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Fourier-transform spectroscopy in dye-doped polymers using the femtosecond accumulated photon echo

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Fourier-transform spectroscopy using the technique of femtosecond accumulated photon echo with incoherent light has been performed in dye-doped polymers. Several types of interference effect or quantum beat between the zero-phonon line and other spectral components including the phonon sideband, the vibronic lines, and the photoproduct state have been observed. Based on the density matrix incorporating the transition-frequency modulation, it is pointed out that the factorization approximation for the relaxation function holds rigorously in the accumulated photon echo. We also clarified that the Fourier cosine transform of the heterodyne-detected echo signal provides the hole-burning spectrum.

I. INTRODUCTION

Fourier-transform spectroscopy[1] using a two-beam interferometer with a white light source has become a general technique in far-infrared spectroscopy when high resolution is required, or when a wide spectral range is to be explored. The extension of this method to nonlinear spectroscopy is desirable to develop a new type of site-selection spectroscopy which enables us to extract the wide-range homogeneous spectrum from the inhomogeneously broadened absorption spectrum. Recently, in several nonlinear spectroscopies,[2,3] coherent or incoherent broadband dye lasers having a spectral bandwidth of several hundred wave numbers have been employed to get higher time resolution. It is now possible to develop Fourier-transform nonlinear spectroscopy using a broadband dye laser as a quasi-white-light source and time-domain nonlinear spectroscopy, in particular, photon-echo spectroscopy. Among several types of photon-echo measurement, the heterodyne-detected accumulated photon echo[4,5] is known to possess high sensitivity. It has several advantages: the time resolution is determined by the correlation time of the excitation field and the phase-sensitive detection in this method enables us to determine the signal phase which is indispensable for identifying the physical origin of the echo signal. A drawback of this method is that it is only applicable to samples which have a long absorption-recovery time. Thus samples of dye-doped polymers are appropriate for this technique because of the presence of triplet state with a long relaxation time. Dye molecules embedded in polymers have been investigated so far using photon echo[6,7] and resonant Rayleigh-type mixing,[8] and the results have revealed the presence of ultrafast phase relaxation even at liquid-helium temperature. We have recently pointed out[9] that the ultrafast phenomena previously reported for dye-doped polymers originate from the contribution of the phonon sideband. In addition to the zero-phonon line and the phonon sideband, other spectral components such as vibronic lines and antiholes due to the photoproduct show in the persistent hole-burning spectra. However, it has not been elucidated how the latter spectral components affect the temporal behavior of the echo.

The purpose of this work is to demonstrate Fourier-transform nonlinear spectroscopy with a wide spectral range, and to identify the physical origin of several interference effects observed in the femtosecond photon echo by virtue of comparison between the Fourier-transformed spectrum of the echo signal and the persistent hole-burning spectrum.

II. THEORY

Based on the density matrix incorporating the transition frequency modulation, we derive the expression for the signal strength of the heterodyne-detected accumulated photon echo and also derive the expression for the persistent hole-burning spectrum. We consider a three-level system consisting of the ground state $|g\rangle$, the excited state $|e\rangle$, and a third level as the bottleneck state. The transition energy between the states $|g\rangle$ and $|e\rangle$ is assumed to experience frequency modulation from the electron-phonon interaction. From the third-order density-matrix expansion, we get the expression for the signal strength of the heterodyne-detected accumulated photon echo,[5]

$$\begin{aligned} S=\mathrm{Re}\int_{-\infty}^{\infty} dt \int_0^{\infty}\int_0^{\infty}\int_0^{\infty} d\tau\, d\tau'\, d\tau'' \int g(\omega_0)\, d\omega_0 \\ \times E_4^*(t-t_4)E_3(t-\tau-t_3)E_2(t-\tau-\tau'-t_2)E_1^*(t-\tau-\tau'-\tau''-t_1) \\ \times e^{(-i\omega_0-\gamma)\tau''}(1+e^{-2\gamma\tau'})e^{(i\omega_0-\gamma)\tau} \\ \times \left\langle \exp\left[-i\int_0^{\tau''}\delta\omega(t)dt+i\int_{\tau'+\tau''}^{\tau+\tau'+\tau''}\delta\omega(t)dt\right]\right\rangle . \end{aligned} \qquad (1)$$

The heterodyne-detection scheme for the accumulated photon echo utilizes exactly the same experimental arrangement as the pump-probe method. We designate the relevant electric fields as E_1 and E_3 for the pump beam and E_2 and E_4 for the probe beam, where E_2 and E_4 are, respectively, the optically delayed replicas of E_1 and E_3. In Eq. (1), 2γ is the natural decay rate of the excited state, $g(\omega_0)$ is the inhomogeneous broadening, $\delta\omega(t)$ is the modulation of the transition energy, and t_i is the arrival time of an E_i pulse. The function with angular brackets in Eq. (1) is called the relaxation function[10] and the brackets denote an average over the modulation process. Evaluation of the relaxation function has been performed by several authors using a dynamical model[11] or a Gaussian stochastic model.[12,13] In particular, Aihara[11] has derived an explicit expression for the localized-electron phonon system using the cumulant expansion method and the electron-phonon interaction Hamiltonian up to the quadratic interaction. The most important feature of the accumulated photon echo is that the write-in process due to E_1, E_2 pulses and the read-out process due to E_3, E_4 pulses can be temporally distinguished due to the long absorption recovery time. This means that the write-in process is accumulated by the sequential excitation of mode-locked pulses, and the echo signal is generated through the population change in the ground state. This feature leads to the result that the relaxation function as a second-order optical process can be factorized as the product of the corresponding first-order relaxation functions:

$$\left\langle \exp\left[-\gamma(\tau+\tau'')-i\int_0^{\tau''}\delta\omega(t)dt+i\int_{\tau'}^{\tau+\tau'+\tau''}\delta\omega(t)dt\right]\right\rangle=\left\langle \exp\left[-\gamma\tau''-i\int_0^{\tau''}\delta\omega(t)dt\right]\right\rangle\left\langle \exp\left[-\gamma\tau+i\int_0^{\tau}\delta\omega(t)dt\right]\right\rangle . \tag{2}$$

Therefore, the factorization approximation holds rigorously in the accumulated photon echo. It makes a striking contrast with other nonlinear optical processes,[14] in which the factorization approximation has been well known to lead to inaccurate result. If the inhomogeneous spectral width is assumed to be extremely broad, we get the expression

$$S=\int_0^{\infty} |G(\tau-t_{21})|^2 \times\left|\left\langle \exp\left[-\gamma\tau-i\int_0^{\tau}\delta\omega(t)dt\right]\right\rangle\right|^2 d\tau , \tag{3}$$

where G is the field correlation function of the excitation pulse and $t_{21}=t_2-t_1=t_4-t_3$ is the delay time between the pump and probe pulses. Further assuming that the excitation pulse has a white spectrum, the signal strength can be written as

$$S(t_{21})=\left|\left\langle \exp\left[-\gamma t_{21}-i\int_0^{t_{21}}\delta\omega(t)dt\right]\right\rangle\right|^2 . \tag{4}$$

Similarly, we derive the expression for the persistent hole-burning spectrum. The imaginary part of the nonlinear susceptibility which the probe beam with the frequency ω_2 sees after burning by the pump beam with the frequency ω_1 is written as

$$\begin{aligned} H(\Delta\omega)=\mathrm{Re}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}d\tau\, d\tau'\, d\tau''\int g(\omega_0)d\omega_0 \\ \times e^{[-i(\omega_0-\omega_1)-\gamma]\tau''}(1+e^{-2\gamma\tau'})e^{[i(\omega_0-\omega_2)-\gamma]\tau} \\ \times\left\langle \exp\left[-i\int_0^{\tau''}\delta\omega(t)dt+i\int_{\tau'+\tau''}^{\tau+\tau'+\tau''}\delta\omega(t)dt\right]\right\rangle , \end{aligned} \tag{5}$$

where $\Delta\omega=\omega_2-\omega_1$. Under the assumption of the extreme inhomogeneous broadening, and considering that burning and probing of the hole are temporally distinguished due to the persistency of the burnt hole, Eq. (5) results in

$$H(\Delta\omega)=\int_0^{\infty} d\tau \cos\Delta\omega\tau S(\tau) . \tag{6}$$

Therefore the hole-burning spectrum can be obtained from the Fourier-cosine transform of the echo signal. It is worthwhile to remark the difference between the hole-burning spectrum and the power spectrum of the electron-phonon coupling. Using the power spectrum defined as

$$J(\Delta\omega)=\mathrm{Re}\int_0^{\infty}\left\langle \exp\left[-\gamma\tau-i\int_0^{\tau}\delta\omega(t)dt\right]\right\rangle e^{i\Delta\omega\tau}d\tau , \tag{7}$$

the hole-burning spectrum $H(\Delta\omega)$ can be expressed as

$$H(\Delta\omega)=\int J(\omega)J(\omega+\Delta\omega)d\omega . \tag{8}$$

This means that the hole-burning spectrum corresponds to the autocorrelation function of the power spectrum. Based on the relaxation function which was derived from the four-time correlation function of the transition dipole, Berg *et al.*[15] have recently pointed out that the relaxation function is sensitive to dynamics on a different time scale and varies depending on the type of nonlinear spectroscopy. Therefore, the deviation from Eq. (6) might be observed in actual experiments, depending on the sample material and the experimental conditions.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The echo measurements were performed by the high-frequency modulated heterodyne method[16] using a synchronously pumped rhodamine-6G dye laser. In order to get a broader spectral width, the dye laser was operated without birefringent filters. Then the spectral width is 100 Å around the center wavelength of 5900 Å. An acoustooptical modulator (ISOMET 1205C) was employed for intensity modulation of the pump beam at 5 MHz. The signal has been amplified by a tuned preamplifier and then fed into a high frequency lock-in amplifier (PAR-5202). In order to avoid the persistent hole-burning effect to some extent, the experiment was made under simultaneous irradiation with 5145-Å Ar-laser light, which refills the burned hole. The samples we have employed are ionic dyes such as rhodamine-640, resorufin, and 3,3′-diethyloxadicarbocyanine iodide (DODCI), which were doped in several polymers including polyvinyl alcohol (PVOH), polymethylmethacrylate (PMMA), polyacrylic acid, and polystyrene. The optical density of the samples ranged from 0.5 to 1.0 at the peak of the low-energy absorption band. The samples were kept at 2 K in an immersion-type superfluid helium cryostat.

The host polymer dependence of the temporal behavior of the echo was investigated for rhodamine-640 which was doped in four different host polymers. As shown in Fig. 1(a), the echo signal consists of a sharp spike and a slowly decaying component. The relative weight of the two signals was found to depend on the host polymer. We have previously determined that the zero-phonon line and the phonon sideband are associated with the two components, and the dip observed after the spike reflects the quantum beat between them.[9] This assignment was further confirmed by the Fourier cosine transform of the echo signal which is shown in Fig. 1(b). The present laser excites the longer wavelength side of the absorption spectrum in rhodamine-640, hence the two spectral components of the zero-phonon line (Z) and the phonon sideband (W) are generally excited. However, since the hole-burning spectrum corresponds to the autocorrelation function of the power spectrum, four spectral components expressed as ZZ, ZW, WZ, and WW appear in the hole-burning spectrum, where WZ, for example, denotes the zero-phonon holes burned through the phonon sideband of the absorption spectrum. In a host polymer such as PVOH which exhibits a weak electron-phonon coupling, the contribution from the WW component is negligibly small. Therefore, the spectrum with an isolated phonon-sideband is observed. On the other hand, in host polymers such as PMMA and polystyrene in which the electron-phonon coupling is relatively strong, the WW component predominates in the hole-burning spectrum. To interpret the Fourier-transformed spectrum, the comparison with the persistent hole-burning spectrum shown in Fig. 1(c) is useful. These spectra have been obtained by means of the spatial modulation method.[6] It is well known that the experimentally observed hole-burning spectrum is nonsymmetric around the zero-phonon hole. This is due to the fact that under the heavy irradiation of the burning light, the zero-phonon line which has a narrower spectral width is easily saturated relative to the phonon sideband, hence the WW and WZ components become prominent. Anyway, observed spectra in both the Fourier transform of the echo

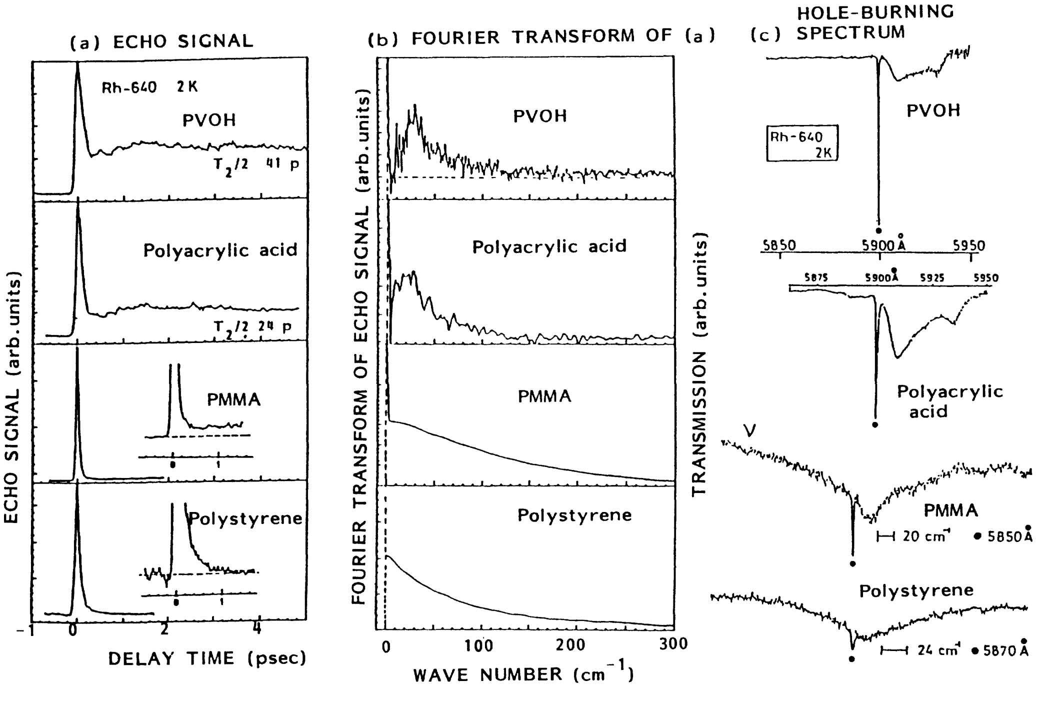

FIG. 1. (a) Accumulated photon echo in rhodamine-640 doped in four different polymers including PVOH, polyacrylic acid, PMMA, and polystyrene. (b) Fourier cosine transformed spectra of (a). The intensity of the zero-phonon line is off scale in PVOH and polyacrylic acid. (c) Persistent hole-burning spectra. Solid circles indicate the burning wavelength.

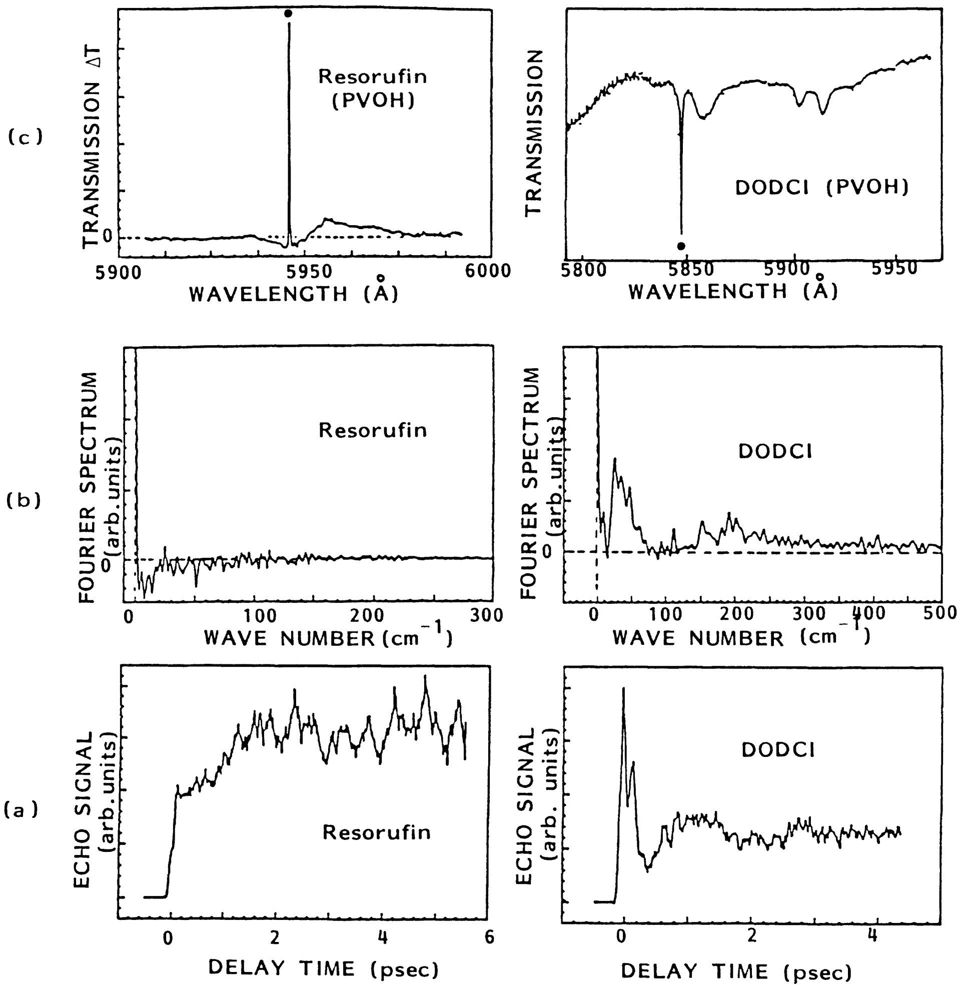

FIG. 2. (a) Accumulated photon echo in resorufin and DODCI doped in PVOH. (b) Fourier cosine transformed spectra of (a). The intensity of the zero-phonon line is off scale. (c) Persistent hole-burning spectra. Solid circles indicate the burning wavelength.

signal and persistent hole-burning spectroscopy indicate that the electron-phonon interaction strength in the samples of rhodamine-640 decreases in the order of host polymer polystyrene, PMMA, polyacrylic acid, and PVOH. With regard to this point, we have previously pointed out that there is a correlation between the electron-phonon coupling strength and the size of side groups on the polymer chain.[9]

In the samples of resorufin and DODCI doped in PVOH, we observed further interesting temporal behavior of the photon echo. As shown in Fig. 2(a), the echo signal in resorufin does not exhibit the spike around the time origin, which means that the electron-phonon interaction strength is weak in this sample. Although the echo signal was very noisy, it is evident that the signal height does not take the maximum value at the time origin; rather it gradually rises up to the delay time of 2 psec. The Fourier transform of this signal shown in Fig. 2(b) indicates that the leading part of the echo signal is associated with the spectrum with a negative sign. From the persistent hole-burning spectrum of Fig. 2(c), we observe that this negative spectrum corresponds to the antihole due to the photoproduct. Furthermore, from the comparison between Figs. 2(b) and 2(c), we notice that the appearance of the pseudophonon sideband in Fig. 2(c) is caused by saturation of the zero-phonon hole due to the heavy irradiation of the burning light, while the photon echo signal has not suffered seriously from the persistent hole-burning effect.

As a final example of the present Fourier-transform spectroscopy, the result in DODCI is also shown in Fig. 2. The most interesting result is that the spike in the echo signal exhibits substructures. From the comparison between the Fourier-transformed spectrum and the persistent hole-burning spectrum, it was found that the substructure is caused by the quantum beat between the zero-phonon line and the low-frequency vibrational lines in the excited state, whose frequencies are about 150 and 200 cm^{-1}, respectively.

To summarize, Fourier-transform photon-echo spectroscopy using the femtosecond accumulated photon echo was demonstrated in dye-doped polymers. Using this method, the host-polymer dependence of the electron-phonon coupling strength was experimentally clarified, and the spectral origin of several interference effects observed in the femtosecond photon echo was also identified. The recent advance in femtosecond optical technology, especially the self-phase modulation technique in optical fibers, makes it possible to expand the laser bandwidth up to several thousand wave numbers. The combination of such a quasi-white-light source and the present Fourier-transform photon echo spectroscopy will enable us to realize new site-selection spectroscopy with more wide spectral range.

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