

Theory of the phonon perturbed photon echo experiment: Direct determination of electronic excitation-phonon coupling

William L. Wilson,^{a)} G. Wäckerle,^{b)} and M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305

(Received 11 September 1986; accepted 18 August 1987)

A theory is presented describing the proposed phonon perturbed photon echo experiment. This experiment is a combination of picosecond time scale stimulated Raman pumping and photon echo experiments. The theory demonstrates that the phonon perturbed photon echo can directly measure electronic excitation-phonon coupling matrix elements by observing the influence of a well defined coherent phonon wave on the photon echo signal. The theory predicts that the echo pulse area (integrated intensity) is reduced. The size of this change is related to the strength of the excitation phonon coupling. In addition, a realistic estimate is made of the size of the effect, and it is shown that the experiment is feasible with available laser equipment.

I. INTRODUCTION

The interaction of the electronic degrees of freedom of an isolated impurity with the mechanical degrees of freedom (i.e., vibrations) of the host environment has been the subject of many experimental and theoretical studies. The coupling of impurity electronic states and bulk phonon states (the excitation-phonon coupling, EPC) besides its intrinsic interest has drawn considerable attention because it is directly involved in effects such as energy transfer between impurities in concentrated crystals,¹ exciton scattering in pure crystals,^{2(a),2(b)} photochemistry in proteins,³ and electron transfer.⁴

For isolated impurities (no impurity-impurity interactions) the EPC manifests itself in several ways. By producing a nonzero transition moment for simultaneous electron and acoustic phonon transitions, EPC leads to the appearance of phonon sidebands in optical absorption and emission spectra.^{5(a)} Phonon sideband spectra have been analyzed in detail for favorable systems to yield the integrated coupling strength of an optical excitation to the acoustic phonon branches. In addition to the phonon sidebands, generally a narrow purely electronic transition [the zero-phonon line (ZPL)] is observed in absorption and emission spectra. The ZPL is shifted and broadened by EPC. In principle, the broadening and shift of this ZPL can be measured directly from absorption and emission spectra.^{5(b)} At low temperatures, however, the homogeneous linewidth is very narrow and inhomogeneous broadening prevents extraction of the homogeneous linewidth from optical spectra. In this case, one can use photon echo,⁶⁻⁸ hole burning,⁹ and fluorescence line narrowing¹⁰ techniques, which are capable, in some instances, of measuring the homogeneous linewidth in spite of dominant inhomogeneous broadening.

A number of authors have extensively investigated the temperature dependence of the broadening and shift of the ZPL.¹¹⁻¹⁵ Theoretically, quadratic coupling of a guest mole-

cule to acoustic phonons in the Debye approximation results in a low temperature linewidth which is proportional to T^7 .¹¹ Quadratic EPC to optical phonons or guest librations yield exponential and biexponential activation laws, respectively.¹⁶ Linear EPC does not lead to line broadening at any temperature for harmonic phonons.¹⁷

Experimental observation of one particular coupling mechanism is only possible in rare cases.¹³ In general, at a given temperature many phonon modes are thermally populated and contribute to the broadening of the ZPL. This hampers an unambiguous interpretation of the experimental data. The problem is that the guest electronic states are coupled to many phonon branches each having a complex three-dimensional density of states. In the best circumstances, a particular bulk mechanical degree of freedom can dominate the temperature dependent dephasing at low temperature. If this is the case it may be possible to extract EPC matrix elements which are averaged over all directions and magnitudes of the phonon wave vector. Therefore, information on the directional anisotropy of the coupling is lost, and it is not possible to examine the influence of other mechanical degrees of freedom on the impurity electronic states.

In this paper we propose a new method for studying the EPC of isolated impurities in condensed matter systems. The approach circumvents the nonselective thermal excitation of phonons and excites a particular phonon by a stimulated Raman process¹⁸ at low temperature where the thermal population of phonons is negligible. The effect of the selective phonon excitation is then monitored with a photon echo pulse sequence. The phonon excitation is produced by two short time coincident laser pulses of different frequencies crossed in the sample. The phonon of interest is excited by tuning the difference of the laser frequencies to the phonon frequency ($\omega_1 - \omega_2 = \omega_{ph}$) and obeying symmetry selection rules and wave vector matching conditions. The phonon excited in this way is a coherent wave with well-defined phase and in this sense contrasts with thermally excited phonons. Shortly after this phonon excitation step the system is probed by a regular photon echo sequence. It will be shown that the effect of EPC on the photon echo can be observed by detecting the integrated echo intensity.

^{a)} Permanent address: AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.

^{b)} Present address: 2. Physikalisches Institut der Universität Stuttgart, 7 Stuttgart 80/Pfaffenwaldring 57, Federal Republic of Germany.

The proposed phonon-perturbed photon echo (P³E) experiment closely parallels a magnetic resonance^{19(a),19(b)} experiment in which the external field is modulated. In the optical experiment (in the limit of high phonon occupation), the phonon wave modulates the optical transition frequency of the impurity by EPC, producing frequency sidebands on the homogeneous absorption line analogous with the NMR result. However, unlike the NMR case, the size of the sample in the optical experiment is large compared to the phonon wavelength, and therefore it is necessary to average over all phases of the modulation.

The influence of the phonon on the photon echo is distinctly different from the normal homogeneous dephasing measured in a conventional photon echo experiment.⁶ In a conventional echo experiment, random fluctuations in molecular site energies produced by thermally excited phonons, which span a wide range of frequencies and are generated with random phases, destroy the phase relationships among the electronic coherent superposition states. The decay of the echo signal as the time between the two echo excitation pulses is increased, measures the time dependent decay of the electronic excited state phase. For a two level system, the echo measures the decay of the off diagonal matrix elements of the reduced density matrix which describes the electronic states. The echo decay is the Fourier transform of the homogeneous electronic absorption line.

In the P³E experiment, a single phonon wave with well defined wave vector, frequency and phase is generated. This does not cause homogeneous dephasing, i.e., it does not result in an irreversible loss of the phase relationships among the electronic superposition states. Rather, EPC causes the transition frequency of each isochromat to oscillate instead of randomly fluctuate. In the absence of phonon coupling, the precession frequency of a single molecule's electronic superposition state is a constant. Coupling to the single phonon wave causes this precession frequency to oscillate. The oscillation of the precession frequencies of all the superposition states results in a reduction of the area of the photon echo. In the absence of phonon damping, *this reduction is independent of the pulse separation in the echo pulse sequence.* This effect is not conventional phonon induced dephasing.

The change in the echo signal pulse area is directly related to the amplitude of the phonon wave and the excitation-phonon coupling matrix element. Since the phonon amplitude can be determined by coherent anti-Stokes Raman scattering (CARS)²⁰ or other methods, the EPC matrix element can be determined. By generating the phonon with various propagation directions, directional anisotropy in the EPC can be mapped out. Tuning the frequency difference of the pulses used for the stimulated Raman process in resonance with different phonon modes, permits EPC to a variety of phonons to be independently investigated.

The P³E experiment described below should be practical experimentally. Both coherent Raman and photon echo techniques have evolved to standard methods in the research of dynamical processes in the solid state. The P³E experiment is essentially a combination of photon echo and stimulated Raman experiments. Detailed estimates of the size of

the P³E effect show that readily available laser equipment can be used to produce sizable signals.

This paper is organized as follows: In Sec. II we give the general theoretical model for an optical two-level system that is coupled to a single phonon mode. The general expression for the evolution of the density matrix for an echo pulse sequence is given. In Sec. III we employ a semiclassical description that treats the phonon as a classical wave. The P³E observable is calculated in Sec. IV. Relaxation of both the electronic and phonon system is added phenomenologically. It is demonstrated how EPC constants can be extracted from the P³E observable. Before we conclude (Sec. IV), we give an order of magnitude estimate of the size of the P³E effect for an impurity coupled to a typical phonon in a molecular crystal using optical parameters for common picosecond laser equipment.

II. THEORETICAL MODEL

Consider an ensemble of atoms or molecules in which the electronic states of interest can be described as a two-level system. The molecules are embedded in a host lattice in very low concentration and at very low temperature. The molecules are near resonance with a laser field of frequency Ω . The density of impurities is such that impurity-impurity interactions are negligible. The two-level system (ground state $\equiv |0\rangle$, excited state $\equiv |1\rangle$) interacts with a single coherent phonon mode of a particular wave vector which can be created via a picosecond stimulated Raman process. At the temperature of the experiment, thermal populations of this and other phonon modes are negligible and we will initially ignore the lifetime and dephasing of the phonon wave. This system can be described by the following Hamiltonian:

$$H = H_0 + H_p + H_{E-p} + H_{\text{int}}, \quad (2.1a)$$

$$H_0 = \hbar\omega a^\dagger a, \quad (2.1b)$$

$$H_p = \hbar\omega_{\text{ph}}(b^\dagger b + 1/2), \quad (2.1c)$$

$$H_{E-p} = [\hbar g_l(b^\dagger + b) + \hbar g_g(b^\dagger + b)^2] a^\dagger a, \quad (2.1d)$$

$$H_{\text{int}} = \hat{\mu}(a^\dagger + a) \frac{E(t)}{2} \{ \exp[i(\Omega t - \mathbf{k}\cdot\mathbf{r})] + \text{c.c.} \}. \quad (2.1e)$$

$\hbar\omega$ is the energy of electronically excited state $|1\rangle$. The zero of energy is the energy of the ground state, $|0\rangle$. $\hbar\omega_p$ is the phonon energy. $a^\dagger(a)$ and $b^\dagger(b)$ are the creation (annihilation) operators for the electronic excited state and the phonon, respectively. $\hat{\mu}$ is the transition dipole for the electronic transition and $E(t)$ is the time dependent magnitude of the electric field of the laser beam. It is a function that describes the entire pulse envelope and varies slowly with respect to the optical frequency Ω . The EPC is included up to the quadratic term with the linear and quadratic coupling constants g_l and g_g , respectively. The dynamics of this system can be obtained utilizing the Liouville-von Neumann equation of motion for the density operator ρ ²¹:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho]. \quad (2.2)$$

Relaxation is omitted and will be added later phenomenologically. We remove the time dependence of the applied

optical field by transforming to the rotating frame^{21,22} using the unitary transformation

$$\tilde{\rho} = W^\dagger \rho W, \quad (2.3)$$

where

$$W = \exp(-i a^\dagger a \Omega t). \quad (2.4)$$

After invoking the rotating wave approximation²² the equation of motion becomes

$$\frac{\partial \tilde{\rho}}{\partial t} = -i[\tilde{H}_0 + \tilde{H}_{\text{int}} + \tilde{H}_{E-P} + \tilde{H}_p \tilde{\rho}], \quad (2.5)$$

where

$$\begin{aligned} \tilde{H}_0 &= (\omega - \Omega) a^\dagger a = \Delta_0 a^\dagger a, \\ \tilde{H}_{\text{int}} &= -\frac{\hat{\mu} E(t)}{2\hbar} [\exp(i\mathbf{k}\cdot\mathbf{r}) a^\dagger + \exp(-i\mathbf{k}\cdot\mathbf{r}) a], \\ \tilde{H}_{E-P} &= [g_l (b^\dagger + b) + g_q (b^\dagger + b)^2] a^\dagger a, \\ \tilde{H}_p &= \omega_{\text{ph}} (b^\dagger b + 1/2). \end{aligned} \quad (2.6)$$

Δ_0 is the detuning of the transition frequency ω from the laser frequency Ω . The vector \mathbf{k} is the propagation direction of the j th pulse.

To simplify the solution of Eq. (2.5) two approximations are employed. The laser pulses are taken to be rectangular and so short in duration that during a pulse the only system dynamics arise from coupling to the radiation field, i.e., EPC, free precession, and relaxation can be ignored during the optical pulses. These assumptions imply the following conditions: (i) the j th excitation pulse has a constant amplitude E for a duration t_{pj} ; (ii) t_{pj} is much shorter than $1/\omega_{\text{ph}}$ and any relaxation time; (iii) $\Delta_0 t_{pj} \ll 1$; (iv) the Rabi frequency $\chi = \hat{\mu} \cdot \mathbf{E}/\hbar$ is much larger than the range of possible detunings spanned by the inhomogeneous electronic absorption line ($\chi \gg \Delta_0$); and (v) $\chi \gg g_l, g_q$. While these conditions are very useful, it should be possible to relax them and still obtain a solution to Eq. (2.5).²³

The solution of Eq. (2.5) after the application of a laser pulse of duration t_p is given by

$$\tilde{\rho}(t_p) = V(t_p) \tilde{\rho}(0) V(t_p)^\dagger, \quad (2.7a)$$

where $V(t_p)$ is the system propagator in the presence of the E field:

$$V(t_p) = \exp(-i \tilde{H}_{\text{int}} t_p). \quad (2.7b)$$

In the free evolution period (no laser field) the solution of

$$\begin{aligned} \tilde{\rho}(t') &\propto \hat{\mu} \langle \sin A_2 \cos^2 A_1 / 2 e^{i\mathbf{k}_2 \cdot \mathbf{r}} e^{-i\Delta_0 t'} e^{i\tilde{H}_p t'} e^{-i(\tilde{H}_p + \tilde{H}_{E-P}) t'} - \sin^2 A_2 / 2 \sin A_1 e^{i(2\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} e^{-i\Delta_0(t' - \tau)} e^{-i\tilde{H}_p \tau} \\ &\quad \times e^{i(\tilde{H}_p + \tilde{H}_{E-P}) \tau} e^{i\tilde{H}_p t'} e^{-i(\tilde{H}_p + \tilde{H}_{E-P}) t'} + \cos^2(A_2/2) \sin A_1 e^{i\mathbf{k}_1 \cdot \mathbf{r}} e^{-i\Delta_0(\tau + t')} e^{i\tilde{H}_p \tau} e^{-i(\tilde{H}_p + \tilde{H}_{E-P}) \tau} \\ &\quad \times e^{i\tilde{H}_p t'} e^{-i(\tilde{H}_p + \tilde{H}_{E-P}) t'} - \sin^2(A_2/2) \sin(A_1/2) e^{i\mathbf{k}_2 \cdot \mathbf{r}} e^{-i\Delta_0 t'} e^{i\tilde{H}_p t'} e^{-i(\tilde{H}_p + \tilde{H}_{E-P}) t'} \rangle. \end{aligned} \quad (2.13)$$

In Eq. (2.13) $A_{1,2} = (\hat{\mu} \cdot \mathbf{E}/\hbar) t_{p1,2}$ are the Rabi flip angles and $\mathbf{k}_{1,2}$ are the wave vectors of the two laser pulses. Equation (2.13) has the same appearance as the result for a normal echo calculation in the limit of zero EPC. The echo propagates in the $2\mathbf{k}_2 - \mathbf{k}_1$ direction. Furthermore, an echo will occur for any two flip angles and the echo intensity is maximum for $A_{1,2} = \pi/2, \pi$ at $t' = \tau$. From these considerations it can be seen that only the second term in Eq. (2.13)

Eq. (2.5) can be written as

$$\tilde{\rho}(t) = U(t) \tilde{\rho}(0) U^\dagger(t), \quad (2.8a)$$

where $U(t)$ is the propagator during the free induction decay:

$$U(t) = \exp[-i(\tilde{H}_0 + \tilde{H}_{E-P} + \tilde{H}_p)t]. \quad (2.8b)$$

In a photon echo experiment, the system is prepared by a first laser pulse of duration t_{p1} , it evolves freely for a time τ before a second pulse of duration t_{p2} is applied. The second pulse is followed by another free precession period. For this excitation sequence the evolution of the density matrix following the second pulse is given by

$$\begin{aligned} \tilde{\rho}(t_{p1} + \tau + t_{p2} + t') \\ = U(t') V(t_{p2}) U(\tau) V(t_{p1}) \tilde{\rho}(0) V^\dagger(t_{p1}) \\ \times U^\dagger(\tau) V^\dagger(t_{p2}) U^\dagger(t'), \end{aligned} \quad (2.9)$$

where t' is the time after the second pulse and $t' = 0$ is the end of the second pulse. The phonon is assumed to have been excited on a time scale comparable to or less than t_{p1} .

The experimental observable is related to the macroscopic polarization of the system, which can be calculated directly from Eq. (2.9):

$$P(t) = \langle \text{Tr}[\hat{\mu}(a^\dagger + a) \cdot \tilde{\rho}(t)] \rangle, \quad (2.10)$$

where $\langle \dots \rangle$ denotes an average over the inhomogeneous excitation energy distribution of the optical system and the evaluation of the expectation values of phonon operators.

This polarization acts as a source term in Maxwell's wave equations. $P(t)$ can be written as

$$P(t) = \tilde{p}(t) \exp[-i(\Omega t)] + \text{c.c.}, \quad (2.11)$$

where $\tilde{p}(t)$ is the polarization in the rotating frame. $\tilde{p}(t)$ can be related directly to the density matrix²¹ in the rotating frame $\tilde{\rho}$:

$$\tilde{p}(t) = \hat{\mu} \langle \tilde{\rho}_{12}(t) \rangle. \quad (2.12)$$

To calculate the polarization after the second excitation pulse at time t' it is necessary to evaluate Eq. (2.9) using the appropriate propagators whose forms are determined by Eqs. (2.5) and (2.6). The matrix elements of $V(t_{pj})$ ($j = 1, 2$) can be determined by taking the Laplace transform of Eq. (2.7b), inverting the resulting matrix, and returning to the time domain by taking the inverse Laplace transform element by element. The matrix elements of $U(t)$ are obtained utilizing Eq. (2.8b). Substituting these results into Eqs. (2.9) and (2.12) yields the polarization at time t' :

describes the echo.

Rewriting Eq. (2.13) keeping only the term which gives rise to the echo,

$$\begin{aligned} \tilde{p}(t > \tau) &\propto \hat{\mu} \langle -\sin^2 A_2 / 2 \sin A_1 e^{i(2\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} \\ &\quad \times e^{-i\Delta_0(t-2\tau)} e^{-i\tilde{H}_p \tau} e^{i(\tilde{H}_p + \tilde{H}_{E-P}) \tau} \\ &\quad \times e^{i\tilde{H}_p(t-\tau)} e^{-i(\tilde{H}_p + \tilde{H}_{E-P})(t-\tau)} \rangle. \end{aligned} \quad (2.14)$$

In Eq. (2.14), $t = 0$ coincides with the first pulse in the echo sequence and the simultaneous generation of the phonon. To simplify the notation, the very short pulse durations t_{p1} and t_{p2} have been included in 2τ . The signal for an optically thin sample can then be calculated:

$$I(t) \propto |\tilde{P}(t)|^2. \quad (2.15)$$

III. SEMICLASSICAL ANALYSIS

To analyze the polarization which applies to the P³E experiment it is sufficient and mathematically less complex to treat the phonon, generated by stimulated Raman pumping, as a coherent "quasiclassical" wave.²⁴ This is valid since there is a high degree of coherent excitation of a single phonon mode. The definition of the phonon operators b^\dagger and b in Eqs. (2.14) and (2.15) are²⁴

$$b = \left(\frac{1}{2mN\hbar\omega_{\text{ph}}} \right)^{1/2} (m\omega_{\text{ph}}Q + i\pi),$$

$$b^\dagger = \left(\frac{1}{2mN\hbar\omega_{\text{ph}}} \right)^{1/2} (m\omega_{\text{ph}}Q - i\pi), \quad (3.1)$$

where Q and π are the displacement and momentum operators of the phonon mode, respectively, and m is the effective mass. Stimulated Raman pumping excites a phonon with wave vector $k \cong 0$. For the $k = 0$ mode of a phonon with frequency ω_{ph} the displacement operator Q can be written as^{6(d)}

$$Q = \left(\frac{\hbar}{2mN\omega_{\text{ph}}} \right)^{1/2} (b + b^\dagger). \quad (3.2a)$$

In the classical limit the phonon amplitude Q is

$$Q = q_0 \cos(\omega t + \phi)$$

or

$$Q = q_0 \sin(\omega t + \phi), \quad (3.2b)$$

depending on the choice of phase factor ϕ . q_0 is the maximum of the phonon displacement. (The phase factor ϕ is discussed further below.) In this approximation a semiclassical operator $\tilde{H}_{\text{ep}}^{\text{class}}$ is constructed:

$$\tilde{H}_{\text{ep}}^{\text{class}} = \alpha \sin(\omega_{\text{ph}}t + \phi) + 2\beta \sin^2(\omega_{\text{ph}}t + \phi) \\ = \Delta(t) \quad (3.3)$$

with

$$\alpha = g_i q_0 \left(\frac{2m\omega_{\text{ph}}N}{\hbar} \right)^{1/2} \quad (3.4)$$

and

$$\beta = g_q q_0^2 \left(\frac{m\omega_{\text{ph}}N}{\hbar} \right). \quad (3.5)$$

\tilde{H}_{E-p} is now time dependent, therefore,

$$U(t) = T \left\{ \exp \left[-i \int_0^t dt'' (\tilde{H}_0 + \tilde{H}_{\text{ep}}^{\text{class}}) t'' \right] + \tilde{H}_p \right\}, \quad (3.6)$$

where $T(\exp[\dots])$ denotes the time ordered exponential. Since the Hamiltonian in question commutes with itself at

different times, in our approximation

$$U(t) = e^{-i\tilde{H}_0 t} \left\{ e^{-i\int_0^t dt'' \tilde{H}_{\text{ep}}^{\text{class}}(t'')} \right\} e^{-i\tilde{H}_p t}. \quad (3.7)$$

The factors of \tilde{H}_p can be eliminated from Eq. (2.14) and the polarization in this approximation becomes

$$\tilde{P}(t > \tau) \propto i\hat{\mu} \left(-\sin^2 A_2 / 2 \sin A_1 e^{i(2\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} e^{-i\Delta_0(t-2\tau)} \right. \\ \left. \times \exp \left[-i \int_\tau^t dt'' \Delta(t'') + i \int_0^\tau dt'' \Delta(t'') \right] \right). \quad (3.8)$$

This result is consistent with the results from NMR studies in modulated fields.¹⁹ Physically, the phonon acts as a mean field modulation of the environment of the impurity, i.e., the time dependent modulation of the spatial positions of the host atoms or molecules act similarly to the modulated H_z field in the NMR case. This oscillation of the impurity local environment will in turn modulate the impurity resonance frequency detuning Δ_0 . In the limit that the number of phonon excitations approaches unity, i.e., $\langle Q \rangle$ is small, the expectation value of Q has significant "quantum corrections" (since the uncertainty in $\langle Q \rangle$ becomes large), which are negligible at high excitation densities. These quantum corrections at low excitation density would require an alternate approach to evaluate the exponential in Eq. (2.14).

Consider the time dependent exponential in Eq. (3.8):

$$\exp[\dots] = e^{-i(t-2\tau)(\Delta_0 + \beta)} e^{-i(2\alpha/\omega_{\text{ph}})\cos(\omega_{\text{ph}}\tau + \phi)} \\ \times e^{i(\alpha/\omega_{\text{ph}})[\cos(\omega_{\text{ph}}t + \phi) + \cos\phi]} \\ \times e^{-i(\beta/\omega_{\text{ph}})\sin 2(\omega_{\text{ph}}\tau + \phi)} \\ \times e^{i(\beta/2\omega_{\text{ph}})[\sin 2(\omega_{\text{ph}}t + \phi) + \sin 2\phi]}. \quad (3.9)$$

Physically, Eq. (3.9) demonstrates that EPC modulates the polarization. This will give rise to frequency sidebands separated by the modulation frequency ω_{ph} as in the magnetic resonance case.¹⁹ The phase ϕ is determined by the spatial position of the molecule in the sample in relation to the locations of the maximum and minimum displacements associated with the phonon wave at $t = 0$, the time the phonon wave is generated by the stimulated Raman pumping.

To calculate observables (Sec. IV), the averages over the inhomogeneous line and the phase, indicated by the brackets in Eq. (2.8), must be performed. The time dependent exponential term [Eq. (3.9)] can be put into a more convenient form using the following expansions in terms of Bessel functions:

$$e^{z \sin \theta} \\ = I_0(z) + 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1}(z) \sin[(2k+1)\theta] \\ + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k}(z) \cos(2k\theta) \quad (3.10a)$$

and

$$e^{z \cos \theta} = I_0(z) + 2 \sum_{k=1}^{\infty} I_k(z) \cos(k\theta), \quad (3.10b)$$

where the I_n are modified Bessel functions. The modified Bessel functions can be replaced with spherical Bessel functions $J_n(z)$ using the relation

$$I_\nu(z) = e^{(i\pi/2)^\nu} J_\nu(z e^{i\pi/2}). \quad (3.10c)$$

Using Eq. (3.10) the echo polarization becomes

$$\begin{aligned} \tilde{p}(t > \tau) \propto i\hat{\mu} \left(-\sin^2 \frac{A_2}{2} \sin A_1 e^{i(2k_2 - k_1)\tau} e^{i(t-2\tau)(\Delta_0 + \beta)} \left\{ J_0\left(\frac{2\alpha}{\omega_{ph}}\right) + 2 \sum_{k=1}^{\infty} J_k \left[\frac{2\alpha}{\omega_{ph}} e^{(i\pi/2)^k} \right] \cos[k(\omega_{ph}\tau + \phi)] \right\} \right. \\ \times \left[J_0\left(\frac{\alpha}{\omega_{ph}}\right) + \dots \right] \left[J_0\left(\frac{\alpha}{\omega_{ph}}\right) + \dots \right] \left\{ J_0\left(\frac{\beta}{\omega_{ph}}\right) + 2 \sum_{k=0}^{\infty} (-1)^k \right. \\ \times J_{2k+1}\left(\frac{\beta}{\omega_{ph}} e^{(i\pi/2)^k}\right) \sin[(2k+1)(\omega_{ph}\tau + \phi)] + 2 \sum_{k=1}^{\infty} (-1)^k \\ \times J_{2k}\left(\frac{\beta}{\omega_{ph}} e^{(i\pi/2)^k}\right) \cos[2k(\omega_{ph}\tau + \phi)] \left. \right\} \left[J_0\left(\frac{\beta}{2\omega_{ph}}\right) + \dots \right] \left[J_0\left(\frac{\beta}{2\omega_{ph}}\right) + \dots \right] \right). \end{aligned} \quad (3.11a)$$

After simplification:

$$\begin{aligned} \tilde{p}(t > \tau) \propto i\hat{\mu} \left(-\sin^2 A_2/2 \sin A_1 e^{i(2k_2 - k_1)\tau} \right. \\ \times e^{i(t-2\tau)(\Delta_0 + \beta)} \left. \left[J_0^2\left(\frac{\alpha}{\omega_{ph}}\right) J_0^2\left(\frac{\beta}{\omega_{ph}}\right) J_0\left(\frac{2\alpha}{\omega_{ph}}\right) J_0\left(\frac{2\beta}{2\omega_{ph}}\right) + \dots \right] \right). \end{aligned} \quad (3.11b)$$

Note that the static detuning frequency Δ_0 is shifted by β , the magnitude of the quadratic coupling term. The linear coupling α does not produce a shift in the time independent detuning. This difference in the role of β and α is analogous to the difference between the effects of quadratic and linear EPC on the temperature dependent homogeneous dephasing of the zero phonon line.¹¹⁻¹³ Quadratic EPC results in homogeneous dephasing while linear coupling does not. However, as will be shown below, in a P³E experiment, both linear and quadratic EPC will affect the signal. Another feature of Eq. (3.11) is that only the first term in the Bessel function series is independent of the phase ϕ . All other terms contain products of infinite sums of Bessel functions which are multiplied by products of sin and/or cos functions of ϕ . The importance of this feature will be seen in Sec. IV.

IV. CALCULATION OF OBSERVABLES

To calculate the P³E observables, it is necessary to perform the ensemble average indicated by the outer brackets in Eq. (3.11). In a conventional photon echo experiment, this requires averaging over the inhomogeneous distribution of transition frequencies. In a photon echo experiment examining the effect of intermolecular interactions among the guest molecules, e.g., it is necessary to average over the range of intermolecular interactions as well as the inhomogeneous distribution of transition energies.²¹ In the P³E experiment, it is necessary to average over phase ϕ and the inhomogeneous spectral line.

Because a macroscopic region of the sample is illuminated which is much larger than the phonon wavelength, any subensemble of molecules possessing the same transition frequency (same Δ_0) will contain molecules experiencing all possible initial phases ϕ . This is assured since the molecules in question will be randomly distributed throughout the illuminated sample volume. Examining Eq. (3.11), it is seen that there is one term independent of ϕ [which is shown in

Eq. (3.11b)] and all other terms are products of higher order Bessel functions multiplied by products of infinite sums of trigonometric functions. Expansion of these sums yield terms of the form

$$\begin{aligned} J_0\left(\frac{\alpha}{\omega_{ph}}\right) \dots J_0\left(\frac{\beta}{\omega_{ph}}\right) \sum_j J_j\left(\frac{\alpha}{\omega_{ph}}\right) J_j\left(\frac{\alpha}{\omega_{ph}}\right) \\ \times \cos[i(\omega\tau + \phi)] \cos[j(\omega\tau + \phi)] \\ \text{and} \\ 2 J_0 \sum_{jkl} J_j\left(\frac{\alpha}{\omega_{ph}}\right) J_j\left(\frac{\alpha}{\omega_{ph}}\right) J_{2k}\left(\frac{\beta}{\omega_{ph}}\right) J_{2l+1}\left(\frac{\beta}{\omega_{ph}}\right) \\ \times \cos[i(\omega\tau + \phi)] \cos[j(\omega\tau + \phi)] \\ \times \sin[(2l+1)(\omega\tau + \phi)] \cos[2k(\omega\tau + \phi)], \end{aligned} \quad (4.1a)$$

for example, where $J_0 \dots J_0$ represent products of zeroth order Bessel functions. There are more than 200 such terms containing up to six orders of sin, cos, and/or Bessel functions. In general, upon integration from 0 to 2π , all trigonometric products with dissimilar arguments vanish (the vast majority of the terms in the expansion), only terms with even powers of pure sin or pure cos will leave residual contributions to the polarization. The largest such term after integration is of the form

$$J_0\left(\frac{\alpha}{\omega_{ph}}\right) \dots J_0\left(\frac{\beta}{\omega_{ph}}\right) \sum_{k=1}^{\infty} (J_k)^2 \frac{\pi}{k}. \quad (4.1b)$$

We shall ignore this term as well as others of this type since at weak to moderate couplings $J_{n>0}^2$ is very small (10^{-3} - 10^{-6} or smaller). (Note: J_0 is always ≤ 1 .) In the strong coupling regime J_0 approaches zero while the $J_{n>0}^2$ terms are still $\ll 1$. Therefore, in all experimental conditions ϕ dependent contributions to the polarization are negligible. With these considerations, the expression for the polarization reduces to

$$\begin{aligned} \bar{p}(t > \tau) \propto i\mu \left(\sin^2 A_2 / 2 \sin A_1 e^{i(2\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} \right. \\ \times e^{i(t-2\tau)(\Delta_0 + \beta)} J_0^2 \left(\frac{\alpha}{\omega_{\text{ph}}} \right) J_0 \left(\frac{2\alpha}{\omega_{\text{ph}}} \right) \\ \left. \times J_0^2 \left(\frac{\beta}{2\omega_{\text{ph}}} \right) J_0 \left(\frac{\beta}{\omega_{\text{ph}}} \right) \right), \end{aligned} \quad (4.2)$$

where the outer brackets now indicate an average over the inhomogeneous line.

To explicitly perform the average over the inhomogeneous line, we assume a Gaussian distribution of optical transition frequencies:

$$G(\Delta_0) = \frac{T_2^*}{\sqrt{\pi}} \exp(-\Delta_0^2 T_2^{*2}), \quad (4.3)$$

where T_2^{*-1} characterizes the width of inhomogeneous distribution. The average over the inhomogeneous line has the form

$$\begin{aligned} \bar{p}(t > \tau) \propto J_0^2 \left(\frac{\alpha}{\omega_{\text{ph}}} \right) J_0 \left(\frac{2\alpha}{\omega_{\text{ph}}} \right) J_0^2 \left(\frac{\beta}{2\omega_{\text{ph}}} \right) J_0 \left(\frac{\beta}{\omega_{\text{ph}}} \right) \\ \times \int_{-\infty}^{\infty} G(\Delta_0) e^{i(t-2\tau)(\Delta_0 + \beta)} d\Delta_0. \end{aligned} \quad (4.4)$$

Upon integration and adding a phenomenological relaxation term for the optical two-level systems, $\exp(-t/T_2)$ where $(\pi T_2)^{-1}$ is the homogeneous optical linewidth, we arrive at an expression for the polarization:

$$\begin{aligned} \bar{p}(t > \tau) \propto e^{i(t-2\tau)\beta} e^{-t/T_2} e^{-(t-2\tau)^2/4T_2^{*2}} \\ \times J_0^2 \left(\frac{\alpha}{\omega_{\text{ph}}} \right) J_0 \left(\frac{2\alpha}{\omega_{\text{ph}}} \right) \\ \times J_0^2 \left(\frac{\beta}{2\omega_{\text{ph}}} \right) J_0 \left(\frac{\beta}{\omega_{\text{ph}}} \right). \end{aligned} \quad (4.5)$$

Using Eq. (2.15) the P³E signal intensity is obtained,

$$\begin{aligned} I(t > \tau) = A \exp\left(-\frac{2t}{T_2}\right) \exp\left(-\frac{(t-2\tau)^2}{2T_2^{*2}}\right) J_0^4 \left(\frac{\alpha}{\omega_{\text{ph}}} \right) \\ \times J_0^2 \left(\frac{2\alpha}{\omega_{\text{ph}}} \right) J_0^4 \left(\frac{\beta}{2\omega_{\text{ph}}} \right) J_0^2 \left(\frac{\beta}{\omega_{\text{ph}}} \right), \end{aligned} \quad (4.6)$$

where the constant A contains experimental parameters such as the excitation pulse areas, the size of the illuminated volume, and the sample concentration.

In the limit where EPC is negligible ($\alpha = \beta = 0$) the echo pulse shape is Gaussian as anticipated for a Gaussian absorption line shape [Eq. (4.3)]. Its peak is at $t = 2\tau$ and the temporal width is determined by T_2^* , the inverse inhomogeneous linewidth. This behavior is identical to the standard echo result. When the excitation-phonon coupling is not negligible, the echo amplitude can change considerably. Equation (4.6) is plotted in Fig. 1. The general feature is the decreasing magnitude of the echo pulse. In Fig. 1 the results are for linear coupling only. Curve 1 has $\alpha = \beta = 0$. This is the unperturbed echo envelope. In curves 2, 3, and 4, α increases with $\beta = 0$. α and β are defined in Eqs. (3.4) and (3.5), respectively. The results for quadratic coupling and various combinations of linear and quadratic coupling are similar. Since the effects of linear and quadratic coupling on

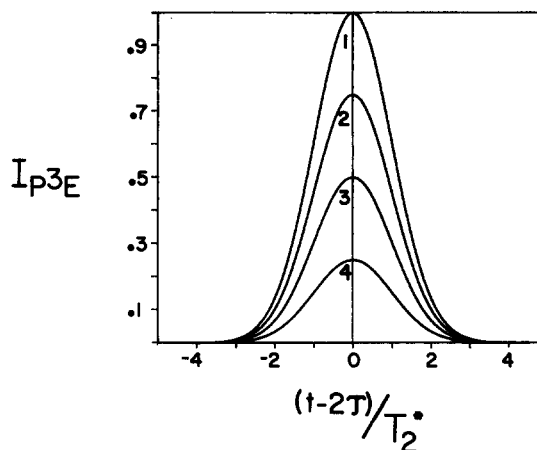


FIG. 1. Phonon perturbed photon echo pulse shapes calculated using Eq. (4.6) for various linear coupling parameters $\alpha/\omega_{\text{ph}}$. (1) $\alpha/\omega_{\text{ph}} = 0$; (2) $\alpha/\omega_{\text{ph}} = 0.30$; (3) $\alpha/\omega_{\text{ph}} = 0.47$; (4) $\alpha/\omega_{\text{ph}} = 0.65$.

the echo depend differently on the maximum amplitude of the phonon wave [q_0 in Eqs. (3.4) and (3.5)], the coupling mechanism can be distinguished.

The coherent phonon wave does not lead to homogeneous dephasing of the optical two-level systems in the conventional sense, in striking contrast to the thermally excited phonon case. The reduction results from lack of correlation of the individual two-level oscillators. In our model for inhomogeneous broadening there is no correlation between the spatial position of the oscillators and its resonance frequency. Therefore, oscillators at frequency ω experience all phases of the phonon field. This "averaging" causes the amplitude reduction not homogeneous dephasing processes. In the absence of conventional T_2 processes, increasing the separation between the pulses in the echo sequence does not result in a further decrease in the echo signal. This is not surprising since the randomness of a thermal phonon bath is absent.

In most photon echo experiments, the echo pulse shape is not detected. The common detection techniques integrate the echo intensity over time. Therefore, we calculate the total echo intensity for a pulse separation τ from Eq. (4.6):

$$I_{\text{echo}}(\tau) = \int_{\tau}^{\infty} dt I(t). \quad (4.7)$$

Figure 2 shows the echo intensity as a function of the parameter $\alpha/\omega_{\text{ph}}$ given by Eq. (4.7) for a fixed pulse separation τ . As $\alpha/\omega_{\text{ph}}$ is increased the echo pulse intensity decreases. The coupling constant can be determined experimentally by measuring the reduction of the echo intensity upon excitation of the coherent phonon wave.

Thus far the perturbing phonon mode has been treated as an ideal nondecaying, nondephasing wave. In reality the phonon has a finite linewidth caused by lifetime and pure dephasing processes. At very low temperatures, the linewidths of many phonons in molecular crystals have been shown to arise because of population relaxation.²⁵ This can be modeled phenomenologically by letting the maximum phonon amplitude decay as

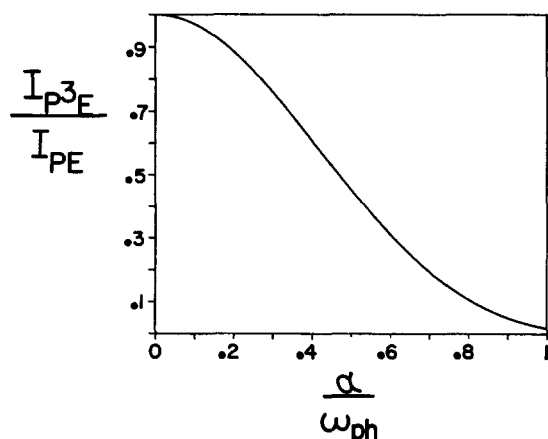


FIG. 2. Phonon-perturbed photon echo energy (integrated intensity) normalized to the unperturbed echo energy as a function of the linear excitation-phonon coupling parameter $\alpha/\omega_{\text{ph}}$. I_{PE} and $I_{\text{P}^3\text{E}}$ are the unperturbed and perturbed echo intensities, respectively.

$$q(t) = q_0 e^{-t/T_{\text{ph}}}, \quad (4.8)$$

where T_{ph} is the phonon lifetime and q_0 is the maximum phonon displacement. Substituting Eq. (4.8) into Eq. (3.4), Eq. (4.7) can be plotted as a function of the laser pulse separation τ . It should be noted that this substitution is valid in the limit $1/T_{\text{ph}} \ll \omega_{\text{ph}}$, i.e., the exponential in Eq. (4.8) is slowly varying relative to the phonon frequency. (This is the regime of experimental interest.) A general expression can be derived by substituting Eq. (4.8) into our original time dependent Hamiltonian and performing the necessary integration. For our purpose the first procedure is sufficient. The results are depicted in Fig. 3 for various coupling constants. The unperturbed photon echo decays at a rate determined by T_2 . The phonon lifetime is taken as $T_{\text{ph}} = T_2/5$. $\alpha/\omega_{\text{ph}}$ takes on values from 0 to 1. As the phonon decays its influence on the echo decreases. This results in an increasing echo signal

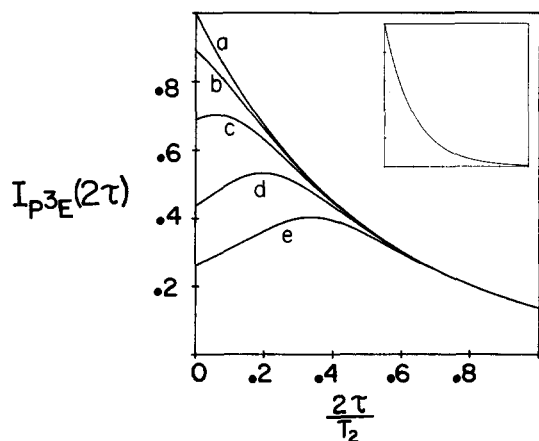


FIG. 3. Phonon perturbed photon echo pulse energy as a function of the pulse separation τ in units of the dephasing time T_2 . Phonon lifetime $T_{\text{ph}} = T_2/5$. (a) $\alpha/\omega_{\text{ph}} = 0$, regular decay; (b) $\alpha/\omega_{\text{ph}} = 0.20$; (c) $\alpha/\omega_{\text{ph}} = 0.35$; (d) $\alpha/\omega_{\text{ph}} = 0.5$; (e) $\alpha/\omega_{\text{ph}} = 0.6$. As the phonon decays its influence on the echo decreases. This results in an interesting echo signal at short time if the phonon perturbation is initially large. Insert: phonon decay obtained from analysis of the difference between curve (a) and any of the perturbed decays using the phonon relaxation model considered in the text.

at short time if the phonon perturbation is initially large. From detailed analysis of the difference between the unperturbed echo decay and the decay with the phonon present, the lifetime of the phonon can be extracted (see inset Fig. 3). This model is appropriate if the phonon population relaxation is either into the thermal bath with no significant temperature increase or if the phonon decays into a small number of modes which have negligible coupling to the optical excitations. One could imagine that there are favorable relaxation paths to phonons with different decay times and nonnegligible EPC constants. This would be manifested in the time dependence of the P³E experiment, giving the possibility of tracking photon decay paths with this method.

V. AN ESTIMATE OF THE SIZE OF THE P³E EFFECT

In the remainder of this article a concrete experiment is considered. An estimate is made of the size of the P³E effect for a typical phonon in a mixed molecular crystal. It is demonstrated that the effect is observable with available laser technology. The method for extracting EPC parameters from the experimental data is also outlined. In order to observe the P³E, we propose the experiment schematically depicted in Fig. 4. One dye laser is tuned to the transition frequency ω_1 of an ensemble of impurity molecules in a molecular crystal. Two pulses from this laser, separated by a time τ , produce the photon echo at 2τ . The phonon of interest is excited in a stimulated Raman process by bringing in a third laser pulse at frequency ω_2 (generated by a second dye la-

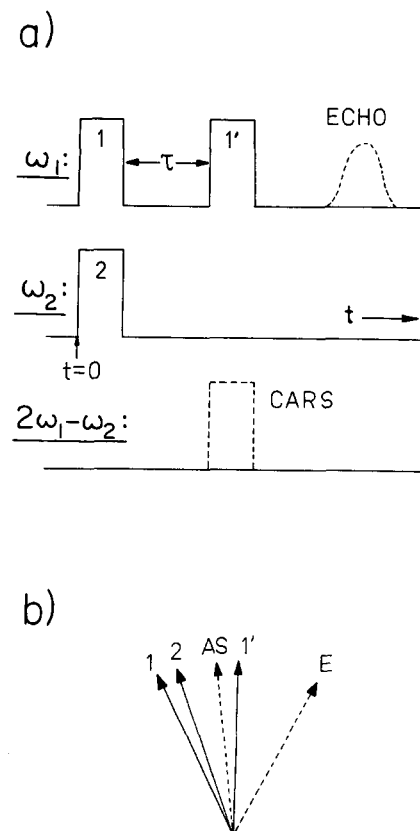


FIG. 4. (a) Pulse sequence for the phonon-perturbed photon echo experiment. (b) Possible phase-matching geometry for the P³E experiment. $1 = \mathbf{k}_{\omega_1}$, $2 = \mathbf{k}_{\omega_2}$, $1' = \mathbf{k}_{\omega_1}$, $\text{AS} = \mathbf{k}_{\text{AS}}$ and $E = \mathbf{k}_{\text{echo}}$.

ser). The ω_2 pulse is time coincident with ω_1 . The difference frequency ($\omega_1 - \omega_2$) equals the phonon frequency of interest (ω_{ph}). The degree of phonon excitation can be determined by detecting the anti-Stokes radiation scattered by the second ω_1 pulse. Both the echo and CARS signal can be detected separately and simultaneously by utilizing the wave vector matching conditions for each, i.e., $\mathbf{k}_{\text{echo}} = 2\mathbf{k}'_1 - \mathbf{k}_1$; $\mathbf{k}_{\text{AS}} = (\mathbf{k}_1 + \mathbf{k}'_1) - \mathbf{k}_2$. In addition, the CARS signal can be frequency filtered since $\omega_{\text{AS}} = (2\omega_1 - \omega_2)$.

The reduction of the echo pulse energy or the change of the echo pulse shape due to EPC can now be detected by either blocking the pulse at ω_2 , moving it before $t = 0$ where there is no overlap between pulses 1 and 2 in time (see Fig. 4), or by tuning ω_2 off the phonon resonance. In all cases the phonon would not be excited and the echo signal should return to its normal level.

In order to determine the magnitude of the P³E effect for a given system, we first need to calculate the phonon amplitude excited by the two pulses ω_1 and ω_2 . To this end we start with the equation of motion for the driven harmonic oscillator²⁶:

$$\frac{\partial^2 Q}{\partial t^2} + \Gamma \frac{\partial Q}{\partial t} + \omega_{\text{ph}}^2 Q = \frac{1}{M} F(t), \quad (5.1)$$

where Q is the normal coordinate, M is the reduced mass of the oscillator, and Γ is the damping constant, which for negligible pure dephasing is related to the phonon lifetime [Eq. (4.11)]. The driving force $F(t)$ is given by the laser fields acting on the vibrating molecules:

$$F(t) = \frac{1}{2} \left(\frac{\partial a}{\partial Q} \right)_{ij} \overline{E^2(t)}. \quad (5.2)$$

$(\partial a / \partial Q)_{ij}$ is the polarizability tensor and $\overline{E^2(t)}$ is the time averaged applied electric field, i.e., the two time-coincident laser pulses of different frequencies. The quantity $(\partial a / \partial Q)_{ij}$ can be determined from the Raman polarizability using the relation

$$a_{ij}^{(r)} = \left(\frac{\hbar}{2\omega_{\text{ph}}} \right)^{1/2} \left(\frac{\partial a}{\partial Q} \right)_{ij}, \quad (5.3)$$

where the indices i, j represent the polarization indices of $\chi_{ijkl}^{(3)}$. $a_{ij}^{(r)}$ can be measured by a spectral analysis of the Raman profile. (This procedure is presented in detail in Ref. 20.)

The fields responsible for the generation of the phonon wave can be written as

$$E(t) = E_1(t) \cos(\omega_1 t + \mathbf{k}_1 \cdot \mathbf{r}) + E_2(t) \cos(\omega_2 t + \mathbf{k}_2 \cdot \mathbf{r}). \quad (5.4)$$

Equation (5.1) with Eqs. (5.2) and (5.4) are solved in Appendix A by assuming identical Gaussian pulse shapes, $E_i(t)$ ($i = 1, 2$), perfectly overlapped in time. There, the Green's function method is used to obtain an analytical expression for q_0 , the phonon amplitude in the slowly varying envelope approximation and for times $t_p \ll t \ll \Gamma^{-1}$, where t_p is the duration of the Gaussian laser pulses:

$$q_0 = \left(\frac{\pi}{32} \right)^{1/2} \left(\frac{J}{C_{\text{ph}} m} \right) \left(\frac{1}{\bar{\omega}^2} \right) \left(\frac{\partial a}{\partial Q} \right)_{ij}, \quad (5.5)$$

where J is the total pulse energy of each laser (ω_1 and ω_2)

and $\bar{\omega}$ is the $1/e$ radius of the E field. To give an order of magnitude estimate, we chose the 1385 cm^{-1} (a_{1g}) mode of naphthalene for which the polarizability along the b crystal-line axes has been determined [$(\partial a / \partial Q)_{bb} = 2.28 \times 10^{-15} \text{ cm}^2$].²⁰ Assuming pulse energies of $750 \mu\text{J}$ and a beam radius of $50 \mu\text{m}$, we get a phonon displacement of $q_0 = 2.59 \times 10^{-10} \text{ cm}$, using the naphthalene reduced molecular mass. For a coherently excited phonon, the number $\langle N_E \rangle$ of excited quanta is related to the expectation value of the displacement by²⁷

$$\langle N_E \rangle = \frac{2m\omega_{\text{ph}} N}{\hbar} q_0^2, \quad (5.6)$$

where N and q_0 are as defined previously.

Redefining Eqs. (3.4) and (3.5) by substituting Eq. (5.6), we have

$$\alpha = g_l (\langle N_E \rangle)^{1/2} = \omega_{\text{ph}} \left(\frac{S_{\text{HR}} \langle N_E \rangle}{N} \right)^{1/2},$$

$$\beta = \frac{g_q}{2} \langle N_E \rangle = \omega_{\text{ph}} \frac{\langle N_E \rangle}{4N} w,$$

where we have introduced coupling parameters S_{HR} and w so that numerical estimates of standard coupling constants could be utilized. These relationships are described in Appendix B.

One common way of expressing the linear EPC strength of color centers in alkali-halide crystals is the Huang-Rhys constant S_{HR} ,²⁸ which is a measure of the displacement of the potential energy surface minimum for a vibration upon electronic excitation. S_{HR} gives the average number of phonons created in the optical emission or absorption process. For example, for $S_{\text{HR}} \geq 5$ the zero-phonon line is not observed and the absorption profile is quasicontinuous (strong coupling). For $S_{\text{HR}} < 1$ there is a dominant zero-phonon line and a pronounced phonon sideband characteristic of the moderate coupling range. Generally for mixed crystals at low concentrations S_{HR} ranges from 0 to 0.1. $S_{\text{HR}} \ll 1$ for molecules in which most of the intensity is in the vibrationless (0,0) band. Taking $S_{\text{HR}} = 0.01$ as our estimate for the calculation and using the conversion from g_l into S_{HR} [Eq. (B5) in Appendix B], we obtain

$$\left(\frac{\alpha}{\omega_{\text{ph}}} \right) = 0.30,$$

where a typical inhomogeneous linewidth of 1 cm^{-1} has been used. According to Fig. 2, this leads to an echo energy reduction of $\sim 30\%$, which would be readily detectable with current picosecond photon echo techniques.

A similar estimate can be made for quadratic EPC. Using the coupling parameter w introduced by Skinner *et al.*¹³ (see Appendix B), which for organic crystals is on the order of $|w| \approx 0.5$, we arrive at

$$\left(\frac{\beta}{\omega_{\text{ph}}} \right) = 1 \times 10^{-4},$$

which corresponds to a reduction of the echo pulse energy of less than 1%.

In the example just described, the linear coupling would be readily observable, but the quadratic coupling would be

very difficult to observe. However, the laser pulse energies (750 μJ) are very reasonable. Picosecond dye lasers can readily produce pulses in the mJ range. In the quadratic coupling case, an increase in laser pulse energy, and therefore an increase in the phonon amplitude will greatly increase the size of the P³E effect. It should be noted that we chose rather modest values for the linear and quadratic coupling parameters. An increase in these parameters would greatly enhance the observed change in the photon echo.

VI. CONCLUDING REMARKS

We have shown that the excitation-phonon interaction of a *coherent* phonon with an optical two-level system leads to interesting new features in photon echo calculations that are strikingly different from the effects of thermally excited (incoherent) phonons. This P³E effect, in principle, can reveal the EPC constants (linear and quadratic) for a particular phonon chosen by the phonon excitation process. In this way coupling constants of different phonon modes with the same electronic system can be investigated individually, rendering information not accessible by recent temperature dependent optical dephasing experiments. By examining the P³E as a function of the direction of propagation of the phonon wave, the anisotropy in excitation-phonon coupling can be mapped out.

This theoretical study represents a departure from the traditional approach to the examination of the interaction of bulk mechanical degrees of freedom with electronic states of a molecule or atom. By avoiding thermal population of the system's phonons, a more selective probing of interactions can be realized.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research No. N00014-85-K-0409 and the National Science Foundation, Division of Materials Research No. DMR 84-16343. We would like to thank Professor R. F. Loring of Cornell University for invaluable conversations leading toward completion of this work. In addition, William L. Wilson would like to thank AT&T Bell Laboratories for a graduate fellowship; and Gerhard Wäckerle would like to thank the Deutsche Forschungsgemeinschaft for partial support. We would like to thank Professor N. Schwentner for interesting conversations pertaining to this work.

APPENDIX A

It has been shown in Ref. 27 that the equation of motion for a two-level system with the polarizability $(\partial a/\partial q)_{ij}$ is equivalent to the classical driven harmonic oscillator

$$\frac{\partial^2 Q}{\partial t^2} + \Gamma \frac{\partial Q}{\partial t} + \omega_{\text{ph}}^2 Q = \frac{1}{M} F(t). \quad (\text{A1})$$

Q is the displacement of the normal coordinate, Γ is the phenomenological damping constant, M is the reduced mass of the oscillator, and $F(t)$ the driving force. The force on the polarizable material is given by

$$F(t) = \frac{1}{2} \left(\frac{\partial a}{\partial Q} \right)_{ij} \overline{E^2(t)}, \quad (\text{A2})$$

where $(\partial a/\partial Q)_{ij}$ is the polarizability along axes i and j and $\overline{E^2(t)}$ is the time averaged E field. The bar indicates averaging over a few optical periods. Consider the exciting field

$$E(t) = E_1(t) \cos(\omega_1 t + \mathbf{k}_1 \cdot \mathbf{r}) + E_2(t) \cos(\omega_2 t + \mathbf{k}_2 \cdot \mathbf{r}), \quad (\text{A3a})$$

$$\overline{E^2(t)} = (1/4) E_1(t) E_2(t) \times \exp[-i(\omega_1 - \omega_2)t], \quad (\text{A3b})$$

where we have eliminated the rapidly oscillating high frequency components of the field. A standard method for constructing the solution to an inhomogeneous linear differential equation is to represent the solution as an integral over a Green's function.²⁹ The Green's function $g(t, t_0)$ associated with Eq. (A1) satisfies the differential equation

$$\frac{\partial^2 g(t, t_0)}{\partial t^2} + \Gamma \frac{\partial g(t, t_0)}{\partial t} + \omega_{\text{ph}}^2 g(t, t_0) = \delta(t - t_0). \quad (\text{A4})$$

Equation (A4) can be solved using standard methods³⁰ yielding an expression for $g(t, t_0)$:

$$g(t, t_0) = \frac{1}{(\omega_{\text{ph}}^2 - \Gamma^2/4)^{1/2}} \exp\left[-\frac{\Gamma}{2}(t - t_0)\right] \times \sin\left[\left(\omega_{\text{ph}}^2 - \frac{\Gamma^2}{4}\right)^{1/2}(t - t_0)\right]. \quad (\text{A5})$$

Using Eq. (A5) $Q(t)$ is readily obtained using the relation

$$Q(t) = \int_{-\infty}^{\infty} F(t_0) g(t, t_0) dt_0. \quad (\text{A6})$$

For identical time coincident Gaussian laser pulses,

$$[E_2^2(t) E_1^2(t)]^{1/2} = E_0^2 \exp(-2t^2/t_p^2), \quad (\text{A7a})$$

where

$$E_0^2 = E_2(t) E_1(t). \quad (\text{A7b})$$

Upon evaluation of Eq. (A6) using Eq. (A8),

$$Q(t) = \frac{1}{8m} \left(\frac{\pi}{2(\omega_{\text{ph}}^2 - \Gamma^2/4)} \right)^{1/2} \left(\frac{\partial a}{\partial Q} \right)_{ij} E_0^2 t_p \times \exp\left[-\frac{\Gamma}{2}t\right] \exp\left[\left(\frac{t_p^2}{2}\right)^2 \left[\frac{(i\omega_R + \Gamma/2)^2}{4} - \frac{(\omega_{\text{ph}}^2 - \Gamma^2/4)}{4} \right] \sin\left[\left(\omega_{\text{ph}}^2 - \frac{\Gamma^2}{4}\right)^{1/2}t - t_p^2 \left(\frac{i\omega_R + \Gamma/2}{4} \right) \left(\omega_{\text{ph}}^2 - \frac{\Gamma^2}{4} \right)^{1/2} \right], \quad (\text{A8})$$

with $\omega_R = \omega_1 - \omega_2$. For the situation of interest $t_p \ll t$ we obtain for the resonant case ($\omega_R = \omega_{\text{ph}}$):

$$Q(t) = \left(\frac{\pi}{2} \right)^{1/2} \left(\frac{1}{8\omega_{\text{ph}} m} \right) \left(\frac{\partial a}{\partial Q} \right)_{ij} E_0^2 t_p \times \exp\left[-\frac{\Gamma t}{2}\right] \sin(\omega_{\text{ph}} t), \quad (\text{A9})$$

where we assume slow damping of the phonon (i.e., negligible damping). Using the relation

$$E = \left(\frac{\mu_0}{\epsilon_0} \right)^{1/4} \left(\frac{J}{2\pi\omega^2 t_p} \right)^{1/2} \quad (\text{A10})$$

for two pulses of equal intensity and duration:

$$E_0^2 t_p = \left(\frac{\mu_0}{\epsilon_0} \right)^{1/2} \left(\frac{J}{2\pi\bar{\omega}^2} \right), \quad (\text{A11})$$

where J is the pulse energy, $\bar{\omega}$ is the $1/e$ radius of the E fields, and μ_0 and ϵ_0 are the vacuum permeability and permittivity, respectively. The amplitude of $Q(t)$ is

$$q_0 = \left(\frac{\mu_0}{2\pi\epsilon_0} \right)^{1/2} \left(\frac{J}{16\omega_{\text{ph}} m} \right) \left(\frac{1}{\bar{\omega}^2} \right) \left(\frac{\partial a}{\partial Q} \right)_{ij}. \quad (\text{A12})$$

Mechanical quantities are commonly measured in cgs units, therefore,

$$q_0 = \left(\frac{\pi}{32} \right)^{1/2} \left(\frac{J}{c\omega_{\text{ph}} m} \right) \left(\frac{1}{\bar{\omega}^2} \right) \left(\frac{\partial a}{\partial Q} \right)_{ij}. \quad (\text{A13})$$

APPENDIX B: NOTATIONS FOR EXCITATION-PHONON COUPLING CONSTANTS

In Ref. 13, the Hamiltonian for EPC is written as

$$H_{E-P} = [A\phi + 1/2w\phi^2]a^\dagger a, \quad (\text{B1})$$

where for a single phonon mode,

$$\phi = \left(\frac{\hbar\omega_{\text{ph}}}{2N} \right)^{1/2} (b^\dagger + b). \quad (\text{B2})$$

A is the linear coupling constant in units of (energy)^{1/2}, w is the dimensionless quadratic coupling constant and N is the number of oscillators. Comparing Eqs. (B1) and (2.1) we have

$$g_l = \left(\frac{\omega_{\text{ph}}}{2N\hbar} \right)^{1/2} A, \quad (\text{B3a})$$

$$g_q = \left(\frac{\omega_{\text{ph}}}{4N} \right) w. \quad (\text{B3b})$$

A common way of expressing linear EPC is the Huang-Rhys constant²⁸ S_{HR} , which gives the average number of phonons emitted after absorption or emission of a photon and thus is a measure of the displacement of the energy surface minimum of the particular vibration in the electronic excited state.

The Hamiltonian for linear EPC in this case is expressed as

$$H_{E-P} = \left[\left(\frac{S_{\text{HR}}}{N} \right)^{1/2} \hbar\omega_{\text{ph}} (b^\dagger + b) \right] a^\dagger a, \quad (\text{B4})$$

and we can complete Eq. (B3a):

$$g_l = \left(\frac{\omega_{\text{ph}}}{2N\hbar} \right)^{1/2} A = N^{-1/2} \omega_{\text{ph}} S_{\text{HR}}^{1/2}. \quad (\text{B5})$$

With Eqs. (B5) and (B3) we can calculate our parameters α and β by

$$\alpha = \omega_{\text{ph}} \left(S_{\text{HR}} \frac{\langle N_E \rangle}{N} \right)^{1/2} \quad (\text{B6})$$

and

$$\beta = \omega_{\text{ph}} \frac{\langle N_E \rangle}{4N} w, \quad (\text{B7})$$

where $\langle N_E \rangle$ is the number of excited phonons.

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