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Chapter 6

Vibrational and Electronic Structure, Electron-Electron and Electron-Phonon Interactions in Organic Conductors Investigated by Optical Spectroscopy

Andrzej Łapiński

Additional information is available at the end of the chapter

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Abstract

The physical properties of organic conductors formed by tetrathiafulvalene (TTF) derivatives have been discussed in this chapter. The results were obtained using spectroscopic methods including infrared (IR), Raman, and UV-Vis. The experimental data were supported by theoretical DFT and TD-DFT calculations. Special attention has been paid to the description of electronic and vibrational structures, electron-electron and electron-phonon interactions and determination of transport parameters.

Keywords: organic conductors, electron-electron and electron-phonon interactions, vibrational end electronic structures, infrared and Raman spectroscopy, DFT calculations

1. Introduction

Research on the development of organic metals and superconductors was stimulated by finding the first organic metal—charge-transfer (CT) complex composed of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) [1–2] and by the discovery of superconductivity in CT salts of tetramethyltetraselenafulvalene (TMTSF) [3].
At the beginning, one of the most important targets in the field of molecular conductors was to search for high electrical conductivity systems [4]. Nowadays, the organic conductors based on the π-electron donors with various anions show a wealth of structural modifications and variety of physical properties [5–8]. They have attracted broad interest from the experimental and theoretical side because they exhibit a lot of fascinating phenomena related to the electronic states near the Fermi level and to relevant interactions. Superconductivity, metal-insulator phase transitions associated with charge-density wave (CDW) or spin-density wave (SDW) condensates and other cooperative states leading to antiferromagnetic-, charge- and dielectric order [9] are highly topical subjects in this field.

The great interest in this field has been sustained by chemists, who produced a huge number of π-electron donors for organic conductors. In many laboratories molecular conductors formed by the organic donors derived from TTF molecule are intensively studied. In designing π-donors, one can distinguish two main strategies. One has evolved mainly from: (a) the planarity for a facile formation of donor stacking, (b) the extension of π-conjugation for a decrease of on-site Coulombic repulsion involved in the formation of a dicationic species, and (c) the introduction of chalcogen atoms for an increase in dimensionality of the conduction pathway. The second approach to the donors design is totally different and it is based on the following requirements: (a) extension of the σ-bond framework which will lead to the lack of planarity, and (b) reduction of the π-electron system, which will increase the on-site Coulombic repulsion. The latter strategy was proposed by Yamada et al. [10]. They believe if donors are synthesized in accordance to these requirements, then it will be possible to produce superconductors using such donors.

In the last years, there is a great interest in the design and study of new molecular-based materials involving interplay between multiple physical properties. This kind of effects leads either to competition, coexistence or cooperation between the desired properties. A possible approach to reach this goal consists of building up hybrid solids formed by two molecular networks. Among these hybrid materials, the highly conducting CT salts formed by TTF-derived donors with various inorganic acceptors with permanent magnetic moments are intensively investigated [7, 11]. A characteristic feature of these salts is a spatial segregation of the organic cations and inorganic anions into alternating layers. These materials are of special interest, because their properties are determined by presence of both the system of delocalized π-electron in the fulvalene-derived stacks or layers and by the localized d-electrons of anions. These systems may exist independently or can interact, leading to new physical properties of the conducting material. One of the most interesting phenomena is a possibility of the
interaction between π-electrons within conducting layers and localized magnetic d-electrons in the counterions. Interaction between these two systems may lead to magnetically ordered conducting structures. The problem of magnetic order and electrical conductivity coexistence is highly topical [5, 8, 12, 13]. Magnetic interactions in these compounds are basically explained by the RKKY-type interaction mediated by the π-d coupling between the donor and the magnetic anions [14]. Moreover, Coulomb interactions between organic (cations) and inorganic (anions) subsystems may also lead to charge-ordering phenomena.

Coulomb interactions between electrons play an important role in organic conductors and have a considerable influence on optical, magnetic and conducting properties [15–17]. In many TTF based one- and two-dimensional organic conductors, the long-range Coulomb interactions are responsible for charge-ordering (CO) phenomena. In the field of CT salts, such behavior is of great interest among researches in many laboratories in the world [18–21]. In order to understand the nature of the charge localization Seo and Fukuyama [22] have performed theoretical calculations [23]. They have shown that a stripe-patterned charge ordering is stabilized in the insulating phase owing to intermolecular Coulomb repulsive forces. Moreover, Tajima et al. [24] have estimated the charge-ordering patterns in bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) salts on the base of the spectral analysis and the mean-field calculations.

The most convenient experimental method to investigate charge distribution in conducting layers [25] and effects of electron-molecular vibration coupling [26, 27] is the vibrational spectroscopy, therefore, study of the vibrational structure in many cases is crucial to understand physical properties of organic conductors. Electron-molecular vibration (EMV) coupling constant is one of the parameters in estimating of critical temperature ($T_c$) of organic superconductors, whereas the degree of ionicity, or average charge per molecule ($\rho$) is one of the fundamental parameters characterizing the physical properties of CT salts [28]. When Coulomb interaction prevails, the salts may undergo a charge-order instability. For the determination of $\rho$ in TTF derivatives, the C=C stretching modes of TTF framework are mainly taken into account. It was shown that such modes are very sensitive to the ionization degree of the molecule [20, 25, 27]. Nevertheless, one should keep in mind that C=C modes can be coupled to the electronic system [29, 30] and hence their positions in infrared (IR) spectra can shift towards lower frequencies [31] due to this coupling; the frequencies of molecular modes may exhibit a non-linear dependence on $\rho$ [30, 31].

The main purpose of the chapter is to present a description of physical properties of the organic conductors using experimental and theoretical methods of molecular spectroscopy. The special attention will be paid to the description of the electronic structure and determination of transport parameters. It will be shown that the most powerful method to investigate the charge ordering phenomena is the vibrational spectroscopy [32–34]. The results presented in this chapter were obtained by the spectroscopic methods including IR, Raman and UV-Vis. The experimental data were supported by theoretical DFT and TD-DFT calculations. It should be emphasized that the spectroscopic methods are very suitable tools for investigations of crystalline organic conductors because they provide a lot of information about electronic and vibrational structures, electron-electron and electron-phonon interactions [35].
2. Electronic structure investigated by optical spectroscopy

The electronic transitions that appear in the spectra of organic conductors recorded in IR, Vis and UV regions fall into two classes. On the one hand, those at high frequencies generally are a result of localized excitations, which are related to intramolecular transitions in which an electron is excited to a higher level on the same molecule. For characterization of such type of excitations, the time-dependent DFT method (TD-DFT) can be applied for organic conductors [36, 37]. The quantitative understanding of such molecular electronic excited states is important in many domains, including spectroscopy, photochemistry and the design of new optical materials.

On the other hand, transitions at lower frequencies that are along the stacking directions or along to the S⋯S short contacts correspond to CT excitations between the molecules. The frequencies and oscillator strengths of these CT bands are clearly related to the electronic structure of these compounds, but they are a consequence of three types of interactions among the unpaired electrons occupying the highest molecular orbital (HOMO): (i) the overlap of the electronic wave functions between sites, (ii) the Coulomb repulsion of two electrons on the same or adjacent sites, and (iii) interactions of the electron with phonons. Theoretical models for the electronic structure of organic conductors have shown the importance of one or the other of these interactions, e.g. tight-binding theory [38], the Hubbard model [39] and the Peierls model [40].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Charge-transfer bands</th>
<th>Intramolecular excitations</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>β&quot;-(ET) 4 NH 4[Cr(C 2 O 4) 3]⋅DMF</td>
<td>3400 10,200</td>
<td>16,300; 20,600; 30,800</td>
<td>[41]</td>
</tr>
<tr>
<td>β&quot;-(ET) 4 K[Cr(C 2 O 4) 3]⋅DMF</td>
<td>3620 9900</td>
<td>16,000; 21,000; 30,000</td>
<td>[42]</td>
</tr>
<tr>
<td>(ET) 3(MoO 4) 3(DMF) 3</td>
<td>2500 7300</td>
<td>11,200; 21,900; 35,400</td>
<td>[43]</td>
</tr>
<tr>
<td>κ-(ET) 4(Co(CN) 6)2[N(C 2 H 5) 4]⋅2H 2 O</td>
<td>2500, 3390 7200</td>
<td>10,000</td>
<td>[44]</td>
</tr>
<tr>
<td>τ-(P-S,S-DMEDT-TTF) 2(AuBr 2)(AuBr 2)y</td>
<td>1000, 5900 12,300</td>
<td>18,100; 22,900; 31,400; 33,500</td>
<td>[45]</td>
</tr>
<tr>
<td>β-(EDT-DTDSF) 4HgI 8</td>
<td>2800 11,700</td>
<td>26,000; 32,500; 40,000</td>
<td>[46]</td>
</tr>
<tr>
<td>(DOEO) 4HgBr 2-TCE</td>
<td>3600 11,500</td>
<td>19,500; 21,800; 28,400; 30,600; 32,000; 33,200</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Table 1. Electronic transitions (in cm⁻¹) observed for selected organic conductors.

The CT bands (denoted as A and B) and intramolecular excitations for selected organic conductors are shown in Table 1. The band A corresponds to a charge transfer of an electron from an occupied A⁺ to a neutral A⁰ molecule (A⁺+A⁰→A⁰+A⁺), whereas band B is associated with the CT from one A⁺ anion to a neighboring A⁺ (A⁺+A⁺→A⁺+A⁺). Within the Hubbard...
theory the position of A band relates to the Coulomb repulsion energy between two electrons on adjacent molecules \((V)\) and hopping integrals \((t)\). The position of B band depends on the value of the effective Coulomb interaction between two electrons reside on the same site. The energy of its transition is proportional to \((U-V)\); \(U\) and \(V\) are the Hubbard parameters for on-site and nearest-neighbor Coulomb repulsion, respectively. From the center position of B band and assuming \(V\) to be small, we can estimate the on-site Coulomb repulsion. Hubbard has also shown that the electron distribution in the ground state can be periodic and may be considered as a generalization of the classical Wigner lattice. The arrangement of the electrons within the period can be non-uniform and then it will give rise to electric fields that can distort the ordinary lattice; distortions can manifest themselves as satellites in the X-ray diffraction pattern. For example, the ground-state configuration for \(\varphi=1/2\) may be presented by two patterns: \(\ldots 101010\ldots\) and \(\ldots 11001100\ldots\) (0 indicates the neutral molecule and 1 corresponds to the monocation). Furthermore, it was also shown that the observed polarizations of optical transitions are consistent with the proposed model [39].

Considerable information about the electronic structure can also be extracted from the oscillator strength sum rule [47]. Such an approach is used very often for organic conductors [41, 42, 46, 48, 49]. The effective number of electrons \((N_{\text{eff}})\) participating in optical transitions for energies less than \(\hbar \omega\) is given by

\[
\left[ \frac{m_0}{m_{\text{eff}}} \right] N_{\text{eff}}(\omega) = \frac{m_0}{32\pi N_e e^2} \int \sigma(\omega') d\omega' \tag{1}
\]

where \(m_{\text{eff}}\) is the effective mass of the carriers; \(m_0\) means the electronic mass; \(N_e\) is the number of molecules per unit volume and \(\sigma\) means optical conductivity.

In order to analyze the electronic dispersion for organic metals and semiconductors the least-squares fits to the experimental data of the reflectance calculated from the Drude and Drude-Lorentz dielectric functions can be performed [41–43, 45, 46, 48, 50, 51]. The Drude model is used for describing the intraband transitions of the free charge carriers, whereas interband transitions can be investigated using the Lorentz model. Within the Drude-Lorentz model the complex dielectric constant can be written as [47]:

\[
\varepsilon(\omega) = \varepsilon_{\text{core}} - \frac{\omega_p^2}{\omega(\omega+i\Gamma)} + \frac{\Omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{2}
\]

where \(\omega_p\) is the plasma frequency of the free charge carries, \(\Gamma\) the relaxation constant of the free charge carries \((\Gamma=1/\tau)\), \(\varepsilon_{\text{core}}\) represents all higher frequency contributions to the dielectric function, \(\Omega_p\), \(\omega_0\) and \(\gamma\) are the oscillator strength, the resonance frequency and the linewidth of the Lorentz oscillators, respectively.

The polarized reflectance and optical conductivity spectra measured for ethylenedithio-dithiadiseleenafulvalene (EDT-DTDSF) salt: \(\beta-(\text{EDT-DTDSF})_n\text{Hg}_3\text{I}_8\) is presented in the Figure 1.
In the bottom panel of this figure there is the inset with sum rule calculations performed for two polarizations of electrical vector. For $E_{\text{max}}$, $(m/m_{\text{eff}})N_{\text{eff}}$ increases rapidly at first and begins to level off at a value near 0.18 and then rises rapidly above 1 eV. The function rises much more slowly and smoothly for the other polarization. For this salt the effective masses of holes ($m_{\text{eff}} = 1.1m_0$ for $E_{\text{max}}$ and $m_{\text{eff}} = 3.8m_0$ for $E_{\text{min}}$) suggest that it belongs to quasi-two-dimensional material with a closed Fermi surface [46].

Figure 1. Polarized reflectance (upper panel) and optical conductivity (lower panel) spectra of $\beta$-(EDT-DTDSF)$_2$Hg$_3$I$_8$ at room temperature. Least-squares fits to the reflectance assuming a Drude dielectric function (upper panel, dotted line) and sum rule calculations based on the optical conductivity data (in the inset). (Reprinted with permission from Łapinski et al. [46]. Copyright © 2006, Elsevier).

The polarized reflectance and optical conductivity spectra measured for pyrazino-S,S-dimethyl-ethylenedithio-tetrathiafulvalene (P-S,S-DMEDT-TTF) salt: $\tau$-(P-S,S-DMEDT-TTF)$_2$(AuBr$_3$)(AuBr$_3$)$_y$ are shown in Figure 2 [45].

Dotted line in the upper panel of this figure was used for display Drude-Lorentz model. The electronic band centered between 5500 and 6050 cm$^{-1}$ observed for this organic conductor is related to the transitions between the lower and upper Hubbard bands. Within the basic Hubbard framework, the optical conductivity spectrum at low-temperature is predicted to show: a Drude-type band centered at zero frequency due to quasi-particle transitions, a resonance at $\omega = U/2$ (where $U$ means the on-site Coulomb repulsion) due to transitions between the Hubbard bands and quasi-particle band; and a contribution which appears at $\omega = U$ due to transitions between lower and upper Hubbard bands [52].

Among the two-dimensional organic CT salts, the $\kappa$-phase ET salts are of particular interest, because the constituting cationic dimers are arranged in an anisotropic lattice [53–55]. To understand the electronic properties of such group of organic conductors Kino and Fukuyama [56–58] considered a triangular lattice. For $\kappa$-(ET)$_2$X family the electronic transition observed
in mid-infrared has the double nature origin. One can identify intraband transitions within the correlated manifold and interband transitions due to CT within the ET dimer. Two-dimensional metallic properties are related to the carriers which can move between the dimer “lattice sites.” In the Mott-insulating state, the strong electronic repulsion limits their mobility and immobilizes them. The other types of carriers are localized on the sites of a triangular lattice. The effective on-site Coulomb interaction is related to the intradimer overlap integrals, whereas the interdimer overlap integrals define the hopping $t$ between the sites.

Figure 2. Polarized reflectance spectra of τ-(P-$S$-$S$-DMEDT-TTF)$_2$(AuBr$_2$)$_2$ at room temperature and 10 K (represented by solid and dashed lines, respectively). Least-squares fits to the reflectance assuming a Drude-Lorentz dielectric function (upper panel, dotted line) and the optical conductivity spectra derived from the reflectance spectra by the Kramers-Krönig transformation. (Reprinted with permission from Łapiński et al. [45]. Copyright © 2003, Elsevier).

Figure 3 shows the electronic feature A for κ-(ET)$_4$[Co(CN)$_6$][N(C$_2$H$_5$)$_4$]·2H$_2$O [44] which can be explained by two contributions: CT inside the dimer “lattice sites” (from 3300 to 4700 cm$^{-1}$) and interdimer CT by correlated charge carriers (from 2500 to 3000 cm$^{-1}$).

Rice [59], Yartsev and coworkers [60–62] have shown that the electronic feature with a maximum at around 3500 cm$^{-1}$ is related to the CT within a dimer; $A_g$ vibrations of ET molecule can be coupled with such transition. Moreover, the electronic band at about 2700 cm$^{-1}$ reveals transitions between the Hubbard bands formed by the correlated conduction electrons [15, 16, 52, 63].

The family of two-dimensional ET salts with half-filled band are especially interesting for the charge disproportionation phenomena and has been extensively investigated [64–71], with the special focus on the κ-phase salts [72–79]. However, such phenomenon in such group of salts
with an effectively half-filled band was very rarely observed. It has been reported only for a few salts, such as for κ-(ET)$_4$PtCl$_2$·C$_6$H$_5$CN, the triclinic κ-(ET)$_4$[[M(CN)$_6$]]$\cdot$3H$_2$O and the monoclinic κ-(ET)$_4$[[M(CN)$_6$]]$\cdot$2H$_2$O (with M = Co$^{III}$, Fe$^{III}$ and Cr$^{III}$). For κ-(ET)$_4$[Co(CN)$_6$][N(C$_2$H$_5$)$_4$]$\cdot$2H$_2$O and κ-(ET)$_4$[Fe(CN)$_6$][N(C$_2$H$_5$)$_4$]$\cdot$2H$_2$O salts [44] the crystallographic studies have been performed at different temperatures at about 100, 200 and 293 K [78]. At ambient temperature, both salts exhibit rather poor conductivity and large paramagnetic susceptibility, which allows us to assert that they are on the insulator side of the Mott-Hubbard criterion as in κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu[N(CN)$_2$]Cl [80, 81]. Both investigated salts undergo a charge-ordering phase transition at T$_{CO}$=150 K [78]. Above 150 K they are in the Mott insulating state with a uniform charge distribution among ET molecules (ET$_A$$^+$$^0.5$ET$_A$$^+$$^0.5$, ET$_B$$^0$$^0$ET$_B$$^0$), whereas below this temperature a charge pattern (ET$_A$$^+$$^1$ET$_A$$^+$$^1$, ET$_B$$^0$ET$_B$$^0$) is observed.

The phase transition at 150 K induces considerable modifications in electronic structures. Due to the charge ordering phase transition, some new bands related to the fully ionized and neutral ET molecules appear in the spectra. One of the most important spectral changes is appearance of the new band at about 7000 cm$^{-1}$ [44] (see Figure 3; band B). This electronic band can be attributed to intermolecular electronic transitions between neighboring ET$^+$ cations. The appearance of this feature is a consequence of the charge-ordering phenomenon. Below 150 K the intensity of this band increases on cooling down. For polarisation E$\perp$b we can also find this band above 150 K which means that even at room temperature charge density fluctuations are present and hence we can expect that the relatively short-living dimers (ET$_A$)$_2$$^{2+}$ exist in our system.

**Figure 3.** Temperature dependence of the optical conductivity spectra of κ-(ET)$_4$[Co(CN)$_6$][N(C$_2$H$_5$)$_4$]$\cdot$2H$_2$O. Dotted lines show the deconvolution of the charge-transfer band into two components. (Reprinted with permission from Łapiński et al. [44]. Copyright © 2013, American Chemical Society).
3. Vibrational structure studied by IR and Raman spectroscopy

The most well-known donor in organic conductors is ET molecule. In the solid state, they are never flat and their symmetry is lowered caused by the deformations of outer CH₂-CH₂ groups. Nevertheless, for the classification of normal modes, a planar \( D_{2h} \) molecular symmetry was often taken by many authors, e.g. by Kozlov et al. [82, 83] and Eldridge et al. [84]. The equilibrium geometry of a neutral ET has a boat conformation (\( C_2 \) symmetry). An ionized ET can be either staggered (\( D_2 \) molecular symmetry) or eclipsed (\( C_{2h} \) symmetry) [85]. Correlations between the spectral predictions based on \( D_{2h} \) and on \( D_2 \) symmetry can be easily made, the difference being associated with the lack of inversion center (\( A_g \) and \( A_u \) become \( A_1g \) and \( B_{1u} \), \( B_{1g} \) and \( B_{1u} \) become \( B_{1g} \) and \( B_{1u} \), \( B_{2g} \) and \( B_{2u} \) become \( B_{2g} \) and \( B_{2u} \), \( B_{3g} \) and \( B_{3u} \) become \( B_{3g} \)). Moreover, \( A_1 \) and \( B_1 \) modes in \( D_2 \) correlate with \( A \) in \( C_2 \) and \( B_2 \) in \( D_2 \) with \( B \) in \( C_2 \).

For ET molecule, there are three normal modes related to C=C stretching vibrations, which exhibit the largest ionization frequency shift (120–130 cm\(^{-1}\)) [25, 31, 54]. Assuming \( D_{2h} \) symmetry for the free ET molecule, these modes are called \( \nu_2(A_g) \), \( \nu_3(A_g) \) and \( \nu_{27}(B_{1u}) \) (see Figure 4) where the symbols in parentheses denote the symmetry species [82, 83].

![Figure 4](image)

Figure 4. Schematic views of the three C=C stretching modes in ET molecule.

They have been the first ones to be proposed for the determination of \( \rho \) in ET [25] and the linear dependence of \( \nu_2(A_g) \) and \( \nu_{27}(B_{1u}) \) modes against charge density has been experimentally verified. The Raman-active \( \nu_2 \) and \( \nu_3 \) modes involve the central and symmetric ring C=C stretching vibrations. For the neutral ET molecule, C=C stretching vibrations are mixed almost equally in \( \nu_2 \) and \( \nu_3 \) modes, whereas for the ionized ET, they are almost separated; in the latter case the \( \nu_2 \) and \( \nu_3 \) modes are mainly assigned to ring C=C stretching and bridge C=C stretching, respectively [86, 87]. The IR-active \( \nu_{27}(B_{1u}) \) mode is due to the anti-symmetric ring C=C stretching and is thus completely separated from the central C=C stretching.

Figure 5 shows that for ET salts in their IR spectra a group of strong bands related to C=C bonds vibrations can be found within the spectral region from 1100 to 1400 cm\(^{-1}\). The ionization results in the meaningful red shift of these modes 95 and 60 cm\(^{-1}\) [20, 25, 88]. For organic metals, where electrical conductivity is relatively high, situation becomes a little more complicated, because instead of well defined group of vibrational features, additional broad maxima can be observed (e.g. \( \beta''-(\text{ET})_4A[M(C_2O_4)_{1-x}]\cdot\text{DMF} \) where \( A=\text{NH}_4^+, \text{K}^+ \) and \( M=\text{Cr}^{III}, \text{Fe}^{III} \) [41–42].
(ET)$_2$(MoO$_2$)$_2$(DMF)$_3$ [43]). Such broad bands are a consequence of the coupling of $\nu_2(A_g)$ and $\nu_3(A_g)$ modes with conducting electrons, for which their proximity leads to a strong mixing.

Nevertheless, it should be emphasized that the C=C modes are often used in the study of the nature of different phase transitions. For example, for the salts $\kappa$-(ET)$_4$[Co(CN)$_6$][N(C$_2$H$_5$)$_4$]⋅2H$_2$O and $\kappa$-(ET)$_4$[Fe(CN)$_6$][N(C$_2$H$_5$)$_4$]⋅2H$_2$O where the phase transition from the Mott insulator state to the charge-ordering state is present, the C=C modes have been discussed [44]. The considerable modifications in vibrational structure due to this phase transition at 150 K are presented in Figure 5a. The new bands related to the fully ionized and neutral ET molecules appear in the IR spectra. One of the most important spectral changes is appearance of new bands at 1347 cm$^{-1}$ and 1289, 1297 cm$^{-1}$ related to the $\nu_3(A_g)$ and $\nu_5(A_g)$ modes of ET$^{2+}$ cation, which are activated by coupling with the CT transition observed at about 7000 cm$^{-1}$ [44]. It gives an evidence of doubly charged ET$_2^{2+}$ dimers. The appearance of these features is a consequence of the charge-ordering phenomenon and EMV coupling in these dimers.

Figure 5. Temperature dependence of the conductivity spectra of $\kappa$-(ET)$_4$[Co(CN)$_6$][N(C$_2$H$_5$)$_4$]⋅2H$_2$O salt (a) and temperature variation of the $\nu_{60}(B_{3g})$ ($D_{2h}$) mode ($\nu_{10}(A)$ for $D_2$ symmetry) (frequency and intensity) (b). (Reprinted with permission from Łapiński et al. [44]. Copyright © 2013, American Chemical Society).

For the determination of $\rho$ in ET salts, other vibrational modes as $\nu_{29}(B_1)$ and $\nu_{44}(B_2)$ (for $D_2$ molecular symmetry) can also be used [89]. For example, for $\kappa$-(ET)$_4$[M(CN)$_6$][N(C$_2$H$_5$)$_4$]⋅2H$_2$O (M= Co$^{III}$ and Fe$^{III}$) salts [44], the $\nu_{44}(B_2)$ mode is assigned to weak bands observed in the experimental spectra at 863 cm$^{-1}$ (for ET$^0$), at 875 cm$^{-1}$ (for ET$^{0.5+}$) and at 900 cm$^{-1}$ (for ET$^+$) which are in good agreement with calculated by Girlando values 864, 876 and 903 cm$^{-1}$ for ET$^0$, ET$^{0.5+}$ and ET$^+$, respectively [89]. The 890 cm$^{-1}$ mode, assigned to $\nu_{60}(B_{3g})$ in the $D_{2h}$ symmetry [84] and to $\nu_{10}(A)$ in the $D_2$ symmetry [89], has attracted a special attention as a spectral feature which is so sensitive to the charge disproportion in ET salts [85]. Moreover, if we consider this mode as a totally symmetric one of a distorted, not a perfectly flat ET molecule ($D_{2h}$ symmetry) then this mode can be coupled to the electronic system [89]. This mode appears in the experimental spectra for the ET$^{0.5+}$ at 878 cm$^{-1}$ [90] and for ET$^+$ at 899 cm$^{-1}$ [91]. In the optical conductivity spectra of $\kappa$-(ET)$_4$[M(CN)$_6$][N(C$_2$H$_5$)$_4$]⋅2H$_2$O (M= Co$^{III}$ and Fe$^{III}$) salts this mode at
868 cm\(^{-1}\) (for ET\(^0\)), at 883 cm\(^{-1}\) (for ET\(^{0.5+}\)) and at 894 cm\(^{-1}\) (for ET\(^+\)) can be observed [44]. Figure 5b shows the temperature dependence of the position of the \(\nu_{10}(A)\) mode.

Figure 6. Schematic atomic displacements of C=C in vibrational modes for DIETS, DIET and DIEDO molecules. Note: the position of C=C stretching modes is given for the experimental spectra of these donors. (Reprinted with permission from Łapinski et al. [36]. Copyright © 2010, Elsevier).

In the case of organic unsymmetrical donors derived from TTF molecule: e.g. pyrazino-S,S-dimethyl-ethylenedithio-tetrathiafulvalene (P-S,S-DMEDT-TTF) [45], 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-5-(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (EDDH-TTP) [48], 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP) [48], ethylenedithio-dithiadiiselenafalvalene (EDT-DTDSF) [46], diidooethylidenedithio-dithiaseleenafulvalene (DIETS) [36, 50], diidoethylenedithiotetrafulvalene (DIET) [50], diidoethylene- dioxotetrafulvalene (DIEDO) [36, 50], (1,4-dioxane-diyl-2,3-ditio) ethylenedioxytetrafulvalene (DOEO) [37, 51, 92], dimethyltrimethylenetetrafulvalene

Figure 7. Simulated IR absorption spectra of EDT-DTDSF\(^+\) (a) and EDT-DTDSF\(^0\) (b). (Reprinted with permission from Łapinski et al. [46]. Copyright © 2006, Elsevier).
DMTTF) [93], o dimethyl-tetrathiafulvalene (o-DMTTF) [93] one can find three types of non-equivalent C=C bonds - one central bond and two ring bonds. The schematic picture of atomic displacement of carbon atoms for DIEDO, DIETS, DIET is shown in Figure 6. The theoretical calculations show that a strong mixing of all C=C stretching vibrations is present for all modes related to C=C stretching vibrations.

Except the modes related to the C=C stretching vibration, which show the largest low-frequency shifts when the molecule is oxidized, other active modes also exhibit a significant shift due to the ionicity [36, 46, 51], what is schematically illustrated by dashed line for EDT-DTDSF (see Figure 7).

For the isolated donor molecules, the optimized geometry depends on whether we have a neutral or charged molecule. The TTF framework for neutral molecules is non-planar deforming to a boat conformation, in contrast with cations where the TTF framework is planar (see Figure 8) [36]. The similar situation has also been observed for the other organic donors [37, 51, 94]. In crystal structures of salts derived from TTF, where donors are not isolated molecules, the TTF framework can be flat with small deviations from planarity [95, 96]. For example, for the CT salts derived from DIET, DIEDO and DIETS and the anion [Fe(bpca)(CN)₃]⁻, the donors are almost flat [97]. In Raman spectra of these salts bands assigned to the C=C stretching vibrations are strongly shifted towards lower frequency and this effect is due to ionization [50].

Infrared spectroscopy is a powerful method not only in investigating the charge disproportion phenomena but also in the study of interaction between the organic and inorganic layers in organic conductors and its impact on the physical properties. For κ-(ET)₄[Co(CN)₆] [N(C₂H₅)₄]·2H₂O and κ-(ET)₄[Fe(CN)₆][N(C₂H₅)₄]·2H₂O salts Ota and co-workers [78] showed that the strong electron-electron correlations and Coulomb interaction between ET and inorganic layers play an important role in the phase transition from the Mott insulator state to the charge-ordering state. The role of such interactions and their contributions to the phase transition has been investigated and discussed in Ref. [44]. The temperature dependence of the modes related to C≡N triple bond vibrations (~2100 cm⁻¹) in M(CN)₃⁺ (M=Co(II) and Fe(III)) anions and C-H stretching in ET molecules (~3400 cm⁻¹) is presented in Figure 9. For these modes, the frequency dependences reflect the sensitivity of the CN-CH₂ interaction to the 150 K phase transition. The blue shift of the CN stretching frequency with decreasing temperature proves that the interaction between the hydrogen atom and the CN group of the anions is...
Moreover, the examination of the CH$_2$ stretching frequencies in κ-(ET)$_4$[Co(CN)$_6$]·2H$_2$O and κ-(ET)$_4$[Fe(CN)$_6$][N(C$_2$H$_5$)$_4$]·2H$_2$O salts leads us to the conclusion that in the last salt the degree of donor-anion interaction is slightly smaller.

![Figure 9](image)

Figure 9. Temperature variation of the C-H (a) and C≡N (b) modes (frequency and intensity). (Reprinted with permission from Łapiński et al. [44]. Copyright © 2013, American Chemical Society).

What should be emphasized at this point is the fact that the temperature variation of bands related to C-H stretching indicate that apart from the long-range Coulomb interactions between electrons within the conducting layers, the anions have an influence on the formation of the charge-ordered state as well [44]. Laversanne and co-workers [98] showed that periodic distribution of the anions could play an important role in the physical properties of organic conductors.

They drew attention that the anion potential effects on an terminal part of the donors. The orientation of the anions along the chain influences on the charge density distribution within conducting layers and the description of the anion potential should be taken into account in calculations [98]. Moldenhower et al. [88] investigated the correlation between the $T_c$ temperature and frequencies of the CH$_2$ stretching modes of ET radical salts with the superconducting phase transition. The position of these modes is evidently not charge dependent but it can reflect the strength of the interaction of the donor molecule with the respective anion. They showed that phases with a higher $T_c$ of their superconducting transition exhibit a smaller red shift of these frequencies, which is due to the hydrogen-bonding like interaction of the donor with the anion, i.e., a less attractive donor-anion interaction [88].

For (DOEO)$_4$HgBr$_4$·TCE salt it has been shown in [92] that the role of anion layers cannot be neglected. The temperature evolution of vibrational features reveals that only the bands related to the deformation of the outer ring of DOEO molecule (e.g. 1371, 1092 cm$^{-1}$) are sensitive to the metal-insulator phase transitions (Figure 10a), whereas the bands related to the deformation of C-O bonds in inner part of donor molecule observed at 1000 and 902 cm$^{-1}$ do not show
such behavior (Figure 10b). The systematic analysis of vibrational and electronic structure performed for DOEO salt one can find in [37] and [51].

Figure 10. Temperature dependence of the wave number of the selected bands: 1371 and 1092 cm$^{-1}$ (a) and 902 and 1000 cm$^{-1}$ (b). Note: lines are used as a guide for the eyes. (Reprinted with permission from Łapiński et al. [92]. Copyright © 2012, Elsevier).

In the case of organic conductors formed by iodinated TTFs as DIEDO, DIET, DIETS [36], the position of modes related to C-I and C-S vibrations could be also sensitive to strong interaction between the iodo group of donor and the cyano group or halogen of acceptors [95, 97, 99, 100]. In the experimental IR spectra of these neutral donors, one can find the bands related to the simultaneous deformation of C-S and C-I bonds at 693, 817, 903 cm$^{-1}$ (for DIETS), 696, 817, 917 cm$^{-1}$ (for DIET) and 699, 829, 912 cm$^{-1}$ (for DIEDO) [36].

The strong interaction between donors and acceptors should also have an influence on frequencies of acceptor molecules. For example, for the 2:1 salts formed by the iodine substituted donors DIEDO, DIET, DIETS with the anion [Fe(bpca)(CN)$_3$]$^-$ (where bpca=bis(s-pyridylcarbonyl)amide anion) we have observed the influence of such interactions on frequencies of C≡N and C=O vibrations of acceptor molecule [50].

4. Electron-phonon interaction

Infrared spectra of organic conductors are usually dominated by strong vibrational features related to the coupling between the electrons in the highest occupied molecular orbital (HOMO) and the molecular vibrational modes of molecules [101, 102]. Because of this coupling, the vibrational modes borrow intensity from the nearby CT electronic transition and occur at frequencies lower than the corresponding Raman active modes. These strong bands are polarized perpendicularly to the molecular planes, like the CT transition.

The EMV coupling phenomenon in conducting organic salts can be analyzed in terms of various models depending on structure of the molecular stacks. Microscopic theories for regular stacks or stacks consisting of quasi-isolated dimers, trimers, tetramers or n-mers have been developed [28–30]. The above mentioned models were successfully applied to IR spectra...
of CT salts formed by TTF and its derivatives with various acceptors [62]. More specifically, the dimer model has proven to be especially useful in determining the coupling constants for TTF-containing CT materials. For example, reliable values for the EMV constants were obtained for the salt \((\text{ET})_2[\text{Mo}_6\text{O}_{19}]\) which contained well-isolated \((\text{ET})_2^+\) dimers [91].

According to symmetry considerations, only the totally symmetric vibrational modes within a specified linear approximation of non-degenerate molecular orbitals can couple with electrons [103]. For other symmetry modes, the electron–vibrational interaction is forbidden by the selection rules and is only correct if the molecules within the dimer have the same symmetry. When considering the dimer, where the molecules are asymmetric with respect to one another, if these molecules are different or inequivalent, their modes are no longer degenerate and couple both in-phase and out-of-phase. In this case, the lack of an inversion center suppresses the mutual exclusion rule leading to all of the modes for the constituent molecules within the dimer becoming both IR and Raman active. Additionally, all of their symmetric modes can then couple to the CT electron [104]. Moreover, if we consider the sufficiently fast charge transfer between the dimer molecules due to electromagnetic radiation, their nuclear configurations do not have time to change in response to the charge transfer and their molecular vibrations arise as the result of the relaxation to each molecule’s respective equilibrium configuration. In this case, the symmetry type of the arising vibrational modes depends not only on the final and initial state symmetries, but also on that of the intermediate states from which the transferred charge among the neighboring molecules belongs. These facts could suggest that in some cases non-totally symmetric modes can be also coupled [105].

Figure 11. Experimental and calculated conductivity spectra of \((\text{DMtTTF})\text{Br}\) salt. Note: electric vector along the stacking axis; the logarithmic wave number scale. (Reprinted with permission from Łapiński et al. [93]. Copyright © 2014, Elsevier).
For salts formed by unsymmetrical TTF derivatives such as o-DMTTF, DMTTF and DOEO in the IR spectra one observes vibrational features suggesting the EMV coupling to intramolecular vibrations of donors, especially those related to C=C stretching [106–109]. In the IR spectra of the salts (DOEO)$_4$HgBr$_4$·TCE [51], (DMTTF)Br [93] and (o DMTTF)$_2$[W$_6$O$_{19}$] [93] a clear evidence of the EMV coupling to C=C stretching modes have been found. The observation of vibrational bands shifted towards lower wave numbers with respect to Raman data and, moreover, with characteristic antiresonance deeps, give an evidence of their interaction with CT transition. This effect is very well visible for polarization parallel to the stacking axis; in particular there are distinct antiresonance dips at 1370 and 1379 cm$^{-1}$ for (DMTTF)Br and (o-DMTTF)$_2$[W$_6$O$_{19}$], respectively [93]. Moreover, the bands at 1338 and 1345 cm$^{-1}$ [93] have a characteristic asymmetric Fano-like lineshape [110]. It is observed when the electric field is polarized along the chain and the electronic absorption overlaps with the phonon frequencies; the interaction between electrons and phonons gives rise to characteristically asymmetric Fano lineshape of bands. The analysis of Fano-effect combined with Raman data can lead to quantitative predictions for the various electron phonon couplings [111].

<table>
<thead>
<tr>
<th>(DMTTF)Br [93]</th>
<th>(o-DMTTF)$_2$[W$<em>6$O$</em>{19}$] [93]</th>
<th>(DOEO)$_4$HgBr$_4$·TCE [51]</th>
<th>Assignment</th>
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<tr>
<td>$\omega_\alpha$</td>
<td>$g_\alpha$</td>
<td>$\lambda_\alpha$</td>
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<tr>
<td>1587</td>
<td>97</td>
<td>0.002</td>
<td>1556</td>
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<tr>
<td>1507</td>
<td>161</td>
<td>0.006</td>
<td>1483</td>
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<tr>
<td>1412</td>
<td>597</td>
<td>0.095</td>
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Note: $\omega_\alpha$ and $g_\alpha$ are given in cm$^{-1}$.

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<td>133</td>
<td>1414</td>
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<td>1418</td>
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Table 2. Dimer model parameters by the fit to the polarized conductivity spectrum of (DMTTF)Br, (o-DMTTF)$_2$[W$_6$O$_{19}$] and (DOEO)$_4$HgBr$_4$·TCE salts obtained by Kramers-Krönig transformation from the reflectance spectra.

Table 3. The EMV coupling constants, $g_\alpha$ (meV) of the C=C stretching modes $\omega$ (cm$^{-1}$) for several symmetrical radical cations based on TTF.

**Figure 11** shows the conductivity spectrum of (DMTTF)Br salt obtained by Kramers-Krönig transformation from the experimental reflectance spectrum (upper panel) and conductivity spectrum calculated within the framework of the dimer model proposed by Rice et al. [103] (lower panel). **Table 2** presents the model parameters for the fit to the conductivity spectra of (DMTTF)Br [93], (o DMTTF)$_2$[W$_6$O$_{19}$] [93] and (DOEO)$_4$HgBr$_4$·TCE [51] salts. Comparing the relevant EMV coupling constants for unsymmetrical DMTTF, o-DMTTF and DOEO donors...
with the corresponding ones measured for symmetrical TTF-based electron donor molecules: TTF itself [28–29], ET [91], tetramethyl-tetrathiafulvalene (TMTTF) [112], bis-fused TTF (TTP) [113] (see Table 3) one can see that the values of coupling constants are comparable and the most strongly coupled modes are assigned to the TTF skeleton vibrations, namely the modes related to the stretching vibrations of both central and ring C=C bonds.

It should be also emphasized that the EMV coupling plays a role in the charge-ordering instabilities, as the modulation of the frontier molecular orbitals, pushing charges back and forth, which may in turn provoke their localization on the molecular sites [89].

5. Conclusions

In this chapter, selected problems of solid state physics of organic conductors have been discussed. The IR, Raman and UV-Vis spectroscopies were used providing the information about vibrational and electronic structures, electron-electron and electron-phonon interactions. The detailed spectral analysis led to a wider recognition and provides the necessary information about physical properties of organic conductors.

It was shown that the role of anion layers cannot be neglected. The periodic distribution of anions could play an important role in the physical properties of organic conductors. On the basis of vibration spectra it was shown that the anion potential influences on a terminal part of the molecules, which are close to anions. Apart from the long-range Coulomb interactions between electrons within layers formed by donors also the anions can have a significant influence on the formation of the charge-ordered state. Moreover, it was shown that in the case of organic unsymmetrical donors derived from TTF molecule the values of coupling constants are comparable with another symmetrical TTF derivatives and the most strongly coupled modes are assigned to the TTF skeleton vibrations, namely the modes related to the stretching vibrations of both central and ring C=C bonds. It was also shown that the special attention should be paid to the impact of the EMV coupling on the charge-ordering instabilities.

For characterization of intramolecular and intermolecular transitions the time-dependent DFT method and Drude-Lorentz models can be successfully applied. Considerable information about the electronic structure can also be extracted from the oscillator strength sum rule.

The degree of ionicity or average charge per molecule is one of the fundamental parameters characterizing the physical properties of CT salts. For the organic donors, this parameter can be studied using spectroscopic methods. It was shown that in the case of organic donors derived from TTF molecule the most convenient for this analysis are the C=C stretching modes of TTF framework which show sensitivity to the ionization degree. It was also shown that spectroscopic methods are very powerful tool in the study of the nature of different phase transitions and the interaction between the organic and inorganic layers in organic conductors and its impact on the physical properties.
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