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The photo-induced phase and coherent phonon in the organic conductor (EDO-TTF)₂PF₆

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Abstract

We have investigated the nature of the photo-induced state and coherent phonon in the conducting charge transfer complex (EDO-TTF)₂PF₆ by measuring the ultrafast reflectivity change over a wide photon energy range from 0.069 eV (18 μm) to 2.1 eV (580 nm). The photo-induced spectra just after photo-excitation indicate that the photo-induced phase is similar to but clearly different from that in a thermally induced metal phase though they are the same for general photo-induced phase transition. The temporal profiles at each probe photon energy are accompanied by extraordinarily large amplitude oscillation originating from coherent phonon generation. The period of the coherent phonon depends discretely on the probe photon energy, while the generation efficiency of both the photo-induced phase and coherent phonon reaches a maximum when the peak top of a charge transfer band is excited. These results are probably attributable to the strong electron–vibration coupling in this complex.

1. Introduction

Conducting charge transfer complexes are organic crystals consisting of electron donors and acceptors and have unfilled bands formed from the open-shell donors and/or acceptors. This type of organic conductor often undergoes phase transition to an insulator mainly owing to electron correlation at low temperatures. It has been recently found in some of these complexes that photo-excitation of the insulator phase induces phase transition to the highly conducting phase. It is expected that this will be exploited in new types of photo-switching devices. However, the nature and dynamics of the photo-induced phase remains unclear [1]. (EDO-TTF)₂PF₆ is a conducting charge transfer complex having a quasi-one-dimensional quarter-filled electron system and is known to

have *strong electron–vibration coupling* [2]. It also exhibits an ultrafast gigantic reflectivity change, presumably due to photo-induced phase transition (PIPT) by irradiation of a femtosecond pulse [3]. We have investigated the ultrafast dynamics of this unique organic conductor using wide-range tunable ultrashort pulse lasers and studied the nature of the photo-induced phase and coherently excited vibration, namely, the coherent phonon.

2. Experimental details

Wide-range tunable femtosecond pulses (0.069–2.1 eV or 18 μm–580 nm, 120 fs) were obtained by combining the methods of optical parametric amplification (OPA), difference frequency generation (DFG) and second harmonic generation

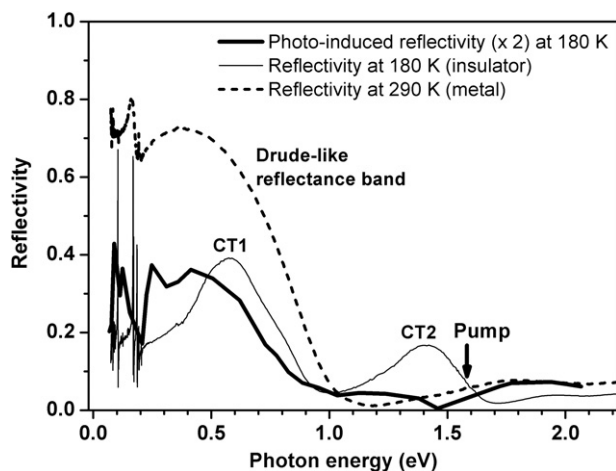


Figure 1. The photo-induced reflectivity spectrum and static reflectivity spectra at 180 and 290 K for $(\text{EDO-TTF})_2\text{PF}_6$.

(SHG) from the output of a Ti:sapphire based regenerative amplifier (1.58 eV or 786 nm, 1 kHz, 1.5 W). The time-resolved reflectivity change spectra were measured by the pump-probe method using any combination of the tunable femtosecond pulses. The polarization of both the pump and probe pulses is parallel to the donor stacking axis (*b* axis) of the sample crystal. The sample was prepared as described in [2], and held inside a cryostat.

3. Results and discussion

Figure 1 shows the photo-induced reflectivity spectrum at 0.1 ps after photo-excitation of the sample in the insulator phase at 180 K (thick line) along with the static reflectivity spectra in the insulator phase at 180 K (thin line) and the metal phase at 290 K (broken line). The photon energy of the pump pulse is 1.58 eV and the photon density is approximately 10^{21} photons cm^{-3} . The photon density is estimated from the number of photons per pulse, irradiation area, penetration depth, and reflectance. The photo-induced spectrum was calculated from the spectrum at 180 K and the doubly enhanced reflectivity change ($\Delta R/R$) measured at each probe photon energy. In the insulator phase, the spectrum has two broad charge transfer (CT) bands centered at 0.6 eV (CT1) and 1.4 eV (CT2), which are assigned to the transition from the ground state ($\text{D}^+\text{D}^0\text{D}^0\text{D}^+$) to the lower excited state ($\text{D}^+\text{D}^+\text{D}^0\text{D}^0 + \text{D}^+\text{D}^0\text{D}^+\text{D}^0$) and to the higher one ($\text{D}^{2+}\text{D}^0\text{D}^0\text{D}^0$) ($\text{D} = \text{EDO-TTF}$), respectively [4]. The many sharp bands below 0.2 eV are assigned to vibrational transition of EDO-TTF and PF_6 . Upon photo-excitation at the tail of the CT2 band in the insulator phase with the 1.58 eV pump pulse, the charge transfer bands vanish and reflectivity below 0.8 eV arises within the pulse duration (<120 fs), as shown in figure 1. Since the shape of this photo-induced reflectivity spectrum is similar to that of free-electron-like (Drude-like) electrons in the metal phase, the electrons in the photo-induced phase move more freely than those in the insulator phase. However, the fact that the absolute reflectivity is only 0.4 even at 0.1 eV and the edge of the

reflectivity rise is lower (~ 0.8 eV) than that in the metal phase (~ 1.0 eV) indicates that the electron motion in the photo-induced phase differs from that in the metal phase and is presumably more localized. This difference between photo-induced and thermally induced phases is most likely due to the strong electron-vibration coupling of this material.

To date, only a few materials have been intensively studied in terms of photo-induced insulator-to-metal phase transition in the low-dimensional organic compounds like $(\text{EDO-TTF})_2\text{PF}_6$. One of them is a halogen-bridged Ni chain compound having a quasi-one-dimensional half-filled electron system [5]. Another example is a layered BEDT-TTF based organic salt having a quasi-two-dimensional quarter-filled electron system [6]. In both cases, photo-excitation of an insulator phase melts charge localization and creates a metal phase. Although there is no theoretical prediction of their photo-induced states themselves, their electronic states in thermal equilibrium are well understood using the extended Hubbard model, which takes only electron-electron correlation into account [7]. In contrast, in $(\text{EDO-TTF})_2\text{PF}_6$, even the charge order pattern in the low temperature phase cannot be reproduced by the model without electron-vibration interaction [8]. Thus, electron-vibration interaction must play an important role in the photo-induced dynamics in $(\text{EDO-TTF})_2\text{PF}_6$.

One effective way to study vibrational dynamics is to measure temporal signal oscillation after excitation with an ultrashort pulse whose duration is less than the period of vibration. This type of oscillation is generally attributed to coherently excited vibrations or phonons, so that it is called a ‘coherent phonon’. The advantage of this method is that low frequency modes in the THz region are easily detected, time-dependent dynamics can be observed, and there is the possibility that the photo-induced phase can be actively controlled using the coherence of the phonon. Thus, in order to reveal the influence of the electron-vibration coupling on the photo-induced dynamics, we measured temporal profiles of reflectivity change at various probe energies. Figure 2 shows examples of temporal profiles under 1.58 eV photo-excitation. These oscillations or coherent phonons in $(\text{EDO-TTF})_2\text{PF}_6$ have unique features compared to those in simple semi-metals and semiconductors [9, 10]. The damping period (~ 3 cycles) is much shorter than those for other materials (>10 cycles) and the oscillation amplitude ($\Delta R/R > 0.1$) is much larger than those for other materials ($\sim 10^{-3}$). Most interestingly, the oscillation period depends discretely on the probe photon energy. The period is ~ 0.5 ps for the probe photon energy ranges of 0.7–1.0 eV and 1.2–1.8 eV, ~ 1.0 ps for 0.5–0.7 eV, and there is no clear period elsewhere as summarized in figure 3. This probe photon energy dependence of the oscillation period cannot be explained by the traditional models of coherent phonon generation, such as impulsive stimulated Raman scattering (ISRS) [11] and displacive excitation of the coherent phonon (DECP) [9]. To explain this behavior, a new theoretical model is required; presumably one that takes into account the electron-vibration coupling.

The oscillation periods of 0.5 ps and 1.0 ps correspond to 66 cm^{-1} and 33 cm^{-1} , respectively. Assignments of these

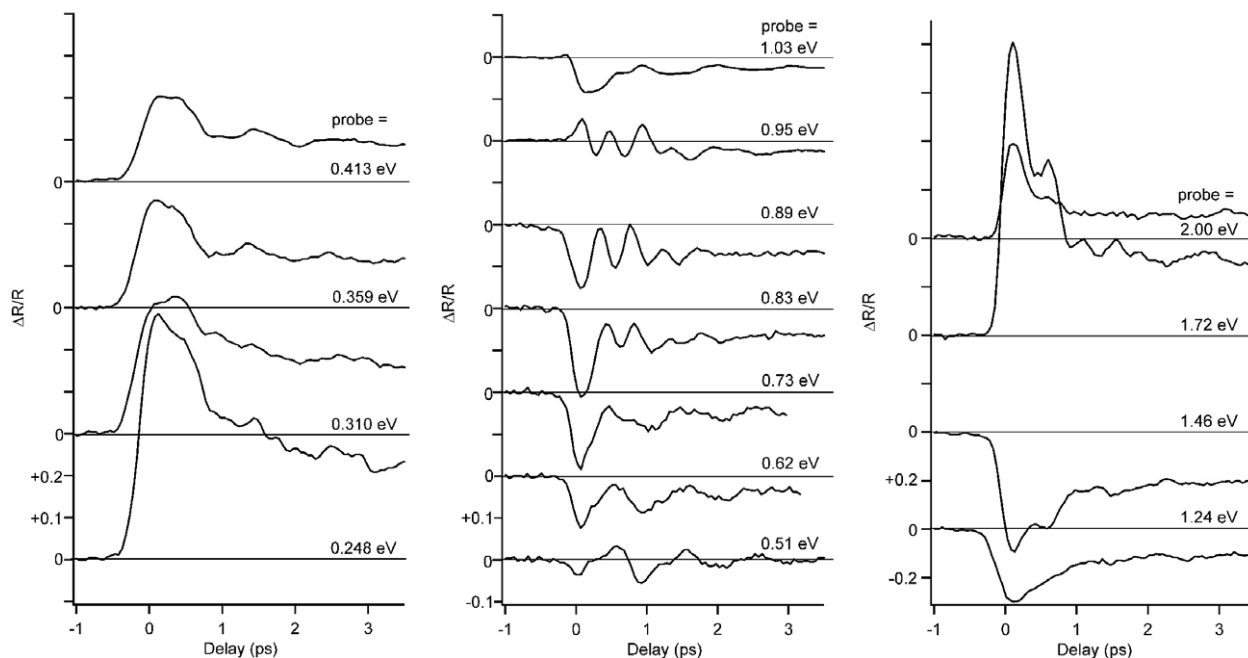


Figure 2. Temporal profiles of reflectivity change ($\Delta R/R$) at various probe photon energies under 1.58 eV excitation.

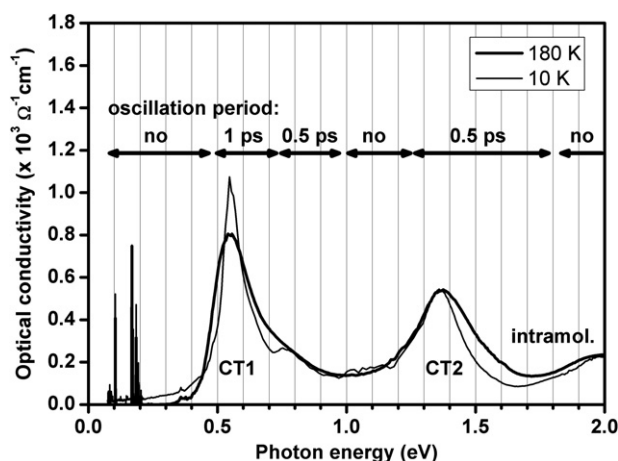


Figure 3. Correlation between oscillation period and charge transfer bands.

frequencies are generally difficult for this kind of molecular crystal; however, they can be done through comparison with the Raman spectra. In the Raman spectra [12], there are two peaks close to 33 and 66 cm^{-1} . Based on molecular orbital calculation for an isolated EDO-TTF molecule and vibrational mode analysis including intermolecular modes, these peaks are assigned to combination modes between the EDO-TTF bending mode and the intermolecular vibrational mode [12]. These assignments agree with the fact that the EDO-TTF molecule in the $(\text{EDO-TTF})_2\text{PF}_6$ crystal bends largely at the thermal phase transition [1], so it is expected that the coherent oscillation of the modes including the EDO-TTF bending mode is excited via the strong electron–vibration coupling under photo-excitation.

In order to investigate the mechanism of coherent phonon generation, we also measured the pump photon energy

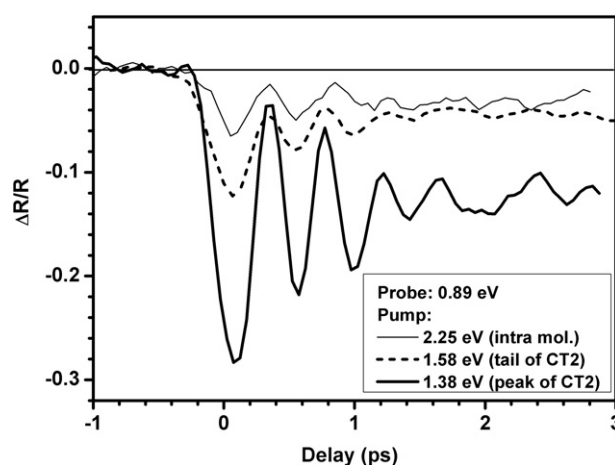


Figure 4. Temporal profiles at 0.89 eV under various pump photon energies. The photon density for all the pump pulses is 0.7×10^{21} photons cm^{-3} .

dependence of coherent phonon oscillation. In addition to the excitation at the tail of the CT2 at 1.58 eV, we excited at the peak top of the CT2 band at 1.38 eV and at the higher energy of 2.25 eV in the intramolecular band. The temporal profiles at a probe photon energy of 0.89 eV are shown in figure 4. The amount of reflectivity change just after the photo-excitation is the largest when the peak top of the CT2 band is excited, and decreases as the pump photon energy increases. Even a difference of 0.2 eV from the peak top to the tail of the CT2 band reduces the reflectivity change to less than half, indicating that the CT2 band is not homogeneous and that the resonance to the charge transfer transition plays an important role for photo-induced phase transition. The relative amplitude of oscillation to the amount of reflectivity change also depends

on the pump photon energy. It is around 90% under 1.38 eV excitation, and less than 70% under excitation of other photon energies, which also indicates that the efficiency of coherent phonon generation is the highest when the peak top of the charge transfer band is excited and that the charge transfer transition plays an important role in generating a coherent photon. In contrast, the period of oscillation is independent of pump photon energy, suggesting that the same phonon mode is excited with even higher pump photon energies.

In conclusion, we measured the ultrafast photo-induced reflectivity change in the charge transfer complex (EDO-TTF)₂PF₆ over a wide photon energy range and found that the photo-induced phase differs from the thermally induced phase. By measuring temporal profiles at each probe photon energy, we also found an extraordinarily large amplitude of the reflectivity oscillations originating from coherent phonon generation. The oscillations clearly emerge only at probe photon energies corresponding to charge transfer bands, and the amplitude reaches a maximum when the peak top of the charge transfer (CT2) band is excited. This unusual behavior of the photo-induced phase and coherent phonon are presumably due to the strong electron–phonon coupling in this complex.

References

- [1] Nasu K 2004 *Photo-induced Phase Transitions* (Singapore: World Scientific)
- [2] Ota A, Yamochi H and Saito G 2002 *J. Mater. Chem.* **12** 2600
- [3] Chollet M, Guerin L, Uchida N, Fukaya S, Shimoda H, Ishikawa T, Yamochi H, Saito G, Tazaki R, Adachi S and Koshihara S 2005 *Science* **307** 86
- [4] Drozdova O, Yakushi K, Yamamoto K, Ota A, Yamochi H, Saito G, Tashiro H and Tanner D B 2004 *Phys. Rev. B* **70** 075107
- [5] Iwai S, Ono M, Maeda A, Matsuzaki H, Kishida H, Okamoto H and Tokura Y 2003 *Phys. Rev. Lett.* **91** 057401
- [6] Iwai S, Yamamoto K, Kashiwazaki A, Hiramatsu F, Nakaya H, Kawakami Y, Yakushi K, Okamoto H, Mori H and Nishino Y 2007 *Phys. Rev. Lett.* **98** 097402
- [7] Seo H, Hotta C and Fukuyama H 2004 *Chem. Rev.* **104** 5005
- [8] Yonemitsu K and Maeshima N 2007 *Phys. Rev. B* **76** 075105
- [9] Zeiger H J, Vidal J, Cheng T K, Ippen E P, Dresselhaus G and Dresselhaus M S 1992 *Phys. Rev. B* **45** 768
- [10] Hase M, Mizoguchi K, Harima H, Nakashima S and Sakai K 1998 *Phys. Rev. B* **58** 5448
- [11] Yan Y-X and Nelson K A 1987 *J. Chem. Phys.* **87** 6240
- [12] Hasegawa T, Iio K, Chollet M, Ishikawa T, Koshihara S, Kawai K, Ota A, Saito G and Yamochi H 2008 in preparation