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Non-Markovian behavior in stimulated photon echoes: Waiting-time dependence

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By using stochastic theory, we analyze the non-Markovian temporal behavior in four types of photon echoes, including the two-pulse echo, stimulated echo, accumulated echo, and heterodyne-detected accumulated echo. In particular, the origin of the $\exp(-ct^3)$ dependence of the two-pulse echo in the limit of slow modulation is discussed in detail. It is also pointed out that, at the slow-modulation limit, the temporal behavior of the stimulated echo changes from $\exp(-ct^3)$ dependence to $\exp(-ct^2)$ dependence as the waiting time (the time interval between the second and the third excitation pulses) is varied.

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Recently, non-Markovian behavior of the photon echo has attracted much interest from both theoretical [1–4] and experimental [5,6] points of view. According to the stochastic theory of Kubo [7], the absorption spectrum varies from Lorentzian to Gaussian as the stochastic fluctuation of the transition frequency changes from the fast-modulation to the slow-modulation regime. Equivalently, the temporal behavior of the photon echo has been considered to vary from exponential to Gaussian as the frequency modulation slows down. This is true in the case where the inhomogeneous broadening is absent, and the previous calculation [1,3,4] of the non-Markovian photon echoes has been performed under this condition.

However, in the inhomogeneously broadened case and at the limit of slow modulation, the temporal behavior of the two-pulse echo signal has been shown to exhibit an $\exp(-ct^3)$ dependence [8,9], although the single-site absorption spectrum is Gaussian. One might consider this paradoxical because of the violation of the Fourier-transform relationship. Here, we discuss the origin of this behavior, and also clarify the non-Markovian behavior in four types of photon echoes, including the two-pulse echo, stimulated echo, accumulated echo, and heterodyne-detected accumulated echo (hereafter referred to as the heterodyne echo). In particular, we point out that the temporal behavior of the stimulated echo changes drastically depending on the waiting time T_W, the time interval between the second and the third excitation pulses. As is evident from Fig. 1, which classifies the four types of photon echoes, the two-pulse echo and accumulated echo correspond, respectively, to the extreme cases of the stimulated echo with $T_W=0$ and $T_W \gg \tau_c$, respectively, where τ_c is the correlation time of the frequency modulation. Therefore, we first discuss the temporal behavior of the stimulated photon echo.

In the stochastic theory, the third-order nonlinear polarization responsible for the stimulated echo is written as

$$P^{(3)}(t)=\int_0^\infty \int_0^\infty \int_0^\infty d\tau_1 d\tau_2 d\tau \int_0^\infty g(\omega_{21})d\omega_{21}\exp[(-i\omega_{21}-\gamma)\tau_2][1+\exp(-2\gamma\tau_1)]\exp[(i\omega_{21}-\gamma)\tau] \times E_3(t-\tau_2-t_{21}-T_W)E_2(t-\tau_2-\tau_1-t_{21})E_1^*(t-\tau_2-\tau_1-\tau)\langle \exp\phi_2\rangle \ , \quad (1)$$

where

$$\phi_2=-i\int_{\tau+\tau_1}^{\tau+\tau_1+\tau_2}\delta\omega(t)dt+i\int_0^\tau \delta\omega(t)dt \ . \quad (2)$$

This expression was derived by assuming a three-level system in which the third level has a long lifetime, like those of the triplet states of dye molecules [10]. 2γ is the natural decay rate of the excited state, $g(\omega_{21})$ is the inhomogeneous broadening, ω_{21} is the transition frequency, and t_{21} is the delay time between the first and the second pulses. The ground-state absorption recovery time was approximated to be infinite. The modulation of the transition frequency $\delta\omega$ is a Gaussian stochastic variable obeying

$$\langle \delta\omega(t_1)\delta\omega(t_2)\rangle=\Delta^2\exp\left[-\frac{|t_2-t_1|}{\tau_c}\right] . \quad (3)$$

Here, τ_c is the correlation time, and Δ is the magnitude of the frequency modulation. $\langle\ \rangle$ is the average over different realizations of a random perturbation. The function $\langle \exp\phi_2\rangle$, named the relaxation function [7], has previously been calculated [2,3] as

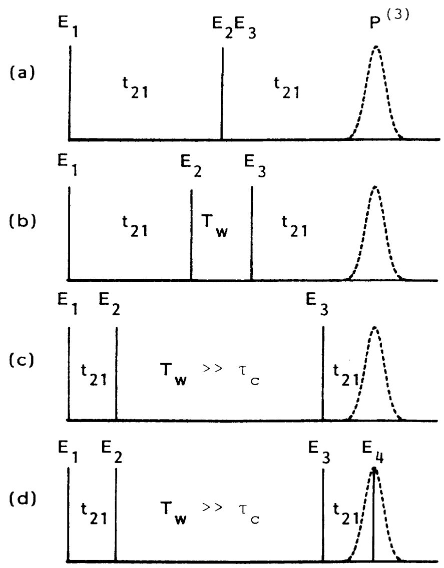

FIG. 1. Pulse sequence for four types of photon echoes, including the two-pulse echo (a), stimulated echo (b), accumulated echo (c), and heterodyne-detected accumulated echo (d). T_W is the waiting time and τ_c is the correlation time of the frequency modulation.

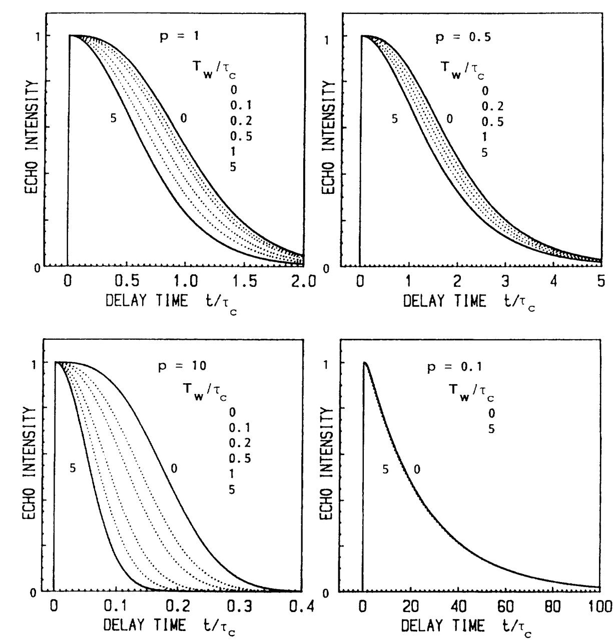

FIG. 2. Waiting time (T_W) dependence of stimulated photon echo signals. The frequency modulation parameter $p=\Delta\tau_c$ was varied from 0.1 to 10.

$$\langle \exp\phi_2 \rangle = \exp\left[-p^2 \left(\frac{\tau_2}{\tau_c} + e^{-(\tau_2/\tau_c)} + \frac{\tau}{\tau_c} + e^{-(\tau/\tau_c)} - 2 - e^{-(\tau_1/\tau_c)} (e^{-(\tau_2/\tau_c)} - 1)(e^{-(\tau/\tau_c)} - 1) \right) \right] \quad (4)$$

with $p=\Delta\tau_c$.

If we assume a δ function for the excitation field, and an extremely broad inhomogeneous spectrum, we get the relations $\tau=\tau_2=t_{21}$, $\tau_1=T_W$, and $t=2t_{21}+T_W$. Under these conditions, the expression for the signal intensity for the stimulated echo is

$$I_{SP}(t_{21},T_W) = \exp\left[-4p^2 \left(\frac{t_{21}}{\tau_c} + e^{-(t_{21}/\tau_c)} - 1 - \tfrac{1}{2} e^{-(T_W/\tau_c)} (e^{-(t_{21}/\tau_c)} - 1)^2 \right) \right] . \quad (5)$$

Equation (5) is plotted in Fig. 2. In the fast modulation case ($p=0.1$), the echo signal always exhibits an exponential decay, irrespective of the values of T_W. As the frequency modulation slows down, i.e., as the value of p increases, the echo decay curve changes markedly, depending on T_W. For example, at $p=10$, the echo curve shows an $\exp(-ct_{21}^3)$ dependence at $T_W=0$, and changes to an $\exp(-ct_{21}^2)$ dependence above $T_W>5\tau_c$. It was found that the decay curve does not change at all over $T_W=5\tau_c$. Hence, the photon echo with $T_W=5\tau_c$ is equivalent to the accumulated echo. The expression for the intensity of the accumulated echo, which corresponds to Eq. (5) with $T_W \gg \tau_c$, is

$$I_{AP}(t_{21}) = \exp\left[-4p^2 \left(\frac{t_{21}}{\tau_c} + e^{-(t_{21}/\tau_c)} - 1 \right) \right] . \quad (6)$$

On the other hand, the expression for the two-pulse echo, which corresponds to Eq. (5) with $T_W=0$, is given by

$$I_{2P}(t_{21}) = \exp\left[-4p^2 \left(\frac{t_{21}}{\tau_c} + e^{-(t_{21}/\tau_c)} - 1 - \tfrac{1}{2}(e^{-(t_{21}/\tau_c)} - 1)^2 \right) \right] . \quad (7)$$

The experiment of the accumulated photon echo has usually been performed by using the optical-heterodyne method [11,12]. In this technique, the fourth optical pulse is irradiated on the sample at the instant that the macroscopic nonlinear polarization is rephased. The echo signal is detected as the change of transmission coefficient of the fourth pulse. The corresponding expression for the signal intensity of the heterodyne echo is given by

$$I_{\mathrm{HAP}}(t_{21})=\exp\left[-2p^2\left[\frac{t_{21}}{\tau_c}+e^{-(t_{21}/\tau_c)}-1\right]\right] . \quad (8)$$

The factor of 2 difference in the exponential between Eqs. (6) and (8) comes from the difference of the experimental arrangement in which $|P^{(3)}|^2$ and $P^{(3)}$ are detected, respectively, in accumulated echo and heterodyne echo.

Here we consider the relationship between the homogeneous spectrum (single-site absorption spectrum) and the echo signals. It is well known that the relaxation function for the first-order optical process, whose Fourier transform gives the absorption spectrum (single-site absorption spectrum), is given by [7]

$$\langle \exp\phi_1\rangle=\left\langle \exp\left[i\int_0^{\tau}\delta\omega(t)dt\right]\right\rangle$$
$$=\exp\left[-p^2\left[\frac{\tau}{\tau_c}+e^{-(\tau/\tau_c)}-1\right]\right] . \quad (9)$$

Therefore, the relaxation functions of the accumulated echo [Eq. (6)] and the heterodyne echo [Eq. (8)] can be factorized as a square of the first-order relaxation function. In contrast, this is not the case for the two-pulse echo, as evidenced by Eq. (7). It is well known that the single-site absorption spectrum, which is related to the first-order relaxation function, varies from Lorentzian to Gaussian as the magnitude of the frequency modulation $p=\Delta\tau_c$ increases [6]. Correspondingly, the temporal behaviors of both the accumulated and the heterodyne echoes change from exponential to Gaussian. Therefore, the Fourier-transform relation is always valid between these two echoes and the single-site absorption spectrum. However, we note that this relation does not generally hold in the two-pulse photon echo.

Strictly speaking, we have to distinguish the single-site absorption spectrum and the hole-burning spectrum. This is evident from the fact that the spectral width in the hole-burning spectrum is twice that of the single-site absorption spectrum. The hole-burning spectrum corresponds to the autocorrelation function of the single-site absorption spectrum. The expression for the hole-burning spectrum is expressed as [10]

$$H(\Delta\omega)=\mathrm{Re}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}d\tau_1 d\tau_2 d\tau\int_0^{\infty}g(\omega_{21})d\omega_{21}e^{[-i(\omega_{21}-\omega_1)-\gamma]\tau_2}(1+e^{-2\gamma\tau_1})e^{[i(\omega_{21}-\omega_2)-\gamma]\tau}\langle\exp\phi_2\rangle , \quad (10)$$

with $\Delta\omega=\omega_1-\omega_2$. This expression corresponds to the imaginary part of the nonlinear susceptibility, which the probe beam with frequency ω_1 "sees" during the burning of the pump beam with frequency ω_2. In the derivation of Eq. (10), we neglected the so-called population modulation term, due to the minor contribution to the persistent hole-burning spectrum [13]. As far as the dye-doped polymer samples are concerned, the burnt spectral hole persists for an extremely long time period. Therefore, the second-order relaxation function in Eq. (10) can be factorized in terms of the first-order relaxation function. In this case, the hole-burning spectrum is rewritten as

$$H(\Delta\omega)=\int d\tau|\langle\exp\phi_1\rangle|^2\cos\Delta\omega\tau$$
$$=\int d\tau\cos\Delta\omega\tau\exp\left[-2p^2\left[\frac{\tau}{\tau_c}+e^{-(\tau/\tau_c)}-1\right]\right] . \quad (11)$$

Comparing Eqs. (8) and (11), we find that the persistent hole-burning spectrum corresponds to the Fourier-cosine transform of the heterodyne echo [10].

As mentioned above, the relaxation function of the accumulated echo corresponds to the square of the relaxation function of the heterodyne echo. This means that the modulation parameter $p=\Delta\tau_c$ of the accumulated echo can be regarded equivalently as being increased by a factor of $\sqrt{2}$ compared with that of the heterodyne echo. This difference of a factor $\sqrt{2}$ is sufficient to give a different temporal behavior between the two types of photon echoes. For example, we can show that, even if the nonexponential behavior is clearly observed in the accumulated echo signal, it happens that the nonexponential behavior is almost undiscernible in the heterodyne echo, provided that the modulation parameter takes a value around $p=0.3$. In such a case, the corresponding hole-burning spectrum has a quasi-Lorentzian spectrum. Furthermore, the two-pulse echo tends to enhance the nonexponential behavior even for a relatively small value of p [9]. To visualize this tendency, the decay curves of three types of photon echoes, including the two-pulse echo (a), accumulated echo (b), and heterodyne echo (c), together with the hole-burning spectra (d), are depicted in Fig. 3 for the modulation parameters $p=0.1$, 0.3, and 1.

Now we discuss the temporal behavior of the photon echoes at both limits of the frequency modulation. In the limit of fast modulation ($p\ll1$, $t_{21}\gg\tau_c$), all types of photon echoes exhibit an exponential decay of $\exp(-\alpha p^2 t_{21}/\tau_c)$, where α depends on the type of the photon echo. On the other hand, in the limit of slow modulation ($p\gg1$, $t_{21}\ll\tau_c$), $\exp[-\beta p^2(t_{21}/\tau_c)^2]$ dependence is observed, where β is 2 and 1, corresponding to the accumulated and the heterodyne echo, respectively. However, the two-pulse echo exhibits a different temporal behavior of $\exp[-\frac{4}{3}p^2(t_{21}/\tau_c)^3]$. In order to explain the $\exp(-ct_{21}^3)$ dependence, we loosen the assumption of the extremely broad inhomogeneous broadening. When the inhomogeneous spectral width is finite, the intensity of the two-pulse photon echo has the

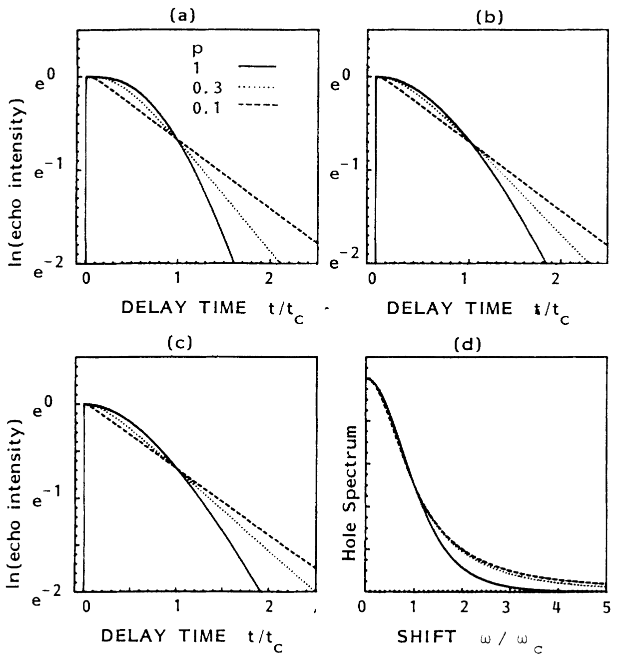

FIG. 3. Echo decay curves of the two-pulse echo (a), accumulated echo (b), and heterodyne echo (c) for the modulation parameters $p=0.1$ (— — —), 0.3, (· · ·), and 1 (——). t_c is the delay time at the half-maximum point of the signal. Also shown are the hole-burning spectra (d) corresponding to the same modulation parameters.

following temporal behavior:

$$I_{2P}(t)=\exp\left[-(t-2t_{21})^2\left[\tfrac{1}{2}\delta\Omega^2+\frac{p^2}{\tau_c^2}\right]-\tfrac{4}{3}p^2\left[\frac{t_{21}}{\tau_c}\right]^3+\frac{p^2}{3\tau_c^3}(t-2t_{21})(t^2-4tt_{21}-2t_{21}^2)+\cdots\right], \tag{12}$$

where the ellipsis represents higher-order terms, $\delta\Omega$ is the spectral width of the Gaussian inhomogeneous broadening, and the term with τ_c^{-n} comes from the nth order Taylor-series expansion of the exponential functions in the exponent of Eq. (4). In the case where $\delta\Omega=0$, the τ_c^{-2} term becomes dominant and an echo decay curve with an error-function shape is obtained, as was previously pointed out in Refs. [3] and [4]. On the contrary, with increasing $\delta\Omega$, the t_{21} dependence of the τ_c^{-2} term vanishes due to strong rephasing at $t=2t_{21}$ [2], and the next-order term, $\exp[-\frac{4}{3}p^2(t_{21}/\tau_c)^3]$, becomes dominant.

As is well known, the photon echo is closely related to the time-reversed optical process; the third pulse plays a role of time reversing the optical dipole induced by the first pulse. The dephasing of the macroscopic dipole due to the static inhomogeneous broadening can be canceled through this time-reversal process. The stochastic theory demands that the single-site absorption spectrum become Gaussian at the slow-modulation limit. However, strictly speaking, this means that, although the Gaussian spectral component that originates from the τ_c^{-2} term in the first-order relaxation function dominates in the absorption spectrum at the slow-modulation limit, the spectral component associated with the higher-order terms with τ_c^{-n} always exists. In this case, if the third excitation pulse is incident on the sample at the waiting time T_W (which is shorter than the correlation time τ_c), the τ_c^{-2} term is canceled, just like the static inhomogeneous broadening [2]. As a result, the next-order term with τ_c^{-3} becomes dominant, and the echo curve gives $\exp[-\frac{4}{3}p^2(t_{21}/\tau_c)^3]$ dependence. However, in the accumulated photon echo with $T_W \gg \tau_c$, the frequency modulations in the periods from 0 to t_{21}, and from T_W+t_{21} to T_W+2t_{21}, are not correlated with each other, and the cancellation does not occur. Therefore, the Gaussian-like decay is observed in the accumulated photon echo.

As mentioned above, at the slow-modulation limit, the temporal behavior of the stimulated echo changes from $\exp(-ct_{21}^3)$ to $\exp(-ct_{21}^2)$ dependence as the waiting time T_W varies from 0 to about $5\tau_c$. Hence, when a nonexponential decay is observed in some material, this T_W dependence of the stimulated echo will provide an important check on whether the nonexponential decay originates from the stochastic fluctuation of the transition frequency. At present, however, there is no experimental demonstration that reveals the difference in non-Markovian temporal behavior between two-pulse echo and accumulated echo. Although nonexponential decay of the echo signals has been observed in several cases [5,9,14,15], the detailed study on the waiting-time dependence of the echo decay curve has not been performed. In this sense, the work of Meijers and Wiersma [14] is very interesting. They investigated the T_W-dependent variation of the phase-relaxation time. Although their interest was focused on spectral diffusion, they briefly reported that the observed nonexponential decay of the echo signals varies depending on the waiting time.

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