Spectroscopy is defined as the interaction of radiation with matter and has both physical and analytical applications. Physical spectroscopists use emitted light, absorbed light or scattered light in order to understand the mechanics of a chemical system. Analytical spectroscopists use the same physical phenomenon/process to determine the content and concentration of the atomic and molecular species present in a chemical system.

Atoms emit electromagnetic radiation ($h\nu$) as they relax from an excited state to their ground state. The emitted radiation can be detected when it is in the vacuum ultraviolet (VUV, 120-185nm), ultraviolet (UV, 185-400nm), visible (VIS, 400-700nm) and near infrared region (NIR, 700-850 nm). Although atoms emit electromagnetic radiations in the infrared, microwave and radiowave regions, the detection systems are less sensitive in this region. Therefore the VUV, UV, VIS, and NIR regions are preferred of these only the VUV needs a special environment devoid of air. Nevertheless, a portion of the VUV spectrum is used by analytical spectroscopy.

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 electronic 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,

\[
E = E_e + E_v + E_r
\]

or

\[
E = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc}
\]

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,

\[
\frac{E}{hc} = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc}
\]

or

\[
T = T_e + G + F
\]

where, \( T_e \) be electronic term value, \( G \) is vibrational term value and \( F \) denotes rotational term values, \( h \) 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,

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

where, \( \omega_e \) is the vibrational frequency and \( \omega_e x_e \) and \( \omega_e y_e \) 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, \( B_v = \left( \frac{h}{8\pi^2 c\mu r^2} \right) \) and \( D_v \) is the centrifugal distortion constant, \( D_v = \left( \frac{4B_v^3}{\omega_e^3} \right) \).
The wave number of the spectral line corresponding to a transition between
two electronic states, in emission or in absorption, is given by
\[
v = T' - T'' = (T_e' - T_e^0) + (G' - G^0) + (F' - F^0)
\]  
(1.6)

\[
v = v_e + v_v + v_r
\]
Where \( v_e = T_e' - T_e^0 \), \( v_v = G' - G^0 \) and \( v_r = F' - F^0 \)
(1.7)

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

Then
\[
v = v_e + \omega_e (v' + \frac{1}{2}) - \omega_e x_e (v' + \frac{1}{2})^2 + \omega_e y_e (v' + \frac{1}{2})^3 + \ldots.
\]
(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 \( \int \Psi_v \Psi_e d\tau \) 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 \( (\Delta v = \pm 1) \)
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 up to a certain point, at which they change suddenly and then slowly change in the separations occurs is the main sequence with $\Delta v = 0$. 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 be derived.

**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:

$$E_r = hc[B_eJ(J+1) - D_eJ^2(J+1)^2 + H_eJ^3(J+1)^3 + L_eJ^4(J+1)^4 + \ldots\ldots\ldots]$$

(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

$$B_e = \frac{h}{8\pi^2 cl}$$

(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

$$\frac{E_r}{hc} = F(J) = B_eJ(J+1) - D_eJ^2(J+1)^2$$

(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

$$v = [B_e J'(J'+1) - D_e J'^2 (J' + 1)^2] - [B_e J''(J''+1) - D_e J''^2 (J'' + 1)^2] \tag{1.13}$$

Application of selection rule $\Delta J = \pm 1$ gives

$$v = 2B_e (J'' + 1) - 4D_e (J''+1)^3 \tag{1.14}$$

This expression shows that the separation between the rotational lines decreases slightly with increasing $J''$. This effect is very small because $D_e < B_e$. One can determine the value of rotational constants ($B_e$ 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 $v_r$ 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

$$v = v_0 + F'(J') - F''(J'') \tag{1.15}$$

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

$$F_e(J) = B_e J (J + 1) - D_e J^2 (J + 1)^2 + \ldots \tag{1.16}$$

Then from the equation (1.15) we have
Here the upper and lower states have different electronic momenta Λ. 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. \( ^1\Sigma^- \rightarrow ^1\Sigma \) 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

\[ v = v_0 + B'_v (J + 1)(J + 2) - B''_v J(J + 1) \]
\[ v = v_0 + B'_v (J^2 + 3J + 2) - B''_v (J^2 + J) \]
\[ v = v_0 + 2B'_v + (3B'_v - B''_v) + (B''_v - B'_v)J^2 = R(J) \]  

(1.22)

Similarly,

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

(1.23)

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

(1.24)

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

\[ v = v_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2 \]  

(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).

$$m_{\text{vertex}} = -\frac{B'_v + B''_v}{2(B'_v - B''_v)}$$

Putting this expression in equation (1.25) we obtain the separation between zero line and vertex as

$$v_{\text{vertex}} - v_0 = -\frac{(B'_v + B''_v)^2}{4((B'_v - B''_v))}$$

(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 $\Delta_2 F_v(J)$ 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

\[ R(J - 1) - P(J + 1) = F_v^-(J + 1) - F_v^-(J - 1) = \Delta_2 F_v^-(J) \]  

(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

\[ R(J) - P(J) = F_v^+(J + 1) - F_v^+(J - 1) = \Delta_2 F_v^+(J) \]  

(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 \( F_v \) is given by

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

(1.30)

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

\[ \Delta_2 F_v(J) = F_v(J + 1) - F_v(J - 1) \]  

(1.31)

\[ \Delta_2 F_v(J) = B_v (J + 1)(J + 2) - B_v (J - 1)J \]

Or

\[ \Delta_2 F_v(J) = 4B_v (J + \frac{1}{2}) \]  

(1.32)

Thus plotting a graph between \( \Delta_2 F_v(J) \) 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

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

Putting this value of \( F_v \) in equation (1.31) we have
\[ \Delta_z F_v(J) = [B_v(J + 1)(J + 2) - D_v(J + 1)^2(J + 2)^2] - [B_v(J - 1)J - D_v(J - 1)^2J^2] \]  

(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 of the cases \( D_v \) is of the order of \( 10^{-5} \), 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

$$
\Delta J F_v (J) = F_v (J + 1) - F_v (J)
$$

$$
\Delta J F_v (J) = B_v (J + 1)(J + 2) - B_v J (J + 1) - D_v (J + 1)^2 (J + 2)^2 + D_v J^2 (J + 1)^2
$$

$$
\Delta J F_v (J) = 2B_v (J + 1) - 4D_v (J + 1)^2
$$

(1.40)

The plot of a graph between $\frac{\Delta J F_v (J)}{(J + 1)^2}$ 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 $M_L (\frac{\hbar}{2\pi})$, where $M_L$ can take values,

$$
M_L = L, L - 1, L - 2, ..., -L
$$

(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

$$
\Lambda = |M_L|
$$

(1.42)

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

$$
\Lambda = 0, 1, 2, 3, ..., L
$$

(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 $M_s \left( \frac{\hbar}{2\pi} \right)$. In case of molecules, $M_s$ is denoted by $\Sigma$. The quantum number $\Sigma$ may take $(2S+1)$ different value i.e.

$$\Sigma=S, S-1, S-2, \ldots, -S \quad (1.44)$$

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,

$$\Omega = |\Lambda + \Sigma| \quad (1.45)$$

**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 $\vec{J}$

$$\vec{\Omega} = \Lambda + \Sigma$$  \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,

$$K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \ldots \ldots$$  \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,

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

**Hund’s Case (c):** 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 $\Lambda$ and $\sum$ 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 $\vec{\Omega}$ of nuclear rotation then form the resultant angular momentum just as in case (a).

**Λ-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 $\Lambda\neq0$ which are doubly degenerate without rotation. With increasing rotation, that is with increasing $J$, in general, this splitting increases. It is called Λ–type doubling and is present for all states with $\Lambda\neq0$.

**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 ±1 (i.e. \( \Delta \Lambda = 0, \pm 1 \))

(4) Both states must be positive or both must be negative, i.e. + ↔ -

(5) For identical nuclei (e.g. \( \text{N}_2 \), \( \text{I}_2 \) 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’.

**Predissociation**

Whenever the potential curves of two different excited electronic states of a molecule intersect such that the discrete energy levels of one curve overlap the continuous range of levels of the other then there is a possibility of a radiationless transition from the discrete state to the continuous state followed by spontaneous dissociation of the molecule. This process is called Predissociation. It is responsible for two characteristic phenomena observed in molecular spectra namely diffuseness of bands and breaking-off of band structure. The study of predissociation has led to many valuable conclusions concerning molecular structure to an explanation of some photochemical processes and to a determination of important heats of dissociation.

Predissociation is established by emission bands breaking off at a certain point in a series. In absorption bands become diffuse. In this case, even with very high resolution, no diffuseness would be hidden by the Doppler width. If the predissociation occurs in the lower state of emission band, no breaking-off occurs,
but the bands become diffuse similar to absorption bands with predissociating upper states.

Predissociation is at least for diatomic molecules, a comparatively rare phenomenon. This is due to the fact that the probability of the radiationless transition into the dissociating state is usually so small that long before the decomposition would have taken place the molecule has already gone over into a lower-lying stable state with emission of radiation. In order for the transition probability to be so large that the bands can be observed to become diffuse or to break off, still further conditions selection rules must be fulfilled in addition to the condition of equal energy. The energy corresponding to the beginning of the diffuseness or in emission to the breaking-off point is called the predissociation limit. The energy of a predissociation limit gives immediately limit of the state causing the predissociation. In addition to line broadening, the predissociation process can cause line shifts. Each discrete or diffuse level can be shifted by its interaction with the entire continuum of the predissociating state, but this effect is considerably smaller than level shifts caused by interactions between discrete levels. The order of magnitude of predissociation induced level shifts and line widths are comparable. Thus in classical spectroscopy, only predissociations observable in absorption, having a width of at least $10^{-1}$ cm$^{-1}$, can be accompanied by detectable level shifts. In principle, rotational constants and fine structure parameters of the predissociated state may also be affected by the predissociating state, as in case of perturbations.
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 of transition metal intermetallics like Cobalt monoselenide (CoSe) and selenium dimmer (Se₂) because of their technological applications in various disciplines.

The normal state electronic configuration of Cobalt (Co) and Selenium (Se) atoms are given by

\[
{_{27}}\text{Co: } 1s^2, 2s^2 \ 2p^6, \ 3s^23p^63d^7, \ 4s^2 \quad \text{-----} \quad {_{4}}\text{F}_{9/2} \\
{_{33}}\text{Se: } 1s^2, 2s^22p^6, \ 3s^23p^63d^{10}, \ 4s^24p^4 \quad \text{-----} \quad {_{3}}\text{P}_{2}
\]

Theoretically the combination of Co and Se forms Co₂, CoSe and Se₂ molecule and higher order of polyatomic molecules of these atoms. However experimentally there are several problems. The most of the diatoms of these elements have been studied using high resolution techniques but such is not the state of affair with the CoSe. The lack of accurate spectroscopic data of CoSe and Se₂ are due to experimental difficulties in generation of transient species because of the following reasons:

The electronic spectra of 3d transition metal oxide and sulfide are generally very complex. The metal atom often has many unpaired electrons that can produce a huge number of low-lying electronic states with high values of spin multiplicity and orbital angular momentum as well as large spin-orbit interactions. These electronic states may perturb one other, thereby complicating their spectra and making analysis difficult. On the other hand theoretical calculation is plagued with similar problems and it is hard to predict the energy order and properties of the low lying electronic states. Despite these difficulties, most of the 3d transition metal monoxides and monosulfide have been well studied partly due to their
importance in astrophysics and as models in understanding the chemical bonding in simple metal systems. In contrast, little data are available for the corresponding sulfide and selenide molecules.

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

In this sequence, the low resolution spectrum of CoSe has been recorded using thermal excitation technique and 2m Plane Grating Spectrograph. The study revealed the presence of entirely new band systems. The chapter III\textsuperscript{rd} consists of findings of new band systems of CoSe molecule in thermal emission.

The technologically important compounds such as Selenium dimer, widely used in photovoltaic action, photoconductive action, rectifiers, xerography, glass industry, photographic toner and as an additive to stainless steel, has been studied using electrodeless discharge technique and Fourier transform spectrometer. The author has recorded high resolution spectra of Selenium dimer using microwave excitation technique (2450 MHz, 100 watt) and BOMEM DA8 Fourier transform spectrometer. The study revealed fruitful results in terms of vibrational constants, rotational constants, perturbation and predissociation. Chapter IV\textsuperscript{th} describes findings of the FT spectrum of selenium dimer 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 different field of science 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 estimated by using spectroscopic data and statistical quantum thermodynamics. Chapter V gives an account of estimation of thermodynamical quantities of Platinum diatomics while Chapter VI presents our findings on tin chalcogenides.

The summary of findings is given below:

(A) New Band Systems of the CoSe Molecule in Thermal Emission

Thermally excited emission spectrum of the mixed vapour of cobalt and selenium has been investigated in the $\lambda \lambda$ 6100 - 6600 Å region for the first time. The spectrum has been photographed about a temperature 2300°C at a reciprocal linear dispersion of 7.3 Å/mm. About 102 entirely new bands, degraded to lower wavelength, have been recorded and are classified into six entirely new systems (viz. A, B, C, D, E & F). The vibrational analysis performed suggests that these systems arise from the ground state ($^4\Delta$) having vibrational frequency 336.0 cm\(^{-1}\). The vibrational constants for the upper and lower state of the different systems have been collected in table 1.1.

**Table 1.1 Vibrational Constants (in cm\(^{-1}\)) of the CoSe Molecule**

<table>
<thead>
<tr>
<th>System</th>
<th>$v_{00}$</th>
<th>$\omega_c$</th>
<th>$\omega_c x_c$</th>
<th>$\omega_c''$</th>
<th>$\omega_c x_c''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15717.7</td>
<td>342.468±0.287</td>
<td>1.46±0.057</td>
<td>335.548±0.287</td>
<td>1.686±0.057</td>
</tr>
<tr>
<td>B</td>
<td>15598.3</td>
<td>347.003±0.246</td>
<td>1.81±0.049</td>
<td>336.758±0.246</td>
<td>1.759±0.049</td>
</tr>
<tr>
<td>C</td>
<td>15685.6</td>
<td>340.738±0.206</td>
<td>1.127±0.044</td>
<td>335.731±0.268</td>
<td>1.737±0.065</td>
</tr>
<tr>
<td>D</td>
<td>15924.2</td>
<td>349.044±0.383</td>
<td>1.605±0.081</td>
<td>336.353±0.497</td>
<td>1.879±0.120</td>
</tr>
<tr>
<td>E</td>
<td>15973.1</td>
<td>340.893±0.969</td>
<td>1.057±0.235</td>
<td>336.588±0.969</td>
<td>1.917±0.0235</td>
</tr>
<tr>
<td>F</td>
<td>15987.1</td>
<td>343.075±0.255</td>
<td>1.229±0.053</td>
<td>336.222±0.251</td>
<td>1.855±0.050</td>
</tr>
</tbody>
</table>
(B) Fourier Transform High Resolution Spectrum of the Se\textsubscript{2} Molecule

The high resolution Fourier Transform spectrum of \textsuperscript{80}Se\textsubscript{2} molecule has been recorded in an electrodeless discharge lamp with microwave excitation in the region 18000 - 26000 cm\textsuperscript{-1}. The observed bands have been classified into a single system $B^3\Sigma_u^- - X^3\Sigma_g^-$. The $B^3\Sigma_u^- - X^3\Sigma_g^-$ system is divided into two subsystems: $B0_u^+ - X0_g^+$ and $B1_u^+ - X1_g^-$. A total of 155 bands are recorded in which 103 bands belong to $B0_u^+ - X0_g^+$ subsystem whereas 52 bands attributed to $B1_u^+ - X1_g^-$ subsystem. Due to diffuseness, perturbation and predissociation, author has been able to analyze rotational structure of 28 bands of $B0_u^+ - X0_g^+$ subsystem. The $B1_u^+ - X1_g^-$ subsystem is very faint and rotational analysis of 5 bands has been performed. The rotational constants determined from analysis have been given in table 1.2. Revised vibrational constants using band origin have been determined. The analysis is further supported by calculating the Franck Condon Factor and r-centroid parameter for \textsuperscript{80}Se\textsubscript{2} molecule. The following vibrational constants (cm\textsuperscript{-1}) have been determined from the analysis:

- $B0_u^+ - X0_g^+$ subsystem
  
  $v_{00} = 25981.58 \pm 0.806$  
  $\omega_c' = 246.24 \pm 0.138$  
  $\omega_c x_e' = 1.056 \pm 0.021$ cm\textsuperscript{-1}  
  $\omega_c' = 385.56 \pm 0.162$  
  $\omega_c x_e'' = 0.989 \pm 0.009$ cm\textsuperscript{-1}
Table 1.2 Rotational Constants (cm$^{-1}$) of the Se$_2$ Molecule: $B^3\Sigma_u^+ - X^3\Sigma_g^-$ System

<table>
<thead>
<tr>
<th>$v''$</th>
<th>$B_{v''}$</th>
<th>$D_{v''}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0888772231(0.438X10$^{-05}$)</td>
<td>0.1983953798X10$^{-07}$ (0.360X10$^{-09}$)</td>
</tr>
<tr>
<td>4</td>
<td>0.0895859915(0.436X10$^{-05}$)</td>
<td>0.2044286044X10$^{-07}$ (0.356 X10$^{-09}$)</td>
</tr>
<tr>
<td>5</td>
<td>0.0882848366(0.430 X10$^{-05}$)</td>
<td>0.2029804171X10$^{-07}$ (0.352 X10$^{-09}$)</td>
</tr>
<tr>
<td>6</td>
<td>0.0879892728(0.430 X10$^{-05}$)</td>
<td>0.2053568171X10$^{-07}$ (0.354 X10$^{-09}$)</td>
</tr>
<tr>
<td>7</td>
<td>0.0876882413(0.423 X10$^{-05}$)</td>
<td>0.2008705623X10$^{-07}$ (0.340 X10$^{-09}$)</td>
</tr>
<tr>
<td>8</td>
<td>0.0873888488(0.424 X10$^{-05}$)</td>
<td>0.2019654373X10$^{-07}$ (0.340 X10$^{-09}$)</td>
</tr>
<tr>
<td>9</td>
<td>0.0871000010(0.441 X10$^{-05}$)</td>
<td>0.2151107518X10$^{-07}$ (0.379 X10$^{-09}$)</td>
</tr>
<tr>
<td>10</td>
<td>0.0867943290(0.433 X10$^{-05}$)</td>
<td>0.2068761968X10$^{-07}$ (0.351 X10$^{-09}$)</td>
</tr>
<tr>
<td>11</td>
<td>0.0864935131(0.429 X10$^{-05}$)</td>
<td>0.2076230820X10$^{-07}$ (0.347 X10$^{-09}$)</td>
</tr>
<tr>
<td>12</td>
<td>0.0861902360(0.428 X10$^{-05}$)</td>
<td>0.2057071513X10$^{-07}$ (0.346 X10$^{-09}$)</td>
</tr>
<tr>
<td>13</td>
<td>0.0858872227(0.425 X10$^{-05}$)</td>
<td>0.2050074168X10$^{-07}$ (0.343 X10$^{-09}$)</td>
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</table>

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$B_{v'}$</th>
<th>$D_{v'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0702558969(0.420X10$^{-05}$)</td>
<td>0.2312033003X10$^{-07}$ (0.334X10$^{-09}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.0699177375(0.428X10$^{-05}$)</td>
<td>0.2275871527X10$^{-07}$ (0.348X10$^{-09}$)</td>
</tr>
<tr>
<td>2</td>
<td>0.0696046879(0.420X10$^{-05}$)</td>
<td>0.2608536412X10$^{-07}$ (0.336X10$^{-09}$)</td>
</tr>
<tr>
<td>3</td>
<td>0.0692697844(0.438X10$^{-05}$)</td>
<td>0.2627282677X10$^{-07}$ (0.360X10$^{-09}$)</td>
</tr>
<tr>
<td>4</td>
<td>0.0689959725(0.439X10$^{-05}$)</td>
<td>0.3313753124X10$^{-07}$ (0.362X10$^{-09}$)</td>
</tr>
<tr>
<td>5</td>
<td>0.0685849901(0.599X10$^{-05}$)</td>
<td>0.4926840683X10$^{-07}$ (0.171X10$^{-08}$)</td>
</tr>
<tr>
<td>6</td>
<td>0.0682437756(0.918X10$^{-05}$)</td>
<td>0.5620819215X10$^{-07}$ (0.313X10$^{-08}$)</td>
</tr>
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</table>

**B1$_v$-X1$_g$ Subsystem**

<table>
<thead>
<tr>
<th>$v''$</th>
<th>$B_{v''}$</th>
<th>$D_{v''}$</th>
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</thead>
<tbody>
<tr>
<td>8</td>
<td>0.0874667963(.371 X10$^{-04}$)</td>
<td>0.9356316794X10$^{-07}$ (.430 X10$^{-08}$)</td>
</tr>
<tr>
<td>9</td>
<td>0.0871818536(.341 X10$^{-04}$)</td>
<td>0.8307384566X10$^{-07}$ (.427 X10$^{-08}$)</td>
</tr>
<tr>
<td>13</td>
<td>0.0858766436(.316 X10$^{-04}$)</td>
<td>0.7368928527X10$^{-07}$ (.459X10$^{-08}$)</td>
</tr>
<tr>
<td>14</td>
<td>0.0856856435(.352 X10$^{-04}$)</td>
<td>0.6361796196X10$^{-07}$ (.418X10$^{-08}$)</td>
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</table>

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$B_{v'}$</th>
<th>$D_{v'}$</th>
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<tbody>
<tr>
<td>0</td>
<td>0.0706489652 (.314X10$^{-04}$)</td>
<td>0.264864285X10$^{-07}$ (.459 X10$^{-08}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.0700458403(.356 X10$^{-04}$)</td>
<td>0.1024762907X10$^{-07}$ (.468X10$^{-08}$)</td>
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</table>

**F$_2$ component**

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<th>$v''$</th>
<th>$B_{v''}$</th>
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<tbody>
<tr>
<td>8</td>
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<td>0.9543296442X10$^{-07}$ (.435 X10$^{-08}$)</td>
</tr>
<tr>
<td>9</td>
<td>0.0872911002(.247 X10$^{-04}$)</td>
<td>0.8291856647X10$^{-07}$ (.417 X10$^{-08}$)</td>
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<td>13</td>
<td>0.0861846820(.290 X10$^{-04}$)</td>
<td>0.77443554421X10$^{-07}$ (.496X10$^{-08}$)</td>
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<tr>
<td>14</td>
<td>0.0857921871(.246 X10$^{-04}$)</td>
<td>0.61235678923X10$^{-07}$ (.418X10$^{-08}$)</td>
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</table>

<table>
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<th>$v'$</th>
<th>$B_{v'}$</th>
<th>$D_{v'}$</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.0744550270(.232 X10$^{-04}$)</td>
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<tr>
<td>1</td>
<td>0.0698403419(.254 X10$^{-04}$)</td>
<td>0.1123567854X10$^{-07}$ (.437X10$^{-08}$)</td>
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**F$_3$ component**
(C) Thermodynamical Quantities of Platinum Diatomics and Tin Chalcogenides from Spectroscopic Data

The thermodynamical quantities such as free energy (F), enthalpy (H), entropy (S) and specific heat ($C_p$) of Platinum diatomics (PtH, PtC, PtN, PtO) and Tin chalcogenides (SnO, SnS, SnSe, SnTe) have been estimated using spectroscopic data and partition function theory in the temperature range 100-3000 K. The partition functions have been calculated by using rotation-vibration energy in ground electronic state including effects of anharmonicity ($\omega_e$), centrifugal stretching ($D_e$) and rotational-vibrational interaction ($\alpha_e$). 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 for platinum diatomics and tin diatomics are collected in table 1.3 and 1.4 respectively.
<table>
<thead>
<tr>
<th>T</th>
<th>F</th>
<th>H</th>
<th>S</th>
<th>C_p</th>
<th>F</th>
<th>H</th>
<th>S</th>
<th>C_p</th>
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<td>100</td>
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<td>249.78</td>
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<td>58.65</td>
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<td>282.73</td>
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<td>S</td>
<td>C_p</td>
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<td>850.58</td>
<td>87.22</td>
<td>319.78</td>
<td>37.25</td>
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</tbody>
</table>

F is energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K) and T is temperature (K)
Table 1.4 Thermodynamical Quantities of Tin Chalcogenides

<table>
<thead>
<tr>
<th>T</th>
<th>F</th>
<th>H</th>
<th>S</th>
<th>C_p</th>
<th>F</th>
<th>H</th>
<th>S</th>
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<table>
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<td>44.25</td>
<td>334.24</td>
<td>37.34</td>
</tr>
</tbody>
</table>

F is energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K) and T is temperature (K)
References


