

Optical Studies of Charge Ordering in Organic Conductors

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In organic conductors, kinetic energy is comparable with on-site and inter-site Coulomb energy. Due to this reason, many organic conductors are located in a boundary area between metallic and localized states, and thus various organic charge-transfer compounds show metal–insulator phase transition. Recently, charge-ordered (CO) state originated from Coulomb interaction is widely found in organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. The CO state attracts much attention, first because charge-mediated superconductivity is theoretically predicted in superconducting compounds neighbored on CO phase, second because some compounds in CO phase show ferroelectricity through the crystallization of conduction electrons. We have investigated the CO state and metallic state near CO employing infrared and Raman, and reflection spectroscopy.

1. Nonuniform Site-Charge Distribution and Fluctuations of Charge Order in the Metallic State of α -(BEDT-TTF) $_2$ I $_3$ ¹

Among a variety of organic conductors, the α -(BEDT-TTF) $_2$ I $_3$ shows rich properties such as charge order, superconductivity, zero-gap state, persistent photoconductivity, photo-induced phase transition, and non-linear optical response. This compound exhibits a first-order metal–insulator (MI) phase transition at $T_{MI} = 135$ K. The MI transition is considered to be driven mainly by on-site and intersite Coulomb interaction. Based on theoretical, 13 C-NMR, Raman, and x-ray studies, the insulating phase is regarded as a charge-ordered state involving a moderate structural change. First, we have quantitatively examined the amplitude of charge order below T_{MI} based on the rational assignment of the charge-sensitive C=C stretching modes. Compared with the insulating phase, the metallic phase of α -(ET) $_2$ I $_3$ has not been thoroughly investigated, although the electronic structure of the metallic phase is related to the superconductivity under uniaxial strain, zero-gap state under hydrostatic pressure, and the excited state

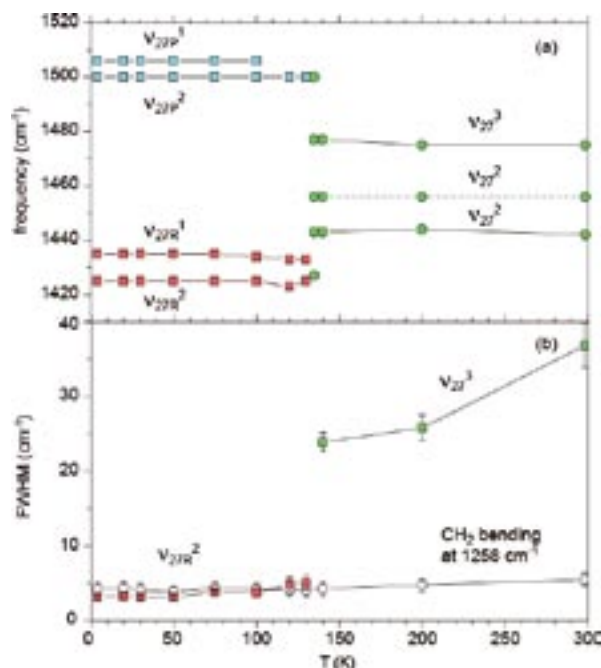


Figure 1. (a) Frequencies of v_{27} modes (C=C stretching) plotted against temperature. The three v_{27} mode largely split into two groups (charge-rich and charge-poor sites) (b) Temperature dependence of the linewidth (FWHM) of the v_{27}^3 (green square) mode, which involves weak v_{27}^2 , and v_{27R}^2 (orange square) modes. The temperature dependence of the CH₂ bending mode (open circle) at 1258 cm⁻¹, the frequency of which is insensitive to site charge, is shown for comparison.

of the photo-induced metal–insulator transition. Second, we have analyzed the linewidth of the charge-sensitive C=C stretching mode, and found a thermally activated short-range charge order in the metallic phase above T_{MI} .

Figure 1 shows the splitting and linewidth of the infrared-active charge-sensitive mode, v_{27} . Below T_{MI} , these modes are largely split into two groups, which correspond to the two charge-rich and two charge-poor sites. From the relationship

between the frequency and site charge, the site charge is deduced to be (0.8₁, 0.7₄, 0.2₆, and 0.2₃). The linewidth of these modes is narrow ($\sim 4 \text{ cm}^{-1}$) as shown in Figure 1b. The large amplitude and narrow linewidth below T_{MI} unambiguously indicates the charge-ordered state with long-range order. In the metallic phase above T_{MI} , this mode is split into three. The site-charge is deduced to be (0.6₈, ~ 0.6 , and 0.4₄). We interpret this small amplitude of site-charge distribution is caused by the distribution of transfer integrals. The most important difference between metallic and charge ordered phases is the linewidth as shown in Figure 1b. We interpret the very broad linewidth as the fluctuation of site charge. Assuming the Gaussian process for the fluctuation, the fluctuation rate was estimated to be $1\text{--}25 \text{ cm}^{-1}$. This slow fluctuation rate suggests a collective motion of short-range ordered charge-ordering stripe. We propose that several short-range ordered charge-ordering stripes are thermally activated in the metallic phase. This idea is consistent with the entropy driven first order MI phase transition. The optical conductivity in the metallic phase obtained from the analysis of reflectivity shows no Drude response, which may be associated with this fluctuation of charge order. According to the high-pressure experiment, this charge-ordering fluctuation is well suppressed.

2. Vibronic Activation of Vibrational Overtone in the Infrared Spectrum of Charge-Ordered Organic Conductors²⁾

Infrared spectrum provides us important knowledge on the valence states in strongly correlated systems. However, there is substantial difficulty in the analysis of the spectrum, because the valence electrons in these systems are affected by various interactions such as electron–electron or electron–phonons, complicating the interpretation of the spectral signals. For instance, even a phonon signal, which has the chemically defined frequency, is difficult to assign unambiguously because of large frequency-shift due to strong vibronic coupling.

In the study, we focused on the identification of the dip-shaped anomaly appearing in the infrared spectrum of a group of organic conductors (the highlighted region in Figure 2). The anomaly appears at approximately the same frequency (*ca.* 2700 cm^{-1}), irrespective of the substances when they transform to charge-ordered phase. By the isotope-shift measurement performed for $\theta\text{-(BEDT-TTF)}_2\text{RbZn(SCN)}_4$, we found that there is a relevance of the anomaly to the overtone of a C=C stretching mode of BEDT-TTF molecule. From the fact that the dip is observed exclusively for the materials showing charge ordering, it is suggested that the anharmonicity activating the overtone does not exist in the potential of individual molecules; instead we suppose, which should be in the electronic potential formed by intermolecular vibronic interactions.

For organic conductors, the electronic potential depends strongly on molecular vibrations *via* the vibronic interaction called electron–molecular vibration (e–mv) coupling. The vibronic phenomenon has been explained within the frame-

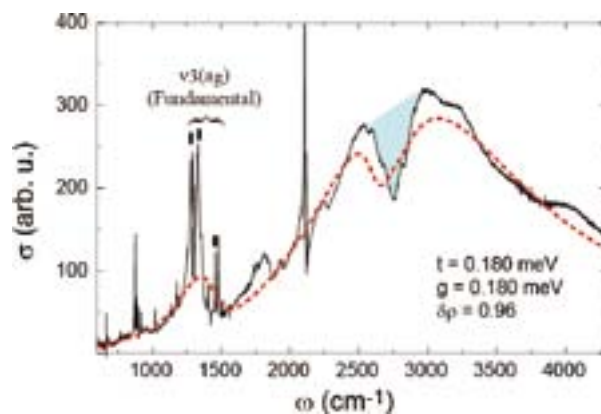


Figure 2. The comparison of the numerical result (dotted line) to the experimentally obtained optical conductivity of $\theta\text{-(BEDT-TTF)}_2\text{RbZn(SCN)}_4$ [$E//a$, $T = 6 \text{ K}$] (solid line). (The parameters used in the calculations: $\omega_{\text{neutral}} = 1494 \text{ cm}^{-1}$, $\omega_{\text{cation}} = 1407 \text{ cm}^{-1}$, line-width of molecular mode: 100 cm^{-1} , linewidth of electronic transition: 1000 cm^{-1} , $t = 180 \text{ meV}$, e–mv coupling constant: 180 meV) The highlighted region denotes the dip-shape anomaly, whereas the sharp peaks labeled by the ticks are the fundamental signals of $\nu_3(a_g)$.³⁾

work of a linear-coupling theory, in which the coupling effect is treated as an energy shift of the valence level. The aim of the present study is to extend the linear-coupling theory to explain the activation mechanism of the overtone of a vibrational mode that behaves otherwise a harmonic oscillator.

We calculated the corrections of the adiabatic electron potential due to the vibronic coupling to higher-ordered terms using a diatomic molecular dimer model. Additionally, the dynamic susceptibility was calculated using the same model. The main arguments derived from the study are summarized: (1) In the energy corrections, there appear two cubic terms—the lowest-order anharmonicity—in terms of the molecular coordinates. (2) One of them is connected with charge separation between the two molecules, which term presumably induces the anharmonicity activating the overtone. (3) The vibronically induced anharmonicity arises from the non-linearity in the adiabatic mixing of the electronic levels in accordance with charge separation. (4) Essential features of the experimentally obtained spectrum were reproduced by the numerical calculation of the dynamical susceptibility based on the cluster mode (Figure 2). (5) There is an intimate relationship between the activation of the overtone and nonlinear electric susceptibility; actually we have demonstrated that an organic conductor $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$, which shows the overtone signal along with charge ordering, generates strong second-order optical nonlinearity.⁴⁾

References

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