

Charge Ordering State of ET, BETS and [Pd(dmit)₂] Salts by Temperature-Dependent Vibrational Spectroscopy

Takashi Yamamoto,[†] Reizo Kato,[†] and Kyuya Yakushi[‡]

[†]Riken, 2-1 Hirosawa, Wako, 351-0198, Japan

[‡]Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

The charge ordering (CO) state has attracted considerable attention since inhomogeneous site charges are observed for the molecular conductors including highly conducting materials and the superconductor.^{1,2} The vibrational spectroscopy is a powerful method to investigate the structure and dynamics of the CO state along with the degree of charge transfer. In this symposium, we will present the vibrational spectra of ET, BETS and [Pd(dmit)₂] salts, and discuss what dictates the CO state.

i) ET₅Te₂I₆ and BETS₅Te₂I₆.³ As shown in Fig. 1, the charge sensitive mode, ν_2 , splits into two bands. Therefore, both compounds are characterized as the CO state. Interestingly, the frequency of the structure sensitive ($e-m\nu$) mode, ν_3 , of the ET-salt is almost equal to that of the BETS-salt, which indicates that the patterns of the CO state are identical to each other. This observation confirms that the CO state is mostly ascribed to the inter-site Coulomb interaction along the stacking direction.¹ Inhomogeneous charges are robust above the metal-insulator transition temperature, T_{MI} . It is likely that the highly conducting state is due to the competition between the most stable and secondary stable patterns.¹

ii) Et₂Me₂Sb[Pd(dmit)₂]₂ and Cs[Pd(dmit)₂]₂.⁴ As shown in Fig. 2, the IR spectra of [Pd(dmit)₂] salts often exhibit two bands around 1300 cm⁻¹. The higher frequency band denoted as “A” is assigned to the asymmetric C=C stretching mode and the lower frequency band denoted as “B” to the symmetric C=C stretching mode. The former is the charge sensitive mode, and the latter is the $e-m\nu$ mode. Both salts undergo the CO phase transition because the band A discontinuously splits into two bands below T_{MI} . Four $e-m\nu$ modes exhibit a localized nature, and these modes are both IR and Raman active. This observation indicates that an organic layer consists of ionic and neutral dimers ([Pd(dmit)₂]₂²⁻ and [Pd(dmit)₂]₂⁰).

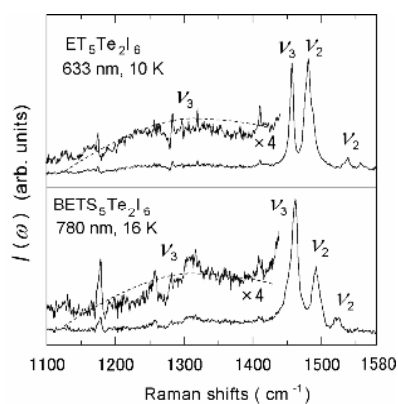


Fig. 1. Raman spectra of ET₅Te₂I₆ and BETS₅Te₂I₆.

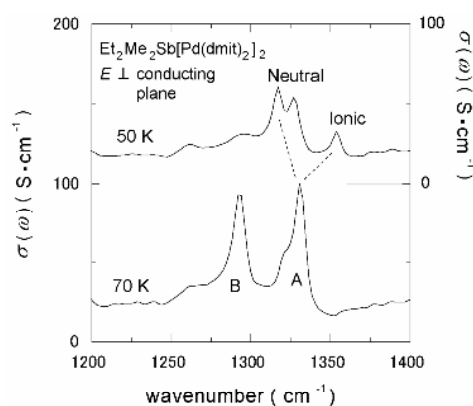


Fig. 2. Conductivity (IR) spectra of Et₂Me₂Sb[Pd(dmit)₂]₂.

[1] T. Yamamoto, et. al. Phys. Rev. B. in press. [2] A. F. Bangura, et. al. Phys. Rev. B. 72 (2005) 014543. [3] M. Fujiwara, et. al. J. Sol. Stat. Chem. 168 (2002) 396. [4] M. Tamura, et. al. Chem. Phys. Lett. 411 (2005) 133.