Accumulated photon echoes generated by synchrotron radiation

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We demonstrate that accumulated photon echoes can be generated by synchrotron radiation. This is an experiment of a nonlinear optical effect carried out by using the radiation from an electron storage ring. A dye-doped polymer film was excited by the visible light from the storage ring, and the accumulated photon echoes from the sample were observed by employing a phase-modulation technique. The use of synchrotron radiation facilitates the extension of the spectral range where we can observe photon echoes with ultrahigh time resolution.

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Much progress has been made in optical transient spectroscopy since the first observation of two-pulse photon echoes [1]. Now various kinds of excitation schemes of photon echoes are known. Stimulated three-pulse photon echoes, for example, can be used to investigate both the optical dephasing time T_2 and the population relaxation time T_1 of the electronic and vibronic transition in many kinds of atoms [2], molecules [3], and solids [4]. When T_1 is sufficiently longer than T_2, the accumulated photon echoes, which are considered as an extension of three-pulse photon echoes, can be employed. In accumulated photon echoes using the pulse trains of high repetition rate or cw broad spectral light, the excitation power needed to generate echo signals is greatly reduced because of the accumulation of the population grating [5]. The incoherent excitation of the two-pulse and accumulated photon echoes has been used to measure the dephasing time of various kinds of materials [6,7]. The unique features of the incoherent excitation are the simplicity of the experimental system and the high time resolution, which is solely determined by the inverse of the spectral bandwidth of the excitation light. Therefore, the incoherent excitation has been expected to readily provide the time resolution of several femtoseconds in the measurement of the dephasing time. However, it has not been the case so far because the spectral bandwidth of light generated by dye lasers [8], stimulated Raman scattering in a single-mode fiber [9], and a superluminescent diode [10] is not broad enough. The available bandwidth is restricted, for example, by the fluorescence spectrum of dyes used. On the other hand, the time resolution of 6 fs has been obtained in the photon echo spectroscopy by using an ultrashort pulse, although the experiment is limited to a narrow wavelength region [11]. Recently, a light-emitting diode (LED) has been used to observe the accumulated photon echoes for the first application of a nonlaser light source in photon echo spectroscopy [12].

In this paper, we report a demonstration that the synchrotron radiation (SR) can be applied as an excitation source of accumulated photon echoes. Though this demonstration is an extension of the photon echo spectroscopy performed by a nonlaser light, the LED, it opens the possibility of photon echo spectroscopy in a vacuum ultraviolet region with femtosecond time resolution because the SR has a very wide spectrum as a point source. From our experimental results, we indicate that the SR will enable us to reach the highest time resolution in the photon echo experiment.

We present in this paper picosecond accumulated photon echoes of the zero-phonon transition of sulforhodamine 640 (SRh 640) doped in a polymer film that was successfully observed by exciting the sample with the SR and employing the phase-modulation method [13]. Although the time resolution obtained by the full bandwidth of the SR can be reduced to 3 fs as described below, we preferred to excite the zero-phonon transition by a reduced bandwidth of 13 nm. This is because our major subject is to verify the applicability of the SR to photon echo spectroscopy and because the echo behavior of the zero-phonon transition has been extensively studied so far, which makes it easy to examine the validity of the observed echo decay time. If the excitation with the full bandwidth is used, it results in the echo signal consisting of contributions from the zero-phonon and vibronic transitions [8] with the latter contribution being dominant. In such a case we need a complicated analysis in order to evaluate the photon echo results. Consequently, we used

the SR passed through a bandpass filter with a bandwidth of 13 nm in order to excite the zero-phonon transition, since its dephasing time is expected to be longer than a few picoseconds at the temperature of our cryostat. The excitation bandwidth corresponds to the time resolution of 133 fs. In addition, when the bandpass filter was removed, the field autocorrelation time of the SR beam decreased to about 3 fs, indicating a possible time resolution of 3 fs in photon echo spectroscopy.

The experiment was performed at a beam line 8A of the UVSOR facility, Institute for Molecular Science, Okazaki, Japan [14]. The SR beam emitted from a bending magnet was loosely focused with a platinum-coated confocal mirror with a horizontal and vertical focal length of 2.8 and 2.6 m, respectively. The concave mirror was located about 2.5 m from the bending magnet in an ultrahigh vacuum chamber. The electron storage ring was operated with an electron energy of 750 MeV and a beam current of 200 mA just after the electron injection. The lifetime of the beam current was 400~500 min during our measurement. The stored electron beam consisted of 16 bunches (multibunch operation) and the output SR pulses had a repetition rate of about 90 MHz and a time duration of 1.5 ns.

The schematic diagram of the accumulated photon echo experiment is shown in Fig. 1. The SR beam passed through a quartz window of the storage ring and was filtered by the interference bandpass filter with a center wavelength of 605 nm and a bandwidth of 13 nm. After the filter, the SR beam was introduced to a Michelson interferometer consisting of a nonpolarized cube beam splitter and two corner-cube prisms. The beam was split into two beams, the pump and probe beams, in the interferometer and the probe beam was temporally delayed relative to the pump beam by using an ultraslow harmonic-geared stepping motor. After the interferometer, the two beams were aligned to collinearly overlap with high precision. The pump beam was phase modulated by vibrating one corner-cube prism bonded on a piezoelectric transducer driven at $f=6.5$ kHz. The collinearly overlapped two beams were focused onto the sample in a cryostat by a lens with a 35-mm focal length, and the transmitted beam through the sample was refocused onto a p-i-n photodiode whose output was fed into a lock-in amplifier. The excitation power of the pump and probe beam was 2.2 and 0.8 μW, respectively. The echo signal was obtained in the $2f$ component of the lock-in detected signal. Under this configuration, the echo signal shows a symmetrical decay profile about the zero delay time, $\tau=0$. In the present experiment, since both the pump and the probe beam had the same polarization, the photon echo signal was distorted near $\tau=0$ due to the direct interference between the two beams. However, this effect could be greatly reduced by using the two excitation beams with the orthogonal polarizations. The sample we used was SRh 640 doped in polyvinyl alcohol (PVA). Figure 2 shows the absorption spectrum of SRh 640 in PVA by a solid curve. The filtered SR beam, whose spectrum is shown in Fig. 2 by a dotted curve, was resonant to the 0-0 transition between S_0 and S_1 levels of SRh 640 in PVA.

When the field correlation time of the pump and probe beams is sufficiently shorter than the dephasing time T_2 of the sample, the signal decay $I(\tau)$ of the heterodyne detected accumulated photon echoes, as in our present case, is expressed as

$$I(\tau)=[J_0^2(M)+2J_0(M)J_2(M)\cos(2ft) + \cdots]\exp(-2\tau/T_2),$$

where $J_i(M)$ denotes the ith order Bessel function and M

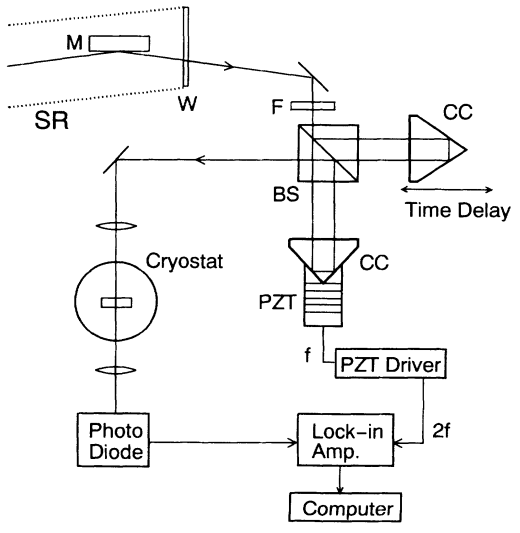

FIG. 1. Experimental setup for the observation of the accumulated photon echoes generated by the SR. The SR beam was loosely focused with a grazing incident concave mirror M; F, interference bandpass filter; CC, corner-cube prism; PZT, piezoelectric transducer; f, modulation frequency of the PZT; BS, a beam splitter.

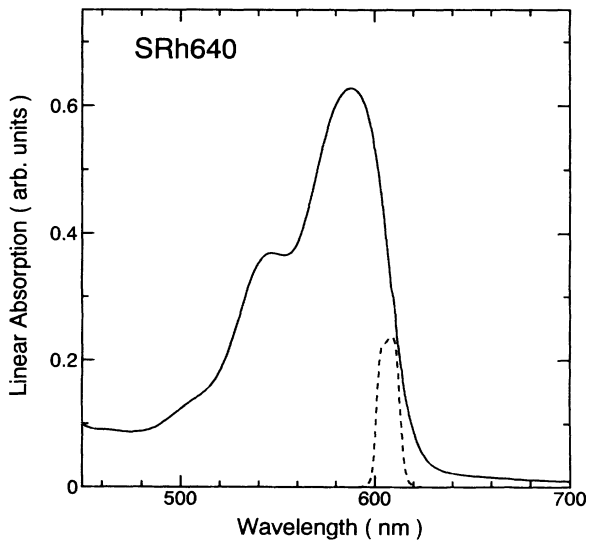

FIG. 2. Solid curve represents the absorption spectrum of SRh 640 doped in PVA. Dotted curve shows the spectrum of the bandpass filtered SR used to generate the accumulated photon echoes.

means the index of the phase modulation induced by the piezoelectric transducer [15]. Since the echo signal of the $2f$ component is proportional to the product of the zeroth- and the second-order Bessel functions, the largest signal can be obtained by adjusting a suitable M value.

We first measured the field autocorrelation of the SR excitation beam that determines the time resolution in the incoherent excitation of photon echoes. Figure 3(a) shows the autocorrelation (interferogram) obtained for the SR beam (the center wavelength of 605 nm and the bandwidth of 13 nm) used in our photon echo experiment. In this measurement, the sample was removed and the f component of the lock-in signal was detected. The depth of the intensity modulation by the interference between the pump and probe beams reached to about 70% of the total dc output at around $\tau=0$ only when the precise spatial overlap between the two beams was accomplished. The precise spatial overlap was a key to the appearance of the interference since only the displacement of about 50 μm between the two beams resulted in no interference. The correlation time full width at half maximum (FWHM) of the filtered SR was measured to be 133 fs. It is rather larger than that estimated from the bandwidth of the bandpass filter, but it clearly indicates that the photon echo decay can be measured with a time resolution of about 130 fs. Side humps in the correlation curve are attributed to the squarish transmission characteristics of the bandpass filter as shown in Fig. 2. The interference modulation occurred with a period of 2.0 fs, which corresponds to the wavelength of the SR (605 nm), though it is not observable in Fig. 3(a).

Figure 3(b) displays the field correlation when the bandpass filter was eliminated, indicating the field correlation time to be about 3 fs. The correlation time measured in this case is basically restricted by the coatings of the dielectric mirrors and the beam splitter used in the Michelson interferometer. Therefore, if we use the mirrors and a beam splitter with the wide-band coatings and a wide-band sensitive optical detector, the SR beam could provide the ultrahigh time resolution over a very wide wavelength region in the photon echo spectroscopy. Such echo spectroscopy is a subject of further research.

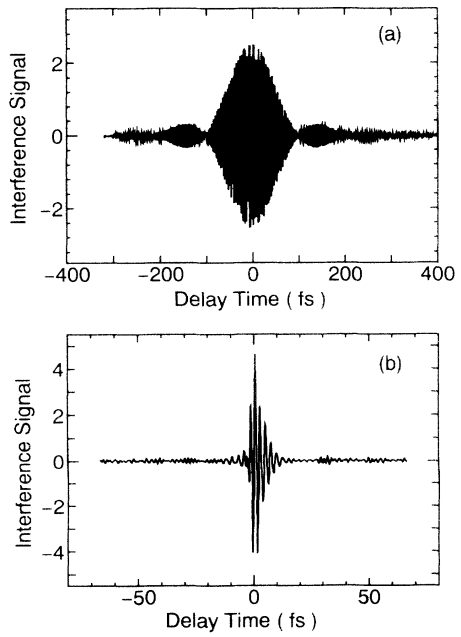

FIG. 3. (a) Field autocorrelation trace of the SR beam corresponding to the spectrum shown in Fig. 2 by a dotted curve. The field correlation time is 133 fs. (b) Field autocorrelation trace of the broadband SR beam, indicating a correlation time of 3 fs.

Figure 4 shows the accumulated photon echo decay on a logarithmic scale measured for SRh 640 in PVA at 29 K, where the delay time τ was scanned from 1.2 to 10 ps. As mentioned previously, the echo signal around $\tau=0$ is severely distorted because of the direct interference between the pump and probe beams. Therefore, the echo data for the delay time from 0 to 1.2 ps were eliminated in Fig. 4. The dephasing time T_2 obtained in Fig. 4 is approximately 4.8 ps. This decay curve is normalized with the SR beam intensity by assuming that the intensity is proportional to the beam current in the storage ring. The beam current of the storage ring changed from 188.7 to 151.4 mA during the measurement. In the measurement, we took ten data into a computer at a fixed delay time after accumulating a population grating for 60 s. Then the accumulated population grating was erased by slowly changing the delay time τ to the next sampling delay time with the two excitation beams on, which took 60 s. The inset of Fig. 4 exhibits the same echo decay on a linear scale.

In order to examine the accumulation rate of the population grating generated by the weak SR beams, we measured the time dependence of the echo signal after the irradiation of the SR beams at a fixed delay time. The echo signal in the present experiment originates from the population grating created as the persistent photochemical hole burning. Therefore, the echo signal is expected to

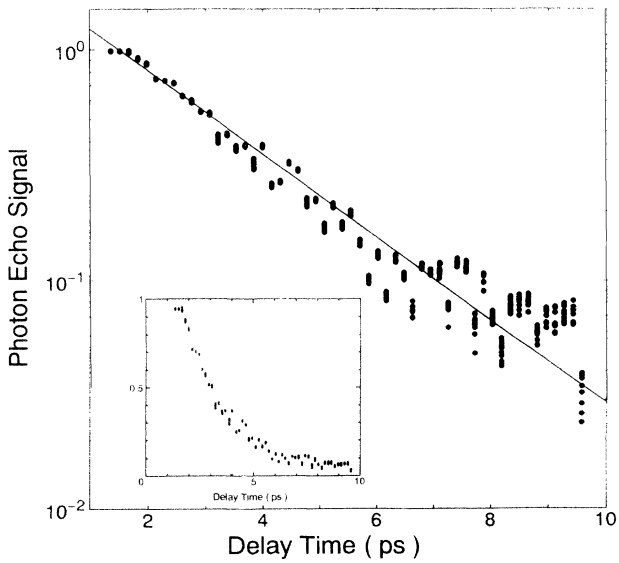

FIG. 4. Accumulated photon echo decay on a logarithmic scale for SRh 640 doped in PVA at 29 K. In the inset, the same curve was plotted on a linear scale.

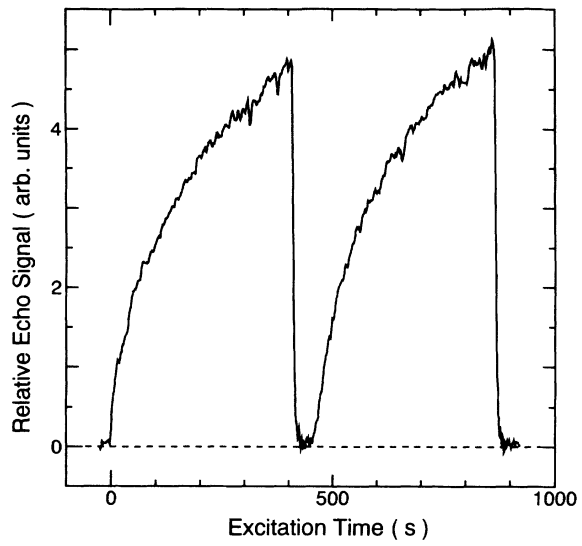

FIG. 5. Buildup of accumulated photon echo signal as a function of the irradiation time at the fixed delay time. After the accumulation time (400 s) of the population grating at a fixed delay time, the delay time was changed to the next sampling delay time for 30 s by smearing out the previous population grating.

grow with the irradiation time. In the period when the delay time is slowly changing, the population grating created at the previous sampling delay time is smeared out completely, resulting in no echo signal. This behavior of the echo signal is shown in Fig. 5, where we accumulated the population grating at a fixed delay time for 400 s and then erased the grating by slowly changing the delay time for 30 s. The echo signal was not greatly saturated by the irradiation of 400 s. As is shown in Fig. 5, the echo intensity was considerably stable in spite of our poor experimental condition that the experimental system be placed in a very noisy storage ring room. As each point of the echo signal shown in Fig. 4 was obtained after the accumulation time of 60 s, the signal-to-noise ratio could be improved if we took more time to accumulate the population grating. It should be noted in Fig. 5 that the hole burning at one delay time has no effect on the echo signal measured at the later sampling delay times, which is confirmed by the null echo signal during the scanning of the delay time. Namely, the null echo signal means the complete erasure of the population grating that gives rise to the echo signal at one delay time, and so the hole-burning process does not affect the echo amplitude at the later delay time.

Moreover, we tried to measure the dephasing time of SRh 640 in PVA at 29 K by using a Q-switched yttrium aluminum garnet (YAG) laser pumped incoherent dye laser [16] at a wavelength of 605 nm to confirm the validity of the dephasing time observed by the SR. Then, it was clearly shown that the two dephasing times agreed well with each other.

In conclusion, we have demonstrated the observation of accumulated photon echoes by the SR beam. We believe that the SR opens a possibility that the measurement of the dephasing time can be carried out with quite high time resolution for various kinds of samples that have absorption from far infrared to vacuum ultraviolet, though the accumulation of the population grating should take place in the sample. Moreover, a resolution time even better than 1 fs may be obtained by means of the SR beam.

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