

# Theory of photon echoes from a pair of coupled two level systems: Impurity dimers and energy transfer in molecular crystals<sup>a)</sup>

James L. Skinner,<sup>b)</sup> Hans C. Andersen, and M. D. Fayer

Department of Chemistry, Stanford University, Stanford, California 94305

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We present the theory of the photon echo and stimulated photon echo from a four level system that results from a pair of weakly coupled two level systems. This model describes an impurity dimer in a molecular crystal. We include the effect of relaxation processes, focusing on energy transfer between delocalized states. We find that both the photon and stimulated echoes contain information about static level splittings and dynamic energy transfer processes. Moreover, these observables show a dramatic dependence on the excitation power. We discuss implications of our results for recent experiments on concentration dependent dephasing of impurities in molecular crystals. Our analysis casts considerable doubt on the intermolecular interaction interpretation of these experiments.

## I. INTRODUCTION

Optical coherence experiments have proven to be extremely useful for obtaining static and dynamic information from systems in which such information is obscured in the absorption spectrum by inhomogeneous broadening.<sup>1</sup> It is sufficient to treat many of these systems as simple or generalized<sup>2-4</sup> two level systems; photon echoes have been observed experimentally from a number of these systems.<sup>1</sup> Recently, related techniques such as the Raman echo,<sup>5,6</sup> the trilevel echo,<sup>7</sup> and the two photon echo<sup>8</sup> have been developed for systems involving three or more well separated electronic levels.

In this paper we discuss the theory of the photon echo and the stimulated photon echo from a pair of weakly coupled two level systems with almost identical excitation energies. If the coupling is weak, so that certain energy splittings are small, then all of the excited levels of the system can be populated with a single excitation frequency. We examine the effects of both (static) level splitting and (dynamic) energy transfer on the time dependence of the echo intensities. Also of interest in the present study is the dependence of the echo intensities on the power of the laser excitation pulses.

The model we discuss here is closely related to the multilevel systems discussed by Schenzle and Brewer.<sup>9</sup> In our model, however, all of the levels can be populated from the ground state with a single optical frequency by one or two (consecutive) photon absorption. In addition, we include relaxation processes, specifically population transfer between excited states. For earlier theoretical work on two photon coherent experiments the reader should consult the papers of Gold and Hahn,<sup>10</sup> Brewer and Hahn,<sup>11</sup> and Hahn and Maxwell.<sup>12</sup>

The theory discussed in this paper is motivated by the

significant interest in coherent processes in molecular crystals<sup>13-15</sup> and by recent photon and stimulated echo experiments on impurities in molecular crystals.<sup>16,17</sup> Current interest focuses on the nature of the (delocalized) eigenstates and energy transfer among these states in both pure and mixed molecular crystals. The prototypical system for the experimental and theoretical study of these processes is an interacting pair of impurities in a molecular crystal. In fact, Olson *et al.*<sup>18</sup> have succeeded in observing a photon echo from a strongly coupled dimer (where the laser is resonant with only one excited level). The study of dimers can also lead to an understanding of (and ability to interpret experiments on) other interacting systems, e.g., impurity bands and pure crystal excitons. The present theory on photon echoes and stimulated photon echoes from dimers complements theoretical studies on the spectra of dimers by Abram and Silbey,<sup>19</sup> and the fluorescence depolarization from dimers by Rahman *et al.*<sup>20</sup>

In Sec. II of this paper we consider a four level system where the frequency splittings between the ground state and the second and third levels is approximately equal to the laser frequency, while the splitting between the ground state and the fourth level is approximately equal to twice the laser frequency. Including relaxation processes, we derive general expressions for the photon and stimulated echo experiments. As a model for a pair of interacting impurities in a molecular crystal, in Sec. III we consider two weakly coupled two level systems, which gives rise to a four level system as discussed in Sec. II. With a simple model of coupling to a (phonon) bath, using Redfield theory we derive relaxation equations that describe energy transfer between the two middle levels. In Sec. IV we evaluate the results of Sec. II with the model of Sec. III. We find that the photon echo exhibits oscillations resulting from the unequal energy splittings, and damping due to energy transfer. Moreover, the form of the time evolution shows a dramatic dependence on excitation power. The time evolution of the stimulated echo is also power dependent. In Sec. V we discuss the implications of our results for the experiments of Cooper *et al.*<sup>16</sup> and Morsink *et al.*<sup>17</sup> on concentration dependent dephasing of impurities in mo-

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<sup>b)</sup> NSF Postdoctoral Fellow 1980-81. Present address: Department of Chemistry, Columbia University, New York, N. Y. 10027.

lecular crystals. Our analysis casts considerable doubt on the intermolecular interaction interpretation of these experiments.

## II. PHOTON ECHOES FROM A FOUR LEVEL SYSTEM

Consider a four level quantum system as shown in Fig. 1. States  $|1\rangle$  and  $|2\rangle$  are in near resonance with the laser frequency  $\Omega$ , while state  $|3\rangle$  is in near resonance with twice  $\Omega$ . Also shown in Fig. 1 are the non-zero dipole matrix elements connecting the four states. Noticeably absent are couplings between states  $|0\rangle$  and  $|3\rangle$ , and between states  $|1\rangle$  and  $|2\rangle$ . The Hamiltonian for this system is

$$H = H_0 + H_1, \quad (2.1)$$

$$H_0 = \hbar\omega_1 |1\rangle\langle 1| + \hbar\omega_2 |2\rangle\langle 2| + \hbar\omega_3 |3\rangle\langle 3|, \quad (2.2)$$

$$H_1 = -\mu E \cos(\Omega t - kz). \quad (2.3)$$

$\hbar\omega_1$ ,  $\hbar\omega_2$ , and  $\hbar\omega_3$  are the energies of the three excited levels (we choose the zero of energy to be the ground state).  $E$  is the time dependent magnitude of the electric field of a laser beam that propagates in the  $z$  direction and is plane polarized in the  $x$  direction.  $\mu$ , the  $x$  component of the transition dipole operator, has the form

$$\begin{aligned} \mu = & \mu_{01} \{ |0\rangle\langle 1| + |1\rangle\langle 0| \} + \mu_{02} \{ |0\rangle\langle 2| + |2\rangle\langle 0| \} \\ & + \mu_{13} \{ |1\rangle\langle 3| + |3\rangle\langle 1| \} + \mu_{23} \{ |2\rangle\langle 3| + |3\rangle\langle 2| \}. \end{aligned} \quad (2.4)$$

We have assumed for simplicity that the matrix elements of  $\mu$  are real.

The Liouville-von Neumann equation of motion for the density operator  $\sigma$  is

$$\frac{\partial \sigma}{\partial t} = -\frac{i}{\hbar} [H, \sigma] - \Lambda \sigma, \quad (2.5)$$

where  $(\Lambda \sigma)_{kl} \equiv \sum_{mn} \Lambda_{klmn} \sigma_{mn}$ .

We have explicitly included relaxation processes via the superoperator  $\Lambda$ , which will be discussed in more detail below and in Sec. III. Making the transformation

$$\tilde{\sigma} = W^\dagger \sigma W, \quad (2.6)$$

where

$$W = \exp[-iS(\Omega t - kz)], \quad (2.7)$$

$$S = |1\rangle\langle 1| + |2\rangle\langle 2| + 2|3\rangle\langle 3|, \quad (2.8)$$

the equation of motion in the rotating wave approximation becomes

$$\frac{\partial \tilde{\sigma}}{\partial t} = -i \left[ \Delta - \frac{\chi}{2}, \tilde{\sigma} \right] - \tilde{\Lambda} \tilde{\sigma}, \quad (2.9)$$

where

$$\begin{aligned} \Delta = & (\omega_1 - \Omega) |1\rangle\langle 1| \\ & + (\omega_2 - \Omega) |2\rangle\langle 2| + (\omega_3 - 2\Omega) |3\rangle\langle 3|, \end{aligned} \quad (2.10)$$

$$\chi = \mu E / \hbar, \quad (2.11)$$

$$\tilde{\Lambda}_{klmn} \equiv W_k^* W_l W_m W_n^* \Lambda_{klmn}. \quad (2.12)$$

For ease of notation  $W_k \equiv W_{kk}$  and (in what follows)  $\Delta_k \equiv \Delta_{kk}$ , since both these operators are strictly diagonal.

To solve Eq. (2.9) in the presence of the laser field

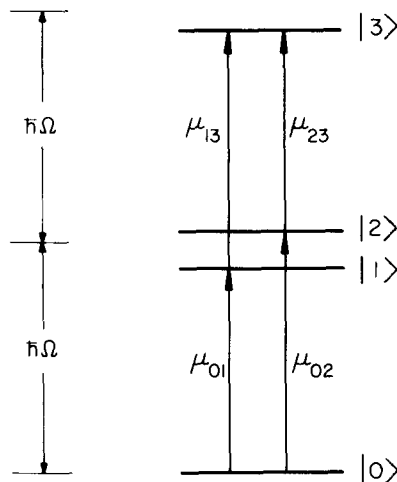


FIG. 1. The four-level system discussed in Sec. II.

we make the following simplifying assumptions: (i) The  $i$ th excitation pulse has a constant amplitude  $E$  for a duration  $\tau_i$  (square pulse); (ii)  $\tau_i$  is much shorter than any relaxation times described by  $\tilde{\Lambda}$ ; (iii)  $\Delta_j \tau_i \ll 1$ ,  $j = 1, 2, 3$ ; (iv) the nonzero matrix elements of  $\chi$  are much larger than  $\Delta_j$ . Assumptions (ii) through (iv) imply that we can neglect both the relaxation operator  $\tilde{\Lambda}$  and  $\Delta$  during each pulse. With assumption (i) the density operator after a pulse of duration  $\tau$  is given by

$$\tilde{\sigma}(\tau) = V(\tau) \tilde{\sigma}(0) V^\dagger(\tau), \quad (2.13)$$

$$V(\tau) = \exp(i\chi\tau/2). \quad (2.14)$$

For our purposes this can be written more conveniently as

$$\tilde{\sigma}(\tau) = g(\tau) \tilde{\sigma}(0), \quad (2.15)$$

where  $g(\tau)$  is a superoperator defined by

$$\tilde{\sigma}_{kl}(\tau) = \sum_{mn} g_{klmn}(\tau) \tilde{\sigma}_{mn}(0), \quad (2.16)$$

$$g_{klmn}(\tau) = V_{km}(\tau) V_{nl}(-\tau). \quad (2.17)$$

In the absence of the laser field, the inclusion of the relaxation term makes the solution of Eq. (2.9) quite complex. In some instances, however (see the discussion in Sec. III), the matrix elements of  $\tilde{\Lambda}$  have the form

$$\tilde{\Lambda}_{klmn} = \delta_{km} \delta_{ln} (1 - \delta_{kl}) \gamma_{kl} + \delta_{kl} \delta_{mn} \lambda_{km}. \quad (2.18)$$

$\gamma$  describes dephasing of the off-diagonal elements, while  $\lambda$  describes population transfer among the diagonal elements. With this form for  $\tilde{\Lambda}$ , the free evolution ( $\chi = 0$ ) solution to Eq. (2.9) can be written as

$$\tilde{\sigma}(t) = G(t) \tilde{\sigma}(0), \quad (2.19)$$

where

$$G_{klmn}(t) = (1 - \delta_{kl}) \delta_{km} \delta_{ln} \exp(i\phi_{kl}t) + \delta_{kl} \delta_{mn} Q_{km}(t), \quad (2.20)$$

$$\phi_{kl} = \Delta_k - \Delta_l - i\gamma_{kl}, \quad (2.21)$$

$$Q(t) = \exp(-\lambda t). \quad (2.22)$$

In a photon echo experiment or variant thereof, one prepares the system with an initial laser pulse of duration  $\tau_1$ , lets it evolve freely for a time  $t_1$ , excites it again with a pulse of duration  $\tau_2$ , lets it evolve freely

for a time  $t_2$ , etc. The evolution of the density operator for such a scheme is

$$\bar{\sigma}(t_1 + t_2 + \dots) = \dots G(t_2)g(\tau_2)G(t_1)g(\tau_1)\bar{\sigma}(0). \quad (2.23)$$

[Due to assumption (iii) above, we have neglected  $\tau_1$  and  $\tau_2$  in the argument of  $\bar{\sigma}$ .]

Assuming that the detector is polarized in the  $x$  direction (the theory can easily be generalized to other situations), we are only concerned with the  $x$  component of the macroscopic polarization of the medium, which is given by

$$p(t) = \text{Tr}[\mu \langle \sigma(t) \rangle]. \quad (2.24)$$

The angular brackets indicate an average over an inhomogeneous distribution of four level systems. Writing

$$p(t) = \bar{p}(t) \exp[-i(\Omega t - kz)] + \text{c. c.}, \quad (2.25)$$

it is easy to see that

$$\begin{aligned} \bar{p}(t) = & \mu_{01} \langle \bar{\sigma}_{10}(t) \rangle + \mu_{02} \langle \bar{\sigma}_{20}(t) \rangle \\ & + \mu_{13} \langle \bar{\sigma}_{31}(t) \rangle + \mu_{23} \langle \bar{\sigma}_{32}(t) \rangle. \end{aligned} \quad (2.26)$$

For an optically thin sample, the intensity of the signal  $s(t)$  is

$$s(t) \propto |\bar{p}(t)|^2. \quad (2.27)$$

To continue further we must specify the nature of the energy level inhomogeneities. We define

$$\Delta_j = x_j + \delta_j, \quad j = 1, 2, 3, \quad (2.28)$$

where  $x_j$  is the average deviation of level  $j$  from  $\Omega$  (or  $2\Omega$ ), and  $\delta_j$  is the inhomogeneous deviation with

$$\langle \delta_j \rangle = 0. \quad (2.29)$$

Depending both on the source of the inhomogeneities (Doppler effect in gases, strain energies in crystals) and on the source of the energy level structure, there are various possibilities for the relationship among the  $\delta_j$ . For the model we discuss in Sec. III, the appropriate choice is

$$\delta_1 \approx \delta_2 \approx \delta_3/2 \equiv \delta. \quad (2.30)$$

To be more precise, we require, for example, that  $(\delta_1 - \delta_2)t_i \ll 1$ , where  $t_i$  are the pulse separations. Equation (2.30) is also valid for Doppler broadened molecules in gases; in this case the approximate equalities become strict equalities.

For the two pulse photon echo experiment, at a time  $t$  after the second pulse, the density operator is given by

$$\bar{\sigma}(t + t_1) = G(t)g(\tau_2)G(t_1)g(\tau_1)\bar{\sigma}(0). \quad (2.31)$$

When written out in terms of matrix elements, this equation contains an enormous number of terms. The average over  $\delta$  reduces the number of terms considerably since we are interested in times such that  $\delta t, \delta t_1 \gg 1$ . Retaining only those terms that produce an echo when  $t = t_1$ , we find [using Eq. (2.26)] that

$$\begin{aligned} \bar{p}(2t_1) = & \sum_{kimn} g_{kimn}(\tau_2)g_{mn00}(\tau_1) \exp[-it_1(\psi_{ki} + \psi_{mn})] \\ & \times (\mu_{01}\delta_{k1}\delta_{i0} + \mu_{02}\delta_{k2}\delta_{i0} + \mu_{13}\delta_{k3}\delta_{i1} + \mu_{23}\delta_{k3}\delta_{i2}) (\delta_{n3}\delta_{m2} + \delta_{n3}\delta_{m1} + \delta_{n2}\delta_{m0} + \delta_{n1}\delta_{m0}), \end{aligned} \quad (2.32)$$

$$\psi_{ki} = x_k - x_i - i\gamma_{ki}. \quad (2.33)$$

As  $t_1$  is varied, the time dependence of the echo amplitude is contained solely in the factor  $\exp[-it_1(\psi_{ki} + \psi_{mn})]$ . In general, it is clear that the echo amplitude is damped by the dephasing factors  $\gamma_{ki}$ , and modulated by the level splittings  $x_k - x_i$ .

For the three pulse stimulated echo experiment, at a time  $t$  after the third pulse the density matrix is given by

$$\bar{\sigma}(t + t_2 + t_1) = G(t)g(\tau_3)G(t_2)g(\tau_2)G(t_1)g(\tau_1)\bar{\sigma}(0). \quad (2.34)$$

Performing the average over  $\delta$ , and retaining terms that lead to an echo when  $t = t_1$ , we obtain

$$\begin{aligned} \bar{p}(2t_1 + t_2) = & \sum_{kimnrs} g_{rs00}(\tau_1) \exp[-it_1(\psi_{ki} + \psi_{rs})] \\ & \times [g_{kimn}(\tau_3)Q_{mn}(t_2)g_{mrs}(\tau_2) + g_{kimn}(\tau_3) \exp(-it_2\psi_{mn})g_{mrs}(\tau_2)(\delta_{m1}\delta_{n2} + \delta_{m2}\delta_{n1})] \\ & \times (\mu_{01}\delta_{k1}\delta_{i0} + \mu_{02}\delta_{k2}\delta_{i0} + \mu_{13}\delta_{k3}\delta_{i1} + \mu_{23}\delta_{k3}\delta_{i2})(\delta_{s3}\delta_{r2} + \delta_{s3}\delta_{r1} + \delta_{s2}\delta_{r0} + \delta_{s1}\delta_{r0}). \end{aligned} \quad (2.35)$$

As  $t_1$  is varied, the time dependence of the stimulated echo amplitude is qualitatively similar to the photon echo amplitude. On the other hand, as  $t_2$  is varied, the time dependence has contributions that are *purely* damped from the population transfer term  $Q_{mn}(t_2)$ , and contributions from  $\exp(-it_2\psi_{mn})$  that are both modulated and damped.

### III. IMPURITY DIMERS IN MOLECULAR CRYSTALS

In this section we show how a simple model of an impurity dimer can be cast into the formalism of Sec. II. We also provide a derivation of the relaxation term in Eq. (2.9), and show how  $\gamma$  and  $\lambda$  from Eq. (2.18) are related to energy transfer rates.

As a model for an impurity dimer in a molecular crys-

tal, we consider a pair of weakly coupled two level systems interacting with a bath. The two level systems model the electronic excitation of the impurities, and the bath consists of lattice phonons, intramolecular vibrations, photons, etc. The Hamiltonian is

$$H = H_0 + H' + H_b, \quad (3.1)$$

$$H_0 = \hbar \epsilon_1 n_1^\dagger n_1 + \hbar \epsilon_2 n_2^\dagger n_2 + \hbar J(n_1^\dagger n_2 + n_2^\dagger n_1), \quad (3.2)$$

and since the laser field is  $x$  polarized, we need the  $x$  component of the transition dipole operator, which is

$$\mu = \mu_1(n_1 + n_1^\dagger) + \mu_2(n_2 + n_2^\dagger). \quad (3.3)$$

$n_i^\dagger$  ( $n_i$ ) is the Fermion creation (annihilation) operator for site  $i$ ,  $i=1, 2$ .  $\hbar\epsilon_1$  ( $\hbar\epsilon_2$ ) is the electronic excitation energy for site 1 (2), and  $\hbar J$  is the static intermolecular interaction which may, for example, arise from dipole-dipole coupling. For convenience we choose  $J$  real and positive.  $H'$  couples the two level systems to bath variables, and  $H_b$  is the bath Hamiltonian.

In what follows we assume that inhomogeneities are manifest only in the site energies and not in  $J$ . Furthermore, we assume that this inhomogeneity is spatially slowly varying (as might result from crystal strain) so that two impurities that are close enough to be considered a dimer have nearly the same bare energy:

$$\epsilon_1 \approx \epsilon_2 \equiv \epsilon. \quad (3.4)$$

Equation (3.4) is further defined by the requirements that  $(\epsilon_1 - \epsilon_2)t_i \ll 1$ , and that  $(\epsilon_1 - \epsilon_2) \ll J$ . The assumption of Eq. (3.4) leads to a modulation of the echo decay, while other assumptions do not. Thus, we invoke Eq. (3.4) since it is precisely this modulation (which when averaged over dimer separations leads to a decay) that is suggested to be responsible<sup>17</sup> for the concentration dependent dephasing in mixed molecular crystals.

To make the connection with Sec. II and to derive relaxation behavior it is necessary to transform to a basis where  $H_0$  is diagonal. The four eigenstates (in increasing energy) are  $|0\rangle$ ,  $|1\rangle$ ,  $|2\rangle$ , and  $|3\rangle$ , where  $|0\rangle$  is the ground state,  $|3\rangle$  is the doubly excited state, and  $|1\rangle$  and  $|2\rangle$  are the (delocalized) singly excited states.  $H_0$  can be written in the form of Eq. (2.2) with

$$\omega_1 = \epsilon - J, \quad (3.5)$$

$$\omega_2 = \epsilon + J, \quad (3.6)$$

$$\omega_3 = 2\epsilon, \quad (3.7)$$

and the dipole moment matrix elements of Eq. (2.4) are given by

$$\mu_{01} = -\mu_{13} = (1/\sqrt{2})(\mu_1 - \mu_2), \quad (3.8)$$

$$\mu_{02} = \mu_{23} = (1/\sqrt{2})(\mu_1 + \mu_2). \quad (3.9)$$

Since only  $\epsilon$  is inhomogeneously broadened, we write (assuming resonance)

$$\epsilon = \Omega + \delta. \quad (3.10)$$

It is clear then that Eqs. (3.5)–(3.7) satisfy the broadening assumption (2.30).

We are interested in deriving the equation of motion (2.5) for the reduced density operator  $\sigma$ . The approach we take here is to assume that  $H'$  is weak and use Redfield theory. For a phonon bath, for example, the usual separation of time scales required by the theory is valid since at low temperatures phonon correlation times are on the order of tens of psec, while echo decays are on the order of nsec. It is known that when the excitation-phonon coupling is not weak, the excitation must be dressed with phonons using a canonical transformation before perturbation theory may be used.<sup>21–23</sup> Here, how-

ever, we ignore this complication since we are primarily interested in deriving a consistent set of model equations for the matrix elements of  $\sigma$ .

We start with the equation of motion for the full (dimer and bath) density operator  $\rho$ :

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho]. \quad (3.11)$$

Using the perturbation formalism of Redfield<sup>24,25</sup> or the projection operator formalism of Hynes and Deutch,<sup>26</sup> we obtain the equation of motion for the reduced density operator

$$\frac{\partial \sigma}{\partial t} = -\frac{i}{\hbar}[H_0, \sigma] - R\sigma, \quad (3.12)$$

where

$$\sigma = \text{Tr}_b[\rho], \quad (3.13)$$

$$R_{kilmn} = \frac{1}{\hbar^2} \int_0^\infty d\tau \left[ \delta_{in} \sum_j \langle H'_{kj}(\tau) H'_{jm} \rangle_b \exp(-i\omega_{jm}\tau) + \delta_{km} \sum_j \langle H'_{nj} H'_{ji}(\tau) \rangle_b \exp(-i\omega_{nj}\tau) - \langle H'_{ni}(\tau) H'_{km} \rangle_b \times \exp(-i\omega_{km}\tau) - \langle H'_{ni} H'_{km}(\tau) \rangle_b \exp(-i\omega_{ni}\tau) \right], \quad (3.14)$$

$$H'_{ki}(\tau) = \exp(iH_b\tau/\hbar) H'_{ki} \exp(-iH_b\tau/\hbar), \quad (3.15)$$

$$\langle \dots \rangle_b = \{ \text{Tr}_b[\exp(-\beta H_b)] \}^{-1} \text{Tr}_b[\exp(-\beta H_b) \dots], \quad (3.16)$$

$$\beta = 1/k_B T, \quad (3.17)$$

and

$$\omega_{ki} = \omega_k - \omega_i. \quad (3.18)$$

In writing this equation we have assumed that

$$\langle H' \rangle_b = 0. \quad (3.19)$$

Using the fact that

$$\int_0^\infty e^{i\omega\tau} d\tau = iP \frac{1}{\omega} + \pi\delta(\omega), \quad (3.20)$$

one can show that<sup>24–27</sup>

$$R_{kilmn} = \delta_{in} \sum_j \gamma_{jkjm}(\omega_{mj}) + \delta_{km} \sum_j \gamma_{jijn}^*(\omega_{nj}) - \gamma_{inkm}(\omega_{mk}) - \gamma_{kmin}^*(\omega_{ni}), \quad (3.21)$$

where

$$\gamma_{kilmn}(\omega) = c_{kilmn}(\omega) + i d_{kilmn}(\omega), \quad (3.22)$$

$$d_{kilmn}(\omega) = \frac{P}{\pi} \int_{-\infty}^\infty d\omega' \frac{c_{kilmn}(\omega')}{\omega - \omega'}, \quad (3.23)$$

$$c_{kilmn}(\omega) = \frac{1}{2\hbar^2} \int_{-\infty}^\infty dt e^{i\omega t} \langle H'_{ki}^\dagger(\tau) H'_{mn} \rangle_b. \quad (3.24)$$

The Hermiticity of the Hamiltonian dictates that

$$H'_{ki}^\dagger = H'_{ik}. \quad (3.25)$$

If the frequencies of the level splittings are all larger than the matrix elements of  $R$ , we only get effective relaxation<sup>24</sup> if  $\omega_k - \omega_i - \omega_m + \omega_n = 0$ . Therefore, if

$$\omega_k - \omega_i - \omega_m + \omega_n \neq 0, \quad R_{kilmn} \equiv 0. \quad (3.26)$$

Furthermore, if we are interested in relaxation rather than energy shifts, we can neglect the imaginary part of  $R_{k1mn}$ . Thus, for the energy level structure of Eqs. (3.5)–(3.7) we find, after making use of Eq. (3.26), that

$$\operatorname{Re}(R_{k1mn}) = \delta_{km} \delta_{ln} \left[ \sum_j c_{jkj}(\omega_{kj}) + \sum_j c_{jjj}(\omega_{jj}) \right] - 2 \operatorname{Re}[c_{lnkm}(\omega_{mk})]. \quad (3.27)$$

These matrix elements can now be identified with the matrix elements of  $\Lambda$  in Eq. (2.5). Using Eqs. (2.12) and (3.26), it is easy to verify that in addition

$$\bar{\Lambda}_{k1mn} = \operatorname{Re}(R_{k1mn}). \quad (3.28)$$

Equation (3.27) can be used to calculate relaxation behavior that for various terms in the perturbation Hamiltonian  $H'$  describes pure dephasing, radiative decay, or energy transfer. In fact, for a physical model of  $H'$  in the site representation these processes are not unrelated. Here, however, for illustrative purposes we only consider terms (in the eigenstate representation) that lead to energy transfer between singly excited states. This energy transfer process is analogous to  $k \rightarrow k'$  scattering in pure crystals, which is of considerable interest.<sup>13–15</sup> Thus, we consider the interaction Hamiltonian

$$H' = T|1\rangle\langle 2| + T^\dagger|2\rangle\langle 1|, \quad (3.29)$$

where  $T$  is a bath (phonon) operator. It is straightforward to show that with this choice for  $H'$ ,  $\bar{\Lambda}$  takes the form of Eq. (2.18), with

$$\lambda = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & k_{12} & -k_{21} & 0 \\ 0 & -k_{12} & k_{21} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (3.30)$$

$$\gamma = \frac{1}{2} \begin{pmatrix} 0 & k_{12} & k_{21} & 0 \\ k_{12} & 0 & k_{12} + k_{21} & k_{12} \\ k_{21} & k_{12} + k_{21} & 0 & k_{21} \\ 0 & k_{12} & k_{21} & 0 \end{pmatrix} \quad (3.31)$$

(the indices of these matrices are associated with the eigenstates in order of increasing energy), where

$$k_{21} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i2J\tau} \langle T^\dagger(\tau) T \rangle_b, \quad (3.32)$$

$$k_{12} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{-i2J\tau} \langle T(\tau) T^\dagger \rangle_b. \quad (3.33)$$

It is easily shown that these rate constants satisfy detailed balance:

$$k_{12} = \exp(-2\beta\hbar J) k_{21}. \quad (3.34)$$

#### IV. RESULTS

In this section we evaluate the general expressions of Sec. II within the model of Sec. III. For mathematical simplicity we consider the case where

$$\mu_1 = \mu_2 = \mu, \quad (4.1)$$

i. e., the  $x$  components of the site transition dipole mo-

ments for molecules 1 and 2 are equal. Therefore, from Eqs. (3.8) and (3.9) we see that in the eigenstate representation only  $\mu_{02}$  and  $\mu_{23}$  are nonzero, with the value

$$\mu_{02} = \mu_{23} = \sqrt{2} \mu. \quad (4.2)$$

With this simplification it is relatively straightforward to evaluate the matrix elements of  $V(\tau)$ . Perhaps the easiest way is with the Laplace transform. Defining

$$\hat{V}(s) = \int_0^\infty e^{-s\tau} V(\tau) d\tau, \quad (4.3)$$

we see from Eq. (2.14) that formally

$$\hat{V}(s) = (s - i\chi/2)^{-1}. \quad (4.4)$$

After inverting the matrix  $(s - i\chi/2)$ ,  $V(\tau)$  can be found from  $\hat{V}(s)$  by the inverse Laplace transform. The result is

$$V_{00}(\tau) = V_{33}(\tau) = (1/2)[1 + \cos(A)], \quad (4.5)$$

$$V_{02}(\tau) = V_{23}(\tau) = (i/\sqrt{2}) \sin(A), \quad (4.6)$$

$$V_{11}(\tau) = 1, \quad (4.7)$$

$$V_{22}(\tau) = \cos(A), \quad (4.8)$$

$$V_{03}(\tau) = (1/2)[\cos(A) - 1], \quad (4.9)$$

$$V_{01}(\tau) = V_{12}(\tau) = V_{13}(\tau) = 0, \quad (4.10)$$

$$V_{k1}(\tau) = V_{1k}(\tau), \quad (4.11)$$

where

$$A = \mu E \tau / \hbar. \quad (4.12)$$

Next we must evaluate  $\mathbf{Q}(t)$  from Eq. (2.22). To this end it is again convenient to use the Laplace transform technique; thus,

$$\hat{\mathbf{Q}}(s) = (s + \lambda)^{-1}. \quad (4.13)$$

For simplicity we will assume that  $k_B T \gg 2\hbar J$ , so that

$$k_{12} = k_{21} = k. \quad (4.14)$$

Then, with Eq. (3.30),  $\hat{\mathbf{Q}}(s)$  can be inverted to find  $\mathbf{Q}(t)$ . The nonzero matrix elements are

$$Q_{00}(t) = Q_{33}(t) = 1, \quad (4.15)$$

$$Q_{11}(t) = Q_{22}(t) = (1/2)[1 + \exp(-2kt)], \quad (4.16)$$

$$Q_{12}(t) = Q_{21}(t) = (1/2)[1 - \exp(-2kt)]. \quad (4.17)$$

#### A. Photon echo

Using the results for  $V(\tau)$  above,  $\gamma$  from Eq. (3.31) with Eq. (4.14), the energy level structure of the dimer model [Eqs. (3.5)–(3.7)], and the simplification of Eq. (4.1), the general expression for the photon echo amplitude [Eq. (2.32)] can be evaluated, with the result

$$\begin{aligned} \bar{p}(2t_1) = & -i\mu e^{-kt_1} \sin(A_1) \sin^2(A_2/2) \\ & \times (1 - \cos(A_2)) \{ [\cos(2Jt_1) - 1] + i \sin(2Jt_1) \cos(A_1) \} \end{aligned} \quad (4.18)$$

[ $A_i = \mu E \tau_i / \hbar$  is in Eq. (4.12)]. As a check of this result, we note that in the limit  $J \rightarrow 0$ ,  $k \rightarrow 0$ , we obtain

$$\bar{p}(2t_1) = -i\mu \sin(A_1) \sin^2(A_2/2), \quad (4.19)$$

which is the correct result for two isolated monomers,

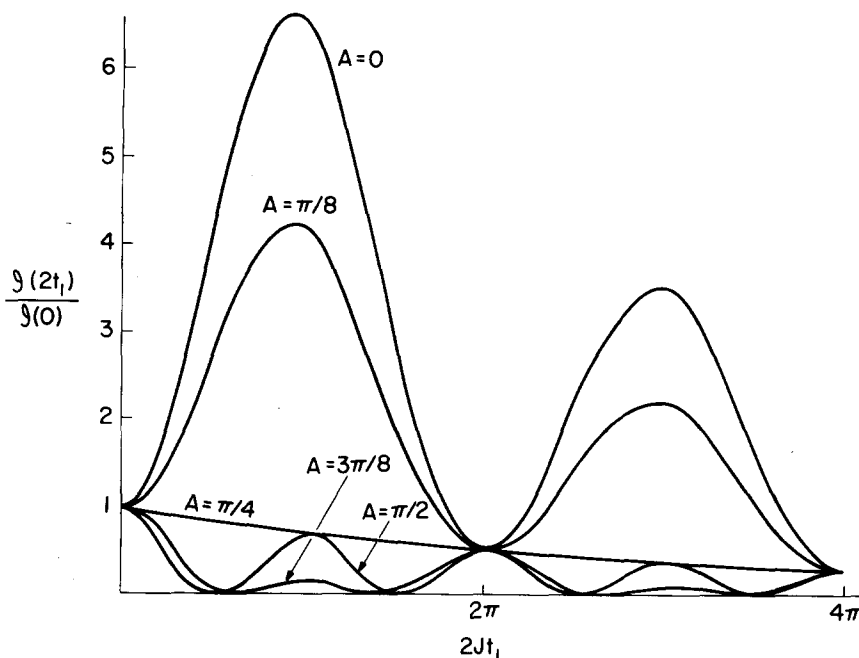


FIG. 2. The photon echo intensity as a function of pulse separation  $t_1$  for various values of the pulse area  $A$ .

as is to be expected in the absence of interaction.

The intensity of the photon echo signal is, from Eq. (2.27),

$$g(2t_1) = g(0) e^{-2kt_1} (\sin^2(2Jt_1) \cos^2(A_1) \cos^2(A_2) + [1 - \cos(A_2)] [\cos(2Jt_1) - 1]^2). \quad (4.20)$$

In Fig. 2 we have plotted  $g(2t_1)/g(0)$  against  $t_1$ , the pulse separation, assuming for the pulse areas  $A_i$  that  $A_1 = A_2/2 = A$ . We consider various values of  $A$ , and take  $k/J = 0.1$ . In the usual situation where  $A = \pi/2$ , the signal is simply a damped oscillation with a maximum value at  $t_1 = 0$ . The oscillation arises from the difference of the energy splitting between  $|0\rangle$  and  $|2\rangle$ , and that between  $|2\rangle$  and  $|3\rangle$ , while the damping is a result of energy transfer. When  $A = \pi/4$ , the beats disappear and the signal decays exponentially. When  $A < \pi/4$ , the signal actually grows from its initial value but as before shows characteristic damped oscillations. This becomes more dramatic as  $A$  decreases. The curve marked  $A = 0$  represents the limit  $A = \mu E \tau / \hbar \ll 1$ , but with the conditions [see assumption (iv) in Sec. II] that  $\mu E / \hbar \gg \delta, J$ . Thus, it is the short pulse limit.

The unusual power dependence that is shown in Fig. 2 is not predicted by theories that only include a manifold of *singly* excited levels,<sup>2-4</sup> and thus is a result of the doubly excited level  $|3\rangle$ . It is interesting that even in the small  $A$  limit the existence of  $|3\rangle$  is crucial in the determination of the echo characteristics. Indeed, in the special case that we have been considering of  $\mu_1 = \mu_2$ , if the presence of  $|3\rangle$  is neglected, there is only one nonzero matrix element of the transition dipole operator and hence there would be no beats at all! Physically, this is not unreasonable since *both* excitation pulses are necessary for the echo signal. Although the first pulse may be less successful in populating  $|3\rangle$  than  $|2\rangle$ , the second pulse can populate  $|3\rangle$  directly from existing population in  $|2\rangle$ . This is a manifestation of one of the differences between nonlinear pulsed experiments and low power absorption experiments. Other differences are discussed elsewhere.<sup>2</sup>

## B. Stimulated echo

To evaluate the general expression for the stimulated echo [Eq. (2.35)] in addition to the results specified in Sec. IVA, we need the expression for  $\mathbf{Q}(t)$  from Eqs. (4.15)–(4.17). The final expression is

$$\bar{p}(2t_1 + t_2) = (-i\mu/4) e^{-kt_1} \sin(A_1) \sin(A_2) \sin(A_3) \{1 + B(t_2) + [1 - B(t_2)] [\cos(2Jt_1) + i \sin(2Jt_1) \cos(A_1)]\}, \quad (4.21)$$

$$B(t_2) = (2 + e^{-2kt_2}) \cos(A_2) \cos(A_3). \quad (4.22)$$

In the limit  $k, J \rightarrow 0$  we obtain

$$\bar{p}(2t_1 + t_2) = (-i\mu/2) \sin(A_1) \sin(A_2) \sin(A_3), \quad (4.23)$$

which is just the stimulated echo result for two monomers.

The echo intensity as a function of the pulse separation  $t_2$  is [from Eq. (2.27)]

$$\frac{g(2t_1 + t_2)}{g(2t_1)} = \frac{C(t_1, t_2)}{C(t_1, 0)}, \quad (4.24)$$

$$C(t_1, t_2) = 4 \cos^2(Jt_1) + \sin^2(2Jt_1)[\cos^2(A_1) - 1] + 2B(t_2) \sin^2(2Jt_1)[1 - \cos^2(A_1)] + [B(t_2)]^2[4 \sin^2(Jt_1) + \sin^2(2Jt_1)[\cos^2(A_1) - 1]] \quad (4.25)$$

In Fig. 3 we plot the intensity as a function of  $t_2$ . We illustrate the effect of power (assuming  $A_1 = A_2 = A_3 = A$ ) and initial pulse separation  $t_1$  on the stimulated echo decay, which in general is nonexponential. It is interesting that in contrast to the photon echo intensity, there are no beats in the stimulated echo decay. We emphasize that this is *not* a general feature of the stimulated echo but only a result of the simplification  $\mu_1 = \mu_2$  that we have used in this section. In general, the four level nature of the problem will result in beats in the stimulated echo [see Eq. (2.35)].

## V. DISCUSSION

The theory we have presented is for a pair of weakly coupled impurities in a molecular crystal. Although no echo experiments have yet been performed on such systems, it is possible to make mixed molecular crystals in which the impurities are well defined molecular dimers.<sup>29,30</sup> This theory will apply directly to understanding experiments on these systems. Furthermore, this theory is valuable as a qualitative guide in understanding recent photon echo and stimulated photon echo experiments in mixed molecular crystals<sup>16,17</sup> and can be viewed as a first step in describing coherent transients from a pure crystal.

In the echo experiments on mixed crystals by Cooper *et al.*<sup>16</sup> and Morsink *et al.*,<sup>17</sup> the excitation lasers were tuned to the zero phonon line of the impurity molecules. Both groups found a photon echo decay whose rate increased with increasing impurity concentration, but observed a stimulated echo decay that was concentration independent. Cooper *et al.*<sup>16</sup> suggested that phonon modulated dipole-dipole interactions were responsible for the enhanced dephasing. In a complete photon echo the-

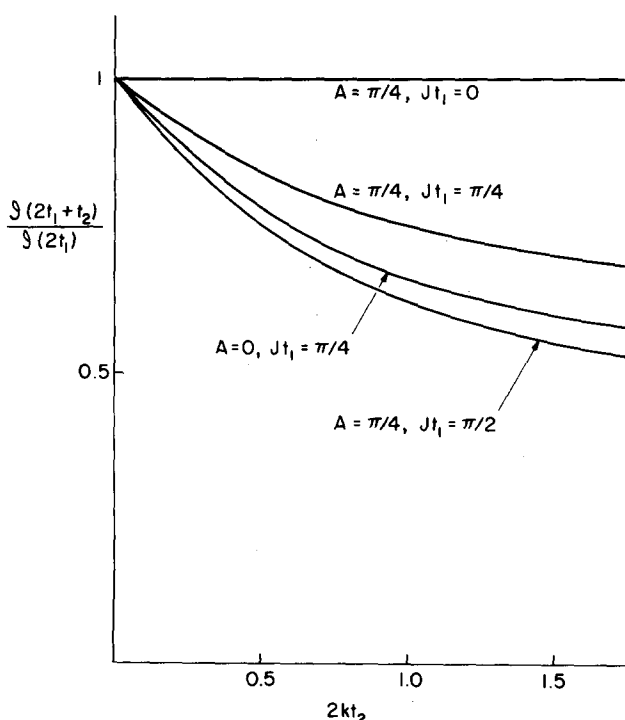


FIG. 3. The stimulated photon echo intensity as a function of pulse separation  $t_2$  for various values of the pulse separation  $t_1$  and the pulse area  $A$ .

ory, static dipole-dipole interactions should also be taken into account. Morsink *et al.*<sup>17</sup> proposed a model based on these static interactions, but appear to neglect the effect of multiple excitations in the impurity band. The present dimer theory provides a rigorous understanding of the photon echo from a pair of interacting systems. Qualitative conclusions from this theory, which are discussed below, raise several important issues relating to the intermolecular interaction interpretation of the experiments described above.

In the dimer model, static intermolecular interactions produce a splitting of  $2\hbar J$  between  $|1\rangle$  and  $|2\rangle$ . From a theoretical perspective, one of the important points of this work is that even for small pulse areas the doubly excited level  $|3\rangle$  must be included in a proper treatment. In addition, the following observations from our results are relevant for discussing the mixed crystal system: (i) In general, the splitting causes oscillatory modulations in both the photon and stimulated echo intensities. (ii) Modulations occur only if the molecules are nearly degenerate in the absence of the interaction  $J$  (see the discussion in Sec. III). (iii) The precise form of the echo time dependence is very power dependent.

To make the qualitative connection to the disordered mixed crystal situation we argue as follows: at a suitably low concentration most of the impurities will behave as isolated monomers. There will be some pairs of molecules that interact quite strongly; at least for short times they will behave as isolated dimers. Averaging the photon and stimulated echo results for dimers with different separations (and hence different  $J$ ) would then give a qualitative picture of the concentration dependence of the experimental observables from disordered crystals at low concentrations and short times. Such an average of the modulations caused by the energy level splittings would result in a smoothed out time dependence. However, as we observed for a simple dimer; (i) the stimulated echo as well as the photon echo should show some time dependence resulting from the averaged splittings; (ii) only interacting molecules with nearly the same bare energies would cause this time dependence in either experiment; and (iii) the time dependence should be very power dependent. Inasmuch as (i) contradicts the experimental results of both groups, and (ii) places a severe restriction on the spatial correlation of bare energies, it seems to us unlikely that static dipole-dipole interactions are the cause of the anomalous dephasing observed in these experiments.

Cooper *et al.*<sup>16</sup> consider a model that involves phonon modulated intermolecular interaction. In our language this corresponds to an off-diagonal perturbation  $H'$  in the site representation. In the eigenstate representation

this perturbation would in general be both diagonal and off diagonal, but when  $\epsilon_1 = \epsilon_2$  it is strictly diagonal and thus would cause pure dephasing. Although we have provided expressions for a general perturbation Hamiltonian  $H'$  in Sec. III, we gave explicit results only for the off-diagonal terms of  $H'$  (in the eigenstate representation) that lead to energy transfer. Therefore, our results do not follow directly from the model of Cooper *et al.*<sup>16</sup> However, a few general remarks about phonon modulated interactions are appropriate. Pure dephasing rates are equal to zero frequency Fourier transforms of correlation functions of the phonon variables that couple diagonally to the excitation (see Sec. III). From theoretical models<sup>27,28</sup> we would expect the dephasing rate to be very temperature dependent at low temperatures and to vanish at  $T=0$  K. On the other hand, as we have seen in Sec. III, energy transfer rates are expressed in terms of Fourier transforms of correlation functions of phonon variables, evaluated at a nonzero frequency of  $2J$ . However, for the experimental systems under consideration the inequality  $2\hbar J \ll k_B T \ll \hbar\omega_D$  ( $\omega_D$  is the Debye frequency) is valid; in other words,  $2J$  is small compared with the reciprocal of the characteristic phonon time scales. Thus, the Fourier transform evaluated at frequency  $2J$  is essentially equal to the zero frequency value, which as we have seen is very temperature dependent. In fact, the photon echo decay of the experiments by Cooper *et al.*<sup>16</sup> is temperature independent,<sup>31</sup> and so it seems unlikely that phonon modulated intermolecular interactions are involved in dephasing in these experiments.

This work suggests that both the static<sup>17</sup> and phonon modulated<sup>16</sup> dipole-dipole mechanisms are incapable of explaining the concentration dependent echo decays. Recent experiments<sup>31</sup> by the Fayer group imply that the apparent concentration dependence is actually an optical density effect arising from the optically thick samples used in the experiments. An understanding of these optical density effects coupled with insight obtained from the present theoretical treatment will facilitate the observation and analysis of the effects of true intermolecular interactions on photon echoes in molecular crystals.

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