\omega(0)=\omega_0+2V$ so that $\omega_1=\omega(0)$. In the second case, the pump beams are detuned by at least an exciton bandwidth ($4V$) from the $k=0$ exciton absorption maximum, $\Delta\omega_1\equiv\omega_1-\omega(0)>4V$, and ω_2 is scanned over a narrow frequency interval centered at ω_1.

Previously it has been shown that $\chi^{(3)}$ is propor-

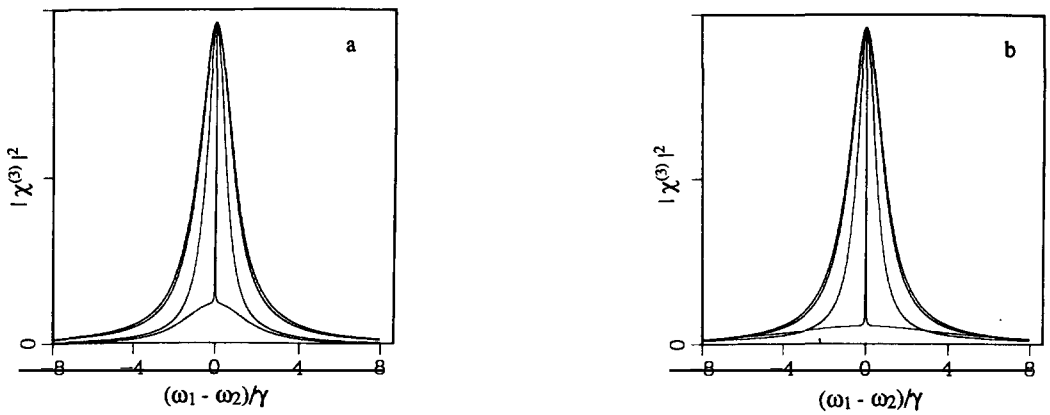

Fig. 2. Phase conjugate DFWM spectra $|\chi^{(3)}(-2\omega_1+\omega_2;\ \omega_1,-\omega_2,\omega_1)|^2$ versus $\omega_1-\omega_2$ for $N=5$ and for $\hat{\Gamma}/N\gamma = 0.01$, 1, 10 and 100. (a) $\Delta\omega_1 = 0$ and (b) $\Delta\omega_1 = 8V$. All curves are normalized to a peak height of unity, and increasing values of $\hat{\Gamma}$ correspond to curves with greater linewidths (at half maximum).

tional to N^2, allowing for so-called giant nonlinearities in semiconductor quantum dots. For near resonance DFWM our calculation of $\chi^{(3)}$ shows that this is only true if the dephasing is much greater than the superradiant rate, $\hat{\Gamma} \gg N\gamma$ and that in the opposite limit, $\hat{\Gamma} \ll N\gamma$, $\chi^{(3)}$ is actually degraded with size! (The peak $\chi^{(3)} \sim N^{-1}$.) Furthermore, the N dependence is a complicated function of the particular nonlinear technique as well as the laser detuning. For example, $\chi^{(3)}$ for third harmonic generation and DFWM have different N dependences. In figs. 1(a) and 1(b) band we show the phase conjugate DFWM spectrum in the case of $\hat{\Gamma} = 0$ and $\hat{\Gamma} = 10^4\ \gamma$ for several aggregate sizes.

The addition of an arbitrarily small dephasing rate $\hat{\Gamma}$ produces a narrow resonance located at the center of the $\hat{\Gamma} = 0$ spectrum. In fig. 2a we show normalized spectra for $N = 5$, $\Delta\omega_1 = 0$ and various values of $\hat{\Gamma}$. In the limit $\hat{\Gamma} \ll N\gamma$, the height and FWHM of the narrow resonance are equal to $1/\gamma$ and $\hat{\Gamma}/N$, respectively (for $N \gg 1$), so that as $\hat{\Gamma}$ approaches zero, the area correctly goes to zero. The physical origin of the narrow resonance arises from the fact that only the $k = 0$ exciton state has a nonzero radiative decay rate and is superradiant. All other exciton states are nonradiative (subradiant). The first interaction with a pump beam directly excites the exciton coherence. After the second interaction (with the probe electric field) the $k = 0$ exciton is populated; during the subsequent evolution period homogeneous dephasing allows a transfer of population to all $N-1$, $k \neq 0$ exciton states. In a time of order $(N\gamma)^{-1}$ the total $k \neq 0$ exciton population grows from zero to $\hat{\Gamma}/(N\gamma)$ times the initial $k = 0$ population. Because these states have no transition dipole moment to the ground state, they cannot radiate and they cannot provide a third interaction with the pump beam to create the phase conjugate beam. For times greater than $(N\gamma)^{-1}$ the $k \neq 0$ population slowly leaks back to the $k = 0$ population at a rate $\hat{\Gamma}/N$ where it is rapidly converted to the ground state population as the $k = 0$ exciton states superradiates. It is this slow build-up of ground state population that is responsible for the narrow resonance. (The grating which diffracts the pump beam in the third interaction to produce the phase conjugate beam is a population *difference* grating, i.e., between the $k = 0$ excited state population and the ground state population.) In the opposite limit, $\hat{\Gamma} \gg N\gamma$, homogeneous dephasing causes the total excited state population to be evenly distributed over all exciton states in a time of order $\hat{\Gamma}^{-1}$ (following the first two interactions). The $k = 0$ and $k \neq 0$ exciton populations now return to the ground state at the monomer rate γ causing the width of the narrow line to converge to γ.

In fig. 2(b) we show the DFWM spectrum when the pump beams are off resonance ($\Delta\omega_1 = 8V$). The superradiant spectrum still appears despite the pump beams being far off resonance. Compared with the on resonance spectrum, the narrow resonance peak height is an additional factor of two larger than the superradiant peak. In both cases, the narrow resonance peak height remains $\sim N$ times larger than the superradiant peak height.

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References

[1] G. Scheibe, Agnew. Chem. 50 (1937) 212;
E.E. Jelly, Nature 10 (1973) 631;
A.H. Hertz, Adv. Coll. Interf. Sci. 8 (1977) 237.

[2] S. DeBoer, K.J. Vink and D.A. Wiersma, Chem. Phys. Lett. 137 (1987) 99;
D.A. Wiersma and D. DeBoer, in: Ultrafast Phenomena VI, eds., T. Yajima, K. Yoshihara, C.B. Harris and S. Shionoya (Springer, Berlin, 1988) p. 354;
V. Sundstrom, T. Gillbro, R.A. Gadonas and A. Piskarskas, J. Chem. Phys. 89 (1988) 2754;
D.V. Brumbaugh, A.A. Muenter, W. Knox, G. Mourou and B. Wittnerhaus, J. Lumin. 31 (1984) 783.

[3] H. Haug, ed., Optical Nonlinearities and Instabilities In Semiconductors (Academic Press, New York, 1988);
A. Stahl and I. Balslev, Electrodynamics of the Semiconductor Band Edge (Springer, Berlin, 1987);
D.S. Chemla, D.A.B. Miller, P.W. Smith, A.C. Gossard and W. Wiegmann, IEEE J. Quant. Elec. QE-20 (1984) 265.

[4] L. Brus, IEEE J. Quant. Elec. 22 (1986) 1909;
Y. Wang, A. Suna, W. Mahler and R. Kasowski, J. Chem. Phys. 87 (1987) 7315;
S. Schmitt-Rink, D.A.B. Miller and D.S. Chemla, Phys. Rev. B35 (1987) 8113;
L. Banyai, Y.Z. Hu, M. Lindberg and S.W. Koch, Phys. Rev. B38 (1988) 8142.

[5] G.W. 't Hooft, W.A.J.A. van der Poel, L.W. Molenkamp and C.T. Foxon, Phys. Rev. B35 (1987) 8281.

[6] E. Hanamura, Phys. Rev. B37 (1988) 1273; Phys. Rev. B38 (1988) 1228.

[7] H. Haken and G. Strobl, Z. Phys. 262 (1971) 135.

[8] M. Gross and S. Haroche, Phys. Rep. 93 (1982) 301;
R.H. Lehmberg, Phys. Rev. 2 (1970) 883.

[9] F.C. Spano and S. Mukamel, Phys. Rev. A40 (1989) 5783.

[10] J.T. Remillard, H. Wang, D.G. Steel, J. Oh, J. Pamulapati and P.K. Bhattacharya, Phys. Rev. Lett. 62 (1989) 2861.