

# Theory of photon echoes from interacting impurities in crystals with inhomogeneously broadened absorption spectra

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We present a theory of photon echoes from impurity molecules in mixed crystals that takes into account electronic interactions among impurity molecules and inhomogeneous broadening of the electronic absorption spectrum. The system is modeled as a collection of randomly placed interacting two level systems with a distribution of transition energies. The observable of the echo experiment is expanded in powers of the density of two level systems, and the first two terms of this expansion are calculated. A scaling argument suggests that the density expansion is rapidly convergent for concentrations of experimental interest, and the density expansion is used to construct a Padé approximant. At times comparable to or less than the inverse of the width of the inhomogeneous distribution of resonance frequencies, the time dependence of the signal is determined primarily by the interactions between the impurities and is independent of the inhomogeneous width. At longer times the inhomogeneity becomes significant and the echo signal displays a much weaker time dependence. We examine the effect of different microscopic models of inhomogeneous broadening on the echo observable. We demonstrate that the photon echo experiment can provide a sensitive probe of interactions between impurities in mixed crystals.

## I. INTRODUCTION

The nature of electronic excited states of impurity molecules or atoms in mixed crystals at low temperature is currently receiving considerable attention. In the limit of very low impurity concentration, the electronic interactions between impurities are negligibly small and the spectroscopic properties of the impurity are determined by its interactions with the host species. If the host species is sufficiently different spectroscopically from the impurity, then the impurity electronic states will be well described as localized molecular or atomic states. The opposite case is the pure crystal limit in which the electronic states are delocalized exciton states. Less is known about the intermediate case, in which the impurity concentration is high enough that electronic interactions among the impurities are significant but in which the impurities still only occupy a small fraction of the lattice sites. The nature of the transition from localized impurity electronic states at very low impurity concentration to delocalized states as the impurity concentration is raised is not well understood. Kopelman and co-workers have carried out an extensive set of experiments on the trapping of singlet and triplet electronic excitations in isotopically mixed naphthalene crystals.<sup>1</sup> The crystals studied are composed of three species: the host, a donor impurity, and a trap impurity. In these experiments the fraction of luminescence from the traps is measured as a function of donor concentration at fixed low trap concentration. The low concentration traps thus act as indirect sensors of donor to donor excitation transport. Kopelman *et al.* find that the fraction of luminescence from the traps is strongly dependent on the donor concentration. From these data they have inferred the existence of a critical donor concentration below which excitation transport among the donors becomes very inefficient. Quantitative interpretation of these results in terms of a

model is complicated by the fact that both the excited state dynamics of the donors and the excitation trapping process must be understood. Their results have been interpreted in terms of percolation models,<sup>1</sup> high temperature kinetic models based on the Pauli Master Equation,<sup>2</sup> and the optical Anderson transition.<sup>3</sup> The excitation trapping observable measured in these experiments yields important information about the photophysics of mixed molecular crystals, but has not provided detailed information about the nature of the electronic states.

For a perfect crystal, information about the onset of changes in the impurity electronic states as the concentration is raised could be obtained from electronic absorption spectra. All real crystals have imperfections such as strains, point defects, and dislocations, which give rise to an inhomogeneously broadened absorption spectrum.<sup>4</sup> Inhomogeneous broadening in general obscures the intrinsic (homogeneous) linewidth, thus ruling out absorption spectroscopy as a useful probe of intermolecular interactions. The development of photon echo and other time domain optical coherence experiments has made it possible to determine the homogeneous linewidth of isolated impurities in crystals whose absorption spectra are overwhelmed by inhomogeneous broadening.<sup>5</sup> These techniques have also been applied to the study of the dynamics of strongly interacting pairs of impurity molecules in mixed crystals.<sup>6</sup> The usefulness of such experiments in these contexts suggests that the photon echo experiment may be applicable to the study of intermolecular interactions in systems whose absorption spectra are inhomogeneously broadened.

Many spectroscopic systems can be accurately modeled as two level systems, and the theory of photon echoes in this case is well established.<sup>5,7</sup> Less is known about the information content of a photon echo signal from a multilevel sys-

tem. Skinner *et al.* have presented a theory of photon echoes from a pair of coupled two level systems in which the laser is resonant with both singly excited levels.<sup>8</sup> They have also developed a theory of photon echoes from a quasi-two-level system in which the ground and excited states are replaced by manifolds of states.<sup>9</sup> Warren and Zewail have presented an analysis of optical coherence experiments on interacting molecules and have proven that the photon echo pulse sequence does not rephase the dephasing caused by intermolecular interactions.<sup>10</sup> Their work is discussed further in Sec. V.

In this work we present a theory of photon echoes from interacting impurities in a crystal with an inhomogeneously broadened absorption spectrum at zero temperature. We model this system with a collection of oriented molecules randomly distributed in space, each with one excited state, that interact by a transition dipole-transition dipole mechanism. Although we refer to molecules, an analogous treatment can be carried out to deal with atomic impurities in inorganic crystals. We calculate the first two terms (monomer and dimer) of a density expansion of the photon echo observable for this model. We demonstrate that this observable is a sensitive probe of intermolecular interactions in inhomogeneously broadened systems. Section II contains a formal discussion of the calculation of the photon echo signal for this model. In Sec. III we present a scaling argument that motivates the use of truncated density expansion as a valid approximation for situations of experimental interest. The density expansion approximation is calculated in Sec. IV. In Sec. V we present numerical calculations and discuss their significance. In that section the effect of different microscopic models of inhomogeneous broadening on the observable is discussed. We also make a comparison to the work by Warren and Zewail.<sup>10</sup> Our conclusions are summarized in Sec. VI. Appendix A contains a calculation of the photon echo signal from a coupled pair of two level systems with different resonance frequencies. Appendix B contains a discussion of the generalization of our treatment to different microscopic models of inhomogeneous broadening.

## II. PHOTON ECHOES FROM INTERACTING TWO LEVEL SYSTEMS

We treat a system of  $N$  oriented molecules whose positions are randomly distributed in a volume  $V$  at zero temperature. This is intended to be a simple model for a molecular crystal in which guest impurity molecules are randomly substituted in a crystal lattice of host molecules. (A more complete model would allow the guest molecules to be at only certain lattice sites, rather than have a continuum of positions. At the low concentrations we are concerned with, the difference between discrete and continuous positions variables is not expected to be of importance because of the large average distance between an impurity molecule and its nearest impurity neighbor.)

Each molecule has a single excited state that is connected to the ground state by an electric dipole transition. The molecules interact by a transition dipole-transition dipole mechanism. The transition energies for molecules may differ because of inhomogeneous broadening. The Hamiltonian for this system is

$$H = H_0 + H_1 + H_2,$$

$$H_0 = \sum_{j=1}^N \hbar\omega_j n_j^+ n_j,$$

$$H_1 = \sum_{j < l = 1}^N \hbar J(\mathbf{r}_{jl}, \boldsymbol{\mu}_j, \boldsymbol{\mu}_l)(n_j^+ n_l + n_l^+ n_j),$$

$$H_2 = - \sum_{j=1}^N \hat{\boldsymbol{\mu}}_j \cdot \mathbf{E}(t) \cos(\Omega t - \mathbf{k} \cdot \mathbf{r}_j), \quad (2.1)$$

$$\hat{\boldsymbol{\mu}}_j = \boldsymbol{\mu}_j(n_j^+ + n_j), \quad (2.2)$$

$$\hbar J(\mathbf{r}_{jl}, \boldsymbol{\mu}_j, \boldsymbol{\mu}_l) = \frac{\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_l}{r_{jl}^3} - 3 \frac{(\boldsymbol{\mu}_j \cdot \mathbf{r}_{jl})(\boldsymbol{\mu}_l \cdot \mathbf{r}_{jl})}{r_{jl}^5}. \quad (2.3)$$

$n_j^+$  and  $n_j$  are the creation and annihilation operators for the excitation on the  $j$ th molecule.<sup>11</sup>  $\hbar\omega_j$  is the energy of the transition on the  $j$ th particle.  $\boldsymbol{\mu}_j$  is the transition dipole of the  $j$ th molecule.  $\hbar J(\mathbf{r}_{jl}, \boldsymbol{\mu}_j, \boldsymbol{\mu}_l)$  is the energy of interaction between the transition dipoles on molecules  $j$  and  $l$ .  $\mathbf{E}(t)$  is the amplitude,  $\Omega$  is the frequency, and  $\mathbf{k}$  is the wave vector of the electric field of the laser beam with which the experiment is carried out. In this work we will assume that all transition dipoles are of equal magnitude and are aligned parallel to the electric field.

The  $N$  body density matrix  $\sigma$  obeys the Liouville equation

$$\frac{d\sigma}{dt} = - \frac{i}{\hbar} [H, \sigma]. \quad (2.4)$$

We transform into the rotating frame with the following unitary transformation<sup>8</sup>:

$$\begin{aligned} \tilde{\sigma} &= W^+ \sigma W, \\ W &= \exp \left[ -i \sum_j n_j^+ n_j (\Omega t) \right]. \end{aligned} \quad (2.5)$$

In the rotating wave approximation,<sup>8,12</sup> the equation of motion for  $\tilde{\sigma}$  becomes

$$\frac{d\tilde{\sigma}}{dt} = -i[Q_0 + Q_f + Q_c, \tilde{\sigma}], \quad (2.6)$$

where

$$\begin{aligned} Q_0 &= \sum_{j=1}^N (\omega_j - \Omega) n_j^+ n_j, \\ Q_f &= - \sum_{j=1}^N \frac{\boldsymbol{\mu}_j \cdot \mathbf{E}(t)}{2\hbar} [e^{i\mathbf{k} \cdot \mathbf{r}_j} n_j^+ + e^{-i\mathbf{k} \cdot \mathbf{r}_j} n_j], \\ Q_c &= \sum_{j < l = 1}^N J(\mathbf{r}_{jl})(n_j^+ n_l + n_l^+ n_j). \end{aligned} \quad (2.7)$$

The formal solution of Eq. (2.6) in the absence of the laser field is

$$\tilde{\sigma}(t) = U(t) \tilde{\sigma}(0) U^+(t), \quad (2.8)$$

where

$$U(t) = \exp[-i(Q_0 + Q_c)t]. \quad (2.9)$$

In order to solve Eq. (2.6) in the presence of the laser field, we make three simplifying assumptions: (i) The echo experiment is carried out with square pulses [ $\mathbf{E}(t)$  in Eq. (2.7) does not vary in time while the pulse is on]; (ii)  $Q_0$  can be neglected in Eq. (2.6) while the pulse is on; (iii)  $Q_c$  can be neglected in Eq. (2.6) while the pulse is on. In order for assumptions (ii) and

(iii) to be valid, the pulse durations must be short relative to the inverse of matrix elements of  $Q_0$  and  $Q_c$ , and the pulses must be sufficiently intense that the Rabi frequency  $\mu E/\hbar$  is large compared to matrix elements of  $Q_0$  and  $Q_c$ .<sup>8,9</sup> These conditions are realizable in the laboratory. (An echo calculation for a strongly coupled electron-phonon system in which the short pulse assumption is not made has been carried out by Skinner.<sup>7</sup>) Under these assumptions,  $\tilde{\sigma}$  after a short intense pulse of duration  $t$  is given by

$$\tilde{\sigma}(t) = R(t) \tilde{\sigma}(0) R^\dagger(t), \quad (2.10)$$

$$R(t) = \exp(-iQ_f t). \quad (2.11)$$

In a photon echo experiment, the sample is irradiated for a time  $t_1$ , allowed to evolve in the absence of radiation for a time  $t_2$ , irradiated for a time  $t_{II}$ , and allowed to evolve for a time  $t_2$ . The density matrix in the rotating frame after this sequence is given by

$$\begin{aligned} \tilde{\sigma}(t_1 + t_1 + t_{II} + t_2) &= U(t_2) R(t_{II}) U^\dagger(t_1) \\ &\times R(t_1) \tilde{\sigma}(0) R^\dagger(t_1) U^\dagger(t_1) R^\dagger(t_{II}) U^\dagger(t_2). \end{aligned} \quad (2.12)$$

We wish to calculate the macroscopic electric polarization of the sample, which is related to the density matrix by

$$\mathbf{p}(\mathbf{r}, t) = \left\langle \sum_j \text{Tr}(\hat{\mu}_j \tilde{\sigma}) \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle, \quad (2.13)$$

where the angular brackets designate a configuration average over the spatial positions and site energies of all molecules. We define  $\tilde{p}(\mathbf{r}, t)$  by

$$p(\mathbf{r}, t) = \tilde{p}(\mathbf{r}, t) e^{-i\Omega t} + [\tilde{p}(\mathbf{r}, t)]^* e^{i\Omega t}, \quad (2.14)$$

where  $p(\mathbf{r}, t)$  is the magnitude of  $\mathbf{p}(\mathbf{r}, t)$  in Eq. (2.13).  $\tilde{p}(\mathbf{r}, t)$  is related to the rotating frame density matrix  $\tilde{\sigma}(t)$  by

$$\tilde{p}(\mathbf{r}, t) = \left\langle \sum_j \text{Tr}(\hat{\mu}_j \tilde{\sigma}) \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle. \quad (2.15)$$

$\hat{\mu}_j$  is a modified transition dipole operator for molecule  $j$  defined by

$$\hat{\mu}_j = \mu_j n_j, \quad (2.16)$$

where  $n_j$  is the excitation annihilation operator defined after Eq. (2.1) and  $\mu_j$  is the magnitude of the transition dipole on molecule  $j$ .

To calculate the intensity of the emitted light, the electric field caused by the macroscopic polarization must be calculated from Maxwell's equations. In the slowly varying envelope approximation, valid in the limit of optically thin samples,<sup>12,13</sup> the field is proportional to the polarization. Therefore the emitted intensity is proportional to the time average of  $[p(\mathbf{r}, t)]^2$ . From Eq. (2.14), we see that the signal is proportional to the absolute square of  $\tilde{p}(\mathbf{r}, t)$ :

$$I(t) \propto |\tilde{p}(\mathbf{r}, t)|^2. \quad (2.17)$$

(Note that the  $\mathbf{r}$  dependence of  $\tilde{p}(\mathbf{r}, t)$  is contained in a complex exponential, so that  $|\tilde{p}(\mathbf{r}, t)|^2$  is independent of  $\mathbf{r}$ .)

The effect of the two pulse sequence of Eq. (2.12) on a system of noninteracting two level systems is to produce an echo that is sharply peaked at  $t_2 = t_1$ . If the wave vectors of the first and second pulses are  $\mathbf{k}_I$  and  $\mathbf{k}_{II}$ , respectively, then the echo will propagate along the direction  $2\mathbf{k}_{II} - \mathbf{k}_I$ .<sup>5(b)</sup> In

the rest of this work, we will be concerned with calculating the magnitude of the echo signal at  $t_2 = t_1$ . We will refer to  $\tilde{p}(\mathbf{r}, t_1 + t_1 + t_{II} + t_1)$  as  $\tilde{p}(\mathbf{r}, 2t_1)$ . We will omit contributions to  $\tilde{p}$  that are not peaked at  $2t_1$ , such as the parts of  $\tilde{p}$  that give rise to the free induction decay signal following each pulse. The free induction decay signal following the  $j$ th pulse propagates with wave vector  $\mathbf{k}_j$  and hence can be spatially separated from the photon echo signal.

In principle, the photon echo signal from a collection of  $N$  interacting molecules in a volume  $V$  with a specified distribution of spatial positions and site energies can be calculated from Eqs. (2.12), (2.15), and (2.17). In practice such an exact calculation is intractable. In the next section we present a scaling analysis of  $\tilde{p}(\mathbf{r}, t)$  that motivates the truncated density expansion approximation that we will make.

### III. SCALING ANALYSIS OF $\tilde{p}(\mathbf{r}, 2t_1)$

In order to proceed, we must specify a microscopic model of inhomogeneous broadening. We assume a Gaussian distribution of site energies and a complete lack of correlation between site energy and spatial position. (In Sec. V, we examine another model of inhomogeneous broadening in which energy and spatial position are correlated.) We define new site energy variables  $\{x_k\}$  [see Eq. (2.7)] by

$$x_k = \omega_k - \Omega. \quad (3.1)$$

For  $N$  molecules in a volume  $V$  with parallel transition dipole moments, the configuration average of a configuration dependent quantity  $F$  is given by

$$\begin{aligned} \langle F \rangle &= \frac{1}{V^N} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \left( \frac{\tau}{\pi^{1/2}} \right)^N \\ &\times \left[ \prod_{j=1}^N \int_{-\infty}^{\infty} dx_j e^{-\tau^2 x_j^2} \right] F. \end{aligned} \quad (3.2)$$

$\tau$  is a time that characterizes the width of the inhomogeneous distribution of  $\{x_k\}$ . We rewrite the dipole-dipole interaction of Eq. (2.2) for parallel dipoles with equal magnitudes as

$$J(\mathbf{r}_{jl}) = K J_{nn} (d/r_{jl})^3. \quad (3.3)$$

The angular factor  $K$  is given by

$$K = 1 - 3 \cos^2 \theta, \quad (3.4)$$

where  $\theta$  is the angle between  $\mathbf{r}_{jl}$  and the direction in which the dipoles are pointing.  $J_{nn}$  is an effective neighbor interaction frequency and  $d$  is an effective nearest neighbor distance. In this model,  $\tilde{p}(\mathbf{r}, 2t_1)$  in the thermodynamic limit ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \rho$ ) depends on the set of variables  $\{\rho, t_1, \tau, J_{nn}, d, \mathbf{k}_I, \mathbf{k}_{II}, \mathbf{r}\}$ .  $\mathbf{k}_I$  and  $\mathbf{k}_{II}$  are the wave vectors of the two pulses. We carry out a scaling analysis to determine the manner in which  $\tilde{p}(\mathbf{r}, 2t_1)$  depends on these variables. This argument is analogous to the procedure developed by Haan and Zwanzig in their analysis of electronic excitation transport.<sup>14</sup>

The configuration of the  $N$  body system is specified by a set of positions  $\{\mathbf{r}_j\}$  and a set of frequencies  $\{x_j\}$ . Let  $\beta_1$  and  $\beta_2$  be arbitrary positive numbers. Consider a new set of configurations in which all distances are scaled by  $\beta_1$  and all site energies are scaled by  $\beta_2$ . From Eqs. (2.12), (2.15), and (3.2), it can be shown that  $\tilde{p}$  has the form

$$\tilde{\rho} = \rho F(\beta_1^{-3} \rho, \beta_2^{-1} t_1, \beta_1^3 J_{nn} d^3 t_1, \beta_2^{-1} \tau, \beta_1 \mathbf{r}, \beta_1^{-1} \mathbf{k}_I, \beta_1^{-1} \mathbf{k}_{II}). \quad (3.5)$$

$\beta_1$  and  $\beta_2$  are arbitrary, so we can pick

$$\beta_1 = (J_{nn} d^3 \tau)^{-1/3}, \quad (3.6)$$

$$\beta_2 = \tau,$$

since  $\tau$ ,  $J_{nn}$ , and  $d$  are all positive. Substitution of Eqs. (3.6) into Eq. (3.5) yields

$$\tilde{\rho} = \rho F(\rho d^3 J_{nn} \tau, t_1/\tau, t_1/\tau, 1, (J_{nn} d^3 \tau)^{-1/3} \mathbf{r}, (J_{nn} d^3 \tau)^{1/3} \mathbf{k}_I, (J_{nn} d^3 \tau)^{1/3} \mathbf{k}_{II}). \quad (3.7)$$

Thus  $\tilde{\rho}$  can be expressed as  $\rho$  times a function that depends on a scaled time  $t_1/\tau$  and a scaled density  $\rho d^3 J_{nn} \tau$ . We define  $\alpha$  to be the latter quantity.

$$\alpha = \rho d^3 J_{nn} \tau. \quad (3.8)$$

Consider the magnitude of  $\alpha$  for situations of interest. The numbers used are typical of molecules in mixed molecular crystals.<sup>15</sup> Let  $J_{nn}$  be  $10 \text{ cm}^{-1}$  and let  $w$ , the full width at half-maximum of the inhomogeneous distribution be  $1 \text{ cm}^{-1}$ .  $\tau$  is related to  $w$  by

$$\tau = \frac{2(\ln 2)^{1/2}}{w}. \quad (3.9)$$

Then  $J_{nn} \tau \approx 17$ . For  $\rho d^3 = 10^{-3}$ ,  $\alpha \ll 1$ . This argument suggests that a perturbation expansion of  $\tilde{\rho}$  in powers of  $\alpha$  (a density expansion) will give useful information about the time dependence of the photon echo signal at experimentally interesting impurity concentrations.

In the next section we show that the first two terms in a perturbation series for  $\tilde{\rho}$ , i.e., the terms of zeroth and first orders in  $\alpha$ , exist for our model. This suggests that  $\tilde{\rho}$  can be written as

$$\tilde{\rho}(\mathbf{r}, 2t_1) = \rho [f_0(\mathbf{r}) + \alpha f_1(\mathbf{r}, t_1/\tau) + o(\alpha)]. \quad (3.10)$$

We have no proof that  $\tilde{\rho}$  is an analytic function of  $\alpha$ , or even that the  $\alpha^2$  term in the Taylor series has a finite coefficient. If there is a transition from states of finite extent to infinite extent at some finite concentration, then this concentration would probably be an upper limit to the radius of convergence of the series. There is also the possibility that the existence of some states with a large but finite spatial extent will lead to a nonanalyticity in the series. This would appear as a divergence in one or more of the subsequent coefficients in the Taylor series. In either case, it is likely that Eq. (3.10) is at least an asymptotic series, if not analytic, and for small enough  $\alpha$  the first two terms will be an accurate approximation.

#### IV. DENSITY EXPANSION OF $\tilde{\rho}(\mathbf{r}, 2t_1)$

Consider the first two terms of a density expansion of  $\tilde{\rho}(\mathbf{r}, 2t_1)$  for  $N$  molecules in a volume  $V$ .

Substituting Eq. (A8) into Eq. (4.6) gives

$$B_2(\mathbf{r}, t_1) = \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \lim_{V \rightarrow \infty} \left( \frac{-i\mu}{2} \right) \sin A_I \sin^2 \left( \frac{A_{II}}{2} \right) V \left( 2 \cos A_{II} \left( \frac{J^2}{J^2 + y^2} \right) \times \sin^2 [(J^2 + y^2)^{1/2} (t_1)] + i \cos A_I \cos A_{II} \frac{J}{(J^2 + y^2)^{1/2}} \sin [(J^2 + y^2)^{1/2} (2t_1)] \right), \quad (4.9)$$

$$\tilde{\rho}(\mathbf{r}, 2t_1) = \frac{N}{V} B_1(\mathbf{r}, V, t_1) + \frac{(N)(N-1)}{V^2} B_2(\mathbf{r}, V, t_1) + \dots \quad (4.1)$$

By setting  $N = 1$  in this equation we can relate  $B_1(\mathbf{r}, V, t_1)$  to  $\tilde{\rho}_1(\mathbf{r}, 2t_1)$ , the average polarization generated by one molecule in a volume  $V$ .

$$B_1(\mathbf{r}, V, t_1) = V \tilde{\rho}_1(\mathbf{r}, 2t_1). \quad (4.2)$$

By setting  $N = 2$ , we can relate  $B_2(\mathbf{r}, V, t_1)$  to  $\tilde{\rho}_1$  and  $\tilde{\rho}_2(\mathbf{r}, 2t_1)$ , the average polarization generated by two molecules in a volume  $V$ :

$$B_2(\mathbf{r}, V, t_1) = (V^2/2) [\tilde{\rho}_2(\mathbf{r}, 2t_1) - 2\tilde{\rho}_1(\mathbf{r}, 2t_1)]. \quad (4.3)$$

If the thermodynamic limit of Eq. (4.1) exists, then

$$\tilde{\rho}(\mathbf{r}, 2t_1) = \rho B_1(\mathbf{r}, t_1) + \rho^2 B_2(\mathbf{r}, t_1) + \dots, \quad (4.4)$$

$$B_1(\mathbf{r}, t_1) = \lim_{V \rightarrow \infty} V \tilde{\rho}_1(\mathbf{r}, 2t_1), \quad (4.5)$$

$$B_2(\mathbf{r}, t_1) = \lim_{V \rightarrow \infty} (V^2/2) [\tilde{\rho}_2(\mathbf{r}, 2t_1) - 2\tilde{\rho}_1(\mathbf{r}, 2t_1)]. \quad (4.6)$$

This result provides a prescription for calculating an approximation to  $\tilde{\rho}(\mathbf{r}, 2t_1)$  for the many body problems from the exact solutions for  $\tilde{\rho}$  in the one and two body problems.  $\tilde{\rho}_1(\mathbf{r}, 2t_1)$  is given by<sup>5(b),8</sup>

$$\tilde{\rho}_1(\mathbf{r}, 2t_1) = \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \left( \frac{-i}{2} \right) \left( \frac{\mu}{V} \right) \times \sin A_I \sin^2 \left( \frac{A_{II}}{2} \right). \quad (4.7)$$

$A_j$  ( $j = I, II$ ), the area of the  $j$ th pulse, is  $\mu E t_j / \hbar$ , where  $t_j$  is the pulse duration. Substituting this result into Eq. (4.5) gives

$$B_1(\mathbf{r}, t_1) = \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \left( \frac{-i}{2} \right) \mu \sin A_I \sin^2 \left( \frac{A_{II}}{2} \right). \quad (4.8)$$

In Appendix A, we calculate  $\tilde{\rho}_2(\mathbf{r}, 2t_1)$  for a coupled pair of two level systems with different resonance frequencies. In performing this calculation we make the following assumption. A pair of molecules with a large enough interaction to behave as a dimer rather than as two monomers for times of interest must be separated by a distance that is small compared to the wavelength of the laser. This assumption allows us to neglect the difference in phase of the electric field at two positions occupied by molecules that have a significant interaction. This approximation is not essential, but greatly simplifies the calculation. We justify this approximation in our discussion of numerical results in the following section. The final result for  $\tilde{\rho}_2(\mathbf{r}, 2t_1)$  is given by Eq. (A8). If we set the coupling  $J$  to zero in this expression, we obtain the polarization generated by two noninteracting molecules in a volume  $V$ . This must be twice the polarization generated by a single molecule. Thus the right-hand side of Eq. (A8) reduces to twice the right-hand side of Eq. (4.7) for  $J = 0$ .

where  $y$  is  $\frac{1}{2}(x_2 - x_1)$ , half of the difference in resonance frequencies of the two molecules in the absence of intermolecular interactions. The first two terms of the density expansion for  $\tilde{p}(\mathbf{r}, 2t_1)$  can now be obtained from Eqs (4.4), (4.8), and (4.9):

$$\begin{aligned} \tilde{p}(\mathbf{r}, 2t_1) = & \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \mu \rho \left( \frac{-i}{2} \right) \sin A_I \sin^2 \left( \frac{A_{II}}{2} \right) \left\{ 1 + \rho \int d\mathbf{r}_{12} \frac{r^2}{\pi} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \right. \\ & \times e^{-r^2(x_1^2 + x_2^2)} \left[ 2 \cos A_{II} \left( \frac{J^2}{J^2 + y^2} \right) \sin^2((J^2 + y^2)^{1/2}(t_1)) \right. \\ & \left. \left. + i \cos A_I \cos A_{II} \frac{J}{(J^2 + y^2)^{1/2}} \sin((J^2 + y^2)^{1/2}(2t_1)) \right] \right\}. \end{aligned} \quad (4.10)$$

## V. RESULTS AND DISCUSSION

In this section we present the results of calculations performed with Eq. (4.10). We wish to evaluate the integrals in Eq. (4.10) for the transition dipole-transition dipole coupling of Eqs. (3.3) and (3.4). These integrals must be evaluated numerically for each value of  $t_1/\tau$ . Equation (4.10) shows that  $\tilde{p}(\mathbf{r}, 2t_1)$  has both real and imaginary parts. For the experimentally interesting case of  $A_I = \pi/2$ , the real part of the two body correction in Eq. (4.10) vanishes exactly, and for other pulse areas its contribution to  $\tilde{p}$  can be shown to be negligible. Henceforth, we will neglect this term. The angular dependence of the dipole-dipole interaction  $J$ , given in Eq. (3.4), is the reason that the real part of the two body correction to  $\tilde{p}$  in Eq. (4.10) is of negligibly small magnitude. The integrand of this contribution to  $\tilde{p}$  is an odd function of  $J$ , and the angular integration leads to considerable cancellation between contributions from pair configurations in which  $J > 0$  and configurations in which  $J < 0$ . Since the integrand of the imaginary part of the two body contribution to  $\tilde{p}$  is an even function of  $J$ , such cancellation does not occur in this case. Equation (4.10) can then be written as

$$\begin{aligned} \tilde{p}_1(\mathbf{r}, 2t_1) = & \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \left( \frac{-i}{2} \right) \mu \rho \sin A_I \sin^2 \left( \frac{A_{II}}{2} \right) \\ & \times \{ 1 + (\cos A_{II}) \alpha f(t_1/\tau) \}, \end{aligned} \quad (5.1)$$

where  $\alpha = \rho d^3 J_{nn} \tau$ . Some values of  $f(t_1/\tau)$  are listed in Table I. Note that Eq. (5.1) has the form of Eq. (3.10), as predicted by the scaling argument of Sec. III.

TABLE I. Representative values of  $f(t_1/\tau)$ , defined in Eq. (5.1).

$t_1/\tau$	$f$
0	0
0.1	1.01
0.25	2.51
0.5	4.95
1.0	9.37
1.5	12.9
2.0	15.6
3.0	19.3
4.0	21.7
6.0	25.1
8.0	27.5
10.0	29.2
12.0	30.7
16.0	33.0
20.0	34.8
24.0	36.2
30.0	38.0
36.0	39.3
40.0	40.2

We can now test the validity of the long wavelength assumption that was made in deriving Eq. (5.1). As discussed in the previous section and in Appendix A, we assumed that pairs of molecules that contribute significantly to the two body correction for times of interest are separated by distances small compared to the wavelength of the laser. The radial integral that must be carried out to evaluate  $f(t_1/\tau)$  converges and hence is dominated by contributions from small intermolecular separations. For  $J_{nn} = 10 \text{ cm}^{-1}$ , an inhomogeneous linewidth of  $1 \text{ cm}^{-1}$  and  $t_1/\tau = 20$  (a long time on the time scale of interest, as discussed below), the fractional contribution to  $f(t_1/\tau)$  for  $r > 25 d$  is approximately 1%. A typical lattice spacing is  $\sim 10 \text{ \AA}$ , so our simplifying assumption that for times of interest the value of this radial integral is determined by contributions from distances small compared to optical wavelengths is justified.

The short time behavior of  $f(t_1/\tau)$  in Eq. (5.1) can be determined analytically from Eq. (4.10):

$$f(t_1/\tau) = \{ [16\pi^2]/[9(3)^{1/2}] \} (t_1/\tau) + O(t_1/\tau)^3. \quad (5.2)$$

Since  $f(t_1/\tau)$  appears in Eq. (5.1) multiplied by  $\alpha$ , which is linear in  $\tau$ , the linear term in an expansion of Eq. (5.1) in powers of  $t_1$  will be independent of  $\tau$ . The next term in the expansion of  $\tilde{p}$  (the cubic term) does depend on  $\tau$ . Thus the short time behavior of  $\tilde{p}(\mathbf{r}, 2t_1)$  is independent of the width of the inhomogeneous distribution of resonance frequencies.

Consider the approximate  $\tilde{p}(\mathbf{r}, 2t_1)$  in Eq. (5.1) for large  $t_1/\tau$ . It can be shown that  $f(t_1/\tau) \sim \ln(t_1/\tau)$  for  $t_1/\tau \gg 1$  and hence that our approximation to  $\tilde{p}$  in Eq. (5.1) is unbounded. However the polarization of a finite density of dipoles has as an upper bound the polarization of that density of dipoles when the dipoles are all in phase. From the upper bound on the polarization and the definition of  $\tilde{p}$  in Eq. (2.14), an upper bound of  $\mu^2 \rho^2 / 4$  can be placed on  $|\tilde{p}|^2$ . This is the value of  $|\tilde{p}|^2$  after a photon echo pulse sequence with  $A_I = \pi/2$  and  $A_{II} = \pi$  in a sample containing a density  $\rho$  of noninteracting two level systems. The fact that Eq. (5.1) is unbounded is not an unexpected result for a truncated density expansion and suggests the use of a Padé approximant.<sup>16</sup> Consider the function

$$\frac{\mu^2 \rho^2}{4} \sin^2(A_I) \sin^4 \left( \frac{A_{II}}{2} \right) \left[ \frac{1 + 2(1 + \cos A_{II}) \alpha f(t_1/\tau)}{1 + 2\alpha f(t_1/\tau)} \right]. \quad (5.3)$$

This expression is a Padé approximant to the square of Eq. (5.1). To zeroth and first orders in  $\alpha$ , it agrees with the approximation to  $|\tilde{p}|^2$  obtained by squaring Eq. (5.1). However Eq. (5.3) has the desirable property that it remains bounded by  $\mu^2 \rho^2 / 4$  for all  $A_I, A_{II}$ , and  $t_1/\tau$ . The exact form of Eq. (5.3) is somewhat arbitrary. For example, for  $A_{II} = \pi$ , (5.3) de-

cays to zero as  $t_1/\tau \rightarrow \infty$ . With a different choice of a rational approximation, we could have forced  $|\bar{p}|^2$  to decay to a non-zero constant in this case. However Eq. (5.3) has the advantage over Eq. (5.1) that one more piece of information about the exact solution (its boundedness) has been included. We will use expression (5.3) henceforth. Figure 1 illustrates the difference between the square of Eq. (5.1) and expression (5.3) for  $A_I = \pi/2$ ,  $A_{II} = \pi$ , and  $(4/3)\pi\alpha = 0.025$ . The lowest curve is obtained by squaring Eq. (5.1), but discarding the term of order  $\alpha^2$ . The middle curve is obtained by squaring Eq. (5.1) and keeping all terms. The top curve is calculated from expression (5.3). The difference between the top and bottom curves gives an estimate of the error in our approximation. Although we use expression (5.3) in the rest of this work, the conclusions we will draw could just as well have been based on any of the other methods of calculating the echo signal from Eq. (5.1).

In Fig. 2, we present the photon echo signal for  $A_I = \pi/2$ ,  $A_{II} = \pi$ , and three values of  $\alpha$ . In all of the calculations presented here, the excited state lifetimes has not been included to emphasize the time dependence that arises from the intermolecular interactions. For an infinite excited state lifetimes and zero temperature, the photon echo signal from noninteracting two level systems has no time dependence [see Eq. (4.7)]. Each curve in Fig. 2 is characterized by an initial rapid drop, followed by a much slower decay on a time scale long compared to  $\tau$ . The value of  $t_1/\tau$  at which the transition occurs from fast decay to slow decay is the same for three curves in Fig. 2. The effect of raising  $\alpha$ , which is equivalent to raising the concentration for fixed  $J_{nm}$  and  $\tau$  is to increase the amount by which the polarization drops before the decay becomes slow. These observations are consistent with the short time analysis of Eq. (4.10) in Eq. (5.2). Equations (5.1) and (5.2) show that the initial slope of the signal is proportional to  $\rho$ . The initial rapid decay is due to the linear term in Eq. (5.2), while the slow decay at longer times arises from the cubic and higher order terms. Equations (5.1) and (5.2) show that the time range over which the transition occurs (times at which Eq. (5.2) is no longer dominated by the linear term) is independent of  $\alpha$ .

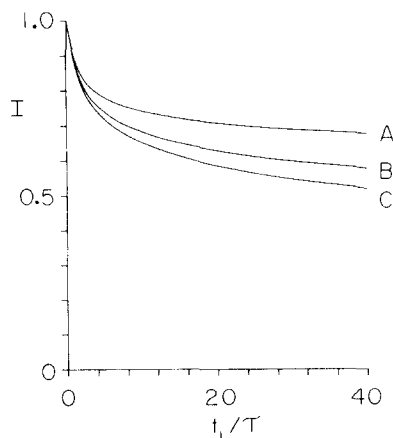


FIG. 1. The photon echo intensity as a function of pulse separation  $t_1$ , calculated from Eq. (5.1) by three methods. See the text for discussion.  $(4/3)\pi\alpha = 0.025$ .  $A_I = \pi/2$ .  $A_{II} = \pi$ . A Padé Approximant [Eq. (5.3)], B square of Eq. (5.1), C square of Eq. (5.1), retaining only terms of zeroth and first order in  $\alpha$ . The excited state lifetime is not included.

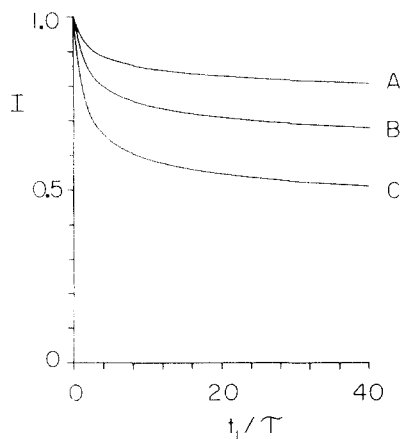


FIG. 2. The photon echo intensity as a function of pulse separation  $t_1$ , calculated from Eq. (5.3) for three reduced concentrations. The excited state lifetime is not included.  $A_I = \pi/2$ .  $A_{II} = \pi$ . A  $(4/3)\pi\alpha = 0.0125$ . B  $(4/3)\pi\alpha = 0.025$ . C  $(4/3)\pi\alpha = 0.05$ .

An important feature of Eq. (5.1) is the strong dependence on pulse areas, particularly on  $A_{II}$ .  $f(t_1/\tau)$  is positive valued for all  $t_1/\tau$ . Therefore for  $A_{II} > \pi/2$ , the initial slope of the echo signal will be negative, and for  $A_{II} < \pi/2$ , the initial slope will be positive. For  $A_{II} = \pi/2$ , the two body correction to  $\bar{p}$  vanishes, and the system will behave as uncoupled monomers in this approximation. Figure 3 shows photon echo signals for  $A_{II} = \pi/4$ ,  $\pi/2$ , and  $3\pi/4$ . The  $t_1/\tau = 0$  values of each curve has been normalized to unity. The relative magnitudes of the three intensities at  $t_1/\tau = 0$  are very different because of the  $\sin^4(A_{II}/2)$  factor in Eq. (5.3). For the same value of  $A_I$ , the relative magnitudes of the echo signal at  $t_1/\tau = 0$  for  $A_{II} = \pi$ ,  $3\pi/4$ ,  $\pi/2$ , and  $\pi/4$  are 1, 0.73, 0.25, and 0.021, respectively.

All results discussed thus far have been based on a model in which there is assumed to be no correlation between spatial position and position in the inhomogeneous line. In Appendix B we show that the truncated density expansion for more general models can be written in terms of a reduced two particle distribution function  $g_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2, V)$ . For the special case of Eq. (4.10),

$$g_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2, V) = \frac{1}{V^2} \frac{\tau^2}{\pi} e^{-\tau^2 x_1^2} e^{-\tau^2 x_2^2}. \quad (5.4)$$

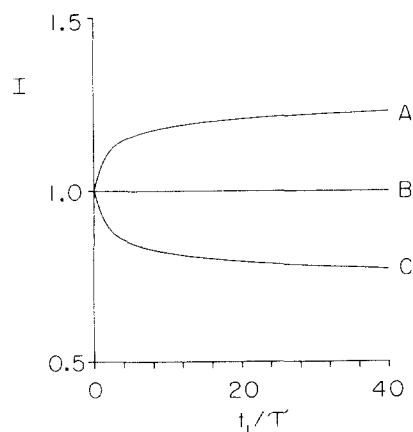


FIG. 3. The photon echo intensity as a function of pulse separation  $t_1$ , calculated from Eq. (5.3) for three values of the pulse area  $A_{II}$ . The excited state lifetime is not included.  $(4/3)\pi\alpha = 0.025$ . Each curve has been normalized as discussed in the text. A  $A_{II} = \pi/4$ . B  $A_{II} = \pi/2$ . C  $A_{II} = 3\pi/4$ .

A simple model in which spatial position and energy are correlated consists of taking the following form for  $g_2$ :

$$g_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{x}_1, \mathbf{x}_2, V) = \frac{1}{V^2} \frac{\tau^2}{\pi} e^{-\tau^2 x_1^2} e^{-\tau^2 x_2^2} \times \left\{ \frac{(2\pi)^{1/2}}{\tau} \delta(x_1 - x_2) [1 - \theta(r_{12} - R)] + \theta(r_{12} - R) \right\}, \quad (5.5)$$

where  $\theta(x)$  is a step function defined to have value 1 for  $x > 0$  and value 0 for  $x < 0$ . Molecules whose separation is less than  $R$  have identical resonance frequencies. The resonance frequencies of molecules whose separation is larger than  $R$  are uncorrelated and are distributed according to a Gaussian distribution. The limit  $R \rightarrow 0$  corresponds to the model discussed previously and the limit  $R \rightarrow \infty$  corresponds to the case in which all molecules are degenerate. For finite  $R$ , Eq. (5.5) provides a simple model of the situation in which the inhomogeneity in molecular resonance frequencies is slowly varying in space, such as might be the case for inhomogeneity induced by crystal strains.<sup>8</sup> In this case, the resonance frequencies of nearby molecules are likely to be very close, while those of molecules separated by large distances will be uncorrelated.

The short time behavior of  $\tilde{p}(\mathbf{r}, 2t_1)$ , calculated from Eqs. (5.5), (B3), and (B4) can be determined analytically. The term linear in  $t_1$  in an expansion of  $\tilde{p}$  in powers of  $t_1$  is identical to the linear term in the expansion of Eq. (4.10). Thus, at short times the photon echo signal calculated using Eq. (5.5) should be very close to that calculated from Eq. (5.4). Figure 4 shows the photon echo signal calculated from Eqs. (5.5), (B3), and (B4) for  $(4/3)\pi\alpha = 0.025$ ,  $\rho d^3 = 5 \times 10^{-4}$ ,  $A_I = \pi/2$ ,  $A_{II} = \pi$ , and several values of  $d/R$ . The scaling analysis of Sec. III no longer applies in this model since we have introduced a new length into the problem. Therefore  $\alpha$  and  $\rho d^3$  must be specified separately. Figure 4 illustrates that the short times behavior of the signal is independent of  $R$ , as indicated by the above short time analysis. At longer times, the signal for  $R < \infty$  decays more slowly than the signal from

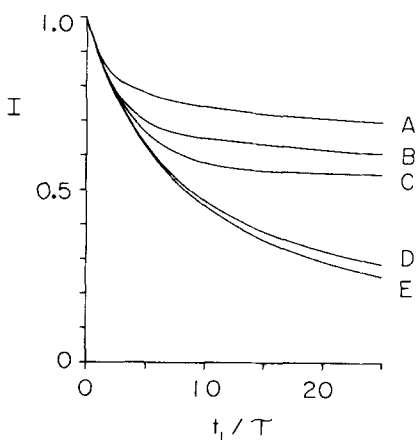


FIG. 4. The photon echo intensity as a function of pulse separation  $t_1$  for a model of inhomogeneous broadening in which molecules separated by less than a distance  $R$  having identical transition energies. The energies of molecules whose separation exceeds  $R$  are uncorrelated and obey a Gaussian distribution.  $\rho d^3 = 5 \times 10^{-4}$ .  $(4/3)\pi\alpha = 0.025$ .  $A_I = \pi/2$ .  $A_{II} = \pi$ . The excited state lifetime is not included. See the text for discussion. A  $d/R = \infty$ . B  $d/R = 0.25$ . C  $d/R = 0.20$ . D  $d/r = 0.10$ . E  $d/R = 0$ .

a system of degenerate two level systems shown in curve E of Fig. 4. The effect of decreasing  $R$  is to decrease the value of the time at which the signal begins to differ significantly from curve E. In the limit  $R \rightarrow \infty$  (curve E), all of the molecules have identical resonance frequencies, and the echo signal no longer depends on  $\tau$ . [ $\tau$  is related to the inverse of the width of the inhomogeneous distribution of resonance frequencies in Eq. (3.9).] To obtain the time dependence (in unscaled time units) of the echo signal in this limit for  $\rho d^3 = 5 \times 10^{-4}$ , a value of  $\tau$  equal to  $\alpha/(\rho d^3 J_{nn})$  should be used with curve E.

In Sec. III, we assumed that the laser pulses had infinite Rabi frequency. Therefore our results include some contributions from pairs of molecules that are sufficiently close in space that their interactions are much larger than the inhomogeneous linewidth. In a real crystal, in which the molecules occupy discrete lattice positions, the existence of such strongly coupled pairs gives rise to discrete peaks in the absorption spectrum that are well separated from the rest of the inhomogeneous line.<sup>6</sup> Such pairs would not contribute to the signal in a real experiment in which the Rabi frequency is large enough to span the main inhomogeneous line but not large enough to include them. We can estimate the contribution to our results from such pairs by carrying out a modified calculation of the two body correction to  $\tilde{p}$  in Eq. (4.6). In this calculation we assume that pairs whose interaction frequency  $J$  exceeds a maximum value  $J_m$  do not contribute to  $\tilde{p}_2$ , the configuration averaged polarization of a pair of molecules. This modification reduces the magnitude of the signal, since some molecules are now excluded. In addition, the analytic structure of the time dependence is changed. The short time behavior of  $\tilde{p}(\mathbf{r}, 2t_1)$  can be determined analytically. The quantity in curly brackets in Eq. (5.1) is replaced by

$$1 - (16 \pi \alpha)/(9(3)^{1/2} J_m \tau) + [\cos A_{II}] [(32 \pi \alpha)/(9(3)^{1/2})] (t_1/\tau) \times \int_0^{J_m t_1} dq \frac{\sin^2 q}{q^2} + O(t_1/\tau)^3. \quad (5.6)$$

For  $t_1 \ll J_m^{-1}$ , the third term in Eq. (5.6) is proportional to  $t_1^2$ , so the echo signal will have zero slope at  $t_1 = 0$ . For  $t_1 \gg J_m^{-1}$ , the value of the integral over  $q$  in Eq. (5.6) approaches  $\pi/2$ , and the time dependence becomes nearly linear. In the limit that the  $q$  integral is replaced by  $\pi/2$ , Eq. (5.6) gives the same linear time dependence as Eq. (5.2), with the same numerical coefficient multiplying  $t_1$ . The magnitude of the effect on the calculated signal of introducing a maximum  $J$  that is comparable to the inhomogeneous linewidth is very small for concentrations of experimental interest. For the parameters used in calculating curve B in Fig. 2 and  $J_m \tau = 2.2$  the magnitude of the signal at  $t_1 = 0$  is reduced by 2%, and the modified curve is essentially indistinguishable from curve B for  $t_1/\tau > 0.1$ .

Because we have used a continuum model in which the molecules are randomly distributed in space, our results contain a contribution from pairs of molecules that are separated by an unphysically small distance. The magnitude of the contribution of such pairs to our results can be estimated by using a reduced two particle distribution function  $g_2$  that

vanishes for unphysically small interparticle separations. This modification also introduces a maximum value of the coupling ( $J_m$ ) into the problem, so that for  $t_1 \ll J_m^{-1}$ , the dimer correction to the polarization is proportional to  $t_1^2$ . At longer times the time dependence of the dimer correction becomes linear, as in the discussion following Eq. (5.6). Since the nearest neighbor interactions in real crystals are typically larger than the width of the inhomogeneous distribution of resonance frequencies, the effect of this modification on our calculation would be even smaller than the effect of introducing a  $J_m$  that is comparable to the linewidth. Thus the finite slope at  $t_1 = 0$  of the echo signals shown in Figs. 1–4 is a consequence of the fact that these calculations were carried out with a continuum model in which there is no maximum value of the intermolecular interaction. If the calculation is modified to include such a maximum value ( $J_m$ ), the echo signal will have zero slope at  $t_1 = 0$  and the time dependence of the signal will be modified for  $t_1 \ll J_m^{-1}$ .

A theoretical investigation of optical coherence experiments on systems of interacting molecules has been carried out by Warren and Zewail.<sup>10</sup> They treat a system whose Hamiltonian includes, in addition to the terms in our Eq. (2.1), permanent dipole–permanent dipole interactions and the possibility that the excitation of one site in a crystal can change the resonance frequencies of nearby sites. These authors do not present results for the case treated here, in which impurities that are sufficiently close in space to have significant interactions can have different resonance frequencies.

Our results can be compared to theirs in the limit in which all impurities are taken to have identical resonance frequencies. This limit corresponds to a simple model of inhomogeneous broadening that is spatially slowly varying. In this model, the crystal consists of macroscopic domains, such that the resonance frequencies of all impurities in a domain are identical, and interactions between impurities in different domains are neglected. In this limit, for a  $\pi/2 - \pi$  pulse sequence, Warren and Zewail predict a decay of the photon echo signal that is exponential for times long compared to the inverse of the maximum value of the intermolecular interaction. This decay is characterized by a  $T_2$  given by

$$T_2^{-1} \sim 1.5f\mu^2 a^{-3} \hbar^{-1} \quad (f \ll 1). \quad (5.7)$$

This result was calculated for an isotropic distribution of parallel transition dipoles of magnitude  $\mu$  and number density  $fa^{-3}$ . The degenerate impurity limit can be taken in our work either by setting  $y = 0$  in Eq. (4.10) or by taking the  $R \rightarrow \infty$  limit of Eq. (5.5). For  $A_I = \pi/2$  and  $A_{II} = \pi$ , the result is

$$\begin{aligned} \tilde{\rho}(\mathbf{r}, 2t_1) = & \exp[i(2\mathbf{k}_{II} - \mathbf{k}_I) \cdot \mathbf{r}] \left( \frac{-i}{2} \right) (\mu\rho) \\ & \times [1 - 10.13f\mu^2 a^{-3} \hbar^{-1} t_1] \end{aligned} \quad (5.8)$$

in the notation of Eq. (5.7). Our approximation in this limit predicts a time dependence that will appear exponential for short times<sup>17</sup> and low concentrations, which is the regime where Eq. (5.8) should be accurate. For purposes of comparison we will calculate an effective  $T_2$  from Eq. (5.8) using the

relation<sup>5(b)</sup>

$$\tilde{\rho}(\mathbf{r}, 2t_1) \propto e^{-2t_1/T_2} \quad (5.9)$$

The result is

$$T_2^{-1} = 5.07 f\mu^2 a^{-3} \hbar^{-1}. \quad (5.10)$$

Equation (5.10) agrees with Eq. (5.7) in predicting a linear concentration dependence for this quantity, but differs from Eq. (5.7) in the magnitude of the numerical factor. Our result in Eq. (5.10) is identical to the expression for  $T_2^{-1}$  obtained in another recent calculation of the echo decay from degenerate impurities following a  $\pi/2 - \pi$  pulse sequence.<sup>18</sup>

Although we define an effective  $T_2$  in Eq. (5.10) for the special case of a  $\pi/2 - \pi$  pulse sequence and noninteracting domains of degenerate impurities, it should be emphasized that our work indicates that there is in general no reason to believe that a photon echo signal from a system of interacting molecules with an inhomogeneously broadened absorption spectrum will have an exponential time dependence. The calculations depicted in Figs. 1–3 do not resemble exponential decays. In fact, as is illustrated in Fig. 3, for certain choices of pulse areas, the echo signal will begin with positive slope.

## VI. CONCLUSIONS

In this work we have presented an approximate calculation of the photon echo signal from a system of interacting molecules with an inhomogeneous distribution of resonance frequencies. The quantity of interest is the magnitude of the echo signal at a time  $t_1$  after the second pulse, where  $t_1$  is the time between pulses. Our approximation is expected to be accurate in the limit of low density. We first considered a model of inhomogeneous broadening in which the inhomogeneous distribution of resonance frequencies is Gaussian and there is no correlations between spatial position and resonance frequency. At shortest times, the signal is of the form  $1 + Bt_1^2$ . At longer times, the signal has the form  $1 + B't_1$ . The signs of  $B$  and  $B'$  are determined by the area of the second pulse. The signal is most strongly time dependent during this linear time regime. At still longer times, the time dependence of the signal becomes weaker. The early time behavior holds for times much less than the reciprocal of the maximum value of the intermolecular interaction, which is determined either by the finite Rabi frequency of the laser or by the largest nearest neighbor interaction in the crystal. (The Rabi frequency is assumed to be large enough to span the main part of the inhomogeneous line, but possibly not large enough to include the most strongly coupled molecular pairs. This point is discussed in Sec V.) The strong time dependence is evident for  $t_1 \approx \tau$  [ $\tau$  is  $2(\ln 2)^{1/2}$  times the inverse of the inhomogeneous linewidth]. As can be seen from Figs. 1–3, the  $t_1$  dependence of the signal becomes significantly weaker for  $t_1 \geq 5\tau$ . We next consider a model of inhomogeneous broadening in which molecules whose separation is less than a distance  $R$  have identical resonance frequencies. The frequencies of molecules whose separation exceeds  $R$  are uncorrelated and are distributed according to a Gaussian distribution. This is a simple model of the situation in which the inhomogeneity is slowly varying in space, as may be the case for inhomogeneous broadening induced by crystal strain. In



this case the resonance frequencies of nearby molecules would be nearly identical. The time dependence of the signal for short times was found to be independent of  $R$ . For finite or zero  $R$ , the time dependence of the signal at long times was found to be weaker than the time dependence of the signal for  $R = \infty$ , in which case all molecules have the same frequency. The time at which the signal for finite  $R$  begins to differ significantly from the signal for  $R = \infty$  decreases as the value of  $R$  is decreased. The echo signals calculated here are in general nonexponential. For arbitrary pulse areas, the optical dephasing due to intermolecular interactions in a system with an inhomogeneously broadened absorption spectrum *cannot* be characterized by a  $T_2$ .

We have shown that intermolecular interactions among impurities in a mixed crystal can be studied with a photon echo experiment. Our results show that the onset of delocalized impurity states in mixed crystals manifests itself in the time dependence of the photon echo signal. Since our approximation is perturbative in concentration, it will not be valid for high impurity concentrations at which a transition to band-like impurity states might occur. However, the results presented here suggest that optical coherence experiments may prove to be an important tool in the investigation of the way in which impurity electronic states in mixed crystals at low temperature change as the impurity concentration is raised.

#### ACKNOWLEDGMENTS

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#### APPENDIX A

The photon echo signal from a pair of interacting two level systems with identical resonance frequencies [ $\omega_1 = \omega_2$  in Eq. (2.1)] has been calculated by Skinner *et al.*<sup>8</sup> In this Appendix we generalize their treatment to the case in which the resonance frequencies are different. The calculation is somewhat more involved than that of Ref. 8, but the procedure is sufficiently similar that we will present only the final results.

The Hamiltonian for this problem is Eq. (2.1) with  $N = 2$ . The formal solution to the Liouville equation in the rotating frame is given in Eq. (2.12). The matrix elements of the propagator  $U(t)$  in the eigenstate basis are

$$\begin{aligned} U_{00} &= 1, \\ U_{11} &= \exp\{-i[x - (y^2 + J^2)^{1/2}]t\}, \\ U_{22} &= \exp\{-i[x + (y^2 + J^2)^{1/2}]t\}, \\ U_{33} &= \exp[-2ix], \\ U_{jk} &= 0; \quad j \neq k, \end{aligned} \quad (\text{A1})$$

where

$$\begin{aligned} x &= \frac{1}{2}(x_1 + x_2), \\ y &= \frac{1}{2}(x_2 - x_1). \end{aligned} \quad (\text{A3})$$

$x_k$  is defined in Eq. (2.1).  $|0\rangle$  is the ground state,  $|1\rangle$  and  $|2\rangle$  are the single excited states, and  $|3\rangle$  is the doubly excited state. The matrix elements of the pulse propagator  $R(t)$  in the eigenstate basis are

$$\begin{aligned} R_{00} &= R_{33} = \frac{1}{2}(1 + \cos A), \\ R_{01} &= i/2(\gamma_1 e^{-ik \cdot r_1} + \gamma_2 e^{-ik \cdot r_2}) \sin A, \\ R_{13} &= i/2(\gamma_1 e^{-ik \cdot r_2} + \gamma_2 e^{-ik \cdot r_1}) \sin A, \\ R_{02} &= i/2(\gamma_3 e^{-ik \cdot r_1} + \gamma_4 e^{-ik \cdot r_2}) \sin A, \\ R_{23} &= i/2(\gamma_3 e^{-ik \cdot r_2} + \gamma_4 e^{-ik \cdot r_1}) \sin A, \\ R_{03} &= \frac{1}{2}(\cos A - 1)e^{-ik \cdot (r_1 + r_2)}, \\ R_{11} &= \cos A + \frac{1}{2}(1 - \cos A) \\ &\quad \times \{1 + 2\gamma_3\gamma_4 \cos[\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)]\}, \\ R_{12} &= \frac{1}{2}(\cos A - 1)[\gamma_1\gamma_4 e^{ik \cdot (r_1 - r_2)} + \gamma_2\gamma_3 e^{ik \cdot (r_2 - r_1)}], \\ R_{22} &= \cos A + \frac{1}{2}(1 - \cos A) \{1 \\ &\quad + 2\gamma_1\gamma_2 \cos[\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)]\}, \\ R_{nm}(\mathbf{k}) &= R_{mn}(-\mathbf{k}), \end{aligned} \quad (\text{A4})$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the positions of the two molecules,  $\mathbf{k}$  is the pulse wave vector,  $A = \mu Et / \hbar$  is the pulse area, and the  $\{\gamma_i\}$  are defined by

$$\begin{aligned} \gamma_1 &= \frac{J}{[2\nu(\nu - y)]^{1/2}}, \\ \gamma_2 &= \frac{y - \nu}{[2\nu(\nu - y)]^{1/2}}, \\ \gamma_3 &= \frac{J}{[2\nu(\nu + y)]^{1/2}}, \\ \gamma_4 &= \frac{y + \nu}{[2\nu(\nu + y)]^{1/2}}, \\ \nu &= (J^2 + y^2)^{1/2}. \end{aligned} \quad (\text{A5})$$

Under the assumption that the molecular transition dipoles are parallel and of equal magnitude  $\mu$ , the matrix elements of  $\hat{\mu}_1$ , the transition dipole operator for molecule 1 in the eigenstate basis are

$$\hat{\mu}_1 = \mu \begin{pmatrix} 0 & \gamma_1 & \gamma_3 & 0 \\ \gamma_1 & 0 & 0 & \gamma_2 \\ \gamma_3 & 0 & 0 & \gamma_4 \\ 0 & \gamma_2 & \gamma_4 & 0 \end{pmatrix}. \quad (\text{A6})$$

The indices of this matrix correspond to the eigenstates in order of increasing energy.

Similarly  $\hat{\mu}_2$  is given by

$$\hat{\mu}_2 = \mu \begin{pmatrix} 0 & \gamma_2 & \gamma_4 & 0 \\ \gamma_2 & 0 & 0 & \gamma_1 \\ \gamma_4 & 0 & 0 & \gamma_3 \\ 0 & \gamma_1 & \gamma_3 & 0 \end{pmatrix}. \quad (\text{A7})$$

The configuration averaged polarization generated in a volume  $V$  containing two interacting molecules by the pho-

ton echo pulse sequence can be calculated from Eqs. (2.12), (2.15), and (A1) through (A7). We now make the simplifying assumption discussed in Secs. IV and V that a pair of molecules whose coupling is of sufficient strength to affect the time dependence of the echo signal for times of interest has a separation that is small compared to the wavelength of the laser. This allows us to set  $\mathbf{k} \cdot \mathbf{r}_1 = \mathbf{k} \cdot \mathbf{r}_2$  in the matrix elements in Eqs. (A4). The final result is

$$\begin{aligned} \bar{p}(\mathbf{r}, 2t_1) = & \exp[i(2\mathbf{k}_{\text{II}} - \mathbf{k}_I) \cdot \mathbf{r}] \left[ \frac{-i\mu}{V} \sin A_I \sin^2\left(\frac{A_{\text{II}}}{2}\right) \right] \\ & \times \left\{ \left[ 1 + \cos A_{\text{II}} \left( \frac{J^2}{J^2 + y^2} \right) \right] [1 - \cos((J^2 + y^2)^{1/2}(2t_1))] \right. \\ & \left. + i[\sin((J^2 + y^2)^{1/2}(2t_1))] \frac{J}{(J^2 + y^2)^{1/2}} \cos A_I \cos A_{\text{II}} \right\}, \end{aligned} \quad (\text{A8})$$

where  $A_I$  and  $A_{\text{II}}$  are the pulse areas defined above.

## APPENDIX B

In this Appendix we generalize our treatment to apply to different microscopic models of inhomogeneous broadening. Equation (3.2) defines the configuration average of a

$$\begin{aligned} \bar{p}(\mathbf{r}, 2t_1) = & \exp[i(2\mathbf{k}_{\text{II}} - \mathbf{k}_I) \cdot \mathbf{r}] \mu \rho \left( \frac{-i}{2} \right) \sin A_I \sin^2\left(\frac{A_{\text{II}}}{2}\right) \\ & \times \left\{ 1 + \rho \int d\mathbf{r}_{12} \int dx_1 \int dx_2 h_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2) \left[ 2 \cos A_{\text{II}} \left( \frac{J^2}{J^2 + y^2} \right) \right. \right. \\ & \left. \left. \times \sin^2((J^2 + y^2)^{1/2}(t_1)) + i \cos A_I \cos A_{\text{II}} \frac{J}{(J^2 + y^2)^{1/2}} \sin((J^2 + y^2)^{1/2}(2t_1)) \right] \right\}, \end{aligned} \quad (\text{B3})$$

where  $h_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2)$  is defined by

$$h_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2) = \lim_{V \rightarrow \infty} V^2 g_2(\mathbf{r}_1, \mathbf{r}_2, x_1, x_2, V). \quad (\text{B4})$$

The calculations shown in Fig. 4 were carried out by substituting Eq. (5.5) for  $g_2$  into Eqs. (B4) and (B3).

<sup>1</sup>R. Kopelman, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), Vol. 4, p. 139.

<sup>2</sup>R. F. Loring, H. C. Andersen, and M. D. Fayer, *Chem. Phys.* **85**, 149 (1984).

<sup>3</sup>J. Klafter and J. Jortner, *J. Chem. Phys.* **71**, 2210 (1978).

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<sup>5</sup>(a) R. L. Shoemaker, *Annu. Rev. Phys. Chem.* **30**, 239 (1979); (b) W. H. Hesselink and D. A. Wiersma, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), Vol. 4, p. 249.

<sup>6</sup>(a) J. B. W. Morsink and D. A. Wiersma, *Chem. Phys. Lett.* **89**, 291 (1982); (b) F. G. Patterson, W. L. Wilson, H. W. H. Lee, and M. D. Fayer (to be published).

<sup>7</sup>J. L. Skinner, *J. Chem. Phys.* **77**, 3398 (1982).

<sup>8</sup>J. L. Skinner, H. C. Andersen, and M. D. Fayer, *J. Chem. Phys.* **75**, 3195 (1981).

<sup>9</sup>J. L. Skinner, H. C. Andersen, and M. D. Fayer, *Phys. Rev. A* **24**, 1994 (1981).

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<sup>11</sup>A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971), p. 121.

<sup>12</sup>(a) J. C. McGurk, T. G. Schmalz, and W. H. Flygare, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York,

configuration dependent quantity  $F$  for  $N$  oriented molecules with parallel dipoles in a volume  $V$  in a model in which spatial position in the inhomogeneous line are uncorrelated. In general, for  $N$  oriented molecules with parallel dipoles in a volume  $V$ , the configuration average of  $F$  is given by

$$\langle F \rangle = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_N g_N[\{\mathbf{r}_i\}, \{x_i\}, V] F, \quad (\text{B1})$$

where  $g_N[\{\mathbf{r}_i\}, \{x_i\}, V]$  is the  $N$  body distribution function of positions and energies. If  $F$  just depends on the positions and energies of the first  $n$  molecules, then Eq. (B1) simplifies to

$$\langle F \rangle = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n g_n(\mathbf{r}_1 \cdots \mathbf{r}_n, x_1 \cdots x_n, V) F, \quad (\text{B2})$$

where  $g_n$  is a reduced distribution function obtained by integrating  $g_N$  over the positions and energies of  $N - n$  molecules. The analysis of Sec. IV can be made more general by replacing Eq. (3.2) with Eq. (B1). If we assume  $g_2$  depends on the molecule positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  only through their difference  $\mathbf{r}_{12}$ , the more general version of Eq. (4.10) is

1974), Vol. XXV, p. 1; (b) R. L. Shoemaker, in *Laser and Coherence Spectroscopy*, edited by J. I. Steinfeld (Plenum, New York, 1978), p. 197.

<sup>13</sup>R. W. Olson, H. W. H. Lee, F. G. Patterson, and M. D. Fayer, *J. Chem. Phys.* **76**, 31 (1982).

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<sup>16</sup>D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

<sup>17</sup>Equation (5.8) is derived from a continuum model in which the magnitude of the interaction between impurities can take on any value. The effect of introducing a maximum value of this interaction  $J_m$  is discussed following Eq. (5.6). In any physical system, such a  $J_m$  always exists. Equation (5.8) should be a valid description of a physical system for a range of times that are long compared to  $J_m^{-1}$ , but still short on the time scale of the echo decay.

<sup>18</sup>L. Root and J. L. Skinner, *J. Chem. Phys.* **81**, 5310 (1984). Root and Skinner have recently completed a theoretical study of photon echoes from interacting impurities in mixed crystals. Their results were communicated to us after the completion of this manuscript. They demonstrate that the method of moments, which was used by Warren and Zewail to derive Eq. (5.7) is internally inconsistent. An expression for  $T_2^{-1}$  for the photon echo decay from a system of degenerate impurities after a  $\pi/2 - \pi$  pulse sequence can be found in terms of any two moments of the frequency domain line shape function. However, the resulting value of  $T_2^{-1}$  depends on which pair of moments is chosen. Root and Skinner calculate  $T_2^{-1}$  for a  $\pi/2 - \pi$  pulse sequence and degenerate impurities with parallel transition dipoles, using an approximation that is based on a cumulant expansion of the ensemble averaged polarization. They obtain a result that is identical to our Eq. (5.10). Their expression is stated to be valid for low impurity concentration and for "intermediate" times that are large compared to the inverse of the interaction frequency of nearest neighbor impurities.