UNIFIED THEORY OF PHOTON ECHOES: THE PASSAGE FROM INHOMOGENEOUS TO HOMOGENEOUS LINE BROADENING

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We calculate the temporal profile of the photon echo signal from a collection of non-interacting two-level systems, whose frequencies undergo Gaussian random modulations. The model is exactly solvable and interpolates continuously between the inhomogeneous broadening limit in which a well-defined echo signal exists and the homogeneous broadening limit in which it is no longer present. The implications for the problem of concentration-dependent dephasing in mixed molecular crystals are discussed.

1. Introduction

The photon echo experiment has become an important tool in elucidating the excited-state dynamics of isolated impurities [1] and strongly coupled impurity dimers [2] in mixed molecular crystals. Currently, there is an interest in applying this technique to the study of more concentrated impurity systems. The problem of calculating the photon echo signal from a mixed crystal for impurity concentrations at which interactions among the impurities are significant, poses a formidable theoretical challenge. The echo experiment probes the effects of a sequence of strong laser pulses on a material characterized by both spatial and energetic disorder. Considerable progress has been made recently in the understanding of the information content of the photon echo signal from interacting impurities [3–5]. These treatments indicate that the photon echo signal is very sensitive to the presence of interactions among the impurities. The behavior of the signal is well understood in two limiting cases: low impurity concentration or short time [3–5] and arbitrary concentration with weak intermolecular interactions [4].

Although the behavior of the echo signal for high impurity concentrations and strong interactions is not completely understood, one can make qualitative predictions regarding the effect of strong interactions among the impurities on the echo signal. In the limit of low impurity concentration, the impurity absorption spectrum is inhomogeneously broadened due to the static distribution of impurity transition energies. In this case, the photon echo pulse sequence will produce a well-defined echo signal. In the limit of high concentrations and strong interactions, we expect the impurity absorption spectrum to be motionally narrowed, and hence, no longer to be completely inhomogeneously broadened [6]. For the extreme case, in which the intermolecular interactions dominate the static transition energy distribution, the absorption line is homogeneously broadened, and we would not expect to detect an echo signal. Thus, the progression from low to high impurity concentration implies a transition from inhomogeneous to homogeneous broadening of the impurity absorption spectrum.

In this Letter, we calculate the photon echo signal from a collection of non-interacting two-level systems whose transition energies are modulated by a Gaussian stochastic process. The absorption lineshape of this system has been calculated by Kubo [7] and forms the basis of the unified theory of spectral lineshapes in single- and multi-photon processes [8]. This simple model, which is exactly solvable, is very useful, since

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by varying a single parameter one may interpolate between an inhomogeneously broadened Gaussian lineshape and a homogeneously broadened Lorentzian line. We show that the temporal profile of the echo signal can be calculated exactly for this model. Our calculation provides a qualitative insight into the complex problem of interacting impurities in which the line broadening can also be homogeneous, inhomogeneous, or between these two limits.

2. The model

Consider N two-level systems randomly distributed in a volume V, interacting with a laser pulse. The system is characterized by the Hamiltonian

$$H = H_0 + H_1 , \tag{1a}$$

$$H_0 = \hbar \sum_{j=1}^{N} a_j^{\dagger} a_j [\Omega + \Delta_j(t)] , \tag{1b}$$

$$H_1 = -\sum_j \boldsymbol{\mu}_j \cdot \boldsymbol{E}(t) \cos(\Omega t - \boldsymbol{k}\cdot\boldsymbol{r}_j) . \tag{1c}$$

$\boldsymbol{\mu}_j$ is the transition dipole operator for the jth two-level system. $\boldsymbol{E}(t)$ is the amplitude, Ω is the frequency, and $\boldsymbol{k}$ is the wavevector of the applied electric field. In what follows, we will assume that all of the molecular transition dipoles are oriented parallel to $\boldsymbol{E}(t)$. $\Delta_j(t)$, the modulation of the transition energy of the jth site is a Gaussian stochastic variable obeying [6,7]

$$\langle \Delta_j(t) \rangle = 0 , \tag{2}$$

$$\langle \Delta_j(t_1) \Delta_m(t_2) \rangle = \delta_{jm} D^2 \exp(-\Lambda |t_2 - t_1|) \tag{3}$$

D represents the magnitude of the frequency modulation, and Λ is its inverse timescale. The dimensionless parameter $\kappa = \Lambda/D$ determines the nature of the absorption lineshape. In the limit of $\kappa \ll 1$, the line is inhomogeneously broadened, and in the limit of $\kappa \gg 1$, the line is homogeneously broadened [7].

In a photon echo experiment, the sample is irradiated with a pulse of duration t_{I}, allowed to evolve in the absence of radiation for a time t_1, and then irradiated with a second pulse of duration t_{II}. A sample with an inhomogeneously broadened absorption line then emits a pulse (the echo), whose temporal profile is peaked at time $2t_1$, and whose wavevector is $2\boldsymbol{k}_{\mathrm{II}} - \boldsymbol{k}_{\mathrm{I}}$, where $\boldsymbol{k}_{\mathrm{I}}$ and $\boldsymbol{k}_{\mathrm{II}}$ are the wavevectors of the first and second pulses, respectively [1]. To obtain the echo signal for the present model, we first calculate the macroscopic electric polarization for a given configuration of the system. A configuration average of this quantity then yields a macroscopic polarization that can be substituted into Maxwell's equations to obtain the echo signal. Within the "slowly varying envelope" approximation, valid for optically thin samples [9,10], the signal is proportional to the square of the polarization.

The configuration averaged electric polarization is related to the system's density matrix ρ by

$$P(r,t) = \langle \Sigma_j \mathrm{Tr}(\boldsymbol{\mu}_j \rho) \delta(r - r_j) \rangle . \tag{4}$$

where the angular brackets denote an average over the fluctuating site energies and the positions of all molecules. It is convenient to define $\tilde{P}(r,t)$, the slowly varying part of the polarization by

$$P(r,t) = \tilde{P}(r,t) \exp(-i\Omega t) + \mathrm{c.c.} \tag{5}$$

This quantity is related to $\tilde{\rho}$, the density matrix in a reference frame that is rotating with the angular frequency of the radiation [3,11], by

$$\tilde{P}(r,t) = \langle \Sigma_j \mathrm{Tr}(\boldsymbol{\mu}_j' \tilde{\rho}) \delta(r - r_j) \rangle \tag{6}$$

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

$$\boldsymbol{\mu}_j' = \boldsymbol{\mu} a_j , \tag{7}$$

where a_j is the excitation annihilation operator of eq. (1) and $\boldsymbol{\mu}$ is the magnitude of the molecular transition dipole. It can easily be shown from eq. (5) that the echo signal will be proportional to the absolute square of $\tilde{P}$.

Since the present model does not include interactions among the impurities, and every molecule is assumed to be initially in the ground state, the many-body density matrix in eq. (4) or eq. (6) factors into a product of one-body density matrices, so we need only calculate the density matrix of a single two-level system after the photon echo pulse sequence. We will make the following approximations. Our calculation of the density matrix is carried out in the rotating wave approximation [9,11]. We assume that the echo experiment is carried out with square pulses. ($\boldsymbol{E}(t)$ in eq. (1) does not vary in time while the pulse is on.) We also assume that the pulses are sufficiently short

and intense that we may calculate the time evolution of the system while a pulse is on, using only H_1 in eq. (1) and neglecting H_0 [11]. Under these conditions, $\tilde{\rho}$ in eq. (6) is given by

$$\tilde{\rho}(t) = G_0(t,t_1)G_1(t_{II})G_0(t_1,0)G_1(t_I)\tilde{\rho}(0) . \quad (8)$$

$G_0(t,t')$ is the tetradic time evolution operator (superoperator) in the rotating frame for the system in the absence of the laser field [11]. $G_1(t)$ is the tetradic time evolution operator in the rotating frame in the presence of the field [11]. Eqs (6) and (8) imply that calculating the echo signal in the short, intense pulse limit involves calculating the average of a product of two G_0 propagators, unlike the ordinary absorption lineshape which requires the average of a single G_0.

3. Results and discussion

Within the approximations of the previous section, the component of the macroscopic polarization in the rotating frame with wavevector $2k_{II} - k_I$ at a time $t > t_1$ is

$$\tilde{P}(2k_{II} - k_I, t) = -\tfrac{1}{2} ic\mu \sin(A_1)\sin^2(A_2/2)R(t,t_1) . \quad (9)$$

A_j is the area of the jth pulse, defined by

$$A_j = \mu E t_j/\hbar . \quad (10)$$

t_j is the duration of the jth pulse, μ is the molecular transition dipole moment, and E is the electric field amplitude. c is the number density of impurities $R(t,t_1)$, the temporal profile of the echo polarization is given by

$$R(t,t_1) = \langle \exp\{-i[\textstyle\int_{t_1}^{t} d\tau \Delta(\tau) - \int_0^{t_1} d\tau \Delta(\tau)]\}\rangle \quad (11)$$

The angular brackets denote an average over the stochastic modulation process. $R(t,t_1)$ can be evaluated by performing a cumulant expansion of eq. (11). For a Gaussian process, all cumulants beyond second order vanish [6,7]. In this case, eq. (11) yields

$$R(t,t_1) = \exp[-2g(t-t_1) - 2g(t_1) + g(t)] , \quad (12a)$$

where

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \Delta(\tau_1 - \tau_2)\Delta(0)\rangle . \quad (12b)$$

Substituting eq. (3) into eqs. (12) yields

$$R(t,t_1) = \exp\{(-D^2/\Lambda^2)[\Lambda t + 2\exp(-\Lambda(t-t_1)) + 2\exp(-\Lambda t_1) - \exp(-\Lambda t) - 3]\} . \quad (13)$$

Let us examine $R(t,t_1)$ for various values of the ratio $\kappa = \Lambda/D$. In the static limit ($\kappa \ll 1$), $g(\tau) = D^2\tau^2/2$ and eq. (13) becomes

$$R(t,t_1) = \exp[(-D^2/2)(t-2t_1)^2] . \quad (14)$$

This is the temporal profile of the echo polarization from a system with Gaussian, static site energy disorder. In this limit, if we detect in the direction $2k_{II} - k_I$, there is a well-defined echo pulse centered at $t = 2t_1$. In the Markovian limit ($\kappa \gg 1$), $g(\tau) = \Gamma\tau$, and eq. (13) becomes

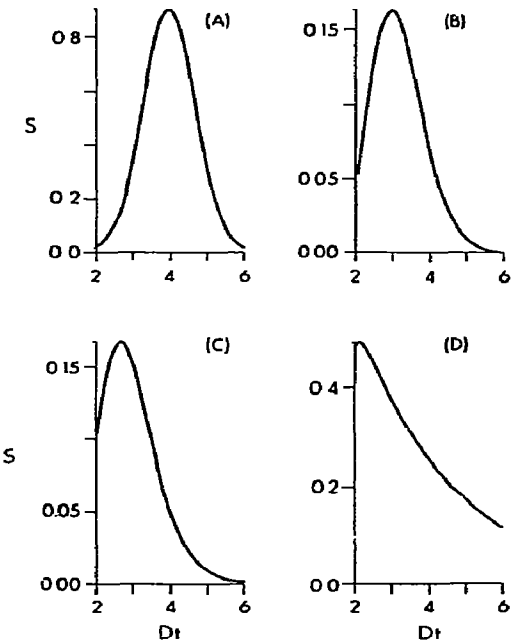

Fig. 1. The temporal profile of the photon echo signal, given by the square of eq (13) The time is scaled by D, defined in eq (3) $Dt_1 = 2$, where t_1 is the time between excitation pulses (A) $\kappa = 0.01$. (B) $\kappa = 0.5$. (C) $\kappa = 1.0$ (D) $\kappa = 5.0$. In (A), the system is close to the inhomogeneous line broadening limit, and there is an echo signal peaked at $t = 2t_1$ As κ is increased, the peak signal shifts to shorter times. In the $\kappa \to \infty$ limit, the signal decays exponentially, starting directly after the second pulse

$$R(t,t_1) = \exp(-\Gamma t)\,, \tag{15a}$$

$$\Gamma = D^2/\Lambda\,. \tag{15b}$$

In this limit, if we detect in the echo direction, we find an exponentially decaying signal that begins immediately after the second pulse. The echo no longer exists, in the sense that there is no longer a signal peaked at $t = 2t_1$. From eq. (13), we can calculate t^*, the time at which the echo signal attains it maximum value for fixed t_1.

$$\Lambda t^* = \ln[2\exp(\Lambda t_1) - 1]\,. \tag{16}$$

In the static ($\kappa \ll 1$) limit, eq. (16) gives the expected result, $t^* = 2t_1$. In the Markovian ($\kappa \gg 1$) limit, it gives $t^* = t_1$. As κ is increased from zero, the peak of the temporal profile of the echo pulse begins to move to shorter times. This behavior is illustrated in fig. 1, in which the echo profile (the square of eq. (13)) is plotted for $Dt_1 = 2$ and $\kappa = 0.01, 0.5, 1$ and 5. Fig. 1 illustrates the manner in which the well-defined temporal profile that characterizes the photon echo signal is lost as we progress from a system with an inhomogeneously broadened absorption spectrum to a system with a motionally narrowed, homogeneously broadened absorption spectrum. This simple model thus provides insight into the far more complicated problem of a photon echo from strongly interacting impurities. As the impurity concentration is raised, and interactions become important, the system passes from the case in which there is an inhomogeneous linewidth from static site energy disorder to the case in which the absorption spectrum is motionally narrowed. We expect the temporal profile of the echo signal to behave in a way that is qualitatively similar to that shown in fig. 1.

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