Photoinduced Ionic to Neutral Phase Transition in TTF-CA Studied by Time-Resolved Infrared Vibrational Spectroscopy

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We studied the photoinduced ionic to neutral phase transition in tetrathiafulvalene-p-chloranil (TTF-CA) using time-resolved infrared vibrational spectroscopy. By monitoring the charge sensitive $b_{1u}\nu_{10}$ band of CA after photoexcitation by a 1.55 eV pulse, we found that the photoinduced N-phase has the same charge of the N-phase in thermal equilibrium and there is no charge variation during the photoinduced phase transition. We also found that the photoinduced N-phase grows through at least two steps over 300 ps.

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1. Introduction

Tetrathiafulvalene-p-chloranil (TTF-CA) is one of the most intensively studied materials in terms of photoinduced phase transition (PIPT) [1–13]. TTF-CA is a mixed stack charge transfer complex consisting of donor (D = TTF) and acceptor (A = CA) molecules. At room temperature, TTF-CA is in the neutral phase (D^0A^0), and it undergoes neutral to ionic phase (D^+A^-) transition at T_c = 81 K by lowering temperature. This phase transition originates from competition between an ionization-energy difference and a long-range Coulomb energy gain [14–16]. To date, both PIPTs from neutral to ionic (N-to-I) and from ionic to neutral (I-to-N) were observed, and various processes and phenomena were revealed while the PIPTs take place [1–13].

In the previous optical spectroscopic studies, only electronic transitions at near-infrared to visible light were measured for knowing characters of photoinduced phases [1, 2, 4–8]; however, the electronic transitions give only indirect information on structure and charge of molecules. In contract, frequencies of vibrational bands in the mid-infrared region are known to shift sensitively according to structure and charge of constituent molecules in charge transfer complexes [17, 18]. Thus, we applied time-resolved infrared vibrational spectroscopy to studying the I-to-N phase transition in TTF-CA. In this report, we focused on temporal variation of the CA $b_{1u}\nu_{10}$ vibrational band whose frequency is sensitive to charge of CA.

2. Experiment

Time-resolved infrared vibrational spectra were measured using a broad-band femtosecond mid-infrared pulse and a MCT (HgCdTe) linear array detector. The broad-band infrared pulse was obtained from an output of a Ti:sapphire regenerative amplifier (Hurricane, Spectra-Physics) using an optical parametric amplifier equipped with difference frequency generation (TOPAS, Light Conversion). The photon energy and temporal width of the output of the regenerative amplifier were 1.55 eV and 120 fs, respectively, and a part of the output was utilized for a pump pulse. The spectral width and tunable range of the infrared pulse were 150 cm^{-1} and 1000–4000 cm^{-1}, respectively. This infrared pulse was focused on the sample held inside a cryostat and the sample temperature was kept at 75 K. The spectra of the reflected probe pulse from the sample were measured with the 64-channel MCT array detector through a 19 cm polychromator (FPAS, Infrared Systems Development). The spectral resolution of the obtained pulse was about 3 cm^{-1}. The single crystalline TTF-CA was obtained by vacuum sublimation of crude TTF-CA powder made from mixed saturated acetonitrile solution of TTF and CA.

3. Results and discussion

Figure 1 shows the linear infrared reflectivity spectra of ionic (75 K) and neutral (100 K) phases of TTF-CA crystal at 1550–1690 cm^{-1}. The polarization of light is perpendicular to a-axis of the crystal. The observed bands at 1611 cm^{-1} for I-phase and at 1640 cm^{-1} for N-phase are assigned to the C=O stretching $b_{1u}\nu_{10}$ mode of CA

molecule [17]. The frequency dependence of this band on charge of CA is already well studied in thermal equilibrium [18], thus we adopted this band as a probe of charge variation of CA during the photoinduced process.
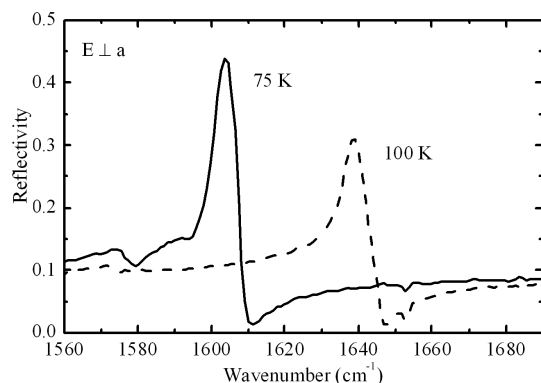

Fig. 1. Linear infrared reflectivity spectra of TTF-CA in the ionic phase at 75 K (solid line) and in the neutral phase at 100 K (broken line). The bands are assigned to the CA $b_{1u}\nu_{10}$ C=O stretching band. The polarization of light is perpendicular to a-axis of the crystal.

Figure 2 shows the three-dimensional (3D) plot of reflectivity change ($\Delta R/R$) after photoexcitation of the ionic phase of TTF-CA at 75 K. The polarization and photon density of the pump pulse were $E \parallel a$ and 4.3×10^{16} photons/cm^2, respectively. The horizontal axis, vertical axis, and colors represent delay time, wave number of probe pulse, and $\Delta R/R$, respectively.
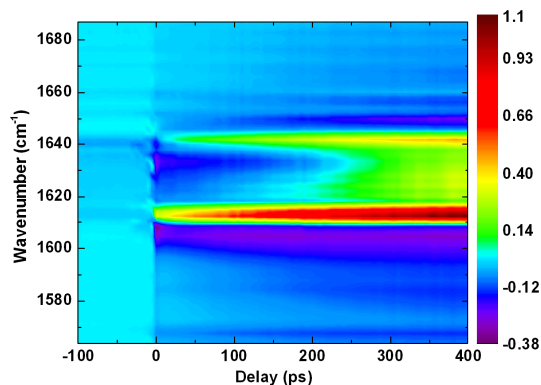

Fig. 2. Three-dimensional (3D) plot of reflectivity change ($\Delta R/R$) after photoexcitation of the ionic phase of TTF-CA at 75 K. The photon energy and photon density of the pump pulse are 1.55 eV and 4.3×10^{16} photons/cm^2, respectively.

In order to be clear about the spectral change, the cross-section spectrum at 350 ps is compared to the reflectivity change spectrum from ionic to neutral phases $(R_N - R_I)/R_I$ in Fig. 3. It is noted here that the reflectivity of N-phase is reduced by 40% for adjusting to the photoinduced reflectivity change. Since these spectral changes are in good agreement with each other, the

CA in the photoinduced N-phase at 350 ps has almost the same charge as the neutral phase in thermal equilibrium. In these spectra, there are two prominent peaks at 1611 cm^{-1} and at 1640 cm^{-1}, and these peaks mainly represent the decrease of I-phase and the increase of the photoinduced N-phase, respectively. In the 3D plot, no wave-number shift and no broadening of these peaks were observed until 400 ps, indicating that the charge of CA is constant from just after photoexcitation at completion of PIPT, that is, the charges in D$^+$A$^-$ and D^{0}A^0 pairs are always the same independent of delay time and domain size in the PIPT process. Thus, the intensity of these peaks simply corresponds to number of D$^+$A$^-$ or D^{0}A^0 pair.
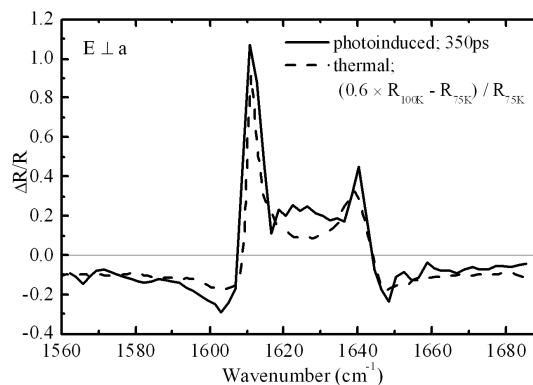

Fig. 3. Comparison of the photoinduced reflectivity change spectrum at 350 ps (solid line) and the estimated reflectivity change spectrum from ionic phase at 75 K to neutral phase at 100 K $(0.6 \times R_{100\,K} - R_{75\,K})/R_{75\,K}$ (broken line).

To reveal the temporal variation of number of D$^+$A$^-$ and DA pairs, the cross-sections at 1611 cm^{-1} and at 1640 cm^{-1} are shown in Fig. 4a and b, respectively. The intensity of the peak at 1611 cm^{-1} first increases rapidly (< 1 ps) and is followed by gradual increase over 300 ps. On the other hand, the intensity of the peak at 1640 cm^{-1} first decreases rapidly followed by increases gradually over 300 ps. To reproduce these temporal variations, at least two steps are required. This result is very close to the result studied by electronic transitions under similar excitation condition (photon energy: 1.55 eV, polarization: $E \parallel a$ and photon density: 4.8×10^{16} photons/cm^2) reported in Ref. [4]. The author proposed the PIPT mechanisms composing of the following three steps: (i) generation of precursor of the N--phase domain, (ii) local proliferation of neutral domains, and (iii) process of forming N-phase order. Our result does not contradict this process. Another result studied by electronic transition was reported in Ref. [5], but the excitation photon energy was different from above results. By photoexcitation by a 0.65 eV pulse which is resonant to charge transfer transition, they observed first one-dimensional N-domains production within 200 fs followed by domain growth over 20 ps. This temporal be-
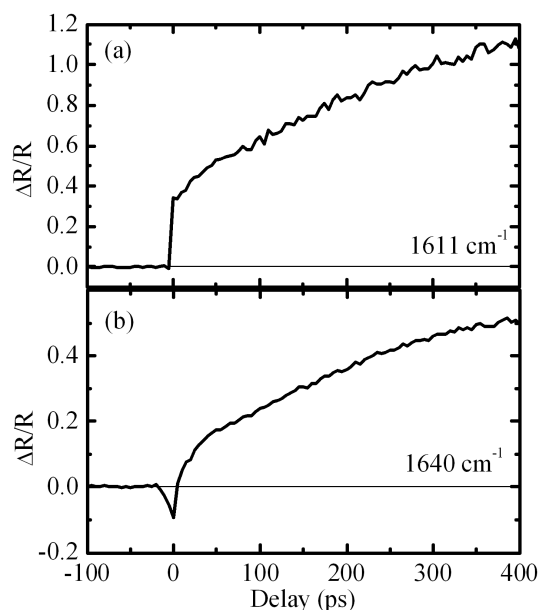
Fig. 4. Temporal profiles of reflectivity change at (a) 1611 cm^{-1} and (b) 1640 cm^{-1} after photoexcitation of TTF-CA in the ionic phase at 75 K (cross-sections of the 3D plot in Fig. 2).

havior is somewhat different from our result probably because of the excess energy from the charge transfer transition.

4. Conclusion

Photoinduced phase transition of TTF-CA has been studied using time-resolved vibrational spectroscopy. By measuring temporal variation of the charge sensitive $b_{1u}\nu_{10}$ band of CA after photoexcitation by a 1.55 eV pulse, we found that the charge of CA does not change during PIPT and it is almost the same as the N-phase in thermal equilibrium. We also found that the number of neutral D^0A^0 pairs increases through at least two steps over 300 ps.

Acknowledgments

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