CHAPTER 4

OPTICAL STUDY AND MAGNETIC MOMENT OF CRYSTALS

4.1 INTRODUCTION

In physics, absorption of electromagnetic radiation is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom. Thus, the electromagnetic energy is transformed to other forms of energy for example, to heat. The absorption of light during wave propagation is often called attenuation. Usually, the absorption of waves does not depend on their intensity (linear absorption), although in certain conditions (usually, in optics), the medium changes its transparency dependently on the intensity of waves going through, and the saturable absorption (or nonlinear absorption) occurs. The absorbance of an object quantifies how much of the incident light is absorbed by it (not all photons get absorbed; some are reflected or refracted instead). This may be related to other properties of the object through the Beer-Lambert law. Precise measurements of the absorbance at many wavelengths allow the identification of a substance via absorption spectroscopy, where a sample is illuminated from one side, and the intensity of the light that exits from the sample in every direction is measured. A few examples of absorption spectroscopy, in different parts of the spectrum, are ultraviolet-visible spectroscopy, infrared spectroscopy, and X-ray absorption spectroscopy. The attenuation coefficient is a quantity that characterizes how easily a material or medium can be penetrated by a beam of light, sound, particles, or other energy or matter. A large attenuation coefficient means that the beam is quickly "attenuated" (weakened) as it passes through the medium, and a small attenuation coefficient means that the medium is relatively transparent to the beam. Attenuation coefficient is measured using units of reciprocal length. The attenuation coefficient is also called linear attenuation coefficient, narrow beam attenuation coefficient, or absorption coefficient.
The measured intensity $I$ of transmitted through a layer of material with thickness $x$ is related to the incident intensity $I_0$ according to the inverse exponential power law that is usually referred to as Beer–Lambert law discussed in next section:

$$I = I_0 e^{-\alpha x}$$

where $x$ denotes the path length. The attenuation coefficient (or linear attenuation coefficient) is $\alpha$.

The Half Value Layer (HVL) signifies the thickness of a material required to reduce the intensity of the emergent radiation to half its incident magnitude. It is from these equations that engineers decide how much protection is needed for "safety" from potentially harmful radiation. The attenuation factor of a material is obtained by the ratio of the emergent and incident radiation intensities $I / I_0$.

The linear attenuation coefficient and mass attenuation coefficient are related such that the mass attenuation coefficient is simply $\alpha / \rho$, where $\rho$ is the density in g/cm$^3$. When this coefficient is used in the Beer-Lambert law, then "mass thickness" (defined as the mass per unit area) replaces the product of length times density. The linear attenuation coefficient is also inversely related to mean free path. Moreover, it is very closely related to the absorption cross section.

### 4.1.1 IR Spectroscopy

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years$^{[1]}$. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material$^{[2-4]}$. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present$^{[1]}$. With
modern software algorithms, infrared is an excellent tool for quantitative analysis.

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis[5-9].

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beamsplitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency.
which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal can not be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis shown in figure 4.1.

![Figure 4.1 - Spectral Information Analysis](image)

4.1.2 Reflectance spectra

Reflectance spectroscopy is used for samples that are difficult to analyze by transmission \[^{[10-13]}\]. The samples can usually be analyzed as is without the need for preparation or any modification. Reflectance measurements can be divided into two basic categories – internal or external reflectance\[^{[14-19]}\]. The technique of Attenuated Total Reflection (ATR) is employed for internal reflectance measurements as the beam of infrared radiation passes through an ATR element (crystal) in contact with the sample. For external reflectance measurements, the infrared beam of radiation is reflected directly from the sample surface. This type of external reflectance measurement can also be divided into two types – Diffuse or Specular.
4.1.2.1 Attenuated total reflectance (ATR)

![Diagram of ATR](image)

**Figure 4.2 - Diagram of ATR**

The diagram in figure 4.2 shows a typical type of ATR experimental set up. In the example a parallelogram shaped ATR crystal is covered on two surfaces with a black sample material. The beam of infrared light traversing through the ATR crystal at a particular angle of incidence is being internally reflected at the top and bottom surfaces and in this instance there are 6 points of contact with the sample material (3 at the top and 3 below). Internal reflection occurs when infrared radiation enters an ATR crystal made of a highly refractive infrared transmitting material. The crystal is designed to enable internal reflection, creating an evanescent wave at the crystal surface. This wave extends into a sample that is held in intimate contact with the crystal material and so absorption spectra can be recorded as a result. The depth of penetration of the evanescent wave into the sample is a function of the crystal material and the angle of incidence for the infrared beam traversing through the crystal to the sample surface interface. Deeper penetration into a sample is achieved with either a smaller incident angle or a lower refractive index ATR crystal. In general the depth of penetration into a sample increases with increasing wavelength of light. The Specac accessories that are used for the analysis of solids and liquids by the ATR technique are the Golden Gate and Silver Gate single reflection ATR accessories, the Gateway 6 reflection ATR system and the 25 reflection ATR accessory.
4.2.2.2 Diffuse reflectance

In external reflectance, incident radiation is focused onto the sample and two forms of reflection can occur – diffuse and specular. Diagram of diffuse reflection shown in figure 4.3. Energy from the incident beam that penetrates one or more particles is reflected in all directions and this component of light is called diffuse reflectance. On a rough or irregular surface material, such as a powder, specularly reflected light is a minor contributor to the overall signal. Therefore Specac accessories are optimized to increase collection of the diffuse reflectance component and decrease the specular component. Collection of the diffusely scattered light can be made directly from a sample or by using an abrasive sampling pad for intractable samples. Many samples will give diffusely reflected spectra including powders, fibers or matt surfaced samples such as textiles. There are two types of Specac diffuse reflectance accessories, the Minidiff Plus and the Selector. Specifically, the Selector has an “off axis” optical design to select for diffusely reflected light. It can also be extended in its capabilities for the study of samples at elevated temperatures and pressurized conditions by using with its complementary Environmental Chamber accessory.

Figure 4.3 - Diagram of DR
4.1.2.3 Specular reflectance

Specular reflectance is a non-destructive method for surface measurements using a mirror-like reflection from the shiny (or matt) surface of a sample as shown in figure 4.5. Specular reflectance occurs when the reflected angle of infrared radiation equals the angle of incidence. The amount of light reflected depends on the angle of incidence, the refractive index, surface roughness and absorption properties of the sample. A particularly useful application for specular reflectance is the study of surface coatings, such as surface treated metals, paints and polymers. Increased path lengths through thin coatings can be achieved using grazing angles of incidence (typically 85° angle) and this gives increased sensitivity. Thicker coatings in the micrometer thickness range can be studied using angles typically at 30° incidence. The band intensities depend on the type and degree of polarization of light. The Specac range of specular reflectance accessories includes both fixed angle and variable incidence angle accessories. The monolayer/grazing angle accessory can be used for range of incident angles from 8 to 85° and with both liquid and solid samples.
4.2 OPTICAL ABSORPTION

4.2.1 Beer–Lambert law

![Diagram of Beer–Lambert absorption](image)

Figure 4.5 - Diagram of Beer–Lambert absorption of a beam of light as it travels through a cuvette of width $\ell$.

The law states that there is a logarithmic dependence between the transmission (or transmissivity), $T$, of light through a substance and the product of the absorption coefficient of the substance, $\alpha$, and the distance the light travels through the material (i.e. the path length), $\ell$. The absorption coefficient can, in turn, be written as a product of either a molar absorptivity of the absorber, $\varepsilon$, and the concentration $c$ of absorbing species in the material, or an absorption cross section, $\sigma$, and the (number) density $N$ of absorbers.

For liquids, these relations are usually written as

$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon c \ell}$$

(4.1)

whereas for gases, and in particular among physicists and for spectroscopy and spectrophotometry, they are normally written

$$T = \frac{I}{I_0} = e^{-\alpha' \ell} = e^{-\sigma \ell N}$$

(4.2)

where $I_0$ and $I$ are the intensity (or power) of the incident light and the transmitted light, respectively; $\sigma$ is cross section of light absorption by a single particle and $N$ is the density (number per unit volume) of absorbing particles.
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The difference between the use of base 10 and base $e$ is purely conventional, requiring a multiplicative constant to convert between them.

The transmission (or transmissivity) is expressed in terms of an absorbance which for liquids is defined as

$$ A = - \log_{10} \left( \frac{I}{I_0} \right) \quad (4.3) $$

whereas for gases, it is usually defined as

$$ A' = - \ln \left( \frac{I}{I_0} \right) \quad (4.4) $$

This implies that the absorbance becomes linear with the concentration (or number density of absorbers) according to

$$ A = \varepsilon \ell c = \alpha \ell \quad (4.5) $$

and

$$ A' = \sigma \ell N = \alpha' \ell \quad (4.6) $$

for the two cases, respectively.

Thus, if the path length and the molar absorptivity (or the absorption cross section) are known and the absorbance is measured, the concentration of the substance (or the number density of absorbers) can be deduced.

Although several of the expressions above often are used as Beer–Lambert law, the name should strictly speaking only be associated with the latter two. The reason is that historically, the Lambert law states that absorption is proportional to the light path length, whereas the Beer law states that absorption is proportional to the concentration of absorbing species in the material.\[1\]

If the concentration is expressed as a mole fraction i.e. a dimensionless fraction, the molar absorptivity ($\varepsilon$) takes the same dimension as the absorption coefficient, i.e. reciprocal length (e.g. m$^{-1}$). However, if the concentration is expressed in moles per unit volume, the molar absorptivity ($\varepsilon$) is used in L·mol$^{-1}$·cm$^{-1}$, or sometimes in converted SI units of m$^2$·mol$^{-1}$.

The absorption coefficient $\alpha'$ is one of many ways to describe the absorption of electromagnetic waves. For the others, and their interrelationships, see the article: Mathematical descriptions of opacity. For
example, $\alpha'$ can be expressed in terms of the imaginary part of the refractive index, $\kappa$, and the wavelength of the light (in free space), $\lambda_0$, according to

$$\alpha' = \frac{4\pi \kappa}{\lambda_0}. \quad (4.7)$$

In molecular absorption spectrometry, the absorption cross section $\sigma$ is expressed in terms of a line strength, $S$, and an (area-normalized) line shape function, $\Phi$. The frequency scale in molecular spectroscopy is often in cm$^{-1}$, wherefore the line shape function is expressed in units of 1/cm$^{-1}$, which can look funny but is strictly correct. Since $N$ is given as a number density in units of 1/cm$^3$, the line strength is often given in units of cm$^2$cm$^{-1}$/molecule. A typical line strength in one of the vibrational overtone bands of smaller molecules, e.g. around 1.5 μm in CO or CO$_2$, is around 10$^{-23}$ cm$^2$cm$^{-1}$, although it can be larger for species with strong transitions, e.g. C$_2$H$_2$. The line strengths of various transitions can be found in large databases, e.g. HITRAN. The line shape function often takes a value around a few 1/cm$^{-1}$, up to around 10/cm$^{-1}$ under low pressure conditions, when the transition is Doppler broadened, and below this under atmospheric pressure conditions, when the transition is collision broadened. It has also become commonplace to express the line strength in units of cm$^{-2}$/atm since then the concentration is given in terms of a pressure in units of atm. A typical line strength is then often in the order of 10$^{-3}$ cm$^{-2}$/atm. Under these conditions

The fact that there are two commensurate definitions of absorbance (in base 10 or e) implies that the absorbance and the absorption coefficient for the cases with gases, $A'$ and $\alpha'$, are ln 10 (approximately 2.3) times as large as the corresponding values for liquids, i.e. $A$ and $\alpha$, respectively. Therefore, care must be taken when interpreting data that the correct form of the law is used. The law tends to break down at very high concentrations, especially if the material is highly scattering. If the light is especially intense, nonlinear optical processes can also cause variances.
4.2.2 Fundamental absorption

The fundamental absorption refers to band or to exciting transitions, i.e. to the excitation of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transition are subject to certain selection rules, the estimation of the energy gap from the “absorption edge” is not a straightforward process—even if competing processes can be accounted for\[13\].

Because the momentum of a photon, \( h/\lambda \) (\( \lambda \) is the wavelength of light thousands of angstroms), is very small compared to the crystal momentum \( h/a \) (‘a’ is the lattice constant, a few angstroms), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient \( \alpha(h\nu) \) for a given photon energy \( h\nu \) is proportional to the probability \( P_{if} \) for the transition from the initial state to the final state and to the density of electrons in the initial state \( n_i \) and also to the density of available (empty) final state \( n_f \), and this process must be summed for all possible transitions between states separated by an energy difference equal to \( h\nu \).

\[
\alpha(h\nu) = A \sum P_{if} n_i n_f
\]

In what follows, for simplicity we shall assume that all the lower states are filled and that all the upper states are empty, a conduction which is true for undoped semiconductors at 0 °K.

Let us consider transition between two direct valleys where all the momentum–conserving transition are allowed (Fig. 4.5) i.e. the transition probability \( P_{if} \) is independent of photon energy. Every initial state at \( E_i \) is associated with a final state at \( E_f \) such that

\[
E_f = h\nu - |E_i|
\]

but in parabolic bonds,
\[ E_f - E_g = \frac{\hbar^2 k^2}{2m^*_e} \]  
\[ E_i = \frac{\hbar^2 k^2}{2m^*_h} \]

and

Hence the absorption coefficient is

\[ \alpha(h\nu) = A^*(h\nu - E_g)^\frac{1}{2} \]

where \( A^* \) is given by [27]

\[ A^* \approx \frac{q^2}{nch^2 m^*_e} \left( 2 \frac{m^*_h m^*_e}{m^*_h + m^*_e} \right)^{\frac{3}{2}} \]

\[ \alpha(h\nu) = 2 \times 10^4 (h\nu - E_g)^\frac{1}{2} \text{ cm}^{-1} \]

\( h\nu \) and \( E_g \) being expressed in eV.

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**Figure 4.6 - Shows direct transition**

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4.3 EXPERIMENTAL

4.3.1 Sample preparation

Gaseous samples require a sample cell with a long path length (typically 5–10 cm), to compensate for the diluteness.

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 or calcium fluoride are also used). 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 analyzed 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 analyzing failed plastic products for example because the integrity of the solid is preserved. FTIR spectrometer shown in figure 4.7 at SICART, V.V.Nagar.

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.
4.3.2 Infrared spectrum study

4.3.2.1 F.T.I.R Spectrometer

**Figure 4.7 - FTIR spectrometer**

**Make Model:** Perkin Elmer Spectrum GX  
**Brief Description:** FT-IR Spectrometer Perkin Elmer Spectrum  
**GX Range:** 30 - 15600 cm\(^{-1}\)  
   - ATR accessory for reflectance measurement; IR Quant software; Spectrum search software.

**Specifications:**
- Sample: Solid, Liquid or Gas
- Operating Mode: NIR and MIR
- Scan Range: 15600 to 30 cm\(^{-1}\)
- Optical system: Source NIR: 15,200 – 1,200 cm\(^{-1}\)
- Beam splitter KBr: 7,800 - 370 cm\(^{-1}\)
- Detector MIRTGS: 10,000 - 220 cm\(^{-1}\)
- Optimum Range: 7,800 - 1,200 cm\(^{-1}\)
- OPD Velocity: 0.20 cm/s
- Interferogram Direction: Bi-Direction

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4.3.2.2 Result and discussion

Infrared spectra of crystals exhibit bands corresponding to Schiff base and metal ions. Bands were observed in far IR region. It is known that in IR spectra of crystals, there are strong coupling and hence, quantitative interpretation of the bands is not possible without the normal coordination analysis. The important infrared absorption bands and spectra of crystals are shown in Table 4.1 and Figures 4.8 to 4.10. The spectra of crystals are obtained in the range of 4000-400 cm\(^{-1}\) using compound in the form of KBr pellets.

The functional groups present in the crystals were identified with their characteristic vibrational frequencies, nature and magnitude of intensity of the absorption bands.

The functional groups present in the schiff base (Not Shown) were identified with their characteristic vibrational frequencies, nature and magnitude of intensity of the absorption bands. Normally N—H stretching bands occur in the region 3400-3100 cm\(^{-1}\). Such strong bands occur in 3411 cm\(^{-1}\) for Schiff base.

The aromatic stretching C—H, -C=C- leads bands in 2810 cm\(^{-1}\), 2920-3060 cm\(^{-1}\). Such bands are observed in spectrum of Schiff base (Not Shown). The phenolic –OH stretching band appear in the range of in 3100 cm\(^{-1}\). A strong intense band appears at 3360 cm\(^{-1}\) which can be attributed to –C=NH. The band similar in behavior to –NH\(_2\) stretching of Schiff base studied complexes is observed in all crystals; but it has shifted to ~3382 cm\(^{-1}\) for Ni(II) crystal, ~3411 cm\(^{-1}\) for Fe(III) crystal and ~3388 for Cu(II) crystal respectively. This shift again accounts for coordination of –NH group of Schiff base with metal ions. Two bands which are strong and are of medium intensity in range

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of 6511-640 and 685-750 cm\(^{-1}\) in studied crystals. These can be M-N and M-N=C stretching respectively. A sharp and strong band obtained ~746 cm\(^{-1}\) in crystals can be attributed to M-NH stretching.

Sharp and medium intensity bands are observed at ~1676 cm\(^{-1}\) in IR spectra of all crystals which represent M-OH\(_2\) stretching.
### Table 4.1 - Infrared Spectral data of the Crystals (cm⁻¹)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\nu$-N-CH₃ (Schiff base)</th>
<th>$\nu$-C=C (Schiff base)</th>
<th>$\nu$-C=NH (Schiff base)</th>
<th>$\nu$-C-H (Schiff base)</th>
<th>$\nu$-CH₂ (Schiff base)</th>
<th>$\nu$-C-N (Schiff base)</th>
<th>$\nu$-M-OH₂ (Metal)</th>
<th>$\nu$-M-N (Metal)</th>
<th>$\nu$-M-N=C (Metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe·L₂·2H₂O]·Cl₃</td>
<td>1529 (m)</td>
<td>-</td>
<td>3411 (b)</td>
<td>-</td>
<td>1323 (m)</td>
<td>1197 (m)</td>
<td>1635 (b)</td>
<td>538 (m)</td>
<td>685 (m)</td>
</tr>
<tr>
<td>[Ni·L₂]·4H₂O Cl₂</td>
<td>1519 (s)</td>
<td>-</td>
<td>3382 (b)</td>
<td>-</td>
<td>1374 (b)</td>
<td>1217 (s)</td>
<td>1607 (s)</td>
<td>633 (m)</td>
<td>746 (m)</td>
</tr>
<tr>
<td>[Cu·L₂]·2H₂O·Cl₂</td>
<td>1519 (s)</td>
<td>3040 (m)</td>
<td>3338 (b)</td>
<td>2941 (m)</td>
<td>1372 (b)</td>
<td>1215 (m)</td>
<td>1676 (s)</td>
<td>511 (b)</td>
<td>746 (s)</td>
</tr>
</tbody>
</table>

L = Schiff Base, (s) = strong, (m) = medium, (b) = broad
Figure 4.8 - IR spectra of [Ni·L₂]·4H₂O Cl₂ crystal
Figure 4.9 - IR spectra of [FeL₂₂H₂O]·Cl₃ Crystal
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Figure 4.10 - Spectra of [Ni·L₂] · 4H₂O Cl₂ Crystal
4.3.3 Reflectance spectra study

The majority of transition metal crystals are colored that is they possess the property of absorbing certain wavelengths in the visible region of the spectrum. Almost invariably, this is accompanied by absorption in the adjacent near infrared and near ultraviolet regions also, so that the expression visible absorption spectrum is usually interpreted somewhat loosely to include these closely neighboring regions.

The considerable attention which has centered on the chemistry of transition metal crystals in recent years can be traced largely to the development of successful theories for interpreting those properties which are peculiarly associated with compounds of metals having an incompletely filled d-sub shell. Such theories needed in the first place, to account particularly for the color and magnetism of crystals. Visible absorption spectra are now known for a vast number of crystals and at the present time the measurement of the visible spectrum is considered to be an essential part of the characterization of any new crystal.

Spectra arise because electrons may be promoted from one energy level to another. Usually ‘d-d’ spectra show broadening of electronic absorption bands of order 1000-3000 cm\(^{-1}\). This diffuseness of spectra is due to close energies of rotational and vibrational transitions which can not be resolved into the separate absorption bands. The electronic spectra of large molecules show spectral congestion- i.e. too many transitions crowded into a small wave number\(^{[21]}\). During crystal formation mixing of ‘d’ and ‘p’ orbitals takes place, so transitions are no longer pure ‘d-d’ transitions in nature. The charge transfer transition originates from redox character of metal ion and the ligand. The charge transfer transitions are of two types\(^{[22]}\).

(i) Metal to ligand charge transfer [MLCT]
(ii) Ligand to metal charge transfer [LMCT]

It is possible to make some general correlations between the nature of an electronic transition and the magnitude of the absorption intensity. These are usually expressed in the form of selection rules which, broadly speaking,
predict whether a transition will be allowed or forbidden and therefore whether the absorption band will be intense or rather weak.

**Spin selection rule:** For a transition to be allowed the number of unpaired electrons in the initial state must be identical with the number in the final state. For a single electron undergoing a transition the spin of the electron must be identical in the initial and final orbitals.

**Laporte selection rule:** A transition is forbidden if it simply involves a redistribution of electrons within the same type of orbital in a single quantum shell. This way of expressing the selection rule is particularly relevant to the spectra of transition metal crystals. Many of the transitions are d-d type, involving only the d-orbitals in a given quantum shell are strictly Laporte forbidden.

**Calculation of Racah Parameter from Electronic Spectra:**
The graphical information contained in the orgel diagrams is more accurately represented by the series of equations that relates the energies of these various states to the Dq values of the ligand. The various equations used for calculation of energies are based on the assumption that the ligands are point charges or point dipoles and that there is no covalence in metal ligand bond. The value of Dq is just substituted in equations \[^{23}\] the energy of metal ion obtained from the atomic spectrum of gaseous ion and the energy of the other levels in the crystal can be calculated. The experimental energies obtained from spectra are lower than the values calculated. Covalency is foreign to crystal field approach and is incorporated into the ligand field by providing an additional parameter ‘B’ called ‘Racah Parameter’. Racach parameter indicated the magnitude of electronic repulsion between various levels in a gaseous ion. The quantity B is constant that enables one to express the energy difference between the levels of high spin multiplicity in terms of some integer, n times B are different for different ions. The same term adjusted for crystal will be nB’. In case of Ni\(^{+2}\) ion, the lowering of 3p is a measure of covalency, among other effects. It is referred as ‘nephelauxetic effect’ and is expressed as a parameter \(\beta^o\), a
percentage lowering of the energy of the 3p state of the crystal compared to 3p in free gaseous ion\textsuperscript{[24]} It is calculated by equation

\[ \beta^o = \left( \frac{(B-B')}{B} \right) \times 100 \]

Where, B is racah parameter for free gaseous ion.

B' is racah parameter for crystal ion.

Most often quantity \( \beta \) is used instead of \( \beta^o \) which is defined as

\[ \beta = \frac{B'}{B} \]

Jorgensen has reported a remarkable set of parameter that enable one to permit 10Dq and \( \beta \) values for various transition metal complexes\textsuperscript{[20]}

There exist a number of different possible origins for the electronic absorption spectra of crystals. These are

I. Spectra associated principally with the ligand
II. Spectra involving electronic transition between the metal and the ligand; charge-transfer spectra
III. Spectra associated principally with the metal, influenced by the presence of the lignds; \( d-d \) spectra
IV. Spectra associated with the counter-ion.

In the present studies UV-visible reflectance spectra of crystals of Ni(II), Fe(III) and Cu(II) are measured on a Beckman Model DK-A UV-VIS-NIR spectrometer. Reflectance spectra and important \( d-d \) transitions are presented in the Figure: 4.13 to 4.15 and Table: 4.2 respectively. Racah parameter, \( \beta^o \), Dq etc. are calculated according to various equations\textsuperscript{[25]} and presented in Table: 4.3.
4.3.3.1 UV-VIS-NIR spectrophotometer

![Image of UV-VIS-NIR spectrophotometer]

**Figure 4.11 - UV-VIS-NIR Spectrophotometer**

**Small Description:**
UV-VIS-NIR Spectrometer Perkin Elmer Lambda 19 Range: 185-3200 nm: Diffuse reflectance attachment; Standards for wavelength and absorption calibration validation traceable to NIST All types of measurements/studies in the region including Absorbance, Transmission and Reflectance spectra; Quantitative analysis.

**Specifications:**
- Double Beam, Double Monochromator, Ratio Recording
- Lamp: Deuterium (UV), Tungsten-Halogen (VIS/NIR)
- Detectors: Photomultiplier tube for UV/Vis Lead-Sulphide cell (PbS) for NIR
- Wavelength Range: 185-3200 nm for Absorbance/Transmission and 200-2500 for Reflectance
- Scan Speed: 0.3 to 1200 nm/min
- Wavelength Accuracy: ± 0.15 nm for UV/VIS & ± 0.6 nm for NIR
- Base line flatness: ± 0.001 A°, 4 nm slit
- Ordinate Mode: Scan, Time Drive, Wavelength Programming, Concentration
- Photometric Accuracy: ± 0.003 A° or ± 0.08 %T

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Beckman Model DK-A spectrophotometer provides a means for analyzing liquids, gases and solids through the use of radiant energy in the far and near ultraviolet, visible and near infrared regions of the electromagnetic spectrum. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the wavelength range between 160 and 3500 millimicrons.

Model DK-A (Fig. 5.3) instrument utilizes a single beam of energy, which is chopped into alternate reference and sample beams to provide a double beam system within the sample compartment. Both sample and reference beams have common detection and amplification components.

Qualitative and quantitative Reflectance data are obtained with the Model DK-A spectrophotometer by directing radiation into a sample and determining what portion of the radiant energy is reflected. Two radiation sources are necessary, since there is no single source that will provide energy over the entire wavelength range of the Model DK-A instrument. Radiation is provided in the wavelength range below 375 millimicron by a hydrogen lamp, the tungsten lamp is used in the 320-3500 millimicrons wavelength range.

From the source, radiation enters the optical system. Fig. 4.12 shows the path followed by a single ray within the radiation beam. The beam is reflected from the condensing mirror (A) to the slit entrance mirror (B), which directs the beam to the chopper (C). The chopped beam passes through the adjustable entrance slit (D) and into the monochromator. The beam is reflected from the collimating mirror (E) in parallel rays through a reflecting quartz prism (F), which disperses the beam into its spectrum of successive wavelengths.
Figure 4.12 - Optical diagram of spectrophotometer

The back surface of the prism is aluminized so that the beam is reflected back through the prism and further dispersed as it emerges. Rotation of the prism relative to collimating mirror changes the angle of incidence and enables selection of a particular group of wave lengths that comprise a spectral band. This band of radiation is directed back to the collimating mirror, which focuses the entrance slit image on the exit slit (G). Upon passing from the monochromator, the radiant energy is directed by lens (H) into the double beam optical system in the sample compartment.

The model DK-A instrument is double beam ratio recording spectrophotometer, i.e. radiant energies transmitted by the reference and sample beams (J and M) are compared, and the ratio of the sample energy to the reference energy is recorded as a percent transmission. The double beam optical system consists of two synchronized semi-circular rotating mirrors (I and N), and two stationary mirrors (L and K) in the sample compartment. The rotating mirrors consequently deflect and pass the radiant energy so that it is directed alternatively into sample and reference cells fifteen (or 12.5) times per second. Energy transmitted by the sample and reference cells is focused by the detector selector mirror (O) onto to the detector.
Detection of transmitted radiant energy requires two detectors to cover the entire wavelength range of the instrument. One - the lead sulphide cell (P) - responds in the region between 400 to 3500 millimicron. For measurements in the wavelength range extending below 700 nm, a photomultiplier tube (Q) is used. Radiant energy that strikes the detector is converted to a proportional alternating current signal.

For obtaining the reflectance spectra using UV-VIS-NIR spectrophotometer from single crystal specimens, thin flakes of approximately 0.20 µm thickness are used. These flakes are pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used is a replica of the black paper, having the cut in exactly the same position as the crystal flake. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. For reflectance measurement standard aluminum coated mirror is used as reference.

4.3.3.2 Ni(II) crystal:

Magnetic moment values 2.83 B.M. suggest tetrahedral geometry in high spin complexes. According Tanabe –Sugano diagram six coordinated Ni(II) crystals belong to 3d⁸ system and there are three spin allowed transition mainly

\[ ^3T_1 \rightarrow ^3T_2 \quad E = 8 \text{ Dq} \]
\[ ^3T_1 \rightarrow ^3A_2 \quad E = 18 \text{ Dq} \]
\[ ^3T_1 \rightarrow ^3T_1(\text{P}) \quad E = 6 \text{ (Dq)} + 15 \text{ B} \]

The crystal of Ni(II) has shown electronic transitions at 5154 cm⁻¹ (ν₁), 11494 cm⁻¹ (ν₂) and 13333 cm⁻¹ (ν₃) respectively.

The value 5154 cm⁻¹ at which the first transitions occur is too high for a tetrahedral crystal. So the transition at 13333 cm⁻¹ is taken as ν₂ and hence Dq is 5154 cm⁻¹. The calculated value for B is 633 cm⁻¹ and β⁰ is 61 %.

4.3.3.3 Fe(III) Crystal:

The ground term is the orbital singlet 6s in high spin complexes. It cannot be split by a field of any symmetry. Since the high spin d⁵ ions is its own ‘hole equivalent’ the same energy level diagram may be used for all cubic
The absence of any other spin sextet terms requires that all transitions in high spin d$^5$ complexes are spin forbidden, as well as Laports forbidden, thus they will generally be very weak.

In an octahedral field, the $(t_{2g})^4 (e_g)$ and $(t_{2g})^2 (e_g)^3$ each give rise to $^4T_{1g}$ and $^4T_{2g}$ states. The $(t_{2g})^3 (e_g)^2$ configuration gives rise to the spin quartets $^4A_{1g}$, $^4A_{2g}$, $^4T_{1g}$, $^4T_{2g}$ and $^4E_g$. It follow that the $^4A_{1g}$, $^4A_{2g}$ and $^4E_g$ states have energies independent of any crystal field and will appear as horizontal lines in the Tanabe-Sugano diagram. In the weak field limit $^4A_{1g}$ and one $^4E_g$ originate from $^4G$, $^4A_{2g}$ from $^4F$ and the remaining $^4E_g$ from $^4D$. Hence the transitions to these levels in the spectra of d$^5$ complexes provide direct evaluation of the energies of the $^4G$, $^4F$ and $^4D$ terms. The $^4T_{1g}$ and $^4T_{2g}$ levels will be scrambled between the three configurations and will have energies dependent upon the ligand field.

Because of the greater oxidizing power of Fe(III) d$^5$ ligand to metal charge transfer bands often obscure the very low intensity d-d absorption. The Dq value for Fe(III) will be higher than for analogous Mn(II) systems. The relative band positions will depend upon whether they have a positive or negative dependence upon Dq. That the forbidden transitions $^4T_1$, $^4T_2$,...$^6A_1$ have a strong negative dependence upon Dq and therefore tetrahedral FeL$_4$ species will exhibit these transition at greater energies than octahedral FeL$_6$ species, the reverse of the usual situation, e.g. the $^4T_1$,...$^6A_1$ transition for Fe(III)O$_6$ and Fe(III)O$_4$ chromophores lie near 11,000 and 22,000cm$^{-1}$ respectively.

The d-d absorption in six coordinate FeS$_6$ species is rarely observed since the strong Fe-S CT absorption will obscure such weak bands. However weak infrared absorption reported for Fe[(Ph$_2$P(S))$_3$ at 9000 and 12,000cm$^{-1}$ is presumably crystal field in origin.

L$\rightarrow$M charge transfer is very common and in Fe(III) crystal and a sharp high absorption transition appears at 37,037cm$^{-1}$ indicating L$\rightarrow$M charge transfer. Fe(III) crystal are assigned following transitions.
The electronic spectrum of Fe(III) crystal exhibits electronic transitions at 4237 cm\(^{-1}\) (\(\nu_1\)), 5208 cm\(^{-1}\) (\(\nu_2\)) and 11494 cm\(^{-1}\) (\(\nu_3\)). The transition at 5208 cm\(^{-1}\) is considered as \(\nu_2\) and 11494 cm\(^{-1}\) as \(\nu_3\). The calculations give \(B = 650\) cm\(^{-1}\), \(\beta = 0.64\) and \(\beta_0 = 64\%\).

**4.3.3.4 Cu(II) crystal:**

A survey of Cu(II) d\(^9\) electronic spectroscopy presents difficulty because of the lack of definitive statements which can be made to relate spectra with structure. Moreover because of the general ease with which Cu(II) crystals can be made, there is an extraordinary amount of spectroscopic information available in the literature.

By far the bulk of this consists of crystals with a single broad poorly resolved absorption band in the visible region. Finally for reasons commented on above Cu(II) crystal frequently exist in highly distorted stereo chemistries. However in parallel with Ni(II), Cu(II) system with square planer stereochemistry will have no electronic absorption below 10000 cm\(^{-1}\). Similarly tetrahedral or close to tetrahedral Cu(II) will absorb primarily in the red and near infrared\[^{[26]}\].

Here, following type of transition are given to Cu(II) crystal

\[
\begin{align*}
^4A_1 & \rightarrow \ ^4E \\
^6A_1 & \rightarrow \ ^4T_1 \\
^6A_1 & \rightarrow \ ^4T_2
\end{align*}
\]

Magnetic moment value of Cu(II) crystal 1.73 B.M suggested for tetrahedral geometry. The dark green colored Cu(II) crystal exhibit bands between 11764 cm\(^{-1}\) - 26315 cm\(^{-1}\) broad band.
Table 4.2 - Electronic Spectra and Magnetic Moment Data for the Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Absorption region (cm⁻¹)</th>
<th>Band assignment</th>
<th>Magnetic moment µ_eff (B.M.)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe·L₂·2H₂O]·Cl₃</td>
<td>4237 cm⁻¹ 5208 cm⁻¹ 11494 cm⁻¹</td>
<td>⁴A₁ → ⁴E ⁶A₁ → ⁴T₁ ⁶A₁ → ⁴T₂</td>
<td>1.73</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Ni·L₂]·4H₂O·Cl₂</td>
<td>5154 cm⁻¹ 11494 cm⁻¹ 13333 cm⁻¹</td>
<td>³T₁ → ³T₂ ³T₁ → ³A₂ ³T₁ → ³T₁</td>
<td>2.83</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>[Cu·L₂]·2H₂O·Cl₂</td>
<td>11764 cm⁻¹ 26315 cm⁻¹ Broad band</td>
<td>T₁----⁴T₂ ³T₂----⁴T₂</td>
<td>1.73</td>
<td>Tetrahedral</td>
</tr>
</tbody>
</table>
### Table 4.3 - Parameters of the Electronic Spectra of Metal Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>d-d transition (cm(^{-1}))</th>
<th>Dq (cm(^{-1}))</th>
<th>B (cm(^{-1}))</th>
<th>(\beta = B/B^o)</th>
<th>(\beta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(\cdot)L₂(\cdot)2H₂O(\cdot)Cl(_3)]</td>
<td>5208</td>
<td>11494</td>
<td>4237</td>
<td>650</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>[Ni(\cdot)L₂(\cdot)4H₂O(\cdot)Cl(_2)]</td>
<td>11494</td>
<td>13333</td>
<td>5154</td>
<td>633</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>[Cu(\cdot)L₂(\cdot)2H₂O(\cdot)Cl(_2)]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

~ 110 ~
Figure 4.13 - Reflectance spectra of [Cu·L₂] .2H₂O·Cl₂ Crystal
Figure 4.14 - Reflectance spectra of [Fe·L₂·2H₂O] · Cl₃ Crystal
Figure 4.15 - Reflectance spectra of [Ni\(\cdot\)L\(_2\)].4H\(_2\)O Cl\(_2\) Crystal
REFERENCE


