CHAPTER – I

Principles of Vibrational Spectroscopy, Infrared & Raman Instrumentation
Vibrational spectroscopy is one of the most valuable branch of science for elucidating the molecular structure and characteristics of organic, inorganic, co-ordination compounds and polymers. Vibrational spectroscopy has contributed significantly to the growth of such other areas such as catalysis, fast reaction dynamics, charge-transfer complexes etc. Its main applications are: to study the intramolecular forces acting between the atoms in the molecule, the intermolecular forces or the degree of association in condensed phases and in the determination of molecular symmetries. Other applications include the identification of functional groups or compound identification, determination of nature and strength of the chemical bond and the calculation of thermodynamic properties.

Molecular vibrational informations can be obtained from the absorption or the emission of infrared radiation and also from the inelastic scattering of light. The study of molecular structure by spectrometry depends primarily on the existence of the vibrating motion of atoms within the molecule. These motions in turn depend on the nature and arrangement of the constituent atoms. Radiant energy, particularly infrared, incident upon the matter, is affected by the presence of such motions. A study of this behaviour of
infrared radiation is thus capable of giving indirect but very valuable information on molecular structure.

Light is scattered by a material in different ways, and the scattering processes are usually named after the scientists who made major contributions to the field. Elastically scattered light that has the same frequency as the incident radiation is known as Rayleigh scattering. Mie scattering is also an elastic scattering process; it is associated with the scattering of large particles. Brillouin scattering, which is in essence a Doppler effect, produces small frequency shifts ($< 0.1 \text{ cm}^{-1}$) of the scattered light and is usually ignored in molecular vibrational spectroscopy. Raman scattering is an inelastic process in which light exchanges energy with the sample and consequently appears at a different frequency. By measuring these frequency differences, details about the vibrational frequencies within the sample molecules can be obtained.

**INFRARED SPECTROSCOPY**

The transition moment for infrared absorption involves the permanent dipole moment operator, instead of the induced dipole moment operator as in the case of Raman scattering. Therefore the transition probability is proportional to the square of

$$[\mathbf{P}]_f = \langle f | \mathbf{P} | i \rangle$$  \hspace{1cm} (1.1)

Where $\mathbf{P}$ is the electric dipole moment operator. It can be shown that the transition moment has the same transformation properties as
Thus, the infrared activity of a non-degenerate fundamental vibration $Q_j$ requires, product of the type $Q_jx$, $Q_jy$ or $Q_jz$ to be totally symmetric. That is, the fundamental vibrational modes, which are in the same symmetry species with $x$, $y$ or $z$ vectors are infrared active.

**INFRARED DICHROISM**

The absorption of infrared radiation by a molecule can be given in terms of the absorbance $A$, by

$$A = \log_{10} \left( \frac{I_o}{I} \right) (M:E)^2$$  \hspace{1cm} (1.3)

where $I_o$ and $I$ are the incident and transmitted intensities of the absorbing frequency, $M$ is the transition moment vector of the normal mode, $M = \frac{\partial \mu}{\partial Q}$, and $E$ is the electrical field vector of the incident beam at the absorbing frequency. For a given normal mode of vibration, the transition moment vector has a definite orientation in the molecule. Consequently, if the angle between $M$ and $E$ is $\theta$, the absorbance is proportional to $\cos^2 \theta$. In the ordered solid state, the molecules are fixed and the direction of the transition moment vector of each molecule has the same orientation space. The absorbance of a given infrared band will then change, depending on (i) the direction of transition moment vector of the particular vibrational mode with respect to the molecular axis and (ii) the polarization of the electric vector of the incident radiation. A maximum absorbance will occur when the electric vector of the polarization light is parallel to the direction of the transition
moment and no absorption will occur when the two vectors are perpendicular. When measurements are made with the electric vector parallel or perpendicular to the preferred direction, a dichroic ratio $R$,

$$R = A_{\parallel} / A_{\perp}$$  \hfill (1.4)

can be measured, where $A_{\parallel}$ is the absorbance with parallel polarized light and the absorbance with perpendicular polarized light is termed $A_{\perp}$.

**MUTUAL EXCLUSION RULE**

For molecules with centre of symmetry, transitions that are allowed in the Raman spectrum are forbidden in infrared and conversely, transitions that are allowed in the infrared spectrum are forbidden in Raman. That is in Raman effect, only transitions between states of same symmetry with respect to the centre of symmetry ($i$), can takes place ($g\leftrightarrow g$, $u\leftrightarrow u$), however in the infrared, only transition between the states of opposite symmetry with respect to the centre of symmetry are allowed ($g\leftrightarrow u$).

It is clear that all the components of electric dipole moment $\vec{P}$, change sign for a reflection at the centre of symmetry, where as, the components of the induced dipole moment which behave as the product of the two components of $\vec{P}$, remain unchanged. Thus for a fundamental vibrational transition, only the vibrational modes ($g$) which are symmetric with respect to the centre of symmetry can be Raman active and those are antisymmetric ($u$)
with respect to centre of symmetry can be infrared active if they also hold the selection rule requirements.

**INSTRUMENTATION – INFRARED SPECTROSCOPY**

Conventional infrared spectrometer suffer from several disadvantages in sensitivity, speed and wavelength accuracy. Most of the light from the source does not in fact pass through the sample to the detector, that is lost in the narrowness of the focusing slits and results in poor sensitivity. Since the spectrum takes minutes to record, the method cannot be applied to fast process. Consequently, the dispersive infrared spectrometers suffer from wavelength inaccuracies associated with the backlash in the mechanical movements, such as in the rotation of mirrors and gratings.

There are two types of infrared spectrometer characterized by the manner in which the infrared frequencies are handled. In the first type, the infrared light is separated into its individual frequencies by dispersion using a grating monochromator or a prism. Whereas in the second type the infrared frequencies are allowed to interact to produce an interference pattern and this pattern is then analysed mathematically using Fourier Tranform to determine the individual frequencies and their intensities.

The essential problem of the prism or grating spectrometer lies with its monochromator. This contains narrow slit at the entrance and exits which limit the wavenumber range of the radiation reaching the detector to one resolution width. When approaching the limiting resolving power of the instrument to
achieve a high-resolution spectrum, the spectral quality deteriorates if the energy reaching the detector becomes severely limited. Weak signals are sometimes due to attempting high resolution by reducing the slit width, which will increase the noise or longer time to obtain spectrum. Samples from which a very quick measurement is needed as, for example, in the eluant from chromatography column or samples decomposition problems then both resolution and signal to noise have to be sacrificed. Hence resolution, noise and time are three interdependent variables. Improvement in one variable reflects in other two.

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

THEORY AND INSTRUMENTATION

Fourier transform infrared (FTIR) spectroscopy is an interference technique through which recent advances in digital computer technology has demonstrated in superiority to dispersive IR techniques. Fourier transform spectroscopy uses the Michelson interferometer as the multiplex optical device[1]. FTIR spectrometer has, for analysts, three major advantages over conventional dispersive infrared spectrometers. Firstly, as the radiation is not constrained to pass through any slit mechanism, it can interact with much larger samples than with a dispersive instrument which is advantageous in getting high quality spectra from samples that are inherently rather opaque.

Secondly, the accuracy of wavelength determination is so high that computer averaging of spectra is easy, i.e., it is easy to enhance the signal to
noise ratio of the spectra allowing studies to be made of weak spectral features or of dilute samples. Thirdly, as the scanning of a spectrum is very rapid, it is possible to record spectra very quickly.

FTIR spectroscopy with its energy advantages, has made it possible now, to obtain spectra under conditions previously considered difficult or impossible. New accessories have been developed just to take advantage of the capabilities of the FT technique. The building blocks of all FTIR instrument have the chain

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SOURCE → INTERFEROMETER → SAMPLE → DETECTOR
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Source

The most commonly used radiation source is globar operating on the basis of the black body radiation. It consists of a SiC (silicon carbide) with dimensions 2 cm in length and 0.5 cm in diameter heated to about 1450 K. The globar is generally used in the spectral range up to 100 μm. The globar is operated in vacuum only. Nernst glower (sintered mixtures of the oxides of Zr, Th, Ce, Y, Er) is also used as source in some spectrometers depending upon the spectral range. For more sophisticated applications gas plasmas must be used as radiation sources. Besides thermic sources semiconductor lasers are also used in FIR, MIR and NIR regions. Microwave generators like kelstrons or magnetrons are also used for wide frequency range.
Interferometer

The interferometer is the heart of the FTIR instrument. The interferometer is the bit that analyses the infrared or near infrared and hence enable us to generate the spectrum. The classic Michelson interferometer is shown in Fig. 1, contain a source, detector, stationary and moving mirrors and a beam splitter.

![Fig. 1 Optical path in Michelson Interferometer](image)

Fig.1 Optical path in Michelson Interferometer
(LS-Light Source, L-Lenses, M-Mirrors, BS-Beam Splitter)

The beam splitter is the crystal of potassium bromide coated with germanium [2], splits the incident light equally reflecting half to the stationary mirror while transmitting the other half to the moving mirror. The white light from the source located at the focus of lens $L_1$ is separated into two parts by
the beam splitter. The reflected part is focused onto the detector D after reflection from the stationary mirror M\textsubscript{1} and after a second split by the beam splitter. The transmitted part of the light is also focused onto the detector after it was reflected from the mirror M\textsubscript{2} and split again by the beam splitter. The mirror M\textsubscript{2} is mobile and can glide a distance \(\Delta x\). In this way interference fringes develop at the detector. Their intensity \(I(x)\) depends on the position \(x\) of the mirror M\textsubscript{2}. \(I(x)\) is termed interferogram function.

If the incident beam is monochromatic of the form \(E(x,t) = E_0 \cos(kx - \omega t)\) the field \(E_D\) at the detector is

\[
E_D = \frac{1}{2} \left\{ E_0 \cos(\omega_0 t - k_0 x) + E_0 \cos[k_0 (x + 2\Delta x) - \omega_0 t]\right\},
\]

where \(2\Delta x\) is the optical path difference between the two beams. The intensity at the detector is given by the following expression

\[
I(x) = c_o E_o <E^2> = \frac{c_o E_o^3}{4} E_o^2 [1 + \cos(4\pi\nu_o x)]
\]

In terms of the spectral intensity \(I(\nu) = c_o E_o^2 \delta(\nu - \nu_o)/2\) the above equation can be written as

\[
I(x) = \frac{1}{2} \int I(\nu)[1 + \cos(4\pi\nu x)] d\nu
\]

Generalising this equation to an arbitrary intensity spectrum \(I(\nu)\) yields the basic relationship for Fourier spectroscopy

\[
I'(x) = I(x) - \frac{1}{2} \int I(\nu) d\nu = \frac{1}{2} \int I(\nu) \cos(4\pi\nu x) d\nu
\]
The interferogram function $I(x)$ or $I'(x)$ contains the whole information about the spectrum $I(v)$. In fact, $I'(x)$ is the Fourier transform of $I(v)$ performed with a cosine function. The observed intensity $I(x)$ oscillates around an average intensity $\int I(v)dv/2 = I_o/2$ which is exactly half of the original total intensity of the beam. For $x = 0$ it reaches its maximum value of $I_o$ as immediately seen from equation (1.7). This position corresponds to zero optical path difference. It is called the white light position. For $x \to \infty$ the coherence of the radiation is lost, results the intensity at the detector becomes then $I_o/2$. A fourier transformation of $I'(x)$ yields for $x = y/2$

$$\int I'(y/2) \cos(2\pi v'y) dy = \frac{1}{2} \int I(v)dv \int \cos(2\pi vy) \cos(2\pi v'y) dy = I(v')/2 \quad (1.9)$$

Since the integration over $y$ gives $\delta(v-v')$. This equation means we obtain the spectral components of the light directly from the interferogram by Fourier transformation, without any spectral dispersion [3]. This Fourier spectroscopy has many basic advantages when compared to dispersive spectroscopy.

The 'energy advantage' originates from the fact that during the whole period of measurement nearly always the total beam intensity hits the detector. This means the detection operates on a high signal level which improves the signal-to-noise ratio, particularly for weak radiation sources.

The 'Fellgett' or the 'multiplex advantage' originate from the simultaneous measurement of full spectrum. To obtain spectra from radiation of very low intensity such as from astronomical sources, all the frequencies
are recorded simultaneously during the whole period $T$ of detection rather than sequentially as in dispersive spectroscopy, they are said to be 'multiplexed'. In dispersive spectroscopy $N$ parts of the widths $\Delta \nu$ of the spectrum will be measured successively so that for each part only the time $T' = T/N$ is available. The signal-to-noise ratio would be smaller by $1/\sqrt{N}$.

Interferometer also have greater 'throughput' than dispersive IR methods. Throughput, a measure of the optical efficiency of the system, is defined as the product of the area and solid angle of the beam passing from the source to the detector. Since there is no slit in FTIR spectrometer, the cross section of the beam of radiation in an interferometer can be much larger than that of a dispersive spectrometer, which leads to considerable improvements in signal-to-noise ratio. But in many chemical and analytical applications the sample size limits the energy advantage. The optimum resolution is obtained by using the theoretical relationship $r = F\sqrt{(2/R_o)}$ where $r$ is the radius of the entrance pinhole and $R_o$ is the resolution. This yields for the brightness of the interferometer

$$E = \frac{r^2 \pi A^2}{F^2} = \frac{(2\pi A^2)}{R_o} = \frac{(2\pi A^2/\nu)\delta \nu}{F}$$

(1.10)

where $A$ is the beam diameter in the spectrometer. For dispersive spectrometer the brightness is given by

$$E = \frac{(AR_o H \delta \lambda)}{F}$$

(1.11)
where $H$ and $F$ are the height of the slit and the focal length of the grating spectrometer respectively. By comparing these two equations it is found that for Fourier spectrometer the enhancement of the brightness is of the order of 500 times greater than the grating and prism spectrometers known as the ‘Jacquinot advantage’.

The dispersive spectrometers suffer from greater wavenumber errors, of a less predictable form owing to their general mechanical and thermal instability and can also be affected by non-uniform illumination across the monochromator entrance slit [4]. FT spectrometers typically use the He-Ne lasers as a reference beam to monitor the displacement of the moving optical element, so providing an active internal absolute wavelength calibration [5]. This feature of FT spectrometers is known as the ‘Connes advantage’.

**Detectors**

There are two commonly used detectors depending upon the energy reaching the detector. A normal detector for routine work functions based on pyroelectric effect. Crystals such as deuterium triglycine sulphate in a temperature resistant alkali halide window, with a permanent electric dipole moment respond to a sudden change in the dipolar order with the generation of compensating surface charges. IR or heat pulses can be the origin of such induced disorder. The voltage accompanying the compensation charges can be used to detect the IR or the heat pulse. The commonly used system is the
Golay detector, which works under a pneumatic principle. A thin film absorbs the incident IR light. The generated heat increases the pressure in the gas chamber, which drives a mirror. The mirror is a part of an optical system that images a grating onto itself. Any small motion of the mirror leads to a change in the overlap between grating and the image and thus gives a signal to the detector. Fig. 2 shows the layout of Bruker IFS 66V spectrometer used to record FTIR and FT-Raman spectra in the present work.

There are a number of advantages of FTIR instrumentation relative to dispersive IR instrumentation including:

- Higher signal-to-noise due to improved detector irradiance.
- Higher energy throughput because no slits are required.
- Accurate wavelength measurements due to calibration with an internal laser.
- High speed as interferometers can be more rapidly scanned than monochromaters.
- Signal-to-noise ratio can be improved by signal averaging.
- Simultaneously records the full spectrum.
- Spectral resolution can be adjusted from 0.5 to 16 cm\(^{-1}\) to the application.
- Large dynamic range: \(10^4\) to \(10^6\).
Fig. 2. Layout of Bruker IFS 66V Fourier Transform Spectrometer
(S-Light Source, M-Gliding Mirror, FM-Fixed Mirror, BS-Beam Splitter, SP-Sample, EB-External Beam, ES-External Source and DTGS, MCT, GB-Detectors)
RAMAN SPECTROSCOPY

The use of Raman spectroscopy for molecular structure has a long and productive history. A characteristic feature of Raman scattering is the change in frequency of the scattered light. As distinct from luminescence where the frequency of the re-emitted radiation is also changed in Raman scattering, the system is not excited for any measurable length of time to a higher energy level.

If the molecule is initially at state \( |i> \) with the energy \( E_i \) and after interaction with the monochromatic radiation of angular frequency \( \omega_o \) goes to state \( |f> \) with energy \( E_f \), from the conservation of energy,

\[
E_i + h \omega_o = E_f + h (\omega_o \pm \omega_f)
\]  

where, \( h \omega_f = E_f - E_i \) and \( h (\omega_o \pm \omega_f) = h \omega_s \), the energy of the scattered photon.

If \( E_f > E_i \), \( \omega_s = \omega_o - \omega_f \) (stokes) \hspace{1cm} (1.13)

\( E_f < E_i \), \( \omega_s = \omega_o + \omega_f \) (anti-stokes) \hspace{1cm} (1.14)

The stokes lines are more intense than the anti-stokes lines, a consequence of the different populations of molecules in the ground and first excited vibrational states, as described by the Boltzmann distribution.

In quantum theory of scattering, the intensity arising from a transition between states \( |i> \) and \( |f> \), under ordinary conditions of Raman scattering experiments, depends on the probability tensor, whose components are:
\[ [\alpha_{xy}]_i = \frac{1}{\hbar} \sum_r \left( \frac{[P_y]_r [P_x]_i}{\omega_{rf} + \omega_o} + \frac{[P_y]_i [P_x]_r}{\omega_{ni} - \omega_o} \right) \]  

(1.15)

where \( |i\rangle, |r\rangle \) and \( |f\rangle \) are initial, intermediate and final states of the molecule respectively; \([P_y]_r = \langle f | P_y | r \rangle\) and here \(P_y\) is the vector component of the electric dipole moment operator; \(\hbar \omega_o\) = incident photon energy; \(\hbar \omega_{rf}\) and \(\hbar \omega_{ni}\) are the transition energies between \(r \rightarrow f\) and \(r \rightarrow i\) states; the summation is over all the states \(r \) of the molecule except \(i\) or \(f\).

For a particular transition to be Raman active, at least one of the six tensor components of the type \([\alpha_{xy}]_i\) must be non-zero. The general condition for \([\alpha_{xy}]_i\) to be non-zero is that the product \(\Psi^*_f xy \Psi_i\) belongs to a representation which contains the totally symmetric species, here \(\Psi_f\) and \(\Psi_i\) are the time independent wave functions of the final and initial states of the molecule, respectively. For the vibrational Raman spectrum, the vibrational eigen functions \(\Psi_{v'}\) and \(\Psi_{v''}\) of the upper and lower states should be substituted for \(\Psi_f\) and \(\Psi_i\). Then, a Raman transition between two vibrational level \(v'\) and \(v''\) is allowed, if at least one of the six products of the type \(\Psi^*_v xy \Psi_{v''}\) is totally symmetrical, i.e., remains unchanged for all the symmetric operations of the molecule.

For a fundamental vibrational transition, where in the initial state, all vibrational quantum numbers are zero and in the final state only the \(j^{th}\) vibrational quantum number has changed to unity, then for Raman activity:
A simple harmonic wave function, $\Psi_{\nu} (Q_j)$ for the ground state ($\nu_j = 0$), is always totally symmetric and a simple harmonic wave function with $\nu_j = 1$ has the same symmetry species as the normal coordinate $Q_j$ [6]. Thus the integral in equation (1.16) is totally symmetric if the product $Q_{xy}$ is totally symmetric. For non-degenerate fundamental vibration, this condition is satisfied if this vibrational mode has the same symmetry species as one of the six products of the type $xx$, $xy$, etc.

**DEPOLARISATION RATIO**

The state of polarisation of the Raman scattering yields valuable information concerning the molecular vibrations. An aspect of the Raman spectrum that differs fundamentally from the infrared is the ability to observe bond polarisation in liquids and gases where the molecules are randomly oriented. Since in a typical Raman experiments the scattering molecule is rotating, the observed scattering will be the average of all orientations of the molecule. To express the scattering intensity in terms of the derived polarisability tensor, it is necessary to find quantities which are invariant under rotation. It is possible to express these invariants in terms of two quantities associated with the tensor,

Mean value $\alpha' = 1/3 \left( \alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz} \right)$

(1.17)
Anisotropy

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

(1.18)

where \( \alpha'_{ij} = \frac{\delta \alpha_{ij}}{\delta Q_0} \)

Then for 90° scattering, the depolarisation ratio \( \rho_n \) representing the ratio of intensities scattered perpendicular and parallel to the direction of the electric vector \( E \) is given by

\[
\rho_n = \frac{6\gamma'^2}{(45\alpha'^2 + 7\gamma'^2)}
\]

(1.19)

Using plane polarised incident radiation, such as for laser radiation

\[
\rho_p = \frac{3\gamma'^2}{(45\alpha'^2 + 4\gamma'^2)}
\]

(1.20)

If \( \rho_p = 0.75 \), then the line is said to be depolarised; if \( \rho_p < 0.75 \), the line is polarised and \( \rho_p = 0 \), the line is completely polarised.

For the symmetric vibrations, the size of the ellipsoid changes but its orientation does not. That is, the change in diagonal elements of the polarisability ellipsoid implies that \( \alpha' \) changes and hence the line must be polarised i.e., \( \rho_p < 0.75 \). Antisymmetric vibrations, on the other hand do not lead to a change in the size and hence \( \alpha' \). Hence Raman lines due to antisymmetric vibrations are depolarized. Information of this type can be of great use in determining the symmetry of vibrations.
INSTRUMENTATION – RAMAN SPECTROSCOPY

The Raman effect is an inherently weak effect, typically $10^{-8}$ of the intensity of the incident exciting radiation. For many years, source stability and intensity, made Raman spectroscopy extremely difficult, particularly in comparison with the faster and less expensive infrared spectrometer that were developed.

It was not until early sixties that the modern Raman renaissance took place with the development of commercial continuous wave visible lasers. In recent years, micro electronics has further improved the technique such that stepper motor drives, photon counting, digital data acquisition and computer processing have provided chemists, physicists and analysts with a technique which is more useful and versatile than infrared spectroscopy.

Due to the ability of visible lasers to penetrate even quite thick glass and the very weak Raman scatter of glass itself, it is possible to construct a wide range of special cells and associated hardware for the examination of systems that are not amenable to study by other analytical techniques. One of the greatest advantages of the technique of Raman spectroscopy is its ability to be used for the spectral examination of the system under a very wide range of temperatures and pressures with comparative ease and in particular, for the time resolved study of such systems. Another valuable feature of the high optical transmission of glass relates to the use of fiber optics. The use of fiber optic probes open up the possibility of extending Raman studies to a wide
range of systems such as in the study of reactions occurring on, or close to electrode surface.

Closely connected with the choice of laser is the choice of external optics associated with the spectrometer. These comprise, apart from any required to steer or adjust the height of laser beam, the filtering system for continuous wave lasers and the photon collection optics. It is an unfortunate feature of the continuous laser, that, associated with any of the individual laser is a series of other outputs, the plasma lines. These are very much weaker than the laser outputs but slightly stronger than Raman bands. This can be resolved using filtering device. Another useful alternative is the pre-monochromator.

The grating of a spectrometer disperses the light entering the monochromator and then passes it through one or more narrow slits so that the light passing through the detector at any one time has a very narrow band width and may be considered as essentially monochromatic. A spectrograph on the other hand uses wider slits and a grating which produces much less dispersion and so gives a relatively broad band of light on a multi-channel detector. The main advantage of the spectrograph is its high throughout and of spectrometer is its high resolution.

The Fourier Transform (FT) Raman Spectroscopy was not successful at the early stages because of the weak nature of Raman effect, and also the problem associated with the removal of exciting line wavelength from the scattered radiation made a considerable amount of the spectrum inaccessible.
In this context, the conventional dispersive systems were far superior and no particular advantage was obtained by using a FT instrumentation. However, there is one area, the near infrared, where several scientists are now actively engaged. This region of spectrum is potentially useful for the analysis of samples which exhibit fluorescence when exposed to the normal visible wavelength radiation from argon or krypton continuous wave lasers.

**FT-RAMAN SPECTROSCOPY**

Raman and infrared spectroscopy give unique information for each chemical substance. In conventional Raman spectroscopy, the strongly interfering fluorescence has always been a great nuisance. Raman has never been as widely used as infrared spectroscopy because majority of the samples either fluoresce or contain impurities, which fluoresce when excited by visible light. The fluorescence arises from the electronic transitions occurring at the visible frequency region and is many times stronger than the Raman scattering. The fluorescence obscures the Raman signal. Fourier transform Raman (FTR) spectroscopy become very attractive to many spectroscopists who could see the advantages of FT-interferometry. The progress in the FTIR techniques, in lasers, NIR detectors, and optical filters made FT-Raman spectroscopy a feasible and finally a very productive method.

The introduction of FT-Raman spectroscopy has brought a new impetus to Raman spectroscopy. It has allowed the study of materials that were
previously “impossible” because of fluorescence [7-9] and provides ready access in the extensive data handling facilities that are available with a commercial FTIR spectrometer. Thus, Raman spectroscopy is taking its place as an equal partner in vibrational spectroscopy.

Fourier Raman spectroscopy is designed to eliminate the fluorescence problem encountered in conventional Raman spectroscopy. Fluorescence can be avoided by using an excitation frequency below the threshold for any fluorescence process. The most common excitation frequency for FT-Raman spectroscopy is the Nd:YAG (Neodimium doped Yttrium Aluminium Garnet) laser source of wavelength 1.064 μm, where there is no electronic transitions and hence fluorescence can be eliminated. A further advantage is that at these low photon energies, sample heating and subsequently photochemical sample degradation are unlikely.

Consequently, the Raman scattering occurs in the near-IR region, and conventional FTIR instrumentation can be used with modification. FT-Raman also benefits from advantages inherent to interferometry: high resolution efficiency, excellent wavelength precision, easily variable resolution, spectral coverage, higher optical throughput and software developments in FTIR.

The restrictions of FT-Raman arise from the low signal-to-noise ratio. This is because the signal-to-noise ratio is limited by detector noise rather than signal shot noise. The result is a signal-to-noise ratio comparable to that for a single channel dispersive system with equal measurement time [10].
The dramatic advantages of FT-Raman over the conventional Raman are: (i) the decrease in fluorescence which enables the researcher to collect good Raman data from nearly all sample. (ii) the wavenumber accuracy of interferometry is exhibited in FT-Raman spectroscopy enabling the analysis to signal average and to perform spectral subtraction. (iii) in Fourier transform spectroscopy all the frequencies are measured at once rather than sequentially as in conventional dispersive spectroscopy. This results in a decrease in data collection time. (iv) an another advantage is the rate at which the spectra can be acquired. Hence it is a useful tool for the study of kinetic processes such as polymer curing. (v) FT-Raman spectroscopy using FTIR instrumentation solves another problem frequently encountered in conventional spectrometers, which is lack of sufficient frequency precision required to perform the spectral subtractions [11].

**FT-Raman Instrumentation**

Recent advances in instrumentation have considerably eased the task of converting an FTIR spectrometer (with NIR capacity) to carry out the FT-Raman experiment and achieve signal-to-noise ratios comparable with those obtainable conventionally [12,13]. The schematic diagram of FT-Raman spectrometer is shown in Fig. 4. The FT-Raman instrument has the following accessories:

(i) a near IR laser excitation source (typically Nd:YAG at 1.064 μm).
(ii) a Fourier transform interferometer equipped with the appropriate beam splitter (quartz).

(iii) a sample chamber with scattering optics that match the input port of the Fourier transform instrument.

(iv) a set of optical filters for rejection of the Rayleigh scattered light.

(v) a low noise detector (InGaAs or Ge) for the near IR region/pre-amp.

Since all of scattered radiation from the sample is collected and Fourier transformed in the FT-Raman experiment, a Rayleigh line filter is used. Dielectric filters or the optical notch filter minimises the amount of Rayleigh scattered light entering the interferometer and is essential for FT-Raman spectroscopy. The sharpness of the cutoff determines the low frequency limit of the FT-Raman spectrometer.
The detector is the liquid nitrogen-cooled high sensitive Indium Gallium Arsenide (InGaAs) detector with specially configured preamplifier required for the low levels of collected radiation typical in Raman experiment. A focusing lens is inserted in the accessory to provide a laser spot size at the sample approximately equal to output beam waist of the laser. The use of attenuators may be necessary where the sample of interest is a very strong scatterer or a sample which has a tendency to heat up with the incident laser energy. Typically, a visible He:Ne laser beam is coaligned with the invisible Nd:YAG laser beam to make it possible to align and focus the Nd:YAG beam. A schematic diagram of Nd: YAG laser, pumped by an arc lamp or diode laser array is given in Fig. 5.

Fig. 5  Schematic diagram of Nd: YAG laser

Another option is to use fiber optics [14]. With fiber optic components, optical alignment is virtually eliminated which allows rapid switching from one sample to another. The spectral advantage of FT-Raman is the removal of
fluorescence. The FT-Raman technique is specifically designed to eliminate fluorescence and the effects are quite dramatic. The spectra of fluorescing dye where obtained with FT-Raman spectroscopy. Recently, Ti:Sapphire lasers which excite at 1.3 μm show beneficial for further minimisation of fluorescence [15].

Given the constraints of a fluorescing sample, the laser of choice is currently a Nd:YAG system. In the future, other lasers operating near 900 nm may be used to take advantage of the $v^4$ gain, while still avoiding the fluorescence problem. For example, diode lasers have made big progress and are now available with reasonable power levels (30–300 mW) at 785 and 830 nm. Tunable excitation in the region 670-1100 nm can be obtained with Ti:Sapphire laser. Pumped by a continuous argon ion laser, output conversions of 10–15% are readily obtained. There is a great deal of interest in changing from Nd:YAG lasers to the diode pumped versions which are coming on to the market.

ADVANTAGES OF FT-RAMAN SPECTROSCOPY

FT-Raman enjoys several distinct advantages over infrared spectrometry. They are,

1. The transparency of water and glass: the very low Raman scattering of water (which is important for living systems) and of glass make it suitable for dilute aqueous solutions of substances as well as for
hygroscopic materials, and permits the use of standard glass cuvettes and capillaries.


3. Very small amounts of materials can be examined, without modification since the laser beam can be focused down to about a spot with a diameter of 100 μm.

4. Symmetrical bonds such as C–C, C=C, C≡C, N=N, O=O, S–S manifests themselves by giving the most intense bands in Raman spectra, while they are inactive in the infrared.

5. Fiber optics can be used for remote sampling.

SAMPLING TECHNIQUES IN RAMAN SPECTROSCOPY

A sample in any state can be examined without difficulty by using Raman spectroscopy. The laser beam is narrow, collimated and unidirectional, so it can be manipulated in a variety of ways depending on the configuration of the sample.

For liquids, a cylindrical cell of glass or quartz with an optically flat bottom is positioned vertically in the laser beam. For solids, the particular method used depends on the transparency of the sample. For clear pellets or the samples, right angle scattering is used. Powdered samples can be analysed by using front surface reflection from a sample holder consisting of a hole in
the surface of a metal block inclined at 90° with respect to beam. One of the advantages of Raman sampling is that glass containers can be used which can be sealed if desired [16].

SAMPLING METHODS IN IR SPECTROSCOPY

A wide range of sampling technique is available for mounting the sample. The technique depends on whether the sample is a gas, liquid, solid or polymer. Sampling techniques plays an important role in recording IR spectrum. A choice of sampling technique is available for all states of matter depending on the application.

Solids are usually examined as a mull, a pressed disc or as deposited glassy films. Mulls are prepared by grinding the solid and then suspending with 1-2 drops of mulling agent followed by further grinding until the suspended particles are less than 2 μm. The mull is then examined as a thin film between flat salt plates. This technique has the advantage of speed but suffers many disadvantages. If the sample concentration is too low, the spectrum is due to mulling agent. On the other hand, if too much sample is used the mull will not transmit radiation. The commonly used mulling agents are Nujol, Hexachlorobutadiene and Voltof 3s oil (halogenated hydrocarban) depending upon the spectral region.
Alkali halide disc

The solid is mixed with suitable dry alkali halide (100-200 mg) grounded in a mortar or ball mill and subjected to a pressure of about 10 ton/sq.inch in an evacuated dye. This sinters the mixture and produces a clear transparent disc of diameter 10-15 mm. The advantage of this method over mull technique is that it eliminates the problem of bands, which appear due to mulling agent. The most commonly used alkali halide is KBr, which is transparent in the commonly scanning region. The commonly used other alkali halides are NaCl, CsI and CsBr.

Solutions

The sample can be dissolved in a solvent and the spectrum of this solution can be recorded. The solution (usually 5%) is placed in a solution cell, which has path length of usually 0.1-1.0 mm. The solvent chosen must satisfy certain criteria: (i) it has to dissolve the compound (ii) it should be non-polar as possible, to minimise solute solvent interactions (iii) it should not react with the sample (iv) it should not absorb IR radiation (v) it should be volatile and not viscous and (vi) it should be pure and dry. CS₂, CCl₄, CHCl₃, CDCl₃ and C₂H₂Cl₄ are some of the solvents commonly used.

Neat liquids can be examined between salt plates without a spacer. Pressing the liquid sample between flat plates produces a film of 0.01 mm or less in thickness. The plates are held together by capillary action. A common
problem is due to sample volatility. Liquids with boiling points below 100°C should be recorded in a solution or in a short path length sealed cell.

ADVANCES IN RAMAN AND INFRARED SPECTROSCOPY

The Resonance Raman Scattering (RRS) is found to have great utility in obtaining vibrational information of the samples that are present in low concentrations [17,18]. There are two important points which are noteworthy in RRS. (i) unlike the Raman spectrum, which yield a great deal of information about the ground state, RRS provides information about the excited electronic state. This helps in estimating atomic displacements between the ground and excited molecule. (ii) the most important phenomena is the resonance enhancement, because of which the active site and other such specific sites of a complex bio-molecule may be probed without interference from other parts of the molecule or from solvents.

Another method of increasing sensitivity of Raman effect is to increase the efficiency of the emission process known as Stimulated Raman Scattering (SRS). While Raman effect in the form of normal and RRS has been known to be associated with the studies of vibrational and rotational transitions in ground states, the application of Electronic Raman (ER) to study such transitions between ground and low energy excited electronic states is theoretically possible.
A non-linear optical technique known as Coherent Anti-stokes Raman Scattering (CARS) has been used to obtain the coherence and signal strength advantages of SRS while retaining the general applicability of spontaneous Raman spectroscopy. The main advantage of CARS is the large gain in Raman signal in a beam of small divergence. This permits the high resolution Raman study of low pressure gases and luminous samples such as flames and plasmas.

Just as laser revolutionised Raman spectroscopy, the discovery of the Fast Fourier transform (FFT) algorithm [19] revitalised the field of infrared spectroscopy. Infrared spectrum of the components of complex mixtures can also be obtained 'on the fly' by using an FTIR spectrometer coupled with a gas liquid chromatography. Owing to the impact of lasers, detectors and computers, the developments in the FTIR are occurring at a rapid rate.

**STATUS OF VIBRATIONAL SPECTROSCOPY**

A precise and valuable insight on molecular properties can be gained from the continuously perfected instrumentation for recording the vibrational spectra. The quantities that are directly related to the geometrical and electronic structure of molecules are the frequencies and the intensities of vibrational bands. It has been proved recently that vibrational parameters are strongly correlated with the properties of individual chemical bonds [20,21]. Determination of intra-molecular potential from the Raman and infrared
spectra of a given molecule, with those of many of its isotopomers, and in combination with still developing computer, as well as the development and incorporation of analytical derivative methods for the determination of vibrational parameters in most standard programs for ab initio molecular orbital calculations and normal coordinate analysis (NCA) reaches a very significant stage. As a result, the interpretation of frequencies and intensities in infrared and Raman spectra has become strongly interconnected with the appropriate quantum mechanical calculations. Needless to say, these developments have greatly enhanced the reliability and accuracy of vibrational spectral studies. The size of the molecule subjected to such an analysis is increasing from year to year.

A molecule in a higher vibrational, an electronically excited molecule, intermediate species in a thermal decomposition, a molecule adsorbed on an adsorbent, intermediate species in a catalytic reaction, radical and a molecule under high pressure are the subjects of infrared and Raman spectroscopic examination.

The analysis of vibrational frequencies via., normal coordinate analysis is well established and provides appropriate theoretical procedures for evaluating the parameters of the potential force field of molecule [22]. The valance force field is now generally accepted as the most plausible representation of the intermolecular forces [23,24]. The interpretation of the
vibrational intensities is based on the application of a number of different theoretical approaches and molecular parameters [25-27].

NORMAL MODES OF OSCILLATION

The motion of a molecule of n atoms is defined by the variation of 3n coordinates; i.e., molecules possess 3n degrees of freedom. If the centre of gravity does not undergo the translation and system itself is restricted from undergoing rotation, only 3n–6 coordinates (or 3n–5 in the case of linear molecule) will be required. It can be shown that for simple harmonic motion, a molecule of n atoms can vibrate in 3n–6 ways, in which, each atom is moving in-phase and at the same frequency. These 3n–6 vibrations are the normal vibrations of the molecule, and the displacements of the atoms from their equilibrium positions are the normal coordinates.

The classical methods of obtaining the normal mode is as follows: Let the position of the systems be represented by the coordinates q_1, q_2, q_3, ......, q_n. If the oscillations are regarded as having infinitesimally small amplitudes in comparison with the nuclear distances, both the kinetic and potential energies may be expressed as

\[ 2T = \sum_{i=1}^{3n} \dot{q}_i^2 \]  \hspace{1cm} (1.21)

\[ 2V = \sum_{j=1}^{3n} f_{ij}q_iq_j \]  \hspace{1cm} (1.22)
The $f_{ij}$ coefficients are called force constants, since they represent the forces acting to restore a displaced atom to its equilibrium for displacement $q_i$ and $q_j$. The equations of motion for a vibrating molecule can be obtained from the expression of $T$ and $V$. It is convenient to write Newton's second law of motion with the Lagrange form

$$\frac{d}{dt} \left[ \frac{\partial T}{\partial q_j} \right] + \left[ \frac{\partial V}{\partial q_j} \right] = 0$$

(1.23)

If equation (1.23) is applied successively with each coordinate in turn, using equations (1.21) and (1.22) to supply the values of $T$ and $V$, there will result a series of simultaneous differential equations. The general solutions of these equations of the form

$$q_i = A_i \cos(\lambda^{1/2} t + \phi)$$

(1.24)

in which $\lambda = 4\pi^2 c^2 \nu^2$, where $\nu$ is the frequency of vibration in cm$^{-1}$ and $c$ is the velocity of light; $\phi$ is the phase factor and $A_i$ is the amplitude of vibration of $i^{th}$ atom. Then from equations (1.23) and (1.24),

$$\sum_{i=1}^{3n} (f_{ij} - \delta_{ij})A_i = 0 \quad j = 1,2, \ldots, 3N$$

(1.25)

Apart from the trivial solution $A_i = 0$, the solutions are given by the conditions

$$|f_{ij} - \delta_{ij}| = 0$$

(1.26)

The above equation is the secular equation. The values of $\lambda$, obtained as solutions of secular equations are known as eigen values.
The evaluation of the determinant is simplified by the transformation to a new set of coordinates $Q_i$, such that the cross product terms in kinetic and potential energy equations disappears. By employing the orthogonal transformation

$$q_i = \sum_{i=1}^{3n} C_{ii} Q_i$$

(1.27)

upon which, the kinetic and potential energy become

$$2V = \sum \lambda_i Q_i^2$$

(1.28)

$$2T = \sum \dot{Q}_i^2$$

(1.29)

This normal coordinate transformation gives, analogously to equation (1.24), the expression

$$Q_i = B_i \sin(\lambda_i^{1/2} t + c')$$

(1.30)

To each value of $\lambda$ which is a root of secular equation, there corresponds a normal vibration of the molecule in which all coordinates $Q_i$ vibrate with the same frequency and phase. Thus the atoms attain their positions of maximum displacement simultaneously.

The vibrational problem is much easier to describe by means of matrix algebra. The displacement coordinates are expressed as a column matrix $X$ and the force constant can be represented as a symmetric square matrix $F_x$. The kinetic and potential energies in quadratic form are given by

$$2V = X^T F X$$

(1.31)
\[ 2T = \dot{X}^T M \dot{X} \]  
\[ (1.32) \]
where \( M \) is a diagonal matrix. The kinetic and potential energies in mass adjusted coordinates are,

\[ 2V = q^T F_q q \]  
\[ (1.33) \]
\[ 2T = \dot{q}^T \dot{q} \]  
\[ (1.34) \]
where \( F_q \) is the force constant matrix.

**SOLUTION OF SECULAR EQUATION IN INTERNAL COORDINATES**

The vibrational problem can be considerably simplified by an approximate choice of the coordinate system. The Cartesian coordinate system is desirable from the point of view of defining the kinetic energy, in that \( M \) is a diagonal matrix of the masses of nuclei and as a result, the kinetic energy of the molecular system is simple to calculate. However, the descriptions of the force constants, except for linear molecules, are difficult to interpret physically. The number of possible orientations of the molecule within the frame makes impossible the transfer of the force field from a bond in one molecule to a similar bond in another molecule.

These difficulties can be overcome by using a set of internal coordinates that describe the bond distortions, such as bond stretching, angle deformations, and torsion. The size of the secular equation in internal coordinate is smaller and hence easier to solve. The principle advantage of
internal coordinates is the representation of the potential energy or force
constant matrix in terms of bond stiffness and resistance to bond angle
deformations, which make these constants physically comprehensible.

The linear transformation between Cartesian and internal coordinates in
matrix form is \( \mathbf{R} = \mathbf{BX} \), similarly between internal coordinates and mass
adjusted coordinates is \( \mathbf{R} = \mathbf{Dq} \), where \( \mathbf{B} \) and \( \mathbf{D} \) matrices are related by the
expression \( \mathbf{D} = \mathbf{BM}^{-1/2} \). The kinetic energy in terms of mass weighted
Cartesian coordinate in matrix form is given by

\[
2T = \mathbf{q}^T \mathbf{q}
\]

In order to express the kinetic and potential energy in terms of internal
coordinates \( \mathbf{R} \), it is necessary to define a quantity \( \mathbf{P} \), which is a momentum
conjugate to \( \mathbf{q} \), as \( \mathbf{p}_j = \dot{\mathbf{q}}_j \).

So that, the kinetic energy can be written as

\[
2T = \mathbf{p}^T \mathbf{p}
\]

(1.35)

after substituting \( \mathbf{p}^T = \mathbf{p}^T \mathbf{D} \), the kinetic energy can be expressed as

\[
2T = \mathbf{p}^T \mathbf{D} \mathbf{D}^T \mathbf{p}
\]

(1.36)

Now the matrix \( \mathbf{G} \) is defined as

\[
\mathbf{G} = \mathbf{D} \mathbf{D}^T
\]

(1.37)

The relation between \( \mathbf{G} \), \( \mathbf{M} \) and \( \mathbf{B} \) is

\[
\mathbf{G} = \mathbf{BM}^{-1} \mathbf{B}^T
\]

(1.38)

The kinetic energy in terms of velocities of internal coordinates is

\[
2T = \mathbf{\dot{R}}^T \mathbf{G}^{-1} \mathbf{\dot{R}}
\]

(1.39)
and potential energy

\[ 2V = R^T FR \]  

(1.40)

Having obtained the kinetic and potential energies in the required form as functions of internal coordinates, the secular determinant can be obtained as

\[ |GF - \lambda E| = 0 \]  

(1.41)

where \( E \) is the unit matrix. The final form of the expression yields the product of \( GF \) first described by Wilson and this method is referred to as the Wilson’s FG matrix method.

**SOLUTION OF SECULAR EQUATION BY SYMMETRY COORDINATES**

The symmetry coordinates were first introduced by Howard et al. [28]. Somewhat different types of symmetry coordinates were also introduced by Rosenthal et al. [29]. The symmetry coordinates are the linear combinations of the equivalent internal coordinates, which are the changes in the bond distances and inter bond angles. The choice of the symmetry coordinates is not arbitrary but is governed by certain conditions: (i) The number of symmetry coordinates corresponding to each symmetry type will be equal to the number of vibrations under each species. (ii) They should be normalised and orthogonal and (iii) They should transform in accordance with their characters of the symmetry type to which they belong.

There are several useful types of coordinates but two of them are most frequently used, known as internal symmetry coordinates and external
symmetry coordinates. The former consists of linear combination of internal coordinates; the latter are constructed from linear combination of Cartesian displacement coordinates.

APPLICATION OF GROUP THEORY TO VIBRATIONAL SPECTROSCOPY

Wigner [30] has shown that the number and symmetry of the normal modes of oscillation of a molecule can be obtained in a less complicated manner by the application of the theory of groups. Every molecule, by virtue of its symmetry, possesses a set of symmetry operations, which transform the molecule into one indistinguishable from itself. The potential and kinetic energies of a molecule in terms of normal coordinates may be expressed in the canonical form as given by the equations (1.21) and (1.22), since under any of the symmetry operations characteristic of the point group, the molecule remains as it is, the potential and kinetic energies should be invariant under all such operations. The choice of the coordinates is accordingly governed by this condition.

Now, a new configuration is considered in which all the normal coordinates except one, say $Q_r$ with frequency $\nu_r$ vanish. Let the configuration obtained by performing symmetry operation $R$ of the group of symmetry operations is denoted by $RQ_k$. If by the operation $r$, the $k^{th}$ atom goes over to the $l^{th}$ atom, then the $l^{th}$ atom remains in its own neighborhood but gets the
motion of the \( k^{th} \) atom. By doing this one obtains a configuration \( R Q_r \) which geometrically identical with \( RQ_r \). \( R Q_r \) represents the normal coordinate having the same frequency \( \nu_r \). With all the covering operations, all the normal modes of the oscillation belonging to the same frequency can be obtained. But all those normal modes of oscillation may not be linearly independent. Let \( Q_1, Q_2, \ldots, Q_f \) be a complete set of linearly independent normal coordinates so obtained of frequency \( \nu_r \). The oscillation of the frequency \( \nu_r \) is \( f \)-fold degenerate. Similarly, the normal coordinates of different frequencies are obtained.

A set of normal coordinates of definite frequency defines an irreducible representation of the group \( G \) and the \( 3n \) Cartesian coordinates \( x_1, y_1, z_1, \ldots, x_n, y_n, z_n \) define a reducible representation. The character of any operation \( r \) may be calculated from the reducible representation defined by the Cartesian coordinates. If the \( k^{th} \) atom is invariant under an operation \( R \), then

\[
\begin{align*}
\bar{R} X_k &= X_k \cos \phi + Y_k \sin \phi \\
\bar{R} Y_k &= -X_k \sin \phi + Y_k \cos \phi \\
\bar{R} Z_k &= Z_k
\end{align*}
\]

When the axis of rotation is the Z-axis and, X and Y-axis lie in a plane perpendicular to it. Then the character of an operation consisting of a rotation through \( \phi \) radians is \( 1+2\cos \phi \). If it is a rotation reflection, the character comes out as \( -1+2\cos \phi \). Thus an invariant atom under the operation \( R \) gives rise to the character \( \pm 1+2\cos \phi_R \), \( \pm \) being used according as the operation is pure
rotation or a rotation-reflection. Hence, in the reducible representation defined by the Cartesian coordinates, if $U_R$ is the number of invariant atoms, the character of any operation $R$ is $U_R(\pm 1 + 2\cos\phi_R)$.

From the knowledge of the group characters in any representation $\Gamma_i$, $n_i$ - the number of times a particular reducible representation $\Gamma_i$ contained in $\Gamma$ is found using the formula,

$$n_i = \frac{1}{N} \sum_{R} \chi_i(R)\chi'(R)$$ (1.45)

where $\chi_i(R)$ and $\chi'(R)$ are respectively the character of $R$ in $\Gamma_i$ and $\Gamma$ and, $N$ the order of the group. $\Gamma$ stands for the reducible representation of the Cartesian coordinates. The number $n_i$ of the normal coordinates that belong to a particular irreducible representation includes translations and rotations of the molecule as a whole. This can be excluded by removing the character arising from pure rotation and translations. The character arising from pure translation is $1 + 2\cos\phi$ for $C(\phi)$ and $-1 + 2\cos\phi$ for $S(\phi)$ and the character from pure rotation is $1 + 2\cos\phi$ for $C(\phi)$ and $1 - 2\cos\phi$ for $S(\phi)$.

**SELECTION RULES**

The activity or otherwise, the modes of oscillations should be discussed to ascertain the number of lines that should appear in the infrared absorption or in the vibrational Raman effect. The important assumption is that the electric moment in the case of the infrared spectrum and the polarisability
tensor ellipsoid in the case of Raman effect have the same symmetry properties as the molecule. The mode is active or inactive in the infrared absorption according as it causes a variation or not in the electric moment of the molecule. The variation itself may be regarded as a vector. Hence, its character is \((±1+2\cos ϕ_R)\) according as \(R\) is a rotation or a rotation-reflection. From the transformation property of electric moment, the selection rule for the infrared is obtained as

\[
\sum_R (±1+2\cos ϕ_R)χ_i(R) = 0 \quad \text{inactive} \quad (1.46)
\]

\[
\neq 0 \quad \text{active} \quad (1.47)
\]

where \(χ_i(R)\) is the character of the irreducible representation \(Γ_i\) to which the normal coordinate belongs. The summation extends over all the operations that constitute the group.

The selection rules for the Raman spectra may be derived in a similar manner. The mode is Raman active if it causes a variation in the optical polarisability and is inactive if there is no variation. The optical polarisability is a symmetry tensor. By the transformation of the polarisability tensor components, it follows that the character of the operation \(R\) in the reducible representation defined by the polarisability tensor components is \(2\cos ϕ_R(±1+2\cos ϕ_R)\). The selection rule for the Raman effect is therefore,

\[
\sum_R (2\cos ϕ_R)(±1+2\cos ϕ_R)χ_i(R) = 0 \quad \text{inactive} \quad (1.48)
\]

\[
\neq 0 \quad \text{active} \quad (1.49)
\]
MOLECULAR FORCE FIELD

Wilson’s method of normal coordinate analysis is based on the classical description of nuclear motions in the harmonic approximations. Although today sufficient computer capacity is available, this method becomes problematic when applied to the large molecules. This is due to the dramatic increase in the number of model parameters, i.e., the force constant matrix $f_i$’s, involved in the procedure. Normal coordinate analysis is primarily a problem involving the determination of appropriate force constants from the observed frequencies. As the number of force constants to be determined is usually greater than the number of experimental wavenumber, it becomes impossible to determine a realistic force field using the vibrational wavenumbers of a single molecule alone.

Symmetry restriction as well as additional experimental data, such as isotope effect, Coriolis coupling constants, vibrational amplitudes, centrifugal distortion constants and inertia defects can solve the difficulties associated with the determination of a suitable force field. In using isotopes of a particular molecule as a source of additional data, it is assumed that the potential energy and geometry of the molecule remain unchanged to a very high degree of approximation by substitution. However the $G$ matrix takes on different values as a result of the change in mass of various atoms. The most frequently encountered isotopes in spectroscopy are deuterated molecules. These isotopes are also extremely useful in making band assignments because
they involve a large percentage change in the mass of specific atoms. Consequently vibrational modes involving large displacements of the substituted hydrogen atoms are subjected to a much greater frequency shift than the modes in which the displacement of this atom are small.

For polymeric materials, additional frequency data can be obtained by using oligomers if available. Often additional sources of information concerning the force constants are obtained from the accurate Coriolis coupling constants and centrifugal distortion constants.

It has been shown that general force field, even in the quadratic approximation, cannot always be determined from experimental data. Consequently, it is usually necessary to assume a model force field by making certain approximations. The ultimate test of such model force field is, of course, the ability to reproduce independent experimental data.

The difficulty in describing the bending of linear molecule is not apparent if valance force field is used. The valance force field is defined in terms of forces resisting stretching, bending, or torsion of chemical bonds. Interaction force constants or forces between non-bonded atoms are not considered in the simple approximation.

This simple force field can be modified in a number of ways to give a better fit between the observed and calculated frequencies. The improvement can be achieved by introducing the interaction force constants that seem physically most necessary. Mainly, Urey-Bradley (UB) force field is a mixing
potential function, employing the principle bond stretching and bond angle, bending diagonal force constants of the simple valance force field, but repulsion between non-bonded atoms are also added. However, the pure UB force field is unsatisfactory for polyatomic molecule except tetrahedral (T_d) molecules and it has been found necessary to introduce additional valance type interactions [31,32]. A force field may be considered to be more reliable when it reproduces the observed wavenumbers of a number of similar type of molecules simultaneously. The simplified general valance force field (SGVFF) has been shown to be very effective in normal coordinate analysis of hydrocarbons, peptides, amides and pyrimidine bases [33] and also the valance force constants can be transferred between the structurally related molecules, which is found to be effective in the normal coordinate analysis of large polyatomic molecules. Besides the stretching and bending force constants, the various possible interactions between the stretching and stretching, bending and bending and, stretching and bending vibrations of neighbouring atoms are also included. Hence in the present investigation the SGVFF method has been used throughout.

**COMPUTER PROGRAMS FOR SOLVING THE SECULAR EQUATION**

There are two major points that should be taken into account when setting up the secular equation in a form suitable for computerised calculations. First is that, it is not always necessary to eliminate redundant
coordinates. However, the problem associated with redundancy cannot be just ignored. Internal symmetry coordinates should be set up so that one of them express the redundancy condition while rest are constructed orthogonal to this symmetry coordinates. The second point to be considered is that, the most efficient methods for solving the secular determinant employ matrix diagonalisation methods that are applicable only to symmetric matrices.

After introducing necessary modifications in the program developed by Fuhrer et al. [34], was used for the calculation of the vibrational frequencies of the molecules. The necessary information that is needed for the calculation is an initial vibrational force field and the structural parameters of the molecule; these parameters may be either the bond lengths and bond angles or the Cartesian coordinates of the atoms with respect to an arbitrary chosen origin. The program is designed to consist of modules so that the output from one serves as a part of the input to the next. The calculated frequencies and the potential energy distributions are obtained as output. The options available in the program are extended to analyse the data and to modify the force field systematically to improve the fit with the experimental values.

POTENTIAL ENERGY DISTRIBUTION

In the normal coordinate analysis, the potential energy distribution (PED) plays an important role to obtain a detailed understanding about the nature of the normal modes. The PED is expressed in terms of the percentage
contribution of each force constant or the displacement coordinate or symmetry coordinate to the potential energy of each normal mode. The potential energy is expressed by the equation (1.28) as

$$2V = \sum \lambda_i Q_i^2$$  \hspace{1cm} (1.50)

If the unit displacements of the normal coordinate $Q_i$ are considered all other normal coordinate being at rest, then $\lambda_i$ is a measure of the potential energy. The normalization condition $L'fL = \lambda$ gives the relations of the form,

$$\lambda_i = \sum_{jk} L_{ji} f_{jk} L_{ki}$$  \hspace{1cm} (1.51)

and after neglecting the cross terms,

$$\lambda_i = \sum_j f_{ji} L_{ji}^2$$  \hspace{1cm} (1.52)

Hence, the normalised PED is expressed as

$$V_{ji} = \frac{f_{ji} L_{ji}^2}{\lambda_i}$$  \hspace{1cm} (1.53)

where $V_{ji}$ is the contribution of the $j^{th}$ symmetry coordinate to the potential energy of the vibration whose frequency is $v_i$. The contribution to the potential energy from the individual diagonal elements gives rise to a conceptual link between the empirical analysis of the vibrational spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computation of the normal modes.

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