RESEARCH ACTIVITIES IV
Department of Molecular Assemblies

IV-A Spectroscopic Study of Charge Carriers in Organic Conductors

The low-frequency reflectivity of an organic conductor provides us with a wealth of information on the nature of charge carriers. For instance, the anisotropy of a band structure, bandwidth, effect of electron-electron correlation, and electron-molecular vibration (*e-mv*) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. We are investigating the polarized reflection spectra of various organic conductors in the spectral region of 50–33000 cm^{-1} and in the temperature range of 6–300 K. Usually the molecular vibrations (local phonons) are screened by strong electronic transition by charge carriers. Therefore, few local phonon bands are detected in the reflection spectrum. In this sense, the Raman spectroscopy is a complementary method to reflection spectroscopy for understanding molecular vibrations in a metallic state. Since some molecules have charge-sensitive vibrational modes, the Raman spectroscopic method is a powerful tool to detect the site-charge distribution (oxidation state of molecule). We are investigating the charge ordering (CO) phenomena in organic conductors using the technique of infrared and Raman spectroscopy. In the organic charge-transfer salts, CO is originated from the localization of the charge carriers. Since the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, CO will be widely found through the phase transition. The charge ordering was first found in inorganic narrow-band systems such as copper, manganese, and vanadium oxides. Recently, CO has been found in several organic conductors, and the electronic phase diagrams of typical organic conductors are re-examined taking CO into account. The CO state is drawing attention, since CO is theoretically considered as being related to the pairing mechanism in superconductivity. The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by an inhomogeneous charge distribution. Our goal is the complete understanding of the CO phase transition through the interpretation of the vibrational spectra, and the drawing of a *P-T* phase diagram.

IV-A-1 Infrared and Raman Evidence for the Charge Ordering in β”-(BEDT-TTF)$_3$(ReO$_4$)$_2$ Studied by Vibrational Spectroscopy

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The charge-ordering (CO) state is drawing attention as a new electronic ground state in narrow-band organic charge-transfer salts which do not have a strong dimer unit. The mechanism of the metal-insulator transition of β”-type ET salts (ET = bis-ethylenedithio-tetrathiafulvalene) has not been understood well. As the first step to investigate the ground state of β”-type ET salts, we started from the 3:2 salts, where the carrier density is higher than those of the 2:1 salts. The infrared and Raman spectra of β”-$(ET)_3(ReO_4)_2$ were measured at various temperatures below 300 K. We investigated the three C=C stretching modes, ν_2, ν_{27} and ν_3. The infrared and Raman spectra discontinuously changed at 80 K. Below 80 K, for example, the doublet ν_2 bands split into three peaks, the doublet ν_{27} also split into three, and a mutual exclusion rule for the vibronic ν_3 modes in the infrared and Raman spectra is broken. This symmetry lowering is consistent with the result of x-ray crystal structure analyses conducted at 100 K and 22 K. The site charges in the unit cell estimated from the splitting of ν_2 are $+0.7_3$, $+0.7_3$, and $+0.5_3$ in the metallic phase above 81 K, and they are changed into +0.2, $+0.8_5$, and $+0.9_5$ in the insulating phase below 80 K. The pattern of the site charge distributions exhibits the re-distribution at 80 K, which is shown in the figures. The frequencies of the vibronic ν_3 modes are reproduced from the numerical calculation by assuming of the patterns in the figures. From these experimental results, the metal-insulator transition of this compound is characterized as the CO transition originated from the localization of charge due to Coulomb interactions.

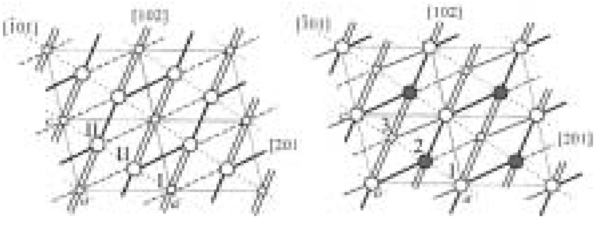

Figure 1. The site charge distributions above 81 K (left) and below 80 K (right). The symbols, ○ and ◦ in the left denote the site charges of 0.7_3 and 0.5_3, and the symbols ○, ●, and ◦ denote the site charges of 0.9_5, 0.8_5, and 0.2. The lines represent the magnitude of transfer integrals, which is schematically shown as follows: double > single > dashed > dotted.

IV-A-2 Charge Ordering State of β”-(ET)$_3$(HSO$_4$)$_2$ and β”-(ET)$_3$(ClO$_4$)$_2$

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In the previous study, we have demonstrated the charge-ordering (CO) phase transition of β”-$(ET)_3(ReO_4)_2$ at 80 K. However, this CO phase transition is accompanied by a drastic structural change. On the other hand, no remarkable structural change is observed in the metal-insulator transition of β”-$(ET)_3(HSO_4)$ and β”-$(ET)_3(ClO_4)$ salts. This enables us to discuss purely the role of the inter-site Coulomb repulsion, *V*, in the CO state. The Raman and IR spectra of β”-$(ET)_3X_2$ (X = HSO_4 and ClO_4) were measured at various temperatures below 300 K. We investigated three C=C stretching modes, namely ν_2, ν_3 and ν_{27}. The spectral patterns of both compounds in the low temperature phases are ascribed to the CO state, where the site charges at charge-poor and charge-rich sites are ~+0.3_3 and ~+0.8_3. The pattern of the CO state in X = HSO_4 salt is identical to that in X = ClO_4 salt but differs from that of X = ReO_4 salt. We have found that the patterns of the CO states are correlated with the inter-molecular distances between the centers of adjacent molecules along the stacking direction. Since the intermolecular distance at the non-slipping point is shorter than that at the slipping point, *V* at the non-slipping point is larger than that at the slipping point. The unit cells of X = HSO_4 and ClO_4 salts contain two non-slipping points whereas an organic layer of the unit cell of X = ReO_4 salt contains one non-slipping point. This structural difference explains the difference in the CO pattern. Through the analyses of the experimental results, we have demonstrated direct evidence for the role of the inter-site Coulomb repulsion in the CO state.

IV-A-3 Inhomogeneous Charge Distributions in β”-$(ET)_4Ga(C_2O_4)_3$sol (sol = $PhNO_2$, Py and Ch_2Cl_2)

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The reason for the strong attention to the charge ordering (CO) is the theoretical prediction that the superconducting (SC) state neighbored on the CO state has a new paring mechanism. Among various non-dimerized ET salts, the β”-type ET salts have attracted attention, because the superconductivity has been found in various β”-type ET salts under hydrostatic pressure. The most interesting point of the title compounds is that they demonstrate superconductivity at ambient pressure. According to the resistivity measurements of the title compounds, the metal-insulator transitions are observed at around 100 K. The electrical resistivity of solvent = Py (pyridine) and CH_2Cl_2 salts keep the insulating behavior down to the liquid-helium temperature. On the other hand, the insulator-superconductor transition is observed at 7.5 K in the electrical resistivity of solvent = $PhNO_2$ (nitrobenzene) salt. The conducting behavior of the title compounds is unique since the SC phase appears with increasing the volume of the unit cell. We have tentatively measured the Raman and IR spectra of these compounds down to 13 K. The ν_{27} and ν_2 modes have the broad line-widths around 300 K. With decreasing temperature, these modes show the peak splitting, suggesting the CO state. The difference in the site charge distributions, $\Delta\rho$, has the large value with increasing the size of the solvent molecule in the crystal. The reflectivity in the infrared region decreases as the size of the solvent molecule increases. Our observations suggest the view that that the SC phase is neighbored on the CO phase.

IV-A-4 Infrared and Raman Study of the Charge-Ordered State of θ-$(ET)_2Cu_2CN[N(CN)_2]_2$

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According to the resistivity measurements of the θ-type ET salts, the conducting behavior can be mapped with the structural parameter, namely the dihedral angle, ϕ, which is defined from the adjacent molecules along the highly conducting direction. The title compound has the largest ϕ among the θ-type ET salts, and the electrical resistivity exhibits an insulating behavior even at 300 K. In order to clarify the electronic state of θ-type ET salts, the polarized Raman and infrared spectra of θ-$(ET)_2Cu_2CN[N(CN)_2]_2$ were measured at various temperatures below 300 K. We investigated the three C=C stretching modes, ν_2, ν_3 and ν_{27}. The spectral pattern below the phase transition temperature, ~220 K, is compatible with the horizontally charge-ordered state, where the site-charge distributions are +0.1_7 and +0.8_3. We have found that the vibronic ν_3 bands correlate to the dihedral angles, ϕ. This relation is well reproduced from the numerical calculation based on the cluster model with C_2 symmetry. Among four independent ν_3 bands, the lowest-frequency vibronic band is the most sensitive to ϕ. With increasing ϕ, the frequency of the vibronic band is elevated due to the decrease of the transfer integral (and increasing the magnitude of the Coulomb repulsions).

The spectral features above the phase transition temperature, ~220 K, also exhibit the peak splitting due to the precursory effect of the CO state. The charges are nearly localized, and perhaps the short-range ordered horizontal CO stripe is dynamically fluctuating in the high-temperature phase above 220 K.

IV-A-5 Re-Examination of the Charge Sensitive Vibrational Modes in ET Molecule

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The phase transition from charge-ordering (CO) phase to superconducting (SC) phase has not been experimentally observed. Such an experiment will be able to be conducted in the β”-type ET salts using vibrational spectroscopic method. However, the Raman technique is inappropriate, because the control of the sample temperature is difficult owing to the heating effect by the excitation lasers. On the other hand, the infrared reflectance technique enables us to measure the vibrational mode around the liquid helium temperature. Among the IR-active modes of the ET molecule, the ν_{27} mode is the candidate of the charge sensitive probe. We can expect that the frequency decreases with increasing the site charges. However, the relation between the frequency and the degree of the charge transfer is not well established. We detected the frequency of the ν_{27} mode of ET^+ through the measurement of the IR reflectance spectra of $(ET)(ClO_4)$, $(ET)(AuBr_2Cl_2)$ and the isotope analogues of $(ET)(AuBr_2Cl_2)$. The decided frequency is ~ 1400 cm^{-1}, which is remarkably different from 1445 cm^{-1} in the previous reports.

The frequency of the ν_{27} mode in the neutral ET crystal is lower than that of the charge-poor site of θ-$(ET)_2Cu_2CN[N(CN)_2]_2$ in the CO state. This contradictory result seems to be ascribed to the fact that the ET molecule in the neutral crystal has a boat structure and those of the charge transfer (CT) salts have a flat structure regardless of the degree of the charge transfer, ρ. This conjecture was verified from the normal mode analysis using the DFT method: the frequency of ν_{27} in boat ET^0 is lower than that of flat ET^0. On the basis of our experimental results and calculations, we deduced the frequency shift of ν_{27} as $\Delta\nu$ ~ 135 cm^{-1}/e. The ν_{27} mode is the efficient probe to the site charges in the ET salts. Finally, we should emphasize that ν_{27} is free from *emv* effect and thus the frequency shift is directly related to the site charge.

IV-A-6 Suppression of the Charge Disproportionation by Hydrostatic Pressure in β"-(ET)(TCNQ)

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Charge disproportionation (CD) and charge ordering (CO) in organic conductors originate from the localization of charge carriers. CO has been investigated in the insulating states of several charge-transfer salts. Last year, we presented dynamically fluctuating CD in the metal-like state of the title compound. We measured the polarized Raman and infrared spectra. First we estimated the charge-transfer degree from ET to TCNQ as 0.5 using the C=C stretching mode (ν_4) of TCNQ. All of the Raman bands of TCNQ are independent of temperature. However, the C=C stretching modes (ν_2 and ν_3) of BEDT-TTF show clear splitting, and the low-frequency component of ν_3 exhibits a broad vibronic feature. This finding indicates that the holes of BEDT-TTF are nearly localized, and thus CD arises near the room temperature. Very interestingly, the split bands of ν_2 merge into a single broad band, and the broad band is sharpened on lowering temperature. The same phenomenon is found in the infrared-active C=C stretching mode ν_{27}. This temperature dependence is well reproduced by motional narrowing model. We interpreted this phenomenon as follows: The lowering the temperature contracts the crystal lattice and increases the transfer integral between the adjacent ET molecules. The slight enhancement of the transfer integral accelerates the hopping speed and causes the merge of the split band.

This compound consists of a segregated stack structure, where BEDT-TTF and TCNQ separately form uniform chains. We found week satellite reflections of 0.5*a** + 0.5*c** on X-ray diffraction patterns exposed for 8 hours. This result and the vibronic band of infrared spectra polarized to TCNQ stack direction are consistent with dimerization of TCNQ. This year, we applied the hydrostatic pressure to contract the crystal lattice. The split bands of ν_2 again merge into a single broad band, and the broad band is sharpened on increasing pressure. All of the Raman bands of TCNQ are independent of pressure. The same phenomenon is found in the temperature dependence of Raman spectra.[1)]

Reference

1) K. Yakushi, M. Uruichi, H. M. Yamamoto and R. Kato, *J. Phys. IV France* **114**, 149–151 (2004).

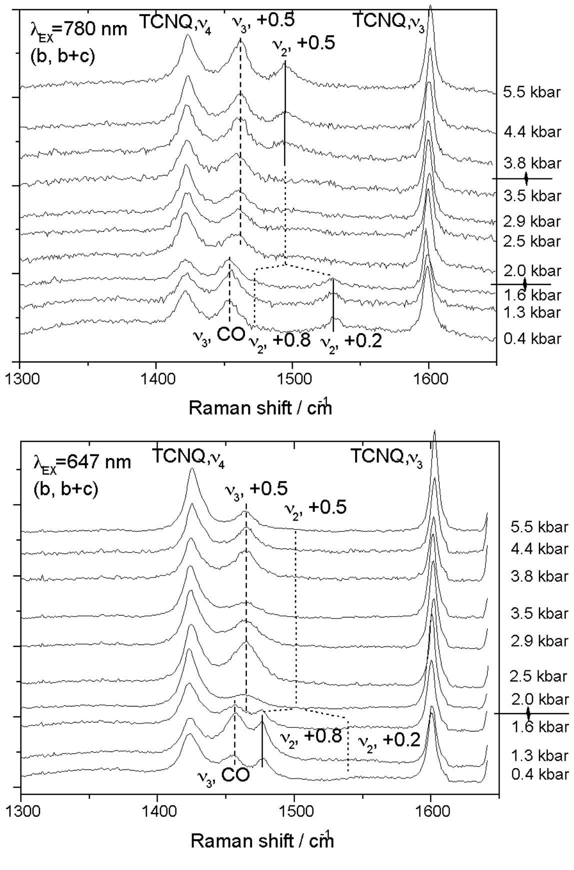

Figure 1. Pressure dependence of the Raman spectra of β"-(ET)(TCNQ) at room temperature.

IV-A-7 Electron-Molecular Vibration Coupling Effect on the Raman Spectrum of Organic Charge Transfer Salts

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Vibrational spectra of dimerized and tetramerized radical clusters have been calculated to understand the features of electron-molecular vibration (EMV) coupling effects for the charge ordered (CO) system. The calculated spectra show that the totally in-phase Raman band, which is usually used as a measure of the molecular ionicity, approaches to the frequency corresponding to the average molecular ionicity in the cluster, as we increase the EMV coupling constant. When the charge disproportionation (CD) ratio is not large, the frequency of this mode is independent of the molecular ionicity. On the other hand, when large CD presents, the in-phase Raman bands show steep shift for small variation of the CD ratio. These results suggest that concerning to the normal modes with a large EMV coupling constant, we should not use the Raman-active band to estimate the molecular ionicity. We should use the Raman-active mode with small EMV coupling constant or infrared-active mode for the estimation of the molecular ionicity.

IV-A-8 Activation of Strong Overtone in the Infrared Spectrum of a Charge Ordered Organic Conductor

YAMAMOTO, Kaoru; YAKUSHI, Kyuya

Activation of overtones (OT) (asterisk in Figure 1) in the IR spectrum of θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$ has been investigated using a diatomic molecular dimer model. When the two molecules are in the charge disproportionation for some reason, deformation of the two molecules along the anti-phase mode ($Q_- = Q_1 - Q_2$; $Q_{1,2}$: normal coordinates of molecule 1 and 2) stabilizes the disproportionation *via* electron-molecular vibration (EMV) coupling effect. This stabilization turns the electronic wavefunction (Ψ) to be dependent on Q_- and induces an unharmonicity in the vibronic energy,

$$\int \Psi^*(n_1 - n_2)Q_-\Psi dr$$

($n_{1,2}$: electron density on the molecule 1 and 2). Taking the Q_- dependence into account, we have calculated the optical conductivity spectrum including one totally symmetric C=C stretching mode (ν_3) using several fitting parameters, such as the vibronic coupling constants and the phenomenological site-energy difference. As shown by the dashed curve in Figure 1, the calculated spectrum reproduces the characteristics of the experimental data including the fundamental and overtone of ν_3. According to the model developed here, the overtone is only visible when the degree of charge disproportionation is large, and thus the emergence of overtone can be referred as evidence for the large charge disproportionation.

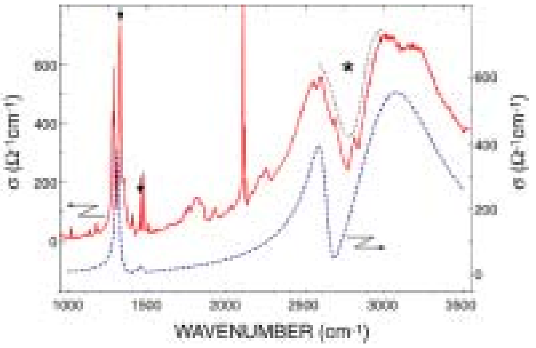

Figure 1. Solid curve shows the optical conductivity spectrum (E_{ph}//*c*-axis) of θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$ measured at 50 K. Arrows and an asterisk indicate the fundamental and overtone of ν_3, respectively. The dashed curve shows the calculation results.

IV-A-9 Bond and Charge Density Waves in the Charge Localized Phase of $(DI\text{-}DCNQI)_2Ag$ Studied by Single-Crystal Infrared and Raman Spectroscopy

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The charge distribution and molecular arrangement of a 1/4-filled quasi-1D system $(DI\text{-}DCNQI)_2Ag$ (DI-DCNQI = 2,5-diiodo-dicyanoquinediimine) have been studied by IR and Raman spectroscopy. The charge localization of this material was believed to be a 1D generalization of a Wigner crystal driven by inter-site Coulomb repulsion. While charge disproportionation (CD) is confirmed *via* the splitting of b_u modes in the infrared (IR) spectrum, the appearance of intense IR vibronic bands of a_g modes strongly suggests the presence of the dimerization that is not expected from the proposed 1010 charge ordering (CO) model (Wigner crystal). In addition, the selection rules for the IR and Raman signals cannot be explained without a further symmetry reduction of the unit cell. To explain the vibrational behavior observed for a single crystal, we show that a more appropriate model for the charge ordering is 0110 ($2k_F$ CDW + $4k_F$ BOW).

IV-A-10 Infrared and Raman Studies of TTM-TTP and TSM-TTP Charge-Transfer Salts

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The bis-fused TTF (tetrathiafulvalene) molecule and its derivatives are good electron donors for synthesis of new conducting ion-radical salts. One of these derivatives, TTM-TTF (see Figure 1) yields mostly quasi-one-dimensional semiconductors, because four $S\text{-}CH_3$ groups attached to the bis-fused TTF skeleton separate efficiently neighboring TTM-TTP stacks. Nevertheless, some TTM-TTP salts exhibit metallic properties. The charge-transfer salt, (TTM-TTP)I_3 was reported as the first organic metal with 1:1 stoichiometry and a highly one-dimensional half-filled band. To investigate the relation between the molecular ionicity and the frequency of characteristic vibrational modes of TTM-TTP molecule, we measured room-temperature infrared and Raman spectra of neutral TTM-TTP molecule and four conducting charge-transfer salts with different molecular ionicity: (TTM-TTP)I_3, (TTM-TTP)AuI_3, (TTM-TTP)$(I_3)_{5/3}$, and (TSM-TTP)$(I_3)_{5/3}$. The vibrational bands related to the C=C stretching modes were analyzed. The frequencies of C=C stretching modes observed both in infrared and Raman spectra depend linearly upon the charge on TTM-TTP (or TSM-TTP) molecules.

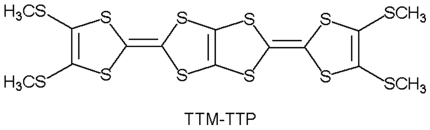

Figure 1. Structural formula of TTM-TTP.