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Modelling κ -Phase Organic Conductors

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Abstract. — κ -phase organic conductors with bidimensional layers of orthogonal molecular dimers are modelled by tetramers and hexamers of appropriate geometry. The complex conductivity is calculated within the Hubbard model including the electron-intramolecular vibration coupling. The polarized optical conductivity data of two κ -phase charge-transfer salts of *bis*-(ethylenedithio)-tetrathiafulvalene: κ -(BEDT-TTF)₂[Hg(SCN)₂Br] and κ -(BEDT-TTF)₂[Hg(SCN)Cl₂], are discussed.

1. Introduction

A rapidly growing family of organic conductors includes ion-radical salts with a variety of crystal structures, which strongly influence their physical properties [1]. The so called “ κ -phase” with bidimensional layers of orthogonal dimers is of special interest, because several of these salts are superconductors with a transition temperature above 10 K at ambient pressure [2]. But even salts of the same donor *bis*-(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) with a common pattern of κ -phase may have rather different electrical properties: the κ -(BEDT-TTF)₂Cu(NCS)₂ and κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X = Br, Br_{0.5}Cl_{0.5}) are superconductors [2, 3] while the κ -(BEDT-TTF)₂[Hg(SCN)_{3-n}X_n] (X = Cl, Br, n = 1, 2) become dielectric at low temperature [4]. Recently, we have undertaken a comparative spectroscopic study [5–7] of some of the κ -phase compounds in order to evaluate the role of electron-molecular vibration (EMV) coupling, which is believed [8] to be responsible for the superconductivity phenomenon in organic materials.

Two alternative approaches are mainly used currently for describing the optical properties of low-dimensional molecular crystals [9]: “phase phonon” theory where charge carriers are supposed to be delocalized and the cluster model where the optical properties are calculated as a superposition of the optical responses of isolated clusters of finite size. The former theory seems to be more appropriate for describing highly conducting materials, but a serious disadvantage of this model is that it is a “one-electron” theory, where electronic correlation can be taken into account only in the effective mass approximation. At the same time low-dimensional molecular crystals are generally classified as strongly-correlated systems,

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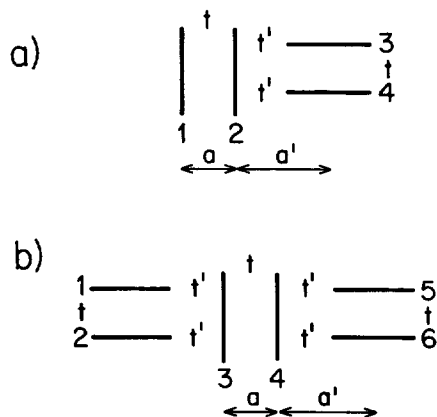


Fig. 1. — Modelling κ -phase compound as the tetramer (a) and the hexamer (b).

because the Coulomb on-site repulsion energy of two radical electrons on the same molecule, U , is known to be of the order of the bandwidth, calculated in a tight-binding approximation. In references [5–7], we used the “phase phonon” theory to interpret our data and found that the salts κ -(BEDT-TTF)₂[Hg(SCN)₂Br] and κ -(BEDT-TTF)₂[Hg(SCN)Cl₂] were characterized by a smaller oscillator strength of the conduction electron transitions and plasma frequency ω_p , compared to the ones in superconductors κ -(BEDT-TTF)₂Cu(NCS)₂ [5] and κ -(BEDT-TTF)₂Cu[N(CN)₂]Br_{0.5}Cl_{0.5} [6]. This observation indicates that electronic correlations are more important in the former salts. Also it has been noted that the optical response of the κ -phase compounds depends on the polarization of the incident light with respect to the crystallographic axes [10]. In the cluster approach, one can model the actual orientation of molecules by a suitable choice of transfer integrals and consider electronic interactions in an explicit way, usually employing the Hubbard Hamiltonian [11] for the purpose. Unfortunately, as cluster dimensions increase, the exact solution of the Hubbard model becomes mathematically difficult.

In this paper, we consider a model of κ -phase as two orthogonal dimers for arbitrary values of the Hubbard model parameters.

2. Theoretical Model

As noted in the Introduction, the crystalline structure of κ -phase organic compounds presents weakly interacting layers composed of orthogonal dimers of donor molecules (*e.g.* BEDT-TTF). Inside each layer, short interdimer (S · · S) distances are observed indicating a rather strong interaction between dimers leading to a quasi-bidimensional electronic system. Within the cluster approach, a simple model for a κ -phase layer is just two orthogonal dimers shown in Figure 1a. Short S · · S contacts are represented by transfer integrals t' . The ratio of t' to the intradimer transfer integral t is a convenient parameter to account for interactions of our dimer with its neighbours. The hexamer shown in Figure 1b will serve to test the convergence of calculated results as a cluster grows for different t'/t values.

Recently we have developed [12] a general formalism to describe the optical properties of molecular clusters with arbitrary geometry and equilibrium charge density distribution.

Applying these results to our model (see Fig. 1 for notation), we get the Hamiltonian

$$H = H_e + H_v + \sum_{\alpha,i} g_{\alpha i} n_i Q_{\alpha i} - \mathbf{p} \cdot \mathbf{E} \quad (1)$$

The first two terms in equation (1) describe, respectively, the radical electrons and the intramolecular vibrations of each monomer in the absence of vibronic coupling. Linear EMV coupling is described by the third term where $g_{\alpha i}$ denotes the EMV coupling constant of the electron density, n_i , on the site i to the dimensionless coordinate $Q_{\alpha i}$ of the vibrational mode α of the same molecule. The last term gives the interaction energy of an external electric field \mathbf{E} with the induced dipole moment \mathbf{p} of the tetramer.

The complex conductivity has the form [12]

$$\sigma(\omega) = -i\omega N_t \left(\mathbf{d}, [\mathbf{I} - \mathbf{X} \cdot \text{diag } \mathbf{D}]^{-1} \cdot \mathbf{X} \cdot \mathbf{d} \right), \quad (2)$$

where N_t is the number of tetramers per unit volume, \mathbf{d} denotes the vector with components $(e(a + a'), ea', 0, 0)$, $\text{diag } \mathbf{D}$ is the diagonal matrix of

$$D_i(\omega) = \sum_{\alpha} \frac{2g_{\alpha i}^2 \omega_{\alpha i}}{\omega_{\alpha i}^2 - \omega^2 - i\omega\gamma_{\alpha i}}, \quad (3)$$

\mathbf{I} is the unitary matrix and \mathbf{X} denotes the matrix of electronic polarizabilities with the elements

$$\chi_{ij}(\omega) = \sum_{\beta} \frac{\langle 1 | n_i | \beta \rangle \langle \beta | n_j | 1 \rangle 2\omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\Gamma_{\beta}} = \chi_{ji}(\omega). \quad (4)$$

In equation (3), $\omega_{\alpha i}$ and $\gamma_{\alpha i}$ are, respectively, frequency and damping factor for the α -th totally symmetric mode of intramolecular vibration. In equation (4), Γ_{β} denotes the phenomenological natural width of the originally uncoupled charge transfer excitation with the energy $\omega_{\beta 1} = E_{\beta} - E_1$; E_{β} and $|\beta\rangle$ are the exact eigenvalues and eigenfunctions of the electronic Hamiltonian H_e in equation (1). $\beta = 1$ labels the ground state.

The electronic Hamiltonian H_e in equation (1) is taken in the Hubbard approximation

$$H_e = \frac{U}{2} \sum_{i,\sigma} n_{i,\sigma} n_{i-\sigma} - t \sum_{\sigma} (c_{1,\sigma}^{\dagger} c_{2,\sigma} + c_{3,\sigma}^{\dagger} c_{4,\sigma} + \text{h.c.}) - t' \sum_{\sigma} (c_{2,\sigma}^{\dagger} c_{3,\sigma} + c_{2,\sigma}^{\dagger} c_{4,\sigma} + \text{h.c.}), \quad (5)$$

where $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) denotes the operator of the hole creation (destruction) on the site i with the spin projection σ , $n_{i,\sigma} = c_{i,\sigma}^{\dagger} c_{i,\sigma}$.

Eigenvalues E_{β} and eigenfunctions $|\beta\rangle$ of the Hamiltonian (5) may be found by using a series

$$|\beta\rangle = \sum_k a_{\beta k} |\vec{k}\rangle \quad (6)$$

over the basis states $|\vec{k}\rangle$, which in the case of two holes per tetramer includes 28 possible distributions. After numerical solution of this problem, we calculate the electronic polarizabilities (4) and finally the complex conductivity given by equation (2). Figure 2 presents the real part of the conductivity calculated for three values of U . We notice that as U increases the optical conductivity spectrum looks more and more as the one calculated for the isolated dimer model. Of course it is not surprising that electronic correlations favour effective charge localization: in

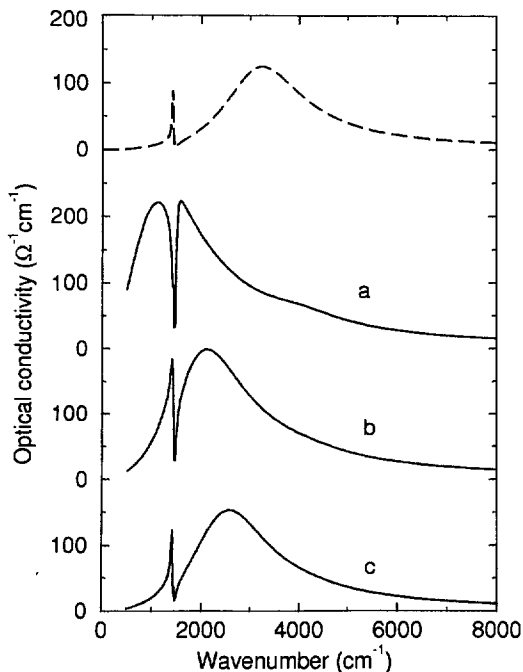


Fig. 2. — Calculated optical conductivity for the tetramer model for the following parameters: $t = 0.2$ eV; $t'/t = 0.4$; $U/4t = 0$ (a), 1 (b), 1000 (c); $\Gamma = 2000$ cm^{-1} ; $\omega_\alpha = 1455$ cm^{-1} ; $g_\alpha = 300$ cm^{-1} , $\gamma_\alpha = 10$ cm^{-1} ; $a = 3.4$ Å, $a' = 3.58$ Å, $N_t = 5.5 \times 10^{20}$ cm^{-3} . The case of isolated dimer ($t' = 0$) is shown by the dashed line.

the case of large U we can imagine our system as a Wigner lattice of molecular dimers with one charge carrier per dimer. It follows from Figure 2, that the curve (c) for $U/t = 4000$ is much closer to the curve (b) corresponding to $U/t = 4$ (typical value for low-dimensional ion-radical salts) than to the curve (a) calculated with the neglect of electronic correlations as is assumed in the "phase phonon" theory. Finite values of U allow high energy transitions resulting in two charges with opposite spins per site, but the coupling of these transitions to intramolecular vibrations is much weaker compared to the low energy excitations permitted in systems with less than half-filled band occupation (κ -phase compounds have a quarter-filled band). We conclude that electronic correlations are important and should be taken into account. Figure 3 presents the calculated spectra for dimer, tetramer and hexamer for $t'/t = 0.2$ and Figure 4 shows the results for $t'/t = 0.4$. It may be seen that for a relatively small value of $t'/t = 0.2$ the resulting spectra seems to converge well with the increase of the size of the cluster, while for $t'/t = 0.4$ the convergence is poor and we would expect that the cluster approach will not be suitable in this case.

3. Discussion of the Experimental Data

It is convenient to consider κ -(BEDT-TTF)₂[Hg(SCN)Cl₂] and κ -(BEDT-TTF)₂[Hg(SCN)₂Br] salts for a discussion of our theoretical results. The crystal structure of both compounds [4,13] is formed by (parallel to bc plane) bidimensional sheets of cation-radicals (BEDT-TTF), which alternate along the a axis with layers of polymer anions. The cation-radical sheets consist of

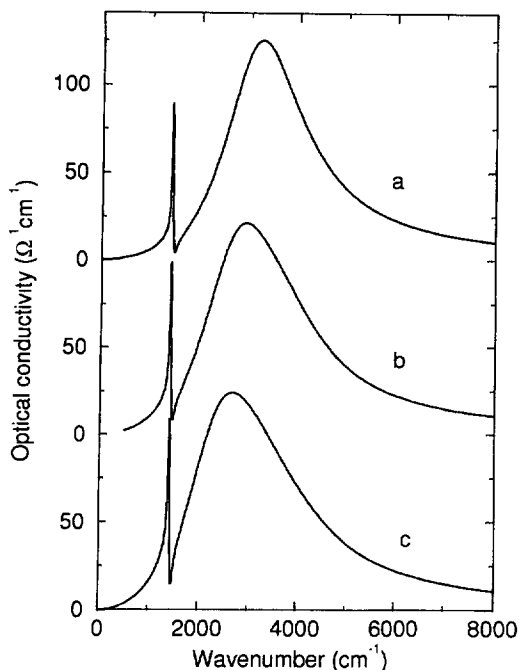


Fig. 3. — Calculated optical conductivity in the case $U/4t = 1000$ of an isolated dimer (a), tetramer (b) and hexamer (c) for $t'/t = 0.2$; the rest of parameters are the same as in Figure 2.

$(\text{BEDT-TTF})_2^+$ dimers, packed in a characteristic κ -phase manner. The interplanar spacings between BEDT-TTF cation-radicals inside the dimer are 3.53 \AA for the salt with Br and 3.59 \AA for the salt with Cl_2 . Also, in the former compound, the dimer contains two shortened (compared to the Van-der-Waals values) intermolecular S...S contacts, which are absent in the salt with Cl_2 , so the intradimer transfer integral t is smaller in the latter case. The cation-radicals of the neighboring dimers have some shortened S...S contacts. The chains of polymer anions in the two compounds are oriented along the c axis.

The experimental room temperature optical conductivity spectra, $\sigma_{\text{exp}}(\omega)$, of κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})_2\text{Br}]$ and κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ in the range $1000 - 4500 \text{ cm}^{-1}$ for polarization $\mathbf{E} \parallel b$ corresponding to the most intense charge-transfer band are shown in Figures 5a and 5b, respectively. The $\sigma_{\text{exp}}(\omega)$ spectra were obtained by Kramers-Kronig transformation of the relevant reflectance spectra as described in reference [7]. The $\sigma_{\text{exp}}(\omega)$ spectra of both compounds exhibit a broad peak at around $2400 - 2800 \text{ cm}^{-1}$ clearly demonstrating that the electronic system in these organic metals does not follow the Drude behavior. The sharp vibrational features observed on the low frequency slope of the broad peak is due to the electron-molecular vibrational (EMV) coupling. A similar but more intense electronic peak is observed in $\sigma_{\text{exp}}(\omega)$ of superconducting κ -salts [5, 6, 14] and has been described by us [5, 6] in the frame of the "phase phonons" theory as electron interband transitions across the energy gap 2Δ . The same analysis of $\sigma_{\text{exp}}(\omega)$ for conductors κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ and κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})_2\text{Br}]$ gives values of plasma frequency ω_p smaller than in the superconductors [5, 6, 14], and consequently larger optical effective mass m^* of charge carriers ($\omega_p^2 = 4\pi N e^2 / m^*$, where N is the charge carriers concentration assumed to be equal to the

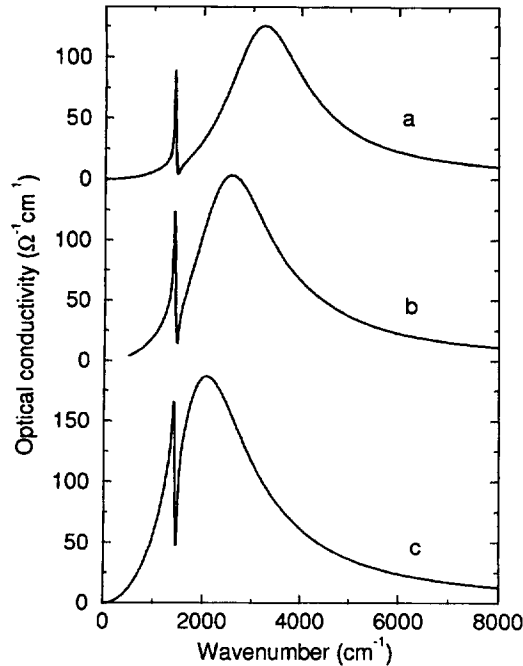


Fig. 4. — Calculated optical conductivity in the case $U/4t = 1000$ of an isolated dimer (a), tetramer (b) and hexamer (c) for $t'/t = 0.4$; the rest of parameters are the same as in Figure 2.

$(\text{BEDT-TTF})_2^+$ dimer concentration, $N_d = 1.1 \times 10^{21} \text{ cm}^{-3}$). We have obtained from this relation $m^* = 8.4 m_0$ ($\parallel b$), for the conductor $\kappa\text{-(BEDT-TTF)}_2[\text{Hg}(\text{SCN})\text{Cl}_2]$, and $m^* = 2.6 m_0$ for the superconductor $\kappa\text{-(BEDT-TTF)}_2\text{Cu}(\text{NCS})_2$ (the latter value found on the basis of the data from Ref. [5] for the corresponding polarization). We can imagine that so large a value of m^* for the conductor as compared to m^* for the superconductor might be due to the stronger EMV coupling and the formation of the molecular polarons. Nevertheless this assumption is not supported by the values of the sum of the dimensionless EMV coupling constants $\lambda = 0.18$ [7] and 0.25 [5] obtained for $\kappa\text{-(BEDT-TTF)}_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ and $\kappa\text{-(BEDT-TTF)}_2\text{Cu}(\text{NCS})_2$, respectively. Therefore one cannot explain the reason for the large value of m^* within the frame work of the “one-electron” band theory for the investigated compounds. The qualitative comparison of the experimental spectra $\sigma_{\text{exp}}(\omega)$ of $\kappa\text{-(BEDT-TTF)}_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ and $\kappa\text{-(BEDT-TTF)}_2[\text{Hg}(\text{SCN})_2\text{Br}]$ with the spectra $\sigma_{\text{theor}}(\omega)$ calculated on the basis of the theory developed in the preceding section (see Figs. 2 to 4) shows that this theory describes the main features of the experimental spectra rather well. Among all spectra calculated for different parameter values, $\sigma_{\text{exp}}(\omega)$ is much closer (by the values of $\sigma_{\text{exp}}(\omega)$, by the location of the electronic band, as well as by the relative location of the electronic band and EMV coupling feature) to the $\sigma_{\text{theor}}(\omega)$ shown in Figure 2c for the tetramer case of the Coulomb on-site repulsion energy $U = 4000 t$ and $t = 0.2 \text{ eV}$; $t'/t = 0.4$; the other parameters are given in the caption to Figure 2. As it was noted above, this case is close to the one of the isolated dimer, and hence we can indeed imagine our system as a Wigner lattice of molecular dimers with one charge carrier per dimer.

Figures 5a and 5b show that the values of $\sigma_{\text{exp}}(\omega)$, including the intensity of the electronic band, for $\kappa\text{-(BEDT-TTF)}_2[\text{Hg}(\text{SCN})_2\text{Br}]$ are nearly twice greater than the ones for

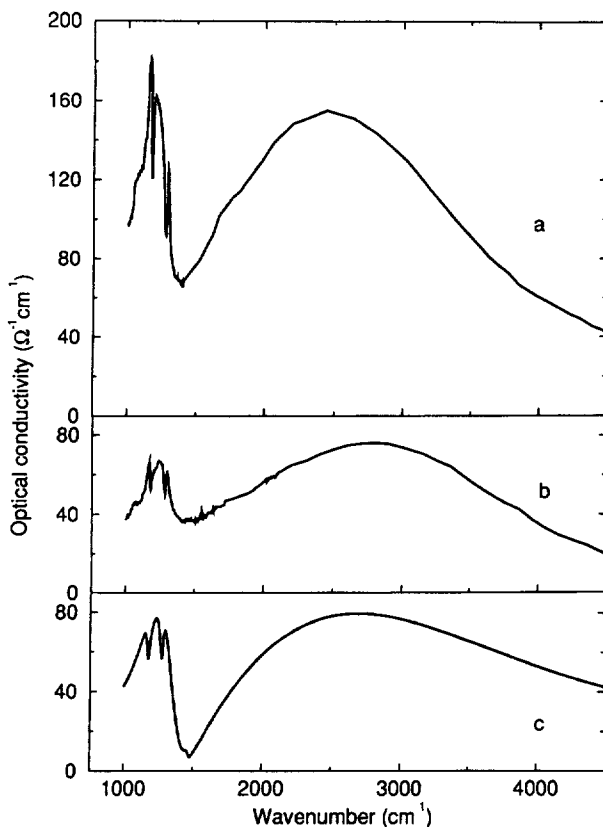


Fig. 5. — Experimental optical conductivity spectra of (a) $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})_2\text{Br}]$ and (b) $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ single crystals for $E \parallel b$ polarization; (c) calculated spectrum for the tetramer model ($U/4t = 1000$) with $t = 0.17$ eV, $t'/t = 0.2$, $\Gamma = 3000$ cm^{-1} , $N_t = 5.5 \times 10^{20}$ cm^{-3} , $a = 3.59$ \AA , $a' = 3.6$ \AA and three vibrational modes discussed in the text.

κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$. We would expect this behavior as a manifestation of the stronger intra- and interdimer interactions (larger transfer integrals t and t') for the former salt. Such an interpretation of the difference between the optical conductivities of the two salts is supported by the crystallographic data. Indeed, for the κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})_2\text{Br}]$ salt: i) the interplanar spacing between the BEDT-TTF molecules inside the dimer is smaller; ii) there are two shortened S · S contacts in the dimer which are absent in the case of the salt with Cl; and iii) each cation-radical BEDT-TTF has 8 shortened S · S contacts, whereas in the structure of the κ - $(\text{BEDT-TTF})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ salt there are 7 or 5 (for the crystallographically different BEDT-TTF molecules) such contacts. As follows from our calculations (see Figs. 3 and 4), the increase of t' leads to the shift of the electronic charge-transfer band to lower wavenumbers and a significant growth of its intensity is predicted.

Figure 5c presents the conductivity spectrum calculated according to the theory developed in the preceding section in the case of $U/t = 4000$. In this calculation, we employed three vibrational modes at 1468, 1274 and 1174 cm^{-1} with the EMV coupling constants 650, 80 and 70 cm^{-1} , respectively, and the damping factor $\gamma_\alpha = 20$ cm^{-1} for all three modes. The wavenumbers for these vibrations were determined (also for $\text{BEDT-TTF}^{+0.5}$) by Eldridge *et*

al. via the careful examination [15] of the infrared and Raman spectra for different isotopes of BEDT-TTF. There is a general agreement to assign the 1468 and 1276 cm^{-1} modes to the totally symmetric a_g ones and their linear coupling to the electronic charge transfer raises no doubt. The matter is more complicated for the 1174 cm^{-1} mode. Eldridge *et al.* [15] has ascribed it to b_{3u} or b_{2g} vibration. According to the calculations of Meneghetti *et al.* [16] performed for BEDT-TTF assuming a lower D_2 symmetry, there is a symmetric vibration at 1195 cm^{-1} for the neutral BEDT-TTF. Our previous analysis of the spectra of some conducting salts of BEDT-TTF [5, 6] also pointed to the existence of the vibration around 1170 cm^{-1} linearly coupled to the electronic excitation. Thus, we believe that the indentations in the $\sigma_{\text{exp}}(\omega)$ spectra at 1179 cm^{-1} for κ -(BEDT-TTF)₂[Hg(SCN)Cl₂] and at 1177 cm^{-1} for κ -(BEDT-TTF)₂[Hg(SCN)₂Br] are a signature of the lowering of the symmetry of the BEDT-TTF in our crystals with respect to D_{2h} symmetry of the isolated molecule.

In conclusion, we have demonstrated the importance of electronic correlations in the optical properties of the κ -phase molecular conductors. A more detailed quantitative analysis will require calculations of the transfer integrals t and t' for different crystallographic directions.

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