

# Real-time molecular vibrational frequency and amplitude probing to resolve instantaneous structure

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Optical and electrical properties of conjugated polymers have attracted enormous attention because of their unique properties as model compounds of one-dimensional electronic systems. Among conjugated polymers polydiacetylenes (PDA's) have special interests because of their large nonlinearity. The ultrafast optical responses in PDA's have been intensively investigated using femtosecond absorption spectroscopy. The mechanism was explained by the following model. First, photoexcited  $^1B_u$  free exciton (FE) relaxes to the nonfluorescent  $^1A_g$  state, which lies lower than the  $^1B_u$  exciton. The nonthermal  $^1A_g$  state relaxes to the bottom of potential curve of the self-trapped exciton (STE) state and then thermalizes and then relaxes to the ground state.

In the present paper, real time evolution of the energies and intensities of features in transmittance change spectra was investigated and real-time vibrational frequencies of several modes were found to provide important information of instantaneous structure of polymers.

In the normalized difference transmission ( $\Delta T/T$ ) spectra, two components with different lifetimes were separated by the singular value decomposition (SVD) method. One is short-lived component of about 60 fs and the other is long-lived component of about 0.9 ps. In the separated spectrum of short-lived component, five positive peaks are found which are assigned to induced emission from the excited-state (ES) vibrational levels to the ground-state (GS) vibrational levels where no population exists because of much larger energies of the levels than the thermal energy of these peaks. Negative peaks in short-lived components could be due to induced absorption, but probe photon energy measured in this study is out of the range of two-photon absorption peaks from the ground state. Therefore only one-photon absorption is to be taken into account in the energy region from 1.68 to 2.28 eV and no induced absorption from  $^1B_u$  is appeared in short-lived component. The time trace of energy of a short-lived peak near 1.88 eV, which disappear within 100 fs, is shown in Fig. 1 with exponential fitting curves.

The transition energy from ES to GS is directly observed and it is found to shift to lower energy associated with the decay process from  $^1B_u$  FE to STE and geometrically relaxed  $2^1A_g$  state after photo-excitation. The time constant of the Stokes shift agrees well with decay time ( $\sim 50$  fs) of the induced emission. This is quite reasonable if we consider the facts that the quantum efficiency of emission is smaller than  $10^{-5}$ . Stokes shift has been estimated to be about 90 meV in PDA-3BCMU and 100 meV in red phase of PDA-4BCMU by stationary fluorescence spectra [4-6]. The binding energy of the STE in red-phase 3BCMU is smaller than that of blue-phase 3BCMU as known from the fact that zero phonon transition energy in the former is larger than that of the latter. Therefore, the configuration in the excited state of 4BCMU is considered to be unstable and hence Stokes shift is larger than in 3BCMU.

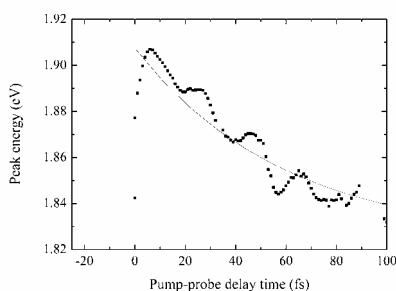


Fig. 1. Energy shifts of peaks due to geometrical relaxation from  $^1B_u$  FE to  $2^1A_g$  STE.

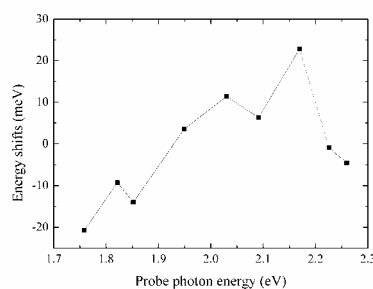


Fig. 2. Energy shifts due to thermalization in  $2^1A_g$  STE during 1400 fs between 100 fs and 1500