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Ultrafast Relaxation in Conjugated Polymers: Femtosecond Raman Gain Spectrum of Excitons with 1.5-PS Life in Polydiacetylene

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ULTRAFAST RELAXATION IN CONJUGATED POLYMERS: FEMTOSECOND RAMAN GAIN SPECTRUM OF EXCITONS WITH 1.5-PS LIFE IN POLYDIACETYLENE

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Abstract Femtosecond time-resolved resonance Raman gain spectroscopy was developed and applied to the study of the geometrical configuration taking place in the process of the self-trapping of excitons in polydiacetylene. Raman signal due to the self-trapped excitons (STE) has been observed for the first time. A new peak at 1200 cm^{-1} is attributed to the butatriene-like structure in the STE and the signal decays biexponentially with the constants of 150fs and 1.5ps. This is consistent with our previous study of induced absorption spectrum due to the nonthermal excitons and due to the quasi-thermal excitons with lifetimes of 150fs and 1.5ps respectively.

INTRODUCTION

Ultrafast relaxation in conjugated polymers are related with the geometrical relaxation due to electron-phonon coupling. This introduces nonlinear excitations such as solitons, polarons, and bipolarons [1]. In order to obtain the structural information of excited species, time-resolved (TR) vibrational spectroscopies such as TR infrared absorption, TR resonance spontaneous Raman scattering, TR resonance coherent Raman scattering (CARS) have been utilized [2,3]. However, these methods have serious disadvantages such as low sensitivity, disturbance by spontaneous florescence, and interference with nonresonant background.

We have developed a Raman gain spectroscopy with femtosecond resolution. The advantage of the method is as follows. (1) The method is not suffered from disturbance by fluorescence as in spontaneous Raman scattering. (2) The interference of signal with nonresonant background does not appear. This is extremely advantageous to the time-resolved CARS spectroscopy. We have applied this new method to the excitons in polydiacetylene (PDA), polythioplenes, and a polyacetylene derivative with

only 1.5 ps lifetime. This offers the vibrational spectrum with the highest time resolution ever reported.

Conjugated polymers have attracted much attention because of their unique properties as model compounds of one-dimensional electronic systems. Conjugated polymers have localized excited states with geometrical relaxation. We have investigated self-trapped exciton (STE) in polydiacetylenes (PDA) using femtosecond spectroscopy [4-15]. The formation process of STE from free-exciton (FE) has been observed as a spectral change of photoinduced absorption with a time constant of about 150 fs [7]. Transient fluorescence from FE in PDA observed by probe saturation spectroscopy (PSS) has a peak at 1.9 eV and decays with the formation of the STE [9].

Time-resolved resonance Raman spectroscopy has been recognized as a powerful method for studying structures of transient species and electronic excited states. Terai et al. have calculated phonon modes of localized excited states in $(CH)_x$ and predicted that solitons and polarons can be distinguished by Raman spectroscopy [16]. However, only a few time-resolved Raman experiments have been performed in conjugated polymers because of the difficulty due to very short lifetime of the excited states [17,18]. However, the observed signals are due to the depletion of the ground state. New phonon modes of excited states in conjugated polymers have not been observed by transient Raman spectroscopy.

EXPERIMENTAL

The femtosecond Raman gain spectroscopy was performed using three pulses of femtosecond durations as shown in Fig. 1. The 1.97-eV femtosecond pulse was generated by a colliding-pulse mode-locked dye laser and amplified by a four-stage dye amplifier [4]. The duration and energy of the amplified pulse were 100 fs and 200μJ, respectively. The amplified pulse was split into three beams. The first beam (pump-1) generated excited states in PDA. A part of white continuum generated from the second one was amplified by a two-stage dye amplifier. The amplified pulse has the center photon energy of 1.78 eV and the duration of 200 fs and was used for the pump pulse of the Raman gain spectroscopy (pump-2). The probe pulse was white continuum generated from the last beam. Using this technique the time dependence and spectra of photoinduced absorption, bleaching, stimulated emission, and Raman gain were observed at the same time. The Raman gain signal was distinguished using the time dependence and sharp structure. Polarizations

of the three beams were parallel to oriented polymer chains of PDA-3BCMU deposited on a KCl crystal [8]. All the experiment was done at room temperature.

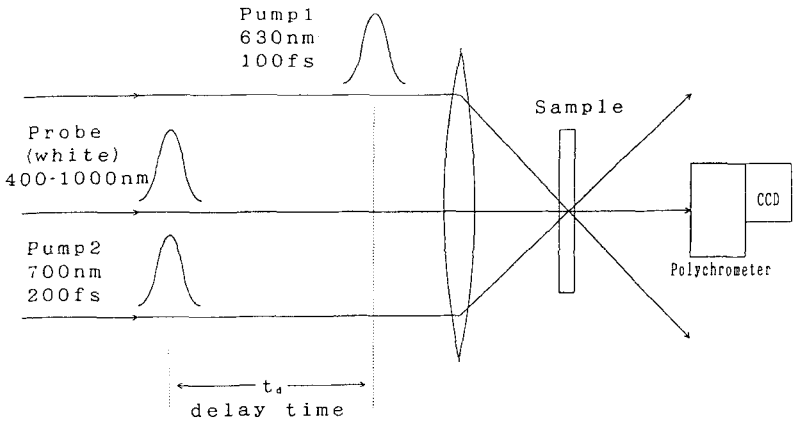

FIGURE 1 Time-resolved Raman gain spectroscopy.

RESULTS AND DISCUSSION

Figure 2 shows Raman gain spectra obtained using the 1.78-eV pulse at several delay times after the 1.97-eV photo-excitation. At -0.5 ps, two Raman gain peaks are observed at 1440 and 2060 cm^{-1}. They are assigned to the stretching vibrations of the C=C and C≡C bonds in the acetylene-like structure of the ground state. The spectrum at 0.0 ps has broad signal below the 1440 cm^{-1} Raman peak down to 1000 cm^{-1}. At delay time longer than 0.2 ps the Raman signal has a clear peak at 1200 cm^{-1}. The spectral change of the Raman signal around 1200 cm^{-1} is reproducible and is observed also in PDA-C_4UC_4. The width of the 2060 cm^{-1} Raman signal becomes slightly broader after the photoexcitation, but no new Raman peak is observed around 2000 cm^{-1}.

Figure 3 shows the transient Raman gain change at 1200 and 1440 cm^{-1}. The negative change at 1440 cm^{-1} is explained by the depletion of the ground state due to the formation of STE. The time dependence is consistent with the decay kinetics of the STE. The signal appears slightly slower than the 1.97-eV pump pulse and decays within several picoseconds. The solid curve is the best fitted curve using time constants of 150 fs and 1.5 ps. The change at 2060 cm^{-1} is also negative and has similar time dependence with the 1440-cm^{-1}

signal. The time dependence of the Raman signal at 1200 cm^{-1} has two components. The long-life component decays within several picoseconds and is assigned to the STE. The short-life component has time constant shorter than the present resolution time of 300 fs and is assigned to the nonthermal STE, because the 1.78-eV pulse can be resonant with the transition between the nonthermal STE and the ground state.

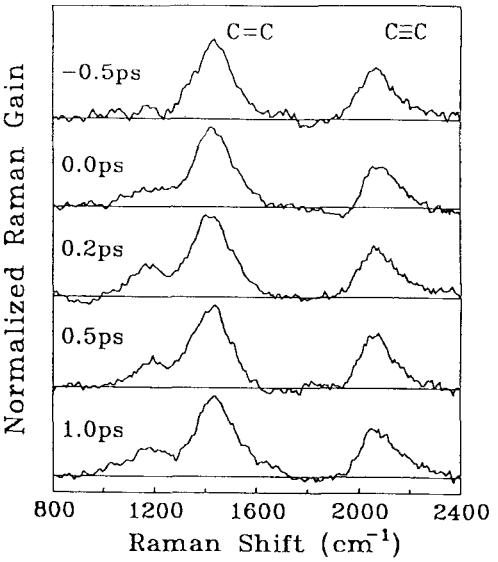

FIGURE 2 Normalized resonance Raman gain spectra at several delay times after the 1.97-eV photoexcitation.

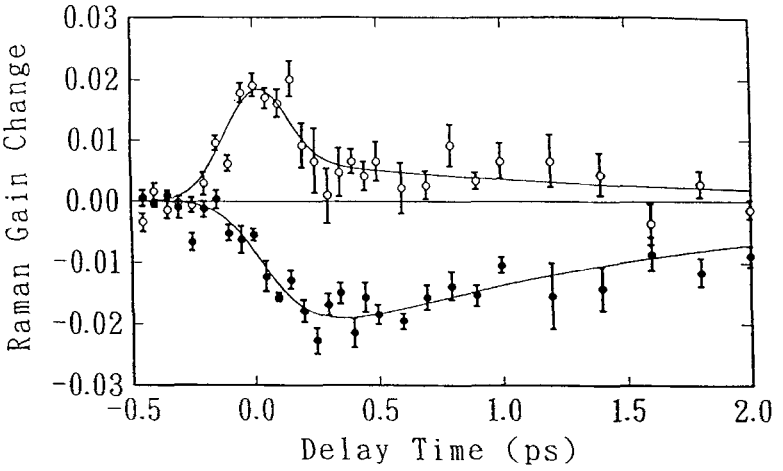

FIGURE 3 Transient Raman gain changes at 1200 cm^{-1} (open circles) and 1440 cm^{-1} (closed circles) after the 1.97-eV photoexcitation. The solid curves are the best fitted curves with time constants of 150 fs and 1.5 ps.

The theoretical calculation has predicted that the localized excitations in *trans*-$(CH)_x$ have several Raman active phonon modes [16]. The expected signal is the reduction of the stretching vibration modes and new Raman lines at lower frequencies than the stretching modes. The Raman signal observed in PDA is similar to this feature. However, the phonon modes of the STE in PDA have not been investigated. Here, the observed Raman frequency is compared with stretching modes of center bonds in unsaturated hydrocarbons with four carbon atoms, i.e. repeat units of PDA [19]. The formation of the STE in PDA is expected to be the geometrical relaxation from the acetylene-like structure $(=CR-C\equiv C-CR=)_x$ to the butatriene-like structure $(-CR=C=C=CR-)_x$. The C=C bond in *trans*-butene-2 (CH_3-CH=CH-CH_3) has a stretching mode with 1675 cm^{-1}, while the frequency of the C-C bond in trans-1,3-butadiene (CH_2=CH-CH=CH_2) is 1202 cm^{-1}. Therefore, the 1200 cm^{-1} Raman peak can be assigned to the C-C bond in the butatriene-like structure. However, Raman signal due to the C=C bond in the butatriene-like structure cannot be observed in this study. It can be explained by close frequencies of the stretching modes of the center C=C bond in butatriene (CH_2=C=C=CH_2) and the C≡C bond in dimetylacetylene (CH_3-C≡C-CH_3), 2079 and 2235 cm^{-1}, respectively. The expected new Raman signal near the 2060 cm^{-1} peak cannot be resolved in this study because of the broad pump spectrum.

In conclusion, we developed a new time resolved Raman spectroscopy and the new Raman peak due to self-trapped exciton in PDA has been observed at 1200 cm^{-1} for the first time by the femtosecond time-resolved Raman gain spectroscopy. The observed Raman signals indicate the butatriene-like structure due to the formation of the STE after the geometrical relaxation from the acetylene-like structure in the FE state.

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