Chapter – 4

FTIR Spectra of charge transfer Complexes of

Tetra methyl Tetra Selena Fulvalene
1. Introduction:

There is a large number of magnetic TTF – based charge transfer complexes. The Bechagaard salts of the \((\text{TMTTF})_{2X}\) and \((\text{TMTSF})_{2X}\) type where \(X = \text{PF}_6, \text{ClO}_4, \text{NO}_3, \text{SiF}_5, \text{BF}_4^-, \text{Cl}^-, \text{Br}^-, \text{I}^-\) are found to be superconducting at ambient or applied high pressure at low enough temperatures. The semiconducting phase of \((\text{TMTSF})_2\text{PF}_6\) results from spin density wave ground state at low temperature. The dynamic response of SDW mode is studied with frequency dependent conductivity (1). Memory effects were studied with transient electrical response (2). Microwave investigations of transverse response of \((\text{TMTSF})_2\text{PF}_6\) were also carried out (3). Superconductivity in \((\text{TMTSF})_2\text{PF}_6\) has also been studied (4). Field angle – resolved calorimetric confirmed phase diagram and anomalous superconductivity in \((\text{TMTSF})_2\text{ClO}_4\) (5). Magnetic – field amplitude and field – angle dependence of the transition temperature for super conduction have been studied for \((\text{TMTSF})_2\text{ClO}_4\) (6). Linear and nonlinear Hall effects in the SDW phase of \((\text{TMTSF})_2\text{AsF}_6\) have been studied (7). The structures of \((\text{TMTSF})_2\text{SiF}_5\) at 293 K and 125 K were studied (8). Synthesis, structure and electrical conductivity of some fulvalenium salts of cobalt (dicarbolide) anions and its derivatives are also reported (9). Phase diagrams of \((\text{TMTTF})_{2X}\) and \((\text{TMTSF})_2X\) type salts were rigorously studied (10). Ferroelectricity in \((\text{TMTTF})_{2X}\) conductors has been reported (11).
In the present work the FTIR spectra of \((\text{TMTSF})_2\text{X}\) where X is an organic acceptor have been investigated. The molecular structures of TMTSF and organic acceptors are shown in (Figure 1).

2. Experimental:

TMTSF (Tetramethyl tetra selena fulvalene) was obtained as a violet powder from Aldrich Chemical company. It was mixed in 2:1 molecular weight proportion with organic acceptors TCNQ (7, 7, 8, 8 – tetracyano – p quino – dimethane), TCNE (tetracyano – p – ethylene), DDQ (2, 3 – dichloro – 5, 6 – dicyno – p – benzoquinone), Chloranil and iodine. The mixtures were grinded in an agate mortar with agate pastle till the colours changed. This formed charge transfer complexes of \((\text{TMTSF})_2\text{X}\) type where X is an organic acceptor. These CTCS in powder forms were mixed with 95 % KBr powder method and circular pellets were prepared using a manually compressing machine.

The spectra in the range 400 – 4000 cm\(^{-1}\) were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin Elmer Company, USA having a resolution of 0.15 cm\(^{-1}\), a scan range of 15,000 – 30cm\(^{-1}\), a scan time of 20 scan/sec, an OPD velocity of 0.20 cm/sec and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800 cm\(^{-1}\) – 370 cm\(^{-1}\). The spectra were recorded in purge mode.

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3. Results and Discussion:

The FTIR spectrum of TCNQ complex in the full mid – IR range is shown figure 2a. The range covers a gaussian band around 3437 cm⁻¹, a half – power beta density in the range between 3050 cm⁻¹ and 1690 cm⁻¹ and a region of nature of transition below 1500 cm⁻¹. The gaussian band described by

\[ A = A_o \exp \left[ -\frac{(K - K_o)^2}{2M_2} \right] \]

is fitted by plotting lnA vs (K – K_o)² (Figure 2b). The half – power beta density is analyzed by plotting T – T_o vs K*¹/₂(1 – K*)¹/₂, where K* = (K – a)/ b (Figure 2c). The absorption edge is analyzed and a forbidden direct transition was found to be the best fit as shown by plotting (Ahν)²/₃ vs hv as a straight line (Figure 2d). The band gap E_g was found to be only 0.06 eV. Thus (TMTSF)₂X TCNQ was found to be a small band gap semiconductor. This should be compared with (TMTSF)⁺ TCNQ⁻ (1:1) complex recently published (12). The 1:1 complex was found to be ionic and a band gap of 0.1 eV was found. The background absorption continued to be monotonically decreasing down to 0.1 eV. The present 2:1 complex is found to be transmitting type below 1500 cm⁻¹, although fitting direct transition as in 1:1 complex. This can be understood by comparing with ternary complexes of 1:1:1 type studied recently (13). The additional donor in two donor and one acceptor type complexes leads to screening of the electrostatic field existing in a 1:1 binary complex. Thus here also TMTSF additional molecules screen in a binary (TMTSF)⁺ TCNQ⁻ complex.

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Actually only half an electron per TMTSF molecule is transferring to TCNQ molecule and \((\text{TMTSF})^+\) and \(\text{TCNQ}^-\) is formed. There is unit positive charge on a dimer of TMTSF molecule. The ionic nature can be concluded by comparing vibrational bands of \(\text{Li}^+ \text{TCNQ}^-\) complex and \((\text{TMTSF})_2 \text{TCNQ}\) complex. The bands of \(\text{TCNQ}^-\) anion are found to be present in the present case (Figure 2a). The resonances – anti – resonances spikes found in 1:1 \(\text{TMTSF}^+ \text{TCNQ}^-\) complex are found to be absent in 2:1 complex studied here. This is because of screening by nearly neutral TMTSF molecules present in \((\text{TMTSF})_2 \text{TCNQ}\) complex here. Electrostatic screening increases the bandwidth of the conduction band and therefore decreases the band gap from 0.1 eV in 1:1 complex to 0.06 eV in 2:1 complex. Band assignments have been carried out for 2:1 complex.

The FTIR spectrum of \((\text{TMTSF})_2 \text{TCNE}\) is shown (Figure 3a). A half – power beta density is found in the range 3440 cm\(^{-1}\) and 1610 cm\(^{-1}\) corresponding to hopping conduction along TMTSF stacks.(Figure 3b). Other range is that of absorption edge below 1200 cm\(^{-1}\). The background absorption keeps monotonically decreasing down to 400 cm\(^{-1}\). A direct allowed transition is found to by plotting \((\Delta \nu)^2 \text{ vs } \nu\) as the best fitting straight line. The band gap is found below 0.05 eV. Again it is a small band gap semiconductor.

The FTIR spectrum of \((\text{TMTSF})_2 \text{DDQ}\) is shown (Figure 4a). In this spectrum a region of nature of transition is found below 1600 cm\(^{-1}\). There is a monotonically decreasing absorption down to 600 cm\(^{-1}\). It is found to be a
forbidden indirect transition with band gap of 0.08 eV (Figure 4b). Below 600 cm\(^{-1}\), there is a low frequency gaussian band which is also fitted (Figure 4c). The FTIR spectrum can be compared with that of 1:1 \((\text{TMTSF})^+ (\text{DDQ})^-\) studied recently (13). In the latter, resonance – anti – resonance spikes were found and an envelope of the asymmetric type fitting \(A = A_0 Ke^{-bk}\) which could be explained with the presence of charge density wave in 1:1 complex. Here \((\text{TMTSF})_2 \text{DDQ}\) is found to be more transmitting type but having only a small band gap. There is screening by additional donor molecules increasing band width and therefore reducing the band gap. The semiquinone ion bands of \((\text{DDQ})^-\) were found in 1:1 ionic complex. In the present case also the semiquinone ion bands of \((\text{DDQ})^-\) are present indicating ionic nature of \((\text{TMTSF})_2 \text{DDQ}\). The presence of semiquinone ion indicates a strong interaction of methyl groups of TMTSF molecules with oxygen atoms of DDQ molecule.

The FTIR spectrum of \((\text{TMTSF})_2 \text{chloranil}\) is also shown (Figure 5a). There is a gaussian band in the range between 3700 cm\(^{-1}\) and 2900 cm\(^{-1}\) (Figure 5b). This follows a range of nature of transition, i.e. optical absorption edge with \(E_g = 1700 \text{ cm}^{-1}(0.22 \text{ eV})\) which is a Peierl gap (Figure 5c). \((\text{TMTSF})_2 \text{chloranil}\) is a one dimensional conductor. Below 1700 cm\(^{-1}\), there are oscillations of density of states corresponding to square root singularities along the homomolecular stacks of Chloranil molecules. Several vibrations of Chloranil \(^-\) anions are found indicating that \((\text{TMTSF})_2 \text{chloranil}\) is an ionic complex.
Finally, an FTIR spectrum of $(\text{TMTSF})_2$ iodine is also shown (Figure 6a). This spectrum has three ranges. The first range consists of a half – power beta density relating to the Bernoulli trials of hopping conduction. The second range is that of optical absorption edge at 0.125 eV (1000 cm$^{-1}$) (Figure 6b). This shows it is a small band gap semiconductor. The third range contains a low frequency gaussian band around 608 cm$^{-1}$ (Figure 6c). This is related with electronic delocalization or free – charge carriers.

4. Conclusions:

The organic CTCS of the type $(\text{TMTSF})_2$ X where X is a standard organic acceptor are found to be small band gap semiconductors. Although these 2:1 donor – acceptor complexes are more transmitting compared to 1:1 $(\text{TMTSF})^+ (\text{DDQ})^-$ and $(\text{TMTSF})^+ (\text{DDQ})^-$ complexes, the band gap reduces due to increase in band width of the conduction band.
Figure 1 Molecular structure of TMTSF and other organic acceptors
Figure 2a FTIR spectrum of (TMTSF)$_2$ TCNQ

Figure 2b Gaussian band around 3400 cm$^{-1}$

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Figure 2c half – power beta density fitted between 3050 cm$^{-1}$ and 1685 cm$^{-1}$

Figure 2d Forbidden direct transition with band gap Eg = 0.06 eV
Figure 3a FTIR spectrum of \((TMTSF)_2 - TCNE\)

Figure 3b half – power beta density fitted between 2920 cm\(^{-1}\) and 1610 cm\(^{-1}\)

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Figure 3c Allowed direct transition with band gap $E_g = 0.05 \text{ eV}$

Figure 4a FTIR spectrum (TMTSF)$_2$– DDQ

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Figure 4b Forbidden indirect transition with band gap

\[ E_g = 0.11 \text{ eV} \]

Figure 4c Gaussian band around 510 cm\(^{-1}\)
Figure 5a FTIR spectrum (TMTSF)$_2$ – Chloranil

Figure 5b Gaussian band around 3420 cm$^{-1}$
Figure 5c Allowed direct transition with band gap $E_g = 0.22 \text{ eV}$

Figure 6a FTIR spectrum (TMTSF)$_2$ – Iodine

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Figure 6b half – power beta density fitted between 2930 cm$^{-1}$ and 1689 cm$^{-1}$

Figure 6c Forbidden direct transition with band gap $E_g = 0.12$ eV

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Figure 6d Gaussian band around 608 cm$^{-1}$
References


5. Shingo Yonezawa, Yoshiteru Maeno, Klaus Bechgaard and Denis Jerome, arXiv: 1112.5974vl (cond – mat.supr – con ) 27 Dec 2011


