Multi-phonon dynamics of the ultra-fast photoinduced transition of (EDO-TTF)$_2$SbF$_6$

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Abstract. We report here the first observation of the photoinduced insulating-to-metal phase transition in the (EDO-TTF)$_2$SbF$_6$ salt, which occurs on the picosecond time-scale. The time-resolved optical experiments performed with 80 fs time-resolution demonstrate that the dynamical process involves several low-frequency phonons, as the crystalline structure is destabilized upon laser excitation.

1. Introduction

Photoinduced phase transitions (PIPT) bring into play subtle couplings between electronic excitations and relaxation of structural degrees of freedom [1,2]. Molecular materials in particular exhibit switching between multi-functional physical properties, which makes them very promising for future applications. The mechanisms driving photoinduced phase transitions are strongly nonlinear and span on different temporal scales and spatial dimensions. They demand thorough analysis of the cooperative effects as well as the physical mechanisms underlying the phase transitions out of thermal equilibrium, which eventually should lead to the photo-control of phase transition.

Here we investigate the photoinduced insulating-to-metal phase transition of the molecular solid (EDO-TTF)$_2$SbF$_6$, for which ethylenedioxytetrahydrofulvalene (EDO-TTF) is an electron donor molecule. This salt undergoes a first-order metal-insulator (M-I) transition around $T_{MI}$ (~ 240 K) with a wide hysteresis region (~22 K) [3]. It is associated with a charge-ordering process on the donor (D) EDO-TTF molecules, driving a structural reorganization associated with cell doubling, as schematically shown hereafter:

Phase I ... (D$^0$ D$^0$ D$^1$ D$^1$) (D$^0$ D$^0$ D$^1$ D$^1$) ... Phase M ... (D$^{1/2}$ D$^{1/2}$) (D$^{1/2}$ D$^{1/2}$) (D$^{1/2}$ D$^{1/2}$) ...

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As shown in figure 1, this phase transition and the associated hysteresis can be tracked by optical reflectivity measurements. (EDO-TTF)$_2$SbF$_6$ is isostructural with the organic conductor (EDO-TTF)$_2$PF$_6$ [4-6], for which an ultra-fast and highly efficient photo-induced phase transition (PIPT) [7] from I-to-M was discovered few years ago. While the nature of the photoinduced M (or highly conducting) state is still a matter of debate [8], the mechanism associated with the switching toward the photoinduced state was demonstrated to involve coherent collective molecular motions (phonons). Investigations of the photoinduced effect in the new (EDO-TTF)$_2$SbF$_6$ derivative cast more light on the mechanism driving such I-to-M transition, and even more generally the PIPT phenomena.

![Figure 1. Reflectivity of (EDO-TTF)$_2$SbF$_6$ salt measured at 635 nm in cooling (▼) and warming (▲) modes. The first-order phase transition is characterized by a thermal hysteresis spanning from 227 K to 249 K.](image)

2. Experimental

Photoinduced phase transition of (EDO-TTF)$_2$SbF$_6$ was investigated by time-resolved reflectivity measurements using 80 fs pump-probe experiments. The measurements were performed utilizing a lock-in amplifier, which significantly enhances the detection sensitivity through band-width narrowing in frequency domain. The excitation wavelength was centered at 850 nm and the probe was set to 720 nm. This wavelength is sensitive to the thermal transition of (EDO-TTF)$_2$PF$_6$ [7,8] as the metalization affects both VIS and IR part of the spectrum. The polarization of the incident laser photons was parallel to the crystal-stacking axis $b$. The fluence per pulse of the pump and probe beams were respectively 5 $\mu$J/mm$^2$ and 100nJ/mm$^2$.

3. Results and discussion

3.1. Evidence of PIPT phenomena in (EDO-TTF)$_2$SbF$_6$

We present in figure 2 the optical reflectivity response of (EDO-TTF)$_2$SbF$_6$ as a function of the delay, $dt$, between pump and probe pulses. The experiment was performed at 100 K, well below the thermal transition. This photo-response is quite similar to the one observed for (EDO-TTF)$_2$PF$_6$ [7,8] and provides the first direct evidence of the PIPT in (EDO-TTF)$_2$SbF$_6$. The photo-response can be described in terms of an instantaneous electronic response (within the experimental resolution), damped oscillation in the 0-7 ps range and a plateau above 7 ps (ps plateau) characteristic of the generation of the highly conducting photoinduced state. Similar oscillations were also reported for (EDO-TTF)$_2$PF$_6$ and the following part of the paper focuses on this particular aspect of the vibration dynamics.
3.2. Multi-phonon dynamics

The accurate structure of the oscillatory component in the response is plotted in figure 3a (thick line). It is clear that such oscillations cannot be described by using a single phonon model as in Bismuth [9], and the inclusion of damping does not improve the model. The FFT of this oscillatory component is presented in figure 3b and shows that several modes are involved in the dynamics, spanning from 0.7 to 3.5 THz. The oscillation was further fitted in by using 5 modes (around 0.7, 1.2, 2.1, 2.5 and 3.4 THz) and their relative contributions were fitted for best match, figure 3a (thin curve). Adding other modes did not improve the fit, whereas decreasing the number of modes markedly deteriorated the fit. The loss of coherence in this part of the signal was accounted for with a single exponential decay, and the resulting damping constant was about 3 ps.

These results clearly indicate that different oscillating components are involved in the dynamical process associated with the PIPT phenomena in (EDOTTF)$_2$SbF$_6$. It should be noticed that the frequencies used correspond to some of the low frequency Raman modes observed in the (EDOTTF)$_2$PF$_6$ compound [10], isostructural to (EDOTTF)$_2$SbF$_6$ investigated here. These low-frequency modes are known to be strongly coupled to the structural reorganization. As the system switches from the stable I phase to the photoinduced one, molecular motions should set in at some stage and the damped oscillation observed here is reminiscent of soft mode behavior around thermal transitions.
The loss of coherence, i.e. the damping of the oscillation, can be interpreted in terms of the establishment and stabilization of the photoinduced lattice structure. The laser excitation promotes the system to a new potential energy surface, thereby defining a new equilibrium position for molecules. The motion from the old equilibrium towards the new one will involve specific phonons sensitive to the related variation of energy surface. The excess energy carried by these specific lattice phonons will be transferred to other degrees of freedom through phonon-phonon or electron-phonon interactions, as discussed in Bismuth for example [9], which causes decoherence.

The extension of this work to the isostructural (EDO-TTF)$_2$XF$_6$ derivatives (X=As and P) for comparing dynamical response, complemented by Raman measurements of lattice vibration modes at thermal equilibrium, will undoubtedly allow deepening the understanding of the dynamical processes involved in the PIPT of these salts, and the role of structural degrees of freedom in the stabilization of the photoinduced state. The development of time-resolved spectroscopies (THz and Raman) also promises a more direct access to the evolution of the phonon distribution from the stable to the photoinduced state.

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