Anomalous photo-induced response by double-pulse excitation in the organic conductor (EDO-TTF)$_2$PF$_6$

Ken Onda, Sho Ogihara, Tadahiko Ishikawa, Yoichi Okimoto, Xiangfeng Shao, Yoshiaki Nakano, Hideki Yamochi, Gunzi Saito and Shin-ya Koshihara

1 Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
2 Non-equilibrium Dynamics Project, ERATO, Japan Science and Technology Agency, c/o KEK, 1-1 Oho, Tsukuba, Ibaraki, 305-0801, Japan
3 Department of Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551 Japan
4 Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
5 Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Sakyoku, Kyoto 606-8501, Japan
6 Research Institute, Meijo University, Tempaku-ku, Nagoya 468-8502, Japan
7 To whom any correspondence should be addressed.

E-mail: konda@chemenv.titech.ac.jp

Abstract. We measured ultrafast reflectivity changes induced by double-pulse excitation in the organic conductor (EDO-TTF)$_2$PF$_6$. Using double-pulse excitation with a relatively high intensity, the sign of reflectivity change became reversed at around 0.8 ps and subsequently the reflectivity change reverted to that of the normal photo-induced state after about 1 ps. Using an optically phase-locked double-pulse with low intensity, we found that the temporal profile excited by an in-phase double-pulse differs from that by an out-of-phase double-pulse despite the time difference between the double-pulses being only 1.31 fs. This was true even when there is almost no overlap between each pulse in the double-pulse. These results indicate that the photo-response in this material to double-pulse excitation differs greatly from the linear sum of the responses to single pulses.

1. Introduction
The quasi-one-dimensional, quarter-filled organic conductor (EDO-TTF)$_2$PF$_6$ has many unusual properties that differ from those of other materials that have a photo-induced phase transition (PIPT) [1-4]. It exhibits a metal-to-insulator phase transition at 280 K accompanied by large molecular distortion [1], indicating that it possesses a strong electron-phonon interaction. Ultrashort pulse excitation induces an ultrafast (< 0.2 ps) and gigantic (> 100 %) reflectivity change [2]. This ultrafast reflectivity change was recently found to originate not from the insulator-to-metal phase transition but

© 2009 Yamada Science Foundation and IOP Publishing Ltd
rather from a change in the charge order pattern from (0110) to (1010) [3]. 10-fs spectroscopy reveals that 20-fs oscillation plays an important role in the nascent stage of PIPT [4]. In this paper, we report a more unusual photo-induced response induced by double-pulse excitation. We have been investigating PIPT by double-pulse excitation because multi-pulse excitation is a promising method for achieving active control of PIPT.

2. Experimental
The light source used for the pump-probe measurements was a Ti:sapphire-based regenerative amplifier (center wavelength: 786 nm = 1.58 eV, pulse duration: 110 fs, repetition rate: 1 kHz). The output of the regenerative amplifier was used as the pump pulse and a tunable infrared beam generated using an optical parametric amplifier was used as the probe pulse. The pump pulse was separated into two pulses by an interferometer. The interval between these two pulses could be controlled not only on a phonon time scale (< 1 ps) but also on an optical-cycle time scale (< 1 fs). The (EDO-TTF)\textsubscript{2}PF\textsubscript{6} crystal was prepared by the procedure given in a previous report [1], and was held at 180 K in a cryostat.

3. Double-pulse excitation on a phonon time scale
Figures 1(a) and (b) show the temporal profiles obtained by double- and single-pulse excitation, respectively. The pump pulse has a photon energy of 1.58 eV, which in the tail of the charge transfer (CT) band named CT2 [5], while the probe pulse has a photon energy of 0.89 eV, which is where the coherent phonon is observed most clearly [6]. In the double-pulse excitation, the pump pulse has a photon density of $0.7 \times 10^{21}$ photons/cm$^3$ and the pulses are separated by a time difference ($\Delta \tau$) of 0.16 ps. The thin lines in figure 1(a) represent the temporal profiles of the reflectivity change ($\Delta R/R$) produced by single pulse excitation, which was achieved by blocking the other pulse in the interferometer. If the photo-induced response follows a linear summation rule, the temporal profile of the reflectivity change produced by double-pulse excitation will be identical to the broken line in figure 1(a), which is the sum of the two profiles obtained by single-pulse excitation. However, the experimental result, which is indicated by the thick line in figure 1(a), greatly differs from the sum of the two single-pulse profiles. $\Delta R/R$ decreases immediately after the first pump pulse but begins to increase near the second pulse and the sign of $\Delta R/R$ becomes reversed. $\Delta R/R$ reaches a maximum about 0.8 ps after the first pulse, and it then reverts to the $\Delta R/R$ profile produced by single-pulse excitation. This reversal in reflectivity change was observed even when $\Delta \tau = 0.5$ ps. For comparison, we also measured the temporal profiles of $\Delta R/R$ induced by single-pulse excitation having a photon density of almost twice that of the previous experiment ($1.2 \times 10^{21}$ photons/cm$^3$); this profile is shown.

![Figure 1](image.jpg)

**Figure 1.** Temporal profiles of reflectivity change in (EDO-TTF)$_2$PF$_6$ by (a) double- and (b) single-pulse excitation. The pump and probe photon energies are 1.58 eV and 0.89 eV, respectively.
in figure 1(b) together with the sum of the profiles obtained by applying single pulses 1 and 2 separately. These temporal profiles are in good agreement with each other, indicating that double-pulse excitation creates a state that single-pulse excitation at 1.58 eV does not reach. Excitation at low photon densities (< 0.1 x 10^{21} photons/cm^3 per pulse) did not produce this reversal in the reflectivity change. This phenomenon is not caused by thermal effects because the time scale of creation and annihilation is approximately 1 ps, which is much faster than that of thermalization and the state does not revert to one of the thermal equilibrium states but to the photo-induced state for this time scale. Moreover, the same state was not produced when the photon density was doubled even although the total energies are the same. We thus conclude that we have found a new type of photo-induced state produced by double-pulse excitation.

4. Optically phase-locked double-pulse excitation
To achieve more precise control of the interval \( \Delta \tau \) between the two pulses, we constructed an interferometer that allows \( \Delta \tau \) to be controlled within 0.1 fs over a wide \( \Delta \tau \) range from 0 ps to 3 ps [7-9]. Using this interferometer, we created a phase-locked double pulse with a photon energy of 1.58 eV and used it as the pump pulse, and used the 0.89-eV infrared pulse as the probe pulse (see schematic diagram in figure 2(a)). The optical cycle of the 1.58-eV photon for the pump pulse is 2.62 fs; thus, a time difference of 1.31 fs corresponds to a phase difference of \( \pi \). Phase-locked in-phase and out-of-phase double-pulses refer to two pulses that are in phase (+0) and out of phase (+\( \pi \)) with each other for even larger \( \Delta \tau \). Figure 2 compares the temporal profiles obtained by in-phase and out-of-phase excitation for four different values of \( \Delta \tau \). The photon density is sufficiently low (~ 0.02 x 10^{21} photons/cm^3) to ensure that the newly discovered photo-induced state described above is not produced. When \( \Delta \tau = 0 \), since the in-phase double pulse is identical to the single pulse before the interferometer while the out-of-phase double pulse vanishes, the temporal profile produced by in-phase double-pulse excitation is the same as that produced by single-pulse excitation without the interferometer, while no

![Figure 2.](image-url)
reflectivity change is observed for out-of-phase excitation. For \( \Delta \tau = 250 \) fs, there is almost no overlap between the two pulses (each pulse has a duration of 110 fs) so the reflectivity change produced by each pulse is expected to be about one-fourth of that produced by in-phase double-pulse for \( \Delta \tau = 0 \) fs. In actual fact, it is approximately half (see figure 2(b)) probably due to a saturation effect. Surprisingly, there is an obvious difference between the temporal profiles produced by in-phase and out-of-phase double-pulse excitations despite the time difference between the pulses being only 1.31 fs, which is equivalent to a phase difference of \( \pi \). This phenomenon lasts for \( \Delta \tau \sim 400 \) fs; no difference was observed for times longer than 500 fs. A possible explanation of this phenomenon is that the spectral profile of the excitation pulse is modulated due to interference between the two pulses but the spectral difference is not so large considering the broad CT band. Another possibility is that the coherence of the electronic excited state has a significant influence on coherent phonon oscillation. This seems to be highly improbable since the coherence time is expected to be short at the sample temperature used in this experiment (180 K); however, a long-lived coherence of \( \sim 400 \) fs has been already reported at 180 K in a photosynthetic reaction center [10]. Thus, we propose that our result is another case of anomaly long-lived coherence.

5. Conclusion
We measured the ultrafast photo-induced reflectivity change of \((\text{EDO-TTF})_2\text{PF}_6\) produced by double-pulse excitation with the goal of achieving active control of the photo-induced phase transition. Using relatively high intensity double-pulse excitation, a reversal in the reflectivity change was observed at around 0.8 ps. It subsequently reverted to the reflectivity change produced by single-pulse excitation after 1 ps. This new photo-induced state emerges at around 0.8 ps and can only be produced by double-pulse excitation. We also produced phase-locked double-pulse excitation using a high precision interferometer and found a difference between the temporal profiles of reflectivity changes produced by in-phase and out-of-phase double-pulse excitation at lower excitation intensities. This result possibly indicates that the coherence of the electronic state affects coherent phonon oscillation. To confirm these speculations, we are currently investigating the effect of using different photon energies and shorter pulse widths.

Acknowledgement
A part of this work was supported by Grant-in-Aid for Scientific Research (B) No.20340074 from MEXT Japan.

References
[1] Ota A, Yamochi H and Saito G 2002 J. Mater. Chem. 12 2600
[2] 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
[3] Onda K, Ogihara S, Yonemitsu K, Maeshima N, Ishikawa T, Okimoto Y, Shao X F, Nakano Y, Yamochi H, Saito G and Koshihara S 2008 Phys. Rev. Lett. 101 067403
[4] Itatani J, Rini M, Cavalleri A, Onda K, Ishikawa T, Ogihara S, Koshihara S, Shao X F, Nakano Y, Yamochi H, Saito G and Schoenlein R W 2009 Ultrafast Phenomena XVI, Springer-Verlag, in press
[5] Drozdova O, Yakushi K, Yamamoto K, Ota A, Yamochi H, Saito G, Tashiro H and Tanner D B 2004 Phys. Rev. B 70 075107
[6] Onda K, Ogihara S, Ishikawa T, Okimoto Y, Shao X F, Yamochi H, Saito G and Koshihara S 2008 J. Phys: Condens. Matter 20 224018
[7] Kubo A, Onda K, Petek H, Sun Z, Jung Y S and Kim H K 2005, Nano. Lett. 5 1123
[8] Onda K, Li B, Zhao J, Jordan K D, Yang J and Petek H 2005 Science 308 1154
[9] Li B, Zhao J, Onda K, Jordan K D, Yang J and Petek H 2006 Science 311 1436
[10] Lee H, Cheng Y-C and Fleming G R 2007 Science 316 1462