Chapter I

Introduction
The study of electronic spectra of molecules provides important information about its geometry and nature of the electronic states. The investigation of gross structure of the electronic spectrum provides the vibrational frequencies of the molecule which in turn enable the determination of force constants and anharmonicities and in many cases, accurate values for dissociation energies. The high resolution studies of electronic spectra yield information related to the equilibrium internuclear distance, type of electronic states, spin-splitting, spin-orbit coupling and other fine structure constants of the ground and excited states. These studies further enable us to understand the electron configurations of the states involved and the nature of the electronic orbitals and their bonding, anti-bonding or non-bonding characters.

Another important aspect in the study of electronic spectra of molecules is study of perturbations and predissociations. Detailed study of these phenomena enables us to elucidate the nature of perturbing states and type of interactions involved. Further, a study of predissociation leads to accurate determination of dissociation energies.

**Vibrational Spectra**

The total energy $E$ of a molecule, to a very good approximation, can be given by the sum of electronic, vibrational and rotational energies as,

$$ E = E_e + E_v + E_r $$

(1.1)

where, $E_e$ represents electronic energy, $E_v$ is vibrational energy and $E_r$ denotes rotational energy.

In terms of term values, we can write,

$$ \frac{E}{\hbar c} = \frac{E_e}{\hbar c} + \frac{E_v}{\hbar c} + \frac{E_r}{\hbar c} $$

(1.2)

or

$$ T = T_e + G + F $$

(1.3)

where, $T_e$ be electronic term value, $G$ is vibrational term value and $F$ denotes rotational term values, $\hbar$ and $c$ represent Planck’s constant and velocity of light respectively.
In a molecule the vibrational and rotational motion take place simultaneously in different electronic states. The vibrational term values are given by,

\[ G = \omega_e (v + \frac{1}{2}) - \omega_e x_c (v + \frac{1}{2})^2 + \omega_e y_c (v + \frac{1}{2})^3 + \ldots \ldots (1.4) \]

where, \( \omega_e \) is the vibrational frequency and \( \omega_e x_c \) and \( \omega_e y_c \) are the anharmonicities of first and second order respectively.

The rotational term values are given by

\[ F = B_v J (J + 1) - D_v J^2 (J + 1)^2 + \ldots \ldots \]

(1.5)

where, \( B_v = \left( \frac{\hbar}{8\pi^2 c \mu r^2} \right) \) and \( D_v \) is the centrifugal distortion constant, \( D_v = \left( \frac{4B_v^3}{\omega^5} \right) \)

The wave number of the spectral line corresponding to a transition between two electronic states, in emission or in absorption, is given by

\[ v = T' - T'' = (T_e' - T_e) + (G' - G') + (F' - F'') \]

(1.6)

where \( v = v_e + v_v + v_r \) \[ \]

Where \( v_e = T_e' - T_e \), \( v_v = G' - G'' \) and \( v_r = F' - F'' \) \[ \]

For a particular electronic transition \( v_e = (T_e' - T_e) \) is constant and therefore need not to be considered. Now, to understand the gross structure or vibrational structure one may consider \( F' = F'' = 0 \), or in other words, transition between rotationless states.

Then

\[ v = v_e + \omega_e (v' + \frac{1}{2}) - \omega_e x_c (v' + \frac{1}{2})^2 + \omega_e y_c (v' + \frac{1}{2})^3 + \ldots \ldots \]

\[ -[\omega_e (v' + \frac{1}{2}) - \omega_e x_c (v' + \frac{1}{2})^2 + \omega_e y_c (v' + \frac{1}{2})^3 + \ldots \ldots ] \]

(1.8)

This equation represents all possible transitions between the different vibrational levels of the two participating electronic states. For electronic transition there is no selection rule for the vibrational quantum number \( v \). Each vibrational level of the upper electronic state, in principle, can combine with each vibrational level of
lower electronic level, but for the restriction imposed by Franck Condon principle which says that only when overlap integral \( \int \Psi_\nu \Psi_\nu^* d\tau \) of the vibrational wave function of the two states is non zero, a transition can take place.

Since the vibrational frequencies of the two electronic states are in general different it is not difficult to characterize the positive and negative \((\Delta \nu = \pm 1)\) sequences in a band system. The positive sequences lie on the higher frequency side of \((0, 0)\) band which is usually the most intense and negative sequences lie on the lower compared to the \((0, 0)\) band.

When, in a band system the sequences are well developed, the vibrational analysis is very easy. If the first band in sequence is considered, starting from longer wave length, separations of the sequences at first gradually increases upto a certain point, at which they change suddenly and then slowly change in the separations occurs is the main sequence with \(\Delta \nu = 0\). In this way the correct arrangement of the bands in a Deslandre’s table is immediately obtained and in turn, upper and lower state vibrational quanta and anharmonicity constants can also derive.

### Rotational Spectra

The transition between rotational levels of the same vibrational level produces the rotational spectra. Such types of spectra arise because of the rotation of the molecule about an axis perpendicular to the internuclear axis and passing through the centre of mass. The bonds by which the atoms of a diatomic molecule are attached are actually not rigid. During the rotation of the diatomic molecule the length of the bond is changed hence the Hamiltonian of the Schrodinger equation is modified. According to the non-rigid rotator model the energy of diatomic molecule is expressed as:

\[
E_r = \hbar c [B_e J(J + 1) - D_e J^2 (J + 1)^2 + H_e J^3 (J + 1)^3 + L_e J^4 (J + 1)^4 + ........] \quad (1.9)
\]
Where \( h \) is Planck’s constant, \( c \) is velocity of light, \( B_e \) is rotational constant, \( J \) is rotational quantum number and \( D_e, H_e, L_e \) are centrifugal distortion constants. The rotational constant \( B_e \) is given as

\[
B_e = \frac{\hbar}{8\pi^2 c I}
\]  

(1.10)

Where \( I \) is moment of inertia of the diatomic molecule about an axis perpendicular to internuclear axis and passing through the centre of mass.

Neglecting higher terms the energy in term value can be written as

\[
\frac{E_e}{\hbar c} = F(J) = B_e J(J+1) - D_e J^2 (J+1)^2
\]

(1.11)

The wave number of the emitted or absorbed quantum is

\[
v = F'(J') - F''(J'')
\]

(1.12)

Where \( F'(J') \) and \( F''(J'') \) are term value of higher and lower states respectively.

Thus from equation (1.11) and (1.12) we have

\[
v = [B_e J'(J'+1) - D_e J'^2 (J'+1)^2] - [B_e J''(J''+1) - D_e J''^2 (J''+1)^2]
\]

(1.13)

Application of selection rule \( \Delta J = \pm 1 \) gives

\[
v = 2B_e (J''+1) - 4D_e (J''+1)^3
\]

(1.14)

This expression shows that the separation between the rotational lines decreases slightly with increasing \( J'' \). This effect is very small because \( D_e \ll (B_e \).

One can determine the value of rotational constants \((B_e \text{ and } D_e)\) by rotational analysis. The knowledge of the value of \( B_e \) and \( D_e \) is used in the determination of internuclear distance and vibrational constant.

**Rotational Fine Structure of Electronic Vibration Spectra**

In the study of coarse structure the contribution due to rotational energy was neglected and only vibrational contribution was considered. We shall now consider the possible change in rotational states for any given vibrational transition. Thus the energy expression in term of frequency can be written as

\[
v = v_e + v_v + v_r
\]
The quantity \( v = v_e + v_v \) is constant for a specific vibrational transition while \( v_v \) is variable and depends on the different values of the rotational quantum number in the upper and lower states. All the possible transitions for a constant value of \( v_0 \) taken together for a single band. We have for such a band

\[
v = v_0 + F'(J') - F''(J'')
\]  
(1.15)

Where \( F'(J') \) and \( F''(J'') \) are the rotational term values of upper and lower states respectively. \( v_0 \) is called band origin or zero line. It should be noted the \( F' \) and \( F'' \) are belonging to the different electronic states and have a different magnitudes.

Now considering the non-rigid rotator model the term value can be written as

\[
F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + \ldots
\]  
(1.16)

Then from the equation (1.15) we have

\[
v = v_0 + B_v(J' + 1) - D_v J'^2(J' + 1)^2 - [B_v J''(J'' + 1) - D_v J''^2(J'' + 1)^2]
\]  
(1.17)

Here the upper and lower states have different electronic momenta \( \Lambda \). If at least one of the two states has \( \Lambda \neq 0 \) the selection rule for \( J \) is

\[
\Delta J = J' - J'' = 0, \pm 1
\]  
(1.18)

If \( \Lambda = 0 \) in both electronic states i.e. \( ^1\Sigma-^1\Sigma \) transition with \( \Delta J = 0 \) is forbidden and only \( \Delta J = \pm 1 \) appears. Thus three or two series of lines (branches) appears respectively whose wave number are given as

- **R Branch**
  \[
v = v_0 + F'_v(J + 1) - F''_v(J) = R(J)
\]  
(1.19)

- **Q Branch**
  \[
v = v_0 + F'_v(J) - F''_v(J) = Q(J)
\]  
(1.20)

- **P branch**
  \[
v = v_0 + F'_v(J - 1) - F''_v(J) = R(J)
\]  
(1.21)

Here, \( J \) is rotational quantum number in lower states.

Putting value of \( F' \) and \( F'' \) and neglecting small correction term i.e. \( D_v \) we have equations (1.19), (1.20) & (1.21) as

\[
v = v_0 + B'_v(J + 1)(J + 2) - B'_v J(J + 1)
\]

\[
v = v_0 + B'_v(J^2 + 3J + 2) - B'_v (J^2 + J)
\]
Similarly,

\[ v = v_0 + (B'_v - B'_v)J + (B''_v - B''_v)J^2 = Q(J) \]  \hspace{1cm} (1.23)

\[ v = v_0 - (B'_v + B'_v)J + (B''_v - B''_v)J^2 = P(J) \]  \hspace{1cm} (1.24)

Here P and R branches can be written by a single formula

\[ v = v_0 + (B'_v + B'_v)m + (B''_v - B''_v)m^2 \]  \hspace{1cm} (1.25)

Where m\(=-J\) for P branch and m\(=J+1\) for R branch. Equations (1.24 and (1.25) are equation of a parabola which is also termed as Fortrat Parabola. Owing to the quadratic term in equation (1.25), one of the two branches turns back and forms a band head. This gives rise to the appearance so characteristic of most bands in visible and ultraviolet region.

A head is formed in R branch if \(B'_v - B'_v\) is negative, since the linear and quadratic terms in equation (1.25) have opposite signs, and therefore a maximum of \(v\) is reached at certain \(J\) value (vertex of parabola). Thus in this case the head lies on the short wavelength side of zero line and band is shaded (degraded) towards the red. A negative value of \(B'_v - B'_v\) implies that \(B'_v\) \((B''_v\) that is the internuclear distance of upper state is greater than the lower state. Conversely, when, \(B'_v - B'_v\) is positive then the internuclear distance of upper state is smaller than the lower and the band head lies in P branch, the band is shaded towards the violet.

The \(m\) value corresponding to vertex of Fortrat parabola can be obtained by putting \(\frac{dv}{dm} = 0\) in equation (1.25).

\[ m_{\text{vertex}} = -\frac{B'_v + B'_v}{2(B''_v - B''_v)} \]  \hspace{1cm} (1.26)

Putting this expression in equation (1.25) we obtain the separation between zero line and vertex as
\[ v_{\text{vertex}} - v_0 = -\frac{(B' + B'')^2}{4((B' - B'')^3)} \]  \hspace{1cm} (1.27)

**Evaluation of rotational constants**

The rotational constants are calculated by the analysis of fine structure using combination relation or combination differences. The rotational spectra may be of two kinds, one without Q-branch and other with Q-branch.

**Evaluation of rotational constants: without Q-Branch**

Consider the case of a band that has only single P-branch and single R-branch. Let the wave numbers of the lines are determined and their correct numbering is assigned. In such a simple band there is to every line in the P branch a corresponding line in R branch with the same upper level. The wave number difference of these two lines is equal to the separation \( \Delta_2 F_r(J) \) of the one of the lower state rotational level from the next but one; for example, the difference between the lines P(5) and R(3) (both having \( J=4 \) in upper state) is equal to the separation of the rotational level \( J=3 \) and \( J=5 \) in the lower state.

Thus

\[ R(J - 1) - P(J + 1) = F_r^\uparrow(J + 1) - F_r^\uparrow(J - 1) = \Delta_2 F_r^\uparrow(J) \]  \hspace{1cm} (1.28)

Similarly, the difference between the wave numbers of two lines with common lower state is equal to the separation of one of the upper state rotational level from the next but one

\[ R(J) - P(J) = F_r^\downarrow(J + 1) - F_r^\downarrow(J - 1) = \Delta_2 F_r^\downarrow(J) \]  \hspace{1cm} (1.29)

The first combination relation depends on the lower state and second combination relation depends on upper state. As we know that the value of \( F_r \) is given by

\[ F_r(J) = B_r J(J + 1) - D_r J^2(J + 1)^2 + \ldots \]  \hspace{1cm} (1.30)

Neglecting \( D_r \) and other higher order terms let us substitute the value of \( F_r(J) \) in equation (1.28) we obtain

\[ \Delta_2 F_r(J) = F_r(J + 1) - F_r(J - 1) \]  \hspace{1cm} (1.31)
\[ \Delta z F_v(J) = B_v (J + 1)(J + 2) - B_v (J - 1)J \]

Or
\[ \Delta z F_v(J) = 4B_v (J + \frac{1}{2}) \] (1.32)

Thus plotting a graph between \( \Delta z F_v(J) \) and \((J+1/2)\) we obtain a straight line and slope of which gives the value of \( 4B_v \). Similarly putting the value of \( F_v(J) \) (neglecting \( D_v \) and other higher order terms) in equation (1.29) we obtain the value of \( 4B_v \).

Again considering the equation (1.30) we have
\[ F_v(J) = B_v J(J + 1) - D_v J^2 (J + 1)^2 + ..... \]

Putting this value of \( F_v \) in equation (1.31) we have
\[ \Delta z F_v(J) = [B_v (J + 1)(J + 2) - D_v (J + 1)^2 (J + 2)^2] - [B_v (J - 1)J - D_v (J - 1)^2 J^2] \] (1.33)
\[ \Delta z F_v(J) = (4B_v - 6D_v)(J + \frac{1}{2}) - 8D_v (J + \frac{1}{2})^3 \] (1.34)

Since in most case \( D_v \) is of the order \( 10^{-5} B_v \). So one can neglect \( 6D_v \) in first bracket and we have
\[ \Delta z F_v(J) = 4B_v (J + \frac{1}{2}) - 8D_v (J + \frac{1}{2})^3 \]

\[ \frac{\Delta z F_v(J)}{(J + \frac{1}{2})} = 4B_v - 8D_v (J + \frac{1}{2})^2 \] (1.35)

The plot of a graph between \( \frac{\Delta z F_v(J)}{(J + \frac{1}{2})} \) and \((J + \frac{1}{2})^2\) gives a straight line having slope \( 8D_v \) and intercept \( 4B_v \). Thus adopting the above process the centrifugal distortion constant \( (D_v) \) for both the upper as well as lower state can be calculated.

**Evaluation of rotational constants: with Q-branch**

If Q-branch is present in bands under investigation, additional combination relation arises. Now three lines have same upper and lower states. The combination relations are as follows:
\[ R(J) - Q(J) = F'_v(J+1) - F'_v(J) = \Delta_1 F'_v(J) \]  
(1.36)

\[ Q(J+1) - P(J+1) = F'_v(J+1) - F'_v(J) = \Delta_1 F'_v(J) \]  
(1.37)

\[ R(J) - Q(J+1) = F'_v(J+1) - F'_v(J) = \Delta_1 F'_v(J) \]  
(1.38)

\[ Q(J) - P(J+1) = F'_v(J+1) - F'_v(J) = \Delta_1 F'_v(J) \]  
(1.39)

From these combination differences the separation \( \Delta_1 F'_v(J) \) of successive rotational levels can be obtained. If two or more bands with same upper state have been measured, the difference that is equation (1.36) and (1.37) formed for these bands must agree exactly for each \( J \) value, while the bands with same lower state the difference that is equation (1.38) and (1.39) must agree exactly. Substituting the value of \( F'_v \) (neglecting higher order terms except \( D_v \)) from equation (1.30) in equation (1.36) we have

\[ \Delta_1 F'_v(J) = F'_v(J+1) - F'_v(J) \]

\[ \Delta_1 F'_v(J) = B_v(J+1)(J+2) - B_v(J+1) - D_v(J+1)^2(J+2)^2 + D_vJ^2(J+1)^2 \]

\[ \Delta_1 F'_v(J) = 2B_v(J+1) - 4D_v(J+1)^2 \]  
(1.40)

The plot of a graph between \( \frac{\Delta_1 F'_v(J)}{(J+1)} \) and \( (J+1)^2 \) gives the value of slope \( 4D_v \) having intercept \( 2B_v \).

**Angular Momenta of the Diatomic Molecule**

In a diatomic molecule the symmetry of field in which the electrons move is reduced to axial symmetry about the internuclear axis. As a consequence only the component of the orbital angular momentum of the electrons about the internuclear axis is a constant of motion. The situation is similar to that of an atom in a strong electric field, which is here the electrostatic field of two nuclei. A precession of orbital angular momentum (L) takes place about the field direction with constant component \( M_L \left( \frac{\hbar}{2\pi} \right) \), where \( M_L \) can take values,

\[ M_L = L, L-1, L-2, \ldots, -L \]  
(1.41)
Unlike in a magnetic field, reversing the directions of motion of all electrons in an electronic field does not change the energy of the system but changes $M_L$ into $-M_L$. Therefore, for diatomic molecules, states differing only in the sign of $M_L$ have the same energy (are degenerate).

The component of the electronic orbital angular momentum along the internuclear axis may be defined as

$$\Lambda = |M_L|$$  \hspace{1cm} (1.42)

For a given value of $L$, the quantum number $\Lambda$ can take values

$$\Lambda = 0, 1, 2, 3, \ldots \ldots \ldots \ldots L$$  \hspace{1cm} (1.43)

The corresponding molecular state is designated as $\Sigma$, $\Pi$, $\Delta$, $\Phi$ …… state. Since $M_L$ can have the two values $+\Lambda$ and $-\Lambda$, the states $\Pi$, $\Delta$, $\Phi$ …… are all doubly degenerated.

Just as in atoms the multiplet structure in the molecule is due to electronic spin. The spins of the individual electron form a resultant $\vec{S}$, the corresponding quantum number $S$ being integral or half integral according as the total number of electron in the molecule is even or odd. The magnetic field in the direction of the internuclear axis resulting from the orbital motion of the electron causes a precession of $\vec{S}$ about the field direction with a constant component $M_s$ ($\frac{\hbar}{2\pi}$). In case of molecules, $M_s$ is denoted by $\Sigma$. The quantum number $\Sigma$ may take $(2S+1)$ different value i.e.

$$\Sigma = S, S-1, S-2, \ldots \ldots \ldots \ldots, -S$$  \hspace{1cm} (1.44)

The total electronic angular momentum about the internuclear axis is denoted by $\vec{\Omega}$ and is obtained by the sum of $\vec{\Lambda}$ and $\vec{\Sigma}$. Thus, for the quantum number of resultant electronic angular momentum about the internuclear axis we have,

$$\Omega = |\Lambda + \Sigma|$$  \hspace{1cm} (1.45)

**Coupling of Rotation and Electronic Motion**
In a molecule, rotation and vibration take place simultaneously with the
electronic motion. Therefore, it is necessary to consider in which way these
different motions influence one another. The influence is brought out in the
coupling of various angular momenta in the molecule, such as electron spin,
electronic orbital angular momentum, angular momentum of nuclear rotation etc.
The resultant of all the angular momentum is designated by $\vec{J}$. The different
modes of coupling of the angular momenta have been classified by Hund.

**Hund’s Case (a):** In this case it is assumed that the interaction of the nuclear
rotation with the electronic motion is very weak and the electronic motion is
coupled very strongly to the line joining the nuclei. The electronic angular
momentum $\vec{\Omega}$ is well defined and together with angular momentum $\vec{N}$ of the
nuclear rotation forms the resultant $\vec{J}$

$$\vec{\Omega} = \Lambda + \vec{\Sigma}$$  \hspace{1cm} (1.46)

and

$$\vec{J} = \vec{N} + \vec{\Omega}$$  \hspace{1cm} (1.47)

The vector $\vec{J}$ is constant in magnitude and direction. $\vec{\Omega}$ and $\vec{N}$ rotate about this
vector and at the same time, the precession of $\vec{L}$ and $\vec{S}$ takes place about the
internuclear axis.

**Hund’s Case (b):** Sometimes $\vec{S}$ may be only very weakly coupled to the
internuclear axis. This weak (or even zero) coupling of $\vec{S}$ to the internuclear axis
is the characteristic of this case. If $\Lambda \neq 0$, then $\Omega = |\Lambda|$. The angular momentum $\Lambda$
(when it is different from zero) and $\vec{N}$ form a resultant which is here designated
as $\vec{K}$. The corresponding quantum number $K$ can have integral values,

$$K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \ldots$$  \hspace{1cm} (1.48)
$\vec{K}$ is the total angular momentum apart from spin. If $\Lambda=0$ the angular momentum $\vec{K}$ is identical with $N$ and is therefore, perpendicular to the internuclear axis; the quantum number $K$ can then take all integral values from zero onward.

The angular momenta $\vec{K}$ and $\vec{S}$ form a resultant $\vec{J}$, the total angular momentum including spin. Thus the positive values of $J$ for a given $K$ are given by,

$$J = (K + S), (K + S - 1), (K + S - 2), \ldots \ldots \ldots \ldots \ldots \ldots |K - S|$$  \hspace{1cm} (1.49)

**Hund’s Case ©:** For heavy molecules the interaction between $\vec{L}$ and $\vec{S}$, in certain cases, may be stronger than the interaction with the internuclear axis. In this case both $\vec{\Lambda}$ and $\vec{\Sigma}$ are not defined. $\vec{L}$ and $\vec{S}$ first form a resultant which is then coupled to the internuclear axis with a component $\vec{\Omega}$. The electronic angular momentum $\vec{\Omega}$ and the angular momentum $\vec{N}$ of nuclear rotation then form the resultant angular momentum just as in case (a).

**$\Lambda$–type doubling:** While considering the interaction of electronic orbital angular momentum $\vec{L}$ with internuclear axis, one should also consider its interaction with rotation of the nuclei. For larger speeds of rotation this interaction is found to produce a splitting into two components for each $J$ values in these states with $\Lambda \neq 0$ which are doubly degenerate without rotation. With increasing rotation, that is with increasing $J$, in general, this splitting increase. It is called $\Lambda$–type doubling and is present for all states with $\Lambda \neq 0$.

**Perturbations:** Many times, in the otherwise regular course of various branches, some lines are found to shift from their expected normal positions. Sometimes even a splitting into two lines appears, or for multiplets bands the multiplet splitting may be abnormally great at a certain place in the band. Also another type of perturbation appears in which the intensity is abnormally small for one or more
lines in the band. Displacement and weakening in intensity may also appear simultaneously. These deviations from their normal behaviour are termed as the perturbations. When the perturbation appears for a number of successive J values; they usually have a resonance like behaviour, the deviation from the normal course increase rapidly to a maximum with increasing J and then decreases.

The perturbations in the fine structure of the band are due to perturbations in the rotational term series of the upper or of the lower state.

Selection rules for the perturbation have been enunciated by Kronig. These are:

1. Both states must have same total angular momentum J, that is $\Delta J=0$
2. For multiplicity we must have $\Delta S=0, \pm 1$
3. The $\Lambda$ values of the two states may differ only by 0 or $\pm 1$ (i.e. $\Delta \Lambda=0, \pm 1$)
4. Both states must be positive or both must be negative, i.e. $+ \leftrightarrow -$
5. For identical nuclei (e.g. $N_2$, $I_2$ etc), both states must have the same symmetry in the nuclei, that is $s \leftrightarrow a$. The third rule ($\Delta \Lambda=0, \pm 1$) holds only as long as $\Lambda$ is defined, that is in Hund's case (a) and (b). In Hund's case (c) it must be replaced by $\Delta \Omega=0, \pm 1$. In Hund's case (b) the quantum number K of the total angular momentum apart from spin is defined. It is obvious that for it, the same selection rule must hold as for J i.e. $\Delta K=0$, provided that pure case (b) applies. However, with increasing coupling of S with the internuclear axis this rule will break down.

Perturbations with $\Lambda=0$ are the perturbations between states of same type and therefore, called ‘Homogeneous perturbation’ and perturbation with $\Delta \Lambda=\pm 1$ are called ‘Heterogenous perturbation’.

**Motivation of Research Problem and Summary of the Results**

The scrutiny of the available literature reveals that there are a large number of diatomic molecules in which experimental study is expected to yield new information in terms of their structure, energy levels, vibrational constants,
rotational constants, dissociation energies, force constants etc. The study shows that there is a vast scope on the molecules like MgBr, YbBr and InBr because of their technological applications in various disciplines such as soil chemistry, agriculture, laser science, heterogeneous catalysis, lamp industry, fiber optic technology etc.

The normal state electronic configuration of Magnesium (Mg), Ytterbium (Yb), Indium (In) and Bromine (Br) atoms are given by

\[
\begin{align*}
12\text{Mg:} & \quad 1s^2, 2s^2 2p^6, 3s^2 \quad \text{----} \quad ^1S_0 \\
70\text{Yb:} & \quad 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6, 6s^2 \quad \text{----} \quad ^1S_0 \\
49\text{In:} & \quad 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^1 \quad \text{----} \quad ^2P_{1/2} \\
35\text{Br:} & \quad 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 \quad \text{----} \quad ^2P_{3/2}
\end{align*}
\]

Theoretically the combination of Mg, Yb and In with Br forms the monobromide. However experimentally there are several problems. The most of the monofluoride and monochloride of these elements have been studied using high resolution techniques but such is not the state of affair with the monobromide. The lack of accurate spectroscopic data of the monobromide of Mg, Yb and In are due to experimental difficulties in generation of transient species because of their photodissociation, hygroscopic nature and smaller value of the rotational constants.

To overcome these difficulties, the transient species have been generated using high temperature excitation technique and microwave discharge technique in presence of buffer gas and recorded with the help of Plane Grating Spectrograph (PGS-2) and Fourier Transform Spectrometer (FTS). While chapter II presents the details of experimental techniques used in the production and detection, the chapter I narrates basics of spectroscopy involved in the interpretation of molecular spectra and summary of the obtained results.

In this sequence, the low resolution spectra of MgBr and YbBr have been recorded using thermal excitation technique and 2m Plane Grating Spectrograph. The study revealed the presence of new band system and addition of new bands.
The chapter III\textsuperscript{rd} consists of finding of new band system of MgBr molecule in thermal emission while chapter IV\textsuperscript{th} gives the details of thermal excitation spectrum of YbBr molecule.

The technologically important compounds such as Indium bromide, widely used in lamp industry, fiber optic technology and in laser science as lasing material in excimer laser, have been studied using microwave technique and Fourier transform spectroscopy. The author has recorded low resolution as well as high resolution spectra of Indium monobromide using microwave excitation technique (2450 MHz, 180 watt) and BOMEM DA8 Fourier transform spectrometer. The study revealed fruitful results in terms of vibrational constant, rotational constants, $\Lambda$- doubling and isotopic species. Chapter V\textsuperscript{th} describes findings of the FT spectrum of InBr molecule.

The knowledge of thermodynamical quantities of a molecule is essential for large number of experimental methods and processes. These quantities plays vital role in the field of sciences such as combustion studies, aeroscience & technology, astrophysics, geochemistry, biotechnology, biomedical, nanotechnology and material sciences etc. Thermodynamical measurements proved to be an important tool to interpret the molecular mechanism of its formation but sometimes it is difficult to determine these quantities by thermal measurement. Therefore standard compilation of these quantities based on theoretical estimates. In the present context these quantities have been determined by using spectroscopic data and statistical quantum thermodynamics. Chapter VI gives an account of estimation of thermodynamical quantities of Mg, Yb and In monobromide using spectroscopic data and Statistical mechanics.

The summary of the molecule wise findings are given below:

(a) A New Band System of the MgBr Molecule

An electronic emission spectrum of magnesium monobromide molecule, excited in high temperature furnace, has been photographed in the
$\lambda 3600 \sim 4050$ Å region at reciprocal linear dispersion of 7.3 Å/mm. The study reveals the presence of new band system B - X in the $\lambda 3600 \sim 3800$ Å region. About 16 single headed bands, degraded to higher wavelength side, have been attributed to this system. The vibrational analysis performed suggests that the system arises from the ground state involving transition B$^2\Sigma$ - X$^2\Sigma$. The following vibrational constants have been determined for the states involved in the transition.

$$v_{00} = 26924.0 \quad \omega_c' = 357.0 \quad \omega_{e'c'} = 2.0 \text{ cm}^{-1}$$

$$\omega_c'' = 374.2, \quad \omega_{e''c''} = 1.2 \text{ cm}^{-1}$$

(b) Thermal Emission Spectrum of the YbBr Molecule

The emission spectrum of the YbBr molecule, lying in the $\lambda \lambda 4400 - 5800$ Å region and attributed to the A$^2\Pi$ - X$^2\Sigma$ and B$^2\Sigma$ - X$^2\Sigma$ transitions, has been reinvestigated using thermal excitation technique. More than 151 bands have been photographed on a reciprocal linear dispersion of 7.3 Å/mm and assigned to the vibrational schemes of the two systems: A-X & B-X. The A - X system vibrational scheme has been extended to include bands involving $\Delta v = \pm 3, +4$ sequences. The B - X system has been analyzed completely. Contrary to the earlier suggestion no perturbation has been found in the B - X system and bands up to $v' = 7$ have been analyzed nicely. More precise vibrational constants of the relevant states have been determined as follows:

For A$^1\Pi_{1/2}$-X$^2\Sigma$ system

$$v_{00} = 17803.0 \quad \omega_c = 212.5 \quad \omega_{e'c'} = 0.90 \quad \omega_c'' = 197.0 \quad \omega_{e''c''} = 0.60 \text{ cm}^{-1}$$

For A$^1\Pi_{3/2}$-X$^2\Sigma$ system

$$v_{00} = 19327.0 \quad \omega_c = 210.5 \quad \omega_{e'c'} = 0.50 \quad \omega_c'' = 197.0 \quad \omega_{e''c''} = 0.60 \text{ cm}^{-1}$$

For B$^3\Sigma$-X$^2\Sigma$ system

$$v_{00} = 19696.0 \quad \omega_c = 215.0 \quad \omega_{e'c'} = 0.60 \quad \omega_c'' = 197.0 \quad \omega_{e''c''} = 0.60 \text{ cm}^{-1}$$
© Fourier Transform High Resolution Spectrum of the InBr Molecule

The emission spectrum of InBr molecule has been recorded in the region 350-400 nm on BOMEM DA8 Fourier transform spectrometer at an apodized resolution of 0.06 cm\(^{-1}\) using microwave excitation technique. About 61 violet degraded and single headed bands have been recorded and are classified into two band systems viz. \(A^3\Pi_0-X^1\Sigma^+\) and \(B^3\Pi_1-X^1\Sigma^+\). A few new bands have been observed and are fitted in the vibrational schemes of the two systems. Revised vibrational constants have been determined. The vibrational assignments have been confirmed by observing isotope effect due to InBr\(^{81}\) in the 30 bands of the \(A^3\Pi_0-X^1\Sigma^+\) system and 19 bands of the \(B^3\Pi_1-X^1\Sigma^+\). The analysis is further supported by calculating the Franck Condon factor for InBr\(^{79}\) and InBr\(^{81}\) molecule. The following vibrational constants (in cm\(^{-1}\)) have been determined from the analysis:

\[
\begin{align*}
\text{A}^3\Pi_0-\text{X}^1\Sigma^+ & \quad \nu_{00}=26599.1 \\
& \quad \omega_c'=226.42 \quad \omega_c \chi_c'=1.24 \text{ cm}^{-1} \\
& \quad \omega_c''=221.19 \quad \omega_c \chi_c''=0.528 \text{ cm}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{B}^3\Pi_1-\text{X}^1\Sigma^+ & \quad \nu_{00}=27380.52 \\
& \quad \omega_c'=223.086 \quad \omega_c \chi_c'=1.446 \text{ cm}^{-1} \\
& \quad \omega_c''=221.19 \quad \omega_c \chi_c''=0.528 \text{ cm}^{-1}
\end{align*}
\]

The rotational structure of (0, 0), (1, 0) and (0,1) bands InBr\(^{81}\) of A-X and (0, 0) band of B-X systems has been analyzed and accurate rotational constants of the \(A^3\Pi_0\) and \(B^3\Pi_1\) states are determined. In the (0, 0) band it is possible to observe rotational lines up to \(J=300\) or so, which has necessitated invoking of \(H_0''\). The analysis is confirmed by assigning rotational lines of isotopic species, InBr\(^{79}\) in the (1, 0) band up to \(J=195\). In \(B^3\Pi_1\) state \(\Lambda\) doubling has been identified for the B-X system and coefficients \(p\) and \(q\) have been evaluated.

The following rotational constants have been determined from the analysis:
Table 5.7 Rotational Constants of $X^1\Sigma^+$, $A^3\Pi_0$ and $B^3\Pi_1$ states of InBr (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>v</th>
<th>$T_v$</th>
<th>InBr$^a$</th>
<th>InBr$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>D×10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^3\Pi_0$</td>
<td>0</td>
<td>26599.10</td>
<td>B=0.057659(62)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>26377.33</td>
<td>B=0.057173(41)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B$_e$=0.05876(95)</td>
<td>D$_e$=0.1614(42)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_e$=0.000499(68)</td>
<td>$\beta_e$=0.003727(23)</td>
</tr>
<tr>
<td>$X^1\Sigma^+$</td>
<td>0</td>
<td>26824.64</td>
<td>B=0.0550000(7)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>26824.64</td>
<td>B=0.053259(57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B$_e$=0.05587(14)</td>
<td>D$_e$=0.13405(11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_e$=0.001741(22)</td>
<td>$\beta_e$=0.002069(21)</td>
</tr>
<tr>
<td>$B^3\Pi_1$</td>
<td>0</td>
<td>27381.75</td>
<td>0.0583479(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1921804989(9)</td>
<td>0.16784(28)</td>
</tr>
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</table>

Values in the parentheses are standard deviations of the constants given in units of the last digit quoted.

(d) Thermodynamical Quantities of Magnesium, Ytterbium and Indium monohalides from Spectroscopic Data

The thermodynamical quantities; enthalpy (H), entropy (S), specific heat ($C_p$) and free energy (F) of MgX, YbX and InX molecules (where X=F, Cl, Br and I) have been estimated using spectroscopic data and partition function theory in the temperature range 100-3000 K. The partition functions have been calculated by explicit summation of rotation-vibration energy level in ground electronic state including effects of anharmonicity ($\omega_e$, $x_e$), centrifugal stretching ($D_e$) and rotational-vibrational interaction ($\alpha_e$). Since spectroscopic constants are microscopic quantities while thermodynamical quantities are macroscopic in nature. By this calculation two properties of molecular gases have been correlated. The method can be used for the estimation of thermodynamical quantities of those molecules whose chemical existence is not possible or where direct thermal measurements are not possible. The calculated values of thermodynamical quantities for selective values of temperature are collected below:
<table>
<thead>
<tr>
<th>T</th>
<th>MgF Molecule</th>
<th>MgCl Molecule</th>
<th>MgBr Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>H</td>
<td>S</td>
</tr>
<tr>
<td>100</td>
<td>17.79</td>
<td>4.58</td>
<td>181.88</td>
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<td>500</td>
<td>102.86</td>
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<td>3000</td>
<td>788.36</td>
<td>92.70</td>
<td>298.59</td>
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Table 1.2 Thermodynamical quantities of YbX (X=F, Cl, Br, I) molecules

<table>
<thead>
<tr>
<th></th>
<th>YbF Molecule</th>
<th></th>
<th>YbCl Molecule</th>
<th></th>
<th>YbBr Molecule</th>
<th></th>
<th>YbI Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
<td>F</td>
<td>H</td>
<td>S</td>
<td>C_p</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>100</td>
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<td>4.58</td>
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<td>Table 1.3 Thermodynamical quantities of InX (X= F, Cl, Br, I) molecules</td>
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<tr>
<td><strong>InF Molecule</strong></td>
<td><strong>InCl Molecule</strong></td>
<td><strong>InBr Molecule</strong></td>
<td><strong>InI Molecule</strong></td>
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<tr>
<td>T</td>
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<td>H</td>
<td>S</td>
<td>C_p</td>
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<td>F</td>
<td>H</td>
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