

Femtosecond time-resolved resonance Raman gain spectroscopy in polydiacetylene

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Geometrical relaxation of the main chain configuration in polydiacetylene (PDA) has been investigated with time-resolved resonance Raman gain spectroscopy with 300-fs resolution. The Raman signal due to a self-trapped exciton in PDA has been observed at 1200 cm^{-1} . The observed Raman signals offer direct evidence of the structure of a self-trapped exciton being a butatrienelike structure after geometrical relaxation from the acetylenelike structure in the free exciton state.

Conjugated polymers have attracted much attention because of their unique properties as model compounds of one-dimensional electronic systems. Their large and ultrafast optical nonlinearities have recently been of great interest because of possible applications to nonlinear optical devices.^{1,2} One-dimensional systems such as conjugated polymers have localized excited states with geometrical relaxation. Solitons and polarons in polyacetylene (PA) can be generated by photoexcitation^{3,4} and have been observed by time-resolved absorption spectroscopy.⁵⁻⁸ Polydiacetylenes (PDA's) ($=CR-C\equiv C-CR'$)_x, with *R* and *R'* being side groups, have a nondegenerate main chain with a so-called "acetylenelike" configuration. The localized excitations that can be generated in PDA are the self-trapped exciton (STE) (exciton polaron), the polaron, and the bipolaron. The formation process of the STE from a photoexcited free exciton (FE) has been observed as a spectral change of photoinduced absorption with a time constant of about 150 fs in several PDA's.⁹⁻¹⁴ Transient fluorescence from FE in PDA-C₄UC₄ [*R*=*R'*=(CH₂)₄CONH(CH₂)₃CH₃] has been observed by probe-saturation spectroscopy (PSS) developed by our group recently.¹⁵ The fluorescence from FE has a peak at 1.9 eV and decays with the formation of the STE.

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.*¹⁶ have calculated phonon modes of localized excited states in PA and predicted that solitons and polarons can be distinguished by Raman spectroscopy. However, only a few time-resolved Raman experiments have been performed on conjugated polymers¹⁷⁻²⁰ because of the difficulties due to its very short lifetime (about 1 ps) and near-infrared absorption of the excited states. Zheng *et al.*¹⁷ have investigated picosecond transient Raman scattering in PDA-4BCMU (4-butoxycarbonylmethylurethane) and observed the reduction of the Raman intensity due to the saturation of the Raman cross section caused by photogenerated excitons.

Lanzani *et al.*¹⁸ have measured transient photoinduced resonance Raman scattering in PA using two-color picosecond dye lasers. However, since the laser pulses are resonant with the absorption from the ground state, the observed signal $\Delta I/I$ is negative and has been explained using the phase-space-filling model. To the best of our knowledge new phonon modes of excited states in conjugated polymers have not been observed by the transient resonance Raman spectroscopy, because two-color ultrashort pulses which are resonant with the absorption from the ground state and from the excited state, respectively, and a near-infrared detector with high sensitivity are needed for the experiment. In the present study, the configuration of main chain in a polydiacetylene PDA-3BCMU (3-butoxycarbonylmethylurethane) has been investigated by femtosecond time-resolved resonance Raman gain spectroscopy.

The femtosecond Raman gain spectroscopy was performed using three pulses of femtosecond durations. The 1.97-eV femtosecond pulse was generated by a colliding-pulse mode-locked dye laser and amplified by a four-stage dye amplifier pumped by the second harmonic of a 10 Hz Q-switched Nd:YAG laser.⁹ The duration and energy of the amplified pulse were 100 fs and 200 μJ , respectively. The amplified pulse was split into three beams. The first beam (pump 1) was resonant with the excitonic absorption and generated excited states in PDA. The second one was focused in a 3-mm cell containing CCl₄ and femtosecond white continuum was generated by self-phase modulation (SPM). A part of the white continuum was selected with a set of prism pairs and a slit and amplified by a two-stage dye amplifier pumped by the second-harmonic of the Q-switched Nd:YAG laser. An interference filter (CORION, S10-700-F) was inset between the amplification stage to suppress the amplified spontaneous emission and to stabilize the wavelength. The amplified pulse has a center photon energy of 1.78 eV and a duration of 200 fs. The 1.78-eV pulse (pump 2) was resonant with the absorption from the STE and was used for the pump pulse of the Raman gain spectroscopy.

The probe pulse was white continuum generated from the last beam by SPM and detected with a polychromator/CCD system. 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, because the photoinduced absorbance change and luminescence in PDA have finite lifetime longer than 150 fs and broad spectra.^{1,2,12-15} Polarizations of the three beams were parallel to oriented polymer chains of PDA-3BCMU deposited on a KCl crystal.² The entire experiment was performed at room temperature.

Figure 1 shows transient absorption spectra induced by the 1.97-eV pulse (pump 1), which is exactly resonant with an excitonic absorption peak. When the pump and probe pulses overlap in time at the sample, three sharp negative peaks are observed. The peak at 1.97 eV is due to saturation of the excitonic absorption and coherent coupling between pump polarization and probe field.² The other two peaks at 1.79 and 1.71 eV are due to the Raman gain of the stretching vibration modes of C=C and C≡C bonds, respectively. The photoinduced absorbance change below 1.8 eV shifts to higher energy with time from 0.0 to 0.5 ps. This spectral change has been explained by the relaxation model shown in Fig. 2.¹²⁻¹⁴ The FE (state 1) photoexcited by the pump-1 pulse is coupled with the stretching modes of carbon atoms within the phonon periods of 10–20 fs and becomes nonthermal STE (state 2). Then the nonthermal STE relaxes to the bottom of the potential surfaces (quasi-thermal STE, state 3) by a quasithermalization process. Therefore, the transient absorption is shifted to higher energy and the transient fluorescence of the FE decays very rapidly as observed by PSS.¹⁵ The STE relaxes to the ground state (*G*) by tunneling in the configuration space before thermalization, which has a time constant of 1.5 ps. The 1.78-eV pulse (pump 2) is resonant with

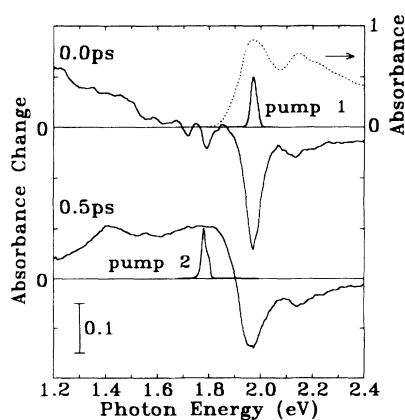


FIG. 1. Transient absorption spectra induced by the 1.97-eV pulse in PDA-3BCMU. The stationary absorption spectrum and the spectra of the 1.97-eV (pump 1) and 1.78-eV (pump 2) pulses are shown together. The excitation photon density is 1.7×10^{15} photons/cm².

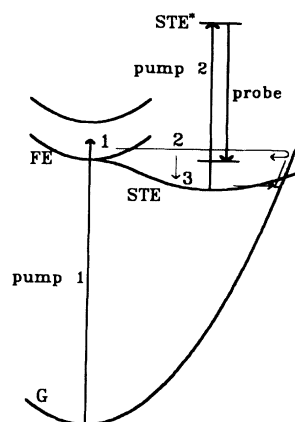


FIG. 2. Relaxation model in polydiacetylene shown in potential surfaces of excitons. States 1, 2, 3, and *G* are free exciton (FE), nonthermal self-trapped exciton (STE), quasi-thermal STE, and the ground state, respectively. STE* is a biexciton state with 1A_g symmetry.

the transition observed at 1.8 eV. This absorption peak is assigned to the transition from the STE to a biexciton with 1A_g symmetry.^{13,14}

The transient absorption spectrum induced by the 1.78-eV pulse (pump 2) is shown in Fig. 3. The pump-2 and probe pulses pass through the sample simultaneously. Two minima due to the Raman gain are clearly observed at 1.60 and 1.52 eV. The broad positive absorbance change is due to the photogenerated excitons, because the 1.78-eV pulse excites the edge of the excitonic absorption. The Raman gain spectra are obtained by subtracting the absorption spectra due to the excitons from the observed absorbance change. The absorption spectra of the excitons are estimated from the data in the regions at 1.42–1.46 eV and 1.67–1.71 eV using a quadratic equation, because the spectra have no sharp structure between 1.4 and 1.8 eV except the Raman gain signals as shown in Fig. 1.

Figure 4(a) shows the normalized Raman gain spectra obtained using the 1.78-eV pulse at several delay times after the 1.97-eV photoexcitation. 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 acetylenelike structure of the ground state. The spectrum at 0.0 ps has a broad signal below

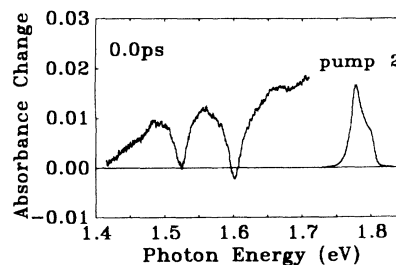


FIG. 3. Transient absorption spectrum of PDA-3BCMU induced by the 1.78-eV pulse (pump 2). The excitation photon density is 9.0×10^{15} photons/cm².

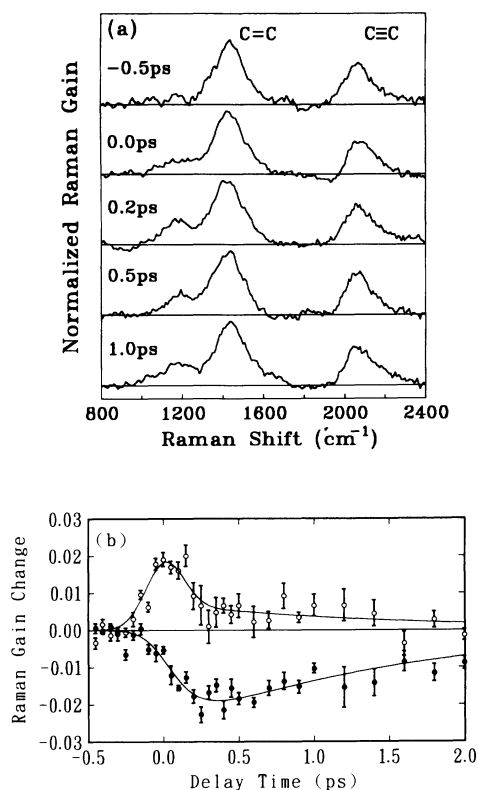


FIG. 4. (a) Normalized resonance Raman gain spectra at several delay times and (b) transient Raman gain changes at 1200 cm^{-1} (open circles) and 1440 cm^{-1} (closed circles) of PDA-3BCMU after the 1.97-eV photoexcitation. The solid curves in (b) are the best fitted curves with time constants of 150 fs and 1.5 ps. The resolution time is 300 fs. The excitation photon densities of the 1.97-eV and 1.78-eV pulses are 2.9×10^{15} and 9.0×10^{15} photons/cm², respectively.

the 1440-cm^{-1} Raman peak down to 1000 cm^{-1} . At a 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-C₄UC₄. 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 4(b) 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 the formation time constant of 150 fs and 1.5 ps. The change at 2060 cm^{-1} is also negative and has a 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 a time constant shorter than the present resolution time of 300 fs and is probably due to the nonthermal STE, because the 1.78-eV pulse can be resonant with the transition between the

nonthermal STE and the ground state.

The Raman signal of the ground state in PDA has a weak peak assigned to the bending mode of the C=C bond around 1200 cm^{-1} .^{21,22} Therefore, the observed 1200-cm^{-1} Raman signal may be explained by the increase in the Raman cross section of the bending mode. However, since the 1200-cm^{-1} spectrum at 0.0 ps is broader than at later times, this spectral change cannot be explained by the increase of the cross section. It suggests that the geometrical relaxation of main chain configuration due to the self-trapping process takes place after the 1.97-eV photoexcitation. Since the wave packet of the nonthermal STE oscillates in the configuration space as shown in Fig. 2, the Raman signal due to the nonthermal STE is broad. After the quasithermalization, the nonthermal STE relaxes to the bottom of the STE potential surface. Therefore, the oscillatory motion in the configuration space becomes smaller and the clear Raman peak is observed at 1200 cm^{-1} .

The theoretical calculation has predicted that the localized excitations in *trans*-PA 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.²³ 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 ($\text{CH}_3\text{-CH=CH-CH}_3$) has a stretching mode with 1675 cm^{-1} , while the frequency of the C-C bond in *trans*-1,3-butadiene ($\text{CH}_2=\text{CH-CH=CH}_2$) is 1202 cm^{-1} . Therefore, the 1200-cm^{-1} Raman peak can be assigned to the C-C bond in the butatrienelike structure. However, the Raman signal due to the C=C bond in the butatrienelike structure cannot be observed in this study. It may be explained by close frequencies of the stretching modes of the center C=C bond in butatriene ($\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$) and the C≡C bond in dimethylacetylene ($\text{CH}_3\text{-C}\equiv\text{C-CH}_3$), 2079 and 2235 cm^{-1} , respectively. The expected new Raman signal near the 2060-cm^{-1} peak is not resolved in this study because of the broad pump spectrum.

The intensity of the 1200-cm^{-1} peak is about one third of that of the 1440-cm^{-1} peak as shown in Fig. 4(a) and the change at 1200 cm^{-1} is also smaller than the change at 1440 cm^{-1} . The resonance Raman signal of the ground state pumped by the 1.78-eV pulse is estimated to be about 15% of that pumped by the 1.97-eV pulse using the homogeneous and inhomogeneous widths of the excitonic absorption of the PDA-3BCMU.¹² The absorbance of the sample at 1.97 eV is 0.8, while the maximum transient absorbance at 1.78 eV is 0.13 when the STE is generated by the 1.97-eV pulse with a density of 2.9×10^{15} photons/cm². Therefore, if the ground state and STE have the same Raman cross section, the Raman signals

due to the STE and the ground state are estimated to have almost the same intensity. The smaller 1200-cm^{-1} signal indicates that the Raman cross section of the STE is smaller than that in the ground state. It is mainly due to a broader absorption spectrum of the transition from the STE to higher excited states than the excitonic absorption from the ground state.

In conclusion, a Raman peak due to photoexcited states in PDA has been observed at 1200 cm^{-1} with femtosecond time-resolved Raman gain spectroscopy. The observed Raman signals indicate that the acetylenelike structure of the main chain relaxes to the butatrienelike structure due to the formation of the self-trapped exciton

with the geometrical relaxation. The formation and decay kinetics of the Raman signals is consistent with the relaxation processes of excitons observed by femtosecond absorption and fluorescence spectroscopies.¹²⁻¹⁵

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