

# Optical characterization of $2k_F$ bond-charge-density wave in quasi-one-dimensional $\frac{3}{4}$ -filled (EDO-TTF) $_2X$ ( $X=PF_6$ and $AsF_6$ )

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We present the electronic and vibrational spectra of quasi-one-dimensional  $\frac{3}{4}$ -filled (EDO-TTF) $_2X$  (EDO-TTF=ethylenedioxy-tetrathiafulvalene,  $X=PF_6$  and  $AsF_6$ ) above and below the metal-insulator phase transition ( $T_{MI}=280$  K for the  $PF_6$  salt and 268 K for the  $AsF_6$  salt). For the low-temperature insulating phase, the pattern of both bond and charge order was identified. Almost all charge density is localized on the strongly bound central pair of 0110 tetramer giving rise to a characteristic spectrum of electronic excitations. Infrared spectra along the stacking axis show evidence of strong electron-molecular vibration coupling between the charge transfer band within the pair and some specific intramolecular vibrations. This charge order is assisted by a molecular deformation.

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## I. INTRODUCTION

Ground states of strongly correlated electron systems involving inhomogeneous site-charge distribution, or charge ordering (CO), have received recently much interest in both experiment and theory.<sup>1,2</sup> Organic charge-transfer solids (CTS) are an important class of materials exhibiting CO owing to a variety of CO states, a chance of coexistence with a commensurate bond order wave (BOW) and spin density wave,<sup>3</sup> tunability of a CO pattern by a small chemical modification of the crystal parameters,<sup>4</sup> and proximity on the phase diagram and likely the similar driving forces leading to CO as well as to a superconducting state.<sup>5</sup> In quasi-one-dimensional (Q1D)  $\frac{3}{4}$ - or  $\frac{1}{4}$ -filled organic CTS, a large on-site ( $U$ ) and nearest-neighbor ( $V$ ) Coulomb repulsion would cause, intuitively, the alternating (Wigner type) pattern of charge distribution 1010 (where 0 and 1 sites have charge densities of  $(0.5-\delta)$  and  $(0.5+\delta)$  electron charge, respectively) corresponding to a  $4k_F$  charge density wave (CDW). A number of theoretical studies have argued that such a periodicity requires  $V$  exceeding some critical  $V_c \sim 2t$  ( $t$  is the intrastack transfer integral).<sup>6</sup> On the other hand, for  $V < V_c$ , the 0110 ground state can be found.<sup>7</sup> This state corresponds to a  $2k_F$  CDW coupled with BOW of SW'SW type (the strongest bond  $S$  connects 1 and 0 sites, and  $W'$  and  $W(<W')$  exist in pairs 11 and 00, respectively) [Fig. 1(a)], which we call below as  $2k_F$  BCDW-I. From numerical calculations, it is expected to have a small site-charge difference  $2\delta$  and a large BOW.<sup>7</sup> Such  $2k_F$  BCDW-I was found, for example, in  $D_2$ (TCNQ) salts, where  $D=MEM$ , TEA tetracyanoquinodimethane (TCNQ);  $N$ -methyl- $N$ -ethyl-morpholinium (MEM); tetraethylammo-

onium (TEA).<sup>7</sup> When  $V$  is further small, 0110 CO can coexist with a different BOW of  $W'SW'W$  sequence Fig. 1(b) called below as  $2k_F$  BCDW-II,<sup>8</sup> which has not previously been definitely confirmed in any organic CTS.

Recently, Q1D organic CTS (EDO-TTF) $_2X$  (where EDO-TTF=ethylenedioxy-tetrathiafulvalene and  $X=PF_6$  and  $AsF_6$ ) have been synthesized.<sup>9</sup> A first order metal-insulator (MI) phase transition was observed at  $T_{MI}=280$  K in the  $PF_6$  salt and 268 K in the  $AsF_6$  salt. The mechanism of the MI transition did not conform to any particular kind of the phase instability found in organic CTS before, and was proposed as a type complying with the simultaneous cooperation of the Peierls, CO, and anion order features.<sup>9</sup> From the x-ray crystal structure analysis, it was determined that the unit cell is doubled. A distinctive deformation of EDO-TTF was found in the low-temperature insulating phase. The molecular bond lengths suggest an "0110" CDW and the calculation of the overlap integrals gives a  $W'SW'W$  type of BOW. Our preliminary optical study of the  $PF_6$  salt<sup>10</sup> has established two types of molecular charges ( $<+0.1$  and  $>+0.9$ ), and two charge-transfer (CT) bands, consistent with a  $2k_F$  BCDW-II. In this paper, we present the full electronic and vibrational spectra and their analysis for both salts with the aim to give a complete optical characterization of the structure and interactions in the rare  $2k_F$  BCDW-II state.

## II. EXPERIMENT

Single crystals grown by an electrocrystallization technique were black lustrous plates of  $1.0 \times 0.3 \times 0.05$  mm<sup>3</sup> dimensions.<sup>9</sup> The most developed crystal face was (001) elongated along the  $b$  axis. The polarized reflectivity data were measured with two spectrometers, Fourier transform infrared Nicolet Magna 760 ( $600-12\,000$  cm<sup>-1</sup>), and multichannel detection system Atago Macs 320 ( $11\,000-33\,000$  cm<sup>-1</sup>), both combined with infrared (IR)



FIG. 1.  $2k_F$  BCDW-I (a) and  $2k_F$  BCDW-II (b).

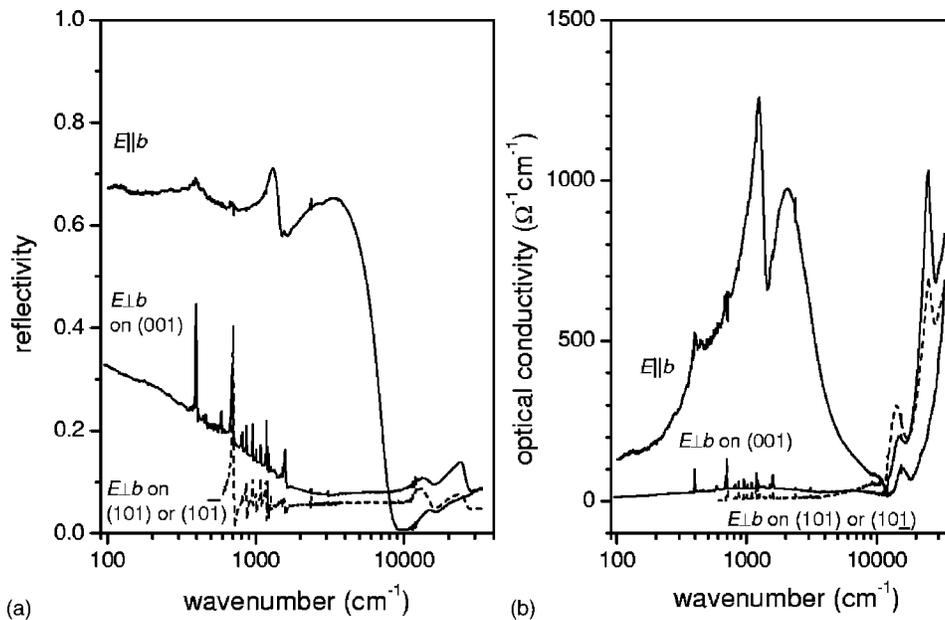


FIG. 2. (a) Polarized reflectivity and (b) optical conductivity spectra of  $(\text{EDO-TTF})_2\text{AsF}_6$  at 300 K.

microscope. Temperature dependence was obtained at slow sample cooling (2–6 K/h) using Oxford CF1104s cryostat. The sample was first heated up to 310 K and then the spectra were taken at 310, 290, 270, 250, 200, 100, and 6 K for  $\text{PF}_6$  salt and at 300, 270, 260, 200, 100, and 6 K for  $\text{AsF}_6$  salt. The far-IR polarized reflectivity (90–700  $\text{cm}^{-1}$ ) at room temperature (RT) was measured on the single crystal of the  $\text{AsF}_6$  salt using Bruker IFS-113v spectrometer. Polarized Raman spectra were measured in  $180^\circ$  backreflecting geometry with Renishaw Ramascope System-1000 equipped with three lasers:  $\text{Ar}^+$  ( $\lambda=515$  nm), He-Ne ( $\lambda=633$  nm), and near-infrared laser diode (LD) ( $\lambda=785$  nm). Spectra were taken at 300, 200, and 4.2 K at slow cooling using the above cryostat system. The isostructural  $\text{PF}_6$  and  $\text{AsF}_6$  salts were found to give almost identical spectra between them while in the same electronic state. Therefore, later in the figures we show the spectra mostly for the  $\text{AsF}_6$  salt and include numerical values for both where appropriate.

### III. RESULTS AND DISCUSSION

#### A. High-temperature phase

##### 1. Electronic spectra

The room-temperature crystal structure is isomorphous to that of the Bechgaard salts, where two donor molecules connected by an inversion center are stacked along the  $b$  axis (weak  $4k_F$  BOW) and form a conducting sheet in the (001) plane.<sup>9</sup> The conducting sheets are separated by anion layers. Reflectance spectra of the  $\text{AsF}_6$  salt at RT for three main crystal directions are shown in Fig. 2(a). Along the stacking axis ( $E||b$ ) the Drude-like feature is prevalent. Although the absolute reflectivity in the low frequency region is high ( $\sim 0.70$  for  $\text{PF}_6$  salt and  $0.65$  for  $\text{AsF}_6$  salt), it does not raise significantly in the far-IR. The spectrum for  $E \perp b$  on (001) is reminiscent of an overdamped plasmon and suggests some weak interstack interaction. The anisotropy of the reflectivity

in the conducting plane resembles that of Bechgaard salts.<sup>11</sup> The spectrum for the third direction is dominated by the intramolecular vibrations on a low flat background. The optical conductivity spectra were obtained after the Kramers-Kronig analysis of the data from Fig. 2(a), where the low frequency region was extrapolated using the Hagens-Rubens formula for the spectra above  $T_M$ , and a constant reflectivity was assumed below  $T_M$ . The result is shown on Fig. 2(b). Along the stack, the conductivity exhibits a broad asymmetric peak in the midinfrared region with the spectral weight extending over 10 000  $\text{cm}^{-1}$ , which is characteristic of a strongly correlated metal. The peak shape is distorted as well by an electron-molecular vibration (e-mv) resonance near 1340  $\text{cm}^{-1}$ , which is consistent with the slightly dimerized structure of the stack. Extrapolating the low-frequency side to  $\omega=0$  gives  $\sigma_0=50 \pm 10 \Omega^{-1} \text{cm}^{-1}$ , which is in good agreement with  $\sigma_{dc}=60 \Omega^{-1} \text{cm}^{-1}$ .<sup>9</sup> Two broad electronic peaks at  $16$  and  $20 \times 10^3 \text{cm}^{-1}$  for  $\text{PF}_6$ , and  $15$  and  $24 \times 10^3 \text{cm}^{-1}$  for  $\text{AsF}_6$  salt were identified as the intramolecular  $\pi \rightarrow \pi^*$  transitions of  $\text{EDO-TTF}^{+1}$  (later called as  $LE_1$ ) and  $\text{EDO-TTF}^0$  ( $LE_2$ ), respectively.

##### 2. Vibrational spectra

In organic molecules built on TTF skeleton, the frequencies of the  $\text{C}=\text{C}$  stretching modes are sufficiently sensitive to the molecular charge to allow them to be used for an accurate quantitative estimation of this charge. EDO-TTF has three  $\text{C}=\text{C}$  bonds, all of which become longer as the molecule acquires positive charge. In the descending order of frequencies we call them  $\nu_i^p$ , where  $i=\alpha, \beta$ , and  $\gamma$  denote stretching of  $\text{C}=\text{C}$  bonds in the EDO-ring, the TTF-ring, and the bridge, respectively, and  $\rho$  shows the molecular (site) charge. The modes were assigned based on the reported data of bis(ethylenedithio)-TTF (BEDT-TTF),<sup>12</sup> bis(ethylenedioxy)-TTF (BEDO-TTF),<sup>13</sup> and ethylenedioxyethylenedithio-TTF (EDOEDT-TTF).<sup>14</sup> Figure 3 shows  $\nu_i^p$  in the Raman spectra of the  $\text{AsF}_6$  salt at room

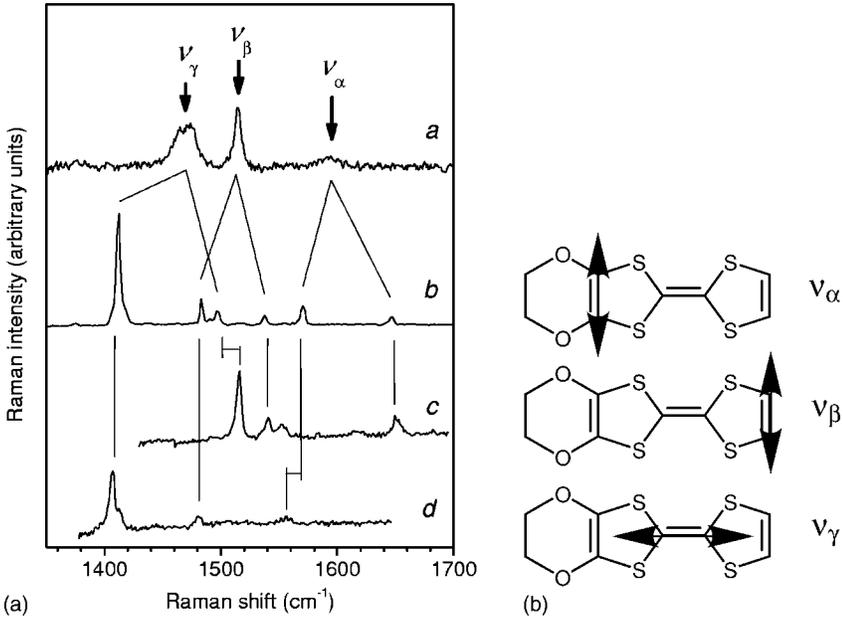


FIG. 3. C=C stretching modes  $\nu_i^\rho$  of EDO-TTF in the Raman spectra of (a) (EDO-TTF)<sub>2</sub>AsF<sub>6</sub> at 300 K; (b) (EDO-TTF)<sub>2</sub>AsF<sub>6</sub> at 6 K; (c) neutral EDO-TTF; and (d) (EDO-TTF)<sup>+</sup>IBr<sub>2</sub><sup>-</sup>.

temperature together with the reference spectra for  $\rho=0^{15}$  and  $+1$ . The observed frequencies of  $\nu_i^\rho$  are summarized in Table I. In the high-temperature phase a single peak for every mode was observed, and the site charges were estimated as (homogeneous)  $+0.5$ . However, the linewidths of  $\nu_i^\rho$  appear to be broadened, although the two sites in the unit cell are crystallographically equivalent to each other. The linewidths of  $\nu^\alpha$  and  $\nu^\gamma$  are significantly broader than that of  $\nu^\beta$ . The larger will be the mode splitting below  $T_{MI}$ , the broader is the linewidth above  $T_{MI}$ . This relation suggests that the line broadening is originated from the dynamical fluctuation of the site-charge density due to the correlation effect. We have simulated the linewidth based on the motional narrowing model taking two equivalent sites and hopping frequency in to account.<sup>16</sup> This simulation reproduced the linewidth of each band shown in Fig. 3(a) (for  $\nu^\gamma$ ,  $\nu^\beta$ , and  $\nu^\alpha$ , respec-

tively, the experimental linewidth, 21, 7, and 22 cm<sup>-1</sup>; the simulated linewidth, 16, 8, and 16 cm<sup>-1</sup>) using the same hopping energy of about 8 meV. This value is interpreted roughly as the hopping energy of the coherently or diffusively moving charge carrier. It should be noted that this hopping energy is more than one order of magnitude small compared with the transfer integrals, which is estimated from the low-temperature electronic spectrum in the next section. From the theoretical point of view, the optical conductivity of strongly correlated system consists of a Drude term and incoherent term.<sup>17</sup> The Drude weight depends upon the effective hopping energy of current carrier.<sup>18</sup> The small hopping energy of the charge carrier is consistent with the observation that the spectral weight of the incoherent part is dominant in the conductivity spectrum.

TABLE I. C=C stretching frequencies of EDO-TTF.

|  | $\nu_\alpha$ (cm <sup>-1</sup> ) | $\nu_\beta$ (cm <sup>-1</sup> ) | $\nu_\gamma$ (cm <sup>-1</sup> ) | Site charge | Symmetry    |
|--|----------------------------------|---------------------------------|----------------------------------|-------------|-------------|
| EDO-TTF  | 1650                             | 1538                            | 1510                             | 0           | (R)         |
|  | 1654                             |                                 | 1515                             |             | (IR)        |
| (EDO-TTF)IBr <sub>2</sub>                      | 1560                             | 1480                            | 1408                             | +1          | (R)         |
|  | 1540                             | 1475                            | 1370                             |             | (IR)        |
| (EDO-TTF) <sub>2</sub> PF <sub>6</sub> at RT   | ~1592                            | 1515                            | 1472                             | +0.5        | $A_g$       |
|  | 1579                             | 1512                            | ~1344                            |             | $A_u(E  a)$ |
| (EDO-TTF) <sub>2</sub> PF <sub>6</sub> at 6 K  | 1649                             | 1539                            | 1499                             | +0.04       | $A_g$       |
|  | 1648                             | 1539                            | 1496                             |             | $A_u$       |
|  | 1572                             | 1484                            | 1412                             | +0.96       | $A_g$       |
|  | 1564                             |                                 | 1383                             |             | $A_u$       |
| (EDO-TTF) <sub>2</sub> AsF <sub>6</sub> at RT  | ~1593                            | 1515                            | 1469                             | +0.5        | $A_g$       |
| (EDO-TTF) <sub>2</sub> AsF <sub>6</sub> at 6 K | 1647                             | 1538                            | 1497                             | +0.04       | $A_g$       |
|  | 1647                             | 1538                            | 1495                             |             | $A_u$       |
|  | 1570                             | 1483                            | 1412                             | +0.96       | $A_g$       |
|  | 1563                             |                                 | 1382                             |             | $A_u$       |

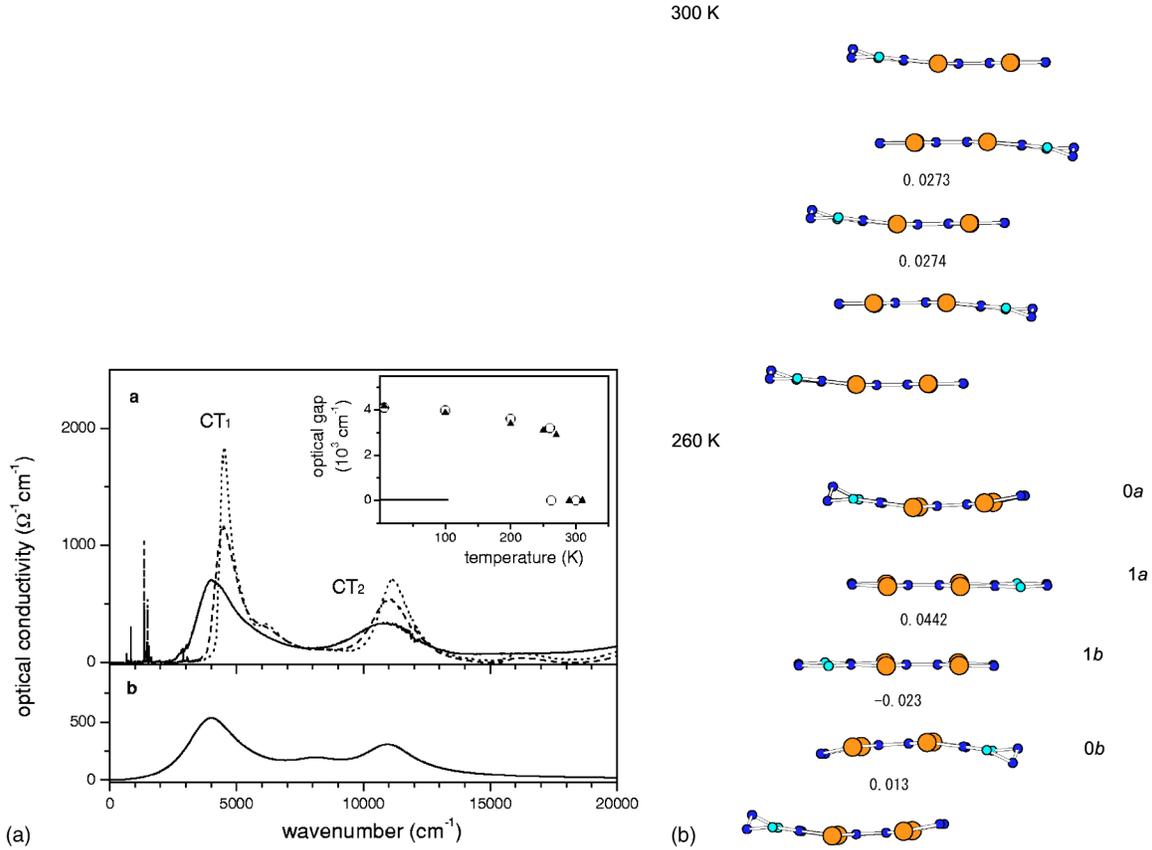


FIG. 4. (a) Stacking-axis optical conductivity spectra of  $(\text{EDO-TTF})_2\text{AsF}_6$  at 260 K (solid line), 100 K (dashed line), and 6 K (dotted line); (b) calculated spectrum (see text). The inset shows the temperature dependence of the optical gap (solid triangles and open circles are for  $\text{PF}_6$  and  $\text{AsF}_6$  salts, respectively). The stacking patterns and the overlap integrals for the  $\text{PF}_6$  salt above (top) and below (bottom)  $T_{\text{MI}}$  are given at the right margin.

## B. Low-temperature phase

### 1. Electronic spectra

As shown in Fig. 4, the low-temperature stack of EDO-TTF forms a tetramer with a small intertetramer overlap integral.<sup>9</sup> The stacking-axis optical conductivity below the phase transition is given in Fig. 4. The broad conductivity peak characteristic of the high-temperature phase [Fig. 2(b)] vanishes abruptly below  $T_{\text{MI}}$  replaced by two rather sharp electronic peaks at 4500 ( $CT_1$ ) and 11 150  $\text{cm}^{-1}$  ( $CT_2$ ), which further sharpen and blueshift at lower temperatures. This drastic spectral change indicates the opening of a wide charge gap below  $T_{\text{MI}}$ , replacing an incoherent feature that exists above  $T_{\text{MI}}$ .  $CT_1$  is the lowest electronic excitation in the insulating phase. Temperature dependence of the optical gap  $E_g$  determined from a linear extrapolation of the leading edge of  $CT_1$  is shown on the inset in Fig. 4. At 6 K  $E_g = 0.52$  eV ( $\text{PF}_6$ ) and 0.51 eV ( $\text{AsF}_6$ ) which is two times lower than the one found from the resistivity measurement (activation energy  $E_A = 0.52$  eV).<sup>9</sup> Such a difference between the optical and electrical gap is sometimes found for organic semiconductors and should be addressed to a proper theoretical evaluation.

The spectral weight of a particular electronic excitation can be obtained using a partial sum rule

$$\frac{m}{m^*} N_{\text{eff}}(\omega) = \frac{m}{32\pi N_c e^2} \int_0^\omega \sigma(\omega') d\omega', \quad (1)$$

where  $m^*$  is the effective mass of the carriers,  $m$  is a free electron mass,  $N_c$  is the carrier density,  $N_{\text{eff}}(\omega)$  is the effective number of the charge carriers taking part in the optical transitions in  $(0, \omega)$  frequency range,  $\sigma(\omega)$  is the optical conductivity, and the upper frequency limit  $\omega$  is chosen as to cover the region of the charge-transfer bands and avoid a contribution from  $LE_1$  and others above.  $(m/m^*)N_{\text{eff}}(\omega)$  is plotted in Fig. 5. At high temperature, the curve rises rapidly at low frequencies and saturates in the visible region to ca. 0.85 ( $\text{AsF}_6$  salt) and 0.80 ( $\text{PF}_6$  salt). Below  $T_{\text{MI}}$ , the total spectral weight does not change, while two distinct plateaus appear associated with the CT bands. The plateaus provide estimations for the oscillator strength  $(m/m^*)N_{\text{eff}}(\omega) = 0.50(CT_1) + 0.35(CT_2)$  for  $\text{AsF}_6$  salt, and  $0.48(CT_1) + 0.32(CT_2)$  for  $\text{PF}_6$  salt.

In order to properly assign  $CT_1$  and  $CT_2$ , we analyzed the electronic spectrum of  $(\text{EDO-TTF})_2\text{PF}_6$  using a Hubbard model for a symmetric tetramer.<sup>19</sup> The sites in the model are denoted as  $0a$ ,  $1a$ ,  $1b$ , and  $0b$  (see Fig. 4, right margin), and the parameters are  $t$ ,  $t_1$ ,  $\Delta$ , and  $U$  (where  $t$  and  $t_1$  are the transfer integrals between the sites  $0a$  and  $1a$  and between

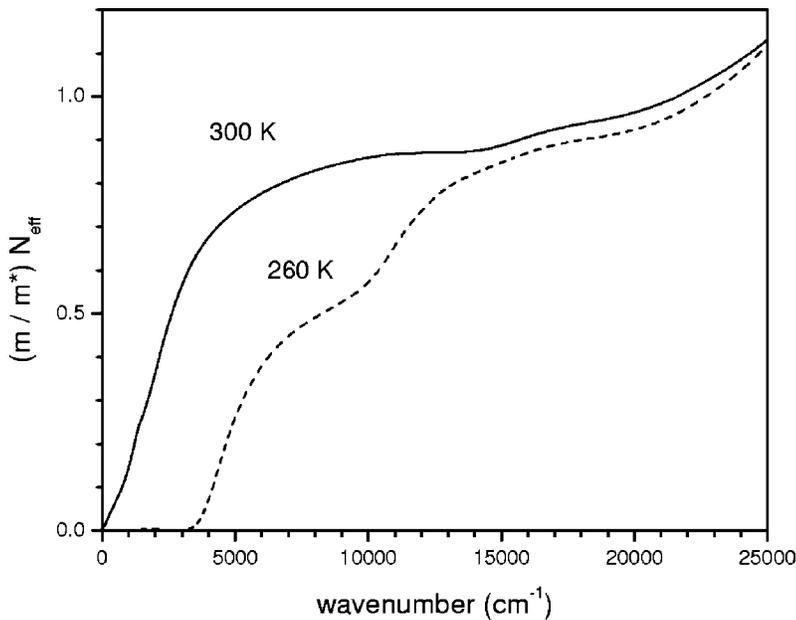


FIG. 5. The sum rule calculation for the  $(\text{EDO-TTF})_2\text{AsF}_6$  along the stacking axis at 300 K (solid line) and 260 K (dashed line).

the sites  $1a$  and  $1b$ ,  $\Delta$  and  $-\Delta$  are the site energies at the sites  $0a$  and  $1a$ , respectively). Although the model describes an isolated tetramer rather than an infinite tetramerized chain, we assume that, on condition of a small intertetramer overlap integral ( $0b-0a$ ), it can reproduce reasonably the general character of the electronic excitations. We searched for the optimal parameters to reproduce the excitation energies, oscillator strengths given earlier, and site charges (0.04 and 0.96), which will be given in the next section. The conductivity spectrum calculated using the optimal parameters ( $t=0.15$ ,  $t_1=0.28$ ,  $\Delta=0.24$ ,  $U=0.93$  eV) is drawn in Fig. 4(b). In this model, the singlet ground state consists of the electronic configurations of  $|0110\rangle$  (70%),  $|0200\rangle$  (16%), and  $|1010\rangle$  (9%) with the site-charge difference of 0.86. There are four optically allowed singlet excited states. The first, second, and third excited states respectively involve  $|1100\rangle$  (55%) and  $|1010\rangle$  (41%);  $|1010\rangle$  (55%),  $|1100\rangle$  (26%), and  $|0200\rangle$  (18%);  $|0200\rangle$  (78%), and  $|1100\rangle$  (16%). The excitation energies of  $CT_1$  and  $CT_2$  are therefore assigned to the electronic transitions to the first and third excited states, respectively. The spectral weight between 0 and  $10\,000\text{ cm}^{-1}$  is interpreted as the sum of the transitions to the first and second excited states, and that between  $10\,000$  and  $15\,000\text{ cm}^{-1}$  as the transition to the third excited state. It should be noted that in order to find a notable intensity of  $CT_2$  in the presence of (main)  $CT_1$ , normally, the band filling should be away from  $\frac{1}{4}(\frac{3}{4})$  and closer to  $\frac{1}{2}$ .<sup>20</sup> The fact that  $CT_2$  holds about 40% of the total spectral weight in the nominally  $\frac{3}{4}$ -filled  $(\text{EDO-TTF})_2X$  ( $X=\text{PF}_6$  and  $\text{AsF}_6$ ) is unique to this family and can be explained by a cooperation of the large site-charge difference and the type of BOW where the largest transfer integral connects two charge-rich sites. Therefore, this distribution of the spectral intensity can be regarded as a characteristic of the  $2k_F$  BCDW-II as opposed to the  $2k_F$  BCDW-I or various  $4k_F$  states. It was confirmed as well by our numerical calculation. The deformation of the molecule plays the most important role to stabilize the  $2k_F$  BCDW-II. As shown in Fig. 4, the deformation of the

molecule not only generates the site energy difference, but also enhances the overlap integral between the flat charge-rich molecules. This enhancement contributes to increase the kinetic energy gain between the charge-rich molecules, in other words, decrease  $V/2t_1$ .

## 2. Vibrational spectra

Each charge-sensitive band of the high-temperature phase [Fig. 2, curve (a)] splits into two bands below  $T_{\text{MI}}$  [curve (b)]. The data in Fig. 3 agree entirely with the factor group analysis. Above  $T_{\text{MI}}$ , six  $v_i^p$  modes of two  $\text{EDO-TTF}^{+0.5}$  are split into  $(3A_g+3A_u; A_g)$ : Raman active,  $A_u$ : infrared active). Below  $T_{\text{MI}}$ , 12  $\text{C}=\text{C}$  modes are split into  $(3A_g+3A_u)$  of the charge-rich molecules, and  $(3A_g+3A_u)$  of the charge-poor ones.<sup>21</sup> As will be shown later from the calculation of the vibronic modes in a symmetric tetramer, the least perturbed modes are  $A_g$  ones. Using the splitting between the charge-poor and charge-rich  $A_g$  branches and taking the weighted average of all three ( $v_i^p$ ) modes, we estimate the site charges below  $T_{\text{MI}}$  as  $\rho=+0.04$  on 0 site, and  $\rho=+0.96$  on 1 site ( $\pm 0.04$ ).

Intensities of the  $A_g$  modes of 0 and 1 site could be enhanced separately using different excitation wavelengths. Figure 6 shows three Raman spectra taken with different lasers, where the excitation wave number of the corresponding laser in relation to the absorption spectra of  $\text{EDO-TTF}^0$  and  $\text{EDO-TTF}^{+1}$  is given in the inset. The frequency of the  $\text{Ar}^+$  laser [curve (a)] is in the region of both  $LE_2$  ( $\text{EDO-TTF}^0$ ) and the second  $\pi \rightarrow \pi^*$  transition  $\text{EDO-TTF}^{+1}$ , so the vibrations of both 0 and 1 sites are enhanced. The frequency of the He-Ne laser is resonant with  $LE_1$  and the corresponding spectrum [curve (b)] shows mainly the modes of the site 1. Because the (intramolecular)  $\pi \rightarrow \pi^*$  transitions are polarized in the molecular plane, this is also the direction of the largest Raman intensity in the earlier cases. In contrast, the frequency of the LD laser [curve (c)] is far from any intramolecular electronic transition but close to the (intermolecular)  $CT_2$  energy. This produces a resonance effect with an

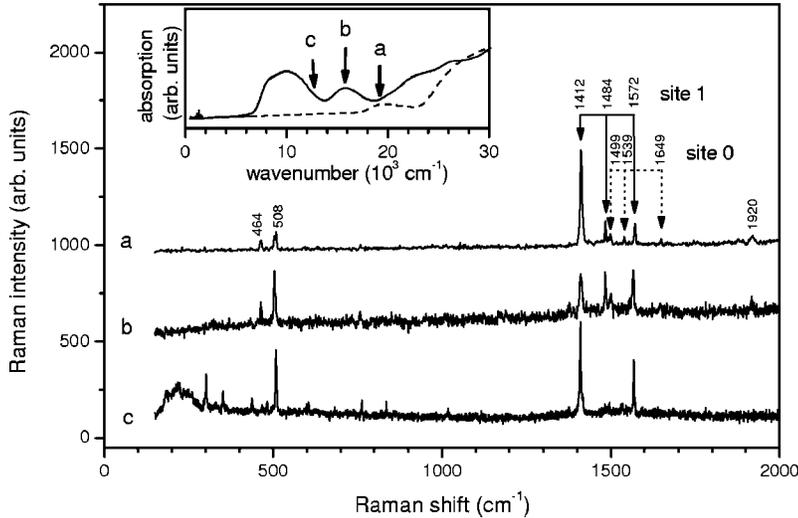


FIG. 6. Raman spectra of  $(\text{EDO-TTF})_2\text{AsF}_6$  at 6 K taken with different excitation wavelengths, which are pointed out in the inset with respect to the absorption spectra of  $(\text{EDO-TTF})^+\text{IBr}_2^-$  (solid line) and neutral EDO-TTF (dashed line). (a)  $\text{Ar}^+$  laser,  $E \perp$  stack; (b) He-Ne laser,  $E \perp$  stack; (c) LD laser,  $E \parallel$  stack.

unusual polarization dependence. While the spectrum polarized in the molecular plane is very weak (not shown), when the polarization is changed to the molecular stack one can observe a strong enhancement of the intensity of some selected modes, among them  $\nu_\alpha^{+0.96}$  ( $\sim 10$  times as compared to the in-plane polarization under the same experimental conditions) and  $\nu_\gamma^{+0.96}$  ( $\sim 50$  times). At the same time, the frequencies are not perturbed.

Next, let us examine the e-mv coupling in the IR spectra ( $A_u$  modes). Below  $T_{\text{MI}}$  the stacking-axis optical conductivity displays a number of sharp peaks below  $2000 \text{ cm}^{-1}$  [Fig. 4(a)], attributed to the e-mv. It is known that for TTF-based donors the bridge C=C bond has the largest e-mv coupling constant.<sup>22</sup> To discuss the e-mv effect in detail, we show in Fig. 7 the six ( $\nu_i^0$ )  $A_g$  modes polarized in the molecular plane [curve (a)] and six  $A_u$  modes found in the optical conductivity spectrum along the stack [curve (b)], both below 6 K. It is seen that the  $A_u$  modes of the 0 site are almost degenerate with the corresponding  $A_g$  counterparts. On the contrary,  $\nu_\alpha^{+0.96}$  ( $A_u$ ) and  $\nu_\gamma^{+0.96}$  ( $A_u$ ) are redshifted from the position of  $A_g$  components by  $-7$  and  $-30 \text{ cm}^{-1}$ , respectively [ $\nu_\beta^{+0.96}$  ( $A_u$ ) was too weak to be safely identified].

In order to understand the effect of the  $2k_F$  BCDW-II electronic structure on the vibrational spectrum, we have calculated the  $A_g$  and  $A_u$  vibronic modes of the symmetric tetramer<sup>19</sup> introduced earlier, using vibronic adiabatic Mulliken theory.<sup>23</sup> Figure 8 shows the site-charge ( $\rho$  at  $0a$  and  $0b$ ) dependence of the frequencies of  $A_g$  (solid lines) and  $A_u$  (broken lines) vibronic modes of  $\nu_\gamma$  (taken as an example), and unperturbed (dotted lines) modes.<sup>24</sup> The effect of the intratetramer interactions is most significant when the charge separation is small. The shifts of the frequencies of  $A_u$  and  $A_g$  branches are large, and the higher mode is almost charge independent in a wide range of the site charge. The deviation from the dashed straight line implies that the estimation of the site charge from the frequency shift of the  $A_g$  vibronic bands is unreliable except the region of  $\rho < 0.1$  and  $\rho > 0.9$ , if the e-mv coupling constant is large. For the  $(\text{EDO-TTF})_2X$  ( $X = \text{PF}_6$  and  $\text{AsF}_6$ ), the frequencies of the four modes are given at  $\rho = 0.04$  shown by the vertical line. This

calculation explains the almost degenerate feature between the  $A_g$  and  $A_u$  modes of charge-poor site and the downshift of the  $A_u$  mode at the charge-rich site. We roughly estimated the coupling constants as  $g_\alpha \sim 0.04$ ,  $g_\beta < 0.01$ , and  $g_\gamma \sim 0.08 \text{ eV}$  to reproduce the splitting between the  $A_g$  and  $A_u$  modes at the charge-rich site. The downshift at charge-rich sites comes from the localized 11 pair at sites 1a and 1b.

#### IV. CONCLUSION

In conclusion, we measured electronic and vibrational spectra of  $(\text{EDO-TTF})_2X$  ( $X = \text{PF}_6$  and  $\text{AsF}_6$ ). Our analysis shows the following things.

(1) The high-temperature metallic phase of  $(\text{EDO-TTF})_2X$  ( $X = \text{PF}_6$  and  $\text{AsF}_6$ ) can be described as a Q1D weak  $4k_F$  BOW with a homogeneous ( $+0.5$ ) charge on each site. The broad width of the Raman bands suggest a nearly localized nature of charge. The e-mv interaction along the stack is evident.

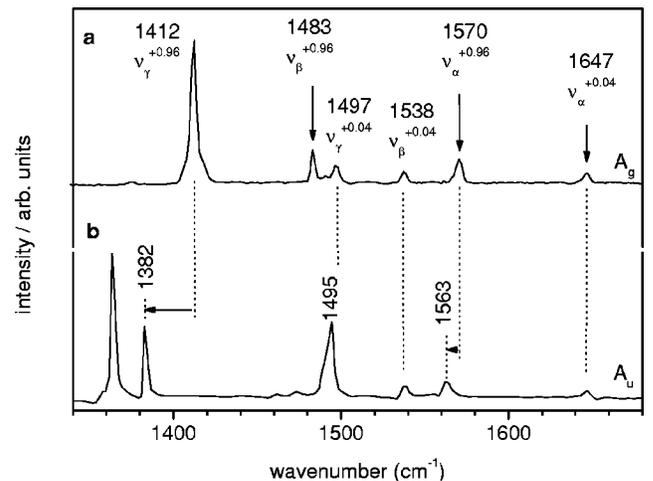


FIG. 7.  $\nu_i^0$  modes of  $(\text{EDO-TTF})_2\text{AsF}_6$  below 6 K: (a)  $A_g$  modes in the Raman spectra and (b)  $A_u$  modes in the optical conductivity spectrum for  $E \parallel$  stack. Arrows show softening of the  $A_u$  modes due to the e-mv coupling.

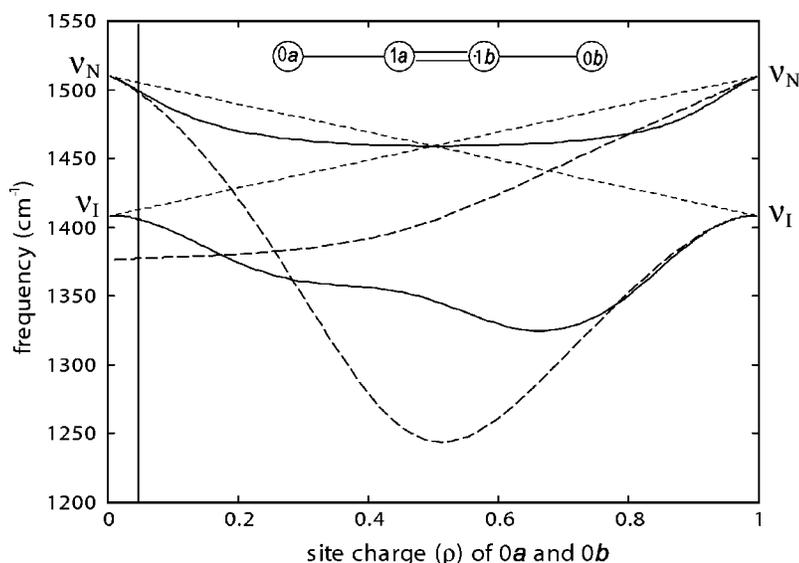


FIG. 8. Site-charge [ $\rho$  at  $0a$  and  $0b$  and  $(1-\rho)$  at  $1a$  and  $1b$ ] dependence of  $2A_g$  (charge-rich and charge-poor branches plotted by two solid lines) and  $2A_u$  (charge-rich and charge-poor branches drawn by two broken lines) vibronic modes and unperturbed (dotted lines) modes in a symmetric tetramer with  $t=0.15$ ,  $t_1=0.28$ ,  $\Delta=0.24$ ,  $U=0.93$ , and  $g=0.08$  eV.  $\nu_N$  and  $\nu_I$  represent the frequencies of neutral and cationic molecules, respectively.

(2) The low-temperature insulating phase is a  $2k_F$  BCDW-II with the large site charge difference ( $2\delta \sim 0.9$ ) and a large bond order amplitude. Because the charge density is localized on the central 11 pair, the electronic spectra manifest a strong  $CT_2$  band (mainly  $|0110\rangle \rightarrow |0200\rangle$ ) and the  $\nu_\alpha^{+0.96}$  and  $\nu_\gamma^{+0.96}$  intramolecular C=C vibrations are strongly coupled to  $CT_2$ .

(3) It is generally agreed that 0110 periodicity requires a large  $U$  to prevent the double occupancy, and a sufficiently small  $V$  to allow two neighboring occupied sites. Most calculations devoted to this problem examine the  $2k_F$  BCDW-I while no study up to date was able to reproduce the  $2k_F$  BCDW-II with such a large charge and bond order in the

framework of the purely electronic extended Hubbard model (except when next-neighbor  $V_2$ , etc., are included). It is clear that in organic CTS the individual properties of the molecule constituting a “site” should not be neglected. This includes the flexibility of EDO-TTF in the studied complexes, which serves as a means of interchange of two processes: variation of the site charge leading to the molecular deformation (and vice versa), and adjustment of the overlap integrals to the molecular geometry. To include such kind of interplay between the molecular charge, molecular deformation, and intermolecular  $\pi$ - $\pi$  overlap, both the Peierls-type<sup>7</sup> and Holstein-type<sup>25</sup> electron-phonon interactions should be included in the extended Hubbard model in the future studies.

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