Ultrafast infrared spectroscopic study of the photo-induced phase transition in (EDO-TTF)$_2$PF$_6$

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Abstract. We have measured ultrafast reflectivity changes of (EDO-TTF)$_2$PF$_6$ in the infrared region (0.51 eV - 1.03 eV) after excitation with a 1.58 eV photon in order to reveal the mechanism of ultrafast photo-induced insulator-to-metal phase transition. We found that the temporal profiles of reflectivity change have two components: a faster component within 3 ps associated with a 1-ps or 0.5-ps period oscillation and a slower component lasting over hundreds of a picosecond. In addition, we found that the sign of a reflectivity change is often different from that expected from the thermally induced phase transition. These results indicate that the PIPT takes place via a complicated process due to strong electron and phonon coupling.

1. Introduction

A quasi-1D, 3/4-filled organic salt, (EDO-TTF)$_2$PF$_6$, is known as a material that has a metal-insulator (M-I) phase transition at near room temperature (T$_c$ = 278 K). In addition, an ultrafast photo-induced Insulator-to-Metal (I-to-M) phase transition (PIPT) has been recently reported [1], and its application to ultrafast switching devices operating around room temperature is expected. In order to explore the ultrafast dynamics of this PIPT, we have been carrying out ultrafast spectroscopy studies in the infrared region. In this energy region, direct information can be obtained on the dynamics of coupling between the electronic excited state and lattice vibration, i.e., photo-induced carriers and phonons.

2. Experimental

The light source for the pump-probe measurement was output from the regenerative amplifier of a Ti:sapphire laser (1.58 eV, 100 fs, 1 kHz). A part of the output was used for the pump pulse, and the rest was used for the generation of an infrared pulse as a probe pulse by optical parametric generation and amplification (OPG/OPA). The typical excitation photon density was $\sim 10^{16}$ photons/cm$^2$. The polarization of both the pump and probe pulse is parallel to the b axis. The procedure for sample preparation was reported in the previous report [2]. The sample temperature was kept at 180 K inside a cryostat.
3. Results and Discussion

Figure 1 shows static reflectivity spectra ranging from 0.12 eV to 2.0 eV at 12 K, 180 K, 275 K, and 290 K. At temperatures below $T_c$ (= 278 K), i.e., the insulator phase, the spectra have several characteristic peaks. The broad peaks at 0.2 eV - 1.7 eV are attributed to charge transfer (CT) states between EDO-TTF molecules, while the sharp peaks at less than 0.2 eV are phonon bands assigned to internal vibrations of the EDO-TTF molecule [3]. At temperatures higher than $T_c$, i.e., the metal phase, these features almost disappear due to disappearance of charge ordering. For our pump-probe measurements, we exited the tail of the highest CT peak (indicated by the vertical arrow in Fig. 1) and probed the lower CT peaks (indicated by the horizontal arrow in Fig. 1) with a tunable infrared pulse. As a result, we found that the temporal profiles of the reflectivity change ($\Delta R/R$) over 1 ns can be divided into fast (~ 3 ps) and slow (~ 500 ps) components.

![Figure 1. Static reflectivity spectra of (EDO-TTF)$_2$PF$_6$ at 12 K, 180 K, 275 K, and 290 K. The arrows indicate the pump and probe energies.](image)

Figure 2 shows the probe energy dependence of $\Delta R/R$ in the region of the fast component. As common behaviors, the reflectivity changes significantly (maximum amplitude = ~ 0.2) just after photo-excitation (at 0 ps) within the time resolution (< 100 fs) and decays over several picoseconds accompanied with approximately 1-ps and 0.5-ps period oscillations. The amplitude and oscillation vary with the probe photon energy; the amplitude reaches its maximum at around 0.7 eV, while the 0.5-ps period oscillation strongly appears at around 0.9 eV.

At around 0 ps, the sign of the $\Delta R/R$ value is different from that expected from the thermally induced I-to-M phase transition. The thermal reflectivity change from the insulator phase (180 K) to the metal phase (290 K) shown in Fig. 3 is always positive at probe energies below 1.03 eV, while the temporal profiles of $\Delta R/R$ just after excitation are basically negative. This result is in contrast to previous results showing that the sign of an $\Delta R/R$ value ranging from 1.3 eV - 2.0 eV is in good agreement with the thermal reflectivity change [1]. This indicates that the dynamics of PIPT on a picosecond time scale actually differs from that of the thermal phase transition and clearly emerges in the infrared energy region. The amplitude of $\Delta R/R$ also varies with the probe energy regardless of that of the thermal reflectivity change and reaches its maximum at 0.7 eV, implying that there are several CT states at 0.5 eV - 1.0 eV and that each CT state has different coupling with excited electrons. The oscillation structure in the temporal profile of $\Delta R/R$ was also observed with the visible probe pulse (1.3 eV - 2.0 eV) [1]. However, in this energy region, it did not show energy dependence, whereas, in the infrared region, the oscillation period obviously depends on the probe photon energy. These oscillation structures seem to consist of two characteristic oscillations: the 1-ps and 0.5-ps periods,
which correspond to 33 cm$^{-1}$ and 66 cm$^{-1}$, respectively. To find vibrations with these characteristic frequencies, we compared them to the bands in the Raman spectra of (EDO-TTF)$_2$PF$_6$ crystal [4]. Although several vibrational bands are observed at around 33 cm$^{-1}$ and 66 cm$^{-1}$, it is difficult to assign them to specific vibrational modes. From the similarity of the energies, we temporally assign the frequency of 33 cm$^{-1}$ to the inter-molecule vibrational mode and that of 66 cm$^{-1}$ to the intra-molecule vibrational mode. The energy dependence of the oscillation structure is as follows: 1-ps oscillation at energies below 0.8 eV, 0.5-ps oscillation at 0.8 eV - 1.0 eV, and a somewhat complicated oscillation at 1.03 eV.

According to Ref. [3], the highest CT band at 1.4 eV consists mainly of a transition from D$^0$D$^+$D$^+$ to D$^0$D$^+$D$^0$, while the lower CT bands consist mainly of transitions from D$^0$D$^+$D$^+$ to D$^+$D$^+$D$^0$ or D$^0$D$^+$D$^0$. Thus, the pump pulse localizes the charge distribution more strongly and initiates the breaking of the charge ordering, but, at this moment (<100 fs), the crystal and molecular structure may stay in the same position because the deformation and displacement of molecules generally take more time (~ps). The results show that a large reflectivity change of more than 20% takes places even at this stage. The oscillations of the reflectivity change in the following time indicate that 33 cm$^{-1}$ and 66 cm$^{-1}$ phonon modes have an important role for the relaxation from the CT excited state. Probing in the infrared region proves that the excitation of the highest CT band strongly affects the lower CT transitions probably via strong electron and phonon interaction. Moreover the result that the sensitive energy dependence of oscillation structure implies that there are several CT states in this infrared energy region and these states have different characters concerning with electron and phonon coupling.

Figure 2. Temporal profiles of the reflectivity change in the fast-component region.

Figure 3. Thermal reflectivity change from the insulator (180 K) to the metal phase (290K).
In the slow-component region, the time profiles also strongly depend on the probe photon energy; however, their behaviors are independent of those of the fast component. Typically, the sign of $\Delta R/R$ is reversed from negative to positive over 100 ps and keeps an amplitude of $\sim 0.03$ even at 1 ns after photo-excitation associated with some slow variations. Figure 4 shows some examples of the time profile of $\Delta R/R$ up to 300 ps. It is noteworthy that these measurements were carried out at 20-ps intervals; as a result, the large reflectivity changes in the fast component disappeared in the temporal profiles. Since the oscillation of $\Delta R/R$ becomes stable after 100 ps, we plot $\Delta R/R$ at 150 ps as a function of probe energy in Fig. 5. Compared to the thermal reflectivity change in Fig. 3, the trend of $\Delta R/R$ at the energies below 0.6 eV seems to be similar to thermal reflectivity change, but $\Delta R/R$ at 0.6 eV - 1.0 eV is not in agreement with the thermal reflectivity change. This behavior of $\Delta R/R$ with respect to the probe energy coincides with that in the fast-component region. Thus, the electron-phonon coupling including CT states in this energy region lasts over 150 ps; in other words, the photo-induced phase transition has not been completed yet on the hundreds-of-picoseconds time scale.

Finally, we consider the possibility that the observed phenomena are thermally induced by laser pulses. From the penetration depth [1], heat capacity [5], and lattice constants [6], the temperature increase with one pump pulse is estimated to be $\sim 0.3$ K. Since the spectrum recovers at a 1-kHz repetition rate, the deposited heat must dissipate sufficiently within 1 ms although the thermal conductivity is unknown. As shown in Fig. 1, the reflectivity change corresponding to a temperature increase of 95 K (180 K to 275 K) in the probe energy region shows only a slight increase (< 20%) but no decrease. Thus, the observed dynamics cannot be explained by simple heat-induced process.

These results clearly indicate that the I-to-M PIPT in (EDO-TTF)$_2$PF$_6$ takes place via complicated processes in the picosecond-nanosecond time region and some intra- and inter-molecular vibrational modes seem to be largely contributing to this phase transition dynamics. To confirm this new finding, we are now measuring temporal profiles in the wider probe energy region from visible to infrared and their dependence on pump-power and sample conditions. In addition, a theoretical analysis will be essential for revealing the detailed mechanisms of this new class of PIPT.
References
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