# Nonlinear optical response functions for a chromophore with linear and quadratic electron–vibration coupling

Mohamad Toutounji and Gerald J. Small<sup>a)</sup>

Department of Chemistry and Ames Laboratory, United States Department of Energy, Iowa State University, Ames, Iowa 50011

Shaul Mukamel

Department of Chemistry, University of Rochester, Rochester, New York 14627

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Two models for the third-order response function of a two-electronic level chromophore are investigated. The first assumes an excited state vibrational Hamiltonian whose phonon modes exhibit both linear and diagonal quadratic electron-phonon coupling. Impulsive stimulated photon echoes are calculated for this model. The second assumes linear electron-phonon coupling including vibrational relaxation and pure electronic dephasing. Impulsive two-pulse photon echo signals and their dependence on temperature and electron-phonon coupling strength are calculated for this model. The initial fast nonexponential (free-induction) decay due to all multiphonon transitions, quantum beats and the slow decay component due to the zero-phonon line (pure electronic dephasing) are identified and correlated with features of the single-site absorption spectrum whose relationship to the hole burned spectrum is well understood. Pure electronic dephasing associated with the zero-phonon line contributes to the decay of the quantum beats. This contribution may be non-negligible at high temperatures in certain systems. An application is made to the special pair absorption band of the bacterial reaction center. © *1999 American Institute of Physics*. [S0021-9606(99)52502-6]

### **I. INTRODUCTION**

Recently, femtosecond photon echo spectroscopies have been used to study optical coherence loss of electronic transitions of molecular chromophores in liquids.<sup>1-12</sup> Of particular interest has been the dephasing due to inertial (librational) modes ("phonons") which couple linearly to the  $S_1 \leftarrow S_0$ electronic transition. The damping of these Franck-Condon active phonons can lead to coherence loss on the femtosecond time scale. We recently suggested that<sup>13,14</sup> the study of optical coherence loss of chromophores in glasses and in the glass forming solvents could lead to a better understanding of the phononic contribution to dephasing in liquids. This suggestion stemmed from the results of persistent spectral hole burning studies of Al-phthalocyanine tetrasulphonate in glassy water<sup>13</sup> and ethanol<sup>14</sup> between 5 K and temperatures close to their glass transition temperature  $(T_g)$ , 135 and 95 K, respectively. In the case of water it was shown that the values of the linear electron-phonon coupling parameters and inhomogeneous broadening of the zero-phonon line [(ZPL), i.e., pure electronic transition] determined from the 5 K spectra, when used with the expression of Hayes et al.<sup>15</sup> for the hole burned spectrum, provided a good accounting of the temperature dependence of APT's hole burned spectrum. The linear electron-phonon coupling is dominated by a 38 cm<sup>-1</sup> phonon with a small Huang–Rhys factor of 0.55 (the width of the one-phonon profile associated with the  $38 \text{ cm}^{-1}$ phonon is 45  $cm^{-1}$ ).<sup>16</sup> The corresponding frequencies for

glassy ethanol and methanol are 26 and 17  $\text{cm}^{-1}$ , respectively.<sup>17</sup> The 38, 26 and 17 cm<sup>-1</sup> phonons were assigned as pseudolocalized with amplitude centered on APT and nearest neighbor solvent molecules. The high resolution of the temperature-dependent hole spectra led to the conclusion that, at temperatures  $\geq 15$  K,<sup>17</sup> the dephasing of the ZPL is due to the exchange coupling mechanism associated with diagonal quadratic electron-phonon coupling.<sup>18,19</sup> The quadratic coupling gives rise to a mode frequency change upon electronic excitation of the chromophore. For glassy water the exchange coupling was found to be due to two phonons with frequencies of 50 and 180  $cm^{-1}$  which correspond to the acoustic modes of water. For glassy ethanol, an exchange coupling mode of 50 cm<sup>-1</sup> was identified which coincides with the lowest energy peak in the spectral density of liquid ethanol.

The combination of spectral hole burning and photon echo spectroscopies is well suited for determination of the similarities and differences between optical coherence loss in glasses and liquids which can be expected to depend on the liquid and the value of  $T-T_g>0$ . Of particular interest would be identification of ultrafast dynamics from inertial modes unique to the liquid. Interpretation of the results of such experiments, however, requires linear and nonlinear response functions for finite temperature that provides a consistent and physically acceptable description of the singlesite absorption, hole-burned and photon echo spectra, as recently pointed out by Nagasawa *et al.*<sup>20</sup> and Bardeen *et al.*<sup>21</sup> in their studies of the temperature dependence of optical coherence loss of chromophores in polymers.

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<sup>&</sup>lt;sup>a)</sup>Electronic mail: gsmall@ameslab.gov

We recently derived an excited state vibrational Hamiltonian  $H_e$  that, in addition to linear coupling, includes diagonal quadratic coupling.<sup>22</sup> This Hamiltonian, which is adequate for mode frequency changes smaller than 30%, was used to obtain the linear response or two-point correlation function and provides a good description of the temperature dependences of the ZPL, multiphonon and sequence transitions. (Sequence transitions correspond to  $n''_i \rightarrow n'_i = n''_i$ , where  $n''_{j}$  and  $n'_{j}$  are the quantum numbers of mode *j* for the ground and exited electronic states, respectively.) For example, in the case of linear coupling only the widths of the  $n''_i = 0 \rightarrow n'_i$  progression members are given by  $\gamma_{el}$  $+n'_{i}\gamma_{i}(n'_{i}=0,1,...)$  where  $\gamma_{i}$  is the damping constant for phonon j. That  $\gamma_{el}$  adds to the widths of the multiphonon transition has a physical basis.<sup>22</sup> The linear dependence on  $n'_{i}$  (folding) is valid for any phonon relaxation mechanism that is linear in the coordinate of the phonon. Such folding has been observed for chromophores in host crystals.<sup>23,24</sup> The structure of the linear response function is such that all transitions in the single-site absorption spectrum carry Lorentzian line shapes. However, the modification required to account for a distribution of values for  $\omega_i$  due to structural heterogeneity is straightforward. The new linear response function was found, for example, to provide a good description of the temperature dependence of the hole-burned spectrum of the special pair band of the bacterial reaction center. The response functions are applicable to systems whose phonons are underdamped,  $\gamma_i < \omega_i$ .

In this paper the temperature dependent third-order response function for the aforementioned Hamiltonian  $H_{e}$  is obtained. In order to demonstrate quantum beats from quadratic coupling, it is used to calculate the impulsive stimulated photon echo (PE) signal in the limit of large inhomogeneous broadening for a linearly and quadratically coupled phonon. The third-order response function which includes both phononic damping and pure electronic dephasing is derived for linear coupling only using the results of Ref. 22 which include an expression for the phonon line shape function,  $g^{\text{ph}}(t;T)$ . The four-point correlation function defines the echo response functions which enter into the expression for the third-order polarization that describes all four-wave mixing spectroscopies including the three-pulse stimulated photon echo (SPE). Applications are made to impulsive echo spectroscopy. The results provide a clear picture of the basic aspects of the echo profile which include the faster and slower components of the echo decay due to the multiphonon transitions (phonon sideband) and ZPL as well as the phonon-induced quantum beats.<sup>25-34</sup> Particular attention is given to the dependency of the two-pulse echo signal for a fixed temperature on the value of the Huang–Rhys factor S of the active phonon, the dependence of the signal for fixed S on the temperature, the relationship between the integrated echo signal and the single-site absorption spectrum and the dynamical information contained in the quantum beat profiles. Consistent with the widths of the multiphonon absorption transitions, vide supra, we find that the pure electronic dephasing  $(\gamma_{el})$  contributes to the decay of the quantum beats. Finally, the two-pulse PE signals are calculated in the low temperature limit for the special pair absorption band of the bacterial reaction center and compared with the results of recent accumulated PE experiments.<sup>35</sup>

# **II. THE THIRD-ORDER RESPONSE FUNCTION**

We begin by reviewing the equations in the book by Mukamel<sup>36</sup> that are the starting point for this work.<sup>37</sup> The nonlinear response function which governs four-wave mixing (4 WM) experiments is

$$S^{(3)}(t_3, t_2, t_1) = 2\hbar^{-3}\theta(t_1)\theta(t_2)\theta(t_3) \times \operatorname{Im}\sum_{\alpha=1}^4 R_{\alpha}(t_3, t_2, t_1),$$
(1)

where  $\{R_{\alpha}(t_1,t_2,t_3)\}_{\alpha=1}^4$  are the nonlinear correlation functions,  $\theta(t_n)$  is the Heaviside step function, and  $t_1,t_2,t_3$  are the interaction intervals between the system and radiation field, *vide infra*. The  $R_{\alpha}$ 's are obtainable from the four-point correlation function

$$F(\tau_1, \tau_2, \tau_3, \tau_4) \equiv \langle V_{ge}(\tau_1) V_{ge}(\tau_2) V_{ge}(\tau_3) V_{ge}(\tau_4) \rangle, \quad (2)$$

with

$$V_{\rm ge}(\tau) = \exp\left(\frac{i}{\hbar}H_g\tau\right)V_{\rm ge}\exp\left(-\frac{i}{\hbar}H_e\tau\right),\tag{3a}$$

$$V_{\rm eg}(\tau) = \exp\left(\frac{i}{\hbar}H_3\tau\right) V_{\rm eg} \exp\left(-\frac{i}{\hbar}H_g\tau\right), \qquad (3b)$$

Here,  $V_{eg}$  is the electronic transition dipole moment which depends on the nuclear coordinates of the system. Later, we will employ the Condon approximation.  $H_g$  and  $H_e$  are the ground and excited state vibrational Hamiltonians. Using the fact that the correlation function is invariant under time translation, it can be shown that

$$R_{1}(t_{3},t_{2},t_{1}) = F(t_{1},t_{1}+t_{2},t_{1}+t_{2}+t_{3},0),$$

$$R_{2}(t_{3},t_{2},t_{1}) = F(0,t_{1}+t_{2},t_{1}+t_{2}+t_{3},\tau_{1}),$$

$$R_{3}(t_{3},t_{2},t_{1}) = F(0,t_{1},t_{1}+t_{2}+t_{3},t_{1}+t_{2}),$$

$$R_{4}(t_{3},t_{2},t_{1}) = F(t_{1}+t_{2}+t_{3},t_{1}+t_{2},t_{1},0),$$
(4)

We mention for what follows that when the field is turned on, the first interaction takes place at time  $t-t_1-t_2-t_3$  and creates an optical coherence which evolves for a period  $t_1$ . The second interaction occurs at time  $t-t_2-t_3$  and converts the coherence state into a population state which evolves for a period  $t_2$ . The third interaction occurs at time  $t-t_3$  and creates a second electronic coherence that evolves for time  $t_3$ . At times  $t > t_3$  the optical polarization is calculated.

## III. FOUR-POINT CORRELATION FUNCTION FOR BOTH LINEAR AND QUADRATIC COUPLING

Consider a system with modes that exhibit both linear and diagonal quadratic electron-phonon coupling. Let  $\omega''$ and  $\omega'$  be the ground and excited electronic state frequencies of such a mode. The dimensionless normal coordinate for the ground state is defined as q and the dimensionless linear displacement between the potential energy minima of the two states as d. The vibrational Hamiltonian for the ground state is J. Chem. Phys., Vol. 110, No. 2, 8 January 1999

$$H_{g} = \hbar \,\omega''(a^{+}a + 1/2), \tag{5}$$

with  $a^+$  and a the raising and lower operators, i.e.,  $q = 2^{-1/2}(a^+ + a)$ . The exact Hamiltonian for the excited state  $H_e$  is given in Ref. 22. We do not give it here, the reason being that even the expression for the two-point correlation function it would give rise to is quite unwieldy. (It is the bilinear terms in  $H_e$  involving  $a^+$  and a that are responsible for this.) For this reason we proposed the following approximate expression for  $H_e$ :22

$$H_{e} = \hbar \omega' [(a^{+}a + \frac{1}{2}) + (2 - r^{-1})d(a^{+} + a)/ \sqrt{2} + (2 - r^{-1})d^{2}/2] + \hbar \Omega, \qquad (6)$$

where  $r = \omega'/\omega''$  and  $\hbar\Omega$  is the adiabatic electronic energy gap. This Hamiltonian is adequate for  $r \ge 0.7$  (without loss of generality we take  $\omega' < \omega''$ ). The adiabatic gap is related to the vertical gap by

$$\Omega_{\nu} = \Omega + S_{\rm eff} \,\,\omega',\tag{7}$$

where

$$S_{\rm eff} = (2 - r^{-1})d^2/2,$$
 (8)

with  $S_{\text{eff}}$  an effective Huang–Rhys factor that equals  $S = d^2/2$  when  $\omega' = \omega''$ . The approximate  $H_e$  was used in Ref. 22 to obtain the linear response (two-point correlation) function J(t;T), for the case of no phonon damping. Coherent states for the phonons, rather than number states, were used in the derivation. We have used the same approach to obtain the temperature-dependent four-point correlation function  $[F(\tau_1, \tau_2, \tau_3, \tau_4)$  for the case of no damping, Eq. (A4) of the Appendix]. It can be used to obtain the echo response functions  $\{R_\alpha(t_3, t_2, t_1)\}_{\alpha=1}^4$ , Eq. (4), which can be used to calculate the third-order polarization for any four-wave mixing experiment.

We consider the impulsive stimulated photon echo in which the three applied pulses are infinitely short. The integrated intensity of the echo signal  $S_{\text{SPE}}$  is:

$$S_{\text{SPE}}(\tau',\tau) = \int_0^\infty dt \big| \mathscr{R}(t,\tau,\tau') \big|^2 \big| \chi(t-\tau') \big|^2, \tag{9}$$

where  $\tau'$  is the delay between the first and second pulses and  $\tau$  is the delay between the second and third pulses. Here,  $\mathscr{R}(t_3, t_2, t_1)$  is the echo response function defined as

$$\mathscr{R}(t_3, t_2, t_1) \equiv R_2(t_3, t_2, t_1) + R_3(t_3, t_2, t_1).$$
(10)

While  $\mathscr{R}(t_3, t_2, t_1)$  governs the homogeneous (dynamical) contribution to the dephasing,  $\chi(t_3 - t_1)$  governs the static inhomogeneous contribution. The form of the inhomogeneous broadening term  $\chi$ , vide infra, results in the maximum of the echo appearing at time  $t = \tau'$  after the interaction with the third pulse which we can now consider to have occurred at t=0. For  $t > \tau'$ , the echo decays due to dephasing. If in the frequency domain the inhomogeneous broadening is far greater than the homogeneous broadening,  $\chi(t - \tau')$  in Eq. (9) can be approximated by a delta function which results in

$$S_{\text{SPE}}(\tau',\tau) = |\mathscr{R}(\tau',\tau,\tau')|^2.$$
(11)

Figure 1 shows an impulsive SPE signal at 300 K for a linearly and quadratically coupled mode defined by  $\omega''$ 



FIG. 1. Impulsive stimulated photon echo signal for a system with very large inhomogeneous broadening and a mode that exhibits both linear and quadratic coupling. It was calculated using Eqs. (A4), (10) and (11) with  $\omega'' = 200 \text{ cm}^{-1}$ ,  $\omega' = 150 \text{ cm}^{-1}$ , S = 2.0,  $\gamma = 0$  and T = 300 K.

=200 cm<sup>-1</sup>,  $\omega' = 150$  cm<sup>-1</sup> and S = 2. It was calculated using Eqs. (A4), (10), and (11). (Again,  $\tau'$  is the delay between the first and second pulses and  $\tau$  the delay between the second and third.) Although damping is not included, Fig. 1 reflects an important feature due to quadratic electron–phonon coupling; namely, quantum beats due to interference of the ground and excited state phonon waves. This is more easily seen by looking at a slice in the frequency domain obtained from Fig. 1. Figure 2 was obtained by performing a Fourier transform of Eq. (11) with  $\tau = 1$  fs as follows:

$$S_{\text{SPE}}(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty d\tau' \, S_{\text{SPE}}(\tau') \exp[(i\omega - \gamma)\tau']. \quad (12)$$

(A damping rate,  $\gamma$ , corresponding to 3 cm<sup>-1</sup> was introduced.) In addition to the ground and excited state fundamentals  $\omega''$  and  $\omega'$ , one observes their difference frequency  $\Delta \omega = 50 \text{ cm}^{-1}$  and its multiple  $2\Delta \omega = 100 \text{ cm}^{-1}$ . The latter two are responsible for the quantum beats indicated by the arrow in Fig. 1. Note that in the absence of temperature-



FIG. 2. Frequency domain slice obtained from Fig. 1 by taking the Fourier transform of Eq. (11) [Eq. (12)] with  $\tau$ =1 fs and uniform damping corresponding to frequency domain widths of 3 cm<sup>-1</sup>.

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dependent data the features in Fig. 2 might be incorrectly assigned to three or four distinct linearly coupled modes. In the calculations which follow a Gaussian profile is used for the inhomogeneous function  $\chi$ :

$$\chi(t_3 - t_1) = \exp[-\frac{1}{2}w^2(t_3 - t_1)^2], \qquad (13)$$

where the parameter w is related to the full width half maximum (FWHM) of the inhomogeneous profile in the frequency domain by FWHM=2.35 w.

### IV. FOUR-POINT CORRELATION FUNCTION WITH DAMPING FOR LINEAR ELECTRON-VIBRATION COUPLING

The correlation function given by Eq. (A4) is a new result which we used in Sec. III to demonstrate the quantum beats that arise from quadratic as well as linear coupling. Unfortunately, inclusion of phonon damping and pure electronic dephasing would lead to a very complicated correlation function which, from a computational point of view, is impractical. This is not the case for linear coupling only. By setting  $\omega' = \omega''$  in Eq. (A4) one obtains

$$F(\tau_1, \tau_2, \tau_3, \tau_4) = \exp[-g(\tau_1 - \tau_2) + g(\tau_1 - \tau_3) -g(\tau_2 - \tau_3) - g(\tau_1 - \tau_4) +g(\tau_2 - \tau_4) - g(\tau_3 - \tau_4)],$$
(14)

which is identical to Eq. (8.14) of Ref. 36. At this point we use the expression for the line shape function g(t;T) from Ref. 22 which is the sum of a phononic (ph) and electron (el) contribution:

$$g(t;T) = g^{\text{ph}}(t;T) + g^{\text{el}}(t;T),$$
 (15)

where

$$g^{\rm ph}(t;T) = \sum_{j=1}^{N} g_{j}^{\rm ph}(t;T), \qquad (16)$$
$$g_{j}^{\rm ph}(t;T) = S_{j} \{ \coth(\beta \hbar \omega_{j}/2) - e^{-\gamma_{j}|t|/2} \}$$

$$\times [\coth(\beta \hbar \,\omega_j/2) \cos(\omega_j t) - i \sin(\omega_j t)] \},$$
(17)

and

$$g^{\rm el}(t;T) = \gamma_{\rm el} |t|/2, \tag{18}$$

where *T* is the temperature, not to be confused with a dephasing time. Insofar as the temperature dependencies of  $\gamma_j$  and  $\gamma_{el}$  are concerned, one needs to consider the different mechanisms and feed their temperature dependencies into the line shape functions, which is standard procedure.

We note that the line shape function, g(t;T) defined by Eq. (15) and the equations that follow yield a single-site absorption spectrum, which is given by

$$\sigma(\omega;T) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty dt \exp[-g(t;T) + i\omega t], \qquad (19)$$

for which the ZPL and multiphonon transitions carry Lorentzian profiles. In amorphous hosts structural heterogeneity can result in a distribution of frequencies for a Franck– Condon active phonon. The modification of the line shape



FIG. 3. Impulsive photon echo (IPE) signals calculated with Eq. (20) for a model system ( $\omega_j$ =30 cm<sup>-1</sup>,  $\gamma_j$ =20 cm<sup>-1</sup>,  $\gamma_{el}$ =2.5 cm<sup>-1</sup>, w=64 cm<sup>-1</sup> and T=0 K) for S=0.01 (top), 0.10 (middle) and 0.50 (bottom). PSB denotes phonon sideband. For comparison, the corresponding single-site absorption spectra calculated according to Eq. (19) are shown in the right panel.

function required to take into account such inhomogeneity is straightforward. For example, if one desires Voigt profiles, one need only multiply  $\exp(-\gamma_j |t|/2)$  in Eq. (17) by  $\exp(-\Delta_j^2 t^2/2)$ , where  $\Delta_j^2$  is the variance of the distribution of  $\omega_i$  frequencies.

The impulsive two-pulse echo (IPE) can be calculated by setting  $\tau=0$  in Eq. (9). Using the echo response function,  $\mathscr{R}(\tau',0,\tau')$ , obtained from Eq. (14) in Eq. (9) yields the integrated impulsive two-pulse echo signal,<sup>36</sup>  $S_{\text{IPE}}(\tau';T)$ :

$$S_{\text{IPE}}(\tau';T) = \int_{0}^{\infty} dt \, \exp[-w^{2}(t-\tau')^{2}] \\ \times \exp\{-2 \operatorname{Re}[2g(t;T) + 2g(\tau';T) \\ -g(t+\tau';T)]\}.$$
(20)

The time resolved two-pulse echo is

$$S_{\text{IPE}}(t;\tau';T) = \exp[-w^2(t-\tau')^2] \\ \times \exp\{-2\operatorname{Re}[2g(t;T)+2g(\tau';T) \\ -g(t+\tau';T)]\}.$$
(21)

Figure 3 shows 0 K results for a linearly coupled mode  $(\omega_j = 30 \text{ cm}^{-1}, \gamma_j = 20 \text{ cm}^{-1}, \gamma_{el} = 2.5 \text{ cm}^{-1}$  and  $w = 64 \text{ cm}^{-1}$ ) for three values of S: 0.01, 0.1, and 0.5. Integrated IPE signals calculated with Eq. (20) are given in the left panel and the corresponding single-site absorption spectra

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calculated with Eq. (19) in the right panel. For S = 0.01, the ZPL of a width 2.5  $cm^{-1}$  dominates the absorption spectrum as expected for such a small S value. Correspondingly, multiphonon transitions make a negligible contribution to the echo signal which is dictated by the ZPL. The decay of the signal is single exponential according to echo  $\exp(-2\gamma_{\rm el}\tau')$ , where  $\tau'$  is the time delay, and  $\gamma_{\rm el}(s^{-1})$  $=2\pi c \gamma_{el}(cm^{-1})$  with  $\gamma_{el}(cm^{-1})=2.5.^{38}$  For S=0.1, the (1,0) phonon transition appears in the single-site absorption spectrum. Its appearance is reflected by that of the fundamental beat at 1.1 ps which is the period  $(\phi_i)$  for  $\omega_i = 30$  $cm^{-1}$ . Increasing S to 0.5 results in resolution of the beat due to sharpening of the feature labeled as PSB (phonon sideband). This sharpening or faster (free-induction) decay which precedes the echo is due to the increase in the Franck-Condon (FC) factors of multiphonon transitions. (The contribution from the slowly decaying ZPL component to the signal at  $\sim 0$  ps is negligible.) One half the inverse of the width of the PSB is an effective or average width for the overall profile of the multiphonon transitions that contribute to the absorption band vide infra. The line shape function g(t;T) of Eq. (15) leads to widths for the cold phonon absorption progression  $n''_{j}0 \rightarrow n'_{j}=0,1,\ldots$  of  $\gamma_{\rm el}=n'_{j}\gamma_{j}$ .<sup>39</sup> The (1,0) absorption transition of Fig. 3 should carry a width of 22.5  $cm^{-1}$ . This was confirmed by "ruler" measurement of the (1,0) band for S = 0.5.<sup>40</sup> Because the resolved fundamental beat in the echo signal for S=0.5 corresponds to the (1,0) absorption transition, the width of the beat profile is inversely proportional to the width of the (1,0) transition. Since we have defined  $\gamma_{el}$  and  $\gamma_j$  as FWHM contributions, the width  $\Gamma(s)$  of the beat equals  $2^{-1}(\gamma_{el} + \gamma_{ph})^{-1}$ , the inverse of the decay constant for the beat, where the unit of  $\gamma_{el}$  and  $\gamma_i$  is circular frequency. Thus,  $2^{-1}\Gamma^{-1}$  is the width of the (1,0) absorption transition, as confirmed by ruler measurement. [To convert to cm<sup>-1</sup> one need multiply  $2^{-1}\Gamma^{-1}$  by  $(2\pi c)^{-1}$ .] That  $\gamma_{el}$  adds to the homogeneous widths of the multiphonon transition has a physical basis which is that the phonon levels build on the zero-point vibrational level. Thus, phononic transitions cannot be sharper than the ZPL. The question arises as to when the contribution from  $\gamma_{el}$  is negligible. For typical dye molecules in amorphous solids at liquid helium temperatures it is, since  $\gamma_{el} \ll 1 \text{ cm}^{-1} (T_2^*)$  $\geq$  10 ps).<sup>41,42</sup> However, this situation may not hold at high temperatures. For example, the dependence of  $\gamma_{\rm el}(T_2^*)$  on temperature (5–100 K) for APT in glassy water<sup>13</sup> and glassy ethanol<sup>14</sup> was satisfactorily explained using the exchange coupling model of Jackson and Silbey.<sup>19</sup> Theoretical extrapolation to room temperature yielded an estimate of  $\sim 0.3$  ps for  $T_2^*$  for both systems. However, the frequency of the exchange coupling mode for both systems is  $\sim 50 \text{ cm}^{-1}$ , which is considerably higher than observed for dye/polymer and dye/protein systems. Thus, it is possible that, in certain systems,  $T_2^*$  could approach 0.1 ps, which is comparable to the time scales for optical coherence loss and solvation dynamics due to low frequency modes that have been reported for dyes in liquids at room temperature.

Figure 4 is a continuation of Fig. 3 with S = 1.7, which corresponds to strong coupling. The three-dimensional (3D) graph calculated with Eq. (21) shows the behavior of the



FIG. 4. Continuation of Fig. 3 with S = 1.7. The 3D graph is the IPE signal as a function of t and  $\tau'$  calculated with Eq. (21). The time-integrated signal calculated with Eq. (20) is shown in the lower frame. Inset B, with the PSB cutoff, shows the phonon quantum beats and the slow decay due to the ZPL. The single site absorption spectrum calculated with Eq. (19) is given in inset (A).

echo along the  $t = \tau'$  diagonal. Following the rapid decay of the intense PSB features associated with the overall profile of the multiphonon transitions, the fundamental beat at 1.1 ps and its first overtone at 2.2 ps are observed. (Since the FC progression in the frequency domain is periodic in  $\omega_i$ , the beat pattern is periodic with features at  $\phi_i, 2\phi_i, \ldots$ , where  $\phi_i$  is the period of the fundamental beat, 1.1 ps for the case at hand.) The time-integrated IPE signal calculated with Eq. (20) is given in the bottom frame. The width of the PSB is  $\sim$ 160 fs which corresponds to a multiphonon profile width of 65 cm<sup>-1</sup> which can be compared with  $S\omega_i = 51$  cm<sup>-1</sup>, where  $S\omega_i$  is approximately the expected width.<sup>43</sup> Inset A is the single-site absorption spectrum [Eq. (19)] with a and b the one- and two-phonon transitions. The second overtone also appears. Folding of the widths of the phonon transitions is apparent. The time-integrated signal with the PSB cutoff is shown in inset B. The correspondence between the ZPL and the beats and the ZPL and multiphonon transitions in absorption is clear.

We next turn to the temperature dependence of the IPE signal. Figure 5 calculated with Eq. (21) shows results for a model system with  $\omega_j = 25 \text{ cm}^{-1}$ , S = 0.30,  $\gamma_j = 10 \text{ cm}^{-1}$ ,  $w = 64 \text{ cm}^{-1}$  and  $\gamma_{\text{el}}(T) = 8\bar{n}(\omega_q^r) \text{ cm}^{-1}$ , where  $\omega_q^r = 50 \text{ cm}^{-1}$  is the ground state frequency of the exchange coupling mode responsible for the pure electronic dephasing.  $\bar{n}(\omega_q^r)$  is the thermal occupation number  $[\exp(\hbar\omega_q^r/kT) - 1]^{-1}$ . This



FIG. 5. IPE signals as a function of temperature calculated with Eq. (21) for a model system  $[\omega_j=25 \text{ cm}^{-1}, S=0.30, \gamma_j=10 \text{ cm}^{-1}, w=64 \text{ cm}^{-1} \text{ and} \gamma_{el}(\text{cm}^{-1})=8\bar{n}(\omega_q^{"})$  where  $\omega_q^{"}=50 \text{ cm}^{-1}$ ]. The top, middle and bottom graphs are for 15, 25 and 100 K, respectively.

model system mimics quite closely APT in glassy ethanol.<sup>14</sup> The top, middle and bottom graphs corresponds to 15, 25, and 100 K, respectively. (Note the changes in time scales.) For comparison of the three  $t, \tau'$  graphs it is useful to know the values of the ZPL FC factor which is given by  $\exp[-S(2\bar{n}\omega_i)+1]$ . They are 0.70, 0.50 and 0.18 for 15, 25 and 100 K. At 15 K the ZPL is strongly allowed and  $\gamma_{el}$  $= 0.07 \text{ cm}^{-1}$  which corresponds to an echo decay constant of  $38 \text{ ps}^{-1}$ . The ZPL contribution dominates the signal seen in the top graph of Fig. 5. Because of the time scale the PSB appears as a sharp spike near  $t = \tau' = 0$ . At 25 K, the FC factor of the ZPL has decreased by 30% and its width is  $\gamma_{\rm el} = 0.50 \text{ cm}^{-1}$ . Its echo decay constant is 5.3 ps<sup>-1</sup>. Following the decay of the PSB, whose amplitude and width have increased, one observes the one-quantum beat at 1.3 ps which is the period of  $\omega_i = 25 \text{ cm}^{-1}$ . Its overtone is also visible and is followed by the relatively slowly decaying ZPL component. At 50 K the ZPL is barely observable on the scale used in Fig. 5 (results not shown). By 100 K, the FC factor of the ZPL is only 0.18 and  $\gamma_{el} = 7.6 \text{ cm}^{-1}$ . Its echo decay constant is  $0.35 \text{ ps}^{-1}$  which means that the ZPL component of the decay should appear near the tail of the PSB. However it, as well as the beats, is too weak to be observable in the bottom graph of Fig. 5. The physics conveyed by Fig. 5 has been observed by Saikan et al. in their accumulated photon echo (APE) studies of octaethylporphine in polystyrene.<sup>34</sup>

As a final application we present results for the special



FIG. 6. Impulsive photon echo signals calculated as Fig. 4 at T=0 K for the special pair absorption band of the bacterial reaction center characterized by two linearly coupled modes ( $\omega_m = 30 \text{ cm}^{-1}$ ,  $\gamma_m = 20 \text{ cm}^{-1}$ ,  $S_m = 1.7$ ;  $\omega_{sp} = 120 \text{ cm}^{-1}$ ,  $\gamma_{sp} = 25 \text{ cm}^{-1}$ ,  $S_{sp} = 1.5$ ; and  $w = 64 \text{ cm}^{-1}$ ,  $\gamma_{el} = 2.5 \text{ cm}^{-1}$ ). The 3D graph shows the fast decay due to the PSB (a), phonon quantum beats (b)–(e) and the slow decay due to the ZPL. For comparison the time-integrated signals are shown in the lower frame.

pair absorption band (P870) of the bacterial reaction center of Rhodobacter sphaeroides. Photochemical hole burning studies of P870 revealed that<sup>44</sup> it is characterized by strong electron-phonon coupling involving two modes with frequencies  $\omega_m = 30 \text{ cm}^{-1}$  and  $\omega_{\text{sp}} = 120 \text{ cm}^{-1}$  and Huang-Rhys factors of  $S_m = 1.8$  and  $S_{\text{sp}} = 1.5$  (where sp denotes special pair and *m* the mean frequency of low frequency protein phonons). Based on the results of Ref. 22 we used  $\gamma_{sp}=25$ cm<sup>-1</sup>,  $\gamma_m = 20$  cm<sup>-1</sup> and w = 64 cm<sup>-1</sup> for the calculations. More recently, Schellenberg *et al.*<sup>35</sup> reported the results of APE experiments performed on P870 at 1.4 K. Following a fast ( $\leq 100$  fs) initial decay due to multiphonon excitation (our PSB), they observed a much weaker decay due to the ZPL with a decay constant determined by the primary charge separation time of 1.9 ps. This time corresponds to  $\gamma_{el} = 2.5$  $cm^{-1}$  which was used in our calculations. An effective S value of 1.7 was determined which most likely corresponds to the 30  $\text{cm}^{-1}$  protein phonons identified by hole burning. Quantum beats were not observed in Ref. 35 and, thus, a mode frequency(ies) could not be determined. Thus, except for  $\gamma_{\rm el} = 2.5 \text{ cm}^{-1}$ , we used the hole burning values for all parameters.

The results are shown in Fig. 6. The 3D graph calculated according to Eq. (21) shows five features: (a)-(e) plus the relatively slowly decaying ZPL but note that feature (a), due

mainly to the PSB, is cut off. The periods of  $\omega_{\rm sp} = 120 \text{ cm}^{-1}$ and the combination band  $\omega_{\rm sp} + \omega_m = 150 \text{ cm}^{-1}$  are 277 and 220 fs. Thus, they are buried by the PSB. The signal in the lower frame with the feature at  $t \approx 0$  labeled as PSB is time integrated [Eq. (20)]. The width of the PSB is 54 fs which corresponds to a width of 196 cm<sup>-1</sup> for the multiphonon profile in the frequency domain. This value is close to the anticipated approximate value of  $S_m \omega_m + S_{sp} \omega_{sp} = 231 \text{ cm}^{-1}$ . Features (b)–(d) can be assigned as follows: (b), (c) and (e) are the first, second and fourth overtones of the fundamental quantum beat of the special pair mode while beat (d) is due to both the fundamental beat of the 30  $cm^{-1}$  mode with a period of 1.1 ps and the third harmonic of the special pair fundamental beat (see inset of bottom frame). With Fig. 6 the difficulty in observing the ZPL decay component and the quantum beats for strong electron-phonon coupling is apparent (see also Fig. 5). As mentioned, Schellenberg et al. were able to detect the relatively weak ZPL component. However, quantum beats are not evident in their time-integrated echo signal, whereas Fig. 6 indicates that if the ZPL component is observed, quantum beats should also be observed. A likely reason for the discrepancy is that in the APE experiment  $\sim 100$  fs pulses with a width of  $\sim 7$  nm were used to pump P870 considerably to the red of its absorption maximum where the probability of exciting the  $120 \text{ cm}^{-1}$  special pair mode is low. This would significantly suppress the quantum beats seen in Fig. 6. In addition, it has been suggested that the one-phonon absorption due to a single mode at  $120 \text{ cm}^{-1}$ could be due to two or more modes in the vicinity of 120 cm<sup>-1</sup>.<sup>45,46</sup> This would have the effect of washing out the structure especially if the damping constants were significantly less than 25  $cm^{-1}$ .

#### **V. CONCLUSIONS**

A new expression for the third-order response function for finite temperatures was obtained for a chromophore whose phonon modes exhibit linear electron-phonon coupling. The line shape function g(t;T) from Ref. 22 used in the response functions includes phonon damping  $(\gamma_i)$  and pure electronic dephasing ( $\gamma_{el}$ ). In that paper it was shown that g(t;T) yields physically reasonable single-site absorption and hole-burned spectra in which  $\gamma_{el}$  contributes to the widths of the phononic transitions and folding of the widths of phonon progression members occurs. Applications of the nonlinear response functions were made to the IPE. Calculated IPE signals for model systems and the special pair band of the bacterial reaction clearly revealed the initial fast decay due to the envelope of multiphonon transitions, quantum beats and the decay of the fundamental beat and the decay due to dephasing of the ZPL and how these features depend on the strength of the electron-phonon coupling and temperature. Based on the results of Ref. 22 it was expected that pure electronic dephasing would contribute to the decay of the quantum beats and this is indeed the case. It was suggested that<sup>13</sup> this contribution could be significant at room temperature for systems whose modes are sufficiently underdamped. The features of the echo profiles/signals were correlated with those of single site absorption spectra which are closely related to hole-burned spectra. The correlations illustrate the complementarity of photon echo and hole burning spectroscopies.

As discussed in Refs. 13, 14 and 20, the combination of temperature-dependent hole burning and echo studies of optical coherence loss of chromophores in glasses and the corresponding liquids should lead to a much better understanding of the inertial modes of liquids responsible for ultrafast dephasing. Our response functions can be helpful in such studies. The question arises as to what types of chromophores are best suited for such studies. The answer is rigid molecules devoid of FC active low frequency intramolecular modes that can interfere with the low frequency inertial (librational) modes of interest. In addition, the linear electron-phonon coupling of such a chromophore in the glass should be weak so that the zero-phonon hole and the phonon sideband structure can be studied up to a temperature sufficiently high to allow for convincing theoretical interpretation of the data. Examples of such a system are Alphthalocyanine tetrasulphonate in glassy water and ethanol. Other phthalocyanines as well as rhodamine and oxazine dyes should also be suitable. Cyanine dyes such as IR 144, which was used in Ref. 20, should be avoided.

The nonlinear response functions can be used to predict finite pulse measurements<sup>47</sup> but at the expense of much longer computational times. Using finite pulses the echo signal can be determined as a function of the pump frequency as it is tuned from the low to high energy sides of the absorption band. The frequency domain analogue of this has been reported with hole burning of the special pair band of the bacterial reaction center.<sup>44</sup>

A temperature-dependent four-point correlation function without damping was calculated for a system whose modes are both linearly and quadratically coupled and used to illustrate quantum beats due to the quadratic coupling which produces a mode frequency change upon electronic excitation. The intensities of such beats are strongly temperature dependent and, therefore, can be distinguished from beats due to linearly coupled modes. Inclusion of phonons damping should be possible but would result in a four-point correlation function of very considerable complexity. A solution for the linear response function is given in Ref. 22.

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### APPENDIX

Here we outline the derivation of  $F(\tau_1, \tau_2, \tau_3, \tau_4)$  in the Condon approximation is outlined. The four-point correlation function is given by:

$$F(\tau_{1},\tau_{2},\tau_{3},\tau_{4}) = \langle e^{iH_{g}\tau_{1}/\hbar}e^{iH_{e}(\tau_{2}-\tau_{1})/\hbar}e^{iH_{g}(\tau_{3}-\tau_{2})/\hbar} \times e^{iH_{e}(\tau_{4}-\tau_{3})/\hbar}e^{-iH_{g}\tau_{4}\hbar}\rho_{g} \rangle.$$
(A1)

Following Ref. 22, where coherent states for the phonon field rather than number states were used to evaluate the two-point correlation function, we use the following closure relation for coherent states to evaluate Eq. (A1):

$$\frac{1}{\pi} \int d^2 z \frac{|z\rangle\langle z|}{\langle z|z\rangle} = 1,$$
(A2)

where  $d^2z = d(\operatorname{Re} z)d\operatorname{Im}(z)$ . Applying Eq. (A2) to Eq. (A1) yields

$$F(\tau_{1},\tau_{2},\tau_{3},\tau_{4}) = \frac{1}{Q\pi} \int_{-\infty}^{\infty} \frac{d^{2}z}{\langle z|z \rangle} \langle z|e^{iH_{g}\tau_{1}\hbar}e^{iH_{e}(\tau_{2}-\tau_{1})/\hbar} \\ \times e^{iH_{g}(\tau_{3}-\tau_{2})/\hbar}e^{-i'H_{g}\tau_{4}/\hbar}e^{-\beta H_{g}}|z \rangle,$$
(A3)

where  $Q \equiv \text{Tr}(e^{-\beta H_g})$ . Evaluation of the integral in Eq. (A3) leads to  $(\Omega = 0)$ 

$$F(\tau_1, \tau_2, \tau_3, \tau_4) = \frac{\exp(-\beta\hbar \,\omega''/2)}{Q} \exp\left(\frac{1}{2}i(\,\omega'' - \omega'\,) \times (\tau_{12} + \tau_{34}) \times b_1^{-1} \exp(b_1^{-1}b_2 + b_3)\right),$$

where  $\tau_{ij} = \tau_i - \tau_j$  and

$$b_1 = 1 - e^{i\omega'(\tau_{21} - \tau_{34}) - \beta\hbar\omega'' + i\omega''\tau_1} e^{i\omega''(\tau_{34} - \tau_2)}, \tag{A5}$$

$$b_{2} \equiv S_{\text{eff}} e^{-\beta \hbar \omega''} [-e^{-i\omega'' \tau_{4}} + e^{i\omega' \tau_{43} - i\omega'' \tau_{4}} - e^{i\omega' \tau_{43} + i\omega'' (\tau_{32} - \tau_{4})} + e^{i\omega' (\tau_{21} + \tau_{43}) + i\omega'' (\tau_{32} - \tau_{4})} ] [-e^{i\omega'' \tau_{1}} + e^{i\omega' \tau_{21} + i\omega'' \tau_{1}} - e^{i\omega' \tau_{21} + i\omega'' (\tau_{12} - \tau_{3})} + e^{i\omega' (\tau_{21} - \tau_{34}) + i\omega'' (\tau_{12} + \tau_{3})} ], \quad (A6)$$

and

$$b_{3} \equiv S_{\text{eff}}(-2 + e^{i\omega'\tau_{21}} + e^{i\omega'\tau_{43}} + e^{i\omega''\tau_{32}} - e^{i\omega'\tau_{21} + i\omega''\tau_{32}} - e^{i\omega'\tau_{43} + i\omega''\tau_{32}}),$$
(A7)

where the effective Huang–Rhys factor  $S_{\text{eff}}$  is given by Eq. (8).

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- <sup>38</sup>We remind the reader that  $\gamma_{el}$  is the FWHM of the ZPL, thus the factor of 2 in the exponential rather than the more usual factor of 4.
- <sup>39</sup>Folding due to  $n'_j$  also occurs for hot  $n''_j \neq 0 \rightarrow n'_j$  transitions. Widths are given by  $\gamma_{el} + (n'_j + n''_j) \gamma_j$ .
- <sup>40</sup>Since  $\gamma_{el} = 2.5 \text{ cm}^{-1}$  is small relative to  $\gamma_j = 20 \text{ cm}^{-1}$ , the uncertainty is quite large,  $\pm 0.5 \text{ cm}^{-1}$ . Thus, we increased  $\gamma_{el}$  to 10 cm<sup>-1</sup> in order to convincingly confirm that the width is  $\gamma_{el} + \gamma_j$ .
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