CHAPTER-1
INTRODUCTION

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1.1. GENERAL:

Advances in techniques such as infrared and Raman spectroscopy during the last decade have greatly increased the interest in optical properties of solids. The information one obtains from these studies are related to rotational and vibrational motion of molecules or molecular ions. The language which is used to describe this interaction and energy level sequence that the interaction reveals is that of group theory and quantum mechanics. The adjective 'molecular' is used in a broad sense to cover all crystalline solids in which there are discernible molecular units, whether these be neutral as in solid $\text{O}_2$, $\text{CO}_2$, $\text{C}_6\text{H}_6$ or charged as in $\text{NH}_4\text{Cl}$, $\text{K}_2\text{SO}_4$, $\text{K}_2\text{CrO}_4$ etc.

The optical spectra of molecules or molecular ions in solids normally are observed in the range from few thousand to about a hundred thousand wave numbers. The electronic absorption technique is employed to understand the energy levels and their ligand field behavior. Infrared technique is used to understand the site symmetry of complex anion in crystals. The Raman spectra can supplement the infrared data. The basic understanding of the optical properties have been
revolutionised by the present day sophisticated IR/Raman spectrometers. These instruments use
(1) holographic gratings and therefore have resolution down to
0.001 cm$^{-1}$,
(2) the high power Laser used as a excitation source in Laser
Raman spectrometers have improved the S/N ratio, also
(3) the use of single-photon counting technique in detection
of scattered radiation, reveal lines of very weak
intensity,
and hence have become indispensable tools for the
structural analysis of molecule.

The low temperature (10 K) can reduce the unwanted
background noise and hence improve the widths of IR/Raman
lines. The present day analysis is obviously more informative
as regards to the structural details of the molecule. The
improved computational techniques have given a new dimension
to the understanding of the molecular vibrations.

The optical properties of solids have been studied either
as a host lattice or as an impurity in a lattice. The
molecule ion when present as an impurity can yield information
about the symmetry of the substituent site. This molecular
impurity can be considered as a defect in solids. The charge on the molecular ion can induce additional defects such as vacancies. A brief review of defects present or deliberately added are discussed.

1.2.1 POINT DEFECTS IN SOLIDS:

A majority of the properties observed in ionic crystals such as, alkali halides are to a large extent influenced by the inevitable presence of point defects, which may be treated as deviation from the perfect periodic lattice [1-5]. Various types of imperfections that are present in a crystal can be broadly classified as, static and transient defects and are listed in Table 1.1. The most important of such static defects are Frenkel and Schottky defects. An ion can be removed from a regular lattice site, causing a vacancy in lattice. The ion thus displaced may find a place in an interstitial position and in such a case, the combined effect consisting of the vacancy and the interstitial ion has come to be known as a Frenkel defect. Alternately, the ion which is removed from the lattice site may be placed on the surface of the crystal to form a new layer. Such vacancies occur equal in number in an anion and cation sublattices to maintain
# Table 1.1

<table>
<thead>
<tr>
<th>POINT DEFECTS</th>
<th>LINE DEFECTS</th>
<th>PLANAR DEFECTS</th>
<th>VOLUME DEFECTS</th>
<th>TRANSIENT DEFECTS</th>
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<tr>
<td>4. Impurities</td>
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<td>4. Mesons</td>
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<td>5. Color centers</td>
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<td>5. Neutrons</td>
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<td>7. Vacancy-Vacancy pairs</td>
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<td>8. Impurity-Vacancy dipoles</td>
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charge neutrality of the crystal and are termed Schottky defects. The concentration of Frenkel and Schottky defects can be calculated on the basis of statistical mechanics.

1.2.2 MOLECULAR DEFECTS IN CRYSTALS:

Impurity ions may already be present in the crystal as background material or may be deliberately added to the starting material from which the crystals are grown. It has been found that the molecular ion impurities can also be added to the starting material and can be used as probes [6]. The molecular ion can be an "isovalent substituent" or "allovalent substituent". Substitution of an impurity of the same charge as the host, causes local changes like displacement of neighbouring ions, while, substitution of an impurity ion of a charge different from that of the host ion will create vacancies in order to maintain stoichiometry of the crystal. These vacancies can occur in the lattice at points close to the impurity ion perturbing it, thus altering the symmetry of the substituent molecular ion. The optical properties of molecular ions in crystal are determined by using standard techniques such as IR, Raman spectroscopy and Optical absorption in the UV-Vis range.
The study of properties of complex molecular impurities in different crystalline lattices is interesting from several points of view. By using isostructral isovalent molecular impurity as a probe the symmetry of the host lattice has been identified using ESR, IR and Raman studies of the molecular impurity. The effect of reduction in symmetry due to the vacancy accompanying the molecular ion, in case, when the molecular impurity ion has different valency than that of substituent host site, can also be studied.

The various molecular impurities that have been studied so far can mainly be classified into two categories: (i) non transition metal molecular ions and (ii) transition metal molecular ions. In the former class are included homonuclear diatomic ions like $S_2^-$, $Se_2^-$, $O_2^-$ and $N_2^-$; triatomic molecular ions like $S_3^-$, $NO_2^-$, $O_3^-$, $SO_2^-$, $NH_2^-\text{ and } H_2O^-$; paraelectric impurities such as $CN^-$ and $OH^-\text{; planar molecular ions like } NO_3^-, CH_3, CO_3^{2-}\text{ and } BO_3^{3-}, \text{ in latter case several transition metal ions like } V^{4+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{2+}\text{ and } Cr^{3+}\text{ have been studied } [7,8], \text{ besides the complex molecular ions like } VO_2^+, CrO_4^{2-}, MnO_4^-\text{ etc.}, [9-11]. \text{ The ionising radiation such as } X\text{-rays and } \gamma\text{-rays when impinged on the crystal knock out electrons changing the valence state of the ion. The}
radicals thus produced are rather rare and otherwise unstable ordinarily not lending themselves for any kind of investigation, have also been studied. These include $\text{SO}_3^-$, $\text{SeO}_3^-$, $\text{CrO}_4^{3-}$, $\text{MnO}_4^{2-}$ etc.,.

1.3.1. TRANSITION METAL OXYANIONS:

The characteristic strong absorption in visible and in near ultraviolet region of electromagnetic spectrum exhibited by first transition series metals has fascinated solid state spectroscopists and inorganic chemists for the last three decades. The transition metal oxyanions have general formula $\text{XO}_n^-$ where, $\text{X} = \text{V}, \text{Cr}, \text{Mg}, \text{Mn}$ etc., and $n = 1, 2, 3$, etc., (typical examples being $\text{CrO}_4^{2-}$ and $\text{MnO}_4^-$). Table 1.2 shows the transition metal oxyanions listed according to their periodic classification and electronic structures. Ions denoted as $d^0$ are termed as 'closed shell ions' since these ions do not have unpaired electrons $\text{CrO}_4^{2-}$ and $\text{MnO}_4^-$ belong to this configuration ($d^0$). Ions termed as $d^1$, $d^2$ have one and two outer electrons respectively. The close shell ions represent the highest valence state of the metal under consideration and their formation is in general the result of vigorous oxidation state of aqueous solution of lower valence.
Table 1.2 Known tetrahedral oxyanions (for ions listed in parentheses there is uncertainty in identification).

<table>
<thead>
<tr>
<th>$d^0$</th>
<th>$d^1$</th>
<th>$d^2$</th>
<th>$d^3$</th>
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</thead>
<tbody>
<tr>
<td>$\text{VO}_4^{3-}$</td>
<td>$\text{CrO}_4^{2-}$</td>
<td>$\text{MnO}_4^-$</td>
<td>$\text{FeO}_4^2-$</td>
</tr>
<tr>
<td>$\text{CrO}_4^{3-}$</td>
<td>$\text{MnO}_4^{3-}$</td>
<td>$\text{FeO}_4^2-$</td>
<td>$\text{FeO}_4^{3-}$</td>
</tr>
<tr>
<td>$\text{NbO}_4^3^-$</td>
<td>$\text{MoO}_4^{2-}$</td>
<td>$\text{TcO}_4^-$</td>
<td>$\text{RuO}_4^-$</td>
</tr>
<tr>
<td>$\text{MoO}_4^{2-}$</td>
<td>$\text{TcO}_4^-$</td>
<td>$\text{RuO}_4^-$</td>
<td>$\text{RuO}_4^{2-}$</td>
</tr>
<tr>
<td>$\text{TaO}_4^{3-}$</td>
<td>$\text{WO}_4^{2-}$</td>
<td>$\text{ReO}_4^-$</td>
<td>$\text{OsO}_4^-$</td>
</tr>
<tr>
<td>$\text{WO}_4^{2-}$</td>
<td>$\text{ReO}_4^-$</td>
<td>$\text{OsO}_4^-$</td>
<td>$\text{ReO}_4^{3-}$</td>
</tr>
<tr>
<td>$\text{W}^{3-}$</td>
<td>$\text{ReO}_4^-$</td>
<td>$\text{ReO}_4^{2-}$</td>
<td>$\text{ReO}_4^{3-}$</td>
</tr>
</tbody>
</table>
states. Sometimes oxyanions having outer electrons are intermediate in such reactions and their salts can be isolated under appropriate conditions. In particular ions like \( \text{CrO}_4^{3-} \), \( \text{MnO}_4^{2-} \) are found to be extremely unstable under ordinary conditions at room temperature [12].

The absorption spectra of crystals with these impurities have been explained in terms of crystal field theory or molecular orbital theory depending on whether the given metal is in ionic or molecular state.

For a clear understanding of the site occupation of these transition metal ions (such as \( \text{Sc}^{2+} \), \( \text{Ti}^{2+} \), \( \text{Cr}^{2+} \), \( \text{Mn}^{2+} \), \( \text{Cu}^{2+} \) etc.,) in various lattices, the electronic spectra have been analysed in terms of crystal field theory and have been confirmed using EPR spectra. The approach is straightforward. If the d\(^1\)-orbital is in octahedral field, then the effect of crystal field on the single electron (\( ^2D \)) state is strong enough to lift the five fold degeneracy of the ion into doubly degenerate \( e_g \) and triply degenerate \( t_{2g} \) representation obtained upon application of group theory. The amount of splitting (10Dq) is an indication of the strength of the crystal field. For lower symmetries, we need other
splitting parameters such as $D_s$ and $D_t$. 

We cannot extend this argument further by treating $\text{CrO}_4^{2-}$ as if it were a $\text{Cr}^{6+}$ ion in a perturbing ligand field of oxygens but must consider it from a general molecular orbital point of view. The molecular orbitals designated as $\sigma$ and $\pi$ orbitals are essentially the linear combination of atomic orbitals.

Let $\Psi_A$ and $\Psi_B$ be the normalized atomic orbitals (real functions) of two atoms $A$ and $B$. Then

$$\Psi_{AB} = C_1 \Psi_A + C_2 \Psi_B$$

is called an LCAO wave function.

The definite integral $\int \Psi_A \Psi_B \, d\tau$ is called the overlap integral 'S' between the two wave functions $\Psi_A$ and $\Psi_B$. By solving the quadratic equation for energy we get two solutions. If the two atoms are homonuclear and if we write the definite integrals

$$H_{AA,BB} = \int \Psi_{A,B} \Psi_{A,B} \, d\tau$$
assuming, $S$ to be $< 1$ we get two energies one larger than $H_{AA}$ (or $H_{BB}$) and the other smaller than $H_{AA}$ (or $H_{BB}$). The lower energy level is called the bonding orbital and the higher energy level is called anti-bonding orbital (Fig. 1.1a).

In order to form a bond the orbitals must have same symmetry relative to the molecular axis. The overlap of various types of atomic orbitals giving rise to different kinds of M.O. are given in Fig.1.1b. One can distinguish various types of molecular orbitals by means of the symmetry of the overlap [13-15]. If the overlap is symmetric for rotation the resulting molecular orbitals are called 'o' (sigma) orbitals. If the overlap gives a nodal plane along the connecting line the resulting molecular orbitals are called 'n' (pi) orbitals. If the overlap has two nodal planes which intersect along the connection line, the molecular orbitals are termed as '6' (delta) orbitals. Since $\pi$ orbital do not point towards center atoms they usually give rise to the weaker bonding than the 'o' orbitals. In many cases, as a first approximation it is possible to neglect $\pi$ bonds and consider the 'o' bonds in the schemes. For complete solution
Fig. 1.1a. The molecular orbital (M.O.) energy diagram for homonuclear molecule.
<table>
<thead>
<tr>
<th></th>
<th>Bonding overlap</th>
<th>Antibonding overlap</th>
</tr>
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<tbody>
<tr>
<td>(a)</td>
<td>( s.s ) ((\sigma))</td>
<td><img src="image" alt="Bonding overlap" /></td>
</tr>
<tr>
<td>(b)</td>
<td>( s.p ) 'end-on' ((\sigma))</td>
<td><img src="image" alt="Bonding overlap" /></td>
</tr>
<tr>
<td>(c)</td>
<td>( s.p ) 'sideways' non-bonding</td>
<td><img src="image" alt="Bonding overlap" /></td>
</tr>
<tr>
<td>(d)</td>
<td>( p.p ) 'end-on' ((\sigma))</td>
<td><img src="image" alt="Bonding overlap" /></td>
</tr>
<tr>
<td>(e)</td>
<td>( p.p ) 'sideways' ((\pi))</td>
<td><img src="image" alt="Bonding overlap" /></td>
</tr>
<tr>
<td>(f)</td>
<td>( p.d ) 'sideways' ((\pi))</td>
<td><img src="image" alt="Bonding overlap" /></td>
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Fig. 1.1b. Overlap of various types of atomic orbitals giving rise to different kinds of molecular orbitals.
If however, π-bonds can be treated as a small perturbation.

1.3.2 MOLECULAR ORBITAL THEORIES:

The isoelectronic \( \text{CrO}_4^{2-} \) and \( \text{MnO}_4^- \) have metal ions in \( 3d^0 \) configuration. These molecular ions have tetrahedral symmetry in their free state. A tetrahedral molecule does not posses a center of symmetry and consequently there is no parity restriction on the electronic transitions. This does not however, mean that the observed absorption bands could be assigned to \( d \rightarrow d \) transitions, because the matrix elements for the electric dipole transition between pure \( d \) orbitals still vanish. Nonvanishing matrix elements are only obtained if there is mixing of the metal \( d \)-orbitals with the \( p \)-orbitals of oxygens. Various M.O. schemes have been proposed to account for this mixing of states and hence explain the observed spectrum. The various M.O. theories depend on various parameters VIZ., (i) values of certain initial parameters such as orbital energies, radial wave functions, (ii) choice of proportionality factor relating the overlap integrals to the energies and (iii) on the number of orbitals and overlaps included in the calculations.
To interpret the observed absorption spectra of transition metal oxyanions the first M.O. scheme was proposed by Wolfsberg and Helmhotz (W and H) [17]. In this method it has been assumed that the nonvalence shell electrons of X and O are unaffected by the bonding and that the X and O nuclei plus these inner shell electrons form an effective core into the field of which the molecular electrons are to be replaced. Thus, only 3d, 4s and 4p atomic orbitals of central atoms and only the 2p atomic orbitals of oxygen atoms have been considered in constructing the M.O.'s. In the present case (CrO$_4^{2-}$) there are 24 valence electrons to be placed in the molecular orbitals in the increasing order of energy. The molecular orbitals for a given molecule reflect its geometric structure and can be classified according to their behavior under the group of rotations and reflections which leave the molecular framework unchanged. For a tetrahedral molecular ion XO$_4$ ($T_d$ group) it can be shown from group theoretical methods that the molecular orbitals belong to one or the another of five distinct types, forming basis for the five irreducible representations of $T_d$. Table 1.3 shows the symmetry behavior of the orbitals and the various combinations which transform under the representations $A_1$, $A_2$, $E$, $T_1$ and $T_2$ of the tetrahedral group. Fig.1.2. shows the orientation of
<table>
<thead>
<tr>
<th>M-Orbitals</th>
<th>O Orbitals</th>
<th>Irreducible Representations</th>
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<tbody>
<tr>
<td>( s ) ((1/2) \left[ \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \right] )</td>
<td>( s ) ((1/4) \left[ \Pi_{x_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4} - \gamma^2 (\Pi_{y_1} + \Pi_{y_2} + \Pi_{y_3} + \Pi_{y_4}) \right] )</td>
<td>( A_1 )</td>
</tr>
<tr>
<td>( d_{z^2} ) ((1/4) \left[ \Pi_{x_1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} - \gamma^2 (\Pi_{y_1} + \Pi_{y_2} + \Pi_{y_3} + \Pi_{y_4}) \right] )</td>
<td>( d_{z^2} ) ((1/4) \left[ \Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4} + \gamma^2 (\Pi_{x_1} + \Pi_{x_2} + \Pi_{x_3} + \Pi_{x_4}) \right] )</td>
<td>( E )</td>
</tr>
<tr>
<td>( d_{x^2-y^2} ) ((1/4) \left[ \Pi_{x_1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} - \gamma^2 (\Pi_{y_1} + \Pi_{y_2} + \Pi_{y_3} + \Pi_{y_4}) \right] )</td>
<td>( d_{x^2-y^2} ) ((1/4) \left[ \Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4} + \gamma^2 (\Pi_{x_1} + \Pi_{x_2} + \Pi_{x_3} + \Pi_{x_4}) \right] )</td>
<td>( E )</td>
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<tr>
<td>( p_{x^1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4} ) ((1/2) \left[ \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} - \Pi_{x_3} - \Pi_{x_4} + \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( p_{x^1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4} ) ((1/2) \left[ \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} - \Pi_{x_3} - \Pi_{x_4} - \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( T_2 )</td>
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<tr>
<td>( p_{y^1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} ) ((1/2) \left[ \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} - \Pi_{x_3} - \Pi_{x_4} + \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( p_{y^1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} ) ((1/2) \left[ \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} - \Pi_{x_3} - \Pi_{x_4} - \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( T_2 )</td>
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<tr>
<td>( p_{z^1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} ) ((1/2) \left[ \sigma_1 - \sigma_2 + \sigma_3 + \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} + \Pi_{x_3} + \Pi_{x_4} + \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( p_{z^1} \Pi_{x_2} \Pi_{x_3} \Pi_{x_4} ) ((1/2) \left[ \sigma_1 - \sigma_2 + \sigma_3 + \sigma_4 \right] ) ((1/4) \left[ -\Pi_{x_1} \Pi_{x_2} + \Pi_{x_3} + \Pi_{x_4} - \gamma^2 (\Pi_{y_1} \Pi_{y_2} \Pi_{y_3} \Pi_{y_4}) \right] )</td>
<td>( T_2 )</td>
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Fig. 1.2. Orientation of the atomic orbitals used by Wolfsberg and Helmholtz. The orientation of the oxygen orbitals relative to the axes on the central atom is shown in this figure. The central metal atom orbitals are defined with respect to the axes on the central atom.
the atomic orbitals that have been used. The calculation of
the molecular orbital energies $E$ and the evaluation of
coefficients of atomic orbitals and sets of atomic orbitals
require the solution of secular determinants (one for each
irreducible representation) of the form

$$|H_{ij} - G_{ij} E| = 0$$

where, $G_{ij}$ is the group overlap integral.

$W$ and $H$ solved secular determinants by making
semiempirical estimates of the matrix elements $H_{ij}$'s. For
example, there will be two pairs of molecular orbitals
belonging to $E$ representation, one pair being of the form

$$A d_2 + (B/4)(\Pi_{x} + \Pi_{y} + \Pi_{z} + \Pi_{z})(\Pi_{x} + \Pi_{y} + \Pi_{z} + \Pi_{z})$$

the other being,

$$C d_2 + (D/4)(\Pi_{x} + \Pi_{y} + \Pi_{z} + \Pi_{z} + \Pi_{z} + \Pi_{z})(\Pi_{x} + \Pi_{y} + \Pi_{z} + \Pi_{z})$$

The values of $H_{ij}$ in general have to be known in order to
determine the energies, $H_{11}$ being the energy of an electron
in the $i^{th}$ orbital in the field of nuclear skeleton and the remaining valence electrons. The experimentally determined ionisation potentials for Cr$^0$ and O$^-$ have been used to estimate the $H_{ij}$ values. However, the values of $H_{ij}$'s ($i \neq j$) were approximated by setting them proportional to the corresponding overlap integrals according to the relation

$$H_{ij} = F_x G_{x(ij)}((H_{ii} + H_{jj})/2)$$

where, $F_x$ is constant and $G_{x(i,j)}$'s are the group overlap integrals. For example

$$G_{A1}(s,\sigma) = \int 4s(x) (1/2)(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \, dx$$

These integrals can be obtained in terms of simple $\sigma$ and $\pi$ diatomic overlaps ($s_{ij}$) by expressing the central atom orbitals in terms of a linear combination of equivalent orbitals oriented relative to the axis on the oxygen atoms [17]. For example

$$G_{A1}(s,\sigma) = 2S (s,\pi\sigma)$$

For $\sigma$ type overlap $F\sigma = 1.67$ and for $\pi$ type overlap
Fig. 1.3 shows the W and H M.O. scheme for CrO$_4^{2-}$ ions. The 24 valence electrons are to be placed in the orbitals of lowest energy. The 1t$_2$ and 2t$_2$ orbitals, each capable of holding six electrons are of bonding type while, 3t$_2$ and 4t$_2$ orbitals are of anti-bonding type. The 2e orbitals are capable of holding four electrons each, 1e being strongly bonding and 2e being anti-bonding. The t$_1$ is a non bonding orbital located on the four oxygen atoms. For the purpose of comparison between the isoelectronic MnO$_4^{-}$ and CrO$_4^{2-}$, the M.O. scheme for MnO$_4^{-}$ is also given in Fig. 1.4. On the basis of Figs. 1.3 and 1.4, the electronic configuration of CrO$_4^{2-}$ and MnO$_4^{-}$ can be written as (1e)$^4$(1t$_2$)$^6$(1a$_1$)$^2$

(2t$_2$)$^6$(t$_1$)$^6$ and (1a$_1$)$^2$(1t$_2$)$^6$(1e)$^4$(2t$_2$)$^6$(t$_1$)$^6$ respectively; $^1$A$_1$ being the ground state in both the cases. The first transition would correspond to ....(t$_1$)$^6$ $\rightarrow$ ....(t$_1$)$^5$(t$_2$)$^1$ in both the cases. This excited configuration gives rise to A$_2^1$, E, T$_1$ and T$_2$ states of which the transition to T$_2$ is the only orbitally allowed one in T$_d$ symmetry, therefore, the lowest energy absorption band responsible for yellow color of chromate has been ascribed to $^1$A$_1$$\rightarrow$$^1$T$_2$. The second excitation accordingly involves the excitation of an electron from 2t$_2$ orbital to 3t$_2$ orbital i.e., (2t$_2$)$^6$(t$_1$)$^8$$\rightarrow$(2t$_2$)$^5$(t$_1$)$^8$(3t$_2$)$^1$. The excited configuration gives rise to A$_1^1$, E, T$_1$ and T$_2$
Fig. 1.3. Molecular orbital energy level schemes for $^{2-} \text{CrO}_4$ ions according to Wolfsberg and Helmholtz.
Fig. 1.4. Molecular orbital energy level schemes for MnO$_4^{2-}$ ions according to Wolfsberg and Helmholtz.
Fig. 1.5. Molecular orbital energy level schemes for $\text{CrO}_4^{2-}$ ions according to Ballhausen and Liehr.
excited states. The observed absorption band in \( \text{CrO}_4^{2-} \) and \( \text{MnO}_4^- \) may therefore be ascribed to \( ^1\text{A}_1 \rightarrow ^1\text{T}_2 \). Although, W and H scheme received apparent initial support from the earlier experiments, their numerical results do not predict the position and intensity of absorption bands correctly. The other weak band at the longer wavelength was interpreted as the forbidden transition, which becomes partially allowed due to the lowering of symmetry (\( T_d \)) of the molecular ion. Ballhausen and Liehr (B and L) therefore, put forward an alternative M.O. scheme [18] by including in the calculation both \( \sigma \) and \( \pi \) molecular orbitals of the ligand. They questioned the puzzling inversion of bonding energy levels on going from \( \text{MnO}_4^- \) to \( \text{CrO}_4^{2-} \) ions, even though, they are isoelectronic. B and L ascribed this discrepancy to the over simplification of the secular equations of W and H. They could account for the observed spectra and intensity of the bands comparing with the calculated oscillator strength with the experimentally observed intensities. Fig.1.5 shows the M.O. scheme proposed by B and L. Comparing Fig.1.3 and Fig.1.5 one can notice that \( t \) orbital is higher than \( e \) orbital in B and L scheme as compared to W and H scheme, i.e., the lowest unoccupied level is a triply degenerate level in W and H scheme while, it is doubly degenerate in B and L.
scheme. The ordering of levels therefore, is in accordance with that predicted by crystal field theory of $d^1$ electron. Hence the two experimentally observed main bands for $\text{CrO}_4^{2-}$ and $\text{MnO}_4^{-}$ were attributed to \((t_1)^6 \rightarrow \ldots (t_1)^5(2e)^1\) and \((t_1)^6 \rightarrow \ldots (t_1)^5(3t_2)^1\), both corresponding to $^1T_2 \rightarrow 1^T_2$.

The B and L scheme could give a better account of observed electronic spectra of $\text{CrO}_4^{2-}$ and $\text{MnO}_4^{-}$ ions. However, when theory was applied to paramagnetic tetrahedral tetroxyanions $\text{MnO}_4^{2-}$, $\text{CrO}_4^{3-}$, $\text{MnO}_4^{-}$, a controversy arose, in which case additional electrons have to be placed in M.O. levels. According to W and H scheme the unpaired electron should go into the triply degenerate $t_2$ orbital while according to B and L scheme it should exist in a doubly degenerate 'e' orbital.

The controversy was resolved when Carrington et al. [19] and Schonland [20] showed from EPR experiments, that the unpaired electrons in $\text{MnO}_4^{2-}$ and $\text{MnO}_4^{-}$ go into a doubly degenerate 'e' orbital. This established that the first unoccupied orbital in $\text{MnO}_4^{-}$ and $\text{CrO}_4^{2-}$ is an 'e' orbital in agreement with B and L scheme.

Although, both B and L and W and H scheme could satisfactorily explain the two main absorption bands of $\text{CrO}_4^{2-}$ and $\text{MnO}_4^{-}$, the experimental data of $\text{MnO}_4^{-}$ in $\text{KClO}_3$ which show
more number of bands which can not be interpreted in terms of these schemes. Viste and Gray (V and G) [21] gave an improved M.O. scheme for tetrahedral tetroxy anions. They stressed the importance of including the core 2s atomic orbitals of oxygen ligands in the calculation of energy of M.O. levels, since they have a good overlap with metal d and p→t$_2$ orbitals. They performed W and H type calculations employing better radial functions for Mn and O and better methods of evaluating H$_{ij}$ and H$_{jj}$ integrals than the ones used in the original calculations [22]. They have shown that $\sigma_3$ overlaps larger than $\sigma_p$ with metal orbitals. When they initially calculated the orbital energies considering only the 2p orbitals they arrived at the W and H scheme i.e., e > t$_2$ ordering. When 2s orbitals were also included they arrived at the t$_2$ > e ordering which explained the EPR results of MnO$_4^-$ ion [19,20].

The M.O. levels of V and G have been shown schematically in Fig.1.6. Including the 2s valence electrons, CrO$_4^{2-}$ and MnO$_4^{-}$ complexes have 32 valence electrons which are to be placed in the orbital of lowest energy. Hence, the levels are filled through t$_1$. According to this scheme the ground state of CrO$_4^{2-}$ and MnO$_4^{-}$ is a nondegenerate singlet given by $^1A_1$ and that of CrO$_4^{-}$ and MnO$_4^{3-}$ is a doubly degenerate level
Fig. 1.6. Molecular orbital energy level scheme of viste and Gray for \( \text{CrO}_4^{2-} \) molecular ion.
represented by $^2E$. The transitions corresponding to the two main bands are given by $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$. The V and G scheme could account well for all the observed features of the tetrahedral oxyanions and received a support from the measurements of Faraday parameters for $\text{CrO}_4^{2-}$ and $\text{MnO}_4^{-}$ and $\text{CrO}_4^{3-}$ ions [23]. V and G's M.O. scheme has been used to interpret the absorption spectra of $\text{CrO}_4^{2-}$ ions in the present case (chapter III) since three main bands have been observed.

There has been attempts to improve the V and G M.O. scheme to explain electronic structure of other isoelectronic molecular ions. Dahl and Johansen [24] have pointed out that one must develop and use a semiquantitative theory independent of empirical parameters. They have employed the same semiquantitative theory that was utilised earlier [25] but varied the atomic orbital basis set systematically. The effect of changes in bond lengths was also examined. They conclude that order and nature of excitation state vary from one tetrahedral system to the next and more theoretical and experimental results are needed in order to arrive at definite conclusions as to the exact nature of the excited states.

The calculations by Dahl and Ballhausen [26] indicate
that the metal 4s and 4p orbitals are heavily engaged in bonding in contrast to the findings of other authors [25]. Oleari et al. [27] have shown that order of the lowest unoccupied M.O. to be different for MnO$_4^-$ and CrO$_4^{2-}$, and it is also known that one can not predict the order of excited states from the order of M.O.'s alone.

As far as the electronic absorption spectra of CrO$_4^{2-}$ in different lattices is concerned, several recent reports show that V and G M.O. scheme can be satisfactorily applied [28-30]. Since, the optical properties of Cr$_2$O$_7^{2-}$ ion come from the charge transfer from ligands to the metal atoms and the effect of metal-metal-ligand is too small on the molecular orbitals, one can consider the dichromate ion to consist of two (T$_d$) chromate ions having a common oxygen for the purpose of explaining optical transitions [31]. Hence, the molecular orbital schemes proposed for CrO$_4^{2-}$ ion can be used for the interpretation of the observed spectra in the case of Cr$_2$O$_7^{2-}$ also.

In the present investigation therefore, V and G M.O. scheme has been used to interpret the observed electronic bands of chromate and dichromate molecular ions.
1.4. NORMAL MODES OF VIBRATION:

During vibration of a molecule the atoms undergo different displacements, with respect to their mean position and also with respect to the center of mass of molecule. In order to carry out the quantum mechanical treatment for molecular vibrations, it becomes necessary to introduce a new set of coordinates, called the normal coordinates, denoted by $Q$'s, which gain importance in a polyatomic molecule, owing to the independent oscillations carried out by each nucleus. To simplify the situation in such a case the concept of normal coordinates were introduced, wherein the system of coupled equations for potential energy and kinetic energy are reduced to the new set of equations which are linear in $Q$'s. In order to analyse such vibrations the usual approach is to represent any of these extremely complicated vibrations in terms of superpositions of a number of normal vibrations [32-48]. In the case of diatomic molecule the situation is relatively simpler as the two nuclei vibrate along the line joining the two nuclei.

It is a well known fact that there is one to one correspondence between the normal coordinate and the normal
mode of vibration. The vibration of a molecule is represented in terms of displacements of \( N \) atoms of a molecule from equilibrium positions in terms of \( 3N \) cartesian coordinates \( q_1, q_2, \ldots, q_{3N} \). The equations of motion of the system under consideration is given by

\[
\sum_j \left( a_{jk} q_j + b_{jk} q_j \right) = 0
\]

(1.1)

where, \( b_{jk} = \left( \frac{\partial^2 V}{\partial q_j \partial q_j} \right) \), and the \( a_{jk} \) are functions of the atomic masses, which appear in potential and kinetic energy expressions [32,33,35,40] the general solution of which is

\[
q_{jk} = A_{jk} \sin \left( \lambda_k^{1/2} t + \xi_k \right).
\]

(1.2)

where, \( \lambda_k = 4\pi^2 \nu^2 \), and \( A_{jk} \) and \( \xi_k \) are the amplitude and phase respectively of the wave motion.

It is evident from the equation (1.2), that each atom is oscillating about its equilibrium position with a simple harmonic motion of amplitude \( A_{ik} = K_k \lambda_k^{1/2} \), frequency \( \lambda_k^{1/2}/2\pi \), and phase \( \xi_k \). Corresponding to a given solution \( \lambda_k \) of the
secular equation, [32,33,35] the frequency and phase of the motion of each coordinate is the same, i.e., each atom reaches its position of maximum displacement at the same time and each atom passes through its equilibrium position at the same time. A mode of vibration having all these characteristics is called a normal mode of vibration, and its frequency is known as normal, or fundamental frequency of the molecule.

Then from equation (1.1) and (1.2),

\[ \sum_{j} (b_{jk} - a_{jk} \lambda) A_{j} = 0 \]  \hspace{1cm} (1.3)

Apart from the trivial solution $A_{j} = 0$, the solutions are given by the condition

\[ \det | b_{jk} - a_{jk} \lambda | = 0 \]  \hspace{1cm} (1.4)

This determinant is the secular determinant, and will give the eigen values of $\lambda$. The evaluation of determinant is complicated by the fact that, the cross product terms appear in the expressions of kinetic and potential energy. Thus, we look for canonical transformation in which $q_{j}$'s are
transformed to a new set of coordinates \( Q_j \)'s the potential
and kinetic energies expressed in terms of which are free from
any cross product terms, thereby considerable reduction in
mathematical complications in dealing with the vibrations.
The corresponding equation of motion in terms of \( Q_j \)'s is given
by

\[ Q_1 = B_1 \sin \left( \lambda_1^{1/2}t + \varepsilon' \right) \]  \hspace{1cm} (1.5)

The solution of the determinant can be further simplified
by the proper choice of the initial coordinates. One of the
approaches is to choose the initial coordinates so as to make
the symmetries correspond to the irreducible representation of
molecule with such a choice, the determinant may be factored
in to different blocks, each of which corresponds to an
irreducible representation of the vibration.

Frequency of the vibration is given by

\[ \nu_1 = \left( \gamma_{_2}^2 \right) / 2\pi \]  \hspace{1cm} (1.6)

The method becomes further more complicated as a molecule
becomes larger. For the vibrational analysis of complex
molecules, the G-F matrix method is employed.

Although apparently there are an infinite number of normal vibrations in a molecule their types differ in their relative directions with respect to the center of mass. Thus the normal vibrations become finite in number because of the symmetry considerations. If a molecule has a number of symmetry elements, the normal vibrations are classified as various species according to the number and the kind of symmetry elements preserved during the vibrations. Thus the number of normal vibrations observable in the IR and Raman spectrum of a molecule is subjected to the selection rules. From a quantum mechanical point of view a vibration is active in IR spectrum if the dipole moment ($\mu_j$) of the molecule is changed during vibration and is active in Raman spectrum if the polarisability ($\alpha_j$) changes during vibration. These selection rules change when a molecule resides in a crystal, because in principle it is subjected only to the symmetry restriction arising out of its crystalline environment. Therefore the vibrational spectra of crystals are treated separately [35].
According to quantum mechanics the selection rules for the IR spectrum are given in terms of matrix elements of the dipole moment ($\mu$) operator between the two eigen functions. Resolving the dipole moment into three cartesian components, nonvanishing of one of these implies that the normal vibration associated with the normal coordinate is IR active, the vibration is IR inactive only in such cases where, all the integrals simultaneously vanish. On similar lines the selection rules for Raman (transition) spectrum is determined by the matrix elements of the electronic polarisability ($\alpha$) of the molecule between the two states under consideration. Again the matrix elements can be resolved into six different components of $\alpha (\alpha_{ij})$. Again the simultaneous vanishing of all the integrals makes the normal vibration Raman inactive, whenever as, nonvanishing of one of them is sufficient to make it Raman active.

The components of the dipole moment $\mu_x$, $\mu_y$, and $\mu_z$ transform as do those of translational motion $T_x$, $T_y$, and $T_z$ respectively [33,35,40]. The character of the representation of the dipole moment is given by
\[ \chi_\mu(R) = (\pm 1 + 2 \cos \theta) \] (1.7)

and character of the representation of the electric polarisability is given by

\[ \chi_a(R) = 2 \cos \theta (\pm 1 + 2 \cos \theta) \] (1.8)

By using the relation

\[ a_j = (1/\hbar) \sum_R \chi(R)\chi^j(R) \]

and character from Table 1.4, one can determine the infrared and Raman activity easily.

For XY\textsubscript{4} type molecule, T\textsubscript{d} point group, the character table and IR and Raman activity of vibrations are tabulated in Table 1.4.

The character \( \chi_\mu(R) \) can be resolved into \( A_1 + E + 2T_2 \) and it is obvious that \( (\mu_x, \mu_y \text{ and } \mu_z) \) all three belong to \( T_2 \) species while, none of \( \mu \) components belong to other species. Therefore, for a T\textsubscript{d} molecule both the T\textsubscript{2} modes are IR active, all the other modes are IR inactive.
Table 1.4.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>8C₃</th>
<th>3C₂</th>
<th>6S₄</th>
<th>8σₜ</th>
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<tbody>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
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<td>1</td>
<td>-1</td>
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<tr>
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</tr>
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<td>-1</td>
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<tr>
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<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>χ_μ(R)</td>
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<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>χ_α(R)</td>
<td>6</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

(α_xx + α_yy + α_zz)

(α_xx + α_yy - α_zz, α_xx - α_yy)

(α_xy, α_yz, α_zx), (μ_x, μ_y, μ_z)
Similarly, the character $\chi_{\alpha}(R)$ can be resolved into $A_1 + E + 2T_2$ and $\alpha$ components belong to $A_1$, $E$ and $2T_2$ species. Therefore, for a $T_d$ molecule all the modes $A_1$, $E$, and $2T_2$ are Raman active.
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