Preface

This thesis deals with the spectroscopic (FTIR spectroscopic and Ultraviolet-visible-near infrared) study of charge transfer complexes of biomolecular compounds.

Chapter 1 is the introductory chapter on introduction of biomolecules, CTCs and semiconducting physics. The biomolecules includes purines and pyrimidines, nucleic acids such as RNA and DNA, proteins and their types such as fibrous, globular and membranes fatty acids and fats, hormones, enzymes, circular molecules and chlorophylls and porphyrins. This follows discussion of charge transfer complexes and radical-ion salts. After this semiconductor physics is discussed particulary involving fundamental absorptions in semiconducting compounds. This includes direct and indirect interband transitions, free-carrier absorption and band tailing.

In chapter 2 The FTIR spectra of charge transfer complexes of purines and pyrimidines with organic acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine are obtained with studied. Adenine, guanine, thymin, cytosine and uracil are the purines and pyrimidines which are found as constituents of DNA and RNA. CT induced hydrogen bonding is concluded on the basis of indirect transitions observed in the infrared range in theses CTCs. Some CTCs show gaussian band revealing delocalization of charge carriers. The CTCs show interband transition in three-dimensions rather than two dimensions unlike CTCs of amino acids. There is no extended hydrogen bonded network spanning the whole crystal; This leads to indirect transition due to locally deformed lattice furnishing a phonon-assisted transition.
Chapter 3 is containing study of FTIR spectra of charge transfer complexes of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). Charge transfer complexes of RNA and DNA with stander organic acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine or KI-I₂ were prepared. The acceptors interact with purines and pyrimidines which are bases of RNA. RNA contains adenine, guanine, thymine, cytosine and uracil in random sequence and RNA molecule is helical with a cavity in center. Small acceptors molecules can go in this cavity and form segregated structure with stacking in one direction. It is form that electronic or polaronic delocalization occurs among RNA molecules and in its charge transfer complexes. Hopping of charge carriers also occurs in two of the complexes. DNA worked as a donor because of purines and pyrimidines (base of DNA) acting as donors. DNA formed only weak molecular lead to oxidative damage of DNA stacks but interacts strongly than donors. DNA is found to be semiconductor with room temperature dc electrical resistivity of the order of 10⁶Ωcm and band gap of about 0.3eV. In the present study, DNA has shown an optical band gap of 0.3eV. However, the CTCs of DNA with acceptors were found to be either semiconducting or semi-metallic. DNA-chloranil and DNA-KI-I₂ were found to be semi-metallic.

Chapter 4 The solid state spectroscopy particularly FTIR spectroscopy of three proteins namely actine, thrombin and γ-globulin and their charge transfer complexes with acceptors such as TCNE, TCNQ, DDQ, chloranil and KI-I2 has been carried out. A half power beta density is found common among these proteins and their CTCs, indicating the folding of one-dimensional chains of polypeptides in three dimensions in tertiary or quaternary structures. Polaron is formed in one-dimensional chain and transported across the chains but hops at chain ends from one molecule to neighboring molecules. This proves fractal
dimensionality one for the globular proteins. Band gaps vs full-width at half-maximum of beta density peaks when plotted shows a straight line.

**Chapter 5** In the present study FTIR spectra of charge transfer complexes of fibrinogen, lipoprotein, albumin and casein are obtained and explained as one or two dimensional conductors. Many of them are semiconductors but some of them are even found to be semi-metallic. Fibrinogen is a fibrous material having chain structure and acting as one-dimensional conductor. Fibrinogen-TCNQ and fibrinogen-TCNE are semimetals. Lipoprotein is a biochemical assembly of protein molecules and lipids having water. Albumin and casein are proteins acting as two-dimensional (layered) conductors. Lipoprotein-TCNQ, Lipoprotein-KI-I$_2$ and Lipoprotein itself are found to be semimetallic. Highly conducting nature of these semimetals may be due to water molecules in the assembly.

**Chapter 6** This chapter divided in two parts. In first part of the chapter results of CTC of arachidic acid and lignoceric acids discussed while in second pare the results of stearic acid and cholesterol are discussed. In the present work, two fatty acids having long chains namely arachidic acid and lignoceric acids are found to form charge transfer complexes with organic acceptors such as TCNQ, TCNE, DDQ, chloranil and KI-I$_2$. These CTCs are studied with FTIR spectroscopy. Most of them are found to be small band gap semiconductors with band gap lying in the infrared range. Some of them are having more than one band-to-band transition because of multiple band transport. Lignoceric acid-TCNE is found to be an organic semi-metal. The FTIR spectra of stearic acid and cholesterol along with their charge transfer complexes with acceptors such as TCNQ, TCNE, DDQ, chloranil and KI-I$_2$ have been studied in the present work.
Nature of transition, band tailing, free-carrier absorption, gaussian distributions, and half-power beta density distributions are analyzed. It is found that the fatty acid molecules conduct with a very small band gap and acceptors only modify this behavior. Cholesterol shows polaron hopping associated with half-power beta density along fractally one-dimensional chains.

**Chapter 7** The FTIR spectroscopy of charge transfer complexes of hormones namely insulin, thyrotropin-releasing hormone, vasopressin and glucagon with organic acceptors is the subject of present study. It is found that these hormones are small band gap semiconductors except glucagon. The CTCs of these hormones with standard organic acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine or KI-I$_2$ are semiconductors having two band transport. Some of them are Peierls semiconductors while others have non-universal Hubbard gaps. Some of them show hopping conduction in amorphous conductors. Intrinsic electronic conduction with very small band gap of pure hormones is because of parallel stacking of molecules in nano-crystalline materials.

**Chapter 8** Solid state FTIR spectroscopy of enniatin B, beuvericin and some enzymes such as hexokinase, catalase, cytochrom c oxides and pepsin and their CTCs has been carried out in the present study. It is found that enzymes catalase, pepsin and hexokinase are semi-metals. Also their CTCs like catalase-TCNQ, catalase-DDQ, catalase-KI-I$_2$ and cytochrome c oxidase-TCNQ are also semimetals. Other CTCs were small band gap semiconductors. Circular molecular compounds such as enniatin B and beuvericin are also semimetals.

**Chapter 9** Charge transfer complexes of etioporphyrin, protoporphyrin, chlorophyll a and chlorophyll b with organic acceptors such as TCNQ, TCNE,
DDQ, chloranil and KI-I$_2$ have been studied in the present work with FTIR spectroscopy. All of them are found to be semiconducting with band gap lying in the infrared range. Many of them have indirect transitions because of substitutions on the outer periphery of porphin ring system. Residual absorption is found in complexes of protoporphyrin excitons. Etioporphrin and its complexes do not show this absorption at the value of the band gap. This may be because of steric effects present in etiporphyrin because of peripheral substitutions.

**Chapter 10** The UV-visible and near IR spectra of the charge transfer complexes of many solid biomolecules are studied in the present work. These include CTCs of purines and pyrimidines, RNA and DNA, fatty acids such as arachidic acid, lignoceric acid and stearic acid, cholesterol, also proteins such as casein, globulin, fibrinogen and lipoprotein, etc. Gaussian distributions of absorption function are found in CTCs of cholesterol, casein, lignoceric acid, γ-globulin and uracil which can be related with electronic delocalization. Near IR spectra are explained with combination modes of various phonons in the solid state and intermolecular vibrations.