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Femtosecond time-resolved Raman spectroscopy using stimulated Raman scattering

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Femtosecond Raman spectroscopy has been developed to investigate ultrafast photoinduced structural changes of materials. Vibrational modes in the photogenerated transient species are measured by stimulated Raman scattering using a Raman pump pulse with narrow bandwidth and a femtosecond supercontinuum probe pulse. The Raman signal can be measured without slowing the temporal response and broadening the spectrum, because the temporal and spectral resolutions of the present method can be improved independently without the restriction of the transform limit. The transient Raman spectra of the *trans- cis* photoisomerization process in the DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-Pyran) dye solution were observed with the resolutions of 250 fs and 25 cm^{-1}.

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I. INTRODUCTION

The recent progress of ultrashort pulse lasers has enabled measurements of ultrafast spectral changes in photoinduced phenomena. Time-resolved Raman spectroscopy, which measures vibrations in photogenerated transient species, has been recognized as a powerful method for studying structural changes in photoinduced phase transitions, photoisomerization, photoinduced chemical reaction, photobiological processes, and so on. The basic technique has been established in the nanosecond region and developed to the picosecond region [1–6]. Measurement of initial ultrafast structural changes is very important to clarify the mechanism of photoinduced phenomena, but the time-resolved Raman spectroscopy has been done mainly in the picosecond region because of difficulty in femtosecond region.

Raman studies using femtosecond lasers have been mainly focused on the different technique called time-resolved coherent Raman spectroscopy. The coherent Raman spectroscopy measures dynamics of the Raman scattering process and gives qualitatively different information from the time-resolved Raman spectroscopy [7–10]. It has been used to investigate dynamics of a vibration in an electronic ground state.

In the coherent Raman spectroscopy, the temporal resolution is important but the spectral resolution is not crucial. On the other hand, the time-resolved Raman spectroscopy needs both the temporal and spectral resolutions, because it measures Raman spectra in transient species and the small change of the spectra must be distinguished from the background signal of the ground state. Iwata *et al.* have reported the picosecond Raman spectroscopy using a transform-limited pulse with the duration of 3.2 ps and the bandwidth of 3.5 cm^{-1} [6]. However, the shorter pulse has the broader bandwidth because of the transform limit. The bandwidth of a 100-fs pulse is broader than 100 cm^{-1}. Since the ordinary time-resolved Raman spectroscopy is restricted by the transform limit of a single pulse, it has essentially poor spectral resolution in the femtosecond region. Therefore, only a few time-resolved Raman experiments have been reported in the subpicosecond and femtosecond regions [11–14].

Infrared spectroscopy is also useful to study vibrations in materials. Since the signal is obtained as a transmittance change of an infrared probe pulse, the spectral resolution can be improved using a spectrometer with high resolution. The time-resolved infrared spectroscopy has been already done by several groups in the femtosecond region [15–18]. However, the transient absorbance change has been measured using monochromatic infrared probe pulses at each wavelength, because the generation and detection of the broad femtosecond infrared pulse is difficult. Therefore, it takes many times to measure the wide spectral region with fine spectral resolution. The reported studies have observed transient phenomena of vibrations in a limited wavelength region.

The present paper describes a different method to measure Raman signals in a wide spectral range with femtosecond resolution and fine spectral resolution. The technique is based on the Raman gain experiment performed by one of us (M.Y.) using a femtosecond dye laser [12]. Our method measures stimulated Raman scattering in photogenerated transient species instead of spontaneous Raman scattering used in the ordinary method. Theoretical calculation shows that the temporal and spectral resolutions can be improved individually free from the transform limit of a single pulse, because they are determined by different pulses. The developed system has been applied to ultrafast *trans-cis* photoisomerization of organic dye in solution.

II. THEORY

A signal of the ordinary time-resolved Raman spectroscopy is obtained using two optical pulses. The first pump pulse excites materials at time 0. Then, the second Raman probe pulse generates spontaneous Raman light in the transient species at delay time t_d. The Raman light is detected by a spectrometer. The temporal dependence on the delay time is determined by the material response and durations of the first and second pulses. The observed spectrum is broadened from the intrinsic Raman line of the material by a bandwidth of the Raman probe pulse and resolution of the spectrometer. Since the Raman probe pulse affects both the temporal and spectral responses, the ability of the instrument is restricted by the transform limit of the Raman probe pulse.

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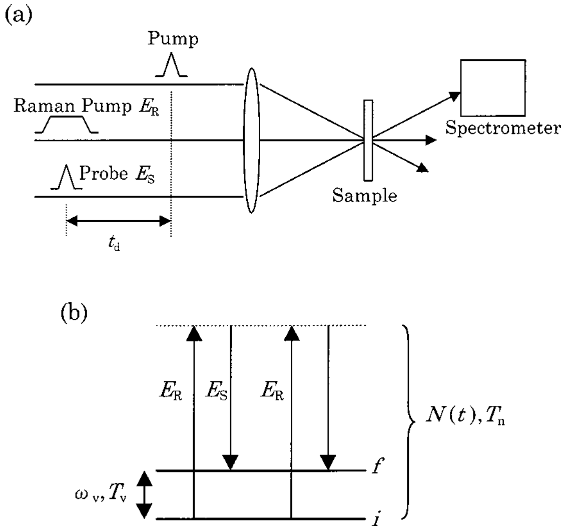

FIG. 1. (a) Schematic diagram of a unique time-resolved Raman spectroscopy using stimulated Raman scattering and (b) Raman gain process in transient species.

The time-resolved Raman spectroscopy in this study is performed using three optical pulses as shown in Fig.1(a). After photoexcitation of the first pump pulse at time 0, the Raman signal in the transient species is measured using stimulated Raman scattering induced by the other two pulses at delay time t_d. The Raman pump pulse has a narrow bandwidth and the probe pulse is an ultrashort and broad pulse such as a femtosecond supercontinuum pulse. The probe pulse is detected by a spectrometer and the Raman signal is obtained as the transmittance change. The temporal response is measured by changing the delay time between the first pump pulse and the other pulses. The signal observed by this method has been theoretically calculated as follows.

We calculate the Raman signal in a transient species which has an initial state *i* and a vibrational excited state *f* as shown in Fig. 1(b). We assume that the transient species is generated instantaneously at $t=0$ and the electrical dephasing is infinitely fast. Therefore, the density of the transient species with lifetime T_n is written as

$$N(t)=\begin{cases} 0 & (t<0), \\ N_0 e^{-t/T_n} & (t\geqslant 0). \end{cases} \tag{1}$$

Electric fields of the second Raman pump pulse (center frequency ω_R) and the supercontinuum probe pulse (center frequency ω_S) are defined as

$$\mathcal{E}_R(t)=E_R(t)e^{-i\omega_R t}+\text{c.c.}, \tag{2}$$

$$\mathcal{E}_S(t)=E_S(t)e^{-i\omega_S t}+\text{c.c.} \tag{3}$$

Nonlinear polarization $\mathcal{P}$ concerning the stimulated Raman scattering is derived from the coherent amplitude generated in the transient species as [19]

$$\mathcal{P}=\mathcal{E}_R\{iQ(t)e^{-i\omega_v t}+\text{c.c.}\}, \tag{4}$$

$$Q(t)=\kappa\int_{-\infty}^{t}dt' N(t')e^{-(t-t')/T_n}E_R(t')E_S^*(t') \times e^{-(t-t')/T_v-i(\omega_R-\omega_S-\omega_v)t'}, \tag{5}$$

where ω_v and T_v are the transition frequency and dephasing time between the initial and vibrational excited states, respectively, and the parameter κ contains material parameters like the Raman cross section. Here, we assume that the lifetime of the transient species is independent of the stimulated Raman process and ignore the resonance of the Raman pump pulse with transition to higher-lying excited states. The obtained nonlinear polarization $\mathcal{P}$ leads Raman gain and coherent anti-Stokes Raman scattering (CARS). The Raman gain signal is obtained from the polarization

$$\begin{aligned}\mathcal{P}_{RG}&=P_{RG}(t)e^{-i\omega_{RG}t}+\text{c.c.}\\ &=-iQ^*(t)E_R(t)e^{-i\omega_{RG}t}+\text{c.c.},\end{aligned} \tag{6}$$

where $\omega_{RG}=\omega_R-\omega_v$. The transmittance change ΔT_{RG} of the probe pulse observed by the spectrometer is calculated using relations

$$\chi_{RG}(\omega)=\frac{P_{RG}(\omega)}{E_S(\omega)} =\frac{\int_{-\infty}^{\infty}dt\, e^{i\omega t}P_{RG}(t)e^{-i\omega_{RG}t}}{\int_{-\infty}^{\infty}dt\, e^{i\omega t}E_S(t)e^{-i\omega_S t}}, \tag{7}$$

$$\Delta T_{RG}(\omega)\propto -\text{Im}\,\chi_{RG}(\omega), \tag{8}$$

where χ_{RG} is the nonlinear susceptibility corresponding to the Raman gain.

First, we consider an ideal case. The Raman pump pulse and the probe pulse are assumed to be monochromatic and a δ-function pulse, respectively, as

$$E_R(t)=E_{R0}, \tag{9}$$

$$E_S(t)=E_{S0}\delta(t-t_d). \tag{10}$$

where t_d is the delay time between the first pump pulse and the probe pulse. The nonlinear susceptibility and transmittance change due to the Raman gain is obtained as

$$\chi_{RG}(\omega,t_d)=\begin{cases} 0 & (t_d<0), \\ \dfrac{\kappa|E_{R0}|^2N_0e^{-t_d/T_n}}{\omega-\omega_{RG}+i(T_v^{-1}+T_n^{-1})} & (t_d\geqslant 0), \end{cases} \tag{11}$$

$$\Delta T_{RG}(\omega,t_d)\propto\begin{cases} 0 & (t_d<0), \\ \dfrac{N_0e^{-t_d/T_n}}{(\omega-\omega_{RG})^2+(T_v^{-1}+T_n^{-1})^2} & (t_d\geqslant 0). \end{cases} \tag{12}$$

The dependence on the delay time t_d follows exactly the density of the transient species given in Eq. (1). Therefore, the temporal resolution of the instrument is infinitely good. The dependence on the probe frequency ω gives the observed spectrum. It has a peak at ω_{RG} and the bandwidth of $T_v^{-1}+T_n^{-1}$. Since both the initial and final states of the Raman process in the transient species have the lifetime of T_n, the broadening becomes T_n^{-1} instead of $T_n^{-1}/2$. The observed spectrum is the intrinsic Raman signal of the transient species. This means that the spectral resolution of the instrument is also infinitely good. Therefore, this method can measure the Raman signal in transient species correctly without slowing the temporal response and broadening the spectrum. Of course the observed signal cannot exceed the transform limit because of the limited material response. The extreme resolutions of the instrument are caused by the assumptions of the δ-function probe pulse and the monochromatic Raman pump light.

Next, we calculate the signal obtained by the probe and Raman pump pulses with finite duration and bandwidth. For simplification, the pulse shapes are assumed to be exponential as

$$E_R(t)=E_{R0}e^{-|t-t_d-\Delta t|/T_R}, \tag{13}$$

$$E_S(t)=E_{S0}e^{-|t-t_d|/T_S}, \tag{14}$$

where T_R and T_S correspond to the durations of the Raman pump and probe pulses, respectively. Δt is the time difference between the Raman pump pulse and the probe pulse and is assumed to be much smaller than T_R. The duration of the probe pulse T_S is assumed to be shorter than the material time constants and the duration of the Raman pump pulse as $T_S<T_v,T_n,T_R$. Then, the transmittance change is obtained as

$$\Delta T_{RG}(\omega,t_d)\propto\frac{N_0 f(\omega,t_d)}{(\omega-\omega_{RG})^2+(T_v^{-1}+T_n^{-1}+T_R^{-1})^2}, \tag{15}$$

$$f(\omega,t_d)=\begin{cases} f_-(\omega,t_d)e^{t_d/T_S} & (t_d<0),\\ e^{-t_d/T_n}-f_+(\omega,t_d)e^{-t_d/T_S} & (t_d\geqslant 0),\end{cases} \tag{16}$$

where $f_\mp(\omega,t_d)$ do not have a term which changes faster than $e^{\pm t_d/T_S}$, respectively. The signal for $t_d<0$ rises with the time constant of T_S, because the temporal dependence of f_- is slower than e^{t_d/T_S}. The first term for $t_d\geqslant 0$ is equal to the density of the transient species. The second term for $t_d\geqslant 0$ decreases with the time constant of T_S. Therefore, the temporal resolution of the instrument is determined by the duration of the probe pulse independently of the Raman pump pulse. The spectrum observed at $t_d\sim 0$ is expected to be complicated by the influence of $f_\pm(\omega,t_d)$, but the spectrum at $t_d\gg T_S$ has a Lorentzian shape with the center frequency of ω_{RG} and the bandwidth of $T_v^{-1}+T_n^{-1}+T_R^{-1}$. The Raman signal of the transient species can be observed only with the broadening due to the bandwidth of the Raman pump pulse, T_R^{-1}. The broad bandwidth of the ultrashort probe pulse is independent of the spectral resolution of the instrument.

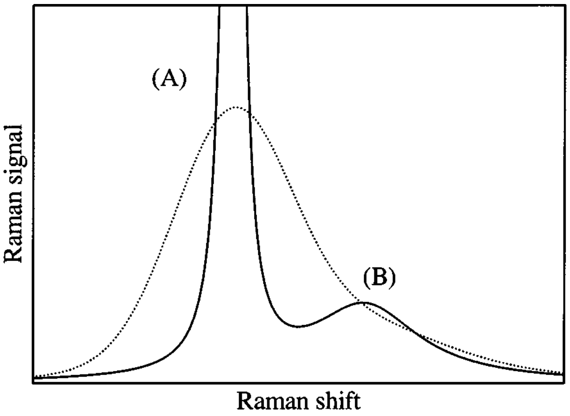

FIG. 2. Simulation of Raman signals obtained by the ordinary time-resolved Raman spectroscopy (dotted curve) and our unique time-resolved Raman spectroscopy (solid curve).

When the Raman pump pulse is resonant or nearly resonant with the transition from the initial state to higher-lying excited states, the temporal dependence of $f_\pm$ is affected by the dynamics of the higher-lying states [20]. The signal due to the resonant excitation can be distinguished from the stimulated Raman signal using the dependence on the time difference Δt between the Raman pump and probe pulses. The temporal resolution on the delay time t_d is limited by the material time constants in the resonant case, but it is usually in the femtosecond region because of ultrafast decay kinetics of the higher-lying states.

In the theoretical calculation, the photogeneration of the transient species is assumed to be instantaneous and the resolution of the spectrometer is not considered. In experiment, the transient species is generated by the first pump pulse with finite duration and the probe pulse is measured by a spectrometer with finite resolution. Therefore, the temporal resolution of the instrument is given by the cross-correlation signal of the first pump and probe pulses. The spectral resolution is determined by the bandwidth of the Raman pump pulse and the resolution of the spectrometer. Full width at half maximum (FWHM) of the Raman pump spectrum observed by the spectrometer gives the spectral resolution of the instrument. Since the resolutions are determined by the different factors, they can be improved individually without the restriction of the transform limit of a single pulse.

Advantage of this method is shown in Fig. 2. We simulate Raman spectra in a model material with two species observed by the ordinary method and our method with equal temporal resolution T_S. The species (A) is a ground state ($T_n=\infty$) and its vibrational excited state has long dephasing time $T_v=20T_S$. The other species (B) is a transient species with a short population lifetime and short vibrational dephasing time $T_n=T_v=T_S$. In the ordinary method, the duration of the Raman probe pulse is T_S for the temporal resolution, so the observed spectrum (dotted curve) is broadened by the bandwidth T_S^{-1} and the signal (B) cannot be distinguished from the signal (A). Even if the transient signal is obtained by the subtraction of the background signal, the observed spectrum is widely broadened from the intrinsic spectrum of the material. On the other hand, the signal observed by our present method (solid curve) has a sharp feature, because the spectral resolution T_R^{-1} is much better than T_S^{-1}. The Raman signal (B) is clearly observed. Our present method can easily distinguish the Raman signals in transient species from the intense background signals due to the ground state.

The essential point of the this method is the combination of the narrow bandwidth Raman pump pulse and the ultrashort probe pulse. This concept can be applied to other stimulated Raman scattering. CARS with the supercontinuum Stokes pulse is obtained from the same polarization in Eq. (4). Polarization in Raman loss and coherent Stokes Raman spectroscopy (CSRS) is induced by an anti-Stokes supercontinuum probe pulse and has similar responses on the delay time and the probe frequency. These measurements give the same resolutions. Therefore, the proper method can be selected according to the condition of materials. The Raman gain and loss are suitable for materials with strong fluorescence. The CARS and CSRS are more sensitive for weak Raman signals in nonfluorescent materials.

III. EXPERIMENTAL RESULTS

The femtosecond light source in this study was a combination of a mode-locked Ti:sapphire laser (Avesta) and a kHz regenerative amplifier (Spectra Physics, Spitfire). Typical characteristics of the amplified pulse were 1 mJ power at 795 nm and a duration of 140 fs. The pulse was separated to three beams using beam splitters. The first beam was passed through a 3-mm (LiB_3O_5) (LBO) crystal for the second-harmonic generation and used as the first pump pulse. The first pump pulse was delayed using an optical variable delay and focused on a sample. The second beam passed through an interference filter (center wavelength 794.7 nm, FWHM 1.5 nm) and used as the Raman pump pulse. The last beam was focused into a 10 mm cell containing water. The generated femtosecond supercontinuum was used as the probe pulse. The Raman pump pulse and the probe pulse were simultaneously focused on the sample. The transmitted probe pulse was detected by a spectrometer with a charge-coupled device (CCD) detector (JOBIN YVON, SR460). The Raman signal is obtained as a transmittance change of the sample.

The temporal resolution of the instrument was determined by measuring a cross-correlation signal of the first pump pulse and the probe supercontinuum. Figure 3 is the correlation signal obtained by the optical Kerr effect in a 1-mm quartz glass plate. The linear polarization of the second-harmonic pump pulse was rotated 45° from the polarization of the probe pulse. The intensity of the probe pulse transmitted crossed polarizers was observed by the spectrometer. The correlation signal can be approximated by a Gaussian function. The FWHM is about 250 fs in the probe wavelength region of 600–1000 nm.

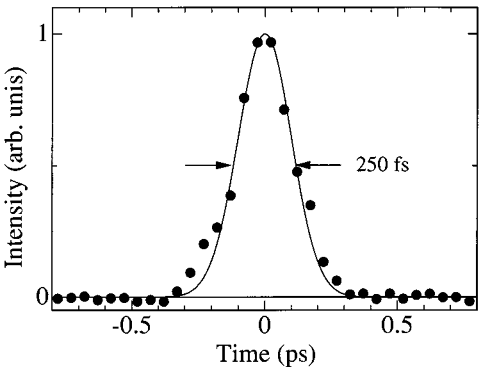

FIG. 3. Optical Kerr gate signal (solid circles) induced by the first pump pulse and observed by the supercontinuum probe pulse at 700 nm. The solid curve is the best-fitted curve of a Gaussian function.

The spectral resolution was obtained as 25 cm^{-1} from the FWHM of the Raman pump spectrum detected by the spectrometer. It is mainly due to the bandwidth of the interference filter (FWHM the 23 cm^{-1}) and partly due to the resolution of the spectrometer (10 cm^{-1}). Figure 4 shows the transmittance change in benzene induced by the 794.7-nm Raman pump pulse. Benzene is suitable for checking the spectral resolution, because it has sharp and intense Raman lines. The observed line at 990 cm^{-1} has the bandwidth of 28 cm^{-1}. It is almost equal to the spectral resolution estimated from the bandwidth of the Raman pump pulse. The instrument can measure the spectral region over 3000 cm^{-1} at one time, but the signal below 200 cm^{-1} has a large uncertainty because of the unstability of the probe pulse and scattering of the Raman pump pulse.

The developed system has been applied to photoisomerization of 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) dye in solution. DCM has a similar structure with stilbene which is well known with *trans-cis* photoisomerization [21,22]. DCM in fresh solution has *trans* form and it changes to *cis* form after photoexcitation [23,24]. In this study, a 1-mm flow cell was used to avoid accumulation of the *cis* form. The concentration of DCM was about 3×10^{-3} mol/l in dimethyl sulfoxide (DMSO) solution.

Figure 5 shows the time-resolved Raman signals in the DCM solution after the 397-nm photoexcitation. The photoinduced absorbance change in DCM around 800-nm is very small, so the Raman pump pulse can be considered to be nonresonant with the transient states. Since the Raman signal at delay time of -1 ps is equal to the signal without the first pump pulse, it is assigned to the ground states of the solu-

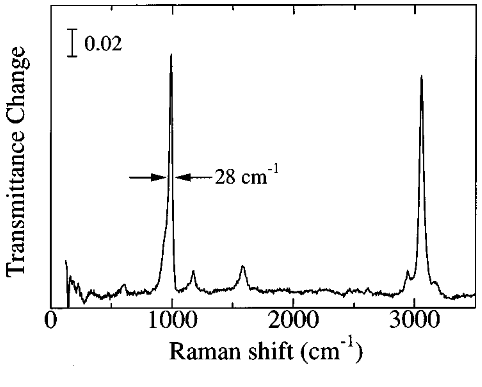

FIG. 4. Transmittance change due to stimulated Raman scattering in benzene induced by the Raman pump pulse.

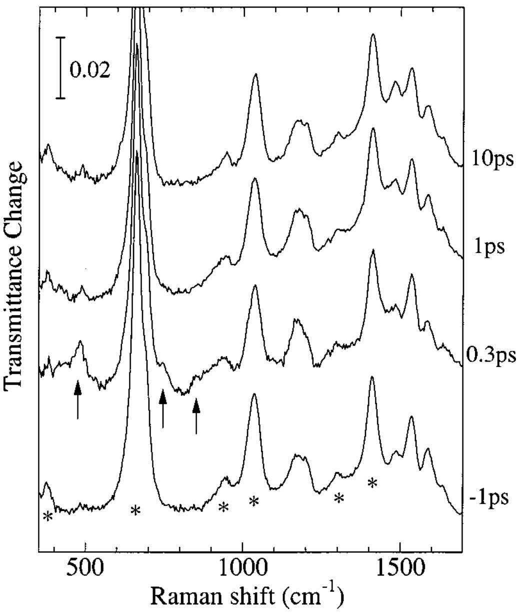

FIG. 5. Transmittance change due to stimulated Raman scattering in a DCM solution at several delay times after photoexcitation. Arrows indicate the Raman signals due to the photogenerated transeint states. Asterisks indicate Raman lines of the solvent (DMSO).

tion. The accumulation of the *cis* form during the measurement is negligible. Intense signals with asterisks are Raman lines of solvent (DMSO). The other lines, a broad Raman signal at 1200 cm^{-1} and four Raman lines at 1490, 1540, 1590, and 1640 cm^{-1}, are assigned to *trans*-DCM. At a delay time of 0.3 ps, the transient Raman signal has new lines at 480, 760, and 850 cm^{-1}. These signals decrease within 1 ps, but the 480-cm^{-1} line remains longer than 10 ps. It should be noted that the ordinary time-resolved Raman spectroscopy cannot observe the 760-cm^{-1} line, because the femtosecond study cannot separate the strong solvent line at 670 cm^{-1} and the picosecond study cannot time resolve the signal.

The new peaks are tentatively assigned to *cis*-DCM or an intermediate state between *trans* and *cis* forms generated by the photoexcitation. Comparing with the resonance Raman spectrum in *cis*-stilbene [22], the observed 480-cm^{-1} line is considered to have torsional character in the *cis* form which is not observed in the *trans* form. The dynamics of the Raman signal is roughly explained by a following model [24]. After photoexcitation, DCM molecules change to the excited state of the *cis* form or to the intermediate state within 0.3 ps. Then, the majority of them recover to the *trans* form within 1 ps and the transient signals decrease, but the rest remain in the *cis* form and relax to the ground state of the *cis* form. The photoisomerization process of DCM will be discussed in more detail elsewhere [25].

IV. SUMMARY

We have developed a different femtosecond time-resolved Raman spectroscopy that measures stimulated Raman scattering in photoinduced transient species using a Raman pump pulse with narrow bandwidth and a femtosecond supercontinuum probe pulse. Since the temporal and spectral resolutions of the instrument are determined by different pulses, they can be improved free from the transform limit of a single pulse. The Raman signals can be observed without slowing the temporal response and broadening the spectrum. This method can apply to any stimulated Raman scattering, i.e., Raman gain, Raman loss, CARS, and CSRS. The temporal resolution of 250 fs and the spectral resolution of 25 cm^{-1} has been obtained simultaneously in this study. The better resolutions can be obtained using shorter pulses and an interference filter with a narrower bandwidth. The validity of the system has been demonstrated by the application to the photoisomerization of organic dye. The transient Raman signal due to the *trans*-*cis* photoisomerization in the DCM solution has been observed perhaps.

ACKNOWLEDGMENT

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