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Photon Echoes as Collective Resonances in Multidimensional Vibrational Spectroscopy of Liquids

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I. INTRODUCTION

Multidimensional vibrational spectroscopy is a powerful tool for studying the dynamics of molecular and atomic liquids. An ideal time-domain technique that can be successfully carried out with very short pulses is the photon echo observed in high-order Raman or infrared measurements [1–6]. In off-resonant fifth-order Raman experiments the system interacts with two pairs of pulses, and a fifth pulse ($\mathbf{k}_f\omega_f$) generates the signal with the wavevector $\mathbf{k}_s = \pm(\mathbf{k}_1 - \mathbf{k}_1') \pm (\mathbf{k}_2 - \mathbf{k}_2') \pm \mathbf{k}_f$ (Fig. 1). The process is described by the fifth-order[1] response function $S^{(5)}$.

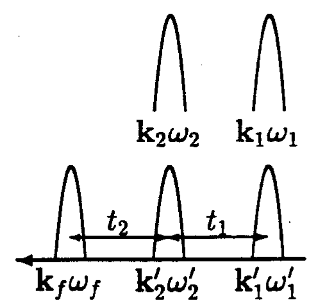


Fig. 1

A close connection between high-order photon echoes in the time domain and collective resonances in the frequency domain was established [7,8]. We compare below two models of a multilevel system with different types of broadening, which produce similar photon echo signals. We first study the effect of static and dynamic correlations in a multilevel system coupled to Brownian oscillator bath. We then consider a model in which the transition frequencies are equal; this corresponds to a harmonic oscillator with a continuous distribution of frequencies, and present numerical simulations of the echo signal. Finally, we analyze the frequency-domain susceptibility of a multilevel system and show how multiphoton resonances appear when the broadening of different levels is correlated. In the time domain these resonances show up as photon echo signals.

II. DYNAMIC CORRELATIONS IN THE BROWNIAN OSCILLATOR MODEL

We study the fifth-order echo signal in a multilevel system (Fig. 2) coupled the Brownian oscillator bath and analyze its dependence on the static and dynamic correlation of the frequencies ω_{ab} and ω_{bc}. We assume short pulses, and the signal is given by $|S^{(5)}(t_1,t_2)|^2$. We consider below only the terms that contribute to the photon echo signal (diagrams in Fig. 3(b)) and denote the contribution of these terms to the fifth-order response by $\mathcal{S}_{\text{PE}}^{(5)}$. We then have

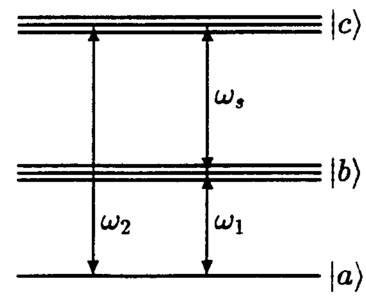


Fig. 2

[1]As far as nuclear dynamics is concerned, the technique has only two time intervals and this response function is equivalent to $S^{(2)}$. Similar resonant infrared results will be described by $S^{(2)}$.

$$S^{(5)}_{\rm PE}(t_1,t_2) = \langle\langle V_{cb}|\mathcal{G}_{bc}(t_2)\mathcal{V}_{bc,ba}\mathcal{G}_{ba}(t_1)\mathcal{V}_{ba,aa}|\rho_g\rangle\rangle + c.c.$$

Here $\mathcal{V}$ is the Liouville-space operator, V being the electronic polarizability, acting on an ordinary operator A through the commutator: $\mathcal{V}A = [V, A]$, and $\mathcal{G}(\tau)$ is the Liouville-space Green function for the system without the radiation field, $\mathcal{G}(\tau) = \theta(\tau)\exp\left(-\frac{i}{\hbar}\mathcal{L}\tau\right)$, $\mathcal{L} \equiv [H, A]$. The coupling to the bath results in fluctuations of the transition frequencies $\omega_{\nu\nu'}$ around $\omega^0_{\nu\nu'}$: $\omega_{ba} = \omega^0_{ba} + \delta\omega_{ba}(t)$, $\omega_{cb} = \omega^0_{cb} + \delta\omega_{cb}(t)$. Then the response function is

$$S^{(5)}_{\rm PE}(t_1,t_2) \propto e^{-i\omega^0_{ba}t_1 + i\omega^0_{cb}t_2}\left\langle \exp\left\{ -i\int_0^{t_1}\delta\omega_{ba}(\tau)\,d\tau + i\int_{t_1}^{t_1+t_2}\delta\omega_{cb}(\tau')\,d\tau'\right\}\right\rangle + c.c.$$

We can calculate the average by expanding the exponent in powers of $\delta\omega$ up to second order; this is known as the second-order cumulant expansion [6].

$$S^{(5)}_{\rm PE}(t_1,t_2) \propto \cos(\omega^0_{ba}t_1 - \omega^0_{cb}t_2)\exp\Big[-g_1(t_1) - g_2(t_2) + g_3(t_1+t_2) - g_3(t_1) - g_3(t_2)\Big], \quad (1)$$

with the line broadening functions

$$g_1(t) \equiv \int_0^t d\tau \int_0^\tau d\tau' \langle\delta\omega_{ba}(\tau)\delta\omega_{ba}(\tau')\rangle,$$
$$g_2(t) \equiv \int_0^t d\tau \int_0^\tau d\tau' \langle\delta\omega_{cb}(\tau)\delta\omega_{cb}(\tau')\rangle,$$
$$g_3(t) \equiv \int_0^t d\tau \int_0^\tau d\tau' \langle\delta\omega_{ba}(\tau)\delta\omega_{cb}(\tau')\rangle.$$

We next assume that $g_1(t) = g_2(t) \equiv g(t)$ and $g_3(t) = (1-\zeta)g(t)$, where the parameter ζ represents the correlation between the fluctuations $\delta\omega_{ba}$ and $\delta\omega_{cb}$. $\zeta = 1$ or 0 correspond to uncorrelated or fully correlated fluctuations, respectively. We further adopt the overdamped Brownian oscillator model for the correlation function of level fluctuations

$$\langle\delta\omega_{ba}(t)\delta\omega_{ba}(0)\rangle = \Delta^2 e^{-\Lambda t}.$$

where Δ is the magnitude and Λ^{-1} is the timescale of the fluctuations. In the static limit $\Lambda \ll \Delta$ we get $g(t) \approx \frac{\Delta^2 t^2}{2}$, and upon substituting in (1), we obtain

$$S^{(5)}_{\rm PE}(t_1,t_2) \propto \cos(\omega^0_{ba}t_1 - \omega^0_{cb}t_2)\exp\left\{-\frac{\Delta^2(t_1-t_2)^2}{2} - \Delta^2\zeta t_1 t_2\right\}. \quad (2)$$

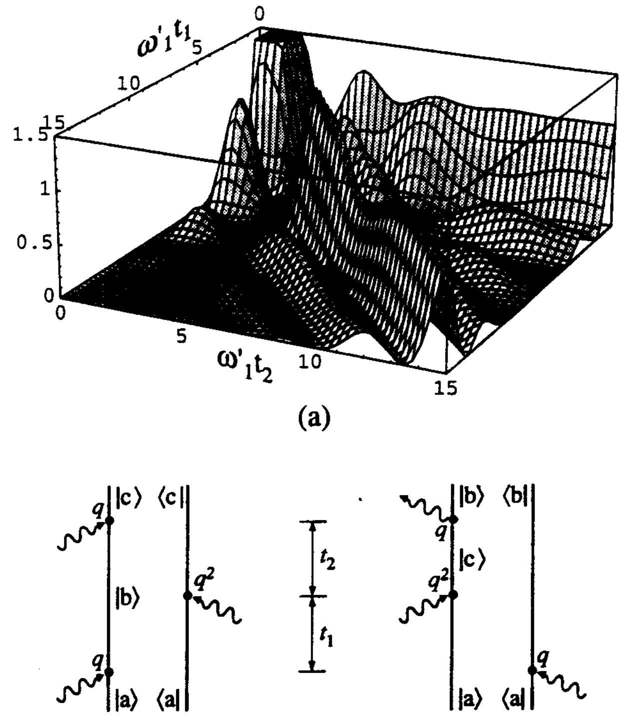
We get an echo signal at $t_1 = t_2$ if the levels are fully correlated ($\zeta = 0$). The temporal width of the echo signal is $\sim \Delta^{-1}$. Thus, the stronger the coupling strenght Δ, the sharper is the echo. In the case of partial correlation $\zeta \neq 0$ the echo (as it appears, for example in Fig. 3(a)) becomes less pronounced, and at $\zeta = 1$ the echo disappears completely.

As the dynamics of fluctuations becomes important (that is, Λ is comparable to or larger than Δ), the echo will be eroded as well; No echo is observed in the motional narrowing (homogeneous) limit $\Lambda \gg \Delta$ where $g(t) \approx \Gamma t$ with $\Gamma \equiv \Delta^2/\Lambda$ and

$$S^{(5)}_{\rm PE}(t_1,t_2) \sim \cos(\omega^0_{ba}t_1 - \omega^0_{cb}t_2)\exp\{-\Gamma(t_1+t_2)\}.$$

III. CONTINUOUS DISTRIBUTION OF HARMONIC OSCILLATORS

We now consider the case of fully correlated levels with $\omega_{ba} = \omega_{cb}$. This system is harmonic [1,9]. We use the Hamiltonian $H = H_0 - E(\mathbf{r},t)V$, where $H_0 = \hbar\omega_0(a^\dagger a + 1/2)$. We also need to specify how the electronic polarizability V depends on nuclear coordinates. With $V(q) = \alpha q$ the response is linear, and all $\mathcal{S}^{(n)}(t_n,\ldots,t_1)$ vanish for $n > 1$. We a-sume $V(q) = V_0 e^{\alpha q}$.



(a)

(b)

Fig. 3

We now consider the nonlinear response to lowest order in α. For $\mathcal{S}^{(5)}$ this is $\sim \alpha^4$. The reason is very simple: there are three interactions with the field, and in the lowest-order nonlinear response we should take one q^2 and two q interactions. This corresponds to expanding the electronic polarizability in the form $V(q) = \alpha q + \frac{1}{2}\alpha^2 q^2$. As a result of each interaction of the q type the system moves either one level up or one level down, whereas the q^2 interaction either moves the system by two levels or does not change its state at all. For the fifth-order response we then have,

$$\mathcal{S}^{(5)}(t_2,t_1;\omega_0) = \frac{V_0^3\alpha^4}{m^2\omega_0^2}\Big\{\cos[\omega_0 t_1] - \cos[\omega_0(t_1+t_2)] + \cos[\omega_0(t_1+2t_2)] - \cos[\omega_0(t_1-t_2)]\Big\}. \quad (3)$$

To introduce inhomogeneous broadening, we assume that the oscillator frequency ω_0 is distributed around some central frequency ω_1 with half-width γ:

$$f(\omega_0) = \frac{1}{2\pi}\frac{\omega_0\gamma}{(\omega_1^2-\omega_0^2)^2+\omega_0^2\gamma^2}. \quad (4)$$

The response is then calculated by averaging (3) over the distribution function (4). Hereafter we consider only the last term in (3) that produces the echo signal. In the underdamped limit $\omega_1 \gg \gamma/2$ we obtain

$$\mathcal{S}^{(5)}_{\rm PE}(t_2,t_1) = \frac{V_0^3\alpha^4}{4m^2(\omega_1')^2}\cos[\omega_1'(t_1-t_2)]e^{-\gamma|t_1-t_2|}. \quad (5)$$

This resembles Eq. (2). Since (5) is written for a harmonic oscillator, for which $\omega_{ba}^0 = \omega_{cb}^0$, the quantum beats, which show up in (2), disappear. Also, the levels of an oscillator are fully correlated, therefore the parameter ζ is zero. Finally, the difference in the echo profile vs $t_1 - t_2$ (Gaussian in (2) and exponential in (5)) reflects the different models used:

the former assumes Gaussian distributions of frequencies, whereas here the distribution is (4), and the parameter γ in (5) plays the role of Δ in (2).

In Fig. 3(a) we show the squared absolute value of the response function (5) as a function of t_1 and t_2 for $\gamma = \omega_1/2$. It is clearly seen that for $t_1 = t_2$ the response does not vanish for long times, resulting in the photon echo signal. The corresponding double-sided Feynman diagrams are given in Fig. 3(b).

IV. COLLECTIVE RESONANCES IN THE FREQUENCY DOMAIN

In this section we analyze the frequency-domain susceptibility of a multilevel system and show how partial correlation in the broadening leads to new multiphoton resonances. In the time domain these resonances show up as photon echo signals. The fifth-order susceptibility of a three-level system is [6]

$$\chi^{(5)}(-\omega_s; -\omega_1, \omega_2) = \frac{1}{\hbar^2}\rho_0 \sum_{\text{perm}} \sum_{a,b,c} P(a) V_{ab} V_{bc} V_{ca} \times \left\{ I_{ab}(\omega_1) I_{ac}(\omega_1 + \omega_2) + I_{ca}(\omega_1) I_{ba}(\omega_1 + \omega_2) - I_{ab}(\omega_1) I_{ca}(\omega_2) \right\} \quad (6)$$

Where $I_{\nu\nu'}(\omega) \equiv (\omega - \omega_{\nu\nu'} + i\Gamma_{\nu\nu'})^{-1}$ are the (frequency-domain) lineshape functions and the levels $|a\rangle$, $|b\rangle$, $|c\rangle$, are shown in Fig. 2. We are interested only in the last term, which gives rise to the desired resonance. In that case,

$$\chi^{(5)}(-\omega_s; -\omega_1, \omega_2) \propto \sum_{\text{perm}} I_{ab}(\omega_1) I_{ca}(\omega_2) = \frac{1}{\omega_1 - \omega_{ba} + i\Gamma} \cdot \frac{1}{\omega_2 - \omega_{ca} - i\Gamma} + c.c'.,$$

where $c.c'.$ denotes complex conjugation with simultaneous changing the signs of ω_1 and ω_2. We now assume that ω_{ba} and ω_{cb} are inhomogeneously broadened with a joint distribution $S(\omega_{ba}, \omega_{cb})$:

$$S(\omega_{ba}, \omega_{cb}) = NS(\omega_{ba})S(\omega_{cb}) \frac{\eta}{(\omega_{cb} - \omega_{ba} - \Omega)^2 + \eta^2}.$$

where N is a normalization factor and Ω represents an anharmonicity. This distribution represents partial correlation. In the limit of noncorrelated levels ($\eta \to \infty$) it factorizes as $S(\omega_{ba})S(\omega_{cb})$. In the other extreme of fully correlated levels ($\eta \to 0$), we have $S(\omega_{ba}, \omega_{cb}) \sim S(\omega_{ba})S(\omega_{cb})\delta(\omega_{cb} - \omega_{ba} - \Omega)$. Then,

$$\langle \chi^{(5)}(-\omega_s; -\omega_1, \omega_2) \rangle \propto \frac{1}{4\pi^2} \int d\omega_{ba} d\omega_{cb} S(\omega_{ba}) S(\omega_{cb}) \times \frac{\eta}{(\omega_{cb} - \omega_{ba} - \Omega)^2 + \eta^2} \cdot \frac{1}{\omega_1 - \omega_{ba} + i\Gamma} \cdot \frac{1}{\omega_2 - \omega_{ca} - i\Gamma} + c.c'. \quad (7)$$

Assuming that the distributions $S(\omega)$ are much broader than the homogeneous width Γ and the correlation parameter η, we have

$$\langle \chi^{(5)}(-\omega_s; -\omega_1, \omega_2) \rangle \propto S(\omega_1) S(\omega_2) \frac{1}{\omega_2 - 2\omega_1 - \Omega - i\varkappa} + c.c'., \qquad \varkappa \equiv \eta + 3\Gamma. \quad (8)$$

We thus obtained a new resonance with width $\varkappa$. If the two levels were fully correlated, that is, $\eta = 0$, the width would be determined by homogeneous broadening. We next show how this resonance corresponds to the photon echo in the time domain. The time-domain response function is related to the susceptibility as

$$\mathcal{S}^{(5)}_{\rm PE}(t_1, t_2) = \frac{1}{2\pi} \int d\omega_1 d\omega_2 \langle \chi^{(5)}(-\omega_s; -\omega_1, \omega_2) \rangle \exp\{-i\omega_1(t_1 + t_2) + i\omega_2 t_1\}. \quad (9)$$

Substituting (8) to (9), we get

$$\mathcal{S}^{(5)}_{\rm PE}(t_1, t_2) \propto e^{i\Omega t_2} e^{-\varkappa t_2} \int d\omega_1 S(\omega_1) S(2\omega_1 + \Omega) e^{i\omega_1(t_2 - t_1)} + c.c. \quad (10)$$

Assuming a Gaussian distribution, $S(\omega_1) = \exp\{-(\omega_1 - \omega_1^0)^2/2\Delta^2\}$. we have,

$$\mathcal{S}^{(5)}_{\rm PE}(t_1, t_2) \propto \cos[\Omega t_2 + \omega_1^0(t_2 - t_1)] \exp\left\{-\frac{\Delta^2(t_2 - t_1)^2}{2} - \varkappa t_2\right\}. \quad (11)$$

This is similar to the response function (2), derived in Sec. II with the correlation parameter $\varkappa$ playing the role of $\Delta^2\zeta$ in (2).

For a Lorentzian distribution $S(\omega_1) = \gamma/[(\omega_1^2 - \omega_1^0)^2 + \gamma^2]$ we obtain

$$\mathcal{S}^{(5)}_{\rm PE}(t_1, t_2) \propto \cos[\Omega t_2 + \omega_1^0(t_2 - t_1)] e^{-\varkappa t_2 - \gamma |t_1 - t_2|}. \quad (12)$$

This recovers the echo signal derived in Sec. III (Eq. (5)).

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