Photoinduced melting and charge order in quarter-filled organic conductors: Itinerant electron systems with competing interactions

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Abstract. Photoinduced charge dynamics in one- and two-dimensional organic conductors are studied theoretically in extended Peierls-Hubbard models. For quasi-one-dimensional (EDO-TTF)₂PF₆, photoinduced change in the charge order pattern from (0110) to (1010) is accompanied by probe-energy-dependent oscillations of conductivity. This is caused by coexistence of charge order and delocalized electrons. For quasi-two-dimensional α-(BEDT-TTF)₂I₃ and θ-(BEDT-TTF)₂RbZn(SCN)₄, photoinduced melting of the horizontal-stripe charge order proceeds easier in the α-type salt than in the θ-type salt. This is because the charge order in the θ-type salt is more strongly stabilized by electron-phonon interactions.

1. Introduction

Organic conductors with low-dimensional electric conductivity have a variety of electronic phases, depending on temperature, pressure, and constituents, so that they are good candidate materials for photoinduced phase transitions. Mechanisms of photoinduced phase transitions and their dynamics in these itinerant electron systems have been studied extensively in recent years [1, 2]. Examples are transitions from Mott insulator to metal phases [3, 4], charge-ordered insulator to metal phases in quasi-one- [5] and two-dimensional [6, 7, 8] systems, charge-density-wave to charge-polarization phases [9, 10], ionic ferroelectric to neutral paraelectric phases [11, 12], and nonmagnetic to paramagnetic phases [13, 14]. The development of theoretical research will be useful in choosing the property of pump light such as wavelength, strength, duration, and pulse shape to obtain desired changes in physical properties.

2. Coexistence of charge order and delocalized electrons in the photoinduced state of (EDO-TTF)₂PF₆

The quarter-filled-band organic salt, (EDO-TTF)₂PF₆ (EDO-TTF=ethylenedioxy-tetrathiafulvalene), is a quasi-one-dimensional conductor, which undergoes a first-order transition from metal to insulator phases by lowering temperature. The insulator phase has a (0110) charge order accompanied by a large structural change based on a doubling of unit cells and deformation of
EDO-TTF molecules [15]. An ultrafast transition from the charge-ordered phase to a highly conducting phase is induced by weak laser light [16] with excitation energy nearly resonant with charge transfer toward the \{0200\} configuration. The photoinduced dynamics is explained in the one-dimensional extended Peierls-Holstein-Hubbard model [5],

\[
H_{1D} = -\sum_{j,\sigma} [t_0 - \alpha(u_{j+1} - u_j)] \left( c_{j+1,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{j+1,\sigma} \right) + U \sum_j n_{j,\uparrow} n_{j,\downarrow} + V \sum_j n_j n_{j+1} - \beta \sum_j v_j (n_j - 1/2) - \gamma \sum_l w_l (n_{2l-1} + n_{2l-1}) + \frac{1}{2} K_\alpha \sum_j (u_{j+1} - u_j)^2 + \frac{1}{2} K_\beta \sum_j v_j^2 + \frac{2 K_\alpha}{\omega_\alpha^2} \sum_j u_j^2 + \frac{K_\beta}{2 \omega_\beta^2} \sum_j v_j^2 + \frac{K_\gamma}{2 \omega_\gamma^2} \sum_l \dot{w}_l^2,
\]

where \( c_{j,\sigma}^\dagger \) (\( c_{j,\sigma} \)) creates (annihilates) a hole with spin \( \sigma \) at site \( j \), \( n_{j,\sigma} = c_{j,\sigma}^\dagger c_{j,\sigma} \), \( n_j = \sum_{\sigma} n_{j,\sigma} \), \( u_j \) denotes the \( j \)th EDO-TTF molecule’s translational mode, \( v_j \) its deformation mode, and \( w_l \) the \( l \)th PF\(_6\) ion’s displacement. The other notations are standard and introduced in Refs. [5, 17]. The parameters are deduced from the charge disproportionation, the optical conductivity spectrum [18], and the photoinduced transient spectra [5].

**Figure 1.** Time dependence of transient spectra on low-energy side of main peak, after photoexcitation from \{0110\} to \{0200\}. The parameters are the same as in Ref. [5].

**Figure 2.** Time dependence of transient spectra on high-energy side of main peak, after photoexcitation from \{0110\} to \{0200\}. The parameters are the same as in Ref. [5].

The time-dependent Schrödinger equation for the exact many-electron wave function is numerically solved by expanding the exponential evolution operator with time slice \( dt = 0.01 \) and by checking the conservation of the norm for the 12-site system with periodic boundary condition [5, 17]. The classical equation of phonon motion is solved by the leapfrog method, where the force is derived from the Hellmann-Feynman theorem. Photoexcitations are introduced with the time-dependent electric field, \( E(t) = E_{\text{ext}} \sin \omega_{\text{ext}} t \). After the field is turned off, the total energy is confirmed to be conserved. The time evolution of the photoinduced reflectivity-change spectrum observed in a wide energy range allows detailed comparison with theoretical calculations. A transition is found to take place from the \{0110\} charge order to a \{1010\} order. After the transition, the transient spectrum shows a single peak due to \{1010\}-to-\{0110\} charge transfer. The time dependence of the transient spectrum depends largely on the probe photon energy. On the low energy side of the peak, it is very irregular (Fig. 1). On the high energy side, the conductivity coherently oscillates (Fig. 2). This behavior is consistent with the experimental
observation and caused by different time scales of observed electronic motion. The low-energy conductivity is due to electrons that are delocalized over different molecules and thus easily scattered by phonons in different positions and timings. Its coherence is easily lost. The high-energy conductivity is due to charge transfers localized spatially and temporally, which are governed by the instantaneous distribution of charge densities and potentials that are electron-phonon-coupling-weighted average quantities. Its coherence is thus robust. This behavior is a manifestation of the coexistence of delocalized electrons and charge order, which are both incomplete: delocalized electrons suffer from strong electron-phonon scatterings, and the charge order is not really long-ranged.

3. Different lattice effects and photoinduced dynamics in α-(BEDT-TTF)$_2$I$_3$ and θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$

The quarter-filled-band organic salts, α-(BEDT-TTF)$_2$I$_3$ and θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ [BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene], are quasi-two-dimensional conductors, which also undergo a first-order transition from metal to insulator phases by lowering temperature. The insulator phases have a horizontal-stripe charge order [19]. Photoinduced melting of the charge order has been observed in these salts by femtosecond reflection spectroscopy [6]. The α-type salt shows critical slowing down as a function of temperature, excitation density [6] and pressure [20], while the θ-type salt shows local melting of the charge order and its ultrafast recovery irrespective of temperature and excitation density. The differences between their electronic states are explained in the two-dimensional extended Peierls-Hubbard model on an anisotropic triangular lattice [7, 8],

$$H_{2D} = \sum_{\langle ij \rangle} (t_{i,j} + \alpha_{i,j} u_{i,j}) \left( c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} V_{i,j} n_i n_j + \sum_{\langle ij \rangle} \frac{K_{i,j}}{2} u_{i,j}^2$$

(2)

where $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (annihilates) an electron with spin $\sigma$ at site $i$, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, $n_i = \sum_{\sigma} n_{i\sigma}$, the displacement $u_{i,j}$ modulates the transfer integral $t_{i,j}$ with coefficient $\alpha_{i,j}$. The band filling is three quarters in terms of electrons. The other notations are standard and introduced in Ref. [7] except for the bare phonon frequency $\omega_{ph}$. We employ the $L \times L$-site lattice with periodic boundary condition. The transfer integrals are deduced from X-ray crystal-structure analyses with the help of extended Hückel calculations [21, 22] and listed in Ref. [7], while the Coulomb and electron-phonon interaction strengths are so taken as to reproduce the horizontal-stripe charge order and the optical conductivity spectra [23] and listed in the figure captions.

Although the charge-order patterns in these salts are quite similar, the lattice effects on them are shown to be quite different by the Hartree-Fock calculations at zero and finite temperatures [7, 24], the exact diagonalization of small clusters, and the strong-coupling perturbation theory up to the third order [8, 23]. The horizontal-stripe charge order is stable even without electron-phonon interaction for the α-type salt, but it needs electron-phonon interactions for the θ-type salt, where molecular rotations are important. The θ-type salt has a crystal structure with higher symmetry and its energy gain from lattice distortion is larger than the α-type salt. The time evolution of charge densities is obtained by numerically solving the time-dependent Schrödinger equation for the Hartree-Fock wave function by expanding the exponential evolution operator with time slice $dt=0.01$ and by checking the conservation of the norm for the $8 \times 8$-site system with periodic boundary condition. The classical equation of phonon motion is solved, where the force is derived from the Hellmann-Feynman theorem. Photoexcitations are introduced with the time-dependent electric field, $E(t) = E_{ext} \sin \omega_{ext} t$, as in the previous section. The charge
disproportionation is weakened by the photoexcitation. Because the linear absorption spectra are broad and large near \( \omega \sim 0.4 \), we use \( \omega_{\text{ext}}=0.4 \) for both salts. For the \( \alpha \)-type salt, the charge order is almost completely destroyed in Fig. 3. For the \( \theta \)-type salt, it survives in Fig. 4 even with slightly larger \( E_{\text{ext}} \). Here, the lattice spacing is denoted by \( a \). For more detailed comparison with different excitation densities, see Ref. [25].

Although the electronic state below the metal-insulator transition temperature is nonmagnetic in the \( \alpha \)-type salt and paramagnetic in the \( \theta \)-type salt, this difference in the magnetic properties does not play an important role as long as we observe the time evolutions of the spin and charge correlation functions in their exact many-electron wave functions (not shown). With the Hartree-Fock wave function, the lattice distortion tends to survive in the \( \theta \)-type salt compared with that in \( \alpha \)-type salt. This difference comes from the way by which the lattice stabilizes the charge order. In the \( \alpha \)-type salt, the distortion due to the coupling \( \alpha_{42} \) locally stabilizes the charge order by strengthening the corresponding bond density locally [7, 8]. The photoinduced charge-transfer process on this bond directly destabilizes the charge order. In the \( \theta \)-type salt, the distortion due to the coupling \( \alpha_{p4} \) globally stabilizes the charge order by strengthening the corresponding bond density globally with molecular rotation [23, 24]. The photoirradiation does not transfer charge between the strengthened bonds and the weakened bonds, so that the charge-transfer process does not directly destabilize the charge order. Thus, the photoinduced dynamics gives a useful hint about how the electronic state is stabilized by electron-phonon interactions.

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**Figure 3.** Time dependence of charge densities during excitations of \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \) with \( L=8, \ U=0.7, \ V_c/U=0.4, \ V_p/V_c=0.6, \alpha_{42}^2/K_{42}=0.07, \omega_{\text{ph}}=0.01, \omega_{\text{ext}}=0.4, \) and \( aE_{\text{ext}}=0.05 \) parallel to stripes.

**Figure 4.** Time dependence of charge densities during excitations of \( \theta-(\text{BEDT-TTF})_2\text{RbZn(SCN)}_4 \) with \( L=8, \ U=0.7, \ V_c/U=0.4, \ V_p/V_c=0.6, \alpha_{p4}^2/K_{p4}=0.1, \omega_{\text{ph}}=0.01, \omega_{\text{ext}}=0.4, \) and \( aE_{\text{ext}}=0.07 \) parallel to stripes.
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