Chapter-2

THEORETICAL ASPECTS

2.1 VIBRATIONAL AND REORIENTATIONAL RELAXATION PROCESS IN LIQUID MOLECULES:

The vibrational and reorientational relaxation study of liquid molecules using Raman technique provides valuable information about the structure and molecular dynamics of the molecule. The vibrational Raman band shapes of molecules are generally characterized by positions of band maxima, intensity and shape (FWHM). These parameters of a reference vibrational mode are sensitive to the molecular environment. These parameters are modulated by the addition of solvent into the reference system. Hence, analysis of the Raman band shape in terms of these parameters provides a wealth of information of particular liquid or liquid systems especially structure, dynamics and intermolecular interactions. Vibrational and reorientational relaxations studies are based on the systematic analysis of the vibrational Raman bandshape [1-4]. Vibrational relaxation originates when a molecule under investigation is close to another molecule in the surrounding and interacts entirely with that molecule. Hence, the vibrational relaxation study is mainly to elucidate what kinds of intermolecular potential of the local field and what types of relaxation processes operate. The vibrational relaxation processes are usually classified into three types [5]:

(a) Energy dissipation: The dissipation of the vibrational energy into all other degrees of freedom of the motion or the heat bath, which includes the translational and rotational motion of molecules and other surrounding modes.

(b) Phase modulation: It is also known as environmental broadening. It arises due to the modulation of the vibrational phase owing to collisions with surrounding molecules or, in other words, the fluctuation of the local field. It seems commonly accepted that phase relaxation is the dominant process in the vibrational relaxation in most liquids so far studied [6].
(c) Resonant energy exchange: It is the exchange of the vibrational energy between oscillators of same kind through the vibrational resonant coupling. It is important to mention that the resonant energy exchange process takes place via transition dipole-transition dipole interaction. It generally appears in pure (or at low solvent concentration region) liquids and is almost disappear in infinite dilute solution.

The isotropic Raman line shape due to solvent induced frequency fluctuations was first studied by Oxtoby [7-8]. It is expressed by the Fourier transform of the vibrational co-ordinate autocorrelation function \( \langle Q_i(t)Q_i(0) \rangle \), where the angular brackets define an ensemble average. The vibrational co-ordinates \( Q_i \) at time \( t \) differ from \( Q_i(0) \) by a phase factor \( \exp \left[ i \langle \Phi_i(t)-\Phi_i(0) \rangle \right] \). It provides direct information about the dephasing rates [9, 10].

The phase difference is given by

\[
\langle \Phi_i(t) - \Phi_i(0) \rangle = \int_0^t dt' \omega_i(t') = \sigma t + \int_0^t dt' \Delta \omega_i(t')
\]

(2.1.1)

where \( \sigma \) is the average vibrational transition frequency in the liquid and \( \Delta \omega_i(t') \) gives the fluctuation in frequency due to the influence of environment.

The vibrational phase relaxation is given by [8, 10]

\[
\langle Q_i(t)Q_i(0) \rangle = \left\langle \exp \left[ \int_0^t dt' \Delta \omega_i(t') \right] \right\rangle
\]

(2.1.2)

and it depends on the statistical properties of \( \Delta \omega_i(t') \). A characteristic time \( \tau_c \) relating to this parameter can be defined as

\[
\tau_c = \int_0^t dt \frac{\langle \Delta \omega_i(t) \rangle \langle \Delta \omega_i(0) \rangle}{\langle \Delta \omega_i^2 \rangle}
\]

(2.1.3)

where \( \langle \Delta \omega_i(t) \Delta \omega_i(0) \rangle \) is the autocorrelation function of \( \langle \Delta \omega_i(t) \rangle \). The nature of the lines shape depends on the relative magnitude of the two characteristic frequencies.
\( \langle \Delta \omega_i^2 \rangle^{1/2} \) and \( \tau_c^{-1} \). A modulation regime can be defined depending on the value of \( \langle \Delta \omega_i^2 \rangle^{1/2} \tau_c \):

(a) When \( \langle \Delta \omega_i^2 \rangle^{1/2} \tau_c >> 1 \), the active species undergo a perturbation for a long time. If it is possible to freeze the environment at a particular time then there occurs frequency shift and vibrational band shape broadened to Gaussian shape. It is generally considered as a static limit.

(b) When \( \langle \Delta \omega_i^2 \rangle^{1/2} \tau_c << 1 \), i.e. the rapid modulation limit where the active species undergo for a short time perturbation and the band shape is narrowed to Lorentzian shape. The full width at half maximum for this is given by

\[
FWMH = \langle \Delta \omega_i^2 \rangle^{1/2} \tau_c / \pi c
\]

(2.1.4)

It is measured in cm\(^{-1}\) unit.

Reorientational motions of molecules have a worthwhile contribution to the vibrational Raman bandshape in liquid molecules. Three approaches have been made to study the molecular reorientations in liquids [11]. In the first approach, the molecules are reoriented by means of free classical rotations. The molecules undergo frequent intermolecular collisions of short duration and their angular momenta are randomized by the impulsive torque associated with the collisions. If the time between the collisions is short compared with the mean free rotational period, then the motion is well-described by rotational diffusion. In second approach, liquid pictures as a pseudo-solid and is demonstrated by the various cell models. A molecule is considered as undergoing solid-like torsional oscillations in a potential well formed by the other molecules and can reorient appreciably only if (a) it can tunnel through the barrier, (b) can acquire sufficient activation energy through collisions to surpass the potential barrier, or (c) if the potential barrier itself dissipates because molecular motions open up the cell and leave free volume, permitting the molecule to rotate freely. The third approach is based on the Vleck-Weisskopf collision-broadening theory which is extended to include the molecular reorientation, in that the molecules reorient instantaneously and randomly upon collisions. The molecules in this picture reorients instantaneously and randomly upon collision.
2.2 VIBRATIONAL AND REORIENTATIONAL RELAXATION TIME:

The isotropic component of a Raman band is broadened by the vibrational relaxation. It can be expressed as a Fourier transform of the vibrational correlation function given by [2]

\[ I_{iso}(\omega) = \int_{-\infty}^{\infty} \phi_{vib}(t) \exp(i\omega t) dt \]  

(2.2.1)

An anisotropic Raman band profile contains both the vibrational and reorientational information. Assuming that the vibrational and reorientational motions are completely decoupled, an anisotropic Raman component can be expressed as Fourier transform of the product of the vibrational and reorientational correlation functions given by

\[ I_{aniso}(\omega) = \int_{-\infty}^{\infty} \phi_{vib}(t) \phi_{reor}(t) \exp(i\omega t) dt \]  

(2.2.2)

Both the vibrational and reorientational functions are assumed to be exponential given as

\[ \Phi_{vib}(t) = \exp(-t / \tau_{vib}) \]  

(2.2.3)

\[ \Phi_{reor}(t) = \exp(-t / \tau_{reor}) \]  

(2.2.4)

where, \( \tau_{vib} \) and \( \tau_{reor} \) are vibrational and reorientational correlation times.

Then, the vibrational and the reorientational correlation times [4] are given by

\[ \tau_{vib} = (\pi c \Gamma_{iso})^{-1} \]  

(2.2.5)

\[ \tau_{reor} = [\pi c (\Gamma_{aniso} - \Gamma_{iso})]^{-1} \]  

(2.2.6)

where, \( c \) is the velocity of light, \( \Gamma_{iso} \) and \( \Gamma_{aniso} \) are the bandwidths of isotropic and anisotropic Raman components respectively.

2.3 MODELS ON VIBRATIONAL RELAXATION:

Vibrational relaxation of a reference mode of liquid molecules depends on molecular environment. Various models have been developed to explain the vibrational relaxation processes in the liquid mixture system and its dependence on concentration. Some of the models are mentioned below.
2.3.1 ISOLATED BINARY COLLISION MODEL:

Fischer and Laubereau [12] developed a model based on semiclassical collision theory to describe the dephasing of vibrational excited molecule in a liquid system. This model quantitatively explores the dephasing process and its interrelation to the energy relaxation. According to this model fluctuations occur in the normal mode frequencies and such fluctuations produces dephasing without involving transitions between vibrational states. In the model, energy dissipation and pure dephasing are assumed to be independent processes and dephasing time is expressed as

\[ \frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{e}} \]  

(2.3.1.1)

where, \( \tau_{ph} \) = the pure dephasing time and 
\( \tau_{e} \) = the energy relaxation time

The pure dephasing time does not affect the excited state population of the vibrational mode. The energy relaxation is due to the non adiabatic transitions between different vibrational states.

Theoretically calculated dephasing time using this model is in good agreement with the experimental dephasing time while giving minor importance to the energy relaxation, that is for \( \tau \approx \tau_{ph} \). However, this model has some limitations in estimating some parameters for complex liquid system. This model describes molecular interaction in the liquid system in terms of binary head-on collisions. Its extension to large molecules is expected to be semi-quantitative nature. Resonant transfer of vibrational quanta is also not included in their calculations for \( \tau_{ph} \).

2.3.2 HYDRODYNAMIC MODEL:

The hydrodynamic model provides a good qualitative vibrational relaxation in terms of dephasing phenomena in molecular liquids. In hydrodynamic model only collective effects are included considering a vibrational molecule as a macroscopic body embedded in a viscoelastic continuum. D.W. Oxtoby [9] developed a hydrodynamic model to study the dephasing phenomenon in the liquid molecular system. His model
also includes the anharmonicity effect. According to this model the dephasing rate for polyanatomic systems depends on viscosity and temperature and is given by

\[ \tau_{ph}^{-1} \propto \eta T \]  

(2.3.2.1)

Hence, viscosity and temperature are playing major role in the vibrational relaxation and leads to line broadening.

Recently, Kim et al. [13] incorporate both the collisional and collective effects of molecular interactions in the dephasing dynamics of fast modulation processes. They developed a theory using the theory of Sung and Stell [14] to the dephasing dynamics by considering atoms in the vibrating molecule as solute particles dissolved in a solvent composed of structureless spherical particle. Then, they explained the isotropic Raman spectra quantitatively incorporating the collisional and collective effects in fluctuating environment for fast modulation.

### 2.3.4 RESONANT ENERGY TRANSFER (RET):

In general RET is a process in which the interaction takes place between the identical molecules through transition dipole- transition dipole coupling (TD-TD) interaction [6]. Several experimental works [15-16] showed the evidences of RET through TD-TD coupling in the liquid phase. In pure liquids vibrations of neighbouring molecules are due to the intermolecular interactions between them. If the molecular orientations are random, the net effect is the broadening of vibrational bands. If, however, the alignment of two neighbouring molecules is not random, then the transition dipole moments of two neighbouring molecules may couple. The coupling may be in-phase or out-of-phase modes. In neat active species (solute), the Raman band shape appears to derive its major contribution through RET process. If the active species is diluted in some inert solvent, its contribution to the bandshape decreases resulting decrease in Raman bandwidth.

### 2.3.5 KUBO MODEL FOR CORRELATION FUNCTION:

Kubo [16] developed a general theory to explain the relaxation process treating the molecule as an oscillator perturbed by random forces. This theory has been applied by several researchers to explain vibrational relaxation or dephasing phenomena
considering that vibrational dephasing mainly occurs due to the RET process.

According to this model, the correlation function for an isotropic band profile which describe the pure dephasing process in is given by [15]

\[
\phi(t) = \exp \left[ -M_2^2 \left( \tau_c^2 \left( e^{-\frac{t}{\tau}} - 1 \right) + t \tau_c \right) \right]
\]

where, \( \tau_c \) is the modulation time, related to the time-scale of the molecular fluctuations in the interacting medium. It can be identified with the average time between perturbed events. \( M_2^2 = \langle w^2 \rangle \) is the second frequency moment. It measures the range of frequency distribution due to various molecular interactions. \( M_2 \) can be obtained from the frequency domain and is given by

\[
M_2 = \frac{\int_{band} I_{iso}(w) w^2 dw}{\int_{band} I_{iso}(w) dw}
\]

where, \( I_{iso} \) is the intensity of the isotropic Raman component. The parameters \( \tau_c \) and \( M_2 \) contains valuable information about the nature of the intermolecular potential. The modulation regime depends on the value of \( \sqrt{M_2 \tau_c} \). In slow modulation limit, \( \sqrt{M_2 \tau_c} \gg 1 \). In such case the active molecule undergoes a perturbation for a long time and its phase rapidly lost. In such modulation broadening of the vibrational band is inhomogeneous and linewidth and shape is assumed to be Gaussian. In fast modulation limit, \( \sqrt{M_2 \tau_c} \ll 1 \). In this case perturbation persists for a short time on the active molecule and its phase is retained for a longer time. The broadening of the vibrational band is homogeneous and the linewidth and shape is assumed to be Lorentzian. For short time approximation \( t < \tau_c \), the bandshape of the equation (2.3.5.1) will be Lorentzian around the centre and Gaussian in the wings.

The vibrational relaxation time \( \tau_v \) can be defined as

\[
\tau_v = \int_0^\infty \phi(t) \, dt
\]

For long time approximation or for fast modulation regime,
\[ \tau_v = (\pi c \ FWHM)^{-1} \]  \hspace{1cm} \text{(2.3.5.4)}

where, FWHM= Full width at half maxima of \( I_{iso}(w) \) and c is the speed of light. For the slow modulation regime

\[ \tau_v = (M_2 \, \tau_c)^{-1} \]  \hspace{1cm} \text{(2.3.5.5)}

Generally, \( \tau_v \) and \( \tau_c \) have time-scales in pico-second range.

Thus, depending upon the nature of modulation process, the isotropic band profile can be predicted. Hence, the Kubo model for correlation function is appropriate in determining the vibrational dephasing. The great advantage of the Kubo model is that the model is essentially an experimental one. Using the facilities of instrumental interface and computers, it is relatively easy to perform Fourier transforms of digitized isotropic spectra.

\textbf{2.4 THEORIES OF NON-COINCIDENCE EFFECT (NCE):}

It has been investigated that in many molecules the peak frequencies of the isotropic and anisotropic components of Raman bands do not coincide in liquid state [18-25]. This difference in peak frequencies is defined as NCE, i.e. \((\nu_{aniso}) - (\nu_{iso}) = \Delta \nu\).

It arises due to the manifestation of vibrational energy transfer induced by transition dipole–transition dipole interaction occurring in the presence of a short-range or long-range orientational order of molecular dipoles. Several workers have taken different approaches to develop theories on NCE [19-26]. Some of the models and theories have been discussed in this section.

\textbf{2.4.1 FINI AND MIRONE’S THEORY:}

Fini and Mirone [19] proposed a model to explain NCE. They made an assumption that aprotic dipolar liquids consists of small molecular clusters within which the dipoles in each cluster can align themselves either parallel or anti-parallel to a common direction. Therefore, the presence of permanent dipole moments allows the formation of some short range order. The transition dipole moment may then couple and RET can take place (due to which NCE occurs). The orientational order may exist up to certain distance such that the electrostatic interaction energy between two dipoles equals
the thermal agitation energy. Characteristically, this distance allows the molecule in the first coordination shell to attain a preferential orientation with respect to the central molecule. Because, RET only occurs between identical molecules, dilution of solute molecule minimizes the strength of coupling of the solute molecules. On further dilution, the effect of RET will reduce resulting decrease in the NCE. This model can also explain the effect of temperature on the NCE. Increase of temperature reduces the size of the clusters and disrupts alignment of the molecular dipoles inside them which reduces the degree of RET resulting decrease in NCE.

In this model, Fini and Mirone [19] derived an empirical equation which relates the NCE ($\Delta \nu$) to the concentration of the solute and solvent. The empirical equation is given by

$$
\Delta \nu = \Delta \nu_{\text{neat}} \frac{\varepsilon_2}{1 - \Phi_0} \cdot \frac{\Phi - \Phi_0}{\varepsilon_1 (1 - \phi) + \varepsilon_2 \Phi}
$$

(2.4.1.1) for $\Phi > \Phi_0$ and

$$
\Delta \nu = 0
$$

(2.4.1.2) for $\Phi < \Phi_0$

where, $\Delta \nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$ (in cm$^{-1}$) is the peak frequency difference at different solute concentration, $\Delta \nu_{\text{neat}} = \nu_{\text{aniso}} - \nu_{\text{iso}}$ for neat solution, $\varepsilon_1$ and $\varepsilon_2$ are dielectric constants of solvent and solute respectively, $\Phi$ is the volume fraction of solute and $\Phi_0$ is the threshold volume below which there is no NCE.

Based on the observation of experimental results, Mirone and Fini [20] pointed out two important points. At first, $\Delta \nu$ decreased as the solution become more dilute and there was a certain “threshold” concentration ($\Phi_0$) below which no NCE occurred. Secondly, the shape of the NCE ($\Delta \nu$) vs. volume fraction graphs depends on the relative values of the dielectric constants of solute and solvent. They explained the second observation on the basis of two assumptions. First, coupling of the two modes takes place by TD-TD coupling. Each molecule contributes to $\Delta \nu$ a term which is proportional to

$$
\left(\frac{\partial \mu}{\partial Q}\right)^2 \frac{1}{r^3},
$$

where $r$ is the distance from the reference molecule and $\frac{\partial \mu}{\partial Q}$ is the dipole derivative. Secondly, the isotropic-anisotropic separation is directly related to
the orientational correlation induced by static dipolar interactions, which is assumed to be represented by \( \tanh \left( \frac{\mu^2}{\varepsilon r^3 k_B T} \right) \) at a given distance from the reference molecule.

Mirone and Fini [20] derived the following relation using these two assumptions

\[
\Delta \nu \propto \left( \frac{\partial \mu}{\partial Q} \right)^2 \frac{N}{V} \int_{d}^{\infty} \frac{\tanh \left( \frac{\mu^2}{\varepsilon r^3 k_B T} \right)}{r^2 dr}
\]

(2.4.1.3)

where,

\[
\frac{N}{V} = \text{number density of solute}
\]

\( k_B T \) = the thermal energy

\( d \) = the minimum distance of approach between two molecules and

\( \varepsilon \) = dielectric constant of solution.

Expanding the term \( \tanh \left( \frac{\mu^2}{\varepsilon r^3 k_B T} \right) \) to third order and integrating equation (2.4.1.3) we get,

\[
\Delta \nu \propto \left( \frac{\partial \mu}{\partial Q} \right)^2 \frac{N}{V} \frac{\mu^2}{3 \varepsilon K_B T d^3} \left[ 1 - \left( \frac{\mu^2}{3 \varepsilon K_B T d^3} \right)^2 \right]
\]

(2.4.1.4)

Thus, \( \Delta \nu \) at different solute concentration depends on \( \varepsilon \). The value of \( \varepsilon \) can be determined by assuming that dielectric constant of the solution depends linearly on the volume fraction (\( \Phi \)) of the two components [22]

\[
\varepsilon = \varepsilon_1 (1 - \phi) + \varepsilon_2 \phi
\]

(2.4.1.5)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are dielectric constants of solvent and solute respectively. For \( \varepsilon_2 \ll \varepsilon_1 \), this model does not agree with the experimental results and it may be due to the following reasons:

(a) \( \varepsilon \) might not be a linear function of volume fraction and

(b) short range interaction might not be adequately described by the bulk dielectric constant. Furthermore, such interactions could affect transition dipole moment leading to further more discrepancies.
2.4.2 MCHALE’S THEORY:

McHale has asserted that the TD-TD interactions are not only responsible for NCE. Other possible sources of contribution to NCE are dipole-dipole (D-D), quadrupole- quadrupole and hydrogen bonding interactions. McHale finds out that orientational intermolecular force can give rise to an NCE even in the absence of local order.

Wang and McHale [21] carry out an extensive and detail theoretical analysis on the NCE. They showed that short-range orientational order is not essential for the NCE, although the presence of short-range order may modify the NCE. However, it is not the basic cause for NCE. The fundamental reason is that the resonance coupling potential between two molecules is angular dependent. The angular dependent intermolecular forces enhance the force constant of the harmonic oscillators, yielding an anisotropic frequency distribution. The isotropic Raman scattering illustrates the average of the frequency distribution but anisotropic Raman scattering illustrates the anisotropy of the frequency distribution. Due to this, the first spectral moments in isotropic and anisotropic Raman bands are different and yields NCE.

It was pointed out that the short-range order may modify significantly the size of the splitting parameter, depending upon the orientational ordering. However, it is not possible to configure its extensive contribution to the splitting parameter. Furthermore, the derived expression for NCE [22] showed that the splitting parameter is proportional to the number density or concentration of the solute and inversely proportional to both the free oscillator frequency and the effective mass. In addition, Wang and McHale pointed out that if the coupling is due to induced dipole interactions, the relative splitting \( \frac{\Delta v}{\Delta v_{\text{ neat}}} \) depends linearly on the infrared intensity parameter \( \left| \frac{\partial \mu}{\partial Q} \right|^2 \) and is always positive.

Considering the transition dipole coupling, McHale [22] adopted the following splitting term for liquid mixture.
\[ \nu_{aniso} - \nu_{iso} = \Delta \nu = \frac{2 \mu^2 \left( \frac{\partial \mu}{\partial Q} \right)^2}{25 \Pi^2 \sigma v_0 K_\beta T d^3 V_M \varepsilon^2} N_0 \phi \]  
(2.4.2.1)

where, \( N_0 \) is the Avogadro’s number, \( \mu \), \( V_M \) and \( \Phi \) are the dipole moment, molar volume and concentration of solute, \( \frac{\partial \mu}{\partial Q} \) is the dipole derivative and \( \nu_0 \) is the free oscillator frequency.

To compare the concentration dependent of equation (2.4.2.1) with the experimental result, it is necessary to know the dependence of the dielectric constant on the concentration of the solution. McHale assumed that the dielectric constant of the solution depends linearly on the volume fraction of the solute and solvent (equation (2.4.1.5))

Applying equation (2.4.1.5) in equation (2.4.2.1) we can write

\[ \Delta \nu = \frac{2 \mu^2 \left( \frac{\partial \mu}{\partial Q} \right)^2}{25 \Pi^2 \sigma v_0 K_\beta T d^3 V_M \varepsilon^2} N_0 \phi \left[ \varepsilon_1 (1 - \phi) + \varepsilon_2 \phi \right]^2 \]

Or \( \Delta \nu = \Delta \nu_{neat} \frac{\varepsilon_2 \phi}{\left[ \varepsilon_1 (1 - \phi) + \varepsilon_2 \phi \right]^2} \)

Or \( \frac{\Delta \nu}{\Delta \nu_{neat}} = \frac{\varepsilon_2 \phi}{\left[ \varepsilon_1 (1 - \phi) + \varepsilon_2 \phi \right]^2} \)  
(2.4.2.2)

Or \( \frac{\Delta \nu}{\Delta \nu_{neat}} = \frac{\phi}{\left[ \phi (1 - x) + x \right]^2} \)  
(2.4.2.3)

where, \( x = \frac{\varepsilon_1}{\varepsilon_2} \)

The equation (2.4.2.3) is the empirical equation formulated by McHale to study the dependence of NCE on the relative dielectric constant and solute concentration.

This empirical model is in good agreement with the experimental results in which \( \frac{\varepsilon_1}{\varepsilon_2} > 1 \) or \( \frac{\varepsilon_1}{\varepsilon_2} = 1 \). However, this model is not appropriate for the case \( \frac{\varepsilon_1}{\varepsilon_2} < 1 \).

Negligence of other molecular parameters such as refractive index, which play an important role in interacting systems, may lead to failure of this model.
2.4.3 MIRONE’S MODIFICATION OF MCHALE’S MODEL:

McHale’s model [22] for NCE is not in good agreement with the experimental results for the case \( \frac{\varepsilon_1}{\varepsilon_2} < 1 \), i.e for polar molecule in non-polar (or slightly polar) solvent molecules. P. Mirone argued that McHale’s equation for NCE was too simplistic and needed to replace and introduced a term refractive index (n). He suggested that McHale’s equation should be re-written as

\[
\Delta \nu = \frac{2 \mu^2 (\frac{\partial \mu}{\partial Q})^2}{25 \pi^2 m \nu_0 K \beta T d^3 V_m} \Phi \cdot \left( \frac{n^2 + 2}{2 \varepsilon + n^2} \right)^2 \varepsilon
\]

where, \( n_2 \) and \( n \) are the refractive indexes of the solute and the solution respectively.

In terms of relative splitting Mirone’s modification of McHale’s model can be expressed as

\[
\frac{\Delta \nu}{\Delta \nu_{neat}} = \frac{2 \varepsilon_2 + n_2^2}{n_2^2 + 2} \left( \frac{n_2^2 + 2}{2 \varepsilon + n_2^2} \right)^2 \frac{\varepsilon}{\varepsilon_2} \Phi
\]

This empirical model shows better agreement with the experimental results for the case \( \frac{\varepsilon_1}{\varepsilon_2} < 1 \).

2.4.4 KIRKWOOD- FRÖHLIC DIELECTRIC MODEL:

Fröhlich [27] developed a model to elucidate the short-range molecular mobility and interaction in self-assembled system. This model gives a relation among the correlation factor \( g \), dielectric constant \( \varepsilon \), dielectric constant of induced polarization \( (\varepsilon_a) \), temperature \( (T) \), the density and the permanent dipole moment. This model represents a dielectric with dielectric constant \( \varepsilon \), consisting of polarizable molecules with permanent dipole moment. The dielectric is considered as a continuum with dielectric constant \( \varepsilon_a \) in which point dipoles having moment \( \mu_d \) are embedded. Each molecule is replaced by a point dipole \( \mu_d \) having the same non-electrostatic interactions with the other point dipoles, while the polarizability of the molecule can be assumed to form a continuum with dielectric constant \( \varepsilon_a \).
The polarization $P$ is composed of two components. That is

$$P = P_{in} + P_{or}$$

(2.4.4.1)

where, $P_{in}$ and $P_{or}$ are the induced and the orientation polarizations respectively.

$P_{in}$ is equal to the polarization of the continuum with the dielectric constant $\varepsilon_\infty$ and can be written as

$$P_{in} = \left[ \frac{\varepsilon_\infty - 1}{4\pi} \right] E$$

(2.4.4.2)

where, $E$ is the applied field.

$P_{or}$ is expressed in terms of dipole density, which is due to dipoles. If $V$ be the volume of a sphere having $N$ dipoles then

$$P_{or} = \frac{1}{V} \langle M_d \cdot e \rangle$$

(2.4.4.3)

where, $M_d = \sum_{j=1}^{N} (\mu_d)_j$

(2.4.4.4)

$\langle M_d \cdot e \rangle$ is the average component of the moment due to dipoles in the sphere, in the direction of the field and is expressed as

$$\langle M_d \cdot e \rangle = \frac{\int dx^N \, M_d \cdot e \exp \left( -\frac{U}{K_B T} \right)}{\int dx^N \cdot \exp \left( -\frac{U}{K_B T} \right)}$$

(2.4.4.5)

Here, $U$ is the energy of the dipoles in the sphere and consists of three parts-

(a) Energy of the dipoles in the external field.

(b) The electrostatic interaction energy between the dipoles and

(c) The non-electrostatic interaction energy between the molecules which is responsible for the short-range correlation between orientation and position of the molecules.

The external field in this model is equal to the field in a spherical cavity filled with a continuum having dielectric constant $\varepsilon_\infty$, while the cavity is situated in a dielectric medium with dielectric constant $\varepsilon$. This field is called the Fröhlich field $E_F$ and expressed as
\[ E_F = \frac{3\epsilon}{2\epsilon + \epsilon_\infty} E \]  

(2.4.4.6)

The derivative of \( P \) w.r.t. \( E \) is equal to \( \frac{\epsilon - 1}{4\pi} \). That is

\[ \frac{\epsilon - 1}{4\pi} = \frac{\partial}{\partial E} (P_m + P_{or}) \bigg|_{E=0} \]  

(2.4.4.7)

Substituting equations (2.4.4.2) and (2.4.4.3) in equation (2.4.4.7), we get

\[ \epsilon - \epsilon_\infty = \frac{4\pi}{V} \left( \frac{\partial}{\partial E} \langle M_d \cdot e \rangle \right) \bigg|_{E=0} \]  

(2.4.4.8)

Rewriting equation (2.4.4.8) with \( E_F \) instead of \( E \) as the independent variable, we have

\[ \epsilon - \epsilon_\infty = \frac{4\pi}{V} \left( \frac{\partial E_F}{\partial E} \right) \bigg|_{E=0} \left( \frac{\partial}{\partial E_F} \langle M_d \cdot e \rangle \right) \bigg|_{E_F=0} \]  

(2.4.4.9)

Again we have,

\[ \langle M_d \cdot e \rangle = \frac{\langle M_d^2 \rangle_0}{3K_bT} E_F \]

Therefore, equation (2.4.4.9) can be written as

\[ \epsilon - \epsilon_\infty = \frac{4\pi}{V} \left( \frac{\partial E_F}{\partial E} \right) \bigg|_{E=0} \frac{\langle M_d^2 \rangle_0}{3K_bT} \]  

(2.4.4.10)

This is the expression for the dielectric constant in Fröhlich model. Using the value of \( E_F \) from equation (2.4.4.6) in the equation (2.4.4.10), we can write

\[ \epsilon - \epsilon_\infty = \frac{4\pi}{V} \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \frac{\langle M_d^2 \rangle_0}{3K_bT} \]  

(2.4.4.11)

Rearranging this equation, we can write

\[ \langle M_d^2 \rangle_0 = \frac{K_bT V}{4\pi} \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon} \]

(2.4.4.12)

Evaluating the value of \( \langle M_d^2 \rangle_0 \), we have

\[ \langle M_d^2 \rangle_0 = N' \mu^2 \sum_{j=1}^{N'} \langle \cos \theta_j \rangle \]

\[ = NV \mu^2 g \]  

(2.4.4.13)
where, \( N = \frac{N'}{V} \), \( g = \sum_{j=1}^{N'} \langle \cos \theta_{ij} \rangle \).

The correlation factor ‘\( g \)’ takes into account the correlation between the orientations due to the short-range order.

Substituting the equation (2.4.4.13) in equation (2.4.4.12), we get

\[
(\varepsilon - \varepsilon_\infty) (2\varepsilon + \varepsilon_\infty) = \frac{N}{12\pi \varepsilon} g \mu_d^2
\]

(2.4.4.14)

The permanent dipole moment \( \mu_d \) in the centre is given by

\[
\mu_d = \frac{\varepsilon_\infty + 2}{3} \mu
\]

(2.4.4.15)

where, \( \mu \) is the dipole moment of the molecule in the gas phase.

Substituting the value of \( \mu_d \) from equation (2.4.4.15) in the equation (2.4.4.14), we get

\[
g \mu_d^2 = \frac{9K_\beta T}{4\pi N} \frac{(\varepsilon - \varepsilon_\infty) (2\varepsilon + \varepsilon_\infty)}{\varepsilon(2 + \varepsilon_\infty)^2}
\]

(2.4.4.16)

This equation is known as the Kirkwood- Fröhlich equation. This equation gives the relation among dielectric constant (\( \varepsilon \)), dielectric constant of induced polarization (\( \varepsilon_\infty \)), temperature, the density and the permanent dipole moment.

Determination of the correlation factor \( g \) is highly important to gather information about the molecular interaction in material. It measures the angular correlation between the dipoles in material. Positive deviation of \( g \) from unity results when short range hindering torques favour parallel orientation of the dipoles of neighbouring molecules, while negative deviation results from antiparallel orientation.

If \( g \) is unity, the position of one dipole does not influence the position of the others except through the long-range electrostatic forces.

The equation (2.4.4.16) is valid only for pure polar liquids. The general expression for solutions of polar compounds in non-polar solvent is given by

\[
g \mu_d^2 = \frac{9k_B T}{4\pi N_0 x_p \varepsilon_\infty (\varepsilon_\infty + 2)^2 (2\varepsilon + 1)} \left[ \frac{\phi(\varepsilon - 1) - 3x_{np} M_{np} (\varepsilon_0 - 1)}{\varepsilon(2\varepsilon + \varepsilon_0) d_{np}} - \frac{3x_p M_p (\varepsilon_\infty - 1)}{(2\varepsilon + \varepsilon_\infty) d_p} \right]
\]

(2.4.4.17)
where, $x_{np}$ and $x_p$ are the molar fractions for the non-polar and the polar component respectively, $d_p$ and $d_{np}$ are the densities of the polar and non-polar compounds in the pure state, $M_p$ and $M_{np}$ are the molecular weights of the polar and non-polar solvents respectively, $N_0$ is the Avogadro’s number and $\phi = \frac{x_{np}M_{np} + x_pM_p}{d}$ is the molar volume of the mixture. Equation (2.4.4.17) is used to determine the Kirkwood correlation factor $g$ from experimental data for solutions of associating compounds in non-polar solvents. It provides vital information about the solute-solvent interaction in the binary mixture.

2.4.5 ONSAGER–FRÖHLICH DIELECTRIC CONTINUUM MODEL (FOR NCE):

This model [24] gives an empirical expression for NCE using a simple dielectric model of Onsager Fröhlich. The theoretical expression for NCE including the screening factors for the interaction energy of the two dipoles is given by

$$\Delta \nu = \frac{2\mu^2 \left( \frac{\partial \mu}{\partial Q} \right)^2}{25\Pi^2 \varepsilon^2 \nu_0 K_B T d^3 V_M} N_0 \phi S$$

Where, $N_0$ is the Avogadro’s number, $\mu$, $V_M$ and $\Phi$ are the dipole moment, molar volume and concentration of solute respectively, $Q$ is the normal coordinates of the isolated molecule, $d$ is the minimum intermolecular distance, $\frac{\partial \mu}{\partial Q}$ is the dipole derivative, $\nu_0$ is the free oscillator frequency, $K_B T$ is the thermal energy and $S$ is the screening factors for the interaction energy of the two dipoles. $S$ comprises two factors, $S_p$ and $S_t$ related respectively to the interaction of permanent and transition dipoles. Owing to the Onsager- Fröhlich dielectric model, which treats the dielectric as a continuum, the polarizability as isotropic and dipoles as point dipoles and molecule as spherical, the two factors are given by [24]

$$S_p = \left( \frac{n^2 + 2}{2\varepsilon + n^2} \right)^2 \varepsilon$$

and
\[ S_i = \left( \frac{n^2 + 2}{2\varepsilon_\infty + n^2} \right)^2 \varepsilon_\infty \]  \hspace{1cm} (2.4.5.3)

where, \( \varepsilon \) is the static dielectric constant of the medium, \( \varepsilon_\infty \) is the dielectric constant at infinite frequency and \( n \) is the refractive index of the solute.

The screening factor \( S_i \) does not vary much with the variation of the solvent as the variation of refractive index is very less, hence the term \( S_i \) can be considered as a constant. Therefore, considering only \( S_\rho \) term, equation (2.4.5.1) takes the form

\[ \Delta \nu = \frac{2\mu^2 \left( \frac{\partial \mu}{\partial Q} \right)^2}{25\Pi^2 c^2 v_0 kT d^3} \frac{N_0}{V_M} \phi \left( \frac{n^2 + 2}{2\varepsilon + n^2} \right)^2 \varepsilon \]

Or \[ \Delta \nu \left( 2\varepsilon + n^2 \right)^2 \frac{1}{\varepsilon} = \frac{2\mu^2 \left( \frac{\partial \mu}{\partial Q} \right)^2 \left( n^2 + 2 \right)^2}{25\Pi^2 c^2 v_0 kT d^3} \frac{N_0}{V_M} \phi \]  \hspace{1cm} (2.4.5.4)

This is another form of expression for NCE using simple dielectric model of Onsager-Fröhlich.

**2.4.6 LOGAN’S MODEL:**

D.E. Logan elucidated the theories on Raman NCE in his two revolutionary research papers [25, 26]. His theories provide detail information about the microscopic thermodynamic state dependences of NCE. His first paper [25] dealt with isotopic binary mixtures and second paper [26] dealt with more general systems. Logan agrees to Wang and McHale’s hypothesis [21] that NCE can arise due to the angular dependent potential which preferably weights the relative alignment of a pair of molecules between which the resonance energy transfer can take place. He also pointed out that many-body molecular interactions are responsible for the details of liquids structure and existence of the NCE.

In the paper [25], Logan developed an expression for the dependence of the Raman NCE on the concentration of the active species for isotopic binary mixtures based on various assumptions. First, he used a model of simple dipolar hard sphere liquid. Second, the active vibrational mode must be non-degenerated and sufficiently separated from all other vibrational transitions that population relaxation effect can be
neglected. Third, he assumed that the permanent dipole moment of the active species lies along the principal molecular axis and that vibration modulates the dipole moment along this axis. In additions to these assumptions, Logan made use of the mean spherical approximation [28]. Logan derived the following expression for NCE using the above assumptions.

\[ \Delta M = M_{aniso} - M_{iso} = \frac{48}{25\pi \varepsilon_0 m \omega_a \sigma^3} \left( \frac{\partial \mu}{\partial Q} \right)_T X_A \zeta(\rho, T) \]  

(2.4.6.1)

where, \( \left( \frac{\partial \mu}{\partial Q} \right)_T = \gamma \) is the dipole moment derivative, M is the reduced mass, \( \sigma \) is hard sphere diameter, \( \omega_a \) is the angular frequency of isolated, uncoupled \( \alpha \) mode of active species ‘A’, \( \rho \) is total number of density of solution, \( \varepsilon_0 \) is the permittivity of a vacuum, \( X_A \) is the mole fraction of the active species ‘A’ and \( M_{aniso} \) and \( M_{iso} \) are the spectral first moment of the anisotropic and isotropic Raman spectrum.

The value of the function \( \zeta(\rho, T) \) can be found by solving the following equation

\[ \frac{(1 + 4\zeta)^2}{(1 - 2\zeta)^2} - \frac{(1 - 2\zeta)^2}{(1 + \zeta)^2} = \frac{\beta \mu_0^2 \rho}{3\varepsilon_0} \]  

(2.4.6.2)

where, \( \mu_0 \) = permanent dipole moment

\[ \zeta = \zeta(\rho, T) \]

\[ \beta = \frac{1}{K_T \rho}, \quad K_T = \text{Boltzmann constant.} \]

\( \zeta(\rho, T) \) is a positive quantity and function of T and \( \rho \) only and independent of \( X_A \).

Therefore, if number density and temperature are constant, then

\[ \Delta M = X_A \Delta M_{neat} \]  

(2.4.6.3)

where, \( \Delta M_{neat} \) is the NCE for neat species ‘A’.

This relation of Raman splitting with the mole fraction of the active species only applied to an isotopic mixture.

Later on Logan elaborated his study of non-isotopic dipolar binary mixtures based on the same assumption as in his previous paper [25]. In non isotopic binary
mixtures, the splitting does not necessarily have a linear dependence of the mole fraction of the active species. Upon the dilution of the solute molecule, new intermolecular forces may arise which may change the ability to align the active pair than in the original.

Logan in his second paper [26] examined a simple dipolar, hard sphere mixture (solute species ‘A’ and solvent species ‘B’) in which the interaction potential consisted of two parts:

(a) A sum of pair wise additive hard sphere interactions with hard sphere diameters \( \sigma_A \) and \( \sigma_b \) of solute A and solvent B respectively and

(b) A dipolar parts arising from the mutual interaction of the permanent dipole moments of both the species.

Logan then defined the function \( \zeta(X_A, \rho, T) \) as

\[
\zeta(X_A, \rho, T) = \frac{\Pi \rho \sigma_A^3}{6} \int_0^\infty \frac{dR}{R} h_D^A(R) dR
\]

(2.4.6.4)

where, \( R \) is the distance between two interacting dipoles.

The function \( h_D^A(R) \) gives the \( R \) dependence of the contribution to the pair distribution function (PDF) associated with angular factor (relative orientation of the active species).

The noncoincidence splitting of the reference mode of a species ‘A’ depends on \( \zeta(X_A, \rho, T) \) is given by

\[
\Delta M_{\alpha A}(X_A, \rho, T) = \frac{X_A}{c T_{\alpha A}} \zeta(X_A, \rho, T)
\]

(2.4.6.5)

where, \( c \) is the speed of light

\[
T_{\alpha A} = \frac{25 \Pi^2 \epsilon_0 m_{\alpha A} \omega_{\alpha A} \sigma_A^3}{24 \gamma_{\alpha A}}
\]

(2.4.6.6)

\( \Delta M_{\alpha A} = \Delta M_{\text{aniso}} - \Delta M_{\text{iso}} \) for the \( \alpha \) mode of species ‘A’, a function of \( X_A, \rho, \text{and } T \); \( \epsilon_0 \) is the permittivity of a vacuum, \( \omega_{\alpha A} \) and \( m_{\alpha A} \) are the free oscillator angular frequency and the effective mass for the \( \alpha \) mode of species ‘A’

\( T_{\alpha A} \) has dimensions of time.

The function \( \zeta(X_A, \rho, T) \) is a function of mole fraction of active species ‘A’, number density (\( \rho \)) and temperature (\( T \)), which determines the thermodynamic state
dependence of the noncoincidence splitting is given by

\[ \zeta(X_A, \rho, T) = \zeta_{A,0}(\rho, T) = \frac{\mu_A^2 \rho}{72 \varepsilon_0 K_{\beta} T} \]  

(2.4.6.7), for low density limit

Hence, equation (2.4.6.7) is independent of \( X_A \). From equation (2.4.6.5) the noncoincidence splitting can be written as

\[ \Delta M_{a,A}(X_A, \rho, T) = \Delta M_{a,A}^0(X_A, \rho, T) \tilde{\zeta}(X_A, \rho, T) \]

(2.4.6.8)

where, \( \Delta M_{a,A}^0(X_A, \rho, T) = \frac{\zeta_{A,0}(X_A, \rho)}{c T_{a,A}} X_A \)

(2.4.6.9)

and \( \tilde{\zeta} \) is defined as

\[ \tilde{\zeta}(X_A, \rho, T) = \frac{\zeta(X_A, \rho, T)}{\zeta_{A,0}(\rho, T)} \]

(2.4.6.10)

Equation (2.4.6.9) is a result for the noncoincidence splitting which asymptotically valid in the \( \rho \to 0 \) limit. In the low number density domain, the permanent dipolar alignment effects responsible for the noncoincidence splitting are solely those due to active pair of ‘A’ molecules between which transitions dipolar RET occurs. The quantity \( \zeta_{A,0}(\rho, T) \) symbolizes the pair alignments of the active molecules and does not depend on any property of species ‘B’. Outside the low number density limit, other molecules of other species will act to preferentially weight the relative alignment of any pair of RET of active molecules. Within the equal-radii MSA [25], \( \tilde{\zeta}(X_A, \rho, T) \) can be calculated from the following expression

\[ 24 Y_0 = \left( \frac{1 + 4 \tilde{\xi} Y_0}{1 - 2 \tilde{\xi} Y_0} \right)^2 - \left( \frac{1 - 2 \tilde{\xi} Y_0}{1 + \tilde{\xi} Y_0} \right)^4 \]

(2.4.6.11)

where, \( Y_0 = X_A \zeta_{A,0}(\rho, T) + (1 - X_A) \zeta_{B,0}(\rho, T) \)

(2.4.6.12)

\( (1 - X_A) = X_B \) is the mole fraction of species ‘B’
These equations (2.4.6.11) and (2.4.6.12) are valid only when the diameters of ‘A’ and ‘B’ are the same. However, Logan pointed out that they should be reasonably successful if hard sphere diameters are within 5-10%. For a given set of $X_A, \rho, \text{and} T$; $Y_0$ is obtained from equations (2.4.6.7) and (2.4.6.12) and $\Delta M^0_{a,A}$ from equations (2.4.6.9) and (2.4.6.6). The experimentally observable $\Delta M_{a,A}(X_A, \rho, T)$ is then found from equation (2.4.6.8). Using an approximation method to solve for $\tilde{\zeta}(X_A, \rho, T)$ the following relationship can be written:

$$
\Delta M_{a,A}(X_A, \rho, T) = \frac{\zeta_{A,0}(\rho, T)}{cT_{a,A}} \left[ \frac{1 + 1.25Y_0(X_A, \rho, T)}{1 + 2.25Y_0(X_A, \rho, T)} \right] X_A
$$

(2.4.6.13)

This expression provides the noncoincidence splitting of dipolar binary mixture within the MSA. McHale [22, 30] and Mirone and his co-workers [21, 31] were also attempted to simplify this result. Simple dielectric screening or continuum dielectric theory arguments were employed to scale the low number density pair alignment effects embodied in $\zeta_{A,0}(\rho, T)$ by a function development on the dielectric constant ($\epsilon$) or refractive index (n) of the solution. These approaches may not adequately reflect the microscopic origin of the NCE.

Finally, Logan expressed Raman NCE in terms of relative splitting of NCE,

$$
\frac{\Delta M}{\Delta M_{\text{neat}}} = \frac{\left[ 1 + 1.25Y_0(X_A) \right] \left[ 1 + 2.5Y_0(1) \right]^2}{\left[ 1 + 2.5Y_0(X_A) \right]^2 \left[ 1 + 1.25Y_0(1) \right]} \phi
$$

(2.4.6.14)

where, $Y_0(X_A) = \xi \left[ \phi + \left( \frac{\mu_B}{\mu_A} \right)^2 \frac{1 - \phi}{R} \right]$

(2.4.6.15)

$$
\xi = \frac{\mu^2 \rho(1)}{72 \epsilon_0 k_B T}
$$

(2.4.6.16)

$R$ is the ratio of molar volumes of solvent and solute $\left( \frac{V_B}{V_A} \right)$ and $\rho(1)$ is the number density of the neat solute.

Various researchers [32-34] studied relative splitting of NCE using Logan’s model and found in good agreement with the experimental results.
2.5 INTERMOLECULAR INTERACTIONS IN LIQUIDS:

In liquids, the densely packed molecules exhibit strong mutual interactions. The rapidly changing configurations due to the random thermal motion of the molecules modify the binding forces of the liquid molecules. Interaction forces which play major role in binding the molecules or atoms in liquid systems are dipole-dipole, dipole-induced dipole, dispersion and hydrogen bonding interactions.

2.5.1 DIPOLE-DIPOLE (D-D) INTERACTION OR KEE som FORCE:

This interaction arises due to the interaction between the permanent dipole moments of the interacting atoms or molecules. The strength of the interaction depends on the dipole centers separation and their spatial orientation (shown in Fig.2.5.1). The potential energy in the D-D interaction is given by [35]

$$U = \frac{\mu_i \mu_j}{r_{ij}^3} \left[2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)\right]$$  \hspace{1cm} (2.5.1.1)

where, $\mu_i$ and $\mu_j$ are the dipole moments of two interacting molecules $i$ and $j$ respectively, $r_{ij}$ is the distance between the centre of the two interacting dipoles and $\theta_i$, $\phi_i$; $\theta_j$ and $\phi_j$ are the polar co-ordinates giving the orientation of the dipoles.

The orientation of the dipoles provides maximum energy while they interact in anti-parallel fashion and minimum energy for parallel interaction. The interacting energy is zero when the two dipoles interact at an angle $90^0$ to each other.

Keesom [35] assumed that the dipoles in liquids or gases did not exist as species rigidly fixed with one another. It depends on temperature. If the thermal energy is greater than the rotational energy of the dipoles in that material, then the dipoles are free to rotate with respect to one another. Depending on thermal energy the interaction energy is averaged over all values of $\theta$ and $\phi$. Hence, depending on thermal energy, the interaction energy can be written as [35, 36]

$$U = -\frac{2\mu_i \mu_j}{r_{ij}^3} \text{ for } K_B T \langle\frac{\mu_i \mu_j}{r_{ij}^3}\rangle$$  \hspace{1cm} (2.5.1.2)
\[ \frac{2 \mu_i^2 \mu_j^2}{3 K_\beta T r_{ij}^6} \text{ for } K_\beta T \] \[ \frac{\mu_i \mu_j}{r_{ij}^3} \] \hspace{1cm} (2.5.1.3)

**Fig. 2.5.1:** Interaction of two dipoles.

The D-D interaction is relatively weak over the long range separation because of \( \frac{1}{r_{ij}^3} \) dependence. However, D-D interaction over short distances of separation is quite important in liquid system.

For binary liquid mixtures, a more precise D-D interaction is given by [37]

\[ U_{D-D} = -\frac{1}{\varepsilon^2} \frac{2 \mu_i^2 \mu_j^2}{3 K_\beta T r_{ij}^6} \text{ for } K_\beta T \] \[ \frac{\mu_i \mu_j}{\varepsilon r_{ij}^3} \] \hspace{1cm} (2.5.1.4)

where, \( \varepsilon \) is the dielectric constant of solvent (medium).

For axially symmetric molecules (having at least threefold symmetry axes), the dipole-dipole term \( U_{11} \) in space-fixed axes is given by

\[ U_{11} = -\frac{\mu_1 \mu_2}{r^3} \left( 3C_1C_2 - C_{12} \right) \] \hspace{1cm} (2.5.1.5)
where, $C_i$ is the cosine angle between $\mu_i$ and $r$, $C_{12}$ is the cosine of the angle between $\mu_1$ and $\mu_2$. The direction of $r$ is chosen from molecule 1 and 2 in the intermolecular frame with polar axes along $r$.

For axially symmetric molecules, the dipole-quadrupole term $U_{12}$ in the space fixed axes [36] is

$$U_{12} = \frac{3}{2} \left( \frac{\mu_1 Q_2}{r^4} \right) \left[ C_1 (5C_2^2 - 1) - 2C_{12} C_2 \right]$$ (2.5.1.6)

The quadrupole-quadrupole term $U_{22}$ in the space fixed axes is

$$U_{22} = \frac{3}{4} \left( \frac{Q_1 Q_2}{r^5} \right) \left( 1 - 5C_1^2 - 5C_2^2 + 2C_{12}^2 + 35C_1^2C_2^2 - 20C_1C_2C_{12} \right)$$ (2.5.1.7)

where, $Q_1$ and $Q_2$ denote the quadrupole moments of molecules 1 and 2 respectively.

The minimum energy orientations for the three orientations $U_{11}$, $U_{12}$ and $U_{22}$ are shown in Fig.2.5.2. The two linear quadrupoles prefer a T configuration which can be understood using a point charge model such as $+ - +$. These minimum energy configurations are of importance for orientational structures of gas dimers, liquids and solids.

![Fig. 2.5.2: Minimum energy orientation for (a) dipole-dipole, (b) dipole-quadrupole and (c) quadrupole-quadrupole](image-url)
2.5.2 DIPOLE- INDUCED DIPOLE (D-ID) INTERACTION:

Dipole-induced dipole interaction arises due to the interaction between the permanent dipole moment and induced dipole moment. When a molecule with spherical symmetric charge distribution encounters a molecule having permanent dipole moment, then the molecule having dipole moment not only align but also polarized the encountered molecule resulting an induced dipole moment.

The potential energy of the two molecules in the D-ID interaction strongly depends on the polarizability of the molecules. The expression which describes the potential energy of the D-ID interaction is given by [35]

\[
U_{D-ID} = -(\alpha_i \cdot \mu_j^2 + \alpha_j \cdot \mu_i^2) \frac{1}{r_{ij}^6}
\]

where, \(\alpha_i\) and \(\alpha_j\) are the polarizabilities of \(i^{th}\) and \(j^{th}\) molecules.

The dipole induction effect results an attractive interaction proportional to \(\frac{1}{r_{ij}^6}\). The D-ID interactions can exist only when the distance of separation is very small, and hence the interaction energy involved for large distance of separation is extremely low. D-ID interaction is also decreased with the increase of temperature. The expression (2.5.2.1) is valid for the situation in which both the interacting molecules have permanent dipole moments and they act upon each other. If one of the molecules does not have a permanent dipole moment then the expression is written as

\[
U_{D-ID} = -\frac{\alpha_i \cdot \mu_j^2}{r_{ij}^6}
\]

2.5.3 DISPERSION INTERACTION:

Dispersion interaction in liquid system is the most important interaction which occurs between all the adjacent molecules even if molecules do not possess a permanent dipole moment. It arises due to the interaction between induced dipole moment and instantaneous dipole moment of the molecules. Electrons in molecules are in constant random motion and at a certain time they are not symmetric about the nucleus. The lack of symmetry causes imbalance in charge resulting an instantaneous dipole moment. This instantaneous dipole then induces an interactive dipole moment in an adjacent
molecule and the resulting dipoles are aligned through an electrostatic interaction. Dispersion interaction accounts for a major part of the energy that keeps molecules in a liquid phase. There are basically two factors that affect the strength of this interaction—the total number of electrons per unit volume and their polarizabilities. The interaction between the instantaneous dipole moment and induced dipole moment called the dispersion interaction was calculated by London in 1930 using quantum mechanics and is given by [38]

\[
U_{\text{Dis}} = -\frac{3}{2} \frac{I_i I_j}{(I_i + I_j)} \frac{\alpha_i \alpha_j}{r_{ij}^6}
\]  \hspace{1cm} (2.5.3.1)

where, \(I_i\) and \(I_j\) are the ionization potentials of \(i\)th and \(j\)th molecules respectively, \(r_{ij}\) is the separation between two interacting dipoles and \(\alpha_i\) and \(\alpha_j\) are the polarizabilities of \(i\)th and \(j\)th molecules respectively.

The expression for dispersion interaction including refractive index is given by [37]

\[
U_{\text{Dis}} = -\frac{1}{2} \frac{I_i I_j}{(I_i + I_j)} \frac{\alpha_i \alpha_j}{n^4 r_{ij}^6}
\]  \hspace{1cm} (2.5.3.2)

If the intermolecular P.E. (U) between the interacting two pairs of molecules or atoms is approximated as the sum of the short range (\(U_{\text{rep}}\)) and long-range (\(U_{\text{D-D}}\), \(U_{\text{D-ID}}\), \(U_{\text{Dis}}\)) potentials then the functional form of the intermolecular potential (U) considering both the potentials is given by [38, 40]

\[
U = 4\delta \left[ \left( \frac{\lambda}{r} \right)^{12} - \left( \frac{\lambda}{r} \right)^{6} \right]
\]  \hspace{1cm} (2.5.3.3)

where, \(\delta\) is the well depth and \(\lambda\) is the intermolecular distance parameter (the parameter \(\lambda\) is an approximation to the sum of the average radii of two molecules).

This intermolecular potential is known as Lennard-Jones potential. The potential has an attractive tail at large \(\lambda\). It reaches a minimum around 1.122 \(\lambda\) and it is strongly repulsive at shorter distance passing through zero at \(r = \lambda\) and increases steeply as \(r\) decreases further. The term \(\frac{1}{r^{12}}\) dominating at short distance, models the repulsion between two atoms when they are brought very close to each other. Its physical origin relates to the pauli’s principle. When electronic clouds surrounding the atoms starts
overlap, the energy of the system increases abruptly. The term \( \frac{1}{r^6} \) dominating at large distance constitute the attractive part. The attractive potential term \( 4\delta \left( \frac{\lambda}{r} \right)^6 \) is originated by D-D, D-ID and instantaneous dipole-ID interactions.

In general terms the interaction potential is written as

\[
U = 4\delta \left( \frac{\lambda^m}{r} - \left( \frac{\lambda}{r} \right)^n \right) \quad \text{for } m\neq n
\]

(2.5.3.4)

where, \( m \) and \( n \) are two integers. The potentials are zero at \( r = \infty \) and \( r = \lambda \) and have a minimum value at \( \lambda_{\min} = r \left( \frac{n}{m} \right)^{\frac{1}{m-n}} \)

(2.5.3.5)

2.5.4 HYDROGEN BONDING:

It is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment Y-H in which Y is more electronegative than H, and an atom or a group of atoms in the same or a different molecule in which there is evidence of bond formation. However, it is not a true bond but particularly a strong dipole-dipole interaction. The strength of hydrogen bond (5 to 10 K cal per bond) is much less than the strength of ordinary covalent bond. Nevertheless, it has a very significant effect on the physical properties such as boiling points, solubility and molecular motions of compounds. It plays important roles in studies of supramolecular, crystal engineering, materials and life sciences.

2.6 THEORY OF RAMAN SPECTROSCOPY:

Raman spectroscopy is a form of optical spectroscopy based on a light scattering phenomenon. It arises from the interaction of photon of incident light with the electrons present in the illuminated molecule. When an incident photon collides with a molecule, its interaction may be elastic or inelastic. The former process is known as Rayleigh scattering and the later is called Raman scattering. In inelastic scattering the molecules make a transition to higher energy state resulting the photon loses energy and scattered with lower frequency and the process is termed as stokes Raman scattering. The molecules which are already in a higher vibrational energy state (\( \nu = 1 \)) may make a
transition to a lower energy state \( (\nu = 0) \). In such case, the photons are scattered with increased frequency and the process is termed as anti-stokes Raman scattering. Fig. 2.6.1 shown below is a diagram with the mechanism of Rayleigh and Raman scattering [41]. Here, \( h\nu \) is the energy of incident photon.

![Diagram with the mechanism of Rayleigh and Raman scattering.](image)

**Fig. 2.6.1:** Diagram with the mechanism of Rayleigh and Raman scattering.

The Raman Effect arises because of an induced oscillating dipole moment generated in the molecules by the interaction of the electric field vector of the incident radiation. When the electric field of the incident radiation is very large, the non-linear contributions to the molecular polarizability become significant. The induced electric dipole moment by a highly intense electric field is given by [41]

\[
\mu = \alpha_1 E + \alpha_2 E^2 + \alpha_3 E^3 + \cdots \tag{2.6.1}
\]

where, \( E \) and \( \mu \) are the electric field and induced dipole moment of the molecule, \( \alpha_1 \) is the polarizability tensor of rank 2 while \( \alpha_2 \) and \( \alpha_3 \) are hyperpolarizabilities of rank
3 and 4 respectively. The first term (linear term) in equation (2.6.1) represents the spontaneous Raman scattering. If the medium is anisotropic, then

\[
\mu_i = \begin{pmatrix}
\alpha_{11} & \alpha_{12} & \alpha_{13} \\
\alpha_{21} & \alpha_{22} & \alpha_{23} \\
\alpha_{31} & \alpha_{32} & \alpha_{33}
\end{pmatrix}
\begin{pmatrix}
E_1 \\
E_2 \\
E_3
\end{pmatrix}
\] (2.6.2)

As the molecule vibrates the polarizability will change. The variation of the polarizability with vibration of molecule can be expressed by expanding each component \(\alpha_{ij}\) of the polarizability tensor in a Taylor series with respect to the normal coordinates of vibration as [42]

\[
\alpha_{ij}(t) = \left(\alpha_{ij}\right)_0 \sum \frac{\partial \alpha_{ij}}{\partial Q_{ij}} Q_k + \frac{1}{2} \sum \frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l} Q_k Q_l
\] (2.6.3)

where, \(Q_k, Q_l \cdots\) are normal coordinates associated with the molecular vibrational frequencies \(\nu_k, \nu_l \cdots\) and the summations are over all normal coordinates. \(\left(\alpha_{ij}\right)_0\) is the polarizability tensor of the molecule in its equilibrium position. For normal linear Raman effect considering simple harmonic approximation.

\[
\left(\alpha_{ij}\right)_k = \left(\alpha_{ij}\right)_0 \frac{\partial \alpha_{ij}}{\partial Q_{ij}} Q_k
\] (2.6.4) (Neglecting higher order term.)

For normal mode undergoing simple harmonic motion

\[
Q_k = Q_k^0 \cos(2\pi c \nu_k t)
\] (2.6.5)

where, \(Q_k^0\) and \(\nu\) are the amplitude and frequency of the vibration.

The ‘x’ component of the oscillating electric field of the incident radiation can be expressed by

\[
E_i = E_i^0 \cos(2\pi c \nu_0 t)
\] (2.6.6)

where, \(E_i^0\) is the amplitude of the electric field vector and \(\nu_0\) is the frequency of the incident light.

Therefore, ‘x’ component of the induced dipole moment

\[
\alpha_{11} E_1 = \left(\alpha_{11}\right)_0 + \frac{\partial \alpha_{11}}{\partial Q_k} Q_k^0 \cos(2\pi c \nu_k t) E_i^0 \cos(2\pi c \nu_0 t)
\]
\[ \left( \alpha_{11} \right)_0 E_1^0 \cos \left( 2 \pi c v_o t \right) + \left( \frac{\partial \alpha_{11}}{\partial Q_k} \right)_0 Q_k^0 \cos \left( 2 \pi c v_k t \right) E_1^0 \cos \left( 2 \pi c v_0 t \right) \]

\[ = \left[ \left( \alpha_{11} \right)_0 E_1^0 \cos \left( 2 \pi c v_o t \right) + \frac{1}{2} E_1^0 \left( \frac{\partial \alpha_{11}}{\partial Q_k} \right)_0 Q_k^0 \cos \left( 2 \pi c (v_0 + v_k) t \right) \cos \left( 2 \pi c (v_0 - v_k) t \right) \right] \quad (2.6.7) \]

The first term on the right hand side of this equation characterizes the intensity of the Rayleigh line and is proportional to \( \left( \alpha_{11} \right)_0 \). Raman intensities occur at \( (v_0 - v_k) \) and \( (v_0 + v_k) \) are Stokes and anti-Stokes lines respectively. The above expression (2.6.7) shows that both Stokes and anti-Stokes lines have the same intensity. Generally stokes lines are more intense than anti-stokes lines [43]. The discrepancy of the classical treatment of Raman effect can be removed quantum mechanically. The correct intensity ratio of Stokes and anti-Stokes lines found quantum mechanically is given by [44]

\[ \frac{I_{\text{anti-stokes}}}{I_{\text{stokes}}} = \frac{(v_0 + v_k)^4}{(v_0 - v_k)^4} e^{-\left( \frac{h v_k}{k T} \right)} \quad (2.6.8) \]

where, \( k \) is the Boltzmann constant and \( T \) is the temperature. The intensity of anti-stokes lines are too low to observed. Hence, most Raman spectroscopy is done by studying stokes lines.

Vibrational Raman spectrum generally observed in terms of wavenumber shift in the unit of cm\(^{-1}\). For a molecule having ‘n’ number of atoms has 3n-6, (3n-5, if linear) normal modes and are anharmonic. The vibrational energy of an anharmonic oscillator is given by [45]

\[ \epsilon_v = \left( \nu + \frac{1}{2} \right) \nu_e - \left( \nu + \frac{1}{2} \right) x_e \nu_e \quad \text{cm}^{-1} \quad (2.6.9) \]

where, \( \nu = 0, 1, 2, \ldots \), \( \nu_e \) is the equilibrium oscillation frequency of the anharmonic system and \( x_e \) is the anharmonicity constant. The selection rule for Raman transition is \( \Delta \nu = \pm 1, \pm 2, \pm 3, \ldots \).
However, we consider only the \( \nu = 0 \rightarrow \nu = 1 \) transition as the population in the \( \nu = 1, 2, 3, \ldots \) will be negligible. Again, Raman scattering is very weak, overtone and combination bands appear seldom in Raman spectra. The energy difference between two vibrational levels (\( \nu = 0 \rightarrow \nu = 1 \)) is given by

\[
\varepsilon_1 - \varepsilon_0 = \nu_e (1 - 2x_e) \text{ cm}^{-1}
\]

Corresponding to each normal mode of vibration, Raman frequency is given by

\[
\nu = \nu_0 \pm \nu_e (1 - 2x_e) \text{ cm}^{-1}
\]

The minus sign corresponds to Stokes lines and plus sign to anti-Stokes lines.

2.7 DEPOLARIZATION RATIO (D.R):

The depolarization ratio is the intensity ratio of the scattered polarized and depolarized Raman components. Let Y axis be the direction of the incident radiation and the direction of observation be perpendicular to the Y axis in the ZX plane (Fig. 2.7.1). If \( I_\perp \) be the intensity of scattered polarized light perpendicular to the ZX plane and \( I_\parallel \) be that of parallel to the ZX plane then the depolarization ratio is defined as [44]

\[
\rho = \frac{I_\perp}{I_\parallel}
\]

(2.7.1)

The intensity of the Raman components is directly related to the polarizability.

In liquids, for plane polarized incident radiation, the intensity of \( I_\perp \) is given by

\[
I_\perp \propto 3 \left( \alpha_i' \right)^2
\]

(2.7.2)

and that of \( I_\parallel \) component is proportional to

\[
I_\parallel \propto 45 \left( \alpha_i' \right)^2 + 4 \left( \alpha_a' \right)^2
\]

(2.7.3)

where, \( \alpha_i' \) and \( \alpha_a' \) are defined as the derivatives of the isotropic and anisotropic polarizabilities

\[
\alpha_i' = \frac{1}{3} \left( \alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz} \right) \text{ and}
\]

\[
\alpha_a' = \frac{1}{2} \left[ \left( \alpha'_{xx} - \alpha'_{yy} \right)^2 + \left( \alpha'_{yy} - \alpha'_{zz} \right)^2 + \left( \alpha'_{zz} - \alpha'_{xx} \right)^2 \right] + 6 \left( \alpha_{xy}' + \alpha_{yz}' + \alpha_{zx}' \right)
\]

Using equations (2.7.2) and (2.7.3) in equation (2.7.1), we get

\[
\rho = \frac{3 \left( \alpha_a' \right)^2}{45 \left( \alpha_i' \right)^2 + 4 \left( \alpha_a' \right)^2}
\]

(2.7.4)
For totally symmetric vibration, the isotropic part of the polarizability only changes and hence $\alpha_i' \neq 0$. With 90° scattering geometry for a polarized incident light the DR will have a value between 0 and 0.75. For totally symmetric vibrations $\rho < 0.75$, while for non-totally symmetric vibrations $\rho = 0.75$ [46].

![Diagram](image)

**Fig. 2.7.1**: Raman scattered radiation using unpolarized light showing polarized components.

### 2.8 HARTREE-FOCK APPROXIMATION [47, 48]:

One of the primary goals in Quantum Mechanics is to solve the Schrödinger equation and to determine the electronic structures of atoms and molecules. The Hartree-Fock (HF) approximation plays an important role in quantum chemistry by solving Schrödinger equation in an iterative method. Describing the electronic wave function by a product of one-electron functions, it is possible to split multidimensional Schrödinger equation into set of one-dimensional equations and solve large many-body problem.

The electronic Schrödinger equation for a fixed set of locations $R$ of nuclei is given by

$$ H \psi (r, R) = E(R) \psi (r, R) $$

(2.8.1)
$E(R)$ is the electronic energy. The electronic wave function $\psi$ depends on the electronic coordinate’s $r$ and parametrically on $R$. The Hamiltonian is expressed as

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2_i - \sum_i \sum_j \frac{Z_i e^2}{4\Pi \varepsilon_0 r_{ij}} + \frac{1}{2} \sum_{ij} \frac{e^2}{4\Pi \varepsilon_0 r_{ij}}$$

(2.8.2)

The critical complication in all electronic structure calculations is the presence of the electron-electron potential energy, which depends on the electron-electron separations $r_{ij}$.

With the inclusion of spin to the electron, the one-electron wave function is represented by a product of the spatial and spin functions ($\alpha_{\pm}$). That is

$$\psi(x) = \psi(r) \alpha_{\pm}$$

(2.8.3)

where, ‘+’ is for spin up and ‘–’ is for spin down.

The wave functions $\psi(x)$ are called spin orbitals, where $x$ is a generalized coordinate which includes spatial and spin coordinates.

The electronic wave function obeys Pauli’s exclusion principle. So, the Hartree-Fock theory uses the wave function in the form of Slater determinant. Therefore, the $n$-electron Slater determinant is given by

$$\psi_e(x_1, x_2, \ldots x_n) = (n!)^{\frac{1}{2}} \det [\psi_1(x_1)\psi_2(x_2)\ldots\psi_n(x_n)]$$

(2.8.4)

The factor $(n!)^{\frac{1}{2}}$ is a normalization factor.

For a wave function in the form of a Slater determinant, the expectation energy is given as a sum of one-electron term and two-electron potential terms. i.e.

$$\langle i | H | i \rangle = -\frac{\hbar^2}{2m_e} \int \psi_i^*(r) \frac{\partial^2 \psi_i(r)}{\partial r_i^2} dr - \frac{e^2}{4\Pi \varepsilon_0} \sum_j \int |\psi_j(r)|^2 \frac{Z_j}{|R_j - r|} dr +$$

$$\frac{1}{2} \sum_{ij} \left[ (ij|ij) - (ij|ji) \right]$$

(2.8.5)

where, $(ij|kl) = \frac{e^2}{4\Pi \varepsilon_0} \int dx_1 dx_2 \psi_i^*(x_1) \psi_j^*(x_2) \frac{1}{|x_1 - x_2|} \psi_k(x_1) \psi_l(x_2)$

(2.8.6)

The first two-electron term of the potential corresponds to the classical Coulomb repulsion; the other is the so called exchange term with no classical analogy, which is
not zero only for electrons with parallel spins. The integrals are usually expressed using
the convenient form of the Coulomb operator $\hat{J}_i$ and the exchange operator $\hat{K}_i$.

$$\hat{J}_i \psi_j(x) = j_0 \int \left( \frac{|\psi_i(x_i)|^2}{|x-x_i|} \right) \psi_j(x_i)$$  \hspace{1cm} (2.8.7)

$$\hat{K}_i \psi_j(x) = j_0 \int \left( \frac{\psi_i(x_i) \psi_j^*(x_i)}{|x-x_i|} \right) \psi_i(x_i)$$  \hspace{1cm} (2.8.8)

where, $j_0 = \frac{e^2}{4\pi\varepsilon_0}$

The exchange integrals arise because of the antisymmetric nature of the wavefunction.

The Hartree-Fock theory is based on the variational principle and to find the best
energy, the function $E[\psi_e] = \left\langle \psi_e \left| \hat{H} \right| \psi_e \right\rangle$ is minimized with respect to the spin orbitals
$\{\psi_i(x_i)\}$.

Introducing the Lagrange multipliers $\varepsilon_i$ and assuming orthonormality of the spin
orbitals, the function $L$ has the form

$$L[\psi_i] = \left\langle \psi_e \left| \hat{H} \right| \psi_e \right\rangle + \frac{1}{2} \sum_{ij} \left[ \langle ij | jj \rangle - \langle ij | ji \rangle \right] - \sum_i \varepsilon_i \left( \langle \psi_i | \psi_i \rangle - 1 \right)$$  \hspace{1cm} (2.8.9)

Minimizing the functional $L$ by setting its first variation to zero, the Hartree-Fock
equations can be expressed as

$$\left[ \hat{h} + \sum_j \left( \hat{\hat{J}}_j - \hat{\hat{K}}_j \right) \right] \psi_i(x_i) = \varepsilon_i \psi_i(x_i) \hspace{1cm} i=1, 2, 3, \ldots, n$$  \hspace{1cm} (2.8.10)

where, $\varepsilon_i = \hat{h} + \sum_j \left( \hat{\hat{J}}_j - \hat{\hat{K}}_j \right)$ is the Fock operator.

These equations are similar to linear eigen value equations. The coulomb and exchange
operators depend on the solutions $\psi_i$. The Hartree-Fock equations are usually solved by
iterative procedures. Starting from an initial guess of the spin orbitals, the equations are
solved to obtain new spin orbitals. The solutions are inserted into the equations again
and new orbitals are calculated. The procedure is repeated until self-consistency is reach
i.e, the spin orbital do not vary. The result of Hartree-Fock calculation depends on the
choice of basis sets. The basis sets used in Hartree-Fock calculation depending on the
method used and the size of the atoms are STO-3G, 4-31G, 3-21G*, 6-31G*, 6-31G**, 6-311G, SDD etc.

2.9 GEOMETRY OPTIMIZATION AND VIBRATIONAL WAVENUMBER CALCULATIONS [49]:

Gaussian software package i.e. Gaussian09 and Gauss View3 have been used as our quantum chemical calculation tool. Hartree-Fock method is used for geometry optimization and vibrational wavenumber calculations. Main calculation is done by Gaussian package while GaussView is a very helpful tool to make the calculation more easily. We can run Gaussian calculation, usually, in two ways: one is to configure input file of calculation directly on the input panel of Gaussian software interface, and another way is to configure input file with the help of Gauss View package. In order to run program directly on Gaussian package we need to declare job type, atomic or molecular specifications such as atomic number, atomic coordinates, bonding types, etc. manually. Usually, the use of Gaussian package is little bit unfriendly and time consuming. On the other hand one can do the above operations with the help of GaussView easily within very short time. Hence the role of GaussView is not only to help for building the molecular structure and to configure the input files but also help to analyze as well as visualize the output of calculations. In our calculation we use GaussView to run the Gaussian calculation because it is possible to run the Gaussian program from the GaussView interface. Once Gaussian package in installed on a computer the further installation of GaussView creates a link with the Gaussian software automatically.

The molecular structures built in Gauss view are not geometrically optimized, that is the initial bond lengths, bond angles obtained by this way should not be used for molecular calculation. The first principle condition of any electronic structure calculation is to obtain optimized geometry of the sample. Geometry optimization refers to the finding of the total energy of the system as minimum as possible and the corresponding bond lengths, bond angles, dihedral etc. The optimized geometry is not
an abstract matter rather it depends on the methods of calculation well as on the choice of basis sets.

The program used to optimization and vibrational wavenumber calculations in Hartree-Fock (HF) method is “RHF/6-31+ G (d, p) Opt Freq”. The polarization and diffuse functions have been used for the better treatment of the calculation. The meaning of the symbolic representation of the basis sets, 6-31+ G (d, p) is that one contracted Gaussian composed of 6 primitives is used to represent each inner shell atomic orbital. The basis set starts with split-valence of 6-31+ G (d, p) basis and adds six polarization functions in the form of 6 d type functions in additions to 3-p type polarization functions for each H atom. Scaling factor 0.9007 has been applied for our vibrational wavenumber calculations and it accounts for systematic errors caused by basis set incompleteness, electron correlation and vibrational anharmonicity [50].
2.10 REFERENCES:


[40] www.fisca.uniud.it