Communication

Femtosecond Time-Resolved Stimulated Raman Gain Spectroscopy in Polydiacetylene

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Conjugated polymers have localized excited states with geometrical relaxation, i.e. soliton, polaron, and self-trapped exciton (STE). The geometrical relaxation due to STE formation from free exciton (FE) in polydiacetylene (PDA) has been observed by femtosecond stimulated Raman gain spectroscopy for the first time.

The femtosecond Raman gain spectroscopy was performed using three femtosecond pulses generated by a colliding-pulse mode-locked dye laser and dye amplifiers [1-3]. The 1.97-eV pulse with 100-fs duration was used for the generation of excited states in PDA. The 1.77-eV pulse with 200-fs duration was used for the pump pulse of the Raman gain spectroscopy. The probe pulse was the white continuum generated by self-phase modulation. Polarizations of the three beams were parallel to the oriented polymer chain of PDA-C4UC4 thin films (side group R=(CH2)4OCONHC4H9).

Figure 1(a) shows the transient absorption spectrum at 0.5 ps after the excitation of the 1.97-eV pulse. Bleaching due to saturation of the excitonic absorption and broad photoinduced absorption below 1.85 eV are observed. The ultrafast relaxation processes in PDA has been explained in terms of STE [1-4]. The absorption peak at 1.78 eV has been assigned to the transition from the STE to a biexciton state.

The transient absorption spectrum excited by the 1.77-eV pulse is shown in Fig. 1(b). Two minima due to the Raman gain are observed at 1.52 and 1.60 eV. The oscillational structures around 2 eV are mainly due to inverse Raman scattering [4]. The Raman gain spectra shown in Fig. 2 are obtained from the transient absorption spectra induced by the 1.77-eV pulse.

At -0.5 ps, two Raman gain peaks are observed at 1450 and 2060 cm⁻¹. They are assigned to the stretching vibrations of the C=C and C≡C bonds in

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acetylene structure \( \{CR=CR=CR\}_x \) of the ground state. The 1450 cm\(^{-1}\) Raman gain peak at 0.0 ps has shoulder at lower frequency and a clear peak is observed at 1200 cm\(^{-1}\) at delay times longer than 0.2 ps. This new peak can be explained by the C=C mode in butatriene structure \( \{CR=CR=CR\}_x \). The 2060 cm\(^{-1}\) Raman peak has no observable change, because the frequency of the middle C=C bond of the butatriene is similar to that of the C=C bond.

In conclusion, the new Raman peak due to self-trapped exciton in PDA was observed for the first time by femtosecond Raman gain spectroscopy. The observed Raman frequency indicates unambiguously the butatriene-like structure due to the formation of the STE after geometrical relaxation from the acetylene structure in the FE state as shown below.

References