CHAPTER - I

INTRODUCTION

1.1. PROCESSES INVOLVED IN INTERACTION OF X-RAYS WITH MATTER

X-ray spectroscopy is an indispensable tool for the study of solid state and molecular structure. The interaction of X-rays with matter involves the following processes:

\[
\text{X-rays} + \text{Matter} \rightarrow \text{Absorption, Transmission, Scattering}
\]

- Mass Absorption
- Photo-electric absorption followed by fluorescence re-emission
- Rayleigh scattering
- Compton scattering
- Raman Scattering

Out of these processes, the photoelectric absorption is most widely used in the study of various chemical and solid state effects. Studies made by fluorescence emission are comparatively few because of the technique involves high intensity X-ray sources. Since the present work consists mainly of the X-rays absorption studies of copper and cobalt complexes, we shall discuss the absorption processes in some detail.
1.1(a) Absorption of X-rays by a free atom

Rare gases are monoatomic in nature and they do not show vibrational and rotational spectra in any range of the spectrum. Process of X-rays absorption by such atoms can be considered as follows:

Fig. 1.1 shows the different X-ray levels together with the continuum at the top. A K-electron if excited by the incident radiation cannot find a place in the L or M shells as they are fully occupied. Apart from the continuum, it can also be accommodated in one of the vacant optical levels (shown in dotted) which may be allowed by the dipole selection rules: \( \Delta l = \pm 1, \ \Delta j = \pm 1 \). Such transitions can occur to different optical levels with varying transition probabilities. Since these optical levels are very close to each other (\( \sim 0.5 \text{ eV} \)) they cannot be resolved in the X-ray region (\( \sim \text{KeV} \)) of the spectrum. The result is that there is a group of absorption lines placed very near to each other as shown schematically in Fig. 1.2. The superposition of such lines results in an absorption curve (in dotted) with fluctuations on the high energy side. The position of first rise in the absorption coefficient (or the first fall in intensity of transmitted X-rays) is called as the position of the absorption edge. The fluctuations on the higher energy side are called the extended structure of the absorption edge.
Fig. 1.1: Energy levels of an atom.
Fig. 1.2: The absorption edge and its extended fine structure.

Fig. 1.3: An illustration of valence band and conduction band and its corresponding absorption edge and $K\beta_{2.5}$ emission line for (a) metal (b) semiconductor (c) insulator.
1.1(b) **Atom in a Molecule**

When an atom is a part of a molecule the outer-most levels become hybridized molecular levels. The optical levels of Fig. 1.1 are now replaced by the electronic optical levels of the molecule. Thus the extended structures observed for such an atom (e.g. Ge in GeCl₄) are characteristic of the molecular structure. These considerations apply to both gases as well as liquid molecular states.

1.1(c) **Atom in a Solid**

(i) **Metals**: From the point of view of the band theory of solids, the crystals are classified as: Metals, Semiconductors and Insulators. Energy level wise these are shown in Fig. 1.3.

In a metal the valence and conduction bands overlap, in a semiconductor there is a gap of \( \sim 1 \text{ eV} \) or less while in an insulator the gap between the conduction and valence bands is large typically \( > 2 \text{ eV} \).

Now an X-ray K-absorption edge transition in a metal corresponds to the transition of the K electron to the bottom of the conduction band, where the conduction band has a vacancy. A \( K_\beta_{2,5} \) emission will correspond to the transition of valence band electrons to the K vacancy. The overlap between the K edge and \( K_\beta_{2,5} \) line will thus give us directly an overlap between the conduction band and valence band.
Semiconductor: In a semiconductor the absorption edge and Kβ₂,₅ emission line are separated narrowly; their distance in energy is a direct measure of the gap between conduction band and valence band. Analogous interpretations for insulators can be given. The above considerations holds true for polycrystalline samples. In single crystals the energy gaps and the overlaps vary with direction. Directional dependence of the absorption edge structure is known in case of single crystals.

Insulators: The insulating class of crystals is classified in the following sub-groups:

a) Ionic crystals
b) Molecular crystals
c) Polymers (semi-crystalline and semi-Amorphous)
d) Complex compounds.

In ionic crystals the extended structure of the absorption edge is decided by the crystal field splitting of the outer levels of the metal ions. In molecular crystals and polymers the situation is very complex and hardly any X-ray spectroscopic work has been ever done. In complex compounds the crystal field splitting of the metal ion levels and the molecular levels of the ligand combine to form the molecular orbitals which are supposed to decide the structures observed on the slope of the absorption edge.

Factors deciding the molecular orbitals of a complex compound are:
1) Valency of the central ion
2) Type and distribution of the ligand
3) Symmetry of the complex ion.

We take the simplest case of $[MA_6]$ type complex compounds which have octahedral symmetry. The qualitative molecular energy level diagram is shown in Fig. 1.4.

Fig. 1.4(a) (for $\sigma$ bonding) and Fig. 1.4(b) (for $\sigma$ and $\pi$ bonding) are the molecular energy level diagrams for the ligand system having mainly the $\sigma$-type bonding and $\pi$-type bonding with the metal ion respectively. We can judge from the qualitative energy level diagram that the atomic orbitals change considerably while combining with the ligand orbitals.

If we change one of the ligands A by a ligand B, so that it forms a $[MA_5B]$ type compound then the molecular symmetry changes from $O_h$ to $C_{4v}$. If one goes on changing A by B successively upto $[MB_6]$, the molecular symmetry undergoes the following series of changes in the symmetry (Table 1.1).

Table - 1.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Symmetry</th>
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<tbody>
<tr>
<td>$MA_6$</td>
<td>$O_h$</td>
</tr>
<tr>
<td>$MA_5B$</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$MA_4B_2$</td>
<td>$C_{2v}$ or $D_{4h}$ (cis or trans)</td>
</tr>
<tr>
<td>$MA_3B_3$</td>
<td>$C_{3v}$ or $C_{2v}$</td>
</tr>
<tr>
<td>$MA_2B_4$</td>
<td>$C_{2v}$ or $D_{4h}$</td>
</tr>
<tr>
<td>$MA_B_5$</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$MB_6$</td>
<td>$O_h$</td>
</tr>
</tbody>
</table>
Fig. 1.4(a): Molecular orbital energy level diagram for \( \sigma \)-type of bonding.
**Fig. 1.4(b):** Molecular orbital energy level diagram for σ- and π-type of bonding.
The lowering of symmetry implies that the irreducible representation of the super group $O_h$ decomposes into irreducible representation of the sub-group. Spectroscopically it implies the splitting of atomic orbitals due to lowering of the symmetry. However, these splittings cannot be observed experimentally in every case. In most of the cases these are very small (of the order of $\sim 1/10$ eV to $1/100$ eV) so that in a crude approximation one can always use the $O_h$ symmetry. Minor deviations from the $O_h$ symmetry can be looked upon as small perturbations, so far as energy levels are concerned. However, the wave functions will change appreciably because they are obtained by an addition of the binding orbital of the ligands (This additivity is valid only approximately because of over simplified assumptions). This is the reason why some times it is advisable not to go through the complete quantitative calculations of the energy levels, since although a minor change in wave-function causes a lot of intricacies, their resultant change in energy levels is very small and some times beyond the reach of experimental resolution. For this reason mostly a qualitative interpretation is preferred.

A transition of the K electron to the outer orbital would correspond to the K absorption edge provided this transition is allowed by the selection rules. Not much can be said about such selection rules. One thing is certain: The atomic selection rules will not hold true, and no rigorously derived rules exist. For this reason the application of this method is rather
limited and one can only speculate about the possible transitions. The next higher transition would possibly correspond to any secondary structure on the slope of the absorption edge. Another difficulty that exists in interpreting the X-ray absorption spectra by the method of molecular orbital theory is that it is necessary to consider the effect of inner electron vacancy (K-hole) on the molecular orbital levels. Calculations of this kind do not exist. Thus the application of the above theory to the X-ray absorption spectra is presently only qualitative and speculative; yet it is an important first step towards future advancements.

For reasons mentioned above we used qualitative methods of interpretation of the X-ray absorption edge. In the absorption spectra of complexes the following features are studied and interpreted:

a) The position of the absorption edge.

b) Structures if any, occurring on the slope of the absorption edge.

c) The principal absorption maximum (1st dip in the intensity curve, see fig. 3.26).

d) The width of the absorption edge.

e) The extended structures on the high frequency side of the absorption edge.

Shift in the absorption edge position is interpreted in terms of the effective charge on the absorbing ion. The structures if any on the slope of the edge are attributed
qualitatively to the electron distribution in the molecular orbitals corresponding to the 3d and 4s atomic orbitals. The first absorption maximum corresponds to the 1s → 4p or its corresponding molecular orbital transition. The width of the edge is discussed in terms of the covalent character in the bonding. The extended structures found in complexes generally depend on the nearest neighbours and the symmetry of the molecule.

1.2. OBJECT AND SCOPE OF THE PRESENT STUDY

X-ray spectra of an atom or an ion in a molecule depends on the electronic structure of the molecule, its symmetry and its constituents. Any change in the electronic structure should be elucidated by X-ray spectra.

Chemical bonding, which is due to the inherent urge of an atom to change its state to a more stable configuration, should cause a redistribution of electrons in the electronic shells as the atom or ion goes in different environments. X-ray spectra of the ion in the compound should correspondingly respond to this chemical change. In X-ray K-absorption spectra some of the trends are well known now, but a number of trends are still to be chalked out. It is therefore an interesting problem to correctly relate the observed change in the X-ray spectra to the molecular or crystallographic structure of the absorbing ion and the nature of the constituent atoms. In the present study, an attempt has been made to systematize the
study of the bonding effects in X-ray spectra.

In transition elements, the penultimate orbit expands from 8 to 18 electrons, the outermost shell remaining the same. A noble element has a stable configuration of 2,8 or 18 electrons. In contrast, the core of transition elements is not stable, and therefore, more susceptible to environmental change. For example, for the first transition series one or more electrons may be drawn out from the inner 3d shell to the outermost shell for valence purpose. It is because of this fact that the energy required for losing an electron and the energy acquired by the formation of bonds are comparable. Thus it shows a wide variety of oxidation states, magnetic moment and symmetry. Hence transition elements offer a wider scope for the study of bonding effects on X-ray K-absorption edge.

We have studied the K-absorption edges of cobalt complex compounds formed by:

a) thiourea
b) phenyl thiourea
c) pyridine
d) 2,2' bipyridine
e) 1,10 phenanthroline
f) 2H - 1,2,4 - Trizole - 3 - thiol, etc.

We have also studied a few complex compounds of copper formed by:

a) pyridine
b) 2,2' bipyridine
c) 1,10 phenanthroline

Apart from these oxypentafluorides of niobium have also been studied. A study of bromine K-absorption edge in some bromine based cobalt complexes has also been included.

It is usually observed that because of the small stability difference between octahedral and tetrahedral complexes of cobalt, both stereochemistries can be taken by them with a particular ligand and sometimes the complexes with different stereochemistries exist even in equilibrium\(^2\)). This behaviour is exemplified with some of the ligands like pyridine. The effect of the molecular symmetry (keeping the ligands the same) can be studied precisely in such cases and we have studied some such complexes in the present work.

In some cases, keeping the coordinating element of the ligand the same, we have changed the nature of ligand by changing the group of atoms attached to the coordinating element. For example, in thiourea the coordinating element is sulphur. In diphenyl thiourea again the coordinating element is sulphur but this time the phenyl group affects the activity of sulphur.

\[
\begin{align*}
\text{NH}_2 & \quad \text{CS} \\
\text{NH}_2 & \quad \text{CS}
\end{align*}
\]

Structure of thiourea and diphenyl thiourea

Thiourea is one of the most versatile complexing agents. It forms well known inclusion complexes with branch
chained hydrocarbons\(^3\) and also has the ability to complex with various other organic substances\(^4\) and with salts of virtually every metal. The latter property is largely a result of the formation of covalent sulphur - to - metal bond\(^5\).

However, thiourea has also been reported to form stable complexes with salts of elements which do not form covalent bonds to coordinate ligands\(^6,7\). If metal ions have \(d\)-electrons, these will have a strong tendency to form a bond of an order higher than one by back donation of \(d\)-electrons from metal to sulphur.

Similarly, pyridine, 2,2' bipyridyl and 1,10 phenanthroline form a systematic series of ligands. Pyridine is planar\(^8\) in structure and acts as a monodentate with a coordinating atom nitrogen. Similarly 1,10 phenanthroline is planar due to the resonance bond character of the constituent rings. The two rings forming 2,2' bipyridyl on the other hand, are connected only by a single bond so the two rings may be rotated about the bond axis. The asymmetry in the compound will be more in 2,2' bipyridyl than in 1,10 phenanthroline\(^9\). Also 1,10 phenanthroline is a stronger \(\pi\)-acceptor than 2,2' bipyridyl. So the back donation of charge from metal into ligand will take place more in 1,10 phenanthroline\(^10\). Both rigid bidentate ligand confer considerable immunity to John – Teller distortion\(^11\).

These facts have been taken into consideration in interpreting X-ray \(K\)-absorption data of complexes for elucidating the nature of these ligands and also the electronic configuration of the absorbing ion.
REFERENCES