CHAPTER - I

INTRODUCTION

1. CHIROPTICAL STUDIES - AN OVERVIEW

1.1. Brief Early History :

More than hundred years ago it was observed that certain liquids such as oil of turpentine, laurel or lemon and certain crystals, such as quartz, rotate the plane of a polarized light passing through them. It was Fresnel who first gave an explanation for such rotation. The plane-polarized light is essentially composed of two circularly polarized light rays rotating in opposite sense. While they travel through the aforesaid media, their velocities differ (and hence their refractive indices) so that one lags behind the other, resulting in a net rotation of the plane of polarization when they recombine. Later, it was seen that the two circularly polarized rays were absorbed unequally. This unequal absorption leads to elliptically polarized light where the major axis of the ellipse is rotated from its original direction. This differential absorption of left- and right circularly polarized light was termed as 'circular dichroism' (CD). Both optical rotation (so called, 'circular birefringence') and CD are different outward expressions of the same general phenomenon known as 'optical activity', and the two expressions are related by 'Kramers-Kronig' trans-
formation. Three years after his explanation of CD, Fresnel\(^2\), came out with the idea that the difference in velocities arose from the helicoidal arrangement of the molecules along the direction of light propagation, which was later proved to be correct by the X-ray analysis of quartz crystal. While studying the symmetry aspects Pasteur observed that molecules which have non-superimposable mirror images are optically active. Since then the spectroscopic problem of optical activity and the stereochemical problem of symmetry have proceeded interdependently.

1.2. Different Techniques for Chiral Studies:

Natural optical activity has by now, evolved into a mature field of study, both experimentally and theoretically. The experimental picture took a new dimension around 1960 when CD measurements in visible and near-UV became commercial. CD measurements have been extended to vacuum-UV region by some groups to cover new chromophoric groups like ethylene, sugars, cyclopropane etc. We refer to the review by Johnson, Jr.\(^3\). Recently the CD technique has been extended to the infrared to cover vibrational transitions. Because of the fingerprint nature of vibrational frequencies, vibrational circular dichroism (VCD) has played an important role in the elucidation of conformations of small organic and bigger biomolecules. Since the vibrational transitions are universal, well-resolved and easily assigned, VCD serves as a good local probe of chirality. It also gives stereochemical information of the entire molecule. Magnetic-field-induced VCD (MVCD) has also
been reported. The potentiality of VCD and MVCD has been reviewed by Keiderling\textsuperscript{4}.

However, it is difficult to extend infrared CD to wavenumber regions below 2000 cm\textsuperscript{-1} or aqueous solution which absorb IR strongly. In such cases, Raman circular intensity differential (RCID) can be used for studying biomolecules in their natural surroundings (i.e. aqueous medium) and for probing the deformation and torsional modes which carry most stereochemical information. Although $\Delta I/I$ in RCID is one order of magnitude higher than $\Delta A/A$ in VCD, signal to noise ratio in RCID is poor, and artifacts, specially for dilute solutions, are more common. Recent developments of multichannel detection techniques have improved the situation\textsuperscript{4-7}.

The emission analogue of CD, called circularly polarized luminescence (CPL), is used as a structural probe of the excited electronic states of inorganic and organic molecules. A good account may be obtained from the review by Richardson and Rieh\textsuperscript{8}. A comparison of CD and CPL throws light on the extent of geometry change on excitation. Mention may also be made here to the technique of fluorescence detected CD (FDOD) developed by Tinoco\textsuperscript{9} and coworkers\textsuperscript{9} where the CD is obtained by the difference in fluorescence intensity of left- and right-circularly polarized excitations.

Various methods have been used to induce optical activity in achiral or racemic molecules. A chiral molecule can induce optical activity in a racemic mixture of labile metal complex.
This is known as 'Pfeiffer effect' and has been reviewed by Gillard\textsuperscript{10} and Kirschner\textsuperscript{11,12}. However, the most universal way of inducing optical activity is by the application of magnetic field which itself has chiral symmetry. Thanks to the development of superconducting magnets, magnetic optical activity (MOA) and magnetic CD (MCD) have become popular methods of determining magnetic moments of electronic states and for throwing lights on bands hidden under broad ones, particularly where conventional Zeeman effect fails. Over the last two decades, MCD and its emission analogue, magnetic CPL (MCPL) have been exploited thoroughly to gain insight into molecular energy levels\textsuperscript{13,14}. Can also be considered

Linear dichroism (LD), as a close analogue of CD and can be induced by stretching a polymer matrix or film. Due to the orientation brought about by stretching, the absorption coefficients ($\varepsilon$) in two mutually perpendicular direction (say, X and Y) may differ. The difference ($\varepsilon_X - \varepsilon_Y$) measures the relative orientations of the polymer molecules in the matrix. Further, if the molecular system is in a non-cubic crystal or in electric or hydrodynamic field etc., the assembly of molecules will produce linear dichroism from which useful electronic and structural information can be elucidated.

The high flux of light photons in a laser beam have facilitated observation of new phenomena, such as two-photon absorption and two-photon CD. While theoretical works have progressed with two-photon CD, experiments reported have been very few\textsuperscript{15-17}.  

\textsuperscript{10} G. Gillard, Rev. Mod. Phys. 21, 120 (1949).  
\textsuperscript{12} Idem., ibid., 2002.  
\textsuperscript{16} Idem., ibid., 2005.  
\textsuperscript{17} S. J. Allen, K. M. Yeh, and J. P. Heremans, J. Appl. Phys. 93, 877 (2003).
1.3. Spectroscopic Information From Chiroptical Studies:

Optical rotatory power \( R_{ab} \) for an electronic transition from state \( |a\rangle \) to state \( |b\rangle \) depends on the imaginary part of the scalar product of the electric-dipole and the magnetic-dipole moments associated with the transition, \( R_{ab} \propto \text{Im} \langle a | \mu | b \rangle \).

\( \langle b | m | a \rangle \), where 'μ' and 'm' are electric- and magnetic-dipole moment operators respectively. The rotational strength (R) can be positive or negative, unlike the dipole strength in absorption which is always positive. In consequence, CD studies give spectroscopic information in more detail than do simple absorption measurements and have been used to detect weak transitions hidden under the contour of a strong one. For example, Misumi et al.\(^{18}\) studied the absorption and CD spectra of 1,2-propanediaminetetraacetic acid and ethylenediaminedisuccinic acid complexes of several lanthanides in aqueous solution at room temperature. They showed that ligand field splitting of J-levels are better resolved in CD than in absorption. However, the principal utility of CD studies lies in the characterization and assignment of electronic transitions and in differentiation between magnetic-dipole-allowed and magnetic-dipole-forbidden transitions. Dissymmetry factor or Anisotropic factor \( g_{ab} \) is defined as

\[
g_{ab} = \frac{4R_{ab}}{D_{ab}}
\]

and if we ignore the magnetic dipole contribution to the dipole strength \( D_{ab} \), \( g_{ab} = 4 \langle m/\mu \rangle \cos \theta \).
Emperically it is found that a value of $|g| > 10^{-2}$ indicates transitions with strong magnetic dipole character and weak electric dipole character. This has been widely used as a criterion to establish the inherent magnetic-dipole-allowedness of electronic transitions in chiral molecular systems and its validity has considerable emperical support\textsuperscript{19}. In transition metal complexes, where transitions are invariably electric-dipole-forbidden to first order, but since many of them are magnetic-dipole-allowed, this criterion can be easily applied. The transitions in near-centrosymmetric ML\textsubscript{n} chromophoric unit generally show $|g| > 10^{-2}$. If the chromophoric unit deviates significantly from centric symmetry, the transitions acquire substantial electric dipole character and consequently, $|g| < 10^{-2} - 10^{-3}$, even when the transitions are magnetic-dipole-allowed. A word of caution is however necessary: $|g| < 10^{-2}$ need not necessarily mean that the transition is magnetic-dipole-forbidden, since $R_{ab}$ depends on the relative orientations of $\mu$ and $m$ through $\cos \theta$.

The sign and splitting patterns observed within the d–d absorption regions of a CD spectrum can also be used to identify and assign specific transitions. For example, nearly degenerate transitions, split out of a common parent state (degenerate) of a $\text{ML}_{n}$ chromophoric cluster, are found quite frequently to exhibit CD bands of opposite signs and very nearly of equal magnitudes (i.e., couplets). This has often been used to identify the components of $A \rightarrow E$ type transitions in chiral complexes of
pseudotetragonal symmetry.

A very interesting case is the Co(III) complex having $D_3$ symmetry. Here the transition $^1A_1 \rightarrow ^1A_1$ is rigorously magnetic-dipole-forbidden and exhibits no optical activity ($g=0$). The trigonal partner of this transition, $^1A_1 \rightarrow ^1E$ is magnetic-dipole-allowed by $D_3$ selection rule but is forbidden by $O_h$ selection rule. This latter transition exhibits only weak optical activity ($|g|<10^{-2}$) in most $D_3$ Co(III) complexes, reflecting its strong octahedral parentage. In contrast, $^1A_1 \rightarrow ^1A_2$ and $^1A_1 \rightarrow ^1E$ transitions in $D_3$ Co(III) complexes are magnetic-dipole-allowed by both $D_3$ and $O_h$ selection rules and so exhibit $|g|>10^{-2}$.

Misumi et al assigned some J-levels on the basis of 'CD-sensitive' bands, which are essentially magnetic-dipole transitions\textsuperscript{20,21}. Pearson and coworkers observed the ORD spectra of lanthanide aminopolycarboxylates and found that at any given wavelength (other than inside of an absorption band) the molecular rotations became more negative as one traversed the lanthanide series. The effect presumably originate from the perturbation caused by the metal ions on the ultraviolet bands of the ligands\textsuperscript{22-24}.

Sen, Chowdhury et al. evaluated relative magnetic dipole contributions for Pr\textsuperscript{3+}, Nd\textsuperscript{3+} and Eu\textsuperscript{3+} transitions in single crystals of Ln-DG\textsuperscript{25-29}. Richardson has proposed some rough selection rules for the optical activity\textsuperscript{30}. Chatterjee and Chowdhury studied the Gd\textsuperscript{3+} transitions (to be reported in this
thesis) and proposed some 'soft' \( \Delta L \)-selection rules. This thesis will also report the magnetic dipole contribution in \( Pr^{3+} \) and \( Nd^{3+} \) transitions in anhydrous double nitrate and \( in \text{Co}^{3+} \)-transitions in pyrogermanate single crystals.

Single crystal spectra of d-d complexes have been studied to find out the relative contributions of electric quadrupole moment transition to the rotational strengths and also to see the relative contributions of site (local) disymmetry vs. unit cell dissymmetry to the overall observed optical activity. Richardson and coworkers have studied CD in single crystal of \( NiSO_4 \cdot 6H_2O \) and \( Cu^{2+} : ZnSeO_4 \cdot 6H_2O \) and concluded that electric dipole-electric quadrupole terms contribute only minimally (~5%), even for transitions which are directly electric-quadrupole-allowed by \( O_h \) selection rule\(^{31,32} \). In the latter system, Kato found out that local (site) symmetry gives the dominant optical activity\(^{33} \). Barron showed that for the \( ^1A_1 \rightarrow ^1E \) transition of Co(III) in \( 2 (\pm) - Co(en)_3Cl_3 NaCl \cdot 6H_2O \), significant contribution to optical activity comes from the electric dipole-electric quadrupole terms\(^{34} \). Though electric quadrupolar transition has not yet been studied in lanthanide, Richardson has calculated theoretically its contributions to some of the transitions in Ln-DG\(^{340} \).

1.4. Spectra-Structure Correlation

Let us focus our attention on the spectra-structure correlation in different systems. Although CD depends critically on
conformation, only limited success has been achieved so far in correlating it precisely with the conformation. Experimental and theoretical generalisations have been possible only within closely similar molecules and we discuss them below for different classes of molecules.

1.4.1. **Small Organic Molecules**

Initially chiroptical studies were largely concentrated on carbonyl chromophore which acts as an ideal probe for many structural subtleties existing in the organic molecules. Experiments with model planar and cyclic ketones indicated that chiral sphere closest to the chromophore mainly determines the sign and magnitude of CD bands. The correlations between structure (or stereochemistry) and CD in carbonyl compounds in general, and ketones in particular, can be done with the help of a simple 'octant rule' which relates the sign and amplitude of the CD to the disposition of atoms in space about the carbonyl groups. Many bicyclic, triterpenoid and especially steroid ketones have been successfully analysed in the light of this rule. The potential contribution of the octant rule is in the field of absolute configuration assignment, particularly where other methods fail.

CD has been used to investigate the solute-solvent interaction of ketones, e.g., the blue shift of their long wavelength transition. Here CD should be more sensitive than absorption, since subtle conformational changes will in general be more important for rotational strengths than for dipole strengths.
This is certainly true if the solute solvent interactions give rise to environmental asymmetries over and above those germane to the solute molecule itself.

The simplest $2\pi$-system is the ethylene chromophore. An ethylene becomes inherently chiral (chirality of the first sphere) if the system is twisted and in such a case electron charge is also rotated during the excitation from $\pi$ to $\pi^*$ orbital. If the angle of the twist is clockwise (positive), these combined movements give rise to a right-handed helix and we get positive CD. However, trans-cyclo-octane does not conform to this idea presumably due to the contribution of another transition and also due to the effect of chiral second and/or third sphere which contribute strongly than the first.

The non-coplanar conjugated diene system was one of the first chromophores where helicity rules were given on a theoretical basis. It was proposed that a positive torsion angle around the bonds between second and third carbon atoms should give a positive CD. Later on, some exceptions were found which were ascribed to the axial allylic groups.

The first sphere can be chiral if either the chromophore belongs to a chiral point group (no $S_n$-axis, including $n=1$ and $2$, is allowed) or if two or more locally achiral chromophores are chirally arranged in close neighbourhood to each other and if the transition considered is connected with a strong electric dipole transition moment, as occurs in exciton interaction. The disulphide chromophore is a case in point. The multiplication
recipe of the rotational strengths in these simple cases gives helicity rule which correlates to the absolute conformation.\textsuperscript{41,42} Mason determined the absolute conformation of the dissymmetric dimer, 2,2'-diamine-1,1'-binapthyl by exciton CD and then correlated it to its absolute configuration.\textsuperscript{43} Actually, most of the investigated chromophores contain one or more \( \pi \)-bonds. But more complicated the systems become, like cross-conjugated polyenes, aromatic compounds, heteroconjugated systems, the less such a qualitative treatment remains valid, and often it fails to predict the correlation between the CD signs and the absolute conformation.

The conformation of the excited state in relation to the ground state has been determined by comparing CPL with CD. A large difference in CPL and CD clearly indicates geometry change in the excited state. A few examples will illustrate the point.

(a) Luk and Richardson\textsuperscript{44} reported CPL and CD for \( \alpha \)-diketone and \( \delta \)-camphorquinone in solution at room temperature and attributed the order of magnitude difference between absorption and emission anisotropies (\( g_{\text{abs}} \) and \( g_{\text{lum}} \)) to ground state/emitting state structural difference within the dicarbonyl chromophore.

(b) Solvent induced CPL has been reported by Brittain and Richardson\textsuperscript{45}. They observed that achiral fluorescing gives polarized luminescence on dissolving in chiral \( \alpha \)-phenyl ethylamine and exciting with an Ar-ion laser. No CD has been observed.

(c) Schlessinger and Warshel\textsuperscript{46} calculated the \( g_{\text{abs}} \) and \( g_{\text{lum}} \) for 1,1'-bianthracene-2,2'-dicarboxylic acid as a function of
the conformational variable, $\phi$, the dihedral angle between the planes of the two anthracene moieties. On comparing with the experimental data they could deduce that $\Delta \phi$ between ground and excited states is about 20°.

(d) Schlessinger, Gafni and Steinberg have reported CD and CPL studies of various cyclic dipeptides, containing luminescent aromatic side chains, particularly diketopiperazines. They could find CD but no CPL and concluded that the fluorescent state of the aromatic chromophores and the ground state sense different chiral environments. In high viscous fluid $g_{\text{abs}}$ almost equals $g_{\text{lum}}$, meaning thereby that the molecular conformations in the two states are similar. They further demonstrated that the rate of rotational (orientational) relaxation of the molecules in the low viscous media (as determined by linear polarization measurements of fluorescence relaxation) is slower than the conformational process responsible for loss of emitting state optical activity (as determined by CPL).

1.4.2. Large Biomolecules:

CD has been utilised for getting information about the environment of a particular chromophore as well as the secondary structure of the whole biopolymer. As an example of the former, we can cite the case of tryptophan residue in $\alpha$, $\beta$ and $\gamma$ crystallins. The near-UV CD points out that the tryptophan residues in $\gamma$-crystallin are mostly buried in a hydrophobic environment whereas $\alpha$-crystallins are least buried. Similarly, tyrosine
residues in β-crystallins are in more polar environments than are α- and γ-crystallins. However, most of the CD studies are concerned with the secondary or tertiary structures or the gross conformation of the biopolymer. α-helix, β-sheet and random structures of proteins, all give different CD spectra. The optical and vibrational CD of enzymes, nucleic acids, Vitamin D, cryoproteins, chromatin etc. have been studied extensively to throw light on conformational aspects. A stepwise synthesis of the soluble polymeric support, i.e. polyoxyethylene by CD, provides a systematic conformational analysis of a number of biologically active peptide and protein sequence determinations. The overall biological activity and functions of proteins, such as enzymes, depend mainly on how the molecule is folded, and in many cases conformational changes dictate the effective biological action. Most biological molecules are asymmetric and CD is extensively exploited for their conformational change particularly in their natural environment i.e., in aqueous solution.

1.4.3. Transition Metal Complexes:

Let us now discuss the chiroptical studies of coordination compounds. The first purely theoretical examination of the origin of optical activity in coordination compounds was made by Kuhn and Bein. Moffitt introduced the quantum-mechanical theory of d-d optical activity by using the crystal field model and one-electron theory proposed by Condon, Altar and Eyring.
and successfully applied it to tris-chelated complexes of Co(III) and Cr(III) which have exact $D_3$ symmetry. The theory has been developed since then, followed by a large quantity of experimental data during last twenty years on a wide variety of metal complexes. Empirical characterisations of the $d-d$ transitions, ligand-metal charge transfer and ligand spectroscopic states of a variety of metal complexes have refined the theoretical models used for interpreting and analysing the chiroptical spectra of metal complexes.

The most complete set of symmetry rules applicable to the $d-d$ optical activity has been set forth by Schipper\textsuperscript{64-66}. These symmetry rules apply to the spectroscopic moments appearing in the rotational strengths and can be related in a straightforward way to sector rules pertaining to ligand stereochemical features. Schipper's work is based on the general independent systems/perturbation model which he calls as 'separable chromophore model'. It includes the 'static' coupling (where a particular charge distribution in the ligand, i.e. of their ground state, perturbs all the metal ion $d$-states) as well as a 'dynamic' coupling (where the induced dipoles in the ligands, brought about by the incident radiation, couple coulombically with the leading charge distribution of the metal ion)\textsuperscript{67}. On the other hand, in a tris-bidentate complex containing unsaturated ligands, a major source of optical activity is the coulombic coupling of the allowed $\pi \rightarrow \pi^*$ transitions in the individual ligand. This coupling gives rise to component transitions, separated
by exciton splitting energy, centered at the individual ligand transition which are intrinsically optically active and whose sign-order along the energy ordinate reflects the particular absolute configuration of the complex\(^\text{43}\). (The signs can be determined by the phase relationships of the individual dipoles).\(^\text{68}\)

The first definite determination of the absolute configuration of a chiral metal complex was reported by Saito and coworkers in 1955 using the anomalous X-ray scattering method\(^\text{69}\). One of the aims of absolute configuration determination is to establish an empirical rule relating the absolute configuration and CD\(^\text{7}\). By doing so, absolute configuration can be determined by simply measuring the CD spectra, a procedure which is much easier to carry out and less time consuming than the tedious X-ray method. Thus, the absolute configuration of the enantiomers of a number of unknown complexes has been determined with reasonable certainty\(^\text{70}\).

As in the case of organic compounds, CPL studies in conjunction with CD give information of geometry change on excitation. However, CPL studies in d-d complexes are comparatively small in number.\(^\text{19}\) For the \((-)\)\(^{546}\) Cr(en)\(_3\)Cl\(_3\) isomer, the absorption and emission anisotropy factors corresponding to the \(4A_2 \rightarrow 2E\) transitions are found to be of similar magnitude and of identical sign indicating similar structure for Cr(en)\(_3\)\(^{3+}\) system in the ground \(4A_2\) and emitting \(2E\) states.\(^\text{71}\)
1.4.4. Chiroptical Studies on Lanthanides:

While intense efforts have been made to investigate the d-d optical activity, much less attention has been focused on analogous studies on the f-f transitions occurring in the lanthanides. We will, however, discuss the lanthanides here a little more elaborately, for the present thesis is concerned with the CD of lanthanide complexes.

1.4.4a. Solution CD:

Most optically active lanthanide complexes studied so far derive their chiroptical properties from their optically-active ligands. Lanthanide complexes of aminopolycarboxylic acids are known to be extremely stable and several of these ligands are potentially resolvable. Pearson and coworkers extensively studied this chiroptical lanthanide aminopolycarboxylates. Later, they studied the kinetics of ligand exchange through changes in their chiroptical properties. Misumi et al examined the effect of pH on the CD sensitive bands of 1,2-propanediaminetetraacetic acid and ethylenediaminedisuccinic acid complexes of several lanthanides and observed that the chiroptical spectra were quite sensitive to changes in complex stereochemistry. Carboxylic acid lanthanide interactions can be quite strong in aqueous solution and generally other functional groups do not interact with Ln(III) ion unless the metal is first bound by carboxylate ligands. Katzin et al reported the CD spectra of
chelate complexes of Eu$^{3+}$ with sugar acids and concluded that complexing takes place through the carboxylate and hydroxyl groups of the sugar acids. Later they also indicated that the lanthanide 'hypersensitive transitions' are due to a binding of an anion which helps to lower the symmetry.$^{73}$ Andersen and others studied the CD spectral changes induced in the Eu$^{3+}$, $7F_0 \rightarrow 5D_1$ transition of the shift reagent Eu(fod)$_3$ when it complexes with optically active alcohols. They indicated that the major species present at standard NMR concentration. ratios is octa-coordinated Eu(fod)$_3$ (ROH)$_2$. Prados and others titrated several aminoacids with lanthanides. They observed more bands in CD than in absorption.$^{75}$

The lanthanide complexes of malic and tartaric acids have received special attention due to the multitude of coordination possibilities presented by these ligands. CD within the infrared region of the spectrum is reported for Pr$^{3+}$/tartarate complexes for several f-f absorption bands.$^{76}$ In a variety of investigations correlation have been made between the absolute configuration of a chiral substrate and the sign of the CD induced in a lanthanide $\delta$-diketone chelate. Nakanishi et al$^{77}$ have determined the chirality of cyclic $\alpha$-glycols by CD and showed that it can be extended to determine the chirality of $\alpha$-glycols containing tert-hydroxyl groups which helps to establish the configurations and conformations of glycol containing natural products in a straightforward manner. They later determined the absolute configuration of the C$_{18}$-juvenile hormone with CD using Tris(dipi-
valoylmethanato) Pr$_3^+$). The basis was the clarification of the epoxide-cleavage mode and concomitant determination of chirality of the resultant α-glycols.

1.4.4b. Solution CPL:

In lanthanide complexes many conformational studies have been made using CPL as the tool instead of CD which becomes difficult to measure for f-f transitions because of their low oscillator strengths. The topic has been elaborately reviewed by Richardson and Rühl$^8$. We only give here some examples of conformational studies by CPL. Camphoratocelates of lanthanides are monomeric in solution and the Eu(III) derivative of 3-trifluoroacetyl-d-camphor CPL lineshapes were found to be solvent dependent. With dimethyl sulfoxide, one of the components of $^5D_0 \rightarrow ^7F_1$ transition came out to be totally circularly polarized$^79$. Brittain and Richardson$^80$ studied CPL of 3-heptafluorobutyryl camphor complexes of Eu$^{3+}$ in different solvents and concluded that metal chirality was due to configurational effects, as the sign of the vicinal effect had to be affected since the α-diketone ring is planar. Chan and Brittain$^81$ prepared and characterized a series of mixed ligand Eu$^{3+}$ compounds, showing conclusively the configurational nature of this solvent induced optical activity. Copeland and Brittain$^82$ took advantage of the fact that Tb(DPA)$^+$ and Tb(DPA)$^-$ contain bound solvent molecules which can be displaced by a second chiral ligand and thus permits CPL studies to be carried out on complexes known to be monomeric at all pH values.
Absolute configuration was determined for Tb(DPM)$_3$ by CPL when it was shown that CD sign within the $^5D_4 \rightarrow ^7F_5$ transition could be related to the chirality of the bound substrate.

Conformational effect in Eu$^{3+}$-δ-diketone complexes was studied by CPL when it was observed that the chiral substrate could attach to these complexes in a bidentate fashion. The CPL for the adducts of Eu(TTFA)$_3$ (TTFA is theonyltrifluoroacetone) with cinchona alkaloids can be successfully correlated to the absolute configuration of one of the substrate asymmetric atoms and it was observed that different alkaloids induce varying degrees of chirality at the metal ion.

CPL proved to be an excellent probe of the solution phase stereochemistry of chiral-lanthanide amino acid complexes, particularly for Eu$^{3+}$ and Tb$^{3+}$ for which the quantum yield of emission is very large. Studies in Tb(DPA)$^+$ and Tb(DPA)$_2^-$, which contain bound solvent molecules, permit an easy method to observe the interactions of Ln$^{3+}$ with only one (or at most two) chiral ligands and thus isolate the bonding situations where vicinal/conformational effects determine the chirality of Tb$^{3+}$ ion. The distinction between CPL associated with pure vicinal versus vicinal/conformational effects was subsequently addressed and found to be a general effect for the Tb(DPA) complexes. If CPL for $^5D_4 \rightarrow ^7F_5$ is single signed, only the vicinal effect is operative. The sign of the vicinal effect CPL is directly relatable to the absolute configuration of the asymmetric atom in the chiral ligand.
CPL was used to investigate the interactions of $\text{Tb}^{3+}$ and $\text{Eu}^{3+}$ ions and a series of potentially terdentate aminoacids (e.g. L-Aspartic acid, L-histidine etc.). CPL was found to be sensitive to pH and generally intense CPL were observed at alkaline pH's. The effect of achiral ligand on CPL was studied and it was shown that if sulfosalicylic and phthallic acid replace the DPA ligand in $\text{Tb}^{3+}$ and $\text{Eu}^{3+}$ complexes, not only the chiroptical properties for a given mode of coordination is changed but can in fact prevent malic acid from binding in the terdentate mode. Brittain and Pearson have found extensive change of sign and magnitude of $\text{Tb}^{3+}$ and $\text{Eu}^{3+}$ complexes of $\text{R}(-)$-PDTA and $\text{R} \text{R}(-)$-CDTA and attributed the anomaly to the formation of hydroxy complexes. Presumably the formation of mixed ligand complexes is accompanied by substantial alteration of the conformation and properties of the $\text{Ln}^{3+}$-ion.

CPL studies are useful to detect energy-transfer occurring between different excited substrates and thus to characterise them. A case in point is the hydroxycarboxylate complexes of lanthanides. Strong CPL was observed for $\text{Eu}^{3+}$-malic acid complex at alkaline pH and a possible energy transfer occurs which indicates polynuclear association. Murata and Morita reported CD and CPL for $\text{Tb}^{3+}$ complex of L-ammonia isopropiondiacetic acid and have examined some details of the intermolecular energy transfer to the analogous $\text{Dy}^{3+}$ and $\text{Ho}^{3+}$ complexes.

Lanthanide complexes of proteins and enzymes have been extensively investigated since lanthanides can be excellent biolo-
gical probes, especially for structural and spectroscopic investigations of binding sites in the macromolecules. CPL/emission of Tb$^{3+}$-protein complexes have been used to probe the metal binding sites of a large number of protein molecules, many of which are known or suspected to be calcium binding sites. The tyrosine and tryptophan aromatic residues of the Tb$^{3+}$-protein complex are irradiated by 290 and 300 nm radiation and the absorbed energy then readily gets transferred to Tb$^{3+}$-ion in a non-radiative fashion. When the two Fe$^{3+}$-ions of transferrin and conalbumin were replaced by Tb$^{3+}$-ion, CPL was observed for the $5D_4 \rightarrow 7F_5$ emission band. Examination of several mixed metal transferrin preparation provided evidence that the two metal sites are equivalent in structure and conformation. It was also observed that the metal binding sites of conalbumin are essentially identical in their stereochemical properties, inspite of the disparity of the origin of these proteins. Donato and Martin studied the conformation of Ca$^{2+}$ binding sites of carp muscle parvalbumin-B by replacing Ca$^{2+}$ by Tb$^{3+}$ and using CPL. These studies indicate no structural change in the protein secondary and tertiary structure accompanied by binding of the Tb$^{3+}$ ion even though the lanthanide ion binds much more tightly than those did by the Ca$^{2+}$ ion. The origin of molecular chirality and the condition of CPL observation can be obtained from CPL intensities and line shapes together with configurational assymmetry. Pure conformational and vicinal effects leading to no configurational assymmetry offers no CPL whereas the chiral environment of the
protein tertiary structure around Ln$^{3+}$ ion leads to CPL observation. Moreover, care has to be taken about resolution since overlapping of emission bands might cancel out CPL lines.

1.4.4c. Crystal CD/CPL:

In solution, lanthanide optical activity is due to the chiral ligands and hence they remain uninterpreted in terms of detailed spectra-structure (i.e. Ln$^{3+}$-environment) correlations. Moreover, the metal ligand stoichiometries in solution are either ill-defined or unknown. The f-orbitals, which take part less in bonding, make metal ligand bond very labile in solution. Though the studies in solution do throw light on f-electron delocalizations, identification of species present and sometimes, determination of absolute configuration, they fail to provide spectroscopic information such as magnetic dipole moments of lanthanide f-f transitions. This is of course, due to the fact that in solution the chirality does not, most often, arise from the immediate vicinity of the lanthanide ion. In order to study the circular dichroism of transitions between states split by crystal field, it is necessary to choose suitable cooled single crystals. Sen, Bera and Chowdhury$^{25}$ were the first to report the single crystal CD spectra of optically active lanthanide Diglycolates. The chiral behaviour of transitions between crystal field (CF.-split components) were studied under high resolution with cooled single crystals$^{26-29}$. Subsequently, they tried a model calculation of the relative magnitudes and signs of CD bands on the basis of
Judd-Ofelt\textsuperscript{96-97} theory. Richardson\textsuperscript{34a} developed a more elaborate theory for the CD of these complexes and gave a set of selection rules. The term-to-term transitions within a chiral environment were classified according to their predicted electric dipole moments, rotatory strengths and the dissymmetry factors. The importance of $\Delta L$ selection rule in Gd$^{3+}$-transitions have been reported by Chatterjee and Chowdhury\textsuperscript{98} and will be discussed in this thesis. The $\Delta J = 0, \pm 1$ selection rule for optical activity has been exploited for spectral assignment in Er$^{3+}$, Tb$^{3+}$ and Tm$^{3+}$ by Chowdhury and co-workers. The same group has also tried to find out the contribution of quadrupolar and still higher order contribution by comparing powder CD with single crystal CD and by comparing CD of different faces of the same cubic crystal.

A great deal of experimental and theoretical work has centered around the chiroptical properties of lanthanide ion in trigonal environments. Schwartz, Banerjee and others\textsuperscript{99} were the first to report the correlation of CD and absolute configuration of the metal ion for any lanthanide complex, when they determined that the $\Delta$-isomer of Eu$^{3+}$-diglycolate exhibited negative CD for the $7F_0 \rightarrow 5D_1$ and $7F_0 \rightarrow 5D_2$ absorption bands. More extensive CD work on the same system along with spectra-structure correlation, has been reported earlier by Chowdhury, Schwartz and coworkers\textsuperscript{27-29}. A detailed CPL investigation on this system was done by Richardson and coworkers\textsuperscript{100,101}. Mason and coworkers\textsuperscript{102} have examined the anisotropic ligand polarization contribution to the f-f transition probabilities of Eu$^{3+}$-ion.
Richardson and coworkers reported the polarized luminescence of Tb$^{3+}$-diglycolate crystal, examining both linear and circular polarization in the emission spectra. They concluded that unlike Pr$^{3+}$-diglycolate system, where a second-order phase transition occurs between 120K and 5K this Tb$^{3+}$-system apparently does not undergo any phase transition at cryogenic temperatures. The details of the nature of the phase transition in Ln-DG crystal has been discussed by Schwartz, Banerjee, Chowdhury and Kuroda.

1.4.4d. Induced Optical Activity:

(1) Pfeiffer effect: No CD study in Pfeiffer-active lanthanide system has been reported so far, but several CPL studies have been done. Madaras and Brittain showed that the enantiomeric equilibrium of the trigonal complex, Ln(DPA)$_3^{3-}$ series in solution can be upset by the addition of resolved tris(ethylenediamine)Cr$^{3+}$. For Tb(DPA)$_3^{3-}$, formation of the expected ion-pair yields strong CPL whose intensity increases on decreasing the dielectric constant of the solvent, clearly supporting the ion-pair formation. On
addition of L-ascorbic acid to the Tb\textsuperscript{3+} complexes. Pfeiffer effect could only be observed as long as the lactone ring remained intact. Hydrolysis of this functionality led to complete loss of CPL which indicates that some hydrophobic site might exist between the DPA rings bound to the metal ion. The nature of this hydrophobic site has been examined in great detail using a wide variety of environmental substances to determine the conditions under which the outer sphere bonding takes place. The Tb(DPA)\textsuperscript{3} and Eu(DPA)\textsuperscript{3} complexes were all found to exhibit the Pfeiffer effect with monoamino and diaminocarboxylic acids\textsuperscript{107}, derivatives of tartaric acids\textsuperscript{108}, phenylalkylamines, phenylalkylamino alcohols and phenylalkylamino acids\textsuperscript{109}. In these studies inversion of CPL sign pattern at elevated pH indicate a change in mechanism for the association not observed for the short chain substances.

(2) MCD: Although the basic matrix element controlling MCD is different from that of CD, we briefly discuss it here. The shape and temperature dependence of the MCD curve yields the Faraday parameters, A, B and C. A major use of MCD has been in the symmetry assignment of excited states using the 'C' term. In many cases this requires only the ground state symmetry and 'g' value to be known (sign and magnitude both). This was first pointed out with f → d transitions of divalent lanthanides\textsuperscript{110,111} and has been pursued extensively since then. For vibration induced electric dipole transitions where the vibrational structure can be resolved, the vibrations involved is assignable via
MCD\textsuperscript{112}. This has been done in cubic elpasolite single crystals of several lanthanides\textsuperscript{113-116} and excited state 'g'-values have been deduced for vibration induced f-f transitions\textsuperscript{117}. Due to its dependence on precise molecular geometry MCD is very helpful to study compounds in solids. Many of the MCD studies of rare earth crystals, such as chalcogenides, garnets, ferrites, oxides, sulfides, tellurides etc. were undertaken from the point of view of band theory and/or magnetic interaction and phase change\textsuperscript{118-125}. Some have used MCD technique to study the relaxation rate processes in lanthanides\textsuperscript{126,127}. Paramagnetic trivalent and bivalent rare earth compounds have been studied with the idea of extracting magnetic moments of excited state and/or assignment of states. Trichlorides of rare earths\textsuperscript{128,129}, Cs\textsubscript{2}NaLnCl\textsubscript{6}\textsuperscript{113-116}, doped CaF\textsubscript{2}\textsuperscript{130-134}, Ethyl sulphates\textsuperscript{135,136} and aqueous solutions\textsuperscript{137-139} have been investigated. Chowdhury and coworkers have carried out MCD measurements along with CD with chiral Pr\textsuperscript{3+} and Nd\textsuperscript{3+}-DG single crystals over broad bands at higher temperatures and tried to test the reliability of MCD data obtained from broad unresolved bands. A few cases of MCD of resolved bands at low temperatures have also been reported by them.\textsuperscript{140-142}

(3) MCPL: It is the emission analogue of MCD. MCPL spectra provides structural information not readily obtainable from the use of other techniques. However, studies of MCPL have been very few. Richardson and coworkers\textsuperscript{143} reported MCPL at high resolution and at various temperatures spanning $^5D_J (J=0-3) \rightarrow ^7F_J (J=0-5)$ for the Eu\textsuperscript{3+} transitions in the cubic Cs\textsubscript{2}NaYCl\textsubscript{6}
crystal. They have obtained excellent agreement between theory and experiment for the MCPL spectra associated with the magnetic dipole allowed origin transitions. Later the same group reported\textsuperscript{144} the MCPL spectra of Pr\textsuperscript{3+} in the same host. MCPL spectra for four different Eu\textsuperscript{3+}/ligand systems in aqueous solution of pH = 8 and with [Eu\textsuperscript{3+}]/[ligand] < 0.33 has been reported\textsuperscript{145} recently. The results revealed the dominant coordination species formed in different concentration ratios of metal and different ligands. It has been shown that MCPL spectra are considerably more useful for eliciting structural information about the complexes.
2. SCOPE OF THE PRESENT WORK:

We have chosen some single crystals of rare earth complexes for chiroptical studies for the following reasons: (1) In solution it is not possible to have optical activity which originates solely from the asymmetry around Ln$^{3+}$ ion. (2) Single crystals have a well-defined symmetry of the coordination polyhedron which enables one to find out precisely the nature of perturbation brought about by the crystal field of the polyhedron. (3) The crystal field lifts the degeneracy of individual J-levels in the Ln$^{3+}$ free ion. The resolved chiroptical spectra of the complexes offer an excellent opportunity for testing model transition to calculations of $f \rightarrow f$ optical activity for each individual crystal-field-split components. This may be expected to help in the evaluation of a sound spectra-structure relationship for the lanthanides. (4) Due to mixed dipolar nature of some of the RE transitions, the spectra of axial crystals occasionally are not well-polarised and therefore may not be amenable to easy assignment. In such cases it becomes necessary to confirm the mixed dipolar nature of the transitions more directly and separate the contribution of the magnetic dipolar part from the electric dipolar contribution. The most elegant way to achieve this is to study the optical activity in conjunction with absorption. The rotational strength depends on the scalar product of the electric dipole and the magnetic dipole moments.
whereas the dipole strength in absorption studies is the sum of the absolute value squares of the two moments. Hence the ratio of rotational strength to dipole strength is capable of throwing light on the role played by magnetic dipole transition moment. (5) In single crystals, electric quadrupolar moment has an additional contribution to optical activity which cancels out on averaging over a random distribution in solution.

Norden et al reported the CD spectra of Ho$^{3+}$ and Sm$^{3+}$ oxydiacetate (Diglycolate or 'DG' as is often called) in powdered form. Their low resolution CD studies could not yield much quantitative information. Subsequently Sen and Chowdhury reported the low temperature highly resolved CD/absorption spectra in single crystals of Pr$^{3+}$ and Eu$^{3+}$-DG. Following this Schwartz, Sen, Banerjee and Chowdhury reported a detailed model calculation on Eu$^{3+}$-DG.

With the idea of relating the site symmetry of the RE ion to the CD at $f^N \rightarrow f^N$ bands, we have studied the chirooptical spectra of optically active single crystals of Gadolinium oxydiacetate (Gd$^{3+}$-DG). The crystal system is trigonal with space group R32 and the site symmetry $D_3$. We have measured the asymmetry factor (i.e., Rotation strength, $R_K$/Dipole strength, $D_K$) for different Gd$^{3+}$ transitions, from the ground state ($^8S_{7/2}$) to $^6P_J$, $^6I_J$ and $^6D_J$ multiplets, to gain insight into the nature of the moments contributing to the transition intensities and thereby tested the applicability of the $\Delta J$ and $\Delta L$ selection rules for diagnostic chirooptical probes.
In course of our work on Ln-DG, the only lanthanide single crystal system on which the chiroptical studies have been made so far, we felt the need for extending similar studies to other lanthanide complexes which are optically active in single crystalline form. With this in view, we focussed our attention on the interesting single crystal system $K_3Ln_2(NO_3)_9$ (Ln = Pr, Nd) - the family of anhydrous double nitrates of rare-earths (Ln-DN). The crystal has an unusual space group $P4_3\overline{2}$. It is cubic and the four body diagonals coincide with the eight $C_3$-axes of the actual site symmetries of the eight RE ions. Each Ln-ion has a coordination number of twelve (12); the twelve oxygen atoms, coming from six-nitrate groups, form a distorted icosahedron. We have investigated the room temperature CD and absorption spectra of the Eu$^{3+}$-doped K$_3$Nd$_2$(NO$_3$)$_9$ single crystal with a view to compare the essentially magnetic-dipole-allowed, but electric-dipole-forbidden, Eu$^{3+}$ transition with electric-dipole allowed Nd$^{3+}$ transitions in identical environment. It has been observed by us that the crystal-field-induced $J$-mixing is more in some of the Nd$^{3+}$ transitions than in Eu$^{3+}$ transitions. We found out that in both Nd$^{3+}$-DN and Eu$^{3+}$-DN, the disymmetry factors are one order of magnitude less than those found for corresponding Ln-DG crystals. The general rule that transitions with high magnetic dipole moments have high disymmetry factors is however obeyed.

With the crystal K$_3$Pr$_2$(NO$_3$)$_9$ we have obtained CD and absorption from room temperature (300K) to 5K in the visible
region. Expectedly, the 5K spectrum is much more simplified. From the splittings of various stark components of the excited states, crystal field parameters are evaluated. The explanation of the sign and magnitude of the CD anomaly of the Ln$^{3+}$-crystals provides a stringent test for the models based on Judd-Ofelt intensity theory. Our success with the Pr-DN case can at most be claimed as modest. Although the models could not explain the observed results quantitatively, presumably due to the simplified assumptions and approximations made, some qualitative features of the spectrum do emerge from the calculation$^{150}$. The possibility of moments higher than dipoles contributing to the CD has been investigated by passing light in different directions of the cubic crystals.

In our bid to put spectra-structure correlation of rare-earth complexes on a better footing, we have taken up yet another single crystal system Ln$_2$Ge$_2$O$_7$ (Ln-PG), the rare-earth pyro-germanates. It has a space group, P4$_1$2$_1$2 (point group D$_4^1$), containing four structural units per unit cell. The oxygen coordination of each Ln is seven and they form a distorted pentagonal bipyramid for the coordination polyhedron. The axis of the polyhedron is almost parallel to the C-axis of the crystal. Eight such Ln-polyhedra in a unit cell are joined along common edges to form infinite spirals of polyhedra. The axes of these spirals are the 4$_1$ screw axis$^{151}$. A model calculation has been made with limited basis set to see how far the CD signs of the transitions to the CF-split components of
\[ {^8S_7/2} \rightarrow {^6P_{7/2,5/2,3/2}} \] can be reproduced. Since the \[ {^8S_7/2} \rightarrow {^6P_{7/2}} \] transitions are magnetic-dipole allowed transitions, in contrast to the \( \text{Pr}^{3+} \)-transition, it was thought that calculations might be more meaningful. Indeed as our calculation showed, the observed CD sign pattern for these transitions has a very good agreement with the calculated signs.