Chapter-1

Introduction
1. Charge Transfer Complexes

A charge transfer complex (or CT complex, electron donor acceptor complex) is a chemical association of two or more molecules or different parts of one very large molecule, in which the attraction between the molecules (or parts) is created by electronic charge which is transferred between the molecules. The charge is transferred from electron donor to the receiving molecule is called the electron acceptor, so the other name, electron-donor acceptor-complex [1,2].

The optical absorption bands are often referred to as charge transfer bands or CT bands. The optical spectroscopy is a powerful technique to characterize the charge transfer bands [3].

In 1973, scientists discover the metal like electronic behaviour of charge transfer complexes. Consisting of an electron donor. Tetra thiafulvalene (TTF) donor with electron accepter. 7,7,8,8. Tetra cyunoqni no dimethane (TCNQ) [4,5].

A widely studied semi conducting polymers is based on oligothiophenes as donator. Here we used the polyaniline, polypyrrole, polythiophene and polypyridine as molecules in conjunction with TCNE, TCNQ, DDQ, Chloranil, and KI-I₂ molecule on the acceptor side. This charge transfer complex (CTC) system has potential applications as an organic semiconductor material and some of its optical and electronic properties have been investigated by photo emission spectroscopy (PES) and electro-luminescence measurements and recently by scanning tunnelling spectroscopy (STS) [6,7].
1.1 Charge transfer complex arrangement

The charge transfer complex interaction with molecule was initially placed above the polymer molecule. Then by gradually decreasing the distance between the molecules a potential minimum was finally achieved. Then symmetry inequivalent initial geometries were chosen by placing the charge transfer complexes centered either above a polymer ring or above the original polymer connection.

In case of thiophene the fully relaxed centered structure is shown in Fig which includes a few key characteristics.

1. The TCNQ is adsorbed paralleled at a medium distance of 3.4 Å
2. Its axis is aligned parallel to the carbon carbon bond of the two underlying thiophene rings
3. There is an alternating twist of the thiophene rings by 4.8\degree with the sulphur atoms pointing away from the TCNQ
4. The end rings are bent downwards, pointing away from the TCNQ [6,8,9].

1.2 Charge transfer complexes in inorganic chemistry

In inorganic chemistry, charge transfer complexes involve electron transfer between metal atoms and ligands. There are two types of inorganic charge transfer complexes

1) Ligand to metal charge transfer complex (LMCT) The electron moves from molecular orbitals (MO) with ligand like character to metal like one, the complex is called ligand to metal charge transfer complex.
2) Metal to ligand charge transfer complex (MLCT) The electron moves from the MO with metal like character to the ligand like one. The complex is called a metal-to-ligand charge transfer complex [3].

1.3 Characterization of charge transfer complexes

The characterization of charge transfer complexes is a well known procedure. Early work on charge transfer complexes was done by Benesi and Hildebrand [10] on Iodine aromatic hydrocarbon complexes. Since this time a great deal of theoretical and experimental interest has been generated on these and other non-ionic complexes.

These complexes are characterized by an intense electronic absorption in the visible or near ultraviolet spectrum. Mulliken [11] considered such complexes to arise from a Lewis acid base type interaction, the bond between the components of the complex arising from partial transfer of a $\pi$-electron from the $\pi$-base (aromatic molecule) to orbitals of the $\pi$-acids. The theory of charge transfer complexes has recently been discussed by Kosower [12].

1.4 Donor acceptor interaction in charge transfer complexes

The molecular charge transfer complexes are based on the interaction between two molecules species, namely donor (D) and accepter (A). The donor molecules has small ionization energy (IP) while the counter pas accepter molecule has a large electronegativity or electron affinity (EA). When donor and accepter intract. The charge is redistributed among the compound. The donor species oxidize by the loss of charge and the
acceptor is reduced. The result is a charge transfer salt $D_mA_n$ described by the following equation [13].

$$[D_m] + [A_n] \rightarrow \frac{3}{4}[D_m] + 0 + [A_n] - 0$$

Where $0$ is the charge transfer ratio and $m$ and $n$ are integers.

In some case, these donor-acceptor interactions mediate the formation of charge transfer crystalline solids in which organic molecules are stacked in homo molecular stacks. Donor and acceptors interact usually weakly to form complexes

$$D + A \xrightleftharpoons{K_c} D, A$$

$K_c$ is complexing constant

The complex absorbs light in a manner different from either $D$ or $A$ such that an electron is transferred from $D$ to $A$

$$D, A \xrightarrow{h\nu} D^+, A^-$$

The theory of charge transfer complexes suggests that the ground state is stabilized by some contribution from the excited state, and that the light absorption process is more accurately described as

$$D, A (\leftrightarrow D^+, A^-) \xrightarrow{h\nu} D^+, A^- (\leftrightarrow D, A)$$

The wave function for the ground ($N$) and excited ($E$) states are given

$$\psi N = a\psi_0(D,A) + b\psi_1(D^+,A^-)$$
$$\psi E = a\psi(D^+,A^-) - b^*\psi(D,A)$$

The complexing constant $K_c$ might be related to the donor and acceptor properties of the components of the complex.
For ultraviolet absorption for the complex. The concentration of the components the value of the equilibrium constant $K$ and molar absorptivity $\varepsilon$ can be determined separately.

$$k = \frac{[c]}{[[A] - [C]][donar]}$$

Where $C$ is constant it may be evaluated from the expression

$$d = [C]\varepsilon_c l$$

Where $d$ is the maximum optical density $\varepsilon_c$ is the molar extinction coefficient of the complex and $l$ is the path length in centimetres solving far[c], substitution and rearrangement give the

$$\frac{[acceptor]l}{d} = \frac{1}{K\varepsilon[donor]} + \frac{1}{\varepsilon}$$

When this expression is multiplied by the [donor]. One arrives at an equation known as scatt equation [12,13].

$$\frac{[donor][acceptor]l}{d} = \frac{1}{K\varepsilon} + \frac{1}{\varepsilon}[donor]$$

TCNQ has two dicyanomethylene termination groups ($C_3N_2$) with strong electrophilic character. The central part of TCNQ consists of a quinonoid ring that stabilizes the anionic system because it allows an efficient charge delocalization (Fig.1.1) TCNQ exhibits in gas phase two successive one-electron reductions, both chemically and electrochemically reversible. This molecule can accommodate up to two electrons in the central ring that, upon charge injection, increases its aromaticity. A most widely studied class of semiconducting polymers that can be rendered conducting upon doping (so far with inorganic acceptors) is based on polythiophene, which has donor character.

Tetracyanoquinodimethane (TCNQ, in Fig.1.2) is one of the strongest known molecular electron acceptors, and has been used for
doping of molecular organic semiconductors. Polymers doped with reticulated crystalline, conducting charge-transfer (CT) complexes are new, recently discovered polymeric conductors (Jeskae ta1 1981a, b) [14].

Figure 1.1 : TCNQ molecular Structure

Figure 1.2 : TCNQ molecular Structure in different phase.

Figure 1.2 : TCNQ molecular Structure in different phase.
The reactions of iodine as an electron acceptor with various electron donor bases have been extensively studied [15-22]. The formed iodine charge-transfer complexes show interesting physical properties such as electrical conductance [20-21]. In the study of the interaction of iodine with metal acetylacetonates as electron donors, Kuleusky and Butamina [22] as well as Singh and Sahai [23] wrongly claimed that the 360 nm band should be assigned to the blue-shifted iodine band, while the lower peak around 290 nm was to be attributed to the intermolecular charge-transfer (CT) in M(acac)\textit{n}–I\textsubscript{2} complex. Formation of the charge-transfer complexes between calyx crowns [24] and iodine in chloroform solution was studied using UV-visible spectrophotometry. The stability constants were found from the thermodynamic properties for acceptors: 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, \textit{pCA}), tetracyanoethylene (TCNE) and 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil). Different colored charge-transfer complexes and radical anions were obtained. Different variables affecting the reactions were studied and optimized [25].

1.5 Effect of solvent

In order to select the most appropriate solvent, the reactions were carried out in different solvents. Small shifts in the position of the maximum absorption peak were observed, and the absorption intensities were also influenced. Methanol gave maximum sensitivity in case of DDQ. Acetonitrile was considered as an ideal solvent for the other-acceptors. This is because it offered maximum sensitivity, which was attributed to the high dielectric constant of acetonitrile that promotes maximum yield of radical anions, in addition to its high solvating power.
for acceptors. UV-visible and IR spectroscopic studies of compounds, are used to deduce the structure and new electrical behaviour of these new compounds. A common procedure was used for the preparation of charge-transfer complexes [26].

Charge-transfer complex of DDQ shows (C≡N) stretching vibration at 2220 cm\(^{-1}\) [27, 28] compared with normal value of (C≡N) vibration (2230 cm\(^{-1}\)) in the free DDQ. The UV-visible spectra were recorded for 200-750 nm. There are two types of electronic transitions, viz., n-\(\pi^*\) and a transitions.

2. One and Two dimensional conductors

2.1 One dimensional conductors

Solid-State devices in which electrons are confined to two dimensional planes have provided some of the most exciting scientific and technological breakthroughs of the last 50 years. From metal-oxide-silicon field effect transistors to high mobility gallium-arsenide hetero structures, these devices have played a key role in the microelectronics revolution and are critical components in a wide array of products from computers to compact-disk players. From a more parochial perspective, the study of electrons in two-dimensional systems has also been responsible for two Nobel prizes in physics – to Klaus von Klitzing in 1985 and to Robert Laughlin, Horst Störmer and Daniel Tsui in 1998. This is testimony to the basic as well as applied interest of such devices (see Heiblum and Stern in further reading). However, 1-D systems are also proving to be very exciting. For many years, studies of quasi 1-D
systems, such as conducting polymers, have provided a fascinating insight into the nature of electronic instabilities in one dimension. In addition, 1-D devices such as “electron waveguides” – in which electrons propagate through a narrow channel of material – have been created. Experiments on these devices have shown, for example, that the conductance of “ballistic” 1-D systems – in which electrons travel the length of the channel without being scattered – is quantized in units of $e^2/h$, where $e$ is the charge on the electron and $h$ is the Planck constant. These systems, however, have been limited by the fact that they are inherently complex and/or difficult to make. What has been lacking is the perfect model system for exploring one dimensional transport.

2.2 Two dimensional conductors

In quasi 1D or 2D conductors in which the (T, pressure) phase diagram exhibits a border line between superconducting and spin density wave (SDW) phases, it is favourable to create a phase segregation in the direct space by forming alternatively superconducting and magnetic slabs [29].

One of the recent remarkable topics in the field of the organic conductors is the hybrid system of organic donor molecules and inorganic magnetic anions. In these systems, the interaction between conduction electrons and magnetic moments has provided some peculiar phenomena such as the field induced superconductivity (FISC), where the internal field created by the magnetic ions plays an essential role [30]. The quasi-two dimensional conductor $k$-(BETS)$_2$FeBr$_4$ (BETS = bis(ethylenedithio)tetrascalenafulvalene), classified into this category, is
the first antiferromagnetic (AF) organic superconductor at ambient pressure [31,32].

Electron transport in amorphous semiconductors has been investigated for decades [33,34]. In recent years, “artificial solids” formed by close packed arrays of monodispersed metallic nanostructures have provided novel model systems for the study of electron transport [35, 36, 37]. Semiconductor nanocrystals [38] can now be synthesized for a wide range of materials with nanometer sizes leading to strong quantum confinement. One of the best characterized systems is CdSe [39].

2.3 Mott transition in two dimensions (2D) organic conductors

For the study of the Mott transition in two dimensions (2D), organic conductors, which are low-dimensional and highly compressible, are suitable. The organic family with a half-filled band [40]. Mott transition is induced by pressure in the organics but by carrier doping in the copper oxides. Furthermore, the exotic pseudogap behaviour is emergent near the Mott transition in both the organics[41] and copper oxides[42,43]. These similarities suggest that they share common physics—the Mott transition in 2D correlated electrons.

The Mott insulator $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (denoted by $\kappa$-Cl hereafter) undergoes an insulator to metal transition when pressure is applied and thus allows us to approach the critical endpoint of the first-order Mott transition[44-47]. This feature provides the foundation of our research because the critical phenomena, which are direct clues to identifying the universality class, are generally found around the endpoint, in analogy to the liquid–gas transition. In the Mott transition,
the conductance in the metallic region was found to describe the critical phenomena very well by Limelette et al.[48].

2.4 Angular effects of the two dimensions (2D) organic conductors

Angular effects of the interlayer magneto-resistance have been extensively studied in organic conductors. These remarkable effects have been explained by the semiclassical Magneto-transport theory considering three-dimensional Fermi surfaces. However, MacKenzie and Moses [49] claimed that the angular-dependent magneto-resistance oscillations (AMRO) could exist even in multilayer systems with incoherent interlayer coupling, where the in-plane scattering happens very often than the interlayer hopping and the three-dimensional Fermi surface no longer exists. On the other hand, existence of the resistance peak in a magnetic field parallel to the layers is not expected in incoherent systems [49]. They applied their theory to low dimensional organic conductors and discussed the interlayer coherency of these compounds. However, no experimental confirmation of their prediction has been done since it is difficult to evaluate the interlayer coherency in organic conductors[50].

Studies over the past decade have clearly demonstrated that the nature of the ground states has many low-dimensional electronic systems are intimately related to the topology of their high-temperature Fermi surfaces, for example, the nesting instabilities associated with spin density- waves SDW and charge-density-waves CDW d states,1,2 momentum-dependent interlayer hopping and scattering mechanisms, and
pseudo gaps and nodal energy gaps in high-temperature superconductors. Consequently, any experimental technique capable of probing FS topology, or even the nature of the quasi particle spectrum locally on the FS, is extremely valuable for studies of broken symmetry states in low-dimensional electronic systems[51].

2.5 Two Dimensional system

A free particle which can move along a plane, but is bound in the direction orthogonal to that plan is said to behave two dimensionally. This occurs in real materials when the thickness of a thin film is of the order of the de Broglie wave length of the electron in the material for example, a thin film in the x-y plane is bound in the \( \hat{z} \) direction the behaviour of the electron along this axis can not be described classically, but rather, by bound states.

The behaviour of the electron in the \( \hat{x}, \hat{y} \) - directions are described by plane waves. The solution to the two dimensional time-independent Hamiltonian.

\[
\left( \frac{\hbar^2}{2m} \nabla^2 + \vartheta \right) \Psi = E_n \Psi
\]

Is given by these plane wave solutions [52].
3. Introduction of hopping conduction

Phonon assisted hopping transitions of particles between spatially distinct locations are a phenomenon encountered in a diverse variety of solid state systems. For instance, in weakly doped and compensated semiconductors the phenomenon of impurity conduction arises from hopping of electrons between impurity sites. Furthermore, in crystals with a narrow conduction band and strong electron-phonon interaction (e.g. orthorhombic sulphur) a new quasi-particle, the small polaron, is formed, which at sufficiently high temperatures moves through the crystal by hopping transitions from site to site.

The elementary hopping process may be either a thermally activated jump over the potential barrier separating neighbouring sites (“over-barrier hopping”) or phonon-assisted tunnelling through the barrier (“under-barrier hopping). Atom hopping is an important transport mechanism, for example, in ionic crystals, metal hydrides, or on surfaces of solids. The hopping of ions or electrons within spatially localized regions represents a well-known dielectric loss mechanism [53, 54, 55].

Another example of hopping motion in solids is the hopping diffusion of Frenkel excitons in molecular crystals [56] which is directly analogous to that of small polarons. Recently, phonon-assisted hopping of electrons between soliton bound states has been discussed as possible dominant conduction mechanism in lightly doped quasi one-dimensional Peierls systems such as polyacetylene [57], and hopping motion of solitons pinned by disorder has been predicted [58].
3.1 General introduction

Hoping conduction is defined as electric conduction in which the carrier transport is via electrons hopping from one localized state to another. Electron transport through localized states (shallow-level states or deep-level states) within the band gap of a semiconductor includes (as shown in Fig. 1.3).

Figure 1.3

1. Electron hops from a state to another state that has a higher energy. A thermal energy is required for this move. Let us denote the energy difference as $E_{\text{hop}}$. This process is thermally assisted tunnelling. It depends on temperature.

2. Electron hops from a state to another state that has equal energy. This transport is tunnelling process. It does not depend on temperature.

Electron hops from a state to another state that has a lower energy. This transport is a tunnelling process with the emission of a phonon(s). It does not depend on temperature.
3.2 The necessary conditions for the occurrence of hopping are:

1. Wave functions of the two localized states must overlap.
2. Occupied and empty states must be present for the hopping to occur. This condition requires the hopping should happen between states close to the Fermi level.

An energy is necessary for the electron hopping from a localized state to another localized state with a higher energy level.[59,60].

3.3 Absorption of radiation by semiconductors

The fundamental absorption in a semiconductor refers to interband (band –to – band) or to exciton transition. There is excitation of an electron from the valence band to conduction band. There is a rapid increase in absorption in the band gap region of frequency. There is threshold near \( E_g \) (band gap) and this is called absorption edge.

The moment of a photon is very small compared to the momentum of the crystal. The phonon absorption process conserves the momentum of an electron. The absorption coefficient is proportional the probability of transition and densities of states of initial and final states [61].

3.4 Allowed indirect transition

In the absorption transitions between two direct valleys all the momentum conserving transitions are allowed. The initial and final states are related by \( E_f = h\nu - E_i \) for parabolic bands as shown in the Figure 1.4.
\[(E_i - E_g) = \frac{\hbar^2 k^2}{2m_*} \quad \text{and} \quad E_i = \frac{\hbar^2 k^2}{2m_*}\]

Therefore,
\[h\nu - E_g = \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_*} + \frac{1}{m_e} \right) = \frac{\hbar^2 k^2}{2m_r}\]

The density of states is given by
\[N(h\nu) \, d(h\nu) = \frac{8\pi k^2 \, dk}{(2\pi)^3} = \frac{(2m_r)^{3/2}}{2\pi^3 \hbar^3} (h\nu - E_g)^{1/2} \, d(h\nu)\]

where \(m_r\) is the reduced mass. This shows that \(\alpha(h\nu) = A (h\nu - E_g)^{1/2}\), \(A\) is a constant. Thus in allowed direct transition the absorption coefficient is proportional to \((h\nu - E_g)^{1/2}\).

### 3.5 Forbidden direct transition

In some materials, quantum selection rules forbid direct transitions at \(k=0\) but allow them at \(k \neq 0\). The transition probability increases with \(k^2\), which is proportional to \((h\nu - E_g)\). The density of states is proportional to \((h\nu - E_g)^{1/2}\). Thus the absorption coefficient is proportional to \((h\nu - E_g)^{3/2}\), i.e., \(\alpha(h\nu) = A (h\nu - E_g)^{3/2}\) where \(A\) is given by \(A = \frac{B}{h\nu}\), here \(B\) is a constant. Thus, \(\alpha h\nu = B (h\nu - E_g)^{3/2}\).

### 3.6 Indirect transitions

When a transition requires a change in both energy and momentum and since a photon can not provide momentum, a two – step process occurs. A phonon is a quantum of lattice vibration. A phonon of the required momentum change is used in a two – step process as shown in the Figure 1.5.
If $E_p$ is the phonon energy, $h\nu_c = E_f - E_i + E_p$, $h\nu_a = E_f - E_i - E_p$ for emission and absorption of phonons.

The densities of states at $E_i$ and $E_f$ are given by

$$N(E_i) = \frac{1}{2\pi^2 h^3} (2m_\text{h}^*)^{3/2} E_i^{1/2}$$

$$N(E_f) = \frac{1}{2\pi^2 h^3} (2m_\text{e}^*)^{3/2} (E_f - E_g)^{1/2}$$

Thus, $N(E_f) = \frac{1}{2\pi^2 h^3} (2m_\text{e}^*)^{3/2} (h\nu - E_g \mp E_p + E_i)^{1/2}$

By integrating above all possible combinations of states,

$$\alpha_a(h\nu) = \frac{A(h\nu - E_g - E_p)^2}{\exp \frac{E_p}{k_B T} - 1}$$

and

$$\alpha_e(h\nu) = \frac{A(h\nu - E_g + E_p)^2}{1 - \exp \frac{E_p}{k_B T}}$$

The total $\alpha$ is given by

$$\alpha = \alpha_e + \alpha_a.$$ 

$\alpha_a$ is valid for $h\nu > E_g - E_p$ and $\alpha_e$ is valid for $h\nu > E_g + E_p$.

Thus there is break in the straight line plot of $\alpha^{1/2}$ vs $h\nu$. Therefore there is a change in slope as indicated in the Figure 1.6.
3.7 Band tailing

There is a perturbation of the bands by the formation of tails of states extending the bands into the forbidden energy gap. This happens due to impurities. An ionized donor exerts attractive and repulsive forces on electrons and holes, respectively. The densities of states lead to conduction band states at lower potential and valence band states at higher potential. At high concentrations of impurities, the impurity states form a band whose distribution tail into the energy gap. Also there is deformation potential. A local mechanical strain is generated by impurities. Either there is compression or dilation. Compression increases energy gap and dilation reduces energy gap. Dislocations generate similar effect.

Because of the above – discussed band tailing effects, one finds an exponentially increasing absorption edge rather than a sharp cut – off with step function. It is found that \( \frac{d(\ln \alpha)}{d(h\nu)} = \frac{1}{K_\alpha T} \) and this is called Urbach’s rule. The final states form an exponential tail described by \( N_f = N_o e^{E/E_0} \). Here \( E_0 \) is called the width of the tail and is calculated by

\[
E_0 = \left( \frac{d(\ln \alpha)}{d(h\nu)} \right)^{-1}
\]
3.8 Burstein – Moss shift

If a semiconductor is heavily doped, the Fermi level is inside the band (the conduction band in an n-type material) by a quantity $\xi_n$ as shown in the Figure 1.7.

The states below $\xi_n$ are already filled, and transitions to states below $E_g + \xi_n$ are forbidden. Thus absorption edge shift to higher energies by about $\xi_n$. This shift in the absorption due to band filling effect is called Burstein – Moss shift. In n-type germanium only phonon emission occurs and edge is shifted to $E_g + E_p + \xi_n$.

In heavily doped indirect – gap semiconductors, momentum is conserved by electron – electron scattering or impurity scattering. The scattering probability is proportional to the number N of scatters and $\alpha = AN (h\nu - E_g - \xi_n)^2$ where A is constant. Heavy doping leads to an effective shrinkage of the energy gap.

3.9 Free – carrier absorption

The Drude model leads to $\alpha_f \sim \lambda^2$ where $\alpha_f$ is the absorption by free carrier and $\lambda$ is the wavelength of light. Thus in a metal $\alpha_f$ is proportional to $\lambda^2$. However, in a semiconductor the absorption by free carrier in a conduction band occurs in a region $h\nu > E_g$ and is proportional to $\lambda^p$ where p- can range from 1.5 – 3.5. The electron must make a transition to a higher energy state within the same valley for absorbing a photon. The transition requires an additional interaction for conserving...
momentum. The change in momentum can be provided by interaction with phonons or ionized impurities. The collision with the semiconductor lattice results in scattering by acoustic phonon leading to absorption increasing as $\lambda^{1.5}$. Scattering by optical phonons gives a dependence of $\lambda^{2.5}$ while scattering by ionized impurities gives dependence on $\lambda^3$ or $\lambda^{3.5}$.

In general, when all the three processes contribute and resultant absorption coefficient is given by,

$$\alpha_f = A \lambda^{1.5} + B \lambda^{2.5} + C \lambda^{3.5}$$

where A, B and C are constants.

The dominant mode of scattering will depend on the impurity concentration.

It is found by experience that $\alpha_f \sim \lambda^3$ for neutral impurities, $\alpha_f \sim \lambda^{3.5}$ for negatively charged impurities, $\alpha_f \sim \lambda^4$ for positively charged hydrogen-like impurities and $\alpha_f \sim \lambda^5$ for impurity band scattering.

From a detailed account of light absorption by electrons [62] in localized states,

$$\alpha = \frac{\hbar \omega - E_i}{\hbar^2 \omega^2 (\hbar^2 \chi^2 + 2m^*(\hbar \omega - E_i))^i}$$

Where $E_i$ is the impurity ionization potential. The quantity $\chi^{-1/2}$ is equal to the distance at which the probability of locating the electron decreases e times. $\alpha$ increases linearly with frequency for $\hbar \omega < 2E_i$ and passes through a maximum then decreases at first slowly ($\sim \omega^{-1}$) but much faster in the end. For $E_i$ very less than $\hbar \omega$, $\alpha_f \sim \omega^{-5}$ or $\alpha_f \sim \lambda^5$ from the above equation.

The theory of absorption of radiation of the hydrogen atom may be applied to the localized states with hydrogen-like spectrum, then the absorption coefficient is given by
\[
\alpha = N_{\text{loc}} \frac{2^{10} \pi^2 e^2}{3ncm^* E_i} \left( \frac{E_i}{\hbar \omega} \right)^4 \left[ \exp \left( \frac{4}{\hbar \omega} \right) \arctan \left( \frac{1}{2 \pi \frac{E_i}{\hbar \omega}} \right) \right] \times \frac{\exp \left( \frac{2 \pi}{\hbar \omega} \right)}{1 - \exp \left( \frac{2 \pi}{\hbar \omega} \right)}
\]

where \( n \) is refractive index, \( E_i \) is the impurity ionization energy and \( m^* \) is the effective mass. For \( E_i \ll h \omega, \alpha_i \sim \omega^{-4} \sim \lambda^4 \) for hydrogen – like impurities from the above equation.

4. **Small polaron model**

A necessary prerequisite of hopping transport is the existence of spatially localized charge carriers. Different mechanisms of charge carrier localization are known one of them is small-polaron model [63, 64, 65]. As mentioned above, in crystals with a narrow conduction band and strong interaction with phonons anew quasi-particle, the small polaron, is formed, the size of which is smaller than the interatomic spacing. Owing to the lattice translational symmetry, in such a system a localized state is quasi-stationary and occurs only at sufficiently high temperatures where the time between consecutive hops is shorter than the decay time of a small-polaron wave packet located are a site. At low temperatures, however, the interaction with phonons leads only to a renormalization (narrowing) of the conduction band and the small-polaron motion is band-like.
5. Charge Density Waves

Density waves are broken symmetry states of metals, due to electron-phonon or electron-electron interactions. The CDW is an electronic-lattice instability (while the electron-electron interaction generates the so-called Spin Density Waves (SDW)), and the driving force behind the CDW instability is the reduction in the energy of electrons in the material as a consequence of establishing a spontaneous periodic modulation of the crystalline lattice with an appropriate wave vector.

CDW were first discussed by Fröhlich in 1954 and by Peierls in 1955; the highly anisotropic band structure is really important to observe this ground state in metals. Indeed the experimental evidence of these ground state was found much later their theoretical prediction, when the so-called low-dimensional materials were discovered and investigated.

Another important concept has to be introduced at this level: the difference between a commensurate and an incommensurate CDW. The former is a CDW for which the charge modulation has a period equal to a rational number of the underlying lattice spacing $a$, while the latter is a CDW for which the ratio between the period of the charge modulation and the lattice spacing is equal to an irrational number. In other words if we think to get a maximum of the charge modulation corresponding to a lattice site, for the commensurate CDW we will always find another lattice site over which the charge modulation is maximum, while for the incommensurate CDW this does not happen[66].
Charge density waves (CDWs) are a type of coupled electronic-lattice instability found in quasi-low dimensional materials. The driving force behind the instability is the reduction in energy of electrons in the material as a consequence of establishing a spontaneous periodic modulation of the crystalline lattice with an appropriate wave vector. The symmetry of the CDW state is very sensitive to the electronic structure of the host material. Charge density wave has been observed in quasi-one dimensional compounds, high temperature superconductors, manganites and many others [67-70]. Conventionally, Fermi surface nesting is the dominant and this mechanism is for CDW. However, it fails to explain the CDW in the 2H-structured transition metal dichalcogenides (2H-TMD’s), which is actually the first two-dimensional CDW materials discovered in 1975[71].

Charge-density waves (CDWs), formed in low dimensional conductors, have attracted considerable attention recently due to their relation to the metal insulator (MI) phase transitions in strongly correlated electronic systems. In order to understand the characteristic properties of CDWs, information about their local structures is extremely important. As a result, numerous studies have been performed using scanning tunneling microscopy (STM) and related techniques [72-77].
6. Polarons to bipolarons

The polaron to bipolaron transition in disordered media under the influence of a broadband ac electric field is suggested: ac conductivity vs. frequency measurements in disordered media with inhomogeneous disorder induce spatio-temporal fluctuations of the density of polarons yielding polaron to bipolaron transformation. The external field results in the transition, alternatively to an increasing doping level. The assertion is confirmed by performing successive complex impedance measurements in disordered media. A systematic increase of the real part of the ac conductivity in the frequency domain, followed by mutual reduction of the magnetic inductivity of conducting polypyrrole, are explained [78].

Conducting polypyrrole is characterized by inhomogeneous disorder: short – range ordering in the polymer chains result in the appearance of conducting grains embedded into an insulating amorphous matrix [79, 80, 81-85]. An electric charge carrier (such as a polaron) can hop along each chain (intra-chain transfer) and over cross linked chain clusters. Charge flow is favored within the ordered polaron-rich grains, while inter-grain transport occurs by penetrating the highly disordered insulating matrix [86]. The system can be virtually described as a network of conducting pathways with distributed effective length [87].

The transitions from the reduced-polaron–bipolaron states of polypyrrole (ppy) were analyzed by in situ Raman spectroelectro chemistry. The distinct vibrational modes presented by the polymer in different oxidation levels were assigned to specific signatures of polaron and bipolaron states. As the polymer was oxidized from the neutral state,
an intermediary phase featuring vibrational bands from both the benzoid (reduced) and the quinoid (oxidized) forms were observed. This intermediary phase was correlated to the polaron state. The results were compared with previous ESR data that confirm the presence of polaron and bipolaron states in the potential region where the vibrational modes of these phases were identified [88].

The polaron–bipolaron model is widely used to explain electrochromic and electrochemical behaviour of conducting polymers. In fact, polaron and bipolaron states are associated to the intermediary energy levels that arise within the electronic band gap region of the polymer due to oxidation [89].

7. Conducting polymers

Conducting polymers were first discovered in 1976. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared by accident by Shirakawa [90,91]. The subsequent discovery by Alan Heeger and Alan MacDiarmid that the polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities, and an intensive search for other conducting polymers soon followed [92]. In 1976, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students found that conductivity of polyacetylene increased by up to 6 orders of magnitude when reacted with iodine (from 10⁻⁴ S/cm to 10² S/cm); this phenomenon, known as doping, is as a result of charge carriers. In addition, it was discovered that varying the level of doping
yielded polymers exhibiting wide range of electrical properties, from insulator, or semi-conductor, to metal [93].

These polymers must be doped (usually meaning altering the number of pi electrons) in order to render the polymers truly conducting. In conjugated polymers the electronic configuration is fundamentally different, where; the chemical bonding leads to one unpaired electron (the electron) per carbon atom. Moreover, bonding, in which the carbon orbitals are in the sp<sup>2</sup>p<sub>z</sub> configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer.

This electronic delocalization provides the highway for charge mobility along the backbone of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e. the number and kind of atoms within the repeat unit, with the result that such polymers can exhibit semiconducting or even metallic properties.
Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electronically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework.

Figure 1.8: Formation of molecular orbitals
The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. Hatano et al [94,95] are the first to report the electrical conductivity of the order of $10^{-5}$ S/cm for trans polyacetylene sample.

Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole, polythiophene, poly paraphenylene, polyphenylene sulphide, polyaniline, polyphenylene vinylene etc.

7.1 Types of Conducting Polymers

Conducting polymers can be classified into different types on the basis of conduction mechanism that renders electrical conductivity to polymers.

- Conducting polymer composites
- Organometallic polymeric conductors
- Polymeric charge transfer complexes
- Inherently conducting polymers.

Brief description of the conducting materials have been given here but as present study deals with the inherently conducting polymers, detail discussion have been done for this type of conducting material.
7.1.1 Conducting Polymer Composites

Conducting polymer composites are mixture or blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastic. Various conductive fillers have been tried such as carbon blacks, graphite flakes, fibers, metal powders etc. The electrical conductivity of the compound is decided by the volume fraction of the filler. A transition from insulating to non-insulating behavior is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%. The various polymers, which have been used as major matrix, are typically PP, Nylon, and PVC etc.

7.1.2 Organometallic Polymeric Conductors

This type of conducting materials is obtained by adding organometallic groups to polymer molecules. In this type of materials the d- orbital of metal may overlap orbitals of the organic structure and thereby increases the electron delocalization. The orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it.

7.1.3 Polymeric Charge Transfer Complexes

Polymeric charge transfer complexes (CTC) are formed when acceptor like molecules are added to the insulating polymers. There are many charge transfer complexes reported in the literature, e.g. CTC of tetrathaifulvalene (TTF) with bromine, chlorine etc is a good conductor. The reason for high conductivity in polymeric charge transfer complexes
and radical ion salts are still somewhat obscure. It is likely that in polymeric materials, the donor – acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhanced electron delocalization.

7.1.4 Inherently Conducting Polymers

Research in the field of inherently conducting polymer started nearly three decades ago when Shirakawa and his group found drastic increase in the electrical conductivity of polyacetylene films when exposed to iodine vapor. The highest crystalline variety of the polyacetylene showed electrical conductivity of the order of $10^{-5}$ S / cm and was in all possibility the trans-form of polyacetylene. Leading on from this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state.

The electronic properties of conjugated polymers are due to the presence of electrons. The conjugated polymers are studied as the intrinsically conductive polymers. The conductivity in such polymers arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. It is therefore necessary for the polymer backbone is necessary for a polymer to behave as an electrical conductor.

This delocalization of electrons may occur through the interaction of n-bonded electrons in a highly conjugated chain or by a similar interaction of n-electrons with nonbonded electrons of electron rich
hetero-atoms (eg, S, N, etc.) in the backbone. For this the molecular structure of the backbone should be planar. There should be no torsion at the bonds, which would decrease the delocalization of the electron system. Some of the examples of conjugated polymers.

![Polyacetylene](image)

![Polyphenylene](image)

![Poly(phenylene vinylene)](image)

![Polyaniline](image)

![Polypyrrole](image)

![Polythiophene](image)

Figure 1.9: molecular structure of some polymers
7.2 Conjugated polymers and Conventional polymers

1. Band gap $E_g$ (electronic band gap) is small (~ 1 to 3.5 eV) with corresponding low excitations and semiconducting behavior.

2. Can be oxidized or reduced through charge transfer reactions with atomic or molecular dopant species.

3. Net charge carrier mobilities in the conducting state are large enough and because of this high electrical conductivity is observed.

4. Quasiparticle, which under certain conditions, may move relatively freely through the material.

7.3 Polyaniline (PANI)

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields.

Among all the conducting polymers, polyaniline is known for it’s

1. Ease of synthesis
2. Environmental stability and
3. Easy to dope by protonic acids.

Polyaniline is well-known as an environmentally stable and highly tunable conducting polymer, which can be produced as bulk powder, cast films, or fibers. This, in conjunction with the feasibility of low-cost, large-scale production, makes it an ideal candidate for various applications. The term Polyaniline corresponds to a class of polymers
having up to 1000 repeat units (also called mers) and was first reported in 1862 [96]. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.

Polyaniline exists in four main oxidation states viz.

1. Leucoemeraldine base,
2. Emeraldine base
3. Emeraldine salt and
4. Pernigraniline
5. Protoemeraldine

7.4 Chemical Synthesis

Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium peroxy-di-sulfate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. In the review article by Gospodinova et al. [97] they had reported that the propagation of polymer chains proceeds by a redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of monomer to the chain end. The high concentration of a strong
oxidant, \((NH_4)_2S_2O_8\), at the initial stage of the polymerization enables the fast oxidation of oligo and polyaniline, as well as their existence in the oxidized form.

**7.5 Charge Transport in Conducting Polymer**

It is well known that polymers with conjugate bonding system, running through the whole molecule are usually electrically conducting. The electrical properties of conducting polymers depend on the electronic band structure. When the bands are filled or empty, no conduction occurs. If the band gap is small compared with thermal excitation energies, electrons are excited to the conduction band and thus conductivity increases. When the band gap is too wide, thermal excitation is insufficient to excite electrons to the conduction band and the material is an insulator.

The conductive polymers carry current without having partially empty or partially filled bands. The most important characteristics, however, is that when the polymers are highly oxidized the charge carriers are spin less. To explain the conduction phenomena, it is proposed that when an electron is removed from the top of the valence band by oxidation a vacancy (hole or radical cation) is created, but it does not delocalize completely.

The energy level associated with the radical cation represents a destabilized bonding orbital and thus has a higher energy than that of the valence band. A radical cation that is partially delocalized over some polymer segment is called a ‘polaron’. A dication or ‘bipolaron’ has two
charges associated with the low oxidation levels yield polarons and higher oxidation levels give the bipolarons. Both polarons and bipolarons are mobile and can move along the polymeric chain by the rearrangement of the double and single bonds in the conjugated system that occurs in an electric field. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polymers with nondegenerate ground states. There are several models for electrical conduction. The most widely used is the one electron band model. This is based on extending the simple model of a bond between two atoms over whole crystalline solid.

Figure 1.10 : One electron band model for electrical conduction
7.6 Doping of Polymers

Conductive polymers generally exhibit poor electrical conductivity \((\sigma \leq 10^{-12} \text{ S/cm})\) in the virgin state and behave as insulators. These virgin polymers need to be treated with a suitable oxidizing or reducing agents to remarkably enhance their conductivities to the metallic region. This phenomenon has been termed as “doping”. Doping can be simply regarded as the insertion or ejection of electrons.

7.6.1 Dopants

Dopants are either strong oxidizing or reducing agents. On doping, either positive or negative charge carriers are created in polymers.

\[
\text{Polymer} + \text{Dopant} \rightarrow [\text{Polymer}^+\text{-Dopant}\text{-}]
\]
(Acceptor) charge transfer complex

\[
\text{Polymer} + \text{Dopant} \rightarrow [\text{Polymer}^-\text{Dopant}^+]
\]
(Donor) charge transfer complex

7.6.2 Different Types of Doping

The expression doping is ambiguous and refers to an uptake into pure material of some other material. This uptake may be diffusion of dopants into the fibers, a chemical reaction with internal or surface chains or simple adsorption on the surface. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase, or by electrochemical
oxidation or reduction. The dopant concentration can be determined by chemical or spectroscopic analysis, or simple weight uptake. Doping of polymers may be done by the following methods including [98].

**Redox doping**

Redox doping is the most common method of doping. This is also known as oxidative doping and accomplished by removing pi electrons from the conjugated pi electrons. All conducting polymers e.g., PPy, PT, Pani etc undergo p- and/ or n- redox doping by chemical and/ or electrochemical processes during which the number of electrons associated with the polymer backbone changes.

**Photo doping**

When trans (CH)x is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and polymer undergoes “photo-doping”.

**Charge injection doping**

Charge injection doping is most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Application of an appropriate potential across the structure can give rise to a surface charge layer.
Non redox doping

Although oxidative doping is available to polyaniline, a more common method of producing doped polyaniline is known as acid- doping (or proton doping).

7.6.3 Types of Doping Agents

Dopants may be classified as:

1. Neutral dopants: I_2, Br_2, AsF_3, Na, K, H_2SO_4, FeCl_3 etc.
2. Ionic dopants: LiClO_4, FeClO_4, CF_3SO_3Na, BuNCIO_4 etc.
3. Organic dopants: CF_3COOH, CF_3SO_3Na, p-CH_3C_6H_4SO_3H
4. Polymeric dopants: PVS, PPS

7.6.4 Doping Techniques

Doping in polymers can be done by following ways,

1. Gaseous doping
2. Solution doping
3. Electrochemical doping
4. Self doping
5. Radiation induced doping
6. Ion exchange doping
7.6.5 Effect of Doping on Conductivity

Doping with acceptor or donor molecules causes a partial oxidation (p-doping) or reduction (n-doping) of the polymer molecule. As a result positively or negatively charged quasi-particles are created presumably polarons in the first step of doping. When doping proceeds, reactions among polarons take place, leading to energetically more favorable quasi-particles, i.e. a pair of charged solitons (bipolarons) in materials with a degenerate ground state. Thus due to the changes in the environment of the chains disorders are created from doping.

Once the radical components of the polarons have combined to form bonds, the remaining charges achieve high mobility along the chain. Example showing formation of polarons –bipolarons in polyprrole chain is given in the Fig. 1.11
Electronic conductivity of conducting polymers depend upon numerous factors. Significant among these are

1. Nature or chemical reactivity of the dopant
2. Process of doping
3. Doping level
4. Method and condition of polymer synthesis
5. Processing of the polymer
7.7 Applications

Research shows that conducting polymers exhibit conductivity from the semiconducting range (~10^-5 S/cm) right up to metallic conductivity (~10^4 S/cm). With this range of electrical conductivity and low density coupled with low cost polymeric conductor pose a serious challenge to the established inorganic semiconductor technology. There are mainly two groups of applications for organic conducting polymers which are briefly described as follows:

Group I

These applications just use the conductivity of the polymers. The polymers are used because of either their lightweight, biological compatibility for ease of manufacturing or cost. Electrostatic materials, Conducting adhesives, Electromagnetic shielding, Printed circuit boards, Artificial nerves, Antistatic clothing, Piezoceramics, Active electronics (diodes, transistors), Aircraft structures.

Group II

This group utilizes the electroactivity character property of the materials. Molecular electronics, Electrical displays, Chemical, biochemical and thermal sensors, Rechargeable batteries and solid electrolytes, Drug release systems, Optical computers, Ion exchange membranes, Electromechanical actuators, 'Smart' structures, Switches.
Reference


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