Chapter 1

Introduction: One-dimensional Conductors
1.1 One-dimensional conductors:

One-dimensional models for systems like a linear lattice, free electron gas, spin systems, etc. are quite common in solid state theory for simplification of the calculations and for the interpretation of physical phenomena [1]. It is now possible to verify some of the conclusion of one-dimensional models directly in low-dimensional solids having highly anisotropic structural and physical properties [2, 3]. A set of new phenomena peculiar to low-dimensional nature has opened a distant possibility of high temperature superconductivity [4].

Low-dimensional systems are important because of possibility of high temperature superconductivity in these conductors. The subject was formulated in present status in 1973. In 1973 several inorganic quasi-one-dimensional conductors were prepared and studied [5]. In 1973, the first organic metal was obtained which was one-dimensional [6].

Fabre-Salts are composed of tetramethyltetrathiafulvalene (TMTTF) and Bechgaard-salts of tetramethyltetraselenafulvalene (TMTSF). These two organic molecules [7] are similar except for the sulfur-atoms of TMTTF being replaced by selenium-atoms in TMTSF. The molecules are stacked in columns (with a tendency to dimerization) which are separated by anions. Typical anions are for example octahedral PF$_6$, AsF$_6$ or tetrahedral ClO$_4$ or ReO$_4$. Both material classes are quasi one-dimensional at room-temperature only conducting along the
molecular stacks and share a very rich phase diagram containing antiferromagnetic ordering, charge order, spin-density wave state, dimensional crossover and of course superconductivity. Only one Bechgaard-Salt was found to be superconducting at ambient pressure which is (TMTSF)$_2$ClO$_4$ with a transition temperature of $T_C = 1.4$ K. Several other salts become superconducting only under external pressure. The external pressure one would have to apply to drive most Fabre-salts to superconductivity is so high, that under lab conditions superconductivity was observed only in one compound.

This dimerization is known as a Peierls transition [8]. Peierls discovered it in the 1930’s when writing a section on one-dimensional models in an introductory solid-state textbook. He put it in the book, but didn’t publish it otherwise. As mentioned in the Introduction, it became very relevant later when some theories suggested that quasi-one-dimensional conductors, materials made up of loosely connected chains, each chain having one electron per atom for a half-filled lowest band, might be high-temperature superconductors. It was found instead that many such materials actually became insulators on cooling: the reason was that at high temperatures, the electrons filled states above and below the point $\pi/2a$ fairly equally, so dimerization did not lower the overall energy much. On lowering the temperature, a point was reached where the Peierls transition gave a lower energy state, and the material became an insulator.
1.2 Models for high-temperature superconductivity:

Superconductivity was discovered on April 8, 1911 by Heike Kamerlingh Onnes [9], who was studying the resistance of solid mercury at cryogenic temperatures using the recently-produced liquid helium as a refrigerant. At the temperature of 4.2 K, he observed that the resistance abruptly disappeared. In the same experiment, he also observed the superfluid transition of helium at 4.2 K, without recognizing its significance. In subsequent decades, superconductivity was observed in several other materials. In 1913, lead was found to superconduct at 7 K, and in 1941 niobium nitride was found to superconduct at 16 K.

The next important step in understanding superconductivity occurred in 1933, when Meissner and Ochsenfeld [10] discovered that superconductors expelled applied magnetic fields, a phenomenon which has come to be known as the Meissner effect. In 1935, F. and H. London [11] showed that the Meissner effect was a consequence of the minimization of the electromagnetic free energy carried by superconducting current.

The electrical resistivity of a metallic conductor decreases gradually as temperature is lowered. In ordinary conductor, such as copper or silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of a normal conductor shows some resistance. In a superconductor, the resistance drops abruptly to zero when the material is cooled below its critical
temperature. An electric current flowing in a loop of superconducting wire can persist indefinitely with no power source.

In 1950, the phenomenological Ginzburg-Landau theory of superconductivity was devised by Landau and Ginzburg [12]. This theory, which combined Landau’s theory of second-order phase transition with a Schrödinger-like wave equation, had great success in explaining the macroscopic properties of superconductors. In particular, Abrikosov showed that Ginzburg-Landau theory predicts [13] the division of superconductors into the two categories now referred to as Type I and Type II. Abrikosov and Ginzburg were awarded the 2003 Nobel Prize for their work (Landau had received the 1962 Nobel Prize for other work, and died in 1968).

The complete microscopic theory of superconductivity was finally proposed in 1957 by Bardeen, Cooper and Schrieffer [14,15]. Independently, the superconductivity phenomenon was explained by Nikolay Bogolyubov. This BCS theory explained the superconducting current as a superfluid of Cooper pairs, pairs of electrons interacting through the exchange of phonons. For this work, the authors were awarded the Nobel Prize in 1972.

In 1986, it was discovered that some cuprate-perovskite ceramic materials have a critical temperature above 90 K (−183 °C). Such a high transition temperature is theoretically impossible for a conventional superconductor, leading
the materials to be termed high-temperature superconductor. Liquid nitrogen boils at 77 K, facilitating many experiments and applications that are less practical at lower temperatures. In conventional superconductors electrons are held together in pairs by an attraction mediated by lattice phonons. The best available model of high-temperature superconductivity is still somewhat crude. There is a hypothesis that electron pairing in HTS mediated by short-range spin waves known as paramagnons.

Most of the physical properties of superconductors vary from material to material, such as the heat capacity and the critical temperature, critical field, and critical current density at which superconductivity is destroyed.

On the other hand, there is a class of properties that are independent of the underlying material. For instance, all superconductors have exactly zero resistivity to low applied currents when there is no magnetic field present or if the applied field does not exceed a critical value. The existence of these "universal" properties implies that superconductivity is a thermodynamic phase, and thus possesses certain distinguishing properties which are largely independent of microscopic details.

Superconductors are also able to maintain a current with no applied voltage whatsoever, a property exploited in superconducting electromagnets such as those found in MRI machines. Experiments have demonstrated that currents in
superconducting coils can persist for years without any measurable degradation. Experimental evidence points to a current lifetime of at least 100,000 years. Theoretical estimates for the lifetime of a persistent current can exceed the estimated lifetime of the universe, depending on the wire geometry and the temperature.

In a normal conductor, an electric current may be visualized as a fluid of electrons moving across a heavy ionic lattice. The electrons are constantly colliding with the ions in the lattice, and during each collision some of the energy carried by the current is absorbed by the lattice and converted into heat, which is essentially the vibrational kinetic energy of the lattice ions. As a result, the energy carried by the current is constantly being dissipated. This is the phenomenon of electrical resistance.

The situation is different in a superconductor. In a conventional superconductor, the electronic fluid cannot be resolved into individual electrons. Instead, it consists of bound pairs of electrons known as Cooper pairs. This pairing is caused by an attractive force between electrons from the exchange of phonons. Due to quantum the energy spectrum of this Cooper pair fluid possesses energy gap, meaning there is a minimum amount of energy $\Delta E$ that must be supplied in order to excite the fluid. Therefore, if $\Delta E$ is larger than the thermal energy of the lattice, given by $kT$, where $k$ is Boltzamann’s constant and $T$ is the temperature,
the fluid will not be scattered by the lattice. The Cooper pair fluid is thus a superfluid, meaning it can flow without energy dissipation.

In a class of superconductors known as type II superconductors, including all known high-temperature superconductors, an extremely small amount of resistivity appears at temperatures not too far below the nominal superconducting transition when an electric current is applied in conjunction with a strong magnetic field, which may be caused by the electric current. This is due to the motion of vortices in the electronic superfluid, which dissipates some of the energy carried by the current. If the current is sufficiently small, the vortices are stationary, and the resistivity vanishes. The resistance due to this effect is tiny compared with that of non-superconducting materials, but must be taken into account in sensitive experiments. However, as the temperature decreases far enough below the nominal superconducting transition, these vortices can become frozen into a disordered but stationary phase known as a "vortex glass". Below this vortex glass transition temperature, the resistance of the material becomes truly zero.

In superconducting materials, the characteristics of superconductivity appear when the temperature $T$ is lowered below a critical temperature $T_c$. The value of this critical temperature varies from material to material. Conventional superconductors usually have critical temperatures ranging from around 20 K to less than 1 K. Solid mercury, for example, has a critical temperature of 4.2 K. As of 2009, the highest critical temperature found for a conventional superconductor
is 39 K for magnesium diboride (MgB$_2$), although this material displays enough exotic properties that there is some doubt about classifying it as a "conventional" superconductor. Cuprate superconductors can have much higher critical temperatures: YBa$_2$Cu$_3$O$_7$, one of the first cuprate superconductors to be discovered, has a critical temperature of 92 K, and mercury-based cuprates have been found with critical temperatures in excess of 130 K. The explanation for these high critical temperatures remains unknown. Electron pairing due to phonon exchanges explains superconductivity in conventional superconductors, but it does not explain superconductivity in the newer superconductors that have a very high critical temperature [16].

Similarly, at a fixed temperature below the critical temperature, superconducting materials cease to superconduct when an external magnetic field is applied which is greater than the critical magnetic field. This is because the Gibbs free energy of the superconducting phase increases quadratically with the magnetic field while the free energy of the normal phase is roughly independent of the magnetic field. If the material superconducts in the absence of a field, then the superconducting phase free energy is lower than that of the normal phase and so for some finite value of the magnetic field (proportional to the square root of the difference of the free energies at zero magnetic field) the two free energies will be equal and a phase transition to the normal phase will occur. More generally, a higher temperature and a stronger magnetic field lead to a smaller fraction of the
electrons in the superconducting band and consequently a longer London penetration depth [17] of external magnetic fields and currents. The penetration depth becomes infinite at the phase transition.

When a superconductor is placed in a weak external magnetic field $H$, and cooled below its transition temperature, the magnetic field is ejected. The Meissner effect does not cause the field to be completely ejected but instead the field penetrates the superconductor but only to a very small distance, characterized by a parameter $\lambda$, called the London penetration depth, decaying exponentially to zero within the bulk of the material. The Meissner effect is a defining characteristic of superconductivity. For most superconductors, the London penetration depth is of the order of 100 nm.

The Meissner effect is sometimes confused with the kind of diamagnetism one would expect in a perfect electrical conductor according to Lenz’s law, when a changing magnetic field is applied to a conductor, it will induce an electric current in the conductor that creates an opposing magnetic field. In a perfect conductor, an arbitrarily large current can be induced, and the resulting magnetic field exactly cancels the applied field.

The Meissner effect is distinct from this it is the spontaneous expulsion which occurs during transition to superconductivity. Suppose we have a material in its normal state, containing a constant internal magnetic field. When the
material is cooled below the critical temperature, we would observe the abrupt expulsion of the internal magnetic field, which we would not expect based on Lenz's law.

Until 1986, physicists had believed that BCS theory forbade superconductivity at temperatures above about 30 K. In that year, Bednorz and Muller discovered superconductivity in a lanthanum-based cuprate perovskite material, which had a transition temperature of 35 K. It was soon found that replacing the lanthanum with yttrium raised the critical temperature to 92 K, which was important because liquid nitrogen could then be used as a refrigerant the boiling point of nitrogen is 77 K at atmospheric pressure. This is important commercially because liquid nitrogen can be produced cheaply on-site from air, and is not prone to some of the problems of helium in piping.

1.3 Little’s model:

In 1964, Little suggested that it might be possible to synthesize a room temperature superconductor using organic materials in which the electrons travelled along certain kinds of chains, effectively confined to one dimension [18]. Little’s idea was that the build up of positive charge by a passing electron could be speeded up dramatically if instead of having to move ions, it need only rearrange other electrons. However, if the conduction electrons moved along a one-dimensional chain, polarizable side chains might be attached, and
rearrangement of the electronic charge distribution in these side chains would respond very rapidly to a passing conduction electron, building up a local positive charge [19].

If this worked, order of magnitude arguments suggested possible enhancement of the transition temperature by a factor square root of \( \frac{M}{m} \) over ordinary superconductors, \( m \) being the electron mass.

In the 1970’s, various organic materials were synthesized and tested, beginning with one called TTF-TCNQ, in which a set of polymer-like long molecules donated electrons to another set, leaving one-dimensional conductors with partially filled bands, seemingly good candidates for superconductivity. Unfortunately, on cooling, these materials surprisingly became insulator rather than superconductors! This was the first example of a, Peierls transition a widespread phenomenon in quasi one-dimensional systems.

The basic mechanism of the Peierls transition can be understood with a simple model. It is a nice example of applied second-order perturbation theory, including the degenerate case.

It should be added that in some newer materials the Peierls transition is (unexpectedly) suppressed under high pressure, and superconductivity has in fact been observed in organic salts, but so far only at transition temperatures around one Kelvin: Little’s dream is not yet realized [20].
1.4 Excitons and electron-hole pairs:

An exciton is a bound state of an electron and hole which are attracted to each other by the electrostatic coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge [21].

An exciton forms when a photon is absorbed by a semiconductor. This excites an electron from the valance band into the conduction band. In turn, this leaves behind a localized positively-charged hole. The electron in the conduction band is then attracted to this localized hole by the coulomb force. This attraction provides a stabilizing energy balance. consequently, the exciton has slightly less energy than the unbound electron and hole. The wavefunction of the bound state is said to be hydrogenic, an exotic atom state akin to that of a hydrogen atom. However, the binding energy is much smaller and the particle's size much larger than a hydrogen atom. This is because of both the screening of the coulomb force by other electrons in the semiconductor and the small effective masses of the excited electron and hole. The recombination of the electron and hole, i.e. the decay of the exciton, is limited by resonance stabilization due to the overlap of the electron and hole wave functions, resulting in an extended lifetime for the exciton.

The electron and hole may have either parallel or anti-parallel spins. The spins are coupled by the exchange interaction, giving rise to exciton fine structure.
In periodic lattices, the properties of exciton show momentum (k-vector) dependence.

The concept of excitons was first proposed by Yakov Frenkel in 1931 [22], when he described the excitation of atoms in a lattice of insulators. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge.

**Frenkel excitons:**

In materials with a small dielectric constant, the Coulomb interaction between an electron and a hole may be strong and the excitons thus tend to be small, of the same order as the size of the unit cell. Molecular excitons may even be entirely located on the same molecule, as in fullerenes. This Frenkel exciton, named after Yakov Frenkel, has a typical binding energy on the order of 0.1 to 1 eV. Frenkel excitons are typically found in alkali halide crystals and in organic molecular crystals composed of aromatic molecules, such as anthracene and tetracene.

**Wannier-Mott excitons:**

In semiconductors, the dielectric constant is generally large. Consequently, electric field screening tends to reduce the Coulomb interaction between electrons and holes. The result is a Wannier exciton [23], which has a radius larger than the
lattice spacing. As a result, the effect of the lattice potential can be incorporated into the effective masses of the electron and hole. Likewise, because of the lower masses and the screened coulomb interaction, the binding energy is usually much less than a hydrogen atom, typically on the order of 0.01eV. This type of exciton was named for Gregory Wannier and Nevill Francis Mott. Wannier-Mott excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constant, but have also been identified in liquids, such as liquid xenon.

In single-wall carbon nanotubes, excitons have both Wannier-Mott and Frenkel character. This is due to the nature of the coulomb interaction between electrons and holes in one-dimension. The dielectric function of the nanotube itself is large enough to allow for the spatial extent of the wave function to extend over a few to several nanometers along the tube axis, while poor screening in the vacuum or dielectric environment outside of the nanotube allow for significant binding energies of 0.4 to 1.0 eV.

Often there is more than one band to choose from for the electron and the hole leading to different types of excitons in the same material. Even high-lying bands can be effective as femtosecond two-photon experiments have shown.
Surface excitons:

At surfaces it is possible for so called image states to occur, where the hole is inside the solid and the electron is in the vacuum. These electron hole pairs can only move along the surface.

Atomic and molecular excitons:

Alternatively, an exciton may be thought of as an excited state of an atom, ion or molecule, the excitation wandering from one cell of the lattice to another. When a molecule absorbs a quantum of energy that corresponds to a transition from one molecular orbital to another molecular orbital, the resulting electronic excited state is also properly described as an exciton. An electron is said to be found in the lowest unoccupied orbital and hole in the highest occupied molecular orbital and since they are found within the same molecular orbital manifold, the electron-hole state is said to be bound. Molecular excitons typically have characteristic lifetimes on the order of nanoseconds, after which the ground electronic state is restored and the molecule undergoes fluorescence. Molecular excitons have several interesting properties, one of which is energy transfer whereby if a molecular exciton has proper energetic matching to a second molecule's spectral absorbance, then an exciton may transfer from one molecule to another. The process is strongly dependent on intermolecular distance between the
species in solution, and so the process has found application in sensing and molecular rulers.

**Dynamics:**

The probability of the hole disappearing (the electron occupying the hole) is limited by the difficulty of losing the excess energy, and as a result excitons can have a relatively long lifetime. (Lifetimes up to several milliseconds have been observed in copper (I) oxide). Another limiting factor in the recombination probability is the spatial overlap of the electron and hole wavefunctions (roughly the probability for the electron to run into the hole). This overlap is smaller for lighter electrons and holes and for highly excited hydrogenic states.

The whole exciton can move through the solid. With this additional kinetic energy the exciton may lie above the band-gap. The exciton propagating through molecular crystal is one that is of greatest concern. Several mechanisms have been proposed in the literature. Two are important. The first one is exciton energy dissipated due to interaction with phonon bath. The other one is energy carried away by radiation. Combinations of the two have also been studied.

Much like molecular systems that have well defined resonances, excitons can undergo internal conversions from energetically higher lying states to lower lying states by coupling to vibrational or electronic degrees of freedom. Internal conversions usually take place of a time scale of a few to tens of femtoseconds.
Also, intersystem crossings are possible when adequate spin orbit interactions are present in the material, and usually take place on a time scale of a few to hundreds of picoseconds.

Excitons are the main mechanism for light emission in semiconductors at low temperature (when the characteristic thermal energy $kT$ is less than the exciton binding energy), replacing the free electron-hole recombination at higher temperatures.

The existence of exciton states may be inferred from the absorption of light associated with their excitation. Typically, excitons are observed just below the band gap.

When excitons interact with phonons a so-called polariton (also exciton-polariton) is formed. These excitons are sometimes referred to as dressed excitons. Provided the interaction is attractive, an exciton can bind with other excitons to form a biexciton, analogous to a dihydrogen molecule. If a large density of excitons is created in a material, they can interact with one another to form an electron-hole liquid, a state observed in k-space indirect semiconductors.

Additionally, excitons are integer-spin particles obeying Bose statistics in the low-density limit. In some systems, where the interactions are repulsive, a Bose-Einstein condensed state is predicted to be the ground state, and indeed such condensate has been already observed in recent experiments (24). The
inference was obtained by cooling an exciton state below 5K and further observing coherent light emission (with interference patterns) from it.

As previously stated there is an energy gap between the conduction and valence band in semiconductors. However the energy required to jump this gap can be supplied to the electrons from heat energy. At room temperature some electrons will have acquired the energy to jump into the conduction band. If the temperature is increased so will the number of electrons in the conduction band. This process is called electron-hole pair generation. This is because by supplying energy we transfer an electron from the valence band to the conduction band. This produces a free electron in the conduction band and leaves a hole in the valence band.

The free electrons are now available to contribute to an electrical current if a voltage is applied to the material. Also the holes (the vacant electron positions) in the valence band will now allow movement of electrons in the valence band, this can also contribute to an electrical current. The net effect is that heat increases the conduction properties of a pure semiconductor.

An exciton comprises an electron and a "hole" bound together by the attractive coulomb interaction. It is the binding energy of the exciton that makes it different than a generic "electron-hole" excitation in which an electron is kicked out of an occupied state and into a previously empty state.
Condensed matter physicists are fond of giving specific names to excitations of solid state systems when those excitations have well-defined quantum numbers (and are in that sense "particle-like"). An exciton comprises an electron and a "hole" bound together by the attractive coulomb interaction (since an electron has charge \(-e\) and a hole has charge \(+e\)). It is the (negative!) binding energy of the exciton that makes it different than a generic "electron-hole" excitation in which an electron is kicked out of an occupied state (leaving behind a hole) and into a previously empty state.

Excitons can exhibit very rich physics. In a 3d crystalline system, excitons can be very analogous to hydrogen-like atoms, or more accurately, positronium, the bound state of an electron and a positron. One can think of the electron and hole as having center of mass momentum, and having an exciton wavefunction that describes the relative displacement of the electron and hole, which would look like a hydrogenic orbital (s-like, p-like, etc.). Like positronium, the electron and hole can annihilate each other and emit a photon. Several important features crop up, however, due to the fact that the exciton exists within a solid host. For example, one cannot ignore the screening of the electron-hole Coulomb interaction by the surrounding host. One approximation commonly shown in textbooks is to treat this screening by using the bulk (relative) dielectric constant of the host material when solving for the exciton wavefunctions. As a result, the exciton is much larger, spatially, than positronium says 5 nm in extent rather than 0.5 nm.
(Note that this had better be true! Otherwise the assumption that the bulk material can screen the interaction would not be internally consistent...) large excitons like this are called Wannier excitons. In contrast, if the screening is relatively weak, the exciton can be small compared to a unit cell of the crystal. Such a small exciton is called a Frenkel exciton.

Furthermore, the electron and hole parts of the exciton wavefunction are really "built" out of the Bloch wave electronic states of the solid. In a semiconductor, the hole states "live" in the valence band, while the electron states live in the conduction band. Hole states often exhibit stronger spin-orbit effects, and as a result, confinement can affect the exciton energy levels quite strongly.

Excitons may be produced by the absorption of light of appropriate energy, and therefore are of intense interest in photovoltaic research. The comparatively strong screening in traditional semiconductors that gives large exciton spatial sizes also leads to modified binding energies. Wannier exciton binding energies in materials like silicon can be of the order of 10 meV (as opposed to electron volts for positronium!). In materials with weaker screening (with Frenkel-like excitons), the exciton binding energy can be higher, more like hundreds of meV. These binding energies are of critical importance. In a silicon pn junction, for example, the built-in electric field due to the junction is large enough to rip apart any light-produced excitons; that is how charge separation happens in a silicon
solar cell. In organic semiconductors, in contrast, the binding energies are stronger, and built in fields are too weak to take apart excitons. Thus, there are no homojunction organic solar cells, and this is one of a number of reasons why organic photovoltaics is challenging.

1.5 Hydrogen bonding:

A hydrogen bond is the attractive interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine that comes from another molecule or chemical group. The hydrogen must be covalently bonded to another electronegative atom to create the bond. These bonds can occur between molecules or within different parts of a single molecule. The hydrogen bond is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond occurs in both inorganic molecules such as water and organic molecules [25]. The hydrogen bond is really a special case of dipole forces. A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine, which has a partial negative charge. The hydrogen then has the partial positive charge.

Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to the other group 16 hydrides that have no hydrogen bonds [26]. Intramolecular hydrogen bonding is partly responsible for the
secondary, tertiary, and quaternary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers, both synthetic and natural [27].

The most ubiquitous, and perhaps simplest, example of a hydrogen bond is found between water molecules. In a discrete water molecule, there are two hydrogen atoms and one oxygen atom. Two molecules of water can form a hydrogen bond between them; the simplest case, when only two molecules are present, is called the water dimer and is often used as a model system. When more molecules are present, as is the case of liquid water, more bonds are possible because the oxygen of one water molecule has two lone pairs of electrons, each of which can form a hydrogen bond with a hydrogen on another water molecule.

This can repeat such that every water molecule is H-bonded with up to four other molecules, (two through its two lone pairs, and two through its two hydrogen atoms). Hydrogen bonding strongly affects the crystal structure of ice helping to create an open hexagonal lattice. The density of ice is less than water at the same temperature; thus, the solid phase of water floats on the liquid, unlike most other substances.

It has been convenient to divide the H bond energy into four components. (1) electrostatic interactions, (2) delocalization effects, (3) dispersion forces, and (4) repulsive forces. Of course, all interatomic forces are electrostatic however; the
above classification is made for the sake of “book keeping” and to gain a clearer understanding of the hydrogen bond. The term “electrostatic” in (1) refers to the forces that would arise if the charges on the atoms could be regarded as point charges without any deformation from polarization. Forces in (2) arise from the fact that mutual polarization of the electron clouds about the atoms does occur, and an account is taken of this distortion in terms of delocalization effects. The small electrostatic interactions resulting from instantaneous charge distribution of electrons in motion produce the dispersion forces, and the forces under (4) are the result of the repulsions between inner-shell electrons during the close approach of the atoms brought together by the H-bond [28].

(1) Electrostatic interactions: The fact that H-bonds are found only between highly electronegative atoms. Suggests that dipole-dipole forces play a dominant role in the H-bond. As a generality it is to be expected that the H-bond strength will increase (a) with increasing polarity of the A-H bond in A-H…B, (b) with an increase in electron-donor character of B, (c) with the stability of the polar structure $A^\delta-\cdot H\cdots B^\delta+$, depending on the relative electronegativities of A and B, (d) and with greater linearity of the H bridge. In accordance with (c) above, spectroscopic data indicate that the O-H…N bond is stronger than the O-H…O bond, while the N-H…O bond is much weaker. This might be expected since oxygen is more electronegative than nitrogen,
which makes the polarized structure $\text{O}^{\delta^-}\text{H} \cdots \text{N}^{\delta^+}$ more stable $\text{O}^{\delta^+}\text{H} \cdots \text{O}^{\delta^+}$.

(2) Delocalization effects: One experimental observation that provides support for this model comes from the measurement of the intensity of infrared absorption by the O-H bond near 3 microns. The intensity of an infrared absorption is proportional to the square of the change in dipole moment during excitation. On this basis the O-H bond dipole can account for only about 30 per cent of the observed intensities. This suggests that there is a much larger fluctuation in charge in the H-bond than in a free O-H bond.

(3) Dispersion forces: Pitzer and coworkers have presented convincing arguments to show that dispersion forces between inner shells of non-bonded atoms are of significant magnitude and have a definite effect on dissociation energies and the conformations of molecules. Thus, the anomalously low dissociation energy of fluorine as compared to chlorine, bromine, and iodine may be partially attributed to the absence of dispersion forces between inner-shell electrons on the fluorine atoms. It is likely that such forces occur between the inner shells of the bridged atoms of an H-bond, particularly for the stronger, shorter H-bonds.
Repulsive forces: As stated above, there must be some counteracting repulsive force in an H-bond because the other types of forces are all attractive and would shorten the H-bond until it collapsed.

Liquid water's high boiling point is due to the high number of hydrogen bonds each molecule can form relative to its low molecular mass. Owing to the difficulty of breaking these bonds, water has a very high boiling point, melting point, and viscosity compared to otherwise similar liquids not conjoined by hydrogen bonds. Water is unique because its oxygen atom has two lone pairs and two hydrogen atoms, meaning that the total number of bonds of a water molecule is up to four. For example, hydrogen fluoride—which has three lone pairs on the F atom but only one H atom can form only two bonds; (ammonia has the opposite problem three hydrogen atoms but only one lone pair).

\[
\text{H–F} \cdots \text{H–F} \cdots \text{H–F}
\]

The exact number of hydrogen bonds formed by a molecule of liquid water fluctuates with time and depends on the temperature. From TIP4P liquid water simulations at 25 °C, it was estimated that each water molecule participates in an average of 3.59 hydrogen bonds. At 100 °C, this number decreases to 3.24 due to the increased molecular motion and decreased density, while at 0 °C, the average number of hydrogen bonds increases to 3.69 [29]. A more recent study found a much smaller number of hydrogen bonds 2.357 at 25 °C [30]. The differences may
be due to the use of a different method for defining and counting the hydrogen bonds.

Where the bond strengths are more equivalent, one might instead find the atoms of two interacting water molecules partitioned into two polyatomic ions of opposite charge, specifically hydroxide (OH⁻) and hydronium (H₃O⁺). (Hydronium ions are also known as 'hydroxonium' ions.)

\[ \text{H}^- \text{O}^- \text{H}_3\text{O}^+ \]

Indeed, in pure water under conditions of standard temperature and pressure this latter formulation is applicable only rarely on average about one in every \( 5.5 \times 10^8 \) molecules gives up a proton to another water molecule, in accordance with the value of the dissociation constant for water under such conditions. It is a crucial part of the uniqueness of water.

It can be that a single hydrogen atom participates in two hydrogen bonds, rather than one. This type of bonding is called "bifurcated" (split in two or 'two-forked'). It can exist for instance in complex natural or synthetic organic molecules [31] It was suggested that a bifurcated hydrogen atom is an essential step in water reorientation [32]. Acceptor type hydrogen bonds (terminating on oxygen’s lone pairs), are more likely to form bifurcation (it is called overcoordinated oxygen, OCO) than donor type, beginning on the same oxygen's hydrogens [33].
Many polymers are strengthened by hydrogen bonds in their main chains. Among the synthetic polymers, the best known example is nylon, where hydrogen bonds occur in the repeat unit and play a major role in crystallization of the material. The bonds occur between carbonyl and amine groups in the amide repeat unit. They effectively link adjacent chains to create crystals, which help reinforce the material. The effect is greatest in aramid fibre, where hydrogen bonds stabilize the linear chains laterally. The chain axes are aligned along the fibre axis, making the fibres extremely stiff and strong. Hydrogen bonds are also important in the structure of cellulose and derived polymers in its many different forms in nature, such as wood and natural fibres such as cotton and flax.

The hydrogen bond networks make both natural and synthetic polymers sensitive to humidity levels in the atmosphere because water molecules can diffuse into the surface and disrupt the network. Some polymers are more sensitive than others. Thusnylons are more sensitive than aramids, and nylon 6 more sensitive than nylon-11.

In 1999, Isaacs et al. [34] proved from interpretations of the anisotropies in the Compton profile of ordinary ice, that the hydrogen bond is partly covalent. Some NMR data on hydrogen bonds in proteins also indicate covalent bonding.

Most generally, the hydrogen bond can be viewed as a metric dependent electrostatic scalar field between two or more intermolecular bonds. This is
slightly different from the intramolecular bound states of for example, covalent or ionic bonds however, hydrogen bonding is generally still a bound state phenomenon, since the interaction energy has a net negative sum. The initial theory of hydrogen bonding proposed by Linus Pauling suggested that the hydrogen bonds had a partial covalent nature. This remained a controversial conclusion until the late 1990s when NMR techniques were employed by F. Cordier et al. to transfer information between hydrogen-bonded nuclei, a feat that would only be possible if the hydrogen bond contained some covalent character [35]. While much experimental data has been recovered for hydrogen bonds in water, for example, that provide good resolution on the scale of intermolecular distances and molecular thermodynamics, the kinetic and dynamical properties of the hydrogen bond in dynamic systems remains unchanged.

1.6 Infrared spectra and hydrogen bonding:

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.
The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near mid and far infrared, named for their relation to the visible spectrum. The higher energy near-IR approximately 14000–4000 cm$^{-1}$ can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm$^{-1}$ may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm$^{-1}$ lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

An invaluable tool in organic structure determination and verification involves the class of electromagnetic (EM) radiation with frequencies between 4000 cm$^{-1}$ and 400 cm$^{-1}$ (wavenumbers). The category of EM radiation is termed infrared (IR) radiation, and its application to organic chemistry known as IR spectroscopy. Radiation in this region can be utilized in organic structure determination by making use of the fact that it is absorbed by interatomic bonds in organic compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. Thus IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum. The frequencies at which there are absorptions of IR radiation ("peaks" or "signals") can be correlated directly to bonds within the compound in question.

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the
vibrational frequency of a bond, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam usually created by an interferometer, but also may have a monochromator before the infrared detector, which changes in wavelength over time. Or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures. Spectra which issues with infrared fluorescense are rare.

Gaseous samples require a sample cell with a long pathlength to compensate for the diluteness. The pathlength of the sample cell depends on the concentration of the compound of the interest. A simple glass tube with length of 5 to 10 cm equipped with infrared windows at the both ends of the tube can be used for concentrations down to several hundred ppm. Sample gas concentrations well below ppm can be measured with a White’s cell in which the infrared light is
guided with mirrors to travel through the gas. White's cells are available with optical pathlength starting from 0.5 m up to hundred meters.

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide calcium or fluoride are also used) [36]. The plates are transparent to the infrared light and do not introduce any lines onto the spectra.

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually Nujol) in a marble or agate mortar with a pestle. A thin film of the mull is smeared onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals).

This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis. The final method is to use microtomy to cut a thin (20–100 µm) film from a solid sample. This is
one of the most important ways of analysing failed plastic products for example because the integrity of the solid is preserved.

In photoacoustic spectroscopy the need for sample treatment is minimal. The sample, liquid or solid, is placed into the sample cup which is inserted into the photoacoustic cell which is then sealed for the measurement. The sample may be one solid piece, powder or basically in any form for the measurement. In example a piece of rock can be inserted into the sample cup and the spectrum measured from it.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

Above figure is schematic of a two-beam absorption spectrometer. A beam of infrared light is produced, passed through an interferometer (not shown), and then split into two separate beams. One is passed through the sample, the other
passed through a reference. The beams are both reflected back towards a detector, however first they pass through a splitter, which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained. This "two-beam" setup gives accurate spectra even if the intensity of the light source drifts over time.

To take the infrared spectrum of a sample, it is necessary to measure both the sample and a "reference" (or "control"). This is because each measurement is affected by not only the light-absorption properties of the sample, but also the properties of the instrument (for example, what light source is used, what detector is used, etc.). The reference measurement makes it possible to eliminate the instrument influence. Mathematically, the sample transmission spectrum is divided by the reference transmission spectrum.

The appropriate "reference" depends on the measurement and its goal. The simplest reference measurement is to simply remove the sample (replacing it by air). However, sometimes a different reference is more useful. For example, if the sample is a dilute solute dissolved in water in a beaker, then a good reference measurement might be to measure pure water in the same beaker. Then the reference measurement would cancel out not only all the instrumental properties (like what light source is used), but also the light-absorbing and light-reflecting properties of the water and beaker, and the final result would just show the properties of the solute (at least approximately).
A common way to compare to a reference is sequentially: First measure the reference, then replace the reference by the sample, then measure the sample. This technique is not perfectly reliable. If the infrared lamp is a bit brighter during the reference measurement, then a bit dimmer during the sample measurement, the measurement will be distorted. More elaborate methods, such as a "two-beam" setup (see figure), can correct for these types of effects to give very accurate results. The Standard addition method can be used to statistically cancel these errors.

An interferogram from an FTIR measurement. The horizontal axis is the position of the mirror, and the vertical axis is the amount of light detected. This is the "raw data" which can be Fourier transformed to get the actual spectrum.

Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an interferometer and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called Fourier transform turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or equivalently, wavenumber). As described above, the sample's spectrum is always compared to a reference.
There is an alternate method for taking spectra (the "dispersive" or "scanning monochromator" method), where one wavelength at a time passes through the sample. The dispersive method is more common in UV-Vis spectroscopy but is less practical in the infrared than the FTIR method. One reason that FTIR is favored is called “Fellgett’s advantage” or the "multiplex advantage": The information at all frequencies is collected simultaneously, improving both speed and signal-to-noise ratio. Another is called "Jacquinot's Throughput Advantage": A dispersive measurement requires detecting much lower light levels than an FTIR measurement [37]. There are other advantages, as well as some disadvantages [37], but virtually all modern infrared spectrometers are FTIR instruments.

Absorption bands

Wavenumbers listed in cm\(^{-1}\).

Because each interatomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR
frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar types of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. For example, neither of the carbon-carbon bonds in ethene or ethyne absorb IR radiation.

Over time organic chemists have recorded and catalogued the types and locations of IR absorptions produced by a wide variety of chemical bonds in various chemical environments. These data can be quickly referenced through tables of IR absorption ranges and compared to the spectrum under consideration. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore the same or similar functional groups in different molecules will typically absorb within the same, specific frequency ranges. Consequently tables of IR absorptions are arranged by functional group it some versions these may be further subdivided to give more precise information.

In IR absorption tables, signal intensities (height) are usually denoted by the following abbreviations w = weak, m = medium, s = strong, v = variable. A broad signal shape is sometimes indicated by br. Occasionally absorption frequency is given as a single approximation denoted with an ~ rather than a range.
Upon first inspection, a typical infrared spectrum can be visually divided into two regions. The left half, above 2000 cm\(^{-1}\), usually contains relatively few peaks, but some very diagnostic information can be found here. First, alkane C-H stretching absorptions just below 3000 cm\(^{-1}\) demonstrate the presence of saturated carbons, and signals just above 3000 cm\(^{-1}\) demonstrate unsaturation. A very broad peak in the region between 3100 and 3600 cm\(^{-1}\) indicates the presence of exchangeable protons, typically from alcohol, amine, amide [38] or carboxylic acid groups (see further discussion of this below). The frequencies from 2800 to 2000 cm\(^{-1}\) are normally void of other absorptions, so the presence of alkyne or nitrile groups can be easily seen here.

In contrast, the right half of the spectrum, below 2000 cm\(^{-1}\), normally contains many peaks of varying intensities, many of which are not readily identifiable. Two signals which can be seen clearly in this area is the carbonyl group, which is a very strong peak around 1700 cm\(^{-1}\), and the C-O bond which can have one or two strong peaks around 1200 cm\(^{-1}\). This complex lower region is also known as the "fingerprint region" because almost every organic compound produces a unique pattern in this area. Therefore identity can often be confirmed by comparison of this region to a known spectrum.

One of the most distinct and easily recognizable peaks in an IR spectrum is the broad O-H absorption of alcohols and phenols. However it important to understand why this broadening takes place and to consider the situations in which
the peak may not have this characteristic shape. First, note that any significant quantity of a compound will contain a very large number of individual molecules, and each of these may be hydrogen bonded to a slightly different extent. Thus as an IR spectrum is acquired IR absorptions will occur at varying frequencies for each of these bonds. The end result is that the IR peak appears broadened, as it is an average of all these slightly different absorptions.

It is possible to acquire IR spectra of hydroxyl containing compounds without seeing this broad signal. By creating a very dilute solution of the sample, or acquiring the IR spectra in the gas phase, hydrogen bonding is prevented through lack of molecular [39] contact. Even in concentrated solution, larger compounds may sterically hinder hydrogen bonding, preventing exchange. In these situations the broad O-H peak is replaced by a sharp signal around 3600 cm$^{-1}$. This effect can be seen in the IR spectra of t-butanol, dilute and concentrated.

We have noted that the covalent bonds of molecules are not rigid, but are more like stiff springs that can be stretched and bent. At ordinary temperatures these bonds vibrate in a variety of ways, and the vibrational energies of molecules may be assigned to quantum levels in the same manner as are their electronic states [40]. Transitions between vibrational energy states may be induced by absorption of infrared radiation, having photons of the appropriate energy. It requires more energy to stretch (or compress) a bond than to bend it, and as might
be expected, the energy or frequency that characterizes the stretching vibration of a given bond is proportional to the bond dissociation energy.

The equation on the right describes the major factors that influence the stretching frequency of a covalent bond between two atoms of mass $m_1$ and $m_2$ respectively. The force constant ($f$) is proportional to the strength of the covalent bond linking $m_1$ and $m_2$. In the analogy of a spring, it corresponds to the spring’s stiffness. For example, a C=N double bond is about twice as strong as a C-N single bond, and the C≡N triple bond is similarly stronger than the double bond. The infrared stretching frequencies of these groups vary in the same order, ranging from 1100 cm$^{-1}$ for C-N, to 1660 cm$^{-1}$ for C=N, to 2220 cm$^{-1}$ for C≡N.

| Approximate Infrared Stretching Frequencies |
| B-H | C-H | N-H | O-H | F-H |
| 2400 cm$^{-1}$ | 3000 cm$^{-1}$ | 3400 cm$^{-1}$ | 3600 cm$^{-1}$ | 4000 cm$^{-1}$ |
| Al-H | Si-H | P-H | S-H | Cl-H |
| 1750 | 2150 | 2350 | 2570 | 2890 |
| Ge-H | As-H | Se-H | Br-H |
| 2070 | 2150 | 2300 | 2650 |
If one of the bonded atoms \( m_1 \) or \( m_2 \) is a hydrogen (atomic mass =1), the mass ratio in the equation is roughly unity, but for two heavier atoms it is much smaller. Consequently, C-H, N-H and O-H bonds have much higher stretching frequencies than do corresponding bonds to heavier atoms. Other X-H stretching frequencies are shown in the table to the left, the trends observed being due chiefly to differences in the force constants. The mass effect on stretching frequencies is particularly evident when deuterium isotope equivalents are compared with corresponding hydrogen functions. Thus, the stretching frequency of a free O-H bond is 3600 cm\(^{-1}\), but the O-D equivalent is lowered to 2600 cm\(^{-1}\). Since deuterium has a mass = 2, the mass term in the equation changes from 1 to 1/2, and the frequency is reduced by the square root of 2. In this discussion we have focussed on stretching vibrations, and it should be noted that bending vibrations may be treated in a similar fashion.

Not all molecular vibrations lead to observable infrared absorptions. In general, a vibration must cause a change in the charge distribution within a molecule to absorb infrared light. The greater the change in charge distribution, the stronger the absorption.

Intramolecular H-bonding has a marked visible effect on ultraviolet absorption whereas intermolecular H-bonding has only small effects. Compounds which exhibit intermolecular H-bonding normally undergo a redshift upon methylation while compounds forming intramolecular H-bonds undergo a blue-
shift upon methylation. The results in a lowering of the stretching frequency and a raise in the bending frequency.

1.7 Absorption edge spectrum and exciton-phonon coupling:

An absorption edge is a sharp discontinuity in the absorption spectrum of a material. These discontinuities occur at wavelengths at which the energy of an absorbed photon corresponds to an electronic transition or ionization potential. Phonon is used to describe a quantized elastic wave or lattice vibration. In the semiconductor the exciton-phonon coupling phenomena is observed for the case of high temperature superconductivity.

It has been experimentally found that the emission spectra of elements of low atomic number, in particular in solid form are characterized by diffuse bands. If the same element exists in the form of vapour, sharp spectral lines are produced. The above noted experimental fact implies that in a solid metal (in which atoms are packed in a crystal lattice) the valence electrons have energies extending over a bond of energies so that there is not a constant difference in energies between a valance electron and electron in a lower shell. The width of the solid state bands is of the order of 1 to 10 eV. In case of sodium 3s and 3p orbitals are broadened as a result of squeezing of the atoms in body centred lattice and as a result they overlap and form a continuous band. Such types of hybridized orbitals are defined by superposition of wave functions.
Uptill now we have taken that mass absorption coefficient increases with the wavelength till the absorption limits is reached. But the refinement of techniques used in the study of spectra have revealed that mass absorption coefficient of a substance for X-rays does not increase in a uniform manner with increasing wavelength upto a critical absorption limit and then decrease abruptly. This uneven variation extends over a region of 200 eV in some cases. The meaning is that absorption edges contain satellites and some fringes. In case of monoatomic gas the structure of simple type were detected. In other cases Kroning recorded the following facts:

1. In case of polyatomic gases sometimes the structures extends within a low range and in some cases it extends over a few hundreds volts.

2. The extended structure, in general, we get in case of solids. It is also noticed that the separation of irregularities increases as the distance from the principle edge increases.

3. As the temperature increases, the irregulatity shifts towards the principal edge and takes a smooth form. At high temperature the secondary structure disappears.

4. At room temperature, the variation of absorption coefficient in the region of short wavelength side of the K limit is about twice as large in Cu as in Rn.
The simple structure observed in case of monoatomic gas finds its application on the basis of Kossel’s theory. He suggested that it is not necessary in an act of absorption, the ejected electron be removed to infinity. It is only necessary that it be displaced to the first incomplete group. If there are no inner incomplete group the electron goes to optical orbits. Thus the short wavelength limits is a sign of removal of infinity, while the long wavelength limit indicates the deposition of electron in an unoccupied orbit. This interpretation hardly covers a range of few ten of volts.

Later on, a comprehensive theory was given by Kroning based on wave-mechanics. In absorbing crystal a periodic array of potential wells corresponding to the lattice is assumed to exist. The ejected electron from the energy level enters into any of the energy levels which are the result of crystal lattice structure. The transition of an electron from a level of an atom to the lowest of these energy bands accounts for the absorption edge. It should be noted that moving electron cannot take all the energies. There are some permitted and forbidden zones. The energy of a level is expressed by the following equation:

\[ E = \frac{n^2 \hbar^2}{8ma^2} \]

where \( n \) is an integer, \( \hbar \) the Plank’s constant, \( m \) the electronic mass, \( a \) the interatomic distance. The fact that intervals between irregularities increases towards higher frequency side is explained with the help of above relation. The
relation states that as \( n \) increases (for higher frequencies), the spacing between forbidden zones is enlarged. At high temperature the value of \( a \) increases, which makes the disappearance of the extended structure. Also that the different atoms within the sharpness of the effect. The more marked effect in Cu is visible than in Zn because room temperature is near the melting point of Zn [43].

In a direct gap semiconductor this process takes place exactly as described but in an indirect gap material a phonon must be absorbed or emitted in the process, because the wave vector of the final state of the electron is not the same as that of the initial. The excitons are thus referred to as direct or indirect. The reverse process, in which the electron and hole recombine can also occur. Since a three body process (electron, hole and phonon) is more unlikely to occur than a two body one the indirect excitons are more stable than direct excitons with respect to decay. The lifetimes of the direct and indirect excitons in germanium are \(~10^{-7}\) and \(~10^{-5}\) seconds, respectively [44].

Excitons may be mobile within the crystal or fixed, for example bound to an impurity. Excitons in germanium may move as much as one millimeter within their lifetime. The movement may be merely the result of diffusion or in response to a strain gradient for example [45].

The optical properties of solids depend on their size. If there is confinement in one direction, e.g. in the \( z \)-direction, the Heisenberg Uncertainty Principle gives an uncertainty in momentum in the \( z \)-direction which is inversely proportional to
the size of the sample in the z-direction. The system under investigation is quasi two-dimensional, which causes momentum conservation in the direction perpendicular to the plane of the sample to be relaxed (so if the system lies in the x/y plane, momentum conservation in the z-direction is relaxed). Excitons interact with 3D ('bulk') phonons. Figure below is a simple diagram showing how bulk LA phonons interact with the quasi-2D excitons.

![Diagram showing how bulk LA phonons interact with quasi-2D excitons.](image)

Above figure is schematic diagram demonstrating how an incoming bulk phonon interacts with a quasi 2D exciton in the QW. The blue disc represents the electron and the red disc represents the hole their sizes are inversely proportional to their masses.

A plot of exciton and phonon dispersion relations. The parabolic surface shows excitonic dispersion; the conical surface shows acoustic phonon dispersion.
The ground state mode couples to a continuum of energy states $E > E_0$ shown by the grey lines.

As seen in Figure-1 $E_0$ is the crossover between exciton and LA-phonon dispersions, and is given by, $E_0 = 2M_x\nu_s^2$, Where $\nu_s$ is the speed of sound in the material. Due to the Heisenberg Uncertainty Principle, a scattered QW exciton can therefore interact with a continuum spectral band of scattering LA phonons $E, E_0$ in a given direction, whereas in bulk semiconductors an exciton can couple via Stokes or anti-Stokes scattering with only one phonon mode in a given direction. As a result, the cooling of hot photoexcited excitons down to the temperature of the lattice is generally much more effective for two-dimensional systems, compared with bulk semiconductors. This fast cooling rate and the long radiative lifetime allow excitons to accumulate in the lowest energy states before they
decay; therefore, hot photoexcited excitons can cool down to low temperatures so that the gas of indirect excitons eventually becomes statistically degenerate.

The electron and hole move together as a bound complex in the two-dimensional structure. Relaxational thermodynamics, optical decay equations and a quantum diffusion equation are used to model excitons in GaAs/AlGaAs CQWs. A simple diagram of the system in real space is shown in Figure 1, where the quantum wells are represented by the two grey layers, and the electron and hole are represented by the blue and red discs respectively. The size of the discs represents their Bohr radius. The effective masses of the electron and hole in GaAs are \( m_e = 0.067 \, m_0 \) and \( m_h \sim 0.2 \, m_0 \) respectively, where \( m_0 \) is the free electron mass, and the electron-hole reduced mass is given by \( (m_e m_h) / (m_e + m_h) = 0.05 \, m_0 \). The Bohr radius of the exciton is \( \sim 14 \, \text{nm} \).

An exciton has integer spin because it consists of two fermions and therefore in the low-density limit is a boson, and obeys Bose-Einstein statistics. The crossover from classical to quantum statistics occurs near the degeneracy temperature \( T_0 \), given by, \( k_B T_0 = 2\pi / (g (\hbar / M_x)) \, n_{2D} \), where \( g \) is the spin degeneracy factor of quantum well excitons, \( n_{2D} \) is the concentration of excitons, \( M_x \) is the in-plane translational mass of an exciton and \( k_B \) is the Boltzmann constant. The gas of quantum well excitons is classical at \( T >> T_0 \), and as \( T \) is decreased and approaches \( T_0 \), Bose-Einstein statistics smoothly develop. If \( T \) is decreased further the lowest energy states have large, non-classical occupation numbers \( >> 1 \).
Note that the exciton mass, $M_x$, is small, even smaller than the free electron mass, so $T_0$ is relatively high because it is inversely proportional to $M_x$.

Relaxational thermodynamics refers to phonon-assisted thermalization kinetics of QW excitons, and is used to study how Bose-Einstein statistics affect the thermalization and photoluminescence of quasi 2D excitons. This approach assumes a hierarchy of interactions exciton-exciton interaction has to be much stronger than exciton-LA-phonon interaction. The concentration of excitons $n_{2D}$, has to be larger than some critical concentration so that the system is able to establish a quasi-equilibrium temperature $T$, and the thermalization of the excitons occurs through a series of quasi-equilibrium thermodynamic states. For GaAs QWs, this critical concentration is $n_{c2D} \sim 1-3 \times 10^9$ cm$^{-2}$ [46].

The temperature of excitons with respect to time, $T(t)$ from the initial value $T_i = T(t=0)$, where $t =$ time, to the lattice temperature $T_b$ (or at least very close to it). This equation deals with the scattering of excitons by bulk LA phonons, where the distribution of the phonons is given by the Planck formula. When the excitons are created they can be hot, but the initial distribution of excitons is assumed to be below the threshold where optical phonon scattering becomes the dominant mechanism (which is $\sim 200$ K, and the threshold for optical phonon emission is $\sim 400$K in GaAs [47]. The excitons then cool down because the lattice is kept very cold. Instead of treating an approximation of the Boltzmann equation, a `microscopic' equation is derived that takes into account all of the excitons in the
Exciton-LA-phonon coupling was researched experimentally by Damen et al. [48,49] and discussed the results of experimental measurements of LA-phonon scattering of hot QW excitons. Piermarocchi et al. made calculations of the photoluminescence rise and decay times, and scattering rates with LA-phonons [50].

There are two ways of creating an exciton, depending on how much energy the electron obtains. If the electron is given enough energy to create an exciton but not enough to become free, it is called a resonant creation, also sometimes called ‘sub-barrier excitation’. This would mean that the energy the electron receives is below $E_g$. If a free electron and free hole are created, which then relax by phonon emission and become a bound pair, it is a nonresonant creation. In this thesis, excitons created resonantly and nonresonantly are modelled only nonresonant creation is used [51].

**Resonant Creation:**

In this case, the excitation energy creates a direct exciton. The generation of indirect excitons is a secondary process, mainly due to quantum tunnelling of the direct excitons to the energetically more favourable states of indirect excitons. There is no significant free carrier generation when resonant excitation is used.
Nonresonant Creation:

If an exciton is created nonresonantly and then relaxes to an indirect exciton, the excess energy $E_i$ of the created indirect exciton is large if it exceeds the energy splitting between the direct and indirect excitons, which is about 20 meV. A substantial amount of research has been conducted into the creation of excitons from e-h pairs. The formation of an exciton from a free electron and a free hole happens very quickly (on the ps time scale) by LO-phonon emission. At temperatures below $\sim 200$ K, LA-phonon emission is the most important relaxation mechanism for exciton formation from free e-h pairs. Yoon et al. state that carrier cooling due to LO-phonon emission occurs on the subpicosecond timescale and after this emission the exciton temperature is of the order of 100 K. Kusano et al. found the formation time to be $\sim 190$ ps and it was deduced from experiments that excitons formed within 20 ps of creation of electron-hole pairs by sub-picosecond optical excitation. Blom et al. studied very narrow GaAs/Al$_x$Ga$_{1-x}$As QWs in which the time for exciton relaxation to the lowest energy states was expected to be small. They measured the exciton formation time to be about 25-40 ps for $n_{2D} = 5 \times 10^{10}$ cm$^{-2}$. Robart et al. stated that the formation time is less than 10 ps for $n_{2D} = 7 \times 10^{10}$ cm$^{-2}$. In GaAs quantum wells Kumar et al. deduced an exciton formation time of 50 ps for an initial carrier density of $n_{2D} = 4 \times 10^{10}$ cm$^{-2}$. Thilagam and Singh were the first to calculate the formation time of excitons theoretically as a function of QW width, by considering the formation of excitons by LA-phonon emission. They calculated generation rates of excitons and found
the exciton formation time from an e-h pair in single GaAs/AlGaAs QWs to be ~ 0.25 - 1 ns however they state that detailed comparison of their theoretical results with experiments may not be possible because of various assumptions involved in the calculations. Zhang et al. theoretically investigated the formation of excitons from an e-h plasma which was created by nonresonant excitation, and calculated a value of 108 ps for the formation of the excitons. More recently, theoretical research by Oh and Singh showed that the rate of formation depends strongly on the temperature of the e-h plasma. Szczytko et al. performed experiments and made calculations for the exciton formation time, and reported that it could vary from 10 ps (for a high concentration of carriers) to several of hundreds of ps (for a low concentration of carriers). However, a lower exciton formation time was found at lower temperatures. They stated that the spread of experimental values for the formation time found in literature is likely to be related to the different experimental conditions. In this thesis, only the scattering of excitons with LA-phonons is taken into account which assumes that the initial energy of excitons does not exceed $E_i/k_B \sim 200$ K. At temperatures higher than this LO-phonon scattering becomes an increasingly significant effect.

Vibrational excitons on the other hand are often defined in the opposite direction. They occur in systems with identical localized vibrational chromophores. Resonant interaction between these localized vibrations then leads to a delocalization of the vibrational wave function. Incidentally, these exciton states can be described by the same theory used to describe Frenkel excitons [52].
which is the main reason for using the same term for this physically quite different excitation. However, in principle vibrational excitons can also be understood as localized phonons, where the localization is due to structural disorder that can happen on various length scales.

The smallest vibrational excitons are found in molecular dimers, where the coupling between two degenerate vibrational modes leads to the so-called Davydov splitting of the vibrational transition frequencies [53], a phenomenon frequently encountered in molecular crystals [54]. The new vibrational eigenstates are often symmetric and antisymmetric, respectively. In some way, even the symmetric/antisymmetric splitting of the stretching vibrations in water and formamide can be understood as formation of, in this case intramolecular, exciton states. Most commonly, vibrational excitons are discussed in proteins and polypeptides where the strongly interacting amide I and II modes form largely delocalized states whose properties are indicative of the polypeptide structure and protein secondary and tertiary structure [55,56,57-72]. But also geometrical constraints such as for nanostructures and structural disorder can lead to localization of phonon modes, i.e. formation of vibrational excitons [73,74].

All these systems however, exhibit essentially static structures. The treatment of the excitonic nature of vibrational excitations in this case relies on an eigenstate analysis, which is referred to as the exciton basis [75]. Small amplitude fluctuations, for example solvent interactions in proteins, can be treated in a statistical manner. Nonetheless, this description relies on structural stability such
that the nature of the excitonic states is conserved, at least on short time scales. It is this assumption that does not hold for vibrational excitons in liquids.

Little is known about vibrational excitons in neat liquids at the moment. Experimental evidence of the existence of delocalized vibrational excitations in liquids was, up until this work, limited to the so-called Raman non-coincidence effect [76,77,78,79-84]. In this polarized Raman experiment, a spectral difference between the peak positions of the isotropic and the anisotropic Raman signal is observed. It was shown that the effect arises from resonant vibrational coupling and is highly sensitive to medium range structural order, i.e. relative arrangement of the molecules. The extent of delocalization defining the size of the structural domain mapped by the excitons is a result of competition between local disorder and resonant coupling strength. These experiments and simulations are however linear, i.e. sensitive only to average liquid structure and the harmonic part of the intermolecular potential.

1.8 Hydrogen bonding and exciton:

When an electron is excited into the conduction band, a hole is created in the valance band. Being of opposite charge, they can attract one another and form a bound pair, rather like a hydrogen atom or positronium. The binding energy accounts for the discrepancy between the expected and experimentally observed onset of absorption [44].
It can be well appreciated that coherent multidimensional spectroscopies [85,86] have emerged to be a very powerful tool in studying dynamics in complex systems. As discussed in preceding chapters, two-dimensional vibrational or infrared (2DIR) spectroscopy allows investigations of structural dynamics, intermolecular coupling, dephasing, and relaxation mechanisms in a wide range of molecular systems. Important applications pertain to the study of polypeptides, proteins [87], DNA [88,90] and liquids [91,92,93-98,99,100,101].

In polypeptide and protein systems, structural changes are slow and the infrared lineshapes are often dominated by excitonic effects indicative of secondary or higher order structure. The evolution of the 2DIR spectra can then be used to track conformational changes on time scales of tens and hundreds of ps. For more site specific information, isotopic substitution is used. In this case, the evolution of the 2DIR cross peaks can reveal the relative structural dynamics of labeled sites in strong analogy to 2D NMR studies. In liquids, an entirely different situation is often encountered. As discussed, most studies use isotopic substitution to eliminate any resonant interaction. The 2DIR spectra are then sensitive to the most immediate structural environment. In these cases, it is the very fast, sub-ps dynamics of the local structure that dictates the 2DIR lineshapes and their evolution. In other words, the structural information gained from most 2DIR studies can be separated into two major regimes: (i) slow structural evolution on big length scales or (ii) fast structural dynamics on very short length scales.
In particular, for systems with extended H-bond networks, it would however be very interesting to also gain access to the dynamics on intermediate length scales. It is in these intermediate regimes that the true network characteristics become important. In the usual protein vocabulary, this is the difference between primary and secondary or higher order structure. Only most recently, it was shown that the 2DIR spectrum of liquid water can be sensitive to intermediate length scales [102] through the delicate balance of local frequency fluctuations and intermolecular couplings. At room temperature, the spectra are still dominated by local structural dynamics, corresponding to the primary structure in the protein language. At lower temperatures however, delocalization of the vibrational excitations becomes important and the 2DIR spectra report on the dynamics of structural correlations between 15-20 molecules, i.e. the secondary structure equivalent.

In this respect, liquid formamide (FA) is an ideal model system. The amide I vibrational oscillator is relatively insensitive to the local environment, electric field fluctuations and H-bonding. On the other hand, the resonant intermolecular couplings via transition dipole coupling (TDC) are comparable to those in water due to the large transition dipole moment. This results in largely delocalized excitons at ambient conditions. The dynamics of these delocalized states are dictated by the dynamics of spatial correlations in the H-bond network that modulate the excitonic states. It is in this sense that 2DIR can give a unique probe
of the H-bond network dynamics in liquid FA. Liquid FA forms an extended H-bond network and for that reason is often used as a model system for other H-bonded liquids such as water. However, it is now believed that the liquid structure, even though generally characterized by structural disorder, contains certain molecular aggregates and maintains some local structural properties of the crystalline phase. The emerging picture exhibits mostly branched linear H-bonded FA chains with a minor appearance of ring-shaped oligomers and cyclic dimers. FA is therefore often considered a well-structured liquid.

The importance of vibrational coupling between the local amide I modes in liquid FA was first discovered in polarized Raman experiments. In these measurements, the difference in peak position between IR, isotropic and anisotropic Raman signals, the so-called Raman noncoincidence effect, is indicative of the resonant vibrational interactions and formation of vibrational excitons. Even though some understanding about prominent structural domains can be extracted, all these studies are limited to time-averaged properties of the FA liquid structure.

1.9 Electron-hole liquids in semiconductors:

A condensed state of nonequilibrium electron-hole plasma is found in a semiconductor [103,104]. An electron-hole liquid is formed when the density of the electrons and holes exceeds some critical value that is a function of
temperature. The electrons and holes may be free or may be bound together to form excitons.

The critical density $n_{cr}$ is easily attained by, for example, injecting carriers into a semiconductor or exposing a semiconductor to light. When $n_{cr}$ is attained, the system of nonequilibrium charge carriers undergoes a phase transition similar to a gas-liquid transition [105,106]. As a result, the system separates into the following two phases: droplets of a relatively dense electron-hole liquid and free carriers; the droplets are surrounded by an exciton gas. When the phase transition occurs, the density and crystal structure of the semiconductor are virtually unaffected.

In contrast to ordinary liquids, an electron-hole liquid contains no heavy particles, that is, no ions or atomic nuclei. Therefore, an electron-hole liquid has pronounced quantum properties. Such a liquid cannot be solidified but remains a liquid down to the lowest temperatures. It cannot be a molecular liquid; that is, it cannot consist of excitons or of exciton molecules. Instead, an electron-hole liquid is composed of quasi-free electrons and holes; that is, it is similar to a liquid metal.

Coulomb interactions bind the particles in an electron-hole liquid. The interactions are weakened by the permittivity of the crystal. Therefore, in comparison with the case of ordinary liquids, the binding energies $E_0$ and densities $n_0$ of the particles in an electron-hole liquid are very low; $E_0 \sim 10^2–10^{-1}$ electron
volt, and \( n_0 \sim 10^{-7} \text{–} 10^{-19} \text{ cm}^{-3} \). By order of magnitude, the range of temperatures \( T \) at which an electron-hole liquid may exist is given by the relation \( T \leq (0.1 E_0/k) \sim 10^{-100} \text{°K} \), where \( k \) is the Boltzmann constant.

The diameter of an electron-hole droplet is usually \( \sim 1 \text{–} 10 \) micrometers. However, droplets with a diameter of up to 1 mm have been observed. The droplets may be accelerated to speeds of up to the speed of sound in a crystal. In other words, electron-hole droplets are mobile regions of high conductivity in a crystal that, at low \( T \), is virtually nonconducting.

An electron-hole liquid may be regarded as “blobs” of excitation energy introduced into a crystal. When electrons and holes recombine, some of the energy is released in the form of electromagnetic radiation that is, as a result of radiative transitions so that the liquid is a strong source of light. Electron-hole liquids have been most comprehensively studied in Ge and Si. However, evidence for the existence of such liquids has also been found in other semiconductors [107,108].

1.10 Infrared excitons and infrared luminescence:

The re-emission of excitation energy as visible or near visible radiation is known as luminescence. Luminescence is a general term denoting the absorption in matter of energy and its re-emission as visible or near visible radiation. The initial excitation may be by light, electron or positive ion bombardment, mechanical strain, chemical reaction or heating. If the emission occurs during
excitation, or within $10^{-8}$ sec of excitation, the process is commonly called fluorescence. The interval $10^{-8}$ sec is chosen as of the order of the lifetime of an atomic state for an allowed electric dipole transition in the visible region of the spectrum. If the emission occurs after excitation has ceased, the process is called phosphorescence or after-glow. The after-glow period may be of the order of microseconds to hour. Most experimental investigations of this region of the phase diagram and indeed of most other properties of excitons and related species are performed using the recombination luminescence technique. In this method excitons etc. are generated and then the light emitted as they annihilate by the recombination of electron-hole pairs is observed. Since the exciton levels in the semiconductors lie just below the conduction band the photon energies observed are all of the order of the band gap energy. It is not possible to differentiate between recombination of excitons in different excited states just one peak is observed. When observations are being made in the transition portion of the phase diagram, the peaks due to the different components (fluid, excitons and plasma) are to an extent superimposed.

In the absorption of far-infrared radiation, the excitons are generated continuously and far-infrared radiation is shone through them. The absorption spectrum is obtained by comparing the spectrum of excitons plus semiconductor with the spectrum due to the semiconductor alone. In these experiments transitions
between the hydrogenic levels of the excitons can be observed and the plasma, exciton and fluid absorptions are clearly differentiated from one another.

Daniel Labrie et al. has done series of experiments was performed to measure the far-infrared (FIR) absorption spectrum of excitons in stressed Ge with the stress axis along the [111] direction. The line position of the 1s-2p and 1s-3p transitions and the relative absorption associated with the 1s-2p transitions were found to be in good agreement with a simple theoretical model. The model only considers the lower conduction band minima and the upper valance band maxima at high streses in the formation of excitons.

Also the FIR absorption spectrum of an exciton bound to an isoelectronic trap is reported. The spectrum provides information on transitions from the even parity ground states to the odd parity excited states. The excited state spectrum of the bound exciton was found to be in excellent agreement with the spectra of acceptors in Si. This shows that FIR spectroscopy applied to the study of bound excitons reveals without ambiguity the nature of the bound exciton.

Daniel Labrie et al. generated the excitons via band gap light excitation. A (sylvana) CW YAG:Nd laser operating at a wavelength of 1.06 µm and with incident power at the sample from 10 to 20 mW was employed in germanium while a krypton laser (spectra physics) operating at a wavelength of 60 µm and with incident power of 60 mW was used in silicon. The FIR radiation is provided
by an interferometer. Both the laser and FIR beam are directed onto the sample. The near infrared beam is absorbed within a few microns at the surface of the sample while the FIR beam is weakly absorbed by the generated exciton gas. The transmitted FIR radiation is received by a detector whose output is processed by a computer to provide the relative transmitted intensity and the absorptance as a function of frequencies. The experiments were conducted in the temperature range from 1.2 K to 34 K. The absorptance by excitons $\alpha_d$ was derived from the following formula,

$$\alpha_d = \ln(I_0/I)$$

$I_0(w)$ represents the transmitted FIR radiation through the sample when there were no excitons present, i.e. when the laser was off and $I(w)$ is the transmitted radiation when excitons were generated i.e. when the laser was on $d$ is the absorption length by excitons.

The most detailed information on the internal structure of free excitons in germanium was obtained by the far-infrared (FIR) absorption experiments. In these experiments, transitions from the even parity ground states to the odd parity excited states were observed. Furthermore, the energy of the even parity ground states was measured by examining the FIR exciton photoconductivity and by looking at the derivative of the near infrared absorption edge. To interpret this series of experimental results, a comprehensive theoretical treatment of the exciton
energy spectrum was made. Despite the complicated band structure good agreement between calculated and measured energy levels was obtained. Nevertheless, some of the observed transitions were not predicted and some of the predicted transitions have not been observed.

Application of a uniaxial compressive stress along the [111] direction simplifies the band structure. In the presence of very large stresses, excitons are formed from one conduction band. Both bands are ellipsoids of revolution with their major axis along the [111] direction. The resulting energy spectrum of excitons is very simple. Muro and Narita and Yamankara et al. determined, from their FIR magneto-absorption of the exciton ground state energy of 2.75 meV. Feldman et al. measured from the luminescence of excitons at intermediate stresses a binding energy of (2.3 ± 0.4) meV and (2.6 ± 1.2) meV respectively [109].

The purpose of this study was to determine the energy spectrum of excitons at very large stresses. The FIR absorption spectra were measured as a function of stress from 9 to 38 Kg/mm² and as a function of the direction of the FIR polarization with respect to the stress axis. At high stress the exciton spectra are similar to those of donors. A theoretical model is used to predict the energy levels and the relative absorption of transition lines. Good agreement is observed between theory and experiment.
The study of bound excitons (BE) was mainly limited to the observation of their even parity states using near-infrared (NIR) spectroscopy. These states are difficult to interpret since they depend on the central cell potential of the binding centre and the line spacing is unique to each impurity. Furthermore, for centres of low symmetry additional lines due to odd parity excited states can also be observed in the even parity state spectrum making the analysis even more difficult.

Far-infrared absorption spectrum of a bound exciton provides information on transitions from the even parity ground states to the odd parity excited states. These odd parity excited states are not shifted by the central cell potential of the binding centre and hence they should give the same spectra. The results of this research show that FIR spectroscopy applied to the study of BE is the best tool for the identification of the BE internal structure.

Hopefield, Thomas and Lynch (HTL) [110] developed a model to explain extrinsic absorption and luminescence lines in ZnTe and GaP crystals. They interpreted these transitions as produced by the formation and the recombination of excitons bound at isoelectronic traps. These traps are electrically neutral because all four bonds to the neighbouring atoms are satisfied and there is no excess of carrier presents. However, the difference in electronegativity between the impurity and lattice atoms produces a short range potential which binds a primary particle, either an electron or a hole, into a very localized state. The secondary particle is then loosely bound by the screened coulomb potential of the
primary particle. Timusk et al. [111] observed a thermal dissociation of the exciton gas in germanium by using the FIR absorption associated with excitons. He explained his results with a kinetic model including a temperature dependent ionization rate of excitons. Mock et al. [112] observed a quadratic decrease of the exciton luminescence with decreasing carrier generation rate at constant temperature. Their results showed the expected behaviour of the dissociation of excitons, in thermal equilibrium with carriers, as a function of carrier generation rate. A more detailed study was done in silicon by Gourley and Wolfe [113], from their steady-state and time resolved luminescence data, they extracted the equilibrium constant of the exciton-carrier gas. The luminescence experiments are mainly sensitive to electron-hole overlap which make them inappropriate to the study of free carriers.
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Chapter 2

Spectroscopic study of hydrogen bonded inclusion compounds of Iodine
2.1 INTRODUCTION:

The inclusion compound of iodine, also known as organic polyiodide chain complexes, have been studied in details (1,2) structural, electrical & optical properties of these complexes had been a subject of interest some time ago (3-7). Pressure-induced peierls instability has been proposed (8-10). Six or seven sugar molecules from a cup or cap shaped molecules connected by glucosidic oxygen atoms. In the present work, many dyes are found to from hydrogen bonding at the site of glucosidic oxygen atoms or at the external O-H groups of these polysaccharides. Mott-Wannier excitons along the dyes resonate with electrons along the iodine chains. Excitons are emitted and absorbed, as required in the Little’s model for high temperature superconductivity. It was proposed that if O-H groups of α or β-cyclodextrins and amylose are replaced by dye molecules, iodine chain may become superconducting (13). We have tried here hydrogen bonding of oxygen atoms or O-H groups with O-H and N-H containing dyes.

2.2 EXPERIMENTAL DETAILS:

α-cyclodextrin, β-cyclodextrin and amylose in analytical reagent grade were obtained from Sigma chemical company. The inclusion compounds of KI-I$_2$ were precipitated by evaporation method from aqueous solution. The blue
coloured inclusion compounds were mixed with pure dyes such as Congo red, Direct red, Para red, Bismark brown, Typan blue and Evans blue and grinded till the colour deepened. Grinding in an agate mortar with agate pastle led to molecular contact between the inclusion compounds and dye molecules.

The spectra in the range 400-4000 cm\(^{-1}\) were recorded using a GXFIR single beam spectrophotometer manufactured by Perkin-Elmer co. USA having a resolution of 0.15 cm\(^{-1}\) a scan range of 15600-30 cm\(^{-1}\) and a scan time 20 scan sec. An optical phase detector (OPD) velocity of 0.20 cm\(^{-1}\) and mid-infrared triglycine sulfate (MIRTGS) and far infrared triglycine sulfate (FIRTGS) detectors. A beam splitter of the opt KBr type was used, having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode.

2.3 RESULTS AND DISCUSSION :

The molecular structure of \(\alpha\)-cyclodextrin is shown along with hydrogen bonded dyes (R) at oxygen atoms. (Figure 1). The dyes provide highly polarizable side chains as required in Little’s model. High polarizability of dye molecules means easy generation of electronic excitations (excitons) which are weakly bound. It was realized that the band gap along the iodine chains was around 0.225 eV and \(\beta\)-cyclodextins (14). Band gap of dyes is also about the same order of magnitude as revealed by infrared spectra of only dyes (Figures 2 & 3). Thus an interband transition along iodine chain and along the dye molecule occur at almost
same energy. The electronic excitation along dye molecules can be referred to generation of Mott-Wannier excitons.

(1)

[Figure 1 Molecular structure of α-cyclodextrin with hydrogen bonded dyes (R)]
[Figure 2 FTIR spectra of (a) Para red, (b) Congo red and (c) Direct red]
Chapter 1

One-dimensional Conductors

(3a)

(3b)
The FTIR spectra of $\alpha$-cyclodextrin–KI-I$_2$-Para red, $\alpha$-cyclodextrin-KI-I$_2$-Congored, $\alpha$-cyclodextrin-KI-I$_2$-Direct red, $\alpha$-cyclodextrin-KI-I$_2$-Bismark brown, $\alpha$-cyclodextrin-KI-I$_2$-Evans blue are shown (Figure 4 & 5). The interband transition (a transition from valance band to conduction band) is analyzed (Figure 6 & 7). In all cases, a break in the slope of straight line in $\alpha$hv vs hv or $(\alpha$hv)$^{1/2}$ vs hv or $(\alpha$hv)$^{1/3}$ vs hv is observed in such a manner that the higher absorption has an intercept lower than the lower absorption cutting hv axis at higher energy. This is in contrast with indirect transition with phonon energy in which higher absorption has higher threshold than lower absorption having lower threshold. This inverted behaviour is also found in some charge transfer complexes such as
Ni(N-H-Salim)$_2$DDQ, Ni(N-H-Salim)$_2$TNF (15), Ni(N-C$_3$H$_7$-Salim)$_2$TCNE (16), Ni(H-dpg)$_2$TCNE (17), (DPPD)$_3$I$_{12}$ (18) and Cu(N-R-Salim)$_2$-PANI (19), where Salim=Salicylaldiminato, hdp=g=diphénylglyoxime, DPPD=diphenyl-p-phenylenediamine, R=H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ and PANI=emeraldine, nigraniline and pernigraniline. In the last case, emeraldine, nigraniline and pernigraniline from hydrogen bonds with Cu(N-R-Salim)$_2$. We assign the inverted behaviour of straight lines to the emission and absorption of excitons. The emission of excitons has lower threshold than the absorption of excitons. This inversion is intrinsically connected to the fact that phonon bands diminish at lower temperature while exciton bands increase in intensity at low temperatures (20). The emission threshold is lower than absorption threshold also shows that first emission of excitons occurs and then absorption of excitons occurs which is logical. An electron along iodine chain first excites a Mott-Wannier exciton (an excitation across the band gap along) of dye molecule and other electron absorbs the exciton. Thus emission of exciton is a primary process and absorption of exciton is consequent secondary process. There is excitonic reduction in the band gap along iodine chains. In α-Cyclodextrin–KI-I$_2$·4H$_2$O, there is allowed direct transition with $(\alpha\nu)^{1/2}$ vs $\nu$ being a straight line. Here $(\alpha\nu)$ vs $\nu$ as in two dimensional conductor or $(\alpha\nu)^{1/2}$ vs $\nu$ or $(\alpha\nu)^{1/3}$ vs $\nu$ plots show straight lines revealing allowed indirect transition or forbidden indirect transition in one dimensional semiconductor. Thus electron phonon interaction along the iodine chains also occurs leading to indirect transition. This is probably due to exciton-phonon
interaction (20). Excitons are also able to excite phonons leading to indirect transition. Exciton-phonon coupling can also be explained with polaronic excitons in which electronic polaron and hole-polaron are forming bound pairs. It is one type of bipolaron.
Figure 4 FTIR spectra of (a) $\alpha$-cyclodextrin-KI-I$_2$-Para red, (b) $\alpha$-cyclodextrin-KI-I$_2$-Conogo red and (c) $\alpha$-cyclodextrin-KI-I$_2$-Direct red.
Figure 5 FTIR spectra of (a) α-cyclodextrin-KI-I$_2$-Bismark brown, (b) α-cyclodextrin-KI-I$_2$-Trypan blue and (c) α-cyclodextrin-KI-I$_2$-Evans blue

\[(a \nu)^{1/2}\]
Figure 6 Analysis of interband transition for (a) $\alpha$-cyclodextrin-KI-I$_2$-Direct red, (b) $\alpha$-cyclodextrin-KI-I$_2$-Para red and (c) $\alpha$-cyclodextrin-KI-I$_2$-Congo red
\[\alpha h \nu (eV)\]

(7a)

\[\sqrt[3]{(\alpha h \nu)}\]

(7b)
The results can also be explained with heavy doping of dye i.e. excitonic medium. Burstein-Moss shift ($\xi_n$ or $\xi_p$) can lead to increase in band gap which is not observed. Rather there is an additional shrinkage ($\Delta_0$ or $\Delta_1$) of the gap due to heavy doping of excitonic medium. $\Delta_0$ is additional shrinkage for direct transition and $\Delta_1$ is the additional shrinkage for indirect transition (23). In this case, the difference in intercept can be in meV and can be explained with $\Delta_0$ or $\Delta_1$.

The electron-electron scattering is a momentum conserving mechanism and an exciton is exchanged between two electron along the iodine chains. The additional shrinkage of the gap is due to electron-electron indirect interaction. There is also an increase absorption or optical conductivity arising from a
conductive (an inverse of resistive transition) transition and exciton-phonon
coupling apart from excitonic intereraction. This decreases activation energy.
Exciton-phonon coupling leads to bumps in absorption or optical conductivity
(23).

The spectra of $\beta$-cyclodextrin-KI-I$_2$-Para red, $\beta$-cyclodextrin-KI-I$_2$-Direct
red, $\beta$-cyclodextrin-KI-I$_2$-Bismark brown, $\beta$-cyclodextrin-KI-I$_2$-Trypan blue and $\beta$-
cyclodextrin-KI-I$_2$-Evans blue are also shown (figures 8 & 9). The interband
transitions are analyzed (Figure 10 & 11). Similarly the spectra of amylose-KI-I$_2$-
Para red, amylose-KI-I$_2$-Congo red, amylose-KI-I$_2$-Direct red and amylose-KI-I$_2$-
Bismark brown are shown (Figures 12 & 13). The interband transitions are also
analyzed (Figure 14). The results and analysis are similar to the hydrogen bonded
complexes of $\alpha$-cyclodextrin-KI-I$_2$-4H$_2$O Only in amylose-KI-I$_2$-Para red a jump
in absorption corresponding to a conductive transition is observed, which
increases conductivity at higher energy. A total increase in conductivity of about
two orders of magnitude is expected from such a conductive transition, exciton-
phonon coupling and additional shrinkage of the band gap.
Figure 8 FTIR spectra of (a) $\beta$-cyclodextrin-KI-I$_2$-Para red,
(b) $\beta$-cyclodextrin-KI-I$_2$-Direct red
Figure 9 FTIR spectra of (a) β-cyclodextrin-KI-I₂-Bismark brown,
(b) β-cyclodextrin-KI-I₂-Trypan blue and (c) β-cyclodextrin-KI-I₂-Evans blue

\[ (\alpha h \nu)^{1/3} \]
Figure 10 Analysis of interband transition for (a) β-cyclodextrin-KI-I₂-Direct red, (b) β-cyclodextrin-KI-I₂-Para red
Figure 11 Analysis of interband transition for (a) β-cyclodextrin-KI-I₂-Bismark brown, (b) β-cyclodextrin-KI-I₂-Trypan blue and (c) β-cyclodextrin-KI-I₂-Evans blue
[Figure 12 FTIR spectra of (a) amylose-KI-I$_2$-Para red,

(b) amylose-KI-I$_2$-Congo red]
[Figure 13 FTIR spectra of (a) amylose-KI-I₂-Bismark brown, (b) amylose-KI-I₂-Direct red]
\[ \alpha \propto h \nu \] (14a)

\[ (\alpha h \nu)^{1/3} \] (14b)
Figure 14 Analysis of interband transition for (a) amylose-KI-I$_2$-Bismark brown,
(b) amylose-KI-I$_2$-Congo red, (c) amylose-KI-I$_2$-Direct red,
(d) amylose-KI-I$_2$-Para red
There is also exciton-exciton coupling due to formation of excitons along the iodine chains. This exciton-exciton coupling are of two types. There can be resonant coupling due to in-phase process of creation and annihilation of excitons or it can be anti-resonant coupling due to out of phase process of creation and annihilation of excitons.

In the present work, the absorption coefficients are found to follow:

\[ \alpha h\nu = A(h\nu - E_g + E_{exc} \pm E_p) \]

corresponding to allowed indirect or direct transition in two dimensions

\[ \alpha h\nu = A(h\nu - E_g + E_{exc} \pm E_p)^2 \]

corresponding to allowed indirect transition or in one dimension;

\[ \alpha h\nu = A(h\nu - E_g + E_{exc} \pm E_p)^3 \]

corresponding to forbidden indirect transition in one-dimension. \( E_{exc} \) is the exciton binding energy in meV for Mott-Wannier type exciton. \( E_p \) is the phonon energy. Band gaps and exciton energies are tabulated (Table 1).
2.4 CONCLUSION:

The FTIR spectra of three inclusion compounds namely $\alpha$-cyclodextrin-KI-I$_2$, $\beta$-cyclodextrin-KI-I$_2$ and amylose-KI-I$_2$ when further hydrogen bonded with various dyes have been obtained and analyzed. The analysis of interband transition reveals an indirect electron-electron interaction through Mott-Wannier exciton across dye molecules.

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Table 1  Band gaps and exciton energy \( (E_{\text{exc}}) \) for various inclusion compounds of iodine hydrogen bonded with dyes.

<table>
<thead>
<tr>
<th>Name of the Complex</th>
<th>Band gap ( E_g ) (eV)</th>
<th>Exciton energy ( E_{\text{exc}} ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Bismark brown</td>
<td>0.218</td>
<td>21.6</td>
</tr>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Direct red</td>
<td>0.215</td>
<td>33.0</td>
</tr>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Evans blue</td>
<td>0.220</td>
<td>31.6</td>
</tr>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Para red</td>
<td>0.208</td>
<td>73.0</td>
</tr>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Congo red</td>
<td>0.156</td>
<td>41.2</td>
</tr>
<tr>
<td>α-cyclodextrin-KI-I(_2)-Typan blue</td>
<td>0.177</td>
<td>83.6</td>
</tr>
<tr>
<td>β-cyclodextrin-KI-I(_2)-Bismark brown</td>
<td>0.213</td>
<td>40.6</td>
</tr>
<tr>
<td>β-cyclodextrin-KI-I(_2)-Direct red</td>
<td>0.224</td>
<td>61.4</td>
</tr>
<tr>
<td>β-cyclodextrin-KI-I(_2)-Evans blue</td>
<td>0.220</td>
<td>31.3</td>
</tr>
<tr>
<td>β-cyclodextrin-KI-I(_2)-Para red</td>
<td>0.224</td>
<td>20.3</td>
</tr>
<tr>
<td>β-cyclodextrin-KI-I(_2)-Typan blue</td>
<td>0.238</td>
<td>59.8</td>
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<tr>
<td>amylose-KI-I(_2)-Bismark brown</td>
<td>0.213</td>
<td>29.4</td>
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<tr>
<td>amylose-KI-I(_2)-Congo red</td>
<td>0.180</td>
<td>48.4</td>
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<tr>
<td>amylose-KI-I(_2)-Direct red</td>
<td>0.165</td>
<td>71.9</td>
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<tr>
<td>amylose-KI-I(_2)-Para red</td>
<td>0.189</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Chapter 3

Spectroscopic study of hydrogen bonded \((\text{Cu-N-R-salim})_2\)

where \(R=\text{H, CH}_3, \text{C}_2\text{H}_5 & \text{C}_6\text{H}_5\) with emeraldine, nigraniline and pernigraniline
3.1 INTRODUCTION:

The theoretical model of high temperature superconductivity on the basis of excitonic interaction was proposed long ago (Little 1964). It was based on polyene polymer substituted with cyanine dyes attached to it. No experimental material could be found even for long time after that. This Little’s model has synthetic problems. The model was revised for organo-metallic complexes containing metal chains (Davis et al 1976). Organometallic chelates are also non-reactive and it becomes difficult to convert a dye-precursor into a real dye molecule. It was suggested that the polyiodine chain complexes which were inclusion compounds of cyclodextrins or amylose may become superconducting provided the external hydroxyl groups of inert host matrices are replaced by dyes (Little 1970). However, the covalent bonding of dyes with amylose or cyclodextrin may not be possible, it should be possible to make hydrogen bonding of dyes with such oxygen and O-H containing molecules. The model was also suggested for cyclopeptides containing naturally-occurring side chains but no transition metal complexes are found to be formed (Oza 1998). Hydrogen bonding of polyanilines with polyacrylonitriles was found in composites recently (Weipen et al 2005). A protonated substitution of one hydrogen atom was also observed for polyaniline derivatives in palladium based systems (Hasik et al 2001). Intermolecular hydrogen bonding was also verified between protonated polyanilines and poly(urethaneamide) and poly(1-naphthylamine) using FTIR spectroscopy (Asharf...
FTIR spectroscopy of partial ordered polyaniline films also revealed organization of PANI chains within film by hydrogen bonds through absorption bands in the 3300-2800 cm\(^{-1}\) region (Trachora et al. 2003). Because of these problems, we try hydrogen bonding of dye-like molecules with metal-organic compounds. Specifically, we try to form hydrogen bonding of polyanilines like emeraldine, nigraniline and pernigraniline with bis(N-R-salicylal-diminato)Cu\(^{II}\). The relevant molecular structures are shown (Figure 1).

Where R= H, CH\(_3\), C\(_2\)H\(_5\) & C\(_6\)H\(_5\)
3.2 EXPERIMENTAL DETAILS:

Bis(N-R-salicylaldiminato)Cu\textsuperscript{II} where R=H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5} were prepared by reacting copper ion with appropriate amines namely ammonia solution, methyl amine, ethylamine and phenylamine (aniline) and salicyldehyde. The medium was rendered alkaline by adding more KOH. The chelates were formed through exothermic reaction.

Emeraldine, nigraniline and pernigraniline were prepared by oxidizing aniline hydrochloride with oxidizing agent hydrogen peroxide, perchloric acid and potassium dichromate respectively in the presence of sulfuric acid. Emeraldine was green, nigraniline was blue and pernigraniline was violet. For reactions to be
complete, mild heating of the reactants was carried out. The heat treatment produced thermally polarized oligoanilines which showed better (more resolved and more quantitative) spectra than the same materials prepared without heating (4).

The chelate powders were mixed with the above polyanilines in 1:4 molecular weight proportions and further grinded in an agate mortar with agate paste till very fine powder was formed by dispersion at very microscopic level. The homogeneous powder was placed in a dye and compressed pallets were prepared by a manually operated high pressure compressing machine after grinding the products with completely dry spectrograde KBr powder which was 90-95 % of the total amount. The semitransparent pallets were kept in a dark chamber of a Perkin-Elmer spectrophotometer. The FTIR spectra in the full range were recorded between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\). It was GXFTIR single beam spectrophotometer of Perkin-Elmer co.,USA having a resolution of 0.15 cm\(^{-1}\), scan range 15,600-30 cm\(^{-1}\), scan time 20 scan/sec and OPD velocity of 0.20 cm/sec. MIRTGS and FIRTGS were used as detectors. The spectra were recorded in purge mode.

3.3 RESULTS AND DISCUSSION:

The band assignments in the infrared spectra of bis(N-R-salicylal-diminato)Cu\(^{II}\) were recently carried out (Prajapati 2006). The infrared spectra of the molecular complexes of these chelates with emeraldine, nigraniline and
pernigraniline are shown (Figures 2 to 5). The band assignments of the spectra of emeraldine, nigraniline and pernigraniline are tabulated (Table 1). These spectra are quantitatively better than those published elsewhere (Prajapati et al 2005). The other details of these thermally polarized oligoanilines were reported recently (Patel et al 2007). The structures of the copper chelates and oligoanilines both having donating groups are such that there is no possibility of charge transfer intermolecular interactions between the chelates and oligoanilines which can be concluded through quantitative comparison between the spectra of pure chelates, pure oligoanilines and the molecular complexes prepared in the present work.
[Figure 2 FTIR spectra of (a) Cu(N-H-salim)$_2$-Emeraldine, (b) Cu(N-H-salim)$_2$-Nigraniline and (c) Cu(N-H-salim)$_2$-Pernigraniline]
Figure 3 FTIR spectra of (a) Cu(N-CH$_3$-salim)$_2$-Emeraldine,

(b) Cu(N-CH$_3$-salim)$_2$-Nigraniline and (c) Cu(N-CH$_3$-salim)$_2$-Pernigraniline
Figure 4 FTIR spectra of (a) Cu(N-C$_2$H$_5$-salim)$_2$-Emeraldine, (b) Cu(N-C$_2$H$_5$-salim)$_2$-Nigraniline and (c) Cu(N-C$_2$H$_5$-salim)$_2$-Pernigraniline.
Looking at the molecular structures, there are two types of reactive sites of the chelates. The NH end group of all three oligoanilines can be hydrogen bonded with two oxygen atoms of the chelate and with $\pi$-clouds of salicyldehyde rings. The N-H group of the chelate cannot form hydrogen bond with NH group of oligoanilines, particularly in the case of bis(N-H-salicylaldihidiminato)Cu$^{II}$. Also the substituent R= CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ prevent any hydrogen bonding in the other chelates. The possibility is left with oxygen atoms which are bonded with ring carbon atoms on one side and covalently bonded to the copper ion in the center. This possibility can be verified with shift in the frequency of carbonyl bond or metal-ligand vibrations. Although most of the spectra in full range are determined
by the spectra of oligoanilines and hardly three or four bands can be only assigned to the vibrations of the chelates, the metal-ligands vibrations below 700 cm\(^{-1}\) are found to be lowered in frequency because of N-H----O hydrogen bond. These bands are summarized in Table II. The red shift of the vibrations can be attributed to the formation of hydrogen bonds.

The other hydrogen bonding is possible between NH group of oligoaniline and the aromatic ring (\(\pi\)-cloud) of salicyldehyde group. This N-H-- \(\pi\)-cloud hydrogen bond is also possible as found in many other compounds (Ferguson 1973). Because of \(\pi\)-cloud on the aromatic ring, the ring behaves like a strongly electronegative complex ion which can form hydrogen bond. The \(\nu_{\text{N-H}}\) stretching vibration frequency of free N-H group of oligoanilines appear at 3433 cm\(^{-1}\) in emeraldine, 3411 cm\(^{-1}\) in nigraniline and 3412 cm\(^{-1}\) in pernigraniline, respectively. In six complexes out of 12 studied here, there is a large red-shift (shift to lower frequencies) of this stretching vibration (Table III). This means that these six complexes have sufficiently strong hydrogen bonds. In the other six complexes, other high frequency bands (higher than 2000 cm\(^{-1}\)) are shifted to lower frequency which can be assigned to asymmetric stretch of N-H bond vibration. The consistent presence of small shifts in most of the complexes reveals existence of at least weak hydrogen bond. Also the \(\nu_{\text{N-H}}\) vibration of the rings can show red-shift when the \(\pi\)-cloud of the ring forms hydrogen bond.
The nature of transition is studied in these disordered materials by plotting $(\alpha h \nu)^{1/r}$ vs $h \nu$ to fit $\alpha h \nu = A(h \nu - E_g)^r$, where $r = 1/2$ or 3/2 for direct allowed and forbidden transition and $r = 2$ or 3 for indirect allowed or indirect forbidden transition. The best fits are plotted (Figure 6 to 9). Cu(N-H-Salim)$_2$-Emeraldine shows $\alpha h \nu$ vs $h \nu$ as a straight line (Fig.6a) indicating either a forbidden direct transition or allowed indirect transition in two-dimension. This shows that this material is a layered conductor. The hydrogen bonding has nature to hold molecules in a plane. Cu(N-H-Salim)$_2$-Nigraniline shows $\alpha h \nu = A(h \nu - E_g)^{1/2}$ as absorption function (Fig. 6c) showing an allowed direct transition. Cu(N-H-Salim)$_2$-Pernigraniline also follows the same function (Fig. 6c). Cu(N-H-Salim)$_2$-Emeraldine again shows $\alpha h \nu = A(h \nu - E_g)$ indicating either direct or indirect transition in two dimension (Fig. 7a) Cu(N-H-Salim)$_2$-Nigraniline shows allowed indirect transition (Fig. 7c). There is a phonon of energy of 0.07 eV is involved. Again Cu(N-CH$_3$-Salim)$_2$-Perniraniline shows 2-D behaves with either direct or indirect transition (Fig.7d). Emeraldine chelate of ethyl-substituted chelate, i.e. Cu(N-C$_2$H$_5$-Salim)$_2$, shows forbidden direct transition by following $\alpha h \nu = A(h \nu - E_g)^{3/2}$ absorption function (Fig. 8a). $\alpha h \nu = A(h \nu - E_g)^3$ function is followed by Cu(N-H-Salim)$_2$-Nigraniline which reveals forbidden indirect transition (Fig.8c) Cu(N-C$_2$H$_5$-Salim)$_2$-Pernigraniline again obeys the function for 2-D material (Fig.8d). Cu(N-C$_6$H$_5$-Salim)$_2$-Emeraldine reveals forbidden indirect transition (Fig. 9a). The nigraniline complex also obeys the same function (Fig.9b). However, Cu(N-C$_6$H$_5$-Salim)$_2$-Pernigraniline indicates allowed indirect transition by following $\alpha h \nu = $
A(h\nu-E_g)^2 (Fig.9d). All the absorption functions and nature of transitions are summarized (Table IV).
\begin{align}
\sigma(h\nu) &\propto (h\nu)^2 \\
\ln \alpha &\propto (K-K_0)^2
\end{align}
\tag{6c}
\tag{6d}
Figure 6 Analysis of spectra of (a) Cu(N-H-salim)$_2$-Emeraldine for nature of transition,
(b) beta density, (c) Cu(N-H-salim)$_2$-Nigraniline for nature of transition, (d) Gaussian band fit,
(e) Cu(N-H-salim)$_2$-Pernigraniline for nature of transition and (f) Gaussian band fit
\[ \alpha h \nu \]  

(7a)

\[ \ln \alpha \]  

(7b)

\[ (K-K_0)^2 \]
Figure 7 Analysis of spectra of (a) Cu(N-CH$_3$-salim)$_2$-Emeraldine for nature of transition, (b) beta density, (c) Cu(N-CH$_3$-salim)$_2$-Nigraniline for nature of transition, (d) Cu(N-CH$_3$-salim)$_2$-Pernigraniline for nature of transition
\( (\alpha h \nu)^{1/3} \) vs. \( h\nu \text{ (eV)} \)

\[(8a)\]

\( \ln \alpha \) vs. \( (K-K_0)^2 \)

\[(8b)\]
Figure 8 Analysis of spectra of (a) Cu(N-C$_2$H$_5$-salim)$_2$-Emeraldine for nature of transition,
(b) beta density, (c) Cu(N-C$_2$H$_5$-salim)$_2$-Nigraniline for nature of transition,
(d) Cu(N-C$_2$H$_5$-salim)$_2$-Pernigraniline for nature of transition

\( (\alpha \hbar \nu)^{1/3} \) vs. \( \hbar \nu \) (eV)

(9a)

\( (\alpha \hbar \nu)^{1/3} \) vs. \( \hbar \nu \) (eV)

(9b)
\[ \ln \alpha \]

\[ (K-K_0)^2 \]

\[ \text{(9c)} \]

\[ (\alpha h\nu)^{1/2} \]

\[ \text{hv (eV)} \]

\[ \text{(9d)} \]
The electronic absorption envelopes at low frequency below 800 cm\(^{-1}\) are found to be either Gaussian (Fig. 6d,6f,7b,8b,9c,9e) or beta density (Fig. 2a,3c,4b,5a). The Gaussian envelope is associated with free charge carriers and beta density is related with hopping mechanism of conduction.

In many cases of interband transition, a break in the slope of straight line of \(\alpha hv\) vs \(h\nu\), \((\alpha hv)^2\) vs \(h\nu\), \((\alpha hv)^{1/3}\) vs \(h\nu\), \((\alpha hv)^{1/2}\) vs \(h\nu\) is found in such a manner that
the higher absorption has an intercept lower than the lower absorption cutting hv axis at higher energy. This is contrary to indirect transition with phonon energy in which higher absorption has a higher threshold than lower absorption having lower threshold. This is found in the cases of Cu(N-H-Salim)$_2$-Emeraldine (Fig-6a), Cu(N-H-Salim)$_2$-Nigraniline (Fig-6c), Cu(N-CH$_3$-Salim)$_2$-Emeraldine (Fig-7a), Cu(N-C$_2$H$_5$-Salim)$_2$-Emeraldine (Fig-8a), Cu(N-C$_2$H$_5$-Salim)$_2$-Nigraniline (Fig-8c), Cu(N-C$_6$H$_5$-Salim)$_2$-Emeraldine (Fig-9a), Cu(N-C$_6$H$_5$-Salim)$_2$-Nigraniline (Fig-9b) and Cu(N-C$_6$H$_5$-Salim)$_2$-Pernigraniline (Fig-9d). This of inverted behaviour is found in many inclusion compounds of iodine with hydrogen bonded dyes recently. This behaviour is also observed in Ni-(N-H-Salim)$_2$-DDQ, Ni-(N-H-Salim)$_2$-TNF, Ni(N-C$_2$H$_5$-Salim)$_2$-TCNE, Ni(Hdps)$_2$-TCNE, DPPD$_5$ I$_{12}$ and Cu(N-H-Salim)$_2$-PANI where salim = salicylaldiminate, Hdpg=diphenylglyoxime, DPPD=N, N-diphenyl-p-phenylenediamine, R=H,CH$_3$C$_2$H$_5$ and C$_6$H$_5$ and PANI = emeraldine, nigranilne and pernigraniline.

We assign the invered behaviour of straight lines to the emission and absorption of excitons. This inversion is intrinsically connected with the fact that phonon bands diminish at low temperature while exciton bands increase in intensity at low temperature. The emission threshold is lower than absorption threshold also showes that the first emission of exciton occurs and then absorption of exciton occur which is also logical. The emission of exciton is a primary process while absorption of exciton is a secondary process. There can be also
exciton-phonon coupling. Excitons are also able to excite phonons leading to indirect transition. Exciton-phonon coupling can also be explained with polaronic excitons in which electronic polaron and hole-polaron are forming bound pairs. It is one type of bipolaron.

The result can also be explained with heavy doping of dye, i.e. excitonic medium. Burstein-moss shift can lead to increase in the band gap but this is not observed. Rather there is additional shrinkage ($\Delta_0$ or $\Delta_1$) of the gap due to heavy doping. $\Delta_0$ is the additional shrinkage for direct transition and $\Delta_1$ is the additional shrinkage for indirect transition. The difference in intercept can be in meV and can be explained with $\Delta_0, \Delta_1$.

The electron-electron scattering is a momentum conserving mechanism and an exciton is exchanged between two electrons along a copper ion chain. There is also an increase in absorption or optical conductivity arising from a conductive (an onverse pf resistive transition) transition and exciton-phonon coupling. Exciton-phonon coupling leads to bumps in absorption or optical conductivity. A total increase in conductivity of about two orders of magnitude is expected from such a conductive transition, exciton-phonon coupling and additional shrinkage of the band gap. Band gaps and exciton energies are tabulated (Table V).
3.4 CONCLUSION:

The bis(N-R-Salicylaldiminato)Cu$^{II}$ forms either strong or weak hydrogen bonding of intermolecular type with polyanilines namely emeraldine, nigraniline and pernigraniline. There are N-H---($\pi$-cloud) hydrogen bonds and N-H---($\pi$-cloud) hydrogen bonds as verified with low frequency shifts of some of the stretching vibrations and metal-ligand vibrations. Both direct and indirect interband transitions are found in either purely organic or organometallic chelate based CT complexes. Some of the complexes are perfectly planar as hydrogen bonding favours such a layered structure.

REFERENCE:

1. Little W A, Phys, Rev A 143 (1964) 416.


Table 1: Band assignments in the infrared spectra of thermally polarized oligoanilines.

<table>
<thead>
<tr>
<th>Emeraldine band assignment (cm⁻¹)</th>
<th>Nigraniline band assignment (cm⁻¹)</th>
<th>Pernigraniline band assignment (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3433 $\nu_{N-H}$</td>
<td>3411 $\nu_{N-H}$</td>
<td><strong>3412</strong> $\nu_{N-H}$</td>
</tr>
<tr>
<td>2988 $\nu_{C-H}$</td>
<td>2977 $\nu_{C-H}$</td>
<td>-</td>
</tr>
<tr>
<td>2883</td>
<td>2884</td>
<td>2888</td>
</tr>
<tr>
<td>2591</td>
<td>2592</td>
<td>2400</td>
</tr>
<tr>
<td>2361</td>
<td>2001</td>
<td>-</td>
</tr>
<tr>
<td>1599 $\delta_{N-H}$/ $\delta_{N-H}$</td>
<td>1571 $\delta_{N-H}$/ $\delta_{N-H}$</td>
<td>1597 $\delta_{N-H}$/ $\delta_{N-H}$</td>
</tr>
<tr>
<td>1497</td>
<td>1496</td>
<td>1497 $\delta_{C-H}$</td>
</tr>
<tr>
<td>1445 $\nu_{cc}$ or $\nu_{C-N}$</td>
<td>1328 $\nu_{cc}$ or $\nu_{C-N}$</td>
<td>1302 $\nu_{cc}$ or $\nu_{C-N}$</td>
</tr>
<tr>
<td>1118</td>
<td>1290</td>
<td>1127</td>
</tr>
<tr>
<td>1025</td>
<td></td>
<td>1112</td>
</tr>
<tr>
<td>741 $\pi_{C-H}$ twisting, rocking &amp; wagging</td>
<td>743 $\pi_{C-H}$ twisting, rocking &amp; wagging</td>
<td>756 $\pi_{C-H}$ twisting, rocking &amp; wagging</td>
</tr>
<tr>
<td>688</td>
<td>686</td>
<td>693</td>
</tr>
<tr>
<td>616</td>
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<td>479</td>
<td>530</td>
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</tr>
<tr>
<td>475</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II Metal Ligand vibrations and their shift due to hydrogen bonding.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M-L Vibration (cm(^{-1}))</th>
<th>Complex with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Em (cm(^{-1}))</td>
<td>Nig (cm(^{-1}))</td>
</tr>
<tr>
<td>Cu(N-H-Salim)(_2)</td>
<td>500</td>
<td>475</td>
</tr>
<tr>
<td></td>
<td>494</td>
<td>400</td>
</tr>
<tr>
<td>Cu(N-CH(_3)-Salim)(_2)</td>
<td>570</td>
<td>526</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>410</td>
</tr>
<tr>
<td>Cu(N-C(_2)H(_5)-Salim)(_2)</td>
<td>614</td>
<td>524</td>
</tr>
<tr>
<td></td>
<td>447</td>
<td>410</td>
</tr>
<tr>
<td>Cu(N-C(_6)H(_5)-Salim)(_2)</td>
<td>523</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>434</td>
<td>420</td>
</tr>
</tbody>
</table>

Table III: Red-shift due to N-H-π-cloud H-bond

(a) Four clear cases of strong hydrogen bonding

<table>
<thead>
<tr>
<th>Complex</th>
<th>N-H Stretching frequency in oligoaniline</th>
<th>Complex with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Em (cm(^{-1}))</td>
<td>Nig (cm(^{-1}))</td>
</tr>
<tr>
<td>Cu(N-H-salim)(_2)-Em</td>
<td>3433</td>
<td>3308</td>
</tr>
<tr>
<td>Cu(N-C(_6)H(_5)-salim)(_2)-Em</td>
<td>3433</td>
<td>3365</td>
</tr>
<tr>
<td>Cu(N-C(_2)H(_5)-salim)(_2)-Nig</td>
<td>3411</td>
<td>-</td>
</tr>
<tr>
<td>Cu(N-CH(_3)-salim)(_2)-Per</td>
<td>3412</td>
<td>-</td>
</tr>
</tbody>
</table>
(a) H-bonds verified with red-shift other high frequency bands above 2000 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Freq. in Oligoanilines</th>
<th>Complex with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>Em cm(^{-1})</td>
</tr>
<tr>
<td>Cu(N-CH(_3)-Salim)(_2)-Em</td>
<td>2591</td>
<td>2587</td>
</tr>
<tr>
<td></td>
<td>2883</td>
<td>2882</td>
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<tr>
<td>Cu(N-C(_2)H(_5)-Salim)(_2)-Em</td>
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<td>2875</td>
</tr>
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<td></td>
<td>2591</td>
<td>2586</td>
</tr>
<tr>
<td>Cu(N-H-Salim)(_2)-Nig</td>
<td>2977</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2592</td>
<td>-</td>
</tr>
<tr>
<td>Cu(N-CH(_3)-Salim)(_2)-Nig</td>
<td>2884</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2592</td>
<td>-</td>
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<tr>
<td>Cu(N-C(_6)H(_5)-Salim)(_2)-Nig</td>
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<td></td>
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<td>-</td>
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<tr>
<td>Cu(N-H-Salim)(_2)-Per</td>
<td>3412</td>
<td>-</td>
</tr>
<tr>
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<td>2888</td>
<td>-</td>
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<tr>
<td>Cu(N-C(_2)H(_5)-Salim)(_2)-Per</td>
<td>2888</td>
<td>-</td>
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<tr>
<td></td>
<td>3412</td>
<td>-</td>
</tr>
<tr>
<td>Cu(N-C(_6)H(_5)-Salim)(_2)-Per</td>
<td>2888</td>
<td>-</td>
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### Table IV: Nature of interband transition.

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<tr>
<th>Molecular Complex</th>
<th>Absorption Function</th>
<th>Nature of transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(N-H-salim)$_2$-Em</td>
<td>$\alpha \nu = A(h\nu - E_g)$</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>Cu(N-H-salim)$_2$-Nig</td>
<td>$\alpha \nu = A(h\nu - E_g)^{1/2}$</td>
<td>Allowed direct</td>
</tr>
<tr>
<td>Cu(N-H-salim)$_2$-Per</td>
<td>$\alpha \nu = A(h\nu - E_g)^{1/2}$</td>
<td>Allowed direct</td>
</tr>
<tr>
<td>Cu(N-CH$_3$-salim)$_2$-Em</td>
<td>$\alpha \nu = A(h\nu - E_g)$</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>Cu(N-CH$_3$-salim)$_2$-Nig</td>
<td>$\alpha \nu = A(h\nu - E_g)^2$</td>
<td>Allowed indirect</td>
</tr>
<tr>
<td>Cu (N-CH$_3$-salim)$_2$-Per</td>
<td>$\alpha \nu = A(h\nu - E_g)$</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>Cu(N-C$_2$H$_5$-salim)$_2$-Em</td>
<td>$\alpha \nu = A(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
</tr>
<tr>
<td>Cu(N-C$_2$H$_5$-salim)$_2$-Nig</td>
<td>$\alpha \nu = A(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Per</td>
<td>$\alpha \nu = A(h\nu - E_g)$</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Em</td>
<td>$\alpha \nu = A(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Nig</td>
<td>$\alpha \nu = A(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Per</td>
<td>$\alpha \nu = A(h\nu - E_g)^2$</td>
<td>Allowed indirect</td>
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Table V: Band gaps and exciton energy for various complexes of Cu(N- R-salim)$_2$ with dyes.

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Band gap $E_g$(eV)</th>
<th>Exciton Energy $E_{exc}$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(N-H-salim)$_2$-Em</td>
<td>0.21</td>
<td>10</td>
</tr>
<tr>
<td>Cu(N-H-salim)$_2$-Nig</td>
<td>0.207</td>
<td>90</td>
</tr>
<tr>
<td>Cu(N-CH$_3$-salim)$_2$-Em</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>Cu(N-C$_2$H$_5$-salim)$_2$-Em</td>
<td>0.20</td>
<td>200</td>
</tr>
<tr>
<td>Cu(N-C$_2$H$_5$-salim)$_2$-Nig</td>
<td>0.14</td>
<td>60</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Em</td>
<td>0.20</td>
<td>60</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Nig</td>
<td>0.16</td>
<td>110</td>
</tr>
<tr>
<td>Cu(N-C$_6$H$_5$-salim)$_2$-Per</td>
<td>0.20</td>
<td>50</td>
</tr>
</tbody>
</table>
Chapter 4

FTIR spectroscopy of hydrogen bonded Cu(N-R-Salim)$_2$

with six dyes.

4.1 Introduction:
Infrared analogies of optical phenomena in soft semiconductors have been an interesting subject. These analogies included nature of transition (1-18) band tailing (9,10,12,13), free-carrier absorption (1,9,10,12,13,14,16), Franz-Keldysh or Redfield effect (9,10,12,13), Burstein-Moss shift, spin-orbit splitting of valence band (19), pairing of charge carriers (20), harmonic generation and heterodyning, two-dimensional absorption functions (21), correlated hopping (19,22), noise in photoconductors (8) and square-root singularity in one dimension (15). Thus the optical phenomena mentioned above which appear in uv-visible range in inorganic compound semiconductors appear in infrared rang in organic and metal-organic semiconductors. Here in the present work, exciton-phonon coupling which occurs in GaP (23-26), SiC (27), CdSe (28), AgBr 29,30), ZnO (31), GaAs (32) and carbon nanotubes (33) is observed in soft semiconductors such as hydrogen bonded dyes with bis(N-R-salicylaldiminato)Cu\textsuperscript{II} metal organic l-d system hydrogen bonded with six dyes.

**4.2 Experimental Details:**

Bis(N-R-salicylaldiminato)Cu\textsuperscript{II} chelates where R=H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5}, were prepared by reactions of nickel ion (ionic solutions of nickel chloride) with salicyldehyde and ammonia solution, methylamine, ethylamine and aniline in the presence of a base. These green coloured chelates were mixed and grinded with six dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue obtained in pure forms from Aldrich chemical company. The fine and
homogeneous powders prepared in this manner were remixed with dry (anhydrous) spectrograde KBr powder in 95% amount and grinded. The semitransparent pallates were prepared by compressing these mixtures in a circular die with the help of a manually operated compressing machine. Then these circular discs were placed in a dark chamber of a spectrophotometer.

The spectra in the range 400-4000 cm$^{-1}$ were recorded using a GXFTIR single beam spectrophotometer manufactured by perking-Elmer co. USA. It was having a resolution of 0.15 cm$^{-1}$ a scan range of 15,600-30 cm$^{-1}$, a scan time of 20 scan sec$^{-1}$, an OPD velocity of 0.20 cm sec$^{-1}$ and MIRTGS and FIRTGS detectors. A bean splitter of opt-KBr type was used having a range of 7800-370 cm$^{-1}$. The spectra were recorded in purge mode.

4.3 Result and Discussion:

The molecular structures of bis(N-R-salicyaldiminato)Cu$^{II}$ where R=H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ and six dyes are shown (figure 1). The dyes show hydrogen bondings of N-H----O type , O-H----O type, N-H----π type and O-H----π type between the dyes and the copper chelats. Hydrogen bonding is confirmed with FTIR spectroscopy. N$^{δ+}$-H----O$^{δ}$, O$^{δ+}$-H----O$^{δ}$, N$^{δ+}$-H----π$^{δ}$ and O$^{δ+}$-H----π$^{δ}$ type bonding lead to excitons due to $δ$+ and $δ$- charges. There are no free electronic excitations in either copper chelates or the six dyes. The electronic excitations are found in hydrogen bonded complexes only. Thus excitons and hydrogen bonds are
related. Highly polarized dyes work as side chains across which electronic oscillations occur and molecular excitons are formed. For long side chains these molecular excitons nearly act as Mott-wannier excitons which are weakly bound. Molecular dipoles oscillate as the long-chain dye molecules have dipole moments of several Debyes. Dipole flip-flop continues without any hindrance. Induced charge appearing along copper chelate molecules moves across the metal chain which acts as a spine.

![Chemical Structure 1](image1.png)

![Chemical Structure 2](image2.png)
[Chapter 1]

[One-dimensional Conductors]

(1g) Molecular structures of Cu(N-R-salim)\textsubscript{2} where R=H,CH\textsubscript{3},C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5}

(1b) Para red, (1c) Congo red, (1d) Direct red, (1e) Bismark brown, (1f) Evans blue and

(1g) Trypan blue

The FTIR spectra of Cu\textsuperscript{II}(N-H-salim)\textsubscript{2} bonded with six dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue are shown (figure 2). The nature of transitions are fitted and best fits are shown (figure 3). Cu(N-H-salim)\textsubscript{2}-Para red shows direct transition by fitting $\alpha h\nu=A(h\nu-E_{g})^{1/2}$ [i.e. $(\alpha h\nu)^{1/2}$ vs $h\nu$]. All other complexes show forbidden indirect transition obeying $\alpha h\nu=A(h\nu-E_{g})^{2}$ [i.e. $(\alpha h\nu)^{1/3}$ vs $h\nu$]. Number of phonon bands vs band gap is plotted and almost shows a linear variation (Fig 4). When the exciton-phonon coupling is weak, more number of phonons are emitted and there are also more number of threshold energies of excitons. The band gap is large in this case. When exciton-phonon coupling is strong there are less number of phonon emission bands and band gap is small. In the former case, the exciton density is high and there is more probability for the formation of electron-hole droplets particularly at low temperatures. In the latter case when band gap is small, there is more probability
of recombinations of electron-hole pairs and consequently more possibility of
infrared luminescence.

(2a)

(2b)
Figure 2 FTIR spectra of complexes of Cu(N-H-salim)$_2$ with (a) Para red,
(b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue
\[(\alpha \hbar \nu)^2\]

\[(\alpha \hbar \nu)^{1/3}\]

(3a)

(3b)
(3b)

(3d)

(3e)
[Figure 3 Nature of transitions in complexes of Cu(N-H-salim)$_2$ with (a) Para red, (b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue]

[Figure 4 Number of phonon bands vs band gap for Cu(N-H-salim)$_2$ complexes]
The FTIR spectra of Cu(N-CH₃-salim)₂ bonded with six dyes are also shown (figure 5). Cu(N-CH₃-salim)₂-Para red shows allowed direct transition, Congo red complex shows forbidden indirect transition, Direct red complex shows allowed indirect transition and Bismark brown, Evans blue and Trypan blue complexes shows forbidden indirect transitions the best fits are shown (Figure 6). Number of phonon bands vs band gap is plotted (Figure 7) which again shows a rectilinear behaviour. Numbers of phonon bands are less for the same dye than those found for Cu(N-H-salim)₂ chelate. This shows that the exciton phonon coupling is stronger for Cu(N-CH₃-salim)₂ chelate than that for Cu(N-H-salim)₂ chelate. The Direct red complex shows strongest exciton-phonon coupling with zero number of phonon bands and behaviour similar to those found in hydrogen bonded inclusion compounds of iodine. In this case, band gap as low as 0.12 eV is found. Exciton energy of 0.08 eV(80 eV) is noted because of Taue energy gap $E_g=0.2$ eV.
[Chapter 1] [One-dimensional Conductors]

(5a)

(5b)
Figure 5 FTIR spectra of the complexes of Cu(N-CH$_3$-salim)$_2$ with (a) Para red,
(b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue

\[(\alpha h \nu)^2\]

![Graph (6a)](image)

\[(\alpha h \nu)^{1/3}\]

![Graph (6b)](image)
\[(\alpha h \nu)^{1/2}\]

\[(\alpha h \nu)^{1/3}\]
Figure 6 Nature of transitions in the complexes of Cu(N-CH$_3$-salim)$_2$ with

(a) Para red, (b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and

(f) Trypan blue.

Figure 7 Number of phonon bands vs band gap for Cu(N-CH$_3$-salim)$_2$ complexes.

The FTIR spectra of Cu(N-C$_2$H$_5$-salim)$_2$ hydrogen bonded with the above mentioned six dyes are shown (Figure 8). Nature of transitions are fitted and best fits are shown (Figure 9). Number of phonon bands vs band gap shows a curve (Figure 10). As the exciton-phonon coupling weakers, band gap shows a saturation. For more number of phonons a plateau is found in band gap. This shows that for bulky substitution like ethyl group or for a larger chelating ligand, no. of phonon bands vs band gap shows a departure or deviation from rectilinear behavior.
Chapter 1  
One-dimensional Conductors

![Graph](8c)

![Graph](8d)
[Figure 8 FTIR spectra of the complexes of Cu(N-C\textsubscript{3}H\textsubscript{5}-salim)\textsubscript{2} with (a)Par red,
(b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue

\[ (\alpha h \nu)^{1/3} \]

\[ (\alpha h \nu)^{1/3} \]

\[ \text{hv (eV)} \]

\[ (\alpha h \nu)^{1/3} \]

\[ \text{hv (eV)} \]

(9a)

(9b)
(9f)

(10)

[Figure 9 Nature of transitions in the complexes of Cu(N-C$_2$H$_5$-salim)$_2$ with

(a)Para red,(b)Congo red,(c)Direct red,(d)Bismark brown,(e)Evans blue and

(f)Trypan blue]

[Figure 10 Number of phonon bands vs band gap for Cu(N-C$_2$H$_5$-salim)$_2$ complexes]
The FTIR spectra of Cu(N-C₆H₅-salim)₂ hydrogen bonded with six dyes are also shown (Figure 11). Nature of transitions are analyzed and best fits are shown (Figure 12). Number of phonon band vs gap again shows a curve for bulky ligand with benzene rings as a substitution (Figure 13). There is a plateau in band gap for large number of phonon bands. However the total no. of phonon bands is not very high indicating sufficient strength of exciton-phonon coupling. This shows more no. of free excitons which are strongly bound to phonons. Cu(N-C₆H₅-salim)₂-Para red complex in spite of having large number of phonon bands has a very small band gap of 0.16 eV only. This does not fall anywhere on no. of phonon bands vs band gap curve and it is an exceptional case. About 10-12 phonon bands are found with weak but band gap is very small. In fact it shows excitonic binding energy almost equal to band gap with the behavior similar to the hydrogen bonded inclusion compounds of iodine. Exciton emission occur first and absorption is a secondary process. Thus an inverted behavior with respect to phonon emission and absorption is found. Emission threshold is lower than absorption threshold.
Figure 11 FTIR spectra of the complexes of Cu(N-C6H5-salim)2 with (a) Par red, (b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue.
\( (\alpha h \nu)^{1/3} \)

![Graph 1](12a)

\( (\alpha h \nu)^{1/2} \)

![Graph 2](12b)
\((\alpha h\nu)^{1/3}\)

(12c)

\((\alpha h\nu)^{1/2}\)

(12d)
Figure 12 Nature of transitions in the complexes of $\text{Cu(N-C}_6\text{H}_5\text{-salam)}_2$ with

(a)Para red,(b)Congo red,(c)Direct red,(d)Bismark brown,(e)Evans blue

and (f)Trypan blue]
Band tailing of either a conduction band or a valence band or both is described by

\[ \alpha = \alpha_0 \exp \left\{ \frac{\hbar \nu - E_1}{E_0} \right\} \]

where \( E_0 \) is called the width of the tail and \( E_1 \) is called the focal point. \( E_0 \) is a measure of amount of disorder and \( E_1 \) is the characteristic of the parent material. When \( E_0 \) is large, disorder is more. When \( E_0 = k_B T \) it is called Urbach tail. \( E_0 \) is found as inverse of the slope of \( \ln \alpha \) vs \( \hbar \nu \) plot, because

\[ E_0 = \left[ \frac{\delta \ln \alpha}{\delta (\hbar \nu)} \right]^{-1} = \frac{1}{\text{slope}} \]

[Figure 13 Number of phonon bands vs band gap for Cu(N-C_6H_5-salim)_2 complexes]
This analysis is done here for Cu(N-R-salim)\(_2\) with six dyes for R = H, CH\(_3\), C\(_2\)H\(_5\) and C\(_6\)H\(_5\) (Figures 14 to 17). The Taue energy gap E\(_T\) found from plots of \((\alpha h \nu)^{1/\tau}\) vs \(h \nu\) and the width of tail E\(_0\) as calculated from slope are plotted (Fig. 14b, 15b, 16b, 17b). It is found as expected that E\(_g\) decreases linearly as E\(_0\) increases. This is also theoretically understood (34). E\(_0\) depends on dye molecule while E\(_1\) depends on chelate Cu(N-R-salim)\(_2\).
Figure 14 (a) Band tailing and focal point analysis for Cu(N-H-salim)$_2$ with six dyes

(b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail

(14b)

(15a)
(15b)

Figure 15 (a) Band tailing and focal point analysis for Cu(N-CH$_3$-salim)$_2$ with six dyes

(b) $E_g$ vs $E_0$, i.e. band gap vs width of the tail

(16a)
Figure 16 (a) Band tailing and focal point analysis for Cu(N-C$_2$H$_5$-salim)$_2$ with six dyes

(b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail

\[ E_g \text{ vs } E_0 \]

\[ \text{(16b)} \]

\[ \ln \alpha \text{ vs } h\nu \]

\[ \text{(17a)} \]
**4.4 Conclusion:**

The FTIR spectra of Cu(N-R-salim)$_2$ where R = H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ hydrogen bonded with six highly polarizable dyes, are studied and analyzed in the present work. Nature of transitions are fitted which are usually found to be indirect transitions. No. of phonon bands vs band gap graphs are plotted which show rectilinear behavior for R = H and CH$_3$ but for R = C$_2$H$_5$ and C$_6$H$_5$ these graphs
show deviation from a linear correlation. Exciton-phonon coupling decreases as
no. of phonon band increases thus band gap decreases with increase in exciton
phonon coupling.

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Chapter 5

FTIR Spectra of Ni(N-R-salim)2 hydrogen bonded with

emeraldine, nigraniline and pernigraniline
5.1 Introduction:

Bis (N-R-Salicylaldiminato)Ni\textsuperscript{II}, Ni(N-R-Salim)\textsubscript{2}, where R=H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5} are likely to have nickel chains along one crystallographic direction. Recently these l-d chelates were found to form charge transfer complexes (CTCs) with organic acceptors such as TCNQ, TCNE, DDQ, Chloronil and iodine and the CTCs were studied with uv-visible near IR and IR spectroscopies (1). The l-d conductors are likely to be excitonic superconductors due to exciton-based mechanism of superconduction as suggested by Little (2,3). In Little’s model, there is a spine which is attached dye molecules in transverse direction which act as an excitonic medium. Spine embedded in tightly packed high exciton density medium may become superconducting due to electron pairing with interaction mediated by excitons. However, the stringent condition of attaching four dye molecules to every atom of a spine through covalent or co-ordination bonding is never fulfilled. Therefore, in the present work, we try hydrogen bonding of highly polarizable systems such as polyanilines with these l-d chelates. The exciton formation and hydrogen bonding are related. The exciton-phonon coupling which occurs in gallium phosphitde (GaP) (4-8), silicon carbide (SiC) (9), cadmium selenide (CdSe) (10), Silver bromide (AgBr) (11,12), Zinc oxide (ZnO) (13), gallium arsenide (GaAs) (14) and carbon nanotubes (15) is observed in soft semiconductors such as hydrogen bonded dyes with Ni(N-R-salim)\textsubscript{2}. Theories of direct and indirect excitons are known (16,17). Phonon-assisted indirect transitions
in Si and Ge are explained with excitonic theory of electroabsorption (18). The Urbach optical absorption edge is also studied in details (19).

5.2 Experimental Details:

Bis(N-R-salicylaldiminato)Ni\textsuperscript{II} chelates where R=H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5} were prepared by reactions of nickel ion with salicyldchylene and ammonia solution or methylamine or ethylamine or aniline in the presence of a base. These green or blue coloured chelates were grinded with six dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue respectively, which were obtained in pure forms from Aldrich chemical company. The fine and homogeneous powders prepared in this manner where remixed with dry (anhydrous) spectrograde KBr powder in 95\% amount and grinded. The semitransparent pallates were prepared by compressing these mixtures in a circular die with the help of a manually operated compressing machine. Then these palates were placed in a dark chamber of spectrophotometer.

The spectra in the range 400-4000 cm\textsuperscript{-1} were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin-Elmer company, USA. It was having a resolution of 0.15 cm\textsuperscript{-1}, a scan range of 15,600-30 cm\textsuperscript{-1}, a scan time of 20 scan sec\textsuperscript{-1}, an OPD velocity of 0.20 cm sec\textsuperscript{-1} and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\textsuperscript{-1}. The spectra were recorded in a purge mode.
5.3 Results and Discussion:

The molecular structures of Ni(N-R-salim)₂ where R= H, CH₃, C₂H₅ and C₆H₅ & the polyanilines are shown (Figure 1). The FTIR spectra of Ni(N-H-salim)₂-emeraldine, Ni(N-H-salim)₂-nigraniline, Ni(N-H-salim)₂-pernigraniline are shown (Figure 2). The optical absorption edge above 1600 cm⁻¹ is found to be modified with large number of absorption bands. These bands can be either due to several levels of Mott-Wannier excitons or phonon bands.

[Figure 1 Molecular structures of Ni(N-R-salim)₂ where R=H,CH₃,C₂H₅ & C₆H₅ and three polyanilines]
The possibility of excitonic bands is discarded because these bands appear for $E > E_g$ where $E_g$ is the point where $\alpha = 0$. If these were excitonic bands due to several levels of a Mott-Wannier exciton they would appear for $E < E_g$, because the position of such bands are given by Rydberg equation (20)

$$E_n = E_g - \frac{(\mu e^4)}{2\hbar^2 c^2 n^2}$$

where $n$ is the principal quantum number. Note that $E_n < E_g$. Thus we assign such bands in the infrared range to the phonon bands. However, there is exciton-phonon coupling which modifies absorption edge. The situation is similar to GaP (4-8)

[Figure 2 FTIR spectra of Ni(N-H-salim)$_2$ bonded with (a) emeraldine, (b) nigraniline and (c) pernigraniline]
where a large number of threshold energies for the formation of excitons are observed with phonon emissions in the absorption edge spectrum.

When the exciton-phonon coupling is weak, there are large no. of phonon bands and when it is strong, there are less no. of phonon bands. This correlation has been found. As the exciton-phonon coupling increases band gap decreases. Here Tauc energy gap $E_g(T)$ is found from extrapolation of higher absorption coefficient than the Urbach band tail range \((21)\). Ni(N-H-salim)$_2$-emeradine shows 
\((\alpha h\nu)^{1/2}\) vs \(h\nu\) as a straight line Ni(N-H-salim)$_2$-nigraniline shows 
\((\alpha h\nu)^{1/3}\) vs \(h\nu\) as a straight line. Thus these absorption functions obeys relations for allowed direct, allowed indirect in two-dimensions and forbidden indirect transitions respectively (Figure 3). When the same range is explored for band tailing range by plotting ln\(\alpha\) vs \(h\nu\) because of

$$
\alpha = \alpha_0 \exp \left[ \frac{(h\nu-E_1)}{E_0} \right]
$$

relation giving the width of the tail \((E_0)\) as

$$
E_0 = \left[ \frac{\delta \ln \alpha}{\delta h\nu} \right]^{-1}
$$

= 1/slope

a straight line plot of background absorption superposed by band spectrum is found (Figure 4).
\[(\alpha \nu)^{1/2}\]

\[(3a)\]

\[\alpha \nu\]

\[(3b)\]
\[(αhν)^{1/3}\]

Figure 3 Nature of transitions in Ni(N-H-salim)2 bonded with (a) emeraldine, (b) nigraniline and (c) pernigraniline

\[(\ln α)\]

Chart Title
The number of phonon bands vs band gap are also noted (Figure 15). As the no. of phonon bands increases, as the exciton-phonon coupling strength decreases, band gap increases. However, the relation is not linear in spite of strong exciton-phonon coupling as found in the case of copper chelates hydrogen bonded with polyanilines. The phonon bands are very pronounced here revealing weaker strengths of exciton-phonon coupling than those found in copper analogs.
\begin{align*}
\text{(15a)} & \quad 
\begin{array}{c}
\text{No. phonon bands} \\
0 & 1 & 2 & 3 & 4 & 5 & 6
\end{array} \\
\begin{array}{c}
\text{Band gap (eV)} \\
0 & 0.05 & 0.1 & 0.15 & 0.2 & 0.25 & 0.3
\end{array} \\
\end{align*}

\begin{align*}
\text{(15b)} & \quad 
\begin{array}{c}
\text{No. of phonon bands} \\
0 & 1 & 2 & 3 & 4 & 5 & 6
\end{array} \\
\begin{array}{c}
\text{Band gap (eV)} \\
0 & 0.05 & 0.1 & 0.15 & 0.2 & 0.25 & 0.3
\end{array} \\
\end{align*}
The FTIR spectra of Ni(N-CH$_3$-salim)$_2$ hydrogen bonded with polyanilines are shown (Figure 5). Here also oscillations in the absorption edge are found but...
phonons bands are very weak compared to the analogous complexes of Ni(N-H-salim)_2 (αhν)^{1/3} vs hν, (αhν)^{1/2} vs hν and (αhν)^{1/2} vs hν are found to the best fits for emeraldine, nigraniline and pernigraniline complexes, respectively. These show forbidden indirect and allowed indirect transitions in these complexes (Figure 6). Ni(N-CH_3-salim)_2-emeraldine reveal very weak phonon bands but inverted behavior for exciton emission and absorption as compared to phonon emission and absorption. It shows that exciton emission threshold is lower than exciton absorption threshold. This means exciton emission process is primary and exciton absorption is a secondary process. This behavior is similar to hydrogen bonded inclusion compounds of iodine. Exciton-phonon coupling is very strong so that band gap is found to be exceptionally small. For Ni(N-CH_3-salim)_2-emeraldine band gap is as small as 0.08 eV. When the urbach tail is analyzed by plotting lnα vs hν, the background absorption is a straight line (Figure 7).
[Figure 5 FTIR spectra of Ni(N-CH$_3$-salim)$_2$ bonded with

(a) emeraldine, (b) nigraniline, (c) pernigraniline]
[Figure 6 Nature of transitions in Ni(N-CH3-salim)2 bonded with (a) emeraldine, (b) nigraniline, (c) pernigraniline]
Figure 7 Analysis of band tailing for Ni(N-CH$_3$-salim)$_2$ bonded with (a) emeraldine, nigraniline and pernigraniline (b) $E_g$ vs $E_0$
The FTIR spectra of Ni(N-C2H5-salim)2 hydrogen bonded with three polyanilines are shown (Figure 8). Here too phonon bands observed in absorption edge spectrum are weak. Here direct transitions obeying $(\alpha\nu)^{2/3}$ vs $\nu$ are found in all of the three complexes (Figure 9). However, transitions are forbidden. The relation is found to be linear as in the case of strong exciton-phonon coupling. When $\ln \alpha$ vs $\nu$ are plotted the background absorption is linear (Figure 10).
[Figure 8 FTIR spectra of Ni(N-C_2H_5-salim)_2 bonded with (a)emeraldine, (b)nigraniline and (c)pernigraniline]
Figure 9 Nature of transitions in Ni(N-C₅H₅-salim)₂ bonded with
(a) emeraldine, (b) nigraniline and (c) pernigraniline
Figure 10 Analysis of band tailing for Ni(N-C$_3$H$_7$-salim)$_2$ bonded with (a) emeraldine, nigraniline and pernigraniline (b) $E_g$ vs $E_0$
The FITR spectra of Ni(N-C₆H₅-salim)₂ hydrogen bonded with the three polyanilines are shown (Figure 11). Nature of transitions are analyzed and best fits are plotted (Figure 12). Ni(N-C₆H₅-salim)₂-emeraldine show \((\alpha h\nu)^{1/2}\) vs \(h\nu\) as the best fit revealing transition to be allowed indirect type. Ni(N-C₆H₅-salim)-nigraniline and Ni(N-C₆H₅-salim)₂-pernigraniline show \((\alpha h\nu)\) vs \(h\nu\) as the best fit revealing indirect allowed transition in layered (two dimensional) materials. Ln\(\alpha\) vs \(h\nu\) plots show linear graph for band tailing (Figure 13). The correlation is not linear indicating that exciton-phonon coupling is weak.
[Figure 11 FTIR spectra of Ni(N-C_{6}H_{5}-salim)_{2} bonded with (a) emeraldine, (b) nigraniline and (c) pernigraniline]
\[(\alpha \hbar \nu)^{1/2}\]

(12a)

\[\alpha \hbar \nu\]

(12b)
Figure 12 Nature of transitions in Ni(N-C\textsubscript{6}H\textsubscript{5}-salim)\textsubscript{2} bonded with (a) emeraldine, (b) nigraniline and (c) pernigraniline.
Apart from the absorption edge spectrum above 1600 cm\(^{-1}\), the FTIR spectra show low-frequency gausssian bands below 1000 cm\(^{-1}\) particularly in the emeraldine complexes. The gausssians are fitted by plotting \( \ln \alpha \) vs \((k-k_0)^2\) because the gausssion function is given by

\[
\alpha = \alpha_0 \exp \left[-(k-k_0)^2/2M_2\right]
\]

where \(\alpha_0\) is absorption maximum, \(k_0\) is the central wave number and \(M_2\) is the second moment of the distribution. These gausssion fits are shown (Figure 14).
\begin{align}
\ln \alpha & = 4.445 + \frac{4.45}{(k-k_0)^2} \\
\ln \alpha & = 4.455 + \frac{4.46}{(k-k_0)^2}
\end{align}
Figure 14 Low-frequency gaussian bands fitted for emeraldine complexes of 
(a)Ni(N-H-salim)$_2$, (b)Ni(N-CH$_3$-salim)$_2$ and (c)Ni(N-C$_2$H$_5$-salim)$_2$]

5.4 Conclusion:

Theories of direct and indirect excitons as discussed elsewhere (16,17) apply to the present hydrogen bonded complexes phonon assisted recombination of electron hole pairs given rise to infrared luminescence particularly in small band gap semiconductor with strong exciton phonon coupling however there is possibility of electron hole droplet formation at low temperatures because of high exciton density in the present hydrogen bonded complexes.
REFERENCES:


Chapter 6

FTIR spectra of Ni(N-R-salim)$_2$ hydrogen bonded with six dyes

6.1 Introduction:
Bis(N-R-salicyldimino)Ni\textsuperscript{II}, Ni(N-R-salim)\textsubscript{2}, where R=H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5} and C\textsubscript{6}H\textsubscript{5} are likely to have nickel chains along one crystallographic direction. Recently these 1-d chelates were found to form charge transfer complexes (CTCS) with organic acceptors such as TCNQ, TCNE, DDQ, chloronil and iodine. These CTCS were studied with uv-visible near IR and IR spectoscopies (1). Some of them were found to be even semimetallic with negative activation energy when studied with temperature dependence of electrical resistivity. Excitonic supercoduction model was proposed (2,3). However the stringent condition of attaching four dye molecules to every atom of the spine is never fulfilled. Therefore, in the present work, we try hydrogen bonding of highly polarizable dyes such as Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue with the nickel chelates. The exciton-phonon coupling which occurs in GaP (4-8), Sic (9), CdSe (10), AgBr (11,12), ZnO (13), GaAs (14) and Carbon nanotubes (15) is observed in soft semiconductors studied in the present work. Theories of direct and indirect excitons are known (16,17) phonon assisted indirect transitions in Si and Ge are explained with excitonic theory of electroabsorption (18). The Urbach optical absorption edge is also studied in details (19).

6.2 Experimental Details:
Bis(N-R-salicylaldiminato)Ni chelates where R=CH$_3$ and C$_2$H$_5$ were prepared by reaction of the nickel ion with salicyldehyde and methylamine or ethylamine in the presence of a base. These green or blue coloured chelates where mixed with dyes and grinded. The fine and homogeneous powder were remixed with dry (anhydrous) spectrograde KBr powder in 95% amount and regrinded. The semitransparent palates were prepared by compressing these mixtures in the form of circular discs with the help of a manually operated compressing machine. Then these palates were placed in a dark chamber of spectrophotometer.

The spectra in the range of 400-4000 cm$^{-1}$ where recorded in a GXFTIR single beam spectrophotometer manufactured by Perkin-Elmer company, USA. It was having a resolution of 0.15 cm$^{-1}$, a scan range of 15,600-30 cm$^{-1}$, a scan time of 20 scan/sec, an OPD velocity of 0.20 cm/ses and MIRTGS and FIRTGS detector. A beam splitter of opt KBr type was used having a range of 7800-370 cm$^{-1}$. The spectra were recorded in purge mode.

6.3 Results and Discussion:

The molecular structures of Ni(N-R-salim)$_2$ where R= CH$_3$, and C$_2$H$_5$ and six dyes are shown (Figure 1). The FTIR spectra of Ni(N-CH$_3$-salim)$_2$ hydrogen bonded with six dyes namely such as Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue are shown (Figure 2).
(1a)

(1b)

(1c)
[Figure (1a) Molecular structures of Ni(N-R-salim)$_2$, where R=CH$_3$ and C$_2$H$_5$ (1b)Para red, (1c) Congo red, (1d) Direct red, (1e) Bismark brown, (1f) Evans blue and (1g) Trypan blue]
Chapter 1 [One-dimensional Conductors]

(2a) [Graph Image]

(2b) [Graph Image]
Figure 2  FTIR spectra of Ni(N-CH$_3$-salim)$_2$ hydrogen bonded with (a)Para red, (b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue and (f) Trypan blue.
Nature of transition above 1700 cm\(^{-1}\) is found in all of the complexes. \(E_g\) is defined as a point at which \(\alpha\) is minimum. As revealed in the theory of direct exciton, residual absorption coefficient is found at \(h\nu=E_g\). In Bismark brown complex, \(\alpha\) is about 8% and in Trypan blue complex, it is about 13% the exciton ionization energy is proportional and this residual value at \(h\nu=E_g\). In all other complexes residual \(\alpha\) is 2.5 % having lower values of exciton ionization energy. This residual value of \(\alpha\) in a direct transition is given by (20)

\[
\alpha(\Delta E_0) = \left(4\pi e^2/m_0^2 c\omega\right)\left(2m^*_{\text{red}}/\alpha\hbar^2\right)^{3/2} \times |P_{nn'}(0)|^2 (E_{1\text{ex}})^{1/2} \\
\]

where \(E_{1\text{ex}}\) is the exciton ionization energy. However, in the present cases, the transitions are indirect (Figure 3) but analogous equation will hold. This shows that ionization energy is highest in Trypan blue complex and next highest in Bismark brown complex. In other complexes, it is very small. In all of the complexes it is a forbidden indirect transition following \(\alpha h\nu=A(h\nu-E_g\pm E_p)^3\) because the best fit is found to be \((\alpha h\nu)^{1/3}\) vs \(h\nu\) plot in all of the complexes. Number of phonon bands vs band gap are noted (Figure 4). In most of cases, the phonon band and threshold energies for formation of excitons are not pronounced. The behavior is similar to the hydrogen bonded complexes of inclusion compounds of iodine. In this case, emission threshold for excitons is lower than their absorption thresholds. This indicates the emission of an exciton is a primary process while absorption of an exciton is a secondary process. Thus the graph is inverted in comparison with phonon absorption and emission. Number of phonon bands vs band gap is also
plotted (Figure 4). This graph is a curve deviating from straight line which indicates that exciton-phonon coupling is weak.

\[(\alpha h\nu)^{1/3}\]

(3a)

\[(\alpha h\nu)^{1/3}\]

(3b)
\[(\alpha \nu)^{1/3}\]

![Graph](image1)

\[(\alpha \nu)^{1/3}\]

![Graph](image2)

\[(\alpha \nu)^{1/3}\]

![Graph](image3)

\[(\alpha \nu h)^{1/3}\]

![Graph of \((\alpha \nu h)^{1/3}\) vs \(\nu h\) in eV.](image)

(Figure 3) Nature of transitions for Ni(N-CH₃-salim)₂ hydrogen bonded with (a) Para red, (b) Congo red, (c) Direct red, (d) Bismark brown, (e) Evans blue, and (f) Trypan blue.

![Graph of band gap (eV) vs number of phonon bands.](image)

(Figure 4) No. of phonon bands vs band gap of Ni(N-CH₃-salim)₂ complexes with six dyes.
The FTIR spectra of Ni(N-C_2H_5-salim)_2 hydrogen bonded with five dyes namely Para red, Congo red, Bismark brown, Evans blue and Trypan blue are shown (Figure 5). Here residual absorption coefficient is 13% in Bismark brown complex and 4% in Trypan blue complex. In all other complexes, it is less than 4% thus exciton ionization energy is high in Bismark brown complex. Only in Trypan blue complexes it is a direct transition across the band gap (Figure 6). A graph of no. of phonon bands vs band gap is also plotted (Figure 7). It shows deviation from straight line indicating that exciton-phonon coupling is weak.
Figure 5 FTIR spectra of Ni(N-C2H5-salim)2 hydrogen bonded with (a) Para red, (b) Congo red, (c) Bismark brown, (d) Evans blue and (e) Trypan blue.
\[(\alpha \nu)_{1/2} \]

\[(\alpha \nu)^{1/3} \]

\[(\alpha \nu)^{1/3} \]
[Figure 6 Nature of transitions for Ni(N-C2H5-salim)2 hydrogen bonded with (a)Para red, (b) Congo red, (c) Bismark brown, (d) Evans blue and (e) Trypan blue]
Conduction band or valence band edges need not be sharp. It has band tailing in the region of forbidden energy gap. This band tailing is described by

\[ \alpha = \alpha_0 \exp \left\{ \frac{(h\nu - E_1)}{E_0} \right\} \]

leading to

\[ E_0 = \left[ \frac{\delta \ln \alpha}{\delta (h\nu)} \right]^{-1} \]

\[ = \frac{1}{\text{slope}} \]

Where \( E_0 \) is called the width of the tail and is given by reciprocal of the slope of \( \ln \alpha \) vs \( h\nu \) plot. \( E_1 \) is called the focal point and is a characteristic of the material. The width of the tail \( (E_0) \) is of the order of \( K_bT \) for crystalline material. However \( E_0 \) can be much larger than \( K_bT \) depending on the disorder present in the material.
In the present work, $E_0$ depends on the dye added (Figure 8 and 9) and $E_1$ depends on the metal chelate. ln$\alpha$ vs $h\nu$ plots are shown (Figure 8a and 9a). $E_g$ vs $E_0$ plots are also shown (Figure 8b and 9b). As $E_0$ increases, $E_g$ decreases almost linearly.

[Figure 8 (a) Band tailing and focal point analysis for Ni(N-CH$_3$-salim)$_2$ with six dyes

(b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail]
Figure 9 (a) Band tailing and focal point analysis for Ni(N-C<sub>2</sub>H<sub>5</sub>-salim)<sub>2</sub> with five dyes

(b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail
6.4 Conclusions :

The FTIR spectra of Ni(N-R-salim)$_2$ where R=CH$_3$ and C$_2$H$_5$ hydrogen bonded with dyes have been studied in the present work. The exciton-phonon coupling is found to be weak from a correlation between number of phonon bands vs band gap. Residual absorption coefficients upto 13% are found indicating high value of exciting ionization energies in some of them. Nature of transitions when analyzed is found to be of indirect type in most of the complexes. Absorption edge spectrum is modified by exciton-phonon coupling.

References :


37. P.S. Kireev, Semiconductor Physics, Mir Publishers, Moscow (p. 552).


Chapter 7

FTIR spectra of lead phthalocyanine hydrogen bonded with emeraldine, nigraniline and pernigraniline
7.1 Introduction:

Lead Phthalocyanine has lead chains in one crystallographic direction and acts as a one-dimensional conductors (1). Thin films were found to be semi-metallic or metallic down to low temperature (2). However, single crystals were found to be semiconducting (3). The uv-visible and IR spectra also have been studied which show a band gap of 0.63 eV along the direction of lead chains. Recently charge transfer complexes of pbpc (lead phthalocyanine) have been studied which show allowed indirect transition in the infrared absorption edge (4). Dielectric property of PbPc has also been studied which show Maxwell-Wagner effect in the nano-crystalline PbPc (5). Polyanilines namely emeraldine, nigraniline and pernigraniline have also been studied using FTIR spectroscopy (6). In the present work, these polyanilines are hydrogen bonded with lead phthalocyanine (PbPc). The molecular structures of PbPc and polyanilines are shown (Figure 1). FTIR spectra were recorded the hydrogen bonded molecular complexes which are studied in details.
7.2 Experimental Details:

Lead Phthalocyanine (PbPc) was prepared by refluxing lead monoxide with nitrobenzene solution of phthalonitrile. PbPc was obtained in this manner as a blue nanocrystalline material. This blue powder was mixed with polyanilines which were also prepared in laboratory by oxidation of aniline with different oxidizing agents (6). The mixtures were grinded till colours deepened and black powders of hydrogen bonded complexes were obtained. These black materials were mixed and grinded with anhydrous spectrograde KBr powder. Finally, round palates were made using a manually operated machine and a circular die which were semitransparent. These circular discs were placed in the dark chamber of a spectrophotometer.
The spectra in the range 400-4000 cm\(^{-1}\) were recorded using a GX-FTIR single beam spectrophotometer manufactured by Perkin-Elmer company USA. It was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), an OPD velocity of 0.2 cm sec\(^{-1}\) and MIRGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode.

**7.3 Results and Discussion:**

The FTIR spectrum of PbPc is shown (Figure-2a). There is monotonic increase in absorption in the range between 1780 cm\(^{-1}\) and 3000 cm\(^{-1}\) as the energy of infrared light increases. This shows that there is an infrared absorption edge with \(E_g=0.223\) eV (1780 cm\(^{-1}\)) which is analyzed (Figure-2b). PbPc is a two-dimensional (layered) material perpendicular to lead chains. There is \(\pi-\pi\) stacking of benzene rings and the fine structure (a large number of weak absorption bands) of the absorption edge is because of non-degenerate ring puckering vibrations of benzene rings. The analysis \(a\nu vs \nu\) shows that it is a two-dimensional conductor perpendicular to lead chains.
The infrared gap of 0.20 eV is between the planar rings of benzene and it is a gap in the phonon dispersion relation between acoustic and optical phonon modes. Rest of the bands below 1780 cm$^{-1}$ are due to several intramolecular vibrations of organic network of phthalocyanine ligand around the lead chains. Some of the bands can be assigned LO and TO modes of lattice vibrations.
vibrations. Metal-ligand vibrations which give rise to allowed indirect transitions in charge transfer complexes of PbPc lie below 700 cm\(^{-1}\). These bands are also shifted by hydrogen bonding of polyanilines.

The FTIR spectrum of PbPc-emeraldine is shown (Figure-3a). The minimum absorption point remains at 1780 cm\(^{-1}\) (0.223 eV) but the nature of absorption edge is complicated by exciton-phonon emission band in this edge followed by a series of threshold energies of excitons. This is similar to what is observed in the absorption edge of GaP(7,8). Gallium Phosphide (GaP) is an ionic semiconductor and has shown electron-hole liquid (EHL) below 45 K of temperature. Electron-hole pairs form a gas at room temperature which condense into a liquid at low temperature (9). Similarly in the present H-bonded complex of PbPc with emeraldine can also undergo a transition to electron-hole liquid phase at low temperature because emeraldine provides a high exciton density medium. The absorption edge of the emeraldine complex of PbPc has been analyzed and \((\alpha h\nu)^{1/2}\) vs \(h\nu\) was found to be the best fit for absorption coefficient (Figure-3b). This shows that it is an allowed indirect transition in a disordered material. The material is disordered and so does not allow calculation of phonon energy from the absorption edge. Only a crystalline material shows a break in straight line in such a plot having two intercepts at \(E_g + E_p\) and \(E_g - E_p\). \((\alpha h\nu)^{1/2}\) vs \(h\nu\) rather than crystalline case where \((\alpha h\nu)^{1/2}\) vs \(h\nu\) is a straight line being a rectilinear plot shows that it is a disordered material. There are four phonon emission bands with four
threshold energies of the formation of excitons. The band gap is obtained by extrapolation of straight line segment at higher energy as an intercept with energy axis. It is found to be about 0.26 eV (Figure 3b).

![Figure 3 (a) FTIR spectrum of PbPc-emeraldine, (b) Allowed indirect transition in disordered PcPc-emeraldine]
There is a shift of absorption edge of 0.200 eV to 0.260 eV in the emeraldine complex. This blue shift of PbPc absorption edge is related with Burstein-Moss shift in heavily doped PbPc with emeraldine. Instead of additional shrinkage of an indirect gap, the Burstein-Moss shift is pronounced. The Burstein-Moss shift parameter $\xi$ is of the order of 0.060 eV. Repulsive effects are dominant in PbPc because of two electrons vibrating across the ligand rather than only one electron found in Ni(Hdmg)$_2$-bis(dimethylglyoximato)Ni$^{II}$. The present case is an infrared analogy of what is found in gallium phosphide. In GaP threshold energies are found in visible range while here these energies lie in infrared range. There is photoluminescence in GaP (9) while here there can be infrared luminescence. Electron-hole pairs are formed across a band gap lying in the infrared range and IR luminescence can occur through recombinations of electrons and holes. In a hard material, IR luminescence can be absorbed but in a soft material there is re-absorption of emitted infrared radiation and phonons are emitted (local strains and thermal phonons) as found here. Probability of recombination is more when band gap is smaller, i.e. when exciton-phonon coupling is stronger. When this coupling is weak, more number of phonons are emitted and band gap is larger.

The FTIR spectrum of PbPc-nigraniline is shown (Figure 4a) and the absorption edge is analyzed similarly finding $(a h \nu)^{1/2}$ vs $h \nu$ as the best fit (Figure 4b). Again a Burstein-Moss shifted edge is found at 0.270 eV which is blue shifted due to heavy doping of nigraniline. The Burstein-Moss shift $\xi$ is nearly 0.07 eV.
There are five phonon emission bands in the absorption edge corresponding to a weaker exciton-phonon coupling compared to emeraldine.

[Figure 4 (a) FTIR spectrum of PbPc-nigraniline (b) Allowed indirect transition in disordered PbPc-nigraniline]
complex. Thus as this coupling weakers, more number of phonon emissions are found and simultaneously band gap increases. The number of threshold energies for the formation of excitons is the same as number of phonon emission bands. There are larger number of thresholds in a large band gap material. This shows that there is more probability of electron-hole droplet formation in materials with large band gap. This is consistent with the fact that electron-hole pairs are stable against recombination in a large band gap material.

The FTIR spectrum of PbPc-pernigraniline is also shown (Figure 5a) and the absorption edge is analyzed to be $\alpha h\nu = B(h\nu-Eg)^2$ as the best fit giving rise to $(\alpha h\nu)^{1/2} \text{ vs } h\nu$ as rectilinear plot at higher energy (Figure 5b). There are six phonon bands in the absorption edge and band gap is nearly 0.275 eV. The Burstein-Moss shift parameter $\xi$ is 0.075 eV. Electron-hole droplet formation at low temperature in this complex is more probable as compared to emeraldine and nigraniline complexes because of large number of excitons.

A comparison can be made with hydrogen bonded complexes of polyanilines with Ni(Hdmg)$_2$. The latter complexes have less band gap than even CTCS of Ni(Hdmg)$_2$ acceptors due to excitonic reduction of band gap. In the present cases of PbPc, band gaps are larger than CTCS of PbPc with acceptors (4) and larger than H-bonded Ni(Hdmg)$_2$ due to Burstein-Moss as a dominating effect. Infrared luminescence is more probable in H-bonded Ni(Hdmg)$_2$ while electron-
hole droplets are more probable in H-bonded PbPc. Exciton-phonon coupling is weaker in PbPc complexes as compared to Ni(Hdmg)$_2$ complexes.

![Figure 5 (a) FTIR spectrum of PbPc-pernigraniline (b) Allowed indirect transition in disordered PbPc-pernigraniline](image-url)
The number of phonon bands which is reciprocal to exciton-phonon coupling is plotted against the band gap and it is found to be nearly a rectilinear plot (Figure 6).

[Figure 6  Number of phonon bands in absorption edge vs band gap of PbPc complexes]

Conduction band or valence band edges may not be sharp and there are exponentially tailing states into the forbidden energy gap. In this case

\[ \alpha = \alpha_0 \exp \left\{ \frac{(h\nu-E_1)}{E_0} \right\} \]

leading to

\[ E_0 = \left[ \frac{\delta \ln \alpha}{\delta (h\nu)} \right]^{-1} = \frac{1}{\text{slope}} \]
\( \ln \alpha \) vs \( h \nu \) is straight line. \( E_0 \) is called the width of the tail and \( E_1 \) is called the focal point. In the present case, \( E_0 \) is determined by the dye added and \( E_1 \) is characteristic of the PbPc. \( E_0 \) is a measure of disorder. \( E_0 \) is large when disorder is more. \( \ln \alpha \) vs \( h \nu \) are plotted (Figure 7a) and \( E_0 \) and \( E_1 \) are found from these graphs. \( E_g \) vs \( E_0 \) is also plotted (Figure 7b). As \( E_0 \) increases, \( E_g \) decreases almost linearly. This is also theoretically established (10).
7.4 Conclusions:

The hydrogen bonded complexes of polyanilines namely emeraldine, nigraniline and pernigraniline are formed with PbPc. These complexes show complicated absorption edge due to exciton-phonon coupling. The absorption edges are Burstein-Moss shifted with respect to only PbPc due to heavy doping of excitonic polyanilines. There is probability of formation of electron-hole liquid at low temperature as large number of excitons found in absorption edge can condense into liquid.

References:


Chapter 8

FTIR spectra of lead phthalocyanine hydrogen bonded with six dyes
8.1 Introduction:

Lead Phthalocyanine (PbPc) is a one-dimensional conductor having one-dimensional lead chains along one-direction of crystals (1). Vibration spectra of CT complexes of PbPc as well as uv-visible spectra of these CTCs are studied (2,3). Here in the present work, hydrogen bonding of PbPc at nitrogen atoms of the ligand with six O-H and N-H containing dyes such as Congo red, Para red, Direct red, Bismark brown, Evans blue and Trypan blue is attempted. It is verified that there is intermolecular hydrogen bonding.

8.2 Experimental Details:

PbPc (lead phthalocyanine) was prepared by refluxing lead monoxide with phthalonitrile in nitrobenzene medium. The blue powder prepared in this manner was mixed with six dyes namely Congo red, Para red, Direct red, Bismark brown, Evans blue and Trypan blue obtained from Aldrich chemical company, USA in pure form. The mixtures were grinded in an agate mortar with a pastle for half an hour for bringing PbPc molecules and dye molecules in molecular contact. The hydrogen bonded complexes prepared were further mixed with 95% spectrograde KBr powder, grinded to form homogeneous mixture and compressed in a die to form circular palates. These round-shaped discs were placed in a 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 Co., USA. It was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15,600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), an OPD velocity of 0.20 cm sec\(^{-1}\) and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode. Molecular structure of PbPc and six dyes are shown (Figure 1).

![Molecular structure of PbPc](image1a)

![Molecular structure of dye](image1b)
8.3 Results and Discussion:

The FTIR spectra of PbPc-Para red, PbPc-Congo red and PbPc-Direct red are shown (Figure 2). The FTIR spectra of PbPc-Bismark brown, PbPc-Evans blue and PbPc-Trypan blue are also shown (Figure 3). All of the spectra show noise in absorption spectrum above 3600 cm\(^{-1}\) in the range of free carrier absorption and noise just above the absorption edge at about 1700 cm\(^{-1}\). The previous one due to photoconducting nature of the hydrogen bonded PbPc complexes and the latter due to localization near the band edges. Band edges are not sharp but having band tailing with localization states near the band edges. The mid-IR spectrum below 1700 cm\(^{-1}\) is governed by the absorption of dye molecules because of a large proportion (1:4 molecular weight proportion) of dyes used in preparing the hydrogen bonded complexes. Bands below 700 cm\(^{-1}\) contain bands due to metal-ligand vibrations of PbPc molecule. These bands are shifted due to hydrogen bonding at nitrogen atoms.
(2a)

(2b)
[Figure 2 FTIR spectra of PbPc hydrogen bonded with (a) Para red, (b) Congo red and (c) Direct red]
Figure 3 FTIR spectra of PbPc hydrogen bonded with (a) Bismark brown, (b) Evans blue and (c) Trypan blue.
The absorption edge spectrum above 1700 cm\(^{-1}\) is modified due to exciton-phonon coupling as discussed elsewhere (4). Threshold energies for the formation of excitons with phonon emission are found as observed in the absorption spectrum of gallium phosphide (5,6). The intrinsic absorption edge spectrum is studied in details (7). At a later date, electron-hole liquid was found in GaP (8) due to high exciton density at low temperature. Because similarity in absorption edge spectra of hydrogen bonded PbPc and crystalline GaP room temperature there is a possibility of electron-hole liquid in the H-bonded PbPc also at low temperatures. The subject of electron-hole liquid is well established (9). In many semiconductors this phenomenon is observed. In the present cases also the absorption edge spectra reveal phonon-assisted creation of free excitons and electrons-hole pairs and high density of excitons at room temperature.

The absorption edge is analyzed by plotting \((\alpha h\nu)\), \((\alpha h\nu)^{1/2}\), \((\alpha h\nu)^{1/3}\), \((\alpha h\nu)^{2/3}\), \((\alpha h\nu)^2\) vs \(h\nu\) and finding the best fit. Here \((\alpha h\nu)\) vs \(h\nu\) is found to the best fit in all cases of PbPc complexes (Figure 4) which reveals allowed indirect transition in two-dimensional (Layered) semiconductor. When exciton-phonon coupling is strong, phonon are emitted limited in number when this coupling is weak, large number of phonons are emitted. The strength of coupling of excitons and phonons is reciprocal to the number of phonon bands in the edge spectrum. The number of phonon bands vs band gap is plotted (Figure 5). This graph indicates that band gap reduces as exciton-phonon coupling increases. This type of
behavior was also found recently in PbPc-emeraldine, PbPc-nigraniline and PbPc-pernigraniline also. Polyanilines were almost symmetric dyes and cannot be highly polarizable like asymmetric dyes chosen in the present work. There are large number of intramolecular vibrations acting as optical phonon modes in asymmetric dyes. These vibrations get decoupled from excitons when exciton-phonon coupling is weak.

(4a)

(4b)
[Figure 4] Nature of transition in (a) PbPc-Para red, (b) PbPc-Congo red, (c) PbPc-Direct red, (d) PbPc-Bismark brown, (e) PbPc-Evans blue and (f) PbPc-Trypan blue.

[Figure 5] No. of phonon bands in the edge spectrum vs band gap.
Usually in a direct band gap semiconductors exciton bands are found just below the gap, while in an indirect band gap semiconductors, steps are found in absorption edge (5). Here in spite of indirect edge, bands are found so most probably these bands are due to lattice absorption and therefore the combination bands of several TO, LO, LA, TA models (5). Multi phonon processes occur due to anharmonic and nonlinear interactions in soft materials studied in the present work. The phonon energies cannot be found because average energy will be zero due to disordered materials studied in the present work. The materials are disordered and therefore, $(\alpha h\nu)$ vs $h\nu$ is straight line rather than $\alpha$ vs $h\nu$, the latter being the absorption function for crystalline material. Indirect transition in metal-organic system due to metal-ligand vibrations are established recently (5,10,11). Here also the best fits were found to be for indirect transition. Phonon bands rather than exciton band in the edge spectrum are more possible because of infrared range of spectra. Also oscillator model of phonons are many time found in the band edges. The phonon bands poke out of the straight line plotted for step function near $E_g$. In this case a linear interpolation to find phonon energy is not valid. Rather there is phonon peak energy. Which can be found out from such indentations.

However, it is possible that broad bands in the absorption edges are due to phonon emissions and one or two sharp bands are due to Mott- Wannier excitons. Then there is real infrared analogy of the excitons found in uv-visible range of
inorganic compound semiconductors. There can be excitons with energies lying in the infrared range. These excitons can lead to infrared luminescence due to electron-hole pairs across the infrared band gap. Also there is remote possibility of all bands found in the edge spectrum being exciton bands. There can be broadening of exciton band. There can be broadening of exciton bands due to exciton-phonon coupling. Then there is infrared analogy of optical phenomena in soft semiconductors.

In soft semiconductors like organic charge transfer complexes and hydrogen-bonded system, the infrared band gap is due to gap in the phonon dispersion curves between acoustic and optical modes. Electron-polaron and hole-polaron are formed and there can be a polaronic exciton or excitonic bipolaron in which there is attractive coupling between electron-polaron and hole-polaron which are oppositely charged. $E_B - 2E_p$ where $E_B$ is the binding energy of a bipolaron and $E_p$ is the polaron binding energy acts as a band gap. Band gap is nothing but dissociation energy of a dipolaron into two polarons. The bipolarons are formed due to exciton-phonon coupling. When phonon is emitted due to weak coupling, bound electron-hole pair results.

The present work and work on polyanilines hydrogen bonded with PbPc clearly show that exciton-phonon coupling is strong for green, blue and violet dyes but weak for yellow, brown and red dyes. Thus band gap is smaller for green, blue and violet dyes hydrogen bonded with one-dimensional conductor than for yellow and red dyes similarly attached.
Moreover, PbPc hydrogen bonded with dyes works as two-dimensional conductor. Exciton density is high on one and two dimensional conductors than three-dimensional (isotropic) conductors. In two-dimensional systems, there are no localization effects which appear in one-dimensional conductors. Two-dimensional electron-hole liquids are also known and studied with both theoretical and experimental points of views (12-14).

Band tailing analysis is also carried out by plotting $\ln \alpha$ vs $\nu$ for the absorption edge spectrum because $\alpha$ is given by,

\[
\alpha = \alpha_0 \exp \left( \frac{(\nu-E_1)}{E_0} \right)
\]

$E_0$ is the width of the band tail and is given by reciprocal of the slope of $\ln \alpha$ vs $\nu$ plot. $E_1$ is a focal point and is a characteristic of the material. $E_1$ may include Burstein-Moss shift parameter ($\xi$) for heavily doped semiconductor apart from $E_g$ and $E_p$ (phonon energy). Band tailing analysis with focal point is shown (Figure 6a) and $E_g$ vs $E_0$ is also plotted (Figure 6b). As $E_0$ increases, $E_g$ decreases almost linearly. This is also expected from theoretical arguments (15).
Figure 6 (a) Bands tailing analysis and focal point (b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail

\[ E_g \text{ vs } E_0 \]


8.4 Conclusions:

The infrared absorption edge spectrum of hydrogen bonded PbPc with six dyes is modified due to exciton-phonon coupling. This spectrum shows several threshold energies for the formation of free excitons or electron-hole pairs with phonon emission. When exciton-phonon coupling is weak several phonons are emitted due to decoupling. The number of phonon bands vs band gap shows a curve which reveals how band gap decreases as exciton-phonon coupling strength increases.

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Chapter 9

FTIR spectra of Ni(Hdmg)$_2$ hydrogen bonded with

emeraldine, nigraniline and pernigraniline
9.1 Introduction:

Bis(dimethylglyoximato)Ni$^{II}$ is a one-dimensional system having metal chains along one crystallographic axis of crystal (1). It has electrical resistivity of the order of $10^{10}$ ohm-cm at room temperature with the band gap of 2.0 eV. It shows and allowed direct transition with an optical band gap of 1.9 eV. The resistivity drops at high pressure (2). Polyanilines namely emeraldine, nigraniline and pernigraniline are semiconductors with highest conductivity in emeraldine (3). Infrared spectra are studied in details (4,5). In the present study, polyanilines are hydrogen bonded with Ni(H-dmg)$_2$ and FTIR spectra are investigated.

9.2 Experimental Details:

Ni(Hdmg)$_2$ was prepared by standard method using NiCl$_2$-6H$_2$O and dimethylglyoxime (6) as a red powder. Polyanilines namely were prepared by oxidising aniline through standard methods by different oxidizing agents (4,5). Ni(Hdmg)$_2$ was mixed in 1:4 proportion with polyaniline and hydrogen bonded systems were prepared by grinding in a mortar for bringing Ni(Hdmg)$_2$ molecules in molecular contact with the molecules of polyanilines. The colours remarkably changed during grinding upon the formation of H-bonded molecular complexes. These coloured powders were again mixed and grinded with spectrograde KBr powder. The fine homogeneous powders prepared in this manner were compressed in a circular dye with manually operated compressing machine to make circular
pallates. These round pallates were then placed in a dark chamber of standard spectrophotometer.

The spectra in the range 400-4000 cm\(^{-1}\) were recorded using a GXFTIR single beam spectrophotometer manufactured by perkin-elmer co.USA. It was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), and OPD velocity of 0-20 cm sec\(^{-1}\). MIRTGS and FIRTGS detectors were used. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode. The molecular structures of Ni(Hdmg)_2 and polyaniline are shown (Figure-1).
9.3 Results and Discussions:

The infrared spectrum of Ni(Hdmg)$_2$ is shown (Figure-2). The spectrum has a transmitting range $1700 \text{ cm}^{-1}$ to $2800 \text{ cm}^{-1}$ showing that the band gap of Ni(Hdmg)$_2$ does not lie in the infrared range. Actually the band gap of about 1.9 eV is in the uv-visible range. Rest of the bands are the phonon bands due to lattice absorption in the infrared range. Several bands are also due to intramolecular vibrations of organic network in this metal chelate. Which can be termed as optical phonons. Metal-ligand vibrations lie below $700 \text{ cm}^{-1}$. These vibrations are found in the range between $400 \text{ cm}^{-1}$ and $700 \text{ cm}^{-1}$. The IR spectrum of Ni(Hdmg)$_2$ has recently been reported (7).

[Figure 2 FTIR spectrum of Ni(Hdmg)$_2$]
The FTIR spectra of emeraldine and \( \text{Ni(Hdmg)}_2 \)-emeraldine complex are shown here (Figure-3a,b). The spectrum of H-bonded complex closely resembles spectrum of emeraldine because of 1:4 proportion having emeraldine in large proportion. Three large gaussian of emeraldine are also approximately visible in \( \text{Ni(Hdmg)}_2 \)-emeraldine complex. There is a range of nature of transition between 1800 cm\(^{-1}\) and 2400 cm\(^{-1}\) in which absorption decreases and wave numbers or energy of infrared light decreases. The infrared absorption edge is not sharp following a step function but complicated by a series of phonon bands. Such a structure can arise out of a complex band gap (8) or optically detected charge density wave (9). The absorption coefficient and optical conductivity show oscillatory behaviour. Such oscillatory patterns are found in metal free phthalocyanine (10), folic acid-KI-I\(_2\) (11) and CT complexes of polypyrrole (9). These two possibilities are discarded here because of heavily damped oscillations are found here rather than periodic undamped oscillations. Thus several bands found in the absorption edge closely resemble to the exciton bands found in the case of Mott-Wannier excitons (12). The nature of transition is analyzed by plotting \((\alpha h \nu)^{1/2}\) vs \(h \nu\) which is the best fit (Figure-4). The graph shows threshold energies of excitons with phonon emission in the absorption edge similar to what is found in gallium phosphide (13).
[Figure 3b FTIR spectra of (b)Ni(Hdmg)$_2$-emeraldine]

[Figure 4  Nature of transition in Ni(Hdmg)$_2$-emeraldine showing threshold energies of excitons with phonon emission in the infrared absorption edge]
The series of thresholds correspond to different excitons rather than several levels of the same Mott-Wannier excitons found elsewhere (12). Thus there is exciton gas in Ni(Hdmg)$_2$-emeraldine similar to that in GaP. It is to be noted that there are electron-hole droplets (exciton liquid) in GaP at low temperatures (14). Thus a similar possibility of electron-hole droplet or exciton liquid is opened in Ni(Hdmg)$_2$-emeraldine. The threshold energies of excitons are in the visible range in GaP while here the threshold energies lie in the infrared range. Thus it is again infrared analogy of optical phenomenon that occurs in uv-visible range in inorganic semiconductors, because band gap of about 0.2 eV lies in infrared range. The exciton-phonon coupling is also discussed for CdTe showing several breaks due to different slopes in the straight line plot of $\alpha^{1/2}$ vs $h\nu$ (15). The greater the exciton ionization energy, the greater is $\alpha$ for $h\nu=\Delta E_0(E_g)$. The theory of indirect exciton transition has also been developed. There is a well-defined long-wave boundary of the fundamental band. The long wave edge of the fundamental absorption band is more or less spread out in the direction of $h\nu<\Delta E_0$. Several straight line sections are clearly visible on the $\alpha^{1/2}$ vs $h\nu$ curve. Extrapolation to $\alpha=0$ leads to energies separated by about 0.021 eV which is close to the energy of a longitudinal optical phonon. The phonons interacting with excitons take part in the formation of absorption edge. The pattern of the intrinsic absorption band edge for exciton-phonon interband transitions in many solids may be described by the urbach equation.
\[ \alpha(hw) = \alpha_0 \exp(\sigma(hw - E_0)/k_B T) \]

\( E_0 \) may be correlated with the energy maximum of the exciton absorption band. However, in the present case the plot of \((\alpha h \nu)^{1/2}\) vs \(h \nu\) show several small bands due to phonon emission rather than broken straight line plots.

Next, the FTIR spectra of nigraniline and Ni(Hdmg)\(_2\)-Nigraniline are shown (Figure-5a,b). In this case also the spectrum is governed by the spectrum of nigraniline because of 1:4 proportion. Two gaussian bands are nearly visible in the spectrum of Ni(Hdmg)\(_2\)-nigraniline. There are three bands in absorption edge of Ni(Hdmg)\(_2\)-emeraldine while there are four bands in Ni(Hdmg)\(_2\)-nigraniline. The band gap of Ni(Hdmg)\(_2\)-emeraldine is about 0.18 eV while the band gap of this nigraniline complex is 0.20 eV. In excition-phonon coupling, phonon screens the electron-hole electrostatic attraction. When phonon is emitted, bound pair of electron and hole gets formed. When exciton-phonon coupling is strong, there are less number of phonon emission bands. When exciton-phonon coupling is weak, the phonons are easily released and therefore, there are large number of phonon emission bands.
The present cases clearly show that when there are less number of phonon bands, the band gap is less. When there are large number of phonon bands the band gap is large. Thus band gap decreases as the excito-phonon coupling strength increases. Exciton-phonon coupling decreases at low temperature because phonon bands diminish at low temperature. Nature of transition in Ni(Hdmg)$_2$-nigraniline is also analyzed (Figure-6).
The kinds in the absorption edge curve are thresholds of excitons and phonon emission bands (four in number) are found. It should be noted that the threshold energies are larger than the band gap. In Mott-Wannier exciton levels are at energies lower than the band gap. This shows that the bands are phonon emission bands and not exciton bands related with excited state of an exciton. Rather several excitons with different thresholds are involved.

The FTIR spectra of pernigraniline and Ni(Hdmg)$_2$-pernigraniline are shown (Figure-7a,b). The data are analyzed to find $(\alpha h\nu)^{1/2}$ vs $h\nu$ as the best fit (Figure-8). Here about five phonon emission bands are observed and band gap is
about 0.22 eV. Thus the exciton-phonon is weaker so that more phonons are emitted. The band gap is large because of weaker strength of exciton-phonon coupling as discussed above. Number of phonon bands vs band gap is plotted which is a rectilinear plot (Figure-9).
Conduction band and valence band edges may not be sharp always. There can be exponential band tailing described by

$$\alpha = \alpha_0 \exp \{((h\nu-E_1)/E_0)\}$$

Where \(E_0\) is the width of band tail and \(E_1\) is the focal point. For this analysis, \(\ln \alpha\) vs \(h\nu\) are plotted (Figure 10 a). \(E_g\) vs \(E_0\) i.e. the band gap vs width of the band tail, also shows a linear relationship (Figure 10b). As \(E_0\) increases, \(E_g\) usually decreases. A linear relationship is also supported by theory (16).
Figure 9: Number of phonon emission bands vs band gap

Figure (10a)
9.4 Conclusions:

The FTIR spectra of three hydrogen bonded complexes of Ni(Hdmg)$_2$ with three polyanilines namely emeraldine, nigraniline and pernigraniline have been studied. Threshold energies of excitons with phonon emission are observed in the absorption edge. It is possible that there is electron-hole liquid in these hydrogen bonded complexes. Also there is possibility of infrared luminescence due to electron-hole recombination. The band gap decreases as the exciton-phonon coupling increases.
References:


Chapter 10

FTIR spectra of Ni(Hdmg)$_2$ hydrogen bonded with six dyes
10.1 Introduction:

Bis(dimethylglyoximato)Ni\textsuperscript{II} [Ni\textsuperscript{II}(Hdmg)\textsubscript{2}], is a one-dimensional system having metal chain in one direction of the crystals (1). This 1-d system is hydrogen bonded with six dyes which contain O-H or N-H group with O-H-O group of dioxime ligand. The hydrogen bonded complexes are studied with FTIR spectroscopy in the present work. Ni(Hdmg)\textsubscript{2} has electrical dc resistivity of $10^{10}$ ohm-cm at room temperature and band gap of 2.0 eV. It shows an allowed direct transition with an optical band gap of 1.9 eV. The resistivity drops at high pressure (2). The charge transfer complexes of Ni(Hdmg)\textsubscript{2} and Ni(Hdp)\textsubscript{2}-the phenyl analog were studied with IR spectroscopy (3).

10.2 Experimental Details:

Ni(Hdmg)\textsubscript{2} was prepared by standard method using NiCl\textsubscript{2}-6H\textsubscript{2}O and dimethylglyoxime (6) as red precipitates. Six dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue were obtained from Aldrich chemical company in pure forms. Ni(Hdmg)\textsubscript{2} and dyes were mixed in 1:4 proportions and grinded in an agate mortar with a pestle till colours changed and till fine homogeneous powders were formed. The mixture were again grinded after mixing them further with dry (anhydrous) spectrograde KBr powder. Round palates were prepared by compressing the powders in a die with manually
operated compressing machine. The semitransparent palates were placed in a 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. It was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), and OPD velocity of 0-20 cm sec\(^{-1}\). MIRTGS and FIRTGS detectors were used. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode.

10.3 Results and Discussions:

The molecular structures of Ni(Hdmg)\(_2\) and six dyes are shown (Figure 1). The hydrogen bonding occurs with O-H---O group of dioxime ligand surrounding the metal ion in the centre. These are bifurcated hydrogen bond because already one intramolecular O-H---O hydrogen bond exists.
[Figure (1a) Molecular structures of Ni(Hdmg)$_2$ (1b) Para red, (1c) Congo red, (1d) Direct red, (1e) Bismark brown, (1f) Evans blue and (1g) Trypan blue]

The FTIR spectra of Ni(Hdmg)$_2$-Para red, Ni(Hdmg)$_2$-Congo red and Ni(Hdmg)$_2$-Direct red are shown (Figure 2). Similar spectra of Ni(Hdmg)$_2$-Bismark brown, Ni(Hdmg)$_2$-Evans blue and Ni (Hdmg)$_2$-Trypan blue are also shown (Figure 3).
Figure 2 FTIR spectra of (a) Ni(Hdmg)$_2$-Para red, (b) Ni(Hdmg)$_2$-Congo red and (c) Ni(Hdmg)$_2$-Direct red.
[Figure 3c FTIR spectra of (a)Ni(Hdmg)$_2$-Bismark brown, (b)Ni(Hdmg)$_2$-Evans blue and (c)Ni(Hdmg)$_2$-Trypan blue]
The intrinsic absorption edge spectrum above 1700 cm$^{-1}$ is analyzed by plotting $(\alpha h \nu)^2$, $(\alpha h \nu)^{1/2}$, $(\alpha h \nu)^{1/3}$, $(\alpha h \nu)^{2/3}$ vs $h \nu$ and finding the best fit. $(\alpha h \nu)^{1/3}$ vs $h \nu$ was found to be the best fit indicating $(\alpha h \nu)=A(h \nu-E_g)^3$ corresponding to forbidden indirect transition in all complexes except the Trypan blue complexes. In Ni(Hdmg)$_2$-Trypan blue, $(\alpha h \nu)=A(h \nu-E_g)^{1/2}$ an allowed direct transition was found to be the best fit. These best fits are shown (Figure 4).
\begin{align*}
(\alpha h \nu)^{1/3} & \quad \text{for (4c)} \\
(\alpha h \nu)^{1/3} & \quad \text{for (4d)} \\
(\alpha h \nu)^{1/3} & \quad \text{for (4e)}
\end{align*}
The absorption edge is modified by exciton-phonon coupling. There are threshold energies for the formation of excitons and electron-hole pairs with phonon emission. If the exciton-phonon coupling is strong, there are less number of phonon emissions. If this coupling is weak, there are large number of phonon emissions. Here there are only two pronounced phonon bands in Bismark brown complex and there are eight phonon bands in the case of Para red complex. Other cases are intermediate cases. The number of phonon bands vs band gap is plotted. Again band gap is found to decrease for strong exciton-phonon coupling (Fig 5).

The excitonic threshold energies are observed in GaP (4,6), SiC (7) and CdTe (8) and absorption edges were found to be modified by exciton-phonon coupling. This coupling for direct excitons is discussed (8). Every atomic system
has an infinite set of discrete energy levels corresponding to finite motion of the electron. When the potential energy of the interaction is normalized to be zero at infinity, the total energy of the electron is negative.

![Figure 5 Number of phonon bands vs band gap (eV)](image)

For positive values of energy the electron is not bound to the ion and is moving freely. The energy spectrum of free motion is continuous. Overlapping transitions into discrete and continuous regions of the energy spectrum prevent the absorption coefficient from turning zero when $\hbar\omega=\Delta E_0$ ($E_g$). The absorption spectrum of direct allowed interband transition is given by

$$\alpha=(2\pi e^2/m_0 \hbar^2 c\omega n)(2m^*_\text{red} / \hbar^2)^{3/2} \times |P_{nn'}(0)|^2 (E_{1e}^{ex})^{1/2} (e^2/sinhz)$$  

where $z=\pi(E_{1e}^{ex} / \hbar\omega-\Delta E_0)^{1/2}$

For $\hbar\omega \to \Delta E_0$ we obtain
\[ \alpha(\Delta E_0) = (4\pi e^2/m_0^2 c^2 \omega n)(2m^*_\text{red}/\hbar^2)^{3/2} |\mathbf{p}_n(0)|^2 (E_1^{ex})^{1/2} \] ------ (2)

i.e. the greater the exciton ionization energy \( E_1^{ex} \) the greater is \( \alpha \) at \( \Delta E_0 \). For \( E_1^{ex} \to 0 \), \( \alpha(\Delta E_0) \to 0. \), and \( \alpha \) takes the form \( \alpha \sim (\hbar \omega - \Delta E_0)^{1/2} \). For direct forbidden transitions the corrections obtained are similar. The theory of indirect exciton transitions has also been developed. There should be a well–defined long–wave boundary of the fundamental band. Actually the long–wave edge of the fundamental absorption band is more or less spread out in the direction of \( \hbar \omega < \Delta E_0 \). The equations (1) and (2) are applied to trypan blue complex where direct transition is observed.

The theory of light absorption resulting in interband transitions of electrons, coulomb interaction between electrons and holes created in the process of photon absorption is not taken into account. Coulomb attraction is instrumental in creating a bound electron-hole system, the exciton, which has a hydrogen-like discrete energy level systems \( E_N^{ex} = E_c - (E_1^{ex}/N^2) \) below the bottom of the conduction band. The fundamental state of the exciton is below \( E_c \) by the amount

\[ E_1^{ex} = (13.5/e^2)(m^*_\text{red}/m_0) \text{ eV} \]

In the course of direct interband transitions from the state \( k = k_n \) a hole with wave vector \( k_p = -k \) is created. since the exciton travels as a whole, it follows that the motion of the electron and the hole is correlated and that their relative velocity is zero. This is possible if the exciton springs from the transitions \( k_n = k_p = 0 \), i.e. if
the transitions take place in the centre of the Brillouin zone or generally in the 
energy extrema. The range of states from which allowed electron transitions 
resulting in the generation of excitons are possible is quite narrow. This is the 
cause of formation of narrow absorption spectral bands adjoining the fundamental 
band from the long-wave side. The formation of narrow discrete absorption bands 
is not the only modification of the exciton states. The exciton states are also 
responsible for the modification of the intrinsic absorption band pattern.

The pattern of the intrinsic absorption band edge for the exciton-phonon 
interband transitions in many solids may be described by the urbach equation valid 
for a wide range of $\alpha$.

$$\alpha (hw) = \alpha_0 e^{-[\sigma(hw-E_0)/KBT]}$$

The parameter $E_0$ may be correlated with the energy maximum of the exciton 
absorption band. This parameter coincides with the value of the absorption 
coefficient in the maximum of the exciton band. $\sigma$ is in range 1-3.

The theory of optical absorption by excitons was developpad (9). Also the 
temperature dependence of the Urbach optical absorption edge was studied (10). A 
early universally observed feature of optical absorption spectra near band edges 
in crystalline and amorphous semiconductors is the Urbach-Martienssen 
absorption edge given by

$$\alpha (w) = \alpha_0 \exp\left[\frac{\hbar w - E_G(T)}{E_0(T)}\right]$$
Where $\hbar w$ is the photon energy and $E_G$ and $E_0$ are temperature-dependent fitting parameters. $E_0$ is the width of the tail. $E_G$ is comparable to the band gap energy. $E_0$ is given by

$$E_0 = \left[ \frac{\delta \ln \alpha}{\delta (\hbar w)} \right]^{-1}$$

and it is in the range 10-100 meV for amorphous semiconductors. $E_G$ and $E_0$ scales almost linearly. $E_G$ decreases as $E_0$ increases. There is a linear scaling relation (Figure 6). This is also supported by theory (10).
The theory for indirect excitons coupled with phonons is also developed. The remainder absorption coefficient at $E=E_g$ remains finite and is proportional to the ionization energy of the exciton. Here the remainder absorption in percentage is plotted vs no. of phonon bands and vs band gap in eV (Figure 7).
As band gap increases, the remainder absorption at $h\nu=E_g$ decreases. When exciton-phonon coupling is strong, the remainder absorption at $E_g$ is more. Since the remainder absorption at $E_g$ is proportional to the ionization energy of exciton, this shows that the excitons with more ionization energy are strongly bound to phonons. Band gap is less when the exciton ionization energy is more.
10.4 Conclusions:

The FTIR spectra of Ni(Hdmg)$_2$ with six dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue have been studied. The intrinsic absorption edge spectrum is modified with threshold energies of excitons by exciton-phonon coupling. The remainder absorption is found at $E_g$ due to this coupling which is proportional to the ionization energy of exciton. Excitons with higher ionization energies are strongly bound to phonons than those with less ionization energy. Band gap reduces with increase in ionization energy of excitons.

References:


Concluding Remarks

1. General Conclusions:

In this thesis, spectroscopic study of one-dimensional conductors hydrogen bonded with dyes and oligomers has been carried out. The exciton model of high temperature superconductivity due to Prof. W.A. Little involved a linear chain polymer or metal-chain system as a spine or a backbone covalently bonded with highly polarizable side chains such as dyes. It was mentioned by Little that organic polyiodide chain complexes can show superconductivity if the hydrogen groups of amylose or cyclodextrin are replaced by dye molecules. The model suffers from synthetic problems. It is not possible to attach four dye molecules to every atom of a spine or convert a dye precursor around a metal chain into a dye molecule. In the present work, we study the effect of hydrogen bonded rather than covalently bonded dyes onto the properties of a linear metal chain as a spine.

Inclusion compounds of iodine such as amylose-iodine and α or β cyclodextrin-KI-I$_2$ contain polyiodine chains. The hydroxyl (OH) groups on outer periphery of inert host matrix forming stacking along one direction in crystals can form hydrogen bonding with dyes or oligomers. Hydrogen bonding is verified with infrared spectra. Hydrogen bonding also leads to formation of excitons due to δ+ and δ- charges involved in hydrogen bonding. There are free charge oscillations across the dye molecule which is highly polarizable. The dipole moments flip-flop along dye molecules when charge moves along spine. There are excitons along the
seemingly polyiodine chain and there is exciton-exciton as well as exciton-phonon coupling. The presence of excitons is verified with infrared spectroscopy. There is inverted behaviour of $\alpha_a$ and $\alpha_e$ for emission and absorption as compared to emission and absorption of phonons in indirect transition. This shows that emission of an exciton is a primary process and absorption of the same is a secondary process quite reverse to the case of phonons. Emission is creation and absorption means annihilation. Excitons are neutral entity formed by electrons and holes. Absorption (annihilation) of excitons is either due to electron-hole recombination or due to ionization of excitons leading to electron-hole plasma. The FTIR spectra of hydrogen bonded inclusion compounds of iodine indicate creation and annihilation of excitons due to heavy doping with excitonic medium.

Similar property is found in bis(N-R-salicylaldiminate)Cu II having copper chains when these metal chain containing organometallic chelates are hydrogen bonded with dyes or oligomers. Threshold energy for emission of excitons is lower than that for absorption of exciton.

Many of the hydrogen bonded systems such as nickel dimethylglyoxime, lead phthalocyanine and nickel salicylaldiminates providing metal chains with dyes or oligomers are showing presence of both of hydrogen bonding and excitons. Heavy doping with exciton media leads to infrared spectra having threshold energies for the formation of excitons with phonon emission. This indicates that there is exciton-phonon coupling. If this coupling strength is weak,
phonons are easily released leading to phonon bands. The forbidden energy gap beyond Urbach tail regime is called Tauc energy gap. This Tauc energy gap is evaluated by extrapolation from higher absorption region. The weak exciton-phonon coupling leads to emission of phonons and the Tauc energy gap shifts to higher value due to base-width of the phonon width of emitted phonons. Thus as exciton-phonon coupling is weaker, there are larger number of phonon bands and the Tauc energy gap is larger. For strong exciton-phonon coupling, there is a linear relationship between the band gap and the number of phonon bands. For weak coupling there is a deviation or departure from a straight line and band gap shows a plateau. The analysis of Urbach tail region leads to focal point for a metal chain system with several dyes. The bonding of a particular dye determines width of the tail $E_0$ and metal chain system decides the focal point $E_1$.

The FTIR spectra of one-dimensional conductor with dyes and oligomers are similar to inorganic semiconductor such as gallium phosphied in which electron-hole liquid is found at low temperatures. Thus we expect electron-hole liquid or droplets at low temperature in these hydrogen bonded one-dimensional conductors. Either there should be infrared luminescence or there should be electron-hole droplets.

Other indication of excitons present in these systems arises from the remainder absorption at the value of the energy gap. Remainder absorption is proportional to exciton ionization energy. This is true for direct as well as indirect
excitons. Higher is the ionization energy, the higher is the value of remainder or residual absorption. Remainder absorption vs Tauc energy gap is also plotted for some of these systems.

2. Further scope of the work:

The hydrogen bonded one-dimensional conductors should be studied at low temperature because the quantum phenomena like Little’s model and electron-hole liquid appear at low temperature. The absorption bands observed in absorption edge spectrum or Urbach regime are assigned to the phonon bands at present because these bands appear in infrared range and they appear for $E > E_g$ rather than $E < E_g$. The low temperature FTIR spectroscopy can only decide whether these are phonon bands or bands due to either Mott-Wannier excitons or polaronic excitons. The intensity of phonon bands should diminish at low temperature while the exciton bands increase in intensity at low temperatures. Whether electron-hole droplet or liquid is formed at low temperature as found in germanium, silicon, gallium phosphide, gallium arsenide, silicon carbide and many other intermetallic and inorganic semiconductors. When coupling with phonon is strong, electron hole liquid due to gas to liquid transition appear at higher temperatures. This transition temperature is found as high as 40K in ionic semiconductors in which electron-phonon coupling strength is appreciable. Also electron-hole liquid is metallic because of electron-hole plasma and metallic phase is first step towards superconductivity at still lower temperature. In the present
study, it is not clear whether electrical conductivity along one-dimensional chain increases due to the effect of electron-exciton interaction. For clarifying this, study of electrical conductivity at low temperature on these materials is extremely necessary. Single crystal growth of hydrogen bonded system is also required for this kind of study. Nanocrystalline material with size of nanocrystal of the order of size of electron-hole droplets can only reveal a semiconductor to metal transition through conductivity study at low temperatures. When electron-hole droplets are formed, dielectric constant increases due to interstitial polarization because of metal-semiconductor boundaries. Thus dielectric studies and their temperature dependence down to low temperature would be essential to determine whether metallic droplets are embedded in rest of the semiconducting medium.

3. Applications :

If electron-hole droplets are formed as expected in hydrogen bonded one-dimensional conductors, there will be metallic droplets in semiconducting medium. This will increase dielectric constant similar to ferroelectric materials or Peirls semiconductors. So wherever ferroelectric material find applications such as laser switching etc., these materials will also find similar applications.

If nanomaterials with nanocrystals having size somewhat larger to the size of electron-hole droplets are prepared, the materials would exhibit behaviour of metal-semiconductor junction or the behaviour (I-V and C-V characteristics) similar to Schottky diodes and such materials will find application similar to
Schottky diodes. The bulk material may behave as heterojunction because of layers of semiconducting and metallic media.

Also, the metallic droplets form an outer sheath of a coaxial line if it contains spine which is metallic. If the spine (central metal chain) remains semiconducting, the assembly will work as a waveguide and pass TE and TM modes with cut-off frequencies. If the spine becomes metallic, the assembly will behaves as a molecular level co-axial line and will freely propagate a TEM mode of electromagnetic waves. If the spine becomes superconducting due to Little’s model or Frohlich model, the assembly being a superconductor-metal junction will show d.c. and a.c. Josephson effects. Thus the observation of Josephson effect will only reveal whether Little’s model due to electron-exciton interaction works or not. Thus one-dimensional conductors hydrogen bonded with highly polarizable dye or oligomers will find applications as either waveguide or coaxial line or Josephson junction devices. If the spine remains semiconducting, there will be hindrance of TEM mode of EM waves and TEM mode will not propagate freely due to change in boundary conditions of EM waves because of semiconducting central boundary.
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