CHAPTER I

INTRODUCTION
1.1 INTRODUCTION

Spectroscopy is concerned with interaction between matter and electromagnetic radiation in which energy is extracted from or added to the radiation field. The extraction of energy from the radiation constitutes the phenomenon of absorption of radiation by matter, while in the emission of radiation, radiation energy appears at the expense of kinetic and potential energies i.e. the total energy of the molecular system.

Broadly speaking, the chemically interesting deductions, which can be made from the spectra, concern mainly two topics; the structure and the energy condition of the molecule. Spectra are primarily determined by the differences of energies of discrete states in which the molecule may exist and the energies are determined by: (i) the nature of the electronic distribution, particularly of the valence electrons with specific angular and spin momenta, (ii) the arrangement of nuclei and (iii) the motion of the atomic nuclei in the molecule. The study of spectra arising from electronic transitions yields results related to distribution of electrons in the molecule and this, in turn, determines such quantities as bond strengths and chemical reactivity of the molecule and also throws light on its size and shape [1-9]. However, direct determination of the positions of atoms in the molecules is possible only for a relatively few organic molecules having highly symmetrical arrangements of the atoms in space from the study of the electronic spectra of the molecule. But in many cases the molecules have complicated arrangement of atoms and only information on the vibrational frequencies of such molecules are easily obtained from a study of their Raman and infrared absorption spectra [2, 10-20]. These data are very helpful in determining certain thermodynamic properties, the structure of the molecule, the bond strengths of various bonds etc., through a complete knowledge of all the frequencies of vibration of the molecule. Further, a critical study of the vibrational spectrum also allows us to obtain information regarding inter and intra-molecular interactions in the molecular system [21, 22].

1.2 RAMAN SCATTERING

When an electromagnetic radiation (light) irradiates an ensemble of molecules, it may be transmitted or absorbed or scattered. As a result, the energy of the outgoing radiation may remain unchanged, partially changed or become zero. In the case of absorption, the energy of the incident photon is equal to a difference of energies of two quantum states of the molecule. The absorption may occur in the ultra-violet, visible, infrared or microwave regions of the electromagnetic spectrum. If the absorption takes place in the ultra-violet and visible region of
the spectrum, it is associated with electronic transitions mostly of the valence electrons in the molecule. While the absorption in the infrared region is concerned with transitions between rotational-vibrational levels of the molecule and those in the microwave region is concerned with transitions between pure rotational levels.

However in the case of scattering, energy of the scattered radiation may be different from that of the incident radiation. When the energy of the scattered radiation remains unchanged, the phenomenon is called Rayleigh scattering, otherwise the process gives rise to Raman scattering [23]. The process for which the energy of the scattered radiation is less than that of the incident radiation, is known as Stokes Raman scattering. For the other case, when the energy of the scattered radiation is greater than that of the incident radiation, the process is known as anti-Stokes Raman scattering [2, 5, 10, 14, 15, 18, 19].

The fraction of the incident photons scattered during Raman process is always found to be very small and thereby the Raman peaks are extremely weak in intensity. It is found that the intensity of Rayleigh line is approximately $10^3$ times the intensity of the incident light and intensity of Raman band is about $10^3$ times that of Rayleigh line. Intense monochromatic laser, therefore, is nowadays used as excitation source to obtain good quality Raman spectra. In the case of normal Raman scattering (NRS) the excitation frequency of radiation is much below the lowest absorption frequency arising from an electronic transition of the system, i.e., the intermediate state (as described below) is not associated with any real molecular eigen state as such and is considered to be a statistical summation of a large number of excited electronic states of the system. When the incident light approaches an electronic absorption band, the concerned electronic state receives more importance and actually summation is dominated by contribution from the relevant electronic state. Thus resonance and pre or post resonance Raman scattering conditions may be obtained by tuning the exciting frequency through the absorption band [10-14, 18, 19, 21].

1.3 THEORETICAL EXPLANATION OF RAMAN EFFECT

In the present work we shall confine our discussion to vibrational Raman effect [2, 10-21]. When the electric field, associated with an electromagnetic radiation, interacts with a molecular system, an oscillating electric dipole moment is induced in the system and it is given by,

$$\vec{P} = \alpha \vec{E}$$

(I.1)
where, ‘$\alpha$’ is the polarizability tensor of rank two as shown below,

$$\alpha = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}$$  \hspace{1cm} (1.2)

If the interaction changes the molecular system from an eigen state $|m\rangle$ to another eigen state $|n\rangle$, then the intensity of the scattered radiation is given by (following the quantum mechanical analogue of electric dipole radiation) [24],

$$I_s = \frac{2}{3} \left| \langle \tilde{P}_{mn} \rangle \right|^2 \frac{1}{C^3}$$  \hspace{1cm} (1.3)

where $\tilde{P}_{mn}$, the induced transition dipole moment between the initial and final molecular eigen states $|m\rangle$ and $|n\rangle$, is given by,

$$\langle \tilde{P}_{mn} \rangle = \langle m | \tilde{P} | n \rangle = \langle m | \alpha E | n \rangle$$  \hspace{1cm} (1.4)

Here the initial and final molecular states are written as,

$$|m\rangle = e^{-\frac{i E_{mf} t}{\hbar}} \left( U_m(\tilde{\phi}) \right)$$

$$|n\rangle = e^{-\frac{i E_{nf} t}{\hbar}} \left( U_n(\tilde{\phi}) \right)$$  \hspace{1cm} (1.5)

Let the electric field associated with the incident radiation is given by,

$$\vec{E} = E_o \cos(2\pi v_o t) = \frac{1}{2} E_o \left[ e^{i2\pi v_o t} + e^{-i2\pi v_o t} \right]$$  \hspace{1cm} (1.6)

Thus the induced transition dipole moment $|\langle \tilde{P}_{mn} \rangle|$ becomes,

$$|\langle \tilde{P}_{mn} \rangle| = \frac{E_o}{2} \left[ e^{i2\pi \left( \frac{v_o E_n - E_m}{\hbar} \right) t} + e^{-i2\pi \left( \frac{v_o E_n - E_m}{\hbar} \right) t} \right] \langle U_m | \alpha | U_n \rangle$$  \hspace{1cm} (1.7)

The equation (1.7) indicates that the scattered radiation will contain frequencies $(v_o - v_{mn})$ and $(v_o + v_{mn})$, where $[v_{mn} = (E_n - E_m)/\hbar]$. Note, as will be shown below, that the second term of the right hand side of equation (1.7), yields some unrealistic results, and so it will not be considered.
Case I: -

When the incident radiation is scattered by the molecule elastically, leaving it in the unchanged state $|m\rangle$, a radiation of frequency ($\nu_o$) is observed. This corresponds to Rayleigh scattering. By absorbing the incident photon (of energy $h\nu_o$), the molecule gets excited to a hypothetical state $|s\rangle$ (whose energy is $h\nu_o$ above that of the initial state $|m\rangle$), wherefrom it is de-excited again to the initial state by emitting a radiation of frequency $\nu_o$. This is shown in figure 1.1. Here $|n\rangle = |m\rangle$ and so $E_n = E_m$.

![Figure 1.1 Rayleigh Scattering](image)

Case II: -

Unlike case I, if the molecule scatters the incident radiation inelastically and is excited from a lower energy initial state $|m\rangle$ to a higher energy final state $|n\rangle$ ($E_n > E_m$), a radiation of frequency $\nu_{Stokes} = \nu_o - \frac{E_n - E_m}{h}$ is found. This is shown in figure 1.2. By absorbing the incident photon, the molecule, being initially in the lower energy state $|m\rangle$, is excited to a hypothetical state $|s\rangle$, and there from returns to the another molecular state $|n\rangle$ ($E_n > E_m$) by
the emission of radiation frequency \( \nu_{\text{Stokes}} = \nu_o - \frac{E_n - E_m}{\hbar} \nu_o \). This radiation is called Stokes Raman radiation. This picture contradicts the process arising from the second term of the right hand side of equation (1.7) and so this term is not considered.

**Case III:**

![Diagram](https://via.placeholder.com/150)

\[
\nu_{\text{anti-Stokes}} = \nu_o + (E_m - E_n)
\]

Figure 1.3 Antistokes Raman Scattering

Here also the molecule scatters inelastically the incident radiation as shown in figure 1.3. The molecule was initially in the state \( |m\rangle \). By absorbing the incident radiation it is excited to the hypothetical state \( |s'\rangle \) wherefrom it comes to the state \( |n\rangle \) \( (E_n \langle E_m \rangle \) by the emission of radiation, known as anti-Stokes Raman radiation. The frequency of this radiation is \( \nu_{\text{anti-Stokes}} = \nu_o - \frac{E_n - E_m}{\hbar} \nu_o \). This is in compliance with the first term on right hand side of equation (1.7), as before, but in contradiction with that arises from the second term of the same equation. So again this term is not taken into consideration.

**1.4 SELECTION RULES**

As stated before, we shall confine our discussion to vibrational spectra of molecules. For vibrational Raman effect the molecular states \( |m\rangle \) and \( |n\rangle \), as described in the previous section, are different vibrational states of the molecule under consideration.

The selection rules for the vibrational Raman effect is determined from the spatial part \( \langle U_m | \alpha | U_n \rangle \) on the right hand side of equation (1.7) [2, 7, 8, 11, 20].

For a polyatomic molecule, the spatial part of initial state \( |m\rangle \) and final state \( |n\rangle \) are,
\[
U_m = \prod_{k=1}^{3n-6(5)} \Psi'_{k'}(Q_k) \\
U_n = \prod_{k=1}^{3n-6(5)} \Psi'_{k}(Q_k)
\]

Here \(k''\) and \(k'\) correspond to vibrational quantum numbers associated with the \(k\)-th normal mode in the initial state \(|m\rangle\) and final state \(|n\rangle\) of the molecule. \(\Psi'(Q_k)\) is the wave function associated with the \(k\)-th normal mode and is assumed to have the form of simple harmonic oscillator type wave function.

Expanding the polarizability operator \((\alpha)\) about the equilibrium nuclear configuration, we have,

\[
\alpha = \alpha_o + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_o (Q_i - (Q_i)_o) + \frac{1}{2} \sum_{i<j} \left( \frac{\partial^2 \alpha}{\partial Q_i \partial Q_j} \right)_o (Q_i - (Q_i)_o)(Q_j - (Q_j)_o) + \ldots
\]

\[
= \alpha_o + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_o Q_i + \frac{1}{2} \sum_{i<j} \left( \frac{\partial^2 \alpha}{\partial Q_i \partial Q_j} \right)_o Q_i Q_j + \ldots
\]

where the subscript \('o'\) correspond to equilibrium nuclear configuration of the molecule concerned and it is assumed that \((Q_j)_o = 0\) for all \(i's\). Then the transition polarizability \(\langle U_m | \alpha | U_n \rangle\) becomes, [using the orthogonal properties of the wave functions of linear harmonic oscillator],

\[
\langle U_m | \alpha | U_n \rangle = \left( \prod_k \Psi'_{k'}(Q_k) \right) \alpha_o + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_o Q_i + \frac{1}{2} \sum_{i<j} \left( \frac{\partial^2 \alpha}{\partial Q_i \partial Q_j} \right)_o Q_i Q_j + \ldots \left( \prod_k \Psi'_{k'}(Q_k) \right)
\]

\[
= \alpha_o \left( \prod_k \Psi'_{k'}(Q_k) \right) \left( \prod_k \Psi_{k'}(Q_k) \right) + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_o \prod_\ell \langle \Psi'_{k'}(Q_k) | \Psi'_{k'}(Q_k) \rangle \langle \Psi_{k'}(Q_k) | \Psi_{k'}(Q_k) \rangle + \ldots
\]

\[
= \alpha_o \prod_k \delta_{k,k'} + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_o \prod_\ell \langle \Psi_{k'}(Q_k) | \Psi_{k'}(Q_k) \rangle \prod_\ell \delta_{k,k'} + \ldots
\]

The first term of the right hand side of equation (1.10) is used in determining the structure of rotational Raman spectra. The second term is non-vanishing corresponding to \(k\)-th normal mode if simultaneously,
Thus this term gives rise to excitation of the fundamental mode (say k-th) in the Raman spectra (Stokes for $\Delta \nu_k = +1$ and anti-Stokes for $\Delta \nu_k = -1$) provided the first gradient \( \frac{\partial \alpha}{\partial Q_i} \) is non-zero. Similarly third term on the right hand side of equation (I.10) given rise to the excitation of the second harmonic of a particular normal mode or simultaneous excitation of two different fundamental modes \((i\text{ and } j)\) if the second gradient \( \frac{\partial^2 \alpha}{\partial Q_i \partial Q_j} \) is non-zero. Since the value of gradient of polarizability decreases with the increase of its order, so the fundamental vibration is stronger than its second harmonics and so on.

For infrared spectrum, absorption intensity is given by [2],

\[
I_{\text{infrared}} = \frac{8\pi^3}{3\hbar c} l_0 (\Delta L) \bar{N} v \left| \langle \bar{P}_{mn} \rangle \right|^2
\]  

(I.12)

Here \( l_0 \) is the incident intensity, \( \Delta L \) is the absorbing path length, \( \bar{N} \) is the number of molecule in ground vibrational state, \( v \) is infrared frequency and here \( \bar{P}_{mn} \) is the transition dipole moment between the initial state \( |m\rangle \) and final state \( |n\rangle \) of the molecule. Here also if we expand the electric dipole moment operator \( \bar{P} \) (as that of polarizability operator \( \alpha \) in equation (I.9)), the transition dipole moment becomes,

\[
\langle \bar{P}_{mn} \rangle = \left( \prod_k \Psi_k^*(Q_k) \right) \bar{P}_0 + \sum_i \left( \frac{\partial \bar{P}}{\partial Q_i} \right)_o Q_i + \frac{1}{2} \sum_{i < j} \left( \frac{\partial^2 \bar{P}}{\partial Q_i \partial Q_j} \right)_o Q_i Q_j + \ldots \left( \prod_k \Psi_k^*(Q_k) \right)
\]

(I.13)

Here the first term on the right hand side of equation (I.13) determines the structure of pure rotational spectra. The second term gives rise to excitation of fundamental vibrations of those normal modes whose first gradient of the dipole moment at equilibrium nuclear configuration is non-zero. Similarly third term and other higher order terms give rise to harmonics (of different order) and various combination bands in the infrared spectra.
Since the activities of the fundamental vibration of a particular normal mode in Raman and infrared spectra depend respectively on the first order gradient of the polarizability and dipole moment with respect to the particular normal mode, the two spectra are said to be complementary to each other.

The activity of a normal mode in the Raman and infrared spectra can easily be determined from the knowledge of group theory [25]. A normal mode is said to be infrared active if the corresponding integrand in the transition dipole moment \( \langle \hat{\mu}_{mn} \rangle \) belongs to the totally symmetric representation for at least one component of the dipole moment operator \( \hat{P} \).

Since ground vibrational state is totally symmetric, so we can say, ‘a fundamental mode will be infrared active (i.e. will give rise to an absorption band) if the normal mode, which is excited, belongs to the same representation as any one or more of the Cartesian coordinates under the concerned point group of the molecule’. Similarly a normal mode is said to be Raman active if at least one component of the integral of the polarizability tensor (i.e. \( \langle U_m | x_{ij} | U_n \rangle \)) belongs to totally symmetric representation. Thus we can say ‘a fundamental vibration will be Raman active (i.e. gives rise to a Raman band) if the normal mode belongs to the same representation as any one or more of the components of the polarizability tensor i.e. linear combination of the quadratic product of the Cartesian coordinates under the concerned point group of the molecule’ [25].

**1.5 DEPOLARIZATION RATIO**

When an electromagnetic radiation interacts with a molecular system, often there is a change in the state of polarization. Incident radiation, which is either polarized or unpolarized, can produce a scattered radiation, which has polarization characteristics different from those of the incident radiation. These changes are important parameters both in Rayleigh as well as in Raman scattering since they are related to the symmetry of the scattering molecule. In gases and liquids, the scattering molecules have completely random orientation. For these systems, the depolarization ratio or the degree of depolarization (\( \rho \)) associated with a particular normal mode of vibration is a very important quantity in the Raman spectroscopy [2, 10, 14]. These ratios give important information regarding the symmetries of different normal modes and structural properties of the molecular system as a whole too.
The general polarizability tensor in a Cartesian coordinate system is given by,

\[
\alpha = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix} = \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & a
\end{pmatrix} + \begin{pmatrix}
\alpha_{xx} - a & \frac{\alpha_{xy} + \alpha_{yx}}{2} & \frac{\alpha_{xz} + \alpha_{zx}}{2} \\
\frac{\alpha_{yx} + \alpha_{xy}}{2} & \alpha_{yy} - a & \frac{\alpha_{yz} + \alpha_{zy}}{2} \\
\frac{\alpha_{zx} + \alpha_{xz}}{2} & \frac{\alpha_{yz} + \alpha_{zy}}{2} & \alpha_{zz} - a
\end{pmatrix}
\]

where \( a = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \)

\( \text{(1.14a)} \)

Note here that the subscript \( \text{iso}, \text{aniso}, \text{sym} \) and \( \text{anti} \) stand for isotropic, anisotropic, symmetric and anti-symmetric parts of the polarizability tensor. For Rayleigh scattering, \( \alpha_y \)'s correspond to various components of polarizability tensor for equilibrium nuclear configuration and for Raman scattering, they are derived polarizability i.e. polarizability derivatives with respect to different normal modes of vibration. This may also be noted here, as found from quantum mechanical description, that various components of polarizability tensor are functions of the frequency of the exciting radiation.

For a freely rotating system, we have to form the space average of various components of polarizability tensor and they are found to be,

\[
\overline{\alpha_{xx}^2} = \overline{\alpha_{yy}^2} = \overline{\alpha_{zz}^2} = \frac{45\alpha^2 + 4\gamma^2}{45}
\]

\( \text{(1.15a)} \)

\[
\overline{(\alpha_{xy})^2_{\text{aniso}}} = \overline{(\alpha_{yz})^2_{\text{aniso}}} = \overline{(\alpha_{zx})^2_{\text{aniso}}} = \frac{\gamma^2}{15}
\]

\( \text{(1.15b)} \)

\[
\overline{(\alpha_{xx} \cdot \alpha_{yy})_{\text{aniso}}} = \overline{(\alpha_{yy} \cdot \alpha_{zz})_{\text{aniso}}} = \overline{(\alpha_{zz} \cdot \alpha_{xx})_{\text{aniso}}} = \frac{45\alpha^2 - 2\gamma^2}{45}
\]

\( \text{(1.15c)} \)

\[
\overline{(\alpha_{\text{sym} \cdot \alpha_{\text{anti}}})} = 0
\]

\( \text{(1.15d)} \)

\[
\overline{(\alpha_{xy})^2_{\text{anti}}} = \overline{(\alpha_{yz})^2_{\text{anti}}} = \overline{(\alpha_{zx})^2_{\text{anti}}} = \frac{8\gamma^2}{9}
\]

\( \text{(1.15e)} \)
and averages of all other terms involving any subscript once only (like $\alpha_{xx} \cdot \alpha_{xy}$ and so on) are zero [10]. Here,

$$\gamma^2 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right] + \
\frac{3}{4} \left[ (\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{yz} + \alpha_{zy})^2 + (\alpha_{zx} + \alpha_{xz})^2 \right]$$

(1.16a)

and

$$\delta^2 = \frac{3}{4} \left[ (\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{yz} - \alpha_{zy})^2 + (\alpha_{zx} - \alpha_{xz})^2 \right]$$

(1.16b)

The quantities $\alpha$, $\gamma^2$ and $\delta^2$ are all rotational invariant although individual components of the polarizability tensor change on rotation of the coordinate axis. One point worth mentioning here is that for non-resonant excitation the polarizability tensor is symmetric i.e. $\alpha_{anti} = 0$. But for resonance excitation, the tensor in general no longer remains symmetric and this unsymmetric nature gives rise to non-vanishing antisymmetric component of the polarizability tensor i.e. $\alpha_{anti} \neq 0$ [10].

For plane polarized incident laser radiation with electric vector parallel to the scattering plane (defined as the plane containing the direction of observation and direction of propagation of the incident radiation), the depolarization ratio of the Rayleigh and Raman lines observed in the direction perpendicular to the incident direction is defined by,

$$\rho_{\parallel}(\pi/2) = \frac{I_{\perp}(\pi/2)}{I_{\parallel}(\pi/2)}$$

(1.17a)

Similarly for incident light, plane polarized perpendicular to the scattering plane, the depolarization ratio is given by,

$$\rho_{\perp}(\pi/2) = \frac{I_{\perp}(\pi/2)}{I_{\parallel}(\pi/2)}$$

(1.17b)

and for unpolarized incident light, the depolarization ratio is defined as,

$$\rho_{\parallel}(\pi/2) = \frac{n I_{\parallel}(\pi/2)}{n I_{\perp}(\pi/2)}$$

(1.17c)

Here $I$ is scattering intensity, the superscript preceding $I$ defines the relation of the electric vector of the incident radiation with respect to the scattering plane and the subscript following $I$ defines the relation of the electric vector of the scattered radiation to the scattering plane. The subscript $n$ indicates unpolarized incident radiation.
Let us consider the scattering from a molecule placed at the origin of the coordinate system. The molecule is excited along negative $Y$-direction and scattered radiation is observed along $Z$-direction as shown in the figure 1.4. For different states of polarization of the incident radiation the depolarization ratio become,

\[
\rho_{\parallel}(\pi/2) = \frac{I_{\perp}}{I_{\parallel}} = \frac{|P_x|^2}{|P_y|^2} = \frac{\alpha_{xx}^2 E_{z0}^2}{\alpha_{xy}^2 E_{x0}^2} = \frac{(\alpha_{xx})^2_{\text{Sym}} + (\alpha_{xy})^2_{\text{anti Sym}}}{(\alpha_{xx})^2_{\text{Sym}} + (\alpha_{yx})^2_{\text{anti Sym}}} = 1.0
\]  

\[
\rho_{\perp}(\pi/2) = \frac{I_{\perp}}{I_{\perp}} = \frac{|P_x|^2}{|P_y|^2} = \frac{\alpha_{yy}^2 E_{z0}^2}{\alpha_{xy}^2 E_{x0}^2} = \frac{(\alpha_{yy})^2_{\text{Sym}} + (\alpha_{yx})^2_{\text{anti Sym}}}{(\alpha_{yy})^2_{\text{Sym}} + (\alpha_{xx})^2_{\text{anti Sym}}} = \frac{3\gamma^2 + 5\delta^2}{45\alpha^2 + 4\gamma^2}
\]  

\[
\rho_{n}(\pi/2) = \frac{n_{\perp}}{n_{\parallel}} = \frac{|P_y|^2}{|P_x|^2} = \frac{\alpha_{xy}^2 E_{x0}^2 + \alpha_{yz}^2 E_{z0}^2}{\alpha_{xx}^2 E_{x0}^2 + \alpha_{xz}^2 E_{z0}^2} = \frac{\alpha_{xy}^2 + \alpha_{yz}^2}{\alpha_{xx}^2 + \alpha_{xz}^2}
\]  

\[
= \frac{(\alpha_{xy})^2_{\text{Sym}} + (\alpha_{yx})^2_{\text{anti Sym}} + (\alpha_{yz})^2_{\text{Sym}} + (\alpha_{yz})^2_{\text{anti Sym}}}{(\alpha_{xx})^2_{\text{Sym}} + (\alpha_{xx})^2_{\text{anti Sym}} + (\alpha_{xz})^2_{\text{Sym}} + (\alpha_{xz})^2_{\text{anti Sym}}} = \frac{6\gamma^2 + 10\delta^2}{45\alpha^2 + 7\gamma^2 + 5\delta^2}
\]  

(because for natural light $E_{x0}^2 = E_{z0}^2$)
Here $P_i(i=x, y, z)$ is the $i$-th component of induced dipole moment, $E_{i0}$ is the amplitude of the $i$-th component of the incident electric field. Here we have considered electric dipole radiation where radiation intensity is proportional to the square of the electric dipole moment.

From the above discussion we see that $\rho_{\downarrow}(\pi/2)$ is always 1.0. So it is not of practical use. For Raman scattering from non-totally symmetric modes, $a = 0$ and then,

$$\rho_{\downarrow}(\pi/2) = \frac{3}{4} + \frac{5 \delta^2}{4 \gamma^2} \tag{1.19a}$$

$$\rho_{n}(\pi/2) = \frac{6}{7} + \frac{40 \delta^2}{49 \gamma^2} \tag{1.19b}$$

If $\delta = 0$, we have normal polarization with $\rho_{\downarrow}(\pi/2) = \frac{3}{4}$. But if $\delta \neq 0$, $\rho_{\downarrow}(\pi/2) > \frac{3}{4}$ which corresponds to anomalous polarization if $\gamma \neq 0$ and $\rho_{\downarrow}(\pi/2) = \infty$ for $\gamma = 0$, which corresponds to inverse polarization.

For totally symmetric modes, $a \neq 0$; then we have for $\delta = 0$,

$$\rho_{\downarrow}(\pi/2) = \frac{3}{45(a^2/\gamma^2) + 4} \tag{1.20a}$$

and

$$\rho_{n}(\pi/2) = \frac{6}{45(a^2/\gamma^2) + 7} \tag{1.20b}$$

So, we see that $0 \leq \rho_{\downarrow}(\pi/2) < \frac{3}{4}$ and $0 \leq \rho_{n}(\pi/2) < \frac{6}{7}$ according to $\infty \geq \left(\frac{a^2}{\gamma^2}\right) > 0$. If however $\delta \neq 0$, the complete formulas (1.18) are to be used. Note that, for excitation polarized in a direction perpendicular to the scattering plane, anomalous polarization will be observed for $\delta^2 > \frac{27}{4} a^2$ and inverse polarization for $a = \gamma = 0$ [obviously for $\delta \neq 0$].

Group theory generally offers help in determining which invariant are non-zero for particular vibrational mode in molecule of a given symmetry. In principle, this requires knowledge of the symmetry properties of the general polarizability tensor. Note that an irreducible representation containing a rotation component also contains the corresponding component of the anti-symmetric tensor $\alpha_{antiSym}$. Thus the corresponding mode may show inverse polarization if $a = \gamma = 0$. 
1.6 RAMAN INTENSITY

In the Raman process of a molecular system, an incident photon is destroyed, a scattered photon is created and the molecular system undergoes a transition from an initial state to a final state. This process is coherent and therefore these three events are not independent and resolvable i.e. we may not view this process as a sequential absorption and then emission of a photon but instead as a process in which the three events occur more or less simultaneously but individually [21, 26, 27]. If the exciting frequency is such that the molecular excitation is close to or in resonance with an available excited state, the process is called resonance Raman scattering. In varying the excitation frequency from off resonance to on resonance, striking changes in intensity, temporal behavior and frequency distribution generally occur. In spite of these exciting frequency dependent differences, the same theoretical treatment is supposed to be applicable independent of the excitation frequency. It may not be necessary to arbitrarily separate out special region of excitation for separate conditions. If we can study the dependence of intensities of different Raman bands on the exciting frequencies [Raman excitation profiles (REPs)], Raman spectroscopy can be used as a very convenient tool for studying many interesting properties of the molecule concerned. Generally there are three theoretical approaches to study Raman intensities and we shall try to present them here very briefly.

1.6.A Sum-over-states method

The total scattering intensity $I_s$ in photons per molecule per second for a molecular transition from the initial ground state $|G\rangle$ to the final state $|F\rangle$ may be written following the standard formula [2, 12, 28, 29],

$$I_s = K\omega_s^2 \sum_{\rho,\sigma} |(\alpha_{\rho\sigma})_{GF}|^2$$

(1.21)

where $K$ is a constant, $I_s$ is the intensity of the incident laser of angular frequency $\omega_s$ and $\omega_s$ is the angular frequency of the scattered radiation. $(\alpha_{\rho\sigma})_{GF}$ is the polarizability (scattering) tensor with incident and scattered polarizations indicated by $\rho$ and $\sigma$ respectively. Here we have taken average over all orientations. The second order perturbation [Kramers-Heisenberg-Dirac (KHD)] expression for the polarizability is [24],

$$(\alpha_{\rho\sigma})_{GF} = \frac{1}{\hbar} \sum I \left[ \frac{\langle F|P_\rho|I\rangle\langle I|P_\sigma|G\rangle}{\omega_{I} - \omega_{\ell} - i\Gamma_{I}} + \frac{\langle F|P_\sigma|I\rangle\langle I|P_\rho|G\rangle}{\omega_{IF} + \omega_{\ell} - i\Gamma_{I}} \right]$$

(1.22)
Here, $|I\rangle$ is an intermediate state and $\Gamma_i$ is the damping term reflecting the homogeneous width of the state $|I\rangle$ and $P_{\rho\sigma}$ is the $\rho$, $\sigma$-th component of the electric dipole moment of the molecule. For simplicity we have not included the effect of damping of the initial and final states, $|G\rangle$ and $|F\rangle$. All other symbols will be explained later on.

Since we shall be concerning with vibrational Raman spectroscopy, all the states $|G\rangle$, $|F\rangle$ and $|I\rangle$ are vibronic states corresponding to ground (first two) and excited (last one) electronic states. Introducing Born-Oppenheimer approximation to signify the states [30],

$$|I\rangle = \Psi_{II}(q, Q) = \Theta_I(q, Q) \varphi_I(Q) \tag{1.23}$$

where, $q$ represents the set of electronic coordinates and $Q$ the set of nuclear coordinates. In this expression $\Theta_I(q, Q)$ is the electronic wave function for the electronic state $I$ and it has a parametric dependence on the nuclear coordinates $Q$. $\varphi_i(Q)$ is the vibrational wave function in the vibrational state $i$ of the electronic state $|I\rangle$. Similar expressions exist for initial and final states and they are,

$$|G\rangle = \Psi_{Gu}(q, Q) = \Theta_G(q, Q) \varphi_u(Q) \tag{1.24a}$$
$$|F\rangle = \Psi_{Gv}(q, Q) = \Theta_G(q, Q) \varphi_v(Q) \tag{1.24b}$$

Here $G$ is ground electronic state. $u$ is the initial and $v$ is the final vibrational states of the electronic state $|G\rangle$.

Using Born-Oppenheimer type vibronic wave functions, the integrals (over electronic coordinate space) used in equation (1.22) becomes of the form,

$$\langle F | P_{\rho} | I \rangle = \langle \Theta_G(q, Q) \varphi_v(Q) | P_{\rho} | \Theta_I(q, Q) \varphi_I(Q) \rangle$$
$$= \langle \varphi_v(Q) | \Theta_G(q, Q) | P_{\rho} | \Theta_I(q, Q) \rangle \bigg| \varphi_I(Q) \bigg>$$
$$= \langle \varphi_v(Q) | P_{\rho} | \Theta_G(q, Q) | \varphi_I(Q) \rangle \bigg> \tag{1.25}$$

Again, the nuclear coordinate dependence of electronic wave function may be expressed by Herzberg-Teller approximation [31]. The Hamiltonian expressing the motion of electrons in a nuclear configuration is given by,

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \sum_k \frac{Z_k e^2}{\theta_{ik}}$$
$$\equiv H_0 + \sum_k \left( \frac{\partial H}{\partial Q_k} \right)_o (Q_k - Q^o_k)$$
Here $m_e$ is the electronic mass, $Z_k$ is the atomic number of the $k$-th atom at a distance $\varphi_{ik}$ from the $i$-th electron. It is also assumed that the equilibrium value of the $k$-th normal coordinate ($Q_i^0$) is zero for all $k$’s. So according to the perturbation theory [30, 32],

$$|I(Q)| = |I(Q_o)| + \sum \sum_{kS} \frac{\langle S|\left(\frac{\partial H}{\partial Q_k}\right)|I\rangle_o}{E_I^o - E_S^o} Q_k |S(Q_o)\rangle \quad (I.27)$$

The second term on the right hand side of equation (I.27) indicates mixing of the electronic states $|I\rangle$ and $|G\rangle$ through the operator $\left(\partial H/\partial Q_k\right)$. The substitution of this equation (I.27) in the equation (I.25), we get,

$$\langle F|P_{\rho}|I\rangle = \langle F|P_{\rho}|G\rangle + \sum \sum_{S \ k} \frac{\langle S|\left(\frac{\partial H}{\partial Q_k}\right)|I\rangle_o}{E_I^o - E_S^o} \langle P_{\rho}|G_S\rangle \langle v|Q_k|i\rangle \quad (I.28)$$

Here the mixing of the ground electronic state with other excited electronic state has been neglected, because of the large value of the energy differences $(E_G^o - E_S^o)$ appearing in the denominator of the mixing part of the perturbed wave function [see equation (I.27)]. Thus under first order perturbation calculation, the scattering tensor $\alpha_{\rho\sigma}$ of the equation (I.22) becomes [12, 29],

$$\alpha_{\rho\sigma} = A + B = A + (B_1 + B_2) \quad (I.29)$$

where,

$$A = \frac{1}{\hbar} \sum \sum_{i} \left[ \frac{(P_{\rho})^o_{GI} (P_{\sigma})^o_{IG} + (P_{\sigma})^o_{GI} (P_{\rho})^o_{IG}}{\omega_{li} + \omega_o - i\Gamma li} \right] \times \langle v|i\rangle \langle i|u\rangle \quad (I.30a)$$

$$B_1 = \frac{1}{\hbar} \sum \sum \sum \sum_{i \ k} \left[ \frac{(P_{\rho})^o_{GI} \left(\frac{\partial H}{\partial Q_k}\right)^o_{IS} (P_{\sigma})^o_{SG}}{\omega_{li} + \omega_o - i\Gamma li} \times \frac{\langle v|i\rangle \langle i|Q_k|u\rangle}{E_I^o - E_S^o} \right. + \left. \frac{(P_{\rho})^o_{GS} \left(\frac{\partial H}{\partial Q_k}\right)^o_{SI} (P_{\sigma})^o_{IG}}{\omega_{li} + \omega_o - i\Gamma li} \times \frac{\langle v|Q_k|i\rangle \langle i|u\rangle}{E_I^o - E_S^o} \right] \quad (I.30b)$$

and
The A-term appears due to the contribution from the Frank-Condon overlap integral (called Albrecht A-term) and the other terms (i.e. Albrecht B-term) appears due to vibronic mixing of two electronic states. These are also known as Herzberg-Teller term [12, 33-90].

For the excitation of the fundamental vibration in the Raman spectra, the A-term can be written as, [changing all the angular frequencies \((\omega's)\) into the corresponding wavenumbers \((\nu's)\) by the relation \(\omega = 2\pi c\nu\)]

\[
A = \frac{1}{ch} \sum_i (P_\rho)_G (P_\sigma)_G \sum \left[ \frac{1}{\nu_{ii} - \nu_o - i\Gamma_{ii}} + \frac{1}{\nu_{ii} + \nu_o - i\Gamma_{ii}} \right] \langle i|j\rangle \langle j|0\rangle
\]

where, \(ch\nu_{ii}G0 = [E_{ii} - E_{G0}]\) and \(ch\nu_{ii}G1 = [E_{ii} - E_{G1}]\). \(\langle i|j\rangle\) and \(\langle i|0\rangle\) are the vibrational overlap integrals. '1' and '0' in the vibrational overlap factor refer to vibrational quantum numbers of the respective normal modes under consideration in the ground electronic state. Again \(P_{\rho/\sigma}\) is \((\rho/\sigma)\)-th component of the electronic dipole moment \((\rho/\sigma = x, y, z)\), \(\nu_o\) is the excitation wavenumber (and is equal to \(\omega_o/2\pi c\)) and \(\Gamma_{ii}\) is the half width of the vibronic state \(|ii\rangle\) in the wavenumber unit.

Under the assumption of no Duschinsky's mixing [91], the multimode expression for the vibrational overlap part of equation (1.31), for the excitation of the \(\alpha\)-th Raman fundamental, becomes,

\[
\langle 1|j\rangle\langle j|0\rangle = \langle 1\alpha|1\alpha\rangle \langle i\alpha|0\alpha\rangle \times \prod_{b\neq\alpha} \langle 0\beta|i\beta\rangle \langle i\beta|0\beta\rangle
\]

The vibrational overlap factors may be determined on the basis of simple harmonic oscillator type vibrational wave function. The overlap integrals, obtained from the recurrence relation of Manneback [92], are found to be functions of the displacement of the potential minimum of the excited electronic state with respect to that of the ground electronic state along the concerned normal coordinates i.e. \(\Delta_{\alpha}^I = (Q_{\alpha I} - Q_{\alpha G})_o\) and of the wavenumbers of the
corresponding normal modes in the excited \((\bar{\nu}_a)_I\) and ground \((\bar{\nu}_a)_G\) electronic states.

In case of small displacement of the excited state potential minimum with respect to that of the ground state, the vibrational overlap integral part of the above equation (I.32) becomes (neglecting the variation of normal mode wavenumbers in different electronic states),

\[
\langle |i\rangle \langle i| \hat{O} \rangle = \langle |i_a\rangle |i_a\rangle \langle 0_a\rangle = + \Delta^E_a \quad \text{for } i_a = 0
\]

\[
= - \Delta^E_a \quad \text{for } i_a = 1
\]

With the simplification as mentioned above, the equation (I.31) becomes,

\[
A = \frac{1}{\hbar} \sum_{l} \sum \left( p_\rho \right)_{GI} \left( p_\sigma \right)_{IG} \nu_a \Delta^I_a \times \frac{1}{(\nu_{IG} - \nu_0 - i\Gamma_I)} \frac{1}{(\nu_{IG} + \nu_0 - i\Gamma_I)}
\]

where, \(\nu_a\) is the wavenumber of the \(a\)-th Raman mode and it is assumed that \((\bar{\nu}_a)_I = (\bar{\nu}_a)_G = \nu_a\) and \(\Gamma_i = \Gamma_I\) all \(i\)'s. For normal Raman excitation (i.e. for excitation far from resonance), \(\nu_a\) and \(\Gamma_I\) can be neglected in comparison with \((\nu_{IG} \pm \nu_0)\), appearing in the denominators of the above equation (I.34). Thus equation (I.34) reduces to,

\[
A = \frac{1}{\hbar} \sum_{l} \sum \left( p_\rho \right)_{GI} \left( p_\sigma \right)_{IG} \nu_a \Delta^I_a \frac{\nu_{IG}^2 + \nu_0^2}{(\nu_{IG}^2 - \nu_0^2)^2}
\]

Under similar kind of assumption, for non-resonance condition, the \(B = B_I + B_2\)-term in equations (I.30b) and (I.30c) can be written as follow,

\[
B = \frac{2}{(\hbar)^2} \sum_{l} \sum \left( p_\rho \right)_{GI} h_{IS}^a \left( p_\sigma \right)_{SG} \left( p_\sigma \right)_{IG} + \left( p_\rho \right)_{GS} h_{SI}^a \left( p_\sigma \right)_{IG}
\]

\[
\times \frac{\nu_{IG} \nu_{SG} + \nu_0^2}{(\nu_{IG}^2 - \nu_0^2)(\nu_{SG}^2 - \nu_0^2)} \langle |i_a\rangle |Q_a\rangle |0_a\rangle
\]

where, \(h_{IS}^a = \langle |i_a| \frac{\partial H}{\partial Q_a} |S\rangle_0 \). Thus it can be shown from equations (I.35) and (I.36) that excitation wavenumber dependence parts of the polarizability tensor are of similar form: the \(A\)-term receives contribution only from a single state, whereas the later receives contribution from two states.
A good idea about the normal modes \( Q_a \)'s and critical studies of REPs may provide some valuable information regarding molecular structures in the excited electronic states in terms of \( \Delta_a^I \)'s, the measure of molecular distortion in the \( I \)-th electronic state along the \( a \)-th normal mode \( Q_a \). This kind of investigation may also throw some light on the nature of vibronic interaction between two electronic states through different normal modes of vibration. For totally symmetric vibration, only diagonal components of the polarizability tensor \( (\alpha_{pp}) \) are expected to take part in the scattering phenomenon and in that case the Raman intensity, when measured in terms of a quantity proportional to the number of scattered photons, (following equation I.) becomes,

\[
I_{0I}^a = K (\overline{\nu}_o - \overline{\nu}_a)^3 |(\alpha_{pp})|^2
\]

\[
= K (\overline{\nu}_o - \overline{\nu}_a)^3 \left[ \sum_i F_A \overline{\nu}_a \Delta_a^i \left( \frac{\nu_{IG}^2 + \nu_o^2}{\nu_{IG}^2 - \nu_o^2} \right) + \sum_j(\nu_{IG}^2 + \nu_{SG}^2 + \nu_o^2) \left( \frac{\nu_{IG}^2 - \nu_o^2}{\nu_{SG}^2 - \nu_o^2} \right) \right]^2
\]

where '\( K \)' is a constant and '\( F_A \)' & '\( F_B \)' are the factors which can be found from equation (1.35) and (1.36), respectively. The first term in the square brackets in equation (1.37) is the A-term and the second term is the B-term contribution. Their interference may sometime be significant, as discussed by Mitra et al. [93], Albrecht et al. [33-37] and Clark et al. [40-45]. The expression shown in the above equation (1.37), describes a steady state scattering process and contains no explicit reference to time. Therefore, the Raman theory, which is based on KHD dispersion relation, is also termed as 'time independent theory'.

In the present investigation, theoretical excitation profiles are calculated on basis of the formula given by equation (1.37) considering the two terms ('A' and 'B') separately. For each normal mode the theoretical A-term or B-term intensities are normalized relative to the respective intensities for a particular excitation wavelength. By comparison of the observed REPs with those calculated from equation (1.37), an idea that which modes produce comparatively large displacements of the potential minima of various electronic states along the relevant normal modes and which ones produce less, can be obtained. Once these are known, employing the idea of multimode phenomenon, the REPs can be calculated by applying the resonant part of equation (1.30) and by introducing, along with others, certain parametric values of \( \Delta_a^I \)'s, to fit the experimental Resonance REPs.
1.6.8 Time dependent picture

The time dependent formulation of Raman scattering (particularly resonance Raman) has been introduced by Hizhnyakov and Tehver [94], Kiffer [95-100] Lee and Heller [101], Heller et al. [102], Tannor and Heller [103], and Mayers et al. [104-106]. Its derivation is strikingly simple. Through a straightforward mathematical transformation [104], the Kramers-Heisenberg-Dirac (KHD) dispersion relation can be transformed into an integral over time only for the vibronic part of the polarizability in the Condon approximation. Considering only the vibronic expression for the polarizability tensor, at resonance condition the A-term as given by equation (I.30a) may be written as,

\[ A = \frac{1}{\hbar} \sum_{i} \left( P_{\rho}^{G} \left( P_{\sigma} \right)^{G}_{i} \left[ \frac{1}{\nu_{li} - \nu_{Gu} - \nu_{o} - i\Gamma_{li}} \right] \right) \langle Gv \mid i \rangle \langle li \mid Gu \rangle \]  

(1.38)

where, \(|u\rangle\) and \(|v\rangle\) are initial and final vibrational states of the electronic ground state \(|G\rangle\) in the Raman process. Using \(c\nu_{li} = c\nu_{li} = \left(E_{i} - E_{u}\right)\), \(\hbar \nu_{o} = E_{\ell}\) and \(c\ell\Gamma_{li} = \Gamma\), the following expression may be obtained,

\[ \alpha_{uv} \propto \sum_{i} \left[ \frac{1}{E_{i} - E_{u} - E_{\ell} - i\Gamma} \right] \langle v \mid i \rangle \langle i \mid u \rangle \]  

(1.39)

Here, the term \(\left( P_{\rho}^{G} \left( P_{\sigma} \right)^{G}_{i} \right)\) is constant, as intensity contribution comes from a particular excited electronic state \(|I\rangle\) when the exciting radiation is at near resonance condition, and so is not included in equation (1.39). Now the denominator of the above equation (1.39) can be transformed into a time dependent expression using a trivial mathematical relation,

\[ \frac{1}{S} = \frac{i}{\hbar} \int_{0}^{\infty} e^{\frac{i}{\hbar} St} dt \]

where, 'S' is a complex quantity, say, \(S = a - ib\), 'a' and 'b' being positive real constants. \(\alpha_{uv}\) then results in

\[ \alpha_{uv} \propto \frac{i}{\hbar} \sum_{i} \int_{0}^{\infty} \langle v \mid i \rangle \langle i \mid u \rangle \exp \left\{ -i(E_{i} - E_{u} - E_{\ell} - i\Gamma)\frac{t}{\hbar} \right\} dt \]  

(1.40)

Since,

\[ \langle i \mid e^{-i\frac{E_{i}}{\hbar}} = \langle i \mid e^{-i\frac{H_{\ell}}{\hbar}} \]  

(1.41)

where, '\(H_{\ell}\)' is the vibrational Hamiltonian of the excited electronic state \(|I\rangle\), the equation (1.40) can be written as,
\[ \alpha_{uv} \propto \frac{i}{\hbar} \int_0^\infty \sum_i \langle v | i | e^{-iHt/\hbar} | u \rangle \exp \left\{ (E_u + E_\ell + i \Gamma) t / \hbar \right\} dt \]  

(1.42)

If the propagator \( \exp(-iHt/\hbar) \) is now considered to operate on the right side, then

\[ e^{-iHt/\hbar} | u \rangle = | u(t) \rangle \]  

(1.43)

The final result can be obtained for \( \alpha_{uv} \) by using closure property to remove the sum over state \( i \):

\[ \alpha_{uv} \propto \frac{i}{\hbar} \int_0^\infty \langle v | u(t) \rangle e^{-i\Gamma t/\hbar} \exp \left\{ (E_u + E_\ell) t / \hbar \right\} dt \]  

(1.44)

The resonance Raman intensity is then obtained by inserting \( \alpha_{uv} \) of equation (1.44) into equation (1.21).

The quantity \( \langle v | u(t) \rangle e^{-\Gamma t/\hbar} \) has been termed Raman overlap [106]. It is the product of the modulus of a time dependent Frank-Condon factor between the final state and the initial wavefunction propagated on the upper electronic state potential energy surface, i.e. \( \langle v | u(t) \rangle \) and a damping factor \( e^{-\Gamma t/\hbar} \) which decreases exponentially with time.

The expressions for \( \alpha_{uv} \) and \( I_{uv} \) have the intuitively appealing interpretation of resonance Raman scattering schematically shown in the figure [1.5] according to Myers and Mathies [106]. The resonance Raman scattering process starts from state \( |u \rangle \), which is a vibrational eigenstate of the ground electronic surface, represented by a harmonic potential function. At time zero, the interaction of the electronic transition moment with the incident radiation causes a vertical transition to the excited electronic surface. The vibrational state \( |u \rangle \), now finding itself under the influence of a Hamiltonian (H), begins to evolve with time. If the ground and excited surfaces are significantly displaced, the wave-packet \( |u(t)\rangle \), quickly moves away from its initial position and reaches the right side of the excited state potential function (dashed line in figure [1.5], panel A). There it is reflected and moves to positions of shorter inter-nuclear distances. In the further process it oscillates between the inner and outer classical turning points until the wavefunction is damped out by the function \( e^{-\Gamma t/\hbar} \). During propagation, \( |u(t)\rangle \) wave packet crosses regions with high overlap with the wavefunction \( |v \rangle \) of the ground electronic state. For the case illustrated in figure [1.5] a maximum overlap is
reached soon (a few fs) after initial propagation (point 1 in panel A). Hence the Raman
overlap function $\langle v | u(t) \rangle e^{-\frac{t^2}{\hbar}}$ has a maximum at this time-point [shown in panel B, where
the Raman overlap is plotted as a function of time]. It then decreases as $|u(t)\rangle$ moves far
away from $|v\rangle$ (point 2), increases to another maximum (point 3) on the return trip with less
amplitude because of small damping, and goes to zero at the end of one full cycle (point 4),
where $|u(t)\rangle$ is orthogonal to $|v\rangle$. Reflection at the left side of the excited state potential
function causes further peaks in the Raman overlaps. This continues until $|u(t)\rangle$ is damped
out. Only three vibrational periods are depicted in panel B of figure [1.5].

Since the Raman intensity $|I_{uv}|$ is proportional to the modulus square of $\alpha_{uv}$, the
Raman excitation profile $[I_{uv} = I_{uv}(v_o)]$ can be directly calculated by a half Fourier
transformation of Raman overlap [equation (1.44)]. This has been done in panel C of figure
[1.5], where for the case discussed in panel B and C, the Raman intensity is plotted as a
function of excitation energy ($E_t = h\nu_o$)

It is very difficult to experimentally obtain the values of scattering cross-section.
However, it is relatively easy to obtain the intensity of a given normal mode (say $k$-th) relative
to that of another mode (say $k'$-th). A simple expression relating to the relative intensities has
been derived by Heller et. al. [103, 107], J. I. Zink [108, 110] for the special conditions of
harmonic oscillators, no Duschinsky rotation, no change in normal mode frequencies on
electronic excitation and pre-resonance (short time) condition spectra. Under these conditions
the relative intensities of two modes is given by,

$$\frac{I_k}{I_{k'}} = \frac{\nu_k^2}{\nu_{k'}^2} \frac{\Delta_k^2}{\Delta_{k'}^2}$$

where, $\Delta_k$'s are the displacements of the upper potential energy curve with respect to the
ground state one along the $k$-th normal mode. The important experimental condition, which
must be fulfilled, is the short time, pre-resonance condition. When the exciting frequency is
slightly off-resonance with the excited electronic state of interest, the propagation time of the
wave packet on the upper potential energy surface is governed by the time-energy uncertainty
principle $\Delta \omega \Delta t \sim 1$, where $\Delta \omega$ is the frequency mismatch. Under short time conditions, the
wave packet moves in a region localized near the equilibrium geometry of the ground
electronic state i.e. Frank-Condon region. The pre-resonance Raman intensity is dominated by
the slope of the upper potential energy surface determined in this region. The greater the
slope, the greater is the motion of the wave-packet, the greater is the overlap with the final state and greater is the intensity.
I.6.C Transform Theory

We know, the study of resonance Raman scattering intensities as a function of incident wavelengths i.e. the excitation profile is an important tool for investigating vibronic coupling in molecules or electron-phonon interactions of impurities in solids. This theory provides a method of calculating the said profile from the available optical absorption spectral data. The relation, through which, the resonance Raman excitation profile is calculated, is valid for arbitrary electron-phonon coupling strengths. Interference effects arising from electron-phonon coupling involving an arbitrary number of normal modes are automatically included. Moreover, it holds for non-zero temperatures.

Here we shall discuss only the basic formalism of the theory developed on the basis of some standard assumptions regarding the scattering system, [111-168] namely : (i) adiabatic (Born-Oppenheimer) and Franck-Condon approximation, (ii) a single excited electronic state, (iii) harmonic approximations for the vibrations (harmonic phonons) and (iv) linear electron-phonon coupling (i.e. linear coupling between excited electronic state and phonons). This theory considers a full adiabatic basis set, as opposed to a “crude” adiabatic basis set [129], which includes just electronic states evaluated at the equilibrium configuration. The Condon approximation consists of replacing the electronic transition dipole matrix elements, which are functions of atomic displacements or normal modes ($R_k$’s or $Q_k$’s), by their values for the equilibrium configuration i.e. ($R_k$’s = 0, $Q_k$’s = 0). This approximation is generally assumed to hold for resonance Raman scattering [34].

The harmonic approximation allows us to write the vibrational hamiltonian appropriate to the ground electronic state in the harmonic oscillator form:

$$H_0(Q_k) = \frac{1}{2} \sum_k Q_k^2 + \omega_k Q_k^2$$  \hspace{1cm} (I.46)

where, $Q_k$ and $\omega_k$ are the normal mode and angular frequencies of the $k$-th mode. Finally, the assumption of linear electron-phonon coupling means that the difference between the system’s vibrational Hamiltonian for the excited and ground electronic states is taken to be linear in atomic displacements ($R_k$’s) or equivalently normal modes ($Q_k$’s):

$$H_i(Q_k) = H_0(Q_k) + \hbar \omega_{lo} + \sum_k A_k Q_k$$  \hspace{1cm} (I.47)

thus the excited and ground state normal coordinates differ only in the equilibrium positions for the former is displaced by $\left(- \frac{A_k}{\omega_k^2}\right)$ from those of the latter.

The relation that allows one to compute Raman intensity profile line-shapes from those
for optical absorption is implicit in any model based upon the use of the standard assumptions to evaluate the KHD formula (with relative damping included) for the case of resonance secondary radiation. In particular, the correlator formulation of Hizhnyaker and Tehver [94, 130] was worked out exactly by them within the standard assumption and for all temperatures. The result for the intensity $I_k(\omega_n)$ of the first order Stokes scattering by $k$-th normal mode for incident light of frequency $\omega_n$ may be expressed as,

$$I_k(\omega_L) = B_k \omega_L \omega_S^3 |\phi(\omega_L) - \phi(\omega_L - \omega_k)|^2$$  \hspace{3cm} (1.48)

where, $\omega_S = \omega_L - \omega_k$ is scattering frequency and $B_k$ is a function of the normal mode $(k)$ but is independent of $\omega_k$. The function $\phi(\omega_L)$ is determined from the optical absorption $\alpha(\omega)$ through normalized line-shape function.

$$I(\omega) = \left[ \int \frac{\alpha'(\omega')}{\omega'} d\omega' \right]^{-1} \frac{\alpha(\omega)}{\omega}$$  \hspace{3cm} (1.49)

according to,

$$\phi(\omega_L) = P \int \frac{I(\omega)}{(\omega - \omega_L)} d\omega - i\pi I(\omega_L)$$  \hspace{3cm} (1.50)

Thus $\phi$ is proportional to the complex susceptibility associated with the electronic transition and for the case of a very strongly phonon broadened absorption band one sees from equation (1.48) that the Raman intensities involve the square magnitude of the frequency derivative of $\phi$.

For optical light frequencies $\omega_S \approx \omega_L$ and therefore it is customary to plot $I_k'(\omega_L)$ versus $\omega_L$, where,

$$I_k'(\omega_L) = \frac{I_k(\omega_L)}{\omega_L^4} = B_k |\phi(\omega_L) - \phi(\omega_L - \omega_k)|^2$$  \hspace{3cm} (1.51)

Equation (1.50) and (1.51) are the basis of the calculation. Optical absorption data are used to form $I(\omega)$, from which $\phi(\omega_L)$ is computed numerically according to equation (1.50). One then simply plot the profile line-shape $I_k'(\omega_L)$ versus $\omega_L$ according to equation (1.51).

Notice that equation (1.51) predicts that two different modes of equal frequencies would give rise to the same profile line-shape, even though their electron-phonon coupling strengths $(A_k's)$ may differ. Variation of the two modes' relative coupling strengths would change both the optical absorption line-shape and the line-shape and relative intensities of the two profiles, but as the absorption and profiles vary, their line-shapes nevertheless remains related through equation (1.50) and (1.51). Insight into this behavior can be obtained by considering the individuals formulas for the absorption and profile line-shapes [111, 112]. It is
thus found (for T = 0 K)

\[ \alpha(\omega) = C \omega \sum_{\beta_1} \ldots \sum_{\beta_N} \frac{\Gamma}{\beta_1! \beta_k!} \left( \omega_L - \sum_{k'} \beta_{k'} \omega_{k'} \right)^2 + \Gamma^2 \]  

(1.52)

and

\[ I_k'(\omega_L) = D b_k^2 \sum_{\beta_1} \ldots \sum_{\beta_N} \frac{\Gamma}{\omega_L - \sum_{k'} \beta_{k'} \omega_{k'} - i \Gamma} \prod_{k'} \beta_{k'}! \]  

(1.53)

Here \( b_k = \left[ (\hbar \omega_k) \beta_k^2 \right]^{-1} A_k \), the sum over \( \beta_k \) run over 0, 1, 2, \ldots and products run over system's \( N \) normal modes. The constants \( C \) and \( D \) are independent of light frequency and do not affect the line-shapes, \( \omega_{i o} \) is the frequency of the zero phonon transition and \( \Gamma \) represents the radiative (natural) broadening of the electronic transition. These formulas are readily derived by generalizing the arguments of Martin and Onari [131] who used the standard assumptions for the case of a single normal mode to evaluate phonon overlap integrals in terms of explicit vibrational wavefunctions. \( \Gamma \) is used as the observed broadening of vibronic lines which does not affect the relation between \( \alpha(\omega) \) and \( I_k'(\omega_L) \) that is the basis of the calculation [equation (1.50) and (1.51)]. Raman spectrum for incident light in resonance with the zero phonon transition may be used to obtain numerical values for the linear coupling parameters \( (A_k)'s \) of different normal modes. These can be used to compute the optical absorption and Raman profiles within the standard assumptions and with the widths [\( \Gamma \) of equation (1.52)] of the vibronic lines adjusted so as to best fit the absorption [132].

We however have presented the transform theory based on the said standard assumptions. This theory on time correlation formalism has been extended far beyond these assumptions inducting non-Condon effect, non-adiabatic terms, multiple excited electronic states, multi-mode effects etc. [11-127, 133-145].
1.6.D Determination of excited state structure of polyatomic molecule

Experimental Raman intensity data from polyatomic molecules can be analysed in order to derive structural information on excited electronic states. The direct modeling approach involves searching for the complete set of excited-state parameters that generate the best fit to the experimental absorption and resonance Raman data. The calculations may be carried out by using either the sum-over-states or the time-dependent method, whichever is more efficient for the specific problem. In the alternative transform method, the experimentally absorption spectrum is used to directly generate a theoretical excitation profile for each observed mode and the excited-state displacement in each mode is then chosen to give the best fit between the calculated and experimental intensities.

1.7 NORMAL COORDINATE CALCULATION

The basic principle in calculating the vibrational frequencies of a molecule is to generate and solve a secular equation [20, 169-171]. For this the kinetic and potential energies are written down and a Lagrangian is formed. Then applying Lagrange's equation a secular equation is made and solved. When ordinary coordinate system (Cartesian coordinate) is used, the method not only becomes inefficient to be useful for molecules even of moderate size, but becomes physically unrealistic in the sense that it is difficult to get any correlation between the force fields of molecules even of similar types. This, on the other hand, means that the idea of transferability of force fields even among molecules of similar types becomes vague.

The difficulty is much remedied when we introduce the idea of internal coordinates such as bond stretching, angle bending, wagging and torsion. These coordinates are physically meaningful and the associated force fields of related compounds can be correlated. Besides, along with the internal coordinate system, when the concept of symmetry and group theory is introduced, the secular equation may be factored into several smaller dimensional equations and hence the method becomes further simplified.

1.7.A Internal Coordinate

The changes in bond lengths and bond angles, wagging and torsional motion of a localized part of a molecule can be used to provide a set of internal coordinates which remain unaffected by translation or rotation of a molecule as a whole. These are practically important because they provide the most significant set to be used in describing the potential energies
of a molecule. The kinetic energy, on the other hand, is more easily set up in terms of Cartesian displacement coordinates of the atoms in the molecule. So a relation between these two types of system is therefore needed.

The $i$-th internal coordinates $R_i$ of the molecule under consideration is related with various Cartesian displacement coordinates ($\xi_i$'s) of the atoms in the molecule by the following equation,

$$R_i = \sum_{i=1}^{3N} B_{ii} \xi_i$$  \hspace{1cm} (I.54)

where, $N$ being the number of atoms in the molecule. $B_{ii}$ are coefficients determined by the geometry of the molecule. Instead of using three Cartesian coordinates to describe the displacement of an atom, it is convenient to introduce a vector $\vec{p}_\alpha$ for each atom $(\alpha)$ whose components along the three coordinate axes are the Cartesian displacement coordinates $\xi_i$, $\xi_i'$ and $\xi_i''$ for that atom $(\alpha)$. Likewise it is useful to group the coefficients $B_{ii}$ for a given $R_i$ into sets of three, each set $B_{ii}$, $B'_{ii}$ and $B''_{ii}$ being associated with a given atom $(\alpha)$. These quantities can be considered as the components of a vector $\vec{s}_{i\alpha}$ associated with that atom $(\alpha)$ corresponding to that internal coordinates $R_i$. Then the above equation (I.54) becomes,

$$R_i = \sum_{i=1}^{N} \vec{s}_{i\alpha} \cdot \vec{p}_\alpha$$  \hspace{1cm} (I.55)

This form has the advantage that it is now unnecessary to specify any axis for the displacement coordinates. Furthermore, simple rules can be worked out for writing down the vectors $\vec{s}_{i\alpha}$.

The physical meaning of this vector $\vec{s}_{i\alpha}$ is as follows: let all the atoms except the atom $(\alpha)$ be in their respective equilibrium position. The direction of $\vec{s}_{i\alpha}$ is the direction which a given displacement of the atom $(\alpha)$ will produce the greatest displacement of $R_i$. The magnitude of $\vec{s}_{i\alpha}$ is equal to the increase in $R_i$ produced by unit displacement of the atom in this most effective direction. This statement comes from the consideration of equation (I.55).

### I.7.B Determination of s-vectors

**{a} Bond stretching:** Let $R_i$ be the increase in the distance between the atoms 1 and 2 (figure 1.6). Clearly the most effective (or efficient) direction to displace the end atoms is along the line connecting them, but in directions away from each other. Furthermore, the vectors $\vec{s}_{11}$ and $\vec{s}_{12}$ should be unit vectors. For the coordinate $R_i$, all other vectors $\vec{s}_{i\alpha}$ ($\alpha \neq$
1, 2) are zero, since displacements of all other atoms will not affect \( R_t \). It is often convenient to express the vectors \( \mathbf{s}_{t\alpha} \) in terms of unit vectors along certain chemical valence bonds. Let \( \mathbf{e}_{\alpha\beta} \) denotes unit vector directed from atom \( \alpha \) towards \( \beta \). Thus when \( R_t \) is the extension of the bond between the atoms 1 and 2, then,

\[
\mathbf{s}_{1t} = \mathbf{e}_{12} = -\mathbf{e}_{21} \\
\mathbf{s}_{2t} = \mathbf{e}_{12} = -\mathbf{e}_{21}
\]

(b) **Valence angle bending:** Let \( R_t \) be the increase in the angle between the valence bonds (connecting the atoms 1 & 3 and the atoms 2 & 3) attached to the atom 3 as shown in figure 1.7. Then the directions of \( \mathbf{s}_{t1} \) and \( \mathbf{s}_{t2} \) of the end atoms are perpendicular to the side 1,3 and 2,3 respectively of the bond angles and are pointed outwards, since these are the directions in which the displacements of the respective atoms 1 and 2 will be most effective in increasing the bond angle. The vector \( \mathbf{s}_{t3} \) of the apex atom 3 is determined from the fact that a rigid displacement of the whole molecule does not alter the bond angles. The \( \mathbf{s} \) vectors, thus found for the increase in bond angle, are,

\[
\mathbf{s}_{t1} = \frac{\mathbf{e}_{31} \cos \varphi - \mathbf{e}_{32}}{r_{31} \sin \varphi} \\
\mathbf{s}_{t2} = \frac{\mathbf{e}_{32} \cos \varphi - \mathbf{e}_{31}}{r_{32} \sin \varphi}
\]
\[ \ddot{\mathbf{s}}_{13} = \left( \frac{r_{31} - r_{32} \cos \phi}{r_{31} r_{32}} \right) \mathbf{e}_{31} + \left( \frac{r_{32} - r_{31} \cos \phi}{r_{31} r_{32}} \right) \mathbf{e}_{32} \]

\[ = -\left( \ddot{\mathbf{s}}_{11} + \ddot{\mathbf{s}}_{12} \right) \quad (1.57c) \]

(c) Wagging: It is an angle between a bond and a plane defined by two bonds. This type of internal coordinate is also very useful and is shown in figure 1.8a and 1.8b. The internal coordinate is the angle formed by the bond 4,1 and the plane of three atoms 2, 3 and 4, all four atoms being in one plane at equilibrium position. From the general consideration, the \( \mathbf{s} \)-vectors for all the atoms will be perpendicular to the equilibrium plane. The length of \( \ddot{\mathbf{s}}_{11} \) is seen to be \( 1/r_{41} \). The effect of displacements of other atoms 2, 3 and 4 can be found by applying rigid rotations and translations to the whole molecule so as to bring 2, 3 and 4 back to their original positions, with a consequent calculable additional displacements of atom 1, the effect of which is now known. The result of this procedure turns out to be, for the absolute values \( R_{\mathbf{s}} \) of the vectors, 

\[ \ddot{\mathbf{s}}_{11} = \frac{1}{r_{41}} \quad \text{"end atom"} \quad (I.58a) \]

\[ \ddot{\mathbf{s}}_{12} = \frac{\sin \phi_2}{r_{42} \sin \phi_1} \quad \text{"anchor atom"} \quad (I.58b) \]

\[ \ddot{\mathbf{s}}_{13} = \frac{\sin \phi_3}{r_{43} \sin \phi_1} \quad \text{"anchor atom"} \quad (I.58c) \]

\[ \ddot{\mathbf{s}}_{14} = \frac{1}{r_{41}} - \frac{\sin \phi_2}{r_{42} \sin \phi_1} - \frac{\sin \phi_3}{r_{43} \sin \phi_1} \quad \text{"apex atom"} \quad (I.58d) \]
Figure 1.8b  Wagging (side view). The position marked by $1'$ is the location of atom 1 would occupy if the distorted molecule is subjected to rigid rotations and translations which restore atoms 2, 3 and 4 to their original plane.

For the general case when all four atoms are not coplanar, the $s$-vectors are,

$$s_t = \Delta \varphi$$

where $\varphi$ is an unit vector along $i$ to $j$.

\[ \begin{align*}
\bar{s}_{t1} &= \frac{1}{r_{41}} \left( \frac{\bar{e}_{42} \times \bar{e}_{43}}{\cos \theta \sin \varphi_1} - \bar{e}_{41} \tan \theta \right) \\
\bar{s}_{t2} &= \frac{1}{r_{42}} \left( \frac{\bar{e}_{43} \times \bar{e}_{41}}{\cos \theta \sin \varphi_1} - \frac{\tan \theta}{\sin^2 \varphi_1} \left( \bar{e}_{42} - \bar{e}_{43} \cos \varphi_1 \right) \right) \\
\bar{s}_{t3} &= \frac{1}{r_{43}} \left( \frac{\bar{e}_{41} \times \bar{e}_{42}}{\cos \theta \sin \varphi_1} - \frac{\tan \theta}{\sin^2 \varphi_1} \left( \bar{e}_{43} - \bar{e}_{42} \cos \varphi_1 \right) \right) \\
\bar{s}_{t4} &= -\bar{s}_{t1} - \bar{s}_{t2} - \bar{s}_{t3}
\end{align*} \]  

(D) **Torsion:** Another type of internal coordinate which may be useful in the change in the dihedral angle $\Gamma$, between the planes determined by atoms 1,2,3 and 2,3,4 respectively, when atoms 1 to 4 are bonded in the sequence (figure 1.9a and 1.9b). The magnitude of the dihedral angle may be determined in accordance with following convention: let $\Gamma$ be restricted to the interval $-\pi < \Gamma \leq \pi$; then $\Gamma$ is positive if, viewing the atoms along the bond 2,3 with 2 nearer the observer than 3, the angle from the projection of 3,4 is faced in the clockwise sense. The $s$-vectors thus found are,
where the expressions in brackets (14) and (23) indicate that the latter vectors can be obtained by permutation of the atom subscripts by 1 & 4, and 2 & 3 in the expressions for the first two vectors.

1.7.C G-Matrix and Kinetic Energy

We define the quantities $G_{tt'}$, which are used very frequently in the vibrational problem, as,

$$G_{tt'} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ti} B_{t'i}^*$$

where, $t$ and $t'$ correspond to two internal coordinates (same or different). Here $m_i$ is the mass of the atom to which the subscript $(i)$ refers and the coefficients $B_{ti}$ have previously been introduced [equation (1.59)] to relate the internal coordinates $R_i$ with the Cartesian displacement coordinates $\xi_i$.

Instead of $3N$ coefficients $B$ (for each $R_i$), it is convenient to use the $N$ vectors $\tilde{s}_{t\alpha}$,
one for each atom. Thus it can be rewritten as,
\[ G_{ii'} = \sum_{\alpha=1}^{N} \mu_{\alpha} \tilde{s}_{i\alpha} \cdot \tilde{s}_{i'\alpha} \]  
(1.62)
and \( \mu_{\alpha} = \frac{1}{m_{\alpha}} \). Therefore, it is seen that no coordinate axes are needed to determine these quantities if the \( \tilde{s} \)-vectors are available. Then it is also possible to tabulate the elements \( G_{ii'} \), which are the common occurrence (for example when \( t \) and \( t' \) correspond to internal coordinates related with valence bond stretching, valence angle bending, wagging torsion etc.). So whenever such internal coordinate combinations occurs these results can be used.

These quantities \( G_{ii'} \), are closely related to the expression for kinetic energy. This can be shown as follows. In terms of mass-weighted Cartesian displacement coordinates, the kinetic energy may be written as,
\[ 2T = \dot{\dot{q}} \]  
(1.63)
The momentum \( p_{i} \) conjugate to the mass-weighted Cartesian displacement coordinate \( q_{i} \),
\[ p_{j} = \frac{\partial T}{\partial \dot{q}_{j}} = \dot{\dot{q}}_{j} \]  
(1.64)
So the kinetic energy can be expressed in terms of the momenta as,
\[ 2T = p^{+} p \]  
(1.65)
Let \( R \) be the column matrix of the internal coordinates (which may include redundant coordinates) and the let the transformation from the mass-weighted Cartesian displacement to internal coordinates be given by,
\[ R = D q \]  
(1.66)
Now,
\[ p_{j} = \frac{\partial T}{\partial \dot{q}_{j}} = \sum_{t} \frac{\partial T}{\partial \dot{R}_{t}} \frac{\partial \dot{R}_{t}}{\partial \dot{q}_{j}} = \sum_{t} P_{t} D_{ij} \]  
(1.67)
where momenta conjugate to the internal coordinate \( R_{t} \) is taken as \( P_{t} = \frac{\partial T}{\partial \dot{R}_{t}} \). Equation (1.67) thus gives,
\[ p^{+} = P^{+} D \]  
(1.68)
which also gives,
\[ p = D^{+} P \]  
(1.69)
Substituting (1.68) and (1.69) in equation (1.65), we have,

$$2T = P^+ \left(D D^+\right) P$$

(1.70)

Now from equations (1.61) and (1.66), we see that,

$$D_{ij} = \frac{l}{\sqrt{m_j}} B_{ij}$$

(1.71)

Thus using equations (1.61) and (1.71) we get that,

$$\left(D D^+\right)_{ii'} = \sum_j D_{ij} D_{ij}^* = \sum_j \frac{l}{m_j} B_{ij} B_{ij}^* = G_{ii'}$$

(1.72)

Thus from equation (1.70),

$$2T = P^+ G P$$

(1.73)

If the determinant $\|G\| \neq 0$, $G^{-1}$ exists. So using Hamilton's equation $\left(\dot{R}_t = \frac{\partial T}{\partial P_t}\right)$, we have,

$$\dot{R} = G P$$

$$P = G^{-1} \dot{R}$$

(1.74)

Thus we get,

$$2T = \dot{R}^+ G^{-1} \dot{R}$$

(1.75)

1.7. D Potential Energy and Secular-equation in terms of Internal Coordinates

Here the potential energy ($V$) is expressed in terms of the internal coordinates as,

$$2V = \sum_{l,l'=l}^{n} F_{ll'} R_l R_{l'}$$

(1.76)

where $n$ is the total number of internal coordinates. Here $F$ is the force constant matrix and the element $F_{ll'}$ connects the internal coordinates $R_l$ and $R_{l'}$.

Thus Lagrangian can be formed as,

$$L = T - V = \frac{1}{2} \sum_{l}^{n} \sum_{l'}^{n} \left[G_{ll'}^{-1} \dot{R}_l \dot{R}_{l'} - F_{ll'} R_l R_{l'} \right]$$

(1.77)

The Lagrange's equation correspond to the internal coordinates $R_l$ i.e. $\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{R}_l} \right) - \frac{\partial L}{\partial R_l} = 0$ gives,

$$\sum_{l}^{n} \left(G_{ll'}^{-1} \dot{R}_l - F_{ll'} R_l \right) = 0$$

(1.78)
Let us now express the internal coordinates $R_i$'s in terms of the normal coordinates $Q_k$'s as,

$$R_i = \sum_{k=1}^{3N-6(5)} L_{ik} Q_k$$  \hspace{1cm} (1.79)

6 and 5 correspond to nonlinear and linear molecules, respectively. Let us assume that the molecule is executing only one particular normal mode (say $k$-th one) of vibration with angular frequency $\sqrt{\lambda_k} = \sqrt{\lambda}$ and phase $\delta_k = \delta$. Then,

$$R_i = L_{ik} Q_k = L_{ik} Q_k^0 \cos(\sqrt{\lambda_k} t + \delta_k) = A_i \cos(\sqrt{\lambda} t + \delta)$$  \hspace{1cm} (1.80)

Substituting this in equation (1.78), we get (substituting the subscript ' $k$ '),

$$\sum_{i=1}^{n} \left[ -\lambda G_i^{ij} + F_i^{ij} \right] A_j = 0$$  \hspace{1cm} (1.81)

So for $n$ such internal coordinates $R_i$, we get $n$ such equations i.e.,

$$\begin{align*}
(F_{11} - \lambda G_{11}^{ij}) A_j + (F_{12} - \lambda G_{12}^{ij}) A_2 + \ldots + (F_{1n} - \lambda G_{1n}^{ij}) A_n &= 0 \\
(F_{21} - \lambda G_{21}^{ij}) A_j + (F_{22} - \lambda G_{22}^{ij}) A_2 + \ldots + (F_{2n} - \lambda G_{2n}^{ij}) A_n &= 0 \\
&\vdots \\
(F_{nn} - \lambda G_{nn}^{ij}) A_j + (F_{n2} - \lambda G_{n2}^{ij}) A_2 + \ldots + (F_{nn} - \lambda G_{nn}^{ij}) A_n &= 0
\end{align*}$$  \hspace{1cm} (1.82)

(since, by definition, in equation (1.62), $G_{ii'} = G_{i'i}$). For non-trivial solution of $A_i$'s, we get the secular equation,

$$\begin{vmatrix}
(F_{11} - \lambda G_{11}^{ij}) & (F_{12} - \lambda G_{12}^{ij}) & \ldots & (F_{1n} - \lambda G_{1n}^{ij}) \\
(F_{21} - \lambda G_{21}^{ij}) & (F_{22} - \lambda G_{22}^{ij}) & \ldots & (F_{2n} - \lambda G_{2n}^{ij}) \\
&\vdots \\
(F_{nn} - \lambda G_{nn}^{ij}) & (F_{n2} - \lambda G_{n2}^{ij}) & \ldots & (F_{nn} - \lambda G_{nn}^{ij})
\end{vmatrix} = 0$$  \hspace{1cm} (1.83a)

i.e.  \hspace{1cm} $|F - \lambda G^i| = 0$  \hspace{1cm} (1.83b)

we shall get $3N-6(5)$ non zero solutions for $\lambda = 4\pi^2v^2$ corresponding to $3N-6(5)$ normal modes of vibration and rest will be zero corresponding to translations, rotations and due to the inclusion of redundancies in selecting the internal coordinates.
For each root of $\lambda$, we can determine the amplitudes $A_i$'s or their ratios from equation (1.82), which is a homogeneous one. These amplitudes connect, excepting a constant undetermined factor $X_k$, the internal coordinates $R_i$'s with the normal coordinates $Q_k$'s. So also with the help of equations (1.79) and (1.80), we can write,

$$R_i = \sum_{k=1}^{3N-6(5)} X_k A_{ik} Q_k = \sum_{k=1}^{3N-6(5)} L_{ik} Q_k$$

(1.84)

$A_{ik}$ being the amplitude of the $i$-th internal coordinates corresponding to $k$-th normal mode of vibration. Substituting equation (1.84) in (1.76), (according to the definition of normal coordinate), we get,

$$2V = \sum_{i} \sum_{i'} F_{ii'} R_i R_{i'} = \sum_{k} \sum_{i} \sum_{i'} F_{ii'} L_{ik} L_{i'k} Q_k^2 = \sum_{k=1}^{3N-6(5)} \lambda_k Q_k^2$$

(1.85)

So we have,

$$\sum_{i} \sum_{i'} (F_{ii'} L_{ik} L_{i'k}) / \lambda_k = 1$$

(1.86)

$(F_{ii'} L_{ik} L_{i'k}) / \lambda_k$ is the fractional contribution of the force constant, connecting the internal coordinates $R_i$ and $R_{i'}$ to the vibrational energy of the $k$-th mode. This is generally expressed in percentage and is called potential energy distribution (PED) which is used in understanding the nature of vibration.

We have earlier shown that $G$ matrix can be determined for various types of internal coordinates (for example: bond stretching, angle bending, wagging and torsion etc.) and determination of $G^{-1}$ is to some extent tedious. So the secular equation (1.83b) can also be expressed in the following form,

$$\|G F - E \lambda\| = 0$$

(1.87)

where $E$ is a $(n \times n)$ order unit matrix. Since both $G$ and $F$ matrices are known, this secular equation can be solved for $\lambda$'s. This technique was developed by G. W. Wilson and is known as Wilson $G$-$F$ Matrix method.

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1.7.E Factoring of the Secular equation

Again if we now define a new coordinate system, which are formed by linear combination of the internal coordinates, such that each such coordinate belongs to one of the symmetry species of the molecular point group, then it can be shown that the secular equation is factored into several blocks, each blocks representing a particular symmetry species. Let the new coordinates called symmetry coordinates be denoted by $S$,

$$S = UR$$

where, $U$ is the transformation matrix from $R$ to $S$. Suppose $S^{(r)}$ and $S^{(r')}$. Then there will always be some operations ($R$) for the group for which,

$$S^{(r)} \xrightarrow{R} + S^{(r)}$$

and

$$S^{(r')} \xrightarrow{R} - S^{(r')}$$

so that

$$S^{(r)}S^{(r')} \xrightarrow{R} - S^{(r)}S^{(r')}$$

Since this reversed of sign is in compatible with the fundamental property that kinetic and potential must be unchanged by an operation of the group, such cross terms must have zero coefficients. The vanishing of all such cross terms makes the secular equation break up into separate factors, one for each species.
1.8 REFERENCES


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[171] Barrow
