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FTIR Spectroscopy of charge transfer Complexes of Decamethylferrocene

[Vishal R. Jain/Ph.D.Thesis (Physics)/S.P.U.-2012]
1. Introduction:

Organic ferromagnetism has become famous among chemists and physicists doing both theories and experiments (1 – 3). Ferromagnetic charge transfer complexes such as $\text{M}^{\text{II}}$ and $\text{M}^{\text{III}}$ decamethylmetalocenes $\text{M}^{\text{II}}(\text{C}_5\text{Me}_5)^{+}$. $\text{A}^-$ and $\text{M}^{\text{II}}(\text{C}_5\text{Me}_5)_2 \text{A}^-$ where $\text{M}^{\text{II}}$ or $\text{M}^{\text{III}}$ is Ni, Co, Fe, Cr and A = TCNQ, TCNE, DDQ, $\text{C}_4(\text{CN})_6$, and $\text{C}_3(\text{CN})_6$, have been studied in details (4). Models for organic ferromagnetism have been reviewed (5). Organic and molecular magnets have been a subject of a review (6). Magnetic TTF – based charge transfer complexes are also reviewed (7).

2. Experimental:

Decamethylferrocene (DMF) was obtained from standard chemical company such as Aldrich-Sigma chemical company and organic acceptors such as 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 were also similarly obtained in pure form.

Tetraphenylporphine in powder form was mixed with organic acceptors such as TCNQ, TCNE, DDQ, Chloranil and iodine in 1:1 molecular proportion. The mixtures were grinded in an agate mortar with agate pastel for half an hour till the colour deepened or changed due to the formation of charge transfer complexes. After forming CTCS, they were
mixed with anhydrous spectrograde KBr powder and again grinded to form homogeneous mixtures. Then they were compressed to form round pellets were placed in the dark chamber of spectrophotometer.

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.

3. Results and Discussion:

Molecular structures of decamethylferrocene and organic acceptors as well as the transfer complexes are shown (Figure 1).

The FTIR spectrum of decamethylferrocene is shown (Figure 2a). This spectrum contains a range of nature of interband transition between 2600 cm\(^{-1}\) and 1700cm\(^{-1}\) as well as oscillations in density of states associated with the repeated structures below 1400 cm\(^{-1}\). The interband transition when analyzed is found to be a forbidden direct transition in one – dimension (Figure 2b). Thus DMF is a one – dimensional semiconductor having a Peierls – Hubbard transition above room temperature. The band gap is about 0.24 eV. Below 1400 cm\(^{-1}\), the structure between 500cm\(^{-1}\) and 1100cm\(^{-1}\) is repeated between 1100 cm\(^{-1}\) and 1400 cm\(^{-1}\). This repetition is associated with the oscillations in the density of states along one – dimensional homomolecular lattice having a square – root singularity like a monoatomic lattice.

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The FTIR spectrum of DMF – TCNQ is also shown (Figure 3). This spectrum has a range of constant absorption like a two – dimensional system. Thus DMF – TCNQ is a two – dimensional conductor having DMF and TCNQ molecules arranged in a layered or planar structure. This range is between 1700 cm\(^{-1}\) and 2700 cm\(^{-1}\). Below 1300 cm\(^{-1}\) there is repetition of structure between 1700 cm\(^{-1}\) and 900 cm\(^{-1}\) below 800 cm\(^{-1}\). This is again related with the oscillations in density of states. The fine structure when closely observed contains vibrational bands of DMF. Thus the chains of DMF molecules are retained as found in only DMF. Thus DMF molecules form semiconducting chains perpendicular to layered structure containing both DMF and TCNQ molecules.

The FTIR spectrum of DMF – TCNE is displayed (Figure 4). It also shows two – dimensional interband transition with constant absorption as observed in TCNQ complex. DMF – TCNE has been studied in earlier work and was found to be a diamagnetic material with magnetic susceptibility of the order of 10\(^{-4}\) (amu / mole) (4). Here it is found to be a layered semiconductor. There is again repetition of structure corresponding to oscillations in the density of states along homomolecular lattice.

The FTIR spectrum of DMF – DDQ is shown (Figure 5a). There is a range of one – dimensional interband transition with \(E_g = 0.24\) eV which is found to be a forbidden direct transition as found in only DMF (Figure 5b). There are three repetitions of a structure below 1700 cm\(^{-1}\). The structure between 400 cm\(^{-1}\) and 700 cm\(^{-1}\) is repeated twice – once between 800 cm\(^{-1}\) and 1200 cm\(^{-1}\) and second time between 1200 cm\(^{-1}\) and 1675 cm\(^{-1}\). This can be along one – dimensional mixed stacks of D\(^+\)A\(^-\) D\(^+\)A\(^-\)… type where D\(^+\) is
DMF$^+$ and A$^-$ is semiquinone ion of DDQ. The repeated structure contains bands of both of these ions. Thus there are oscillations of density of states along mixed stacks with square – root singularities.

The FTIR spectrum of DMF – chloranil is also shown (Figure 6a). There is a region of nature of transition which when fitted shows an allowed direct transition with $E_g = 0.225$ eV (Figure 6b). This is the Peierls – Hubbard gap along one – dimensional conductor. None of the CT complex of DMF shows an indirect transition as observed in CTCS of metal – organic chalets. This is related with peculiar bonding in metallocones between cyclopentadienyl ring and the sandwiched metal ion. It is different from metal – ligand bonding in metal chalets undergoing a metal – ligand vibration. DMF molecules behave like small molecules providing direct rather than indirect transition. The interaction of chloranil molecules with DMF is stronger than that encountered in TCNQ, TCNE and DDQ complexes. The intermolecular distance decreases in the chloranil complex leading to allowed rather than forbidden direct transition. Again oscillations in the density of states leading to thrice repeated structure are observed below 1400 cm$^{-1}$. These structures consist of both DMF and chloranil molecular vibrations. It is a strongly one – dimensional conductor leading to square root singularity more pronounced than those found in TCNQ, TCNE and DDQ complexes. In the cases of TCNQ, TCNE and DDQ the singularities are smoothened due to two – dimensional interactions.

Finally, The FTIR spectrum of DMF – I$_2$ is shown (Figure 7a). This spectrum also shows strong interaction like chloranil complex with iodine being an electronegative halogen. The structure below 1400 cm$^{-1}$ is twice
repeated. There is arranging of nature of transition between 2000 cm\(^{-1}\) and 1600 cm\(^{-1}\) which fits a forbidden indirect transition (Figure 7b). This is due to macromolecular nature of polyiodine chains. The band gap of 0.22 eV is the Peierls gap along polyiodine chains. This is the only complex of DMF which shows indirect transition. The conduction band in this complex is stabilized which is established by fitting free – carrier absorption. There is a range between 2200 cm\(^{-1}\) and 2800 cm\(^{-1}\) where the power – law of free – carrier absorption is fitted by plotting log \(\alpha\) vs. log \(\lambda\) (Figure 7c). This graph shows a straight line due to power – law and a slope of 1.00 corresponding to the scattering of charge carriers by acoustic phonons. Thus DMF – I\(_2\) complex shows presence of a well – defined conduction band along iodine chains.

4. Conclusions:

Decamethylferrocene (DMF) with divalent iron (ferric) ion is a one – dimensional semiconductor having Peierls – Hubbard gap. Its charge transfer complexes with TCNQ and TCNE show two – dimensional conductivity with smoothened square – root singularity in density of states. DDQ and chloranil complexes show one – dimensional conductivity having a Peierls gap. Small intermolecular distance in chloranil complex leads to allowed direct transition. Iodine complex reveals an indirect interband transition associated with macromolecular behavior of polyiodine chains and stabilization of conduction band furnishing a range of free – carrier absorption.
Decamethylferrocene

TCNE

DDQ

Chloranil

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Figure 1 Molecular structure of DMF and other organic acceptors

Figure 2a FTIR spectrum of DMF

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Figure 2b Forbidden direct transition in DMF with $E_g = 0.245$ eV

Figure 3 FTIR spectrum of DMF – TCNQ
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Figure 4 FTIR spectrum of DMF – TCNE

Figure 5a FTIR spectrum of DMF – DDQ

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Figure 5b Forbidden direct transition in DMF – DDQ with $E_g = 0.24$ eV

Figure 6a FTIR spectrum of DMF – chloranil

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Figure 6b Allowed direct transition in DMF – chloranil with $E_g = 0.24$ eV

Figure 7a FTIR spectrum of DMF – Iodine
Figure 7b Forbidden indirect transition in DMF – Iodine with $E_g = 0.22$ eV

Figure 7c Scattering of free – charge carriers by acoustic Phonons

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References:


