Photoinduced melting of charge order in quasi-two-dimensional organic conductors

Yasuhiro Tanaka1 and Kenji Yonemitsu1,2

1Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan
2Graduate University for Advanced Studies, Okazaki, Aichi 444-8585, Japan
E-mail: yasuhiro@ims.ac.jp

Abstract. Photoinduced melting of charge order in quasi-two-dimensional organic conductors \( \alpha-(ET)_2I_3 \) (ET=BEDT-TTF) and \( \theta-(ET)_2RbZn(SCN)_4 \) is investigated theoretically. By solving the time-dependent Schrödinger equation numerically within the Hartree-Fock approximation for an extended Peierls-Hubbard model, we study the photoinduced dynamics in each compound. The obtained charge, spin and lattice dynamics are considered to reflect the different natures of charge ordered states in these systems. In particular, the melting of charge order needs more energy for \( \theta-(ET)_2RbZn(SCN)_4 \) than for \( \alpha-(ET)_2I_3 \), which is a consequence of large lattice distortion and the essential role of electron-phonon coupling in stabilizing the charge order in \( \theta-(ET)_2RbZn(SCN)_4 \).

Low dimensional organic conductors are known to exhibit various ground states which are typical of strongly correlated electron systems[1]. Charge ordering (CO) is one of such phases, where electron-electron as well as electron-phonon (e-ph) interactions have important roles. The photoinduced phase transitions realized by photoirradiation in these systems have been intensively studied for recent years in order to understand the mechanism of electron and lattice dynamics both experimentally and theoretically[2].

The quasi-two-dimensional organic conductors \( \alpha-(ET)_2I_3 \) (\( \alpha-I_3 \)) and \( \theta-(ET)_2RbZn(SCN)_4 \) (\( \theta-RbZn \)) are the typical compounds with a quarter filled \( \pi \)-band which show CO[3, 4, 5]. \( \theta-RbZn \) shows a first-order metal-insulator transition with lattice distortion at \( T_c = 200K \) and a spin gap behavior much below \( T_c \)[6]. On the other hand, \( \alpha-I_3 \) undergoes a CO transition at \( T_c = 135K \)[7], and the magnetic susceptibility[8] indicates a spin gap below \( T_c \). Several experiments such as X-ray scattering[9, 10] show that horizontal-type CO is formed in both compounds.

The photoinduced melting of CO in these systems has been observed by using the femtosecond spectroscopy recently[11]. It indicates that a semimacroscopic metallic domain is generated for \( \alpha-I_3 \), whereas only local melting of CO is created for \( \theta-RbZn \). In particular, the dynamics in \( \alpha-I_3 \) shows critical slowing down and strong dependence on the excitation intensity and temperature[11]. This clear difference is considered to originate from the roles of lattice distortion in stabilizing the COs. In fact, the transition is of first-order with a large structural distortion and large discontinuity in \( \theta-RbZn \), whereas the lattice distortion in \( \alpha-I_3 \) is relatively small. These observations are consistent with the theoretical calculations with Hartree-Fock approximation[12, 13] and exact diagonalization[14, 15]. Therefore, it is of great interest to investigate the photoinduced melting of CO in these systems and compare their dynamics.

In order to describe the horizontal CO with lattice distortion in \( \alpha-I_3 \) and \( \theta-RbZn \), we consider...
Figure 1. Charge densities as a function of increment in total energy for (a) $\alpha$-I$_3$ and (b) $\theta$-RbZn. The parameters are chosen at $U = 0.7$, $V_c/U = 0.4$, $V_p/V_c = 0.4$ and $\omega_{ph} = 0.01$ for both compounds. $s_{b2} = 0.07$ for $\alpha$-I$_3$ and $s_{p4} = 0.1$ for $\theta$-RbZn.

Figure 2. Modulations of transfer integrals as a function of increment in total energy for (a) $\alpha$-I$_3$ and (b) $\theta$-RbZn. The inset shows $\langle n_{i\uparrow}\rangle$ for a hole-rich site with $\langle n_{i\uparrow}\rangle > \langle n_{i\downarrow}\rangle$.

an extended Peierls-Hubbard model[12, 13, 14, 15] which is written as,

\[
H = \sum_{\langle ij\rangle \sigma} (t_{i,j} + \alpha_{i,j} u_{i,j})(\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij\rangle} V_{i,j} n_i n_j + \sum_{\langle ij\rangle} \frac{K_{i,j}}{2} u_{i,j}^2 + \sum_{\langle ij\rangle} \frac{K_{i,j}}{2\omega_{ph}^2} u_{i,j}^4, \tag{1}
\]

where $\langle ij\rangle$ represents the summation over the pairs of neighboring sites, $\hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$ denotes the creation (annihilation) operator for an electron with spin $\sigma$ at the $i$th site, $n_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. The electron density is fixed at 3/4 filling. The e-ph coupling constant, lattice displacement, elastic constant and phonon frequency are denoted by $\alpha_{i,j}$, $u_{i,j}$, $K_{i,j}$ and $\omega_{ph}$, respectively. Further introduce new variables as $y_{i,j} = \alpha_{i,j} u_{i,j}$ and $s_{i,j} = \alpha_{i,j}^2 / K_{i,j}$. The notations of transfer integrals $t_{i,j}$, $V_{i,j}$, $y_{i,j}$ and $s_{i,j}$ are the same as those in ref.[13] for both compounds. For simplicity, we consider only $s_{b2}$ and $s_{p4}$ as the e-ph coupling in $\alpha$-I$_3$ and $\theta$-RbZn, respectively. The photoexcitation is introduced with an oscillating electric field $E(t) = E_{ext} \sin \omega_{ext} t$ for $0 < t < 2\pi N_{ext}/\omega_{ext}$ by the Peierls phase factor of the transfer integrals. We set $N_{ext} = 16$ and $\omega_{ext} = 0.4$ which nearly corresponds to the peak positions of the linear absorption spectra for both compounds. Here $E(t)$ is assumed to be parallel to the horizontal.
stripe CO. The time evolution is obtained by numerically solving the time-dependent Schrödinger equation within the Hartree-Fock approximation [16] for the 8 × 8-site system. The parameters such as the Coulomb interactions and e-ph couplings are so chosen that the horizontal-stripe COs are realized for both compounds [13].

Figure 1 shows the charge densities averaged over $2\pi(N_{\text{ext}} - 3)/\omega_{\text{ext}} < t < 2\pi N_{\text{ext}}/\omega_{\text{ext}}$ as a function of the increment in total energy $\Delta E$ [17]. Similar plots for the modulations of transfer integrals are shown in Fig. 2. In order to see the time evolution of the spin component which is antiferromagnetically ordered on a hole-rich stripe at $t = 0$ within the Hartree-Fock approximation [13], $\langle n_{ij} \rangle$ for a hole-rich site with $\langle n_{i4} \rangle > \langle n_{i3} \rangle$ is shown in the inset of Fig. 2. In the case of $\alpha$-I$_3$, the charge disproportionation is strongly reduced in the region of $\Delta E > 0.04$. For $\theta$-RbZn, on the other hand, the horizontal CO persists up to larger $\Delta E$ than $\alpha$-I$_3$ and the modulation $y_{4d}$ shows no noticeable change for small $\Delta E$. The relative stability of CO in $\theta$-RbZn is understood by an essential role of the e-ph coupling and large lattice distortion compared with $\alpha$-I$_3$ where the lattice effect is small [13, 15]. The spin order on the hole-rich stripe and the CO vanish simultaneously for $\alpha$-I$_3$, while the CO survives even when the spin order is destroyed for $\theta$-RbZn. This may be related to the experimental fact that the spin gap is formed below $T_c$ in $\alpha$-I$_3$, while the paramagnetic state is observed in the wide temperature range in $\theta$-RbZn. The difference in these spin states are expected since the transfer integrals on the hole-rich stripe are alternating in $\alpha$-I$_3$, whereas they are uniform in $\theta$-RbZn [13].

In summary, we have studied the time evolution of CO systems $\alpha$-I$_3$ and $\theta$-RbZn under the photoexcitation by using the time-dependent Hartree-Fock approximation for the relevant extended Peierls-Hubbard models. It is found that the dynamics of charge, spin and lattice degrees of freedom are different in these systems. The melting of horizontal CO needs more energy for $\theta$-RbZn than $\alpha$-I$_3$ because the effect of the e-ph coupling on the stabilization of CO is larger in the case of $\theta$-RbZn.

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