CHAPTER 1

INTRODUCTION
Various physical and chemical processes in molecular systems could be studied only with a detailed knowledge of their internal structure. The recent advancements in the spectroscopy of different regions of the electromagnetic spectrum have provided valuable informations for the investigation of molecular structure. Selection of the particular spectroscopic technique is decided by the nature of the information required. The infrared and Raman spectroscopic methods are the most powerful and useful techniques available for the understanding of molecular structure, conformation analysis, symmetry of molecular groups or ions in crystals, the nature of the co-ordination between atoms etc. [1-13]

1.1 SPECTROSCOPIC METHODS

Most of the experimental methods used in molecular spectroscopy depend on the study of interaction between electromagnetic radiation and the molecular system. A molecule (gas or liquid phase) can have different types of energies.

i. the translational energy $E_t$ due to the translational motion of the molecule.

ii. the electronic energy $E_e$ associated with each atom or bond.

iii. the vibrational energy ($E_v$) due to the periodic displacement of its atoms from their equilibrium positions.
iv.

the rotational energy \( (E_r) \) by virtue of bodily rotation about its centre of gravity.

For a fluid in a container the space available for the translational motion is large compared to the molecular dimension and hence \( E_t \) is not quantised and those quantised alone are considered at least in the case of liquids and gases.

According to Born and Oppenheimer the various forms of energies of a molecule are completely independent of each other. Hence, leaving \( E_v \)

\[
E_{\text{total}} = E_e + E_v + E_r
\]

The quantised levels of these energies for diatomic molecule are shown in Fig(1.1). The rotational, vibrational and electronic energy separations are of the order of \( 1 - 300 \, \text{cm}^{-1}, 300 - 4000 \, \text{cm}^{-1} \) and \( 10^6 \, \text{cm}^{-1} \) respectively.

A spectral line is exhibited when a molecule absorbs radiation of energy \( h\nu \) and goes to an excited state or a molecule in an excited state emits a quantum of energy \( h\nu \) and drops to a lower level. Corresponding to the above energies we have the electronic, vibrational and rotational transitions.

Emission and absorption are the two general areas of spectroscopy. The general experimental method for obtaining an absorption spectrum is shown in Fig (1.2).
In absorption spectroscopy, depending on the region, there are two types of spectrometers - ordinary absorption spectrometer and resonance absorption spectrometer. In the first type the radiation is allowed to pass through the sample and the difference in the intensity level of the incident and emergent beam is measured. In a resonance spectrometer, the absorption is detected as a current or voltage unbalance when the energy of the incident radiation equals the energy separation between the two levels involved.

In addition to emission and absorption, the following important phenomena are also possible when radiation interacts with matter:

i. Fluorescence ($\nu < \nu_o$)

ii. Phosphorescence ($\nu < \nu_o$)

iii. Rayleigh scattering ($\nu = \nu_o$)

iv. Raman scattering ($\nu = \nu_o \pm \nu_m$)

$\nu_o$ - frequency of the incident radiation $\nu$ - the frequency of scattered radiation, $\nu_m$ characteristic frequency of the molecule.

Fluorescence results when an atomic or molecular system is excited into an upper state by absorption of radiation of energy $h\nu_o$ and then decaying back to a lower state in a time less than $10^{-5}$ s. If the emitted radiation is of energy $h\nu_o$, it is called resonance fluorescence.

Phosphorescence is a phenomenon similar to fluorescence, but results when the molecule loses energy by means of a radiationless process and end
up in a metastable state from which it makes a delayed re-emission. It continues even after the removal of the source.

1.2 INFRARED SPECTRA

The goal of IR spectroscopic applications is to determine the chemical functional groups in a particular material. Each functional group absorbs characteristic frequencies of infrared radiation uniquely. Thus the infrared spectrum fingerprints the identifiable chemical groups.

IR spectroscopy deals with the absorption of IR radiation incident on a sample by virtue of periodic changes in the electric dipole moment of the molecules. During the vibrational motion of a molecule, the dipole moment changes periodically with the same frequencies as the normal mode frequencies and only radiation of those frequencies can be absorbed. Such IR absorption is possible only if the molecule has a permanent dipole moment and the intensity of the resulting absorption band is proportional to the square of the change in dipole moment [14]

The selection rules govern the appearance of a band in the IR spectrum. According to quantum mechanics IR absorption or emission takes place only if

1. there is a change in the magnitude or direction of the dipole moment of the molecule during vibration.

ii. the vibrational quantum number changes by ±1 (under harmonic approximation).
In addition the symmetry of the molecule also restricts the activity of the vibration. Since most of the molecules exist in the ground state, the intense IR band will be usually due to the transition from \( v = 0 \) to \( v = 1 \).

1.3 RAMAN SPECTRA

Raman spectra is due to the inelastic scattering of light by matter. When photons are incident on molecules, most of the photons are scattered elastically (Rayleigh scattering). But a few photons (1 in \( 10^6 \)) undergo inelastic scattering. These inelastically scattered photons have frequencies lower and higher than the incident frequency [15, 16] and are called stokes and antistokes lines respectively. The scattered photons have frequency shifts characteristic of the vibrational or rotational energies of the molecule.

The electric field \( E \) associated with the incident radiation produces an induced polarization \( P \) which is responsible for the Raman process. \( P \) and \( E \) are related [14] by

\[
P = \alpha \ E
\]

where \( \alpha \) is the polarizability tensor. Expanding \( \alpha \) in Taylor series and neglecting higher order terms

\[
\alpha = \alpha_0 + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k
\]

\[
\therefore \quad P = \alpha_0 E + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k E
\]
Since $\alpha_0$ is a constant, the first term oscillates with a frequency equal to that of the incident radiation, leading to Rayleigh scattering. The second term is responsible for Raman scattering.

The intensity of a Raman band is proportional to the square of the transition moment [14]. The transition moment arising from the induced polarization $P$ is given by

$$\int \psi_n P \psi_m \, d\tau = E \int \psi_n \alpha \psi_m \, d\tau$$

$$= E \alpha_0 \int \psi_n \psi_m \, d\tau + E \sum_k \frac{\partial \alpha}{\partial Q_k} \int \psi_n Q_k \psi_m \, d\tau$$

One of the conditions for the second term to be non vanishing is that $\frac{\partial \alpha}{\partial Q_k}$ should be non zero. Symmetry considerations based on group theory leads to the second condition that a normal vibration associated with $Q_K$ becomes active when at least one of the components of the polarizability belongs to the same species as that of $Q_K$.

The intensity of the Raman lines are frequency dependent [17, 18] and is related by

$$\frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \frac{(v_o - v_m)^4}{(v_o + v_m)^4} e^{\frac{h v_m}{kT}}$$

$v_o$ - incident frequency
$v_m$ - vibrational frequency of the molecule
$k$ - Boltzmann’s constant
$T$ - Absolute temperature
The lines in the Raman spectrum are found to be plane polarized to different extents even if the exciting radiation is not a polarized one. The intensity of the polarization of the scattered radiation depends on the direction of observation. A study of the polarization characteristics helps to assign the observed Raman lines to their appropriate molecular vibrations.

1.4 THE VIBRATIONS OF POLYATOMIC MOLECULES

A molecule of 'n' atoms has 3n degrees of freedom. The translational movement uses 3 and rotation without change of shape uses 3 of the 3n degrees of freedom. Hence a non-linear molecule of n atoms has 3n - 6 degrees of freedom. If the molecule is linear, there is no rotation about the bond axis and it will have 3n - 5 degrees of freedom. The 3n - 6 or 3n - 5 vibrational modes are called the internal vibrations or normal vibrations or fundamental vibrations of the molecule. A normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency. During a normal vibration, the centre of gravity of the molecule remains unchanged. As a molecule having n atoms has (n - 1) bonds, out of the (3n - 6) / (3n - 5) vibrations (n - 1) would be bond stretching and (2n - 5) / (2n - 4) would be deformation vibrations. In large molecules the nature of the deformation vibrations become more involved.

1.5 NORMAL MODES OF VIBRATION IN CRYSTALS

A crystal containing N primitive unit cells each containing 'n' atoms will have 3 Nn degrees of freedom. The solution of the vibrational problems gives rise to 3n frequencies. These 3n frequencies are functions of the wave vector
\[ K = \frac{2\pi}{\lambda}, \] which can take \( N \) values. At the Brillouin Zone Centre (\( K = 0 \)), three of the frequencies tend to zero. These three frequencies form the acoustic modes and the remaining \((3n - 3)\) are called the optical modes. As the wavelength of exciting radiation in both IR and Raman spectroscopy is very large compared to that of phonons at the Brillouin zone boundaries, the wave vector conservation law allows only the phonons at \( K = 0 \) to be observed in the first order Raman spectra. At the zone centre the motion of the corresponding atoms in all the unit cells will be in phase and it is sufficient to consider only \((3n - 3)\) optical modes. [6, 17, 18].

The \((3n - 3)\) optical modes are further divided into the internal (stretching, bending etc) and external (translation and rotation) modes. The vibrations of an individual molecule in the gas phase are subjected to symmetry restrictions based on its own symmetry whereas in crystals they are subjected to restrictions arising out of the crystalline environment. For interpreting the spectra of solids the following two group theoretical approaches are usually employed.

1.5 1 Unit Cell Approach

This method developed by Bhagavantam and Venkatrayudu provides a systematic classification of vibrations in solids [19, 20]. This model treats the unit cells of the crystal as a giant molecule and the space group operations are applied in order to classify the modes. The symmetry properties of the crystal are determined by studying the effect of each symmetry operation in the factor
group on each type of atom in the unit cell. This requires a complete knowledge of the arrangement of atom in the unit cell which makes this method tedious.

1.5 2 Site Symmetry Approach

When a unit cell contains a large number of atoms the unit cell approach becomes difficult. In such cases the more suitable method is the site symmetry approach developed by Halford [21] and Hornig [22]. The selection of site group is of great importance in this method. The site group is selected such that it is a subgroup of both free ion and factor group. The normal mode distribution in the free ion symmetry is first obtained. Then it is correlated to the factor group using standard correlation tables [23]. Winston and Halford [24] showed that this method gives identical results as the unit cell approach. The correlation method developed by Fateley et al. [25] is a generalization of both the methods.

The irreducible representation can be obtained by correlating the site symmetry species of individual atoms in the crystal to its factor group species or by correlating the molecular free ion symmetry to the crystal’s factor group symmetry through the molecular site symmetry. The spectral activity of each species can be obtained from the character table. The species which contains a translation will be infrared active while the one that contains a component of the polarizability tensor will be Raman active.

1.6 SOLID STATE EFFECTS

Molecular vibrations in gas phase are subjected to the constraints based on molecular symmetry only. But, in crystal it is controlled by the symmetry
restrictions arising out of its crystalline environment. Since the molecules have relatively fixed orientation in crystals, there is an appreciable difference between the symmetry of the molecule in gas and crystal phases. Hence the following changes in the gas phase fundamentals are expected [18]

1.6 1 Site Symmetry Effect

Generally molecular groups or ions in a crystal occupy sites of lower symmetry than the free ion symmetry. The lower symmetry can lead to the shifting of the non-degenerate modes, splitting of the degenerate modes and activation of inactive modes.

1.6 2 Correlation Field Effect

This effect arises from the interaction between vibrating ions or molecules. Within the same unit cell of the crystal, correlation field may cause splitting of degenerate and non-degenerate internal vibrations. One fundamental vibration may split into a maximum of m bands where ‘m’ is the number of molecules in a primitive unit cell. This effect is also known as Davydov effect.

In ionic compounds, site symmetry splitting is greater than correlation field splitting while in covalent crystals, the two have the same orders of splitting. In systems where hydrogen bonding is very strong large correlation field splitting is possible due to strong interaction between internal modes through hydrogen bond. [18]
1.6 3 External Modes

Translational and rotational motions of rigid units cause the appearance of new bands in the low frequency region (below 600 cm\(^{-1}\)).

1.6 4 Internal External Vibrational Coupling

Thermally excited external vibrations are responsible for internal external vibration coupling causing shifting of non-degenerate internal modes and splitting of degenerate modes. This depends on the symmetry of the internal and external modes involved. Usually only splitting of a few cm\(^{-1}\) are expected due to this coupling.

1.7 Influence of Perturbations on Vibrational Spectra

1.7 1 Anharmonicity

The selection rule for the harmonic oscillator allows only transitions for which \(\Delta \nu = \pm 1\), anharmonicity in the oscillations of real molecules gives rise to weak bands in the spectra due to combinations and overtones. Combination band results from the sum or difference of two different fundamentals, while overtone results from multiples of a single fundamental. There are two main sources of anharmonicity [14]. They are mechanical anharmonicity due to deviations from the harmonic potential and electrical anharmonicity due to higher order terms in the dipole moment or polarizability. If overtones or combinations along with its fundamentals are observed in the spectra, it indicates the presence of mechanical anharmonicity. If electrical anharmonicity
is present the overtones and combinations appear even if the fundamental is absent [26].

1.7 2 Fermi Resonance

Two or more levels of a polyatomic molecule belonging to different vibrations or combinations of vibrations may have nearly the same energy, i.e., they may accidentally degenerate. In such cases the anharmonic terms which ordinarily might produce little effect may split the nearly degenerate levels quite considerably. The extent of splitting will depend on how close the unperturbed levels are to one another and on the magnitude of the anharmonic terms. If the wave function of the two nearly degenerate levels have different symmetries or if they belong to different species of the point group of the molecule then there will be no splitting [17]. If the unperturbed levels are not very close, resonance may increase the weaker band considerably but with little change in the frequency. Fermi [27] was the first to recognise such a perturbation in the case of fundamental and the first overtone of CO$_2$.

1.7 3 Hydrogen Bonding

Formation of the hydrogen bond (H - bond) affects the vibrational frequencies of solids considerably. The H - bond is defined as the bond between an atom X and the hydrogen atom of a covalent bond X - H forming the group X - H .... Y. Atoms X and Y have electronegativities greater than H. In general it can be considered as a proton shared by two lone electron pairs. It is an important form of molecular association and can be of inter or intra molecular
type [28]. An H-bond is called intramolecular when it is formed between groups within a single molecule and intermolecular when it involves association of two or more molecules [29]. An H-bond can occur between atoms with electronegativity greater than that of hydrogen. Oxygen, nitrogen and halogen atoms are the most frequent partners and may give rise to strong H-bond.

When a hydrogen bond complex $X-H ... Y$ is formed the following conspicuous changes are usually observed [30, 31, 32] in the vibrational spectrum.

i. the $X-H$ stretching frequency shifts to lower frequencies.

ii. the breadth and intensity of the $X-H$ stretching frequency increase markedly.

iii. the $X-H$ bending frequency shifts to higher frequencies with decrease in intensity.

iv. appearance of new vibrational bands corresponding to $H ... Y$ stretching and deformation at low frequencies.

v. shifting of the vibrational modes involving hydrogen bond acceptor group $Y$.

In Raman and IR spectroscopic studies the main emphasis is on $\nu X-H$ and $\delta X-H$ frequencies since the effects on these are generally larger than those observed for the other frequencies.
1.8 INFRARED SPECTROMETER

There are two types of infrared spectrometer - one using dispersive technique and the other Fourier transform technique. All the IR spectra used in this thesis are recorded on FT-IR spectrometer which uses the Fourier transform technique.

The FT-IR spectrometer has three basic components - a source, a Michelson interferometer and a detector. The Michelson interferometer which consists of a beam splitter, a fixed mirror and a moving mirror, preserves both frequency and intensity information and replaces the conventional monochromator. Fig (1.3) shows a simplified diagram of the FT-IR spectrometer.

Collimated radiation from the broad infrared source, A, is directed into the interferometer and impinges on the beam splitter, B (a very thin film of germanium). The beam splitter splits the beam into two arms of almost equal energy. About 50% of the light is transmitted through the film and is directed on to the fixed mirror, C. The remainder of the light reflects off the beam splitter and is directed on to the moving mirror, D. The beams reflect off the surfaces of the two mirrors and recombine at the beam splitter. Here constructive and destructive interference occurs, depending on the position of the moving mirror relative to the fixed mirror. The resulting beam passes through the sample where selective absorption takes place, and then continues on to the detector.

The scan in the FT-IR spectroscopy is the mechanical displacement of the moving mirror assembly; not a scan of individual frequencies as with a monochromator type system. The detector response for a single frequency
component from the infrared source stimulates a monochromatic source, which is a laser. The single frequency beam passes through the beam splitter. The resulting two beams move through a sequence of constructive and destructive interference depending on the position of the moving mirror relative to the fixed mirror.

Radiation of a single frequency results in an interference pattern that is a cosine wave by the interferometer technique. However this is a modulated or modified cosine wave whose frequency is determined by the velocity of the moving mirror. The higher the velocity, the higher will be the frequency of the modulated cosine function. Mathematically the Fourier transformation of a single frequency is a cosine wave. Therefore the interferometer is actually taking the Fourier transform of the incoming signal.

This same process occurs for every frequency emitted from the broadband infrared source. Fig (1.4) shows the cosine waves of those component frequencies. When three frequencies are sampled at once, the resulting signal observed by the detector is the signed summation of the individual modulated cosine waves. This type of signal shown in Fig (1.5) is called an interferogram or time domain spectrum (intensity versus time within the mirror scan).

From Fig (1.5) it can be seen that all of the cosine waves have a maximum at Zero Path Difference (ZPD). This is the only position within the moving mirror scan where the optical paths are identical, so all of the frequencies are in phase simultaneously. This produces a large signal at the ZPD point in the interferogram with rapid cancellation on either side. Resolution in an FT-IR
system is defined by the length of the mirror travel beyond the ZPD point. The further the mirror moves, the higher will be the resolving power of the instrument.

This phenomenon occurs because the Fourier transformation can only distinguish two different frequencies if there is a difference in their modulated cosine waves. If two frequencies are very similar, the resulting cosine waves will also be similar. Only a longer mirror travel can pick out the subtle differences.

In summary, the interferometer encodes the initial frequencies (by optically taking the Fourier transformation of the incoming signal) into a special form that the detector can observe in time. The inverse Fourier transformation is a mathematical means of resorting the individual frequencies for the final presentation of the infrared spectrum. In other words, a Fourier transformation simply converts from one domain into another, in this case, from the time domain (measured) to the frequency domain (desired). It is this final spectrum that is of importance.

Any data point of the interferogram represents the summation of components from each modulated frequency. Each data point contains information over the entire infrared region to which the detector is sensitive. In reality the detector observes all frequencies simultaneously.
An FT-IR spectrometer has distinctive advantages over the earlier dispersive instruments.

1. There is only one continuously moving component in the FT-IR system: the moving mirror. This results in little system wear and high system reliability.

2. All frequencies are viewed simultaneously (Felgett’s advantage) producing a spectrum in as little as one second.

3. Rapid scan speeds allow the system to monitor kinetic experiments.

4. A large beam is used. There are no slits in the system to define resolution.

5. The use of a laser provides an internal calibration system with frequency accuracy to 0.01 cm⁻¹.

6. There is no equivalent to stray light because each frequency is modulated uniquely.

7. The sample is further removed from the source and has little problem with thermal effects.

8. Emitted radiation by the sample is not modulated and hence is not viewed by the detector.
1.9 Raman Spectrometer

A large Raman Spectrometer consists of four major components, viz, the laser, the sample illuminator, the monochromator and the detector.

1.9.1 Laser

The highly directional and intense laser beam forms an ideal source for Raman spectroscopy as it has a narrow spectral line width, small cross sectional area, low divergence, coherence, good linear polarization and high power. The commonly used sources are He-Ne laser, Argon ion laser, Krypton laser etc.

1.9.2 Sample Illuminator

A laser beam may be focussed to produce a beam of much smaller diameter using a lens. The small diameter beam extends over a short length before beginning to diverge again. The region in which the beam is most concentrated is called the focal cylinder. As the area of the focused beam is about $10^{-3}$ times the area of the unfocused beam the irradiance at the sample is increased by about $10^3$. If high irradiance is harmful to the sample, focussed beam is not used. The sample is placed in such a way that it is illuminated well and the scattered radiations collected effectively. A lens is used to collect the scattered radiation for further dispensation. Additional concave mirrors are used to increase the observed intensity of scattering by 8 to 10 times. Filters and optical devices such as polarizer, polarization analyzer, etc. may be inserted into the incident laser beam or in the scattered laser beam.
1.9 3 Monochromator

A monochromator allows only a narrow wave number band to reach the detector at a time. The monochromator often used is the one based on grating. The most important property of any monochromator is its spectral purity. Essentially this is the ability to distinguish radiation of the narrow wave number band $\nu \pm d\nu$ to which it is set from radiations of other wave numbers. This depends on factors like resolving power, dispersion and slit widths. If two monochromators are used in series the solution will be much better. For the study of vibrational bands, a double monochromator is sufficient. For high resolution work a triple monochromator is used. In scanning spectrometers a scale which translates the grating movements, reads directly the wave number.

1.9 4 Detector

The dispersed radiation is detected photoelectrically. The exit slit allows only a narrow band to reach the photomultiplier tube and the rotation of the grating allows the successive bands to reach the detector. To reduce thermal emission contributing a noise element in the signal, the photomultiplier is cooled. The photomultiplier has a high efficiency and uniform response over the 4000 to 8000 Å range. The output of the PMT is amplified and fed to the strip chart recorder which can be operated in the photon counting mode or direct current mode. The direct current mode is used usually at higher signal level.
1.10 SURFACE ENHANCED RAMAN SCATTERING (SERS)

The discovery of Raman scattering from molecules adsorbed on metal surfaces enhanced by a factor of $10^6$ to $10^7$ times has attracted considerable interest and excitement in recent years. This was first observed by Fleishman, Hendra and Mc Quillan [33] in 1974 on the molecule pyridine adsorbed from aqueous solution on to a roughened silver electrode. By now SERS has shown to be applicable for spectroscopy of numerous systems ranging from simple molecules to large biological molecules like DNA, RNA etc. It has also made physicists to get interested in the territory of stereochemistry, charge transfer etc.

SERS seems to be most intense when excited on metal surfaces containing many, usually coupled, microscopic metal domains. Such surfaces are referred to as SERS active systems. Some of them are given below.

i. Electrode surfaces subjected to one or more oxidation-reduction cycles.

ii. Island films consisting of small metal particles of diameter 50-200 Å resting on glass or quartz substrate formed by vapour deposition of a small quantity of metal on a warm substrate.

iii. Cold deposited films: Metal vapour deposited on cold substrate usually below 120 K forms a rough film as a result of the greatly reduced mobility of the metal atoms on the cold substrate.

iv. Lithographically produced metal spheroid assemblies.
v. Metal solutions are prepared by reducing dissolved metal salt by means of an appropriate reducing agent in either an aqueous or non aqueous solution [34].

1.10 1 Mechanism of Adsorption

The mechanism by which an adsorbed molecule enhances the signal is not yet understood clearly. It is generally accepted that in any given system several enhancement mechanisms may be operating. The intensity of Raman scattering is proportional to the square of the induced dipole moment. The dipole moment is given by the equation

\[ P = \alpha \ E \]

Here \( E \) is the electric field associated with the incident radiation and \( \alpha \) is the molecular polarizability. From the equation it is clear that enhancement of either the molecular polarizability or the electric field experienced by the molecule causes an enhancement of the scattered intensity. Therefore, the theories of surface enhancement are broadly classified into

1. molecular enhancement mechanism in which the molecular polarizability is perturbed by the interaction of the adsorbate with the surface.

ii. electric field enhancement mechanism in which the field experienced by the adsorbate molecule is larger than that it would experience if it is far from the surface.
In most situations, the molecular and electromagnetic effects are mixed in proportions depending on the types of molecules, surface, binding and environment. The manipulation of surface shape and properties can tailor the enhancement to our desire. A molecule may get adsorbed on the metal surface due to dipole - dipole interactions (electrostatic forces) called physisorption. Another type of interaction called chemisorption is related to the creation of a weak chemical bond between the molecule and metal through adsorption sites. For chemisorption to occur, the molecule should have a lone pair electron. Generally the chemisorbed molecules are more strongly bound to the surface than those that are physisorbed. However both the interactions will be weak when compared to chemical bonding. All molecules are physiosorbed to some extent but only some of them can be chemisorbed.

1.10 2 Certain essential facts about SERS Spectra

i. Vibrations involving atoms directly bonded to metal atoms are more pronounced in SERS spectrum.

ii. When the band corresponding to a symmetric mode is enhanced, the shift from normal frequency is small. However asymmetric modes show appreciable shift in frequency. But shift of frequency along with considerable intensity is rarely observed.

iii. Vibrations involving larger component of dipole moment in a direction normal to the surface will be enhanced more.

iv. Chemisorbed molecules give rise to a metal - adsorbate stretching band in the low frequency region. Chemisorption is usually followed by
reduction in the symmetry of the adsorbed moiety leading to splitting of the fundamental modes.

v. For each adsorbate, there is an optimum concentration at which the enhancement is maximum. This corresponds to a monolayer of the adsorbate on the metal surface. At higher concentrations multilayer effect and bulk properties manifest.

vi. It is found that the best SERS spectrum results when the frequency of the emitting radiation matches with the plasma resonance frequency of the colloidal particle.

vii. As SERS selection rules are different from those of normal Raman, combination bands can also show up in the spectrum.

1.10 3 Colloids

A major step forward in the development of SERS was the discovery that silver or gold colloids could be used as absorbent instead of solid metal surface. The colloids consists of small (10-100 nm), well defined, close to spherical particles which are ideal for producing plasmon resonance [35, 36]. SERS usually occurs after aggregation of the colloids which could be caused by adsorbates. The aggregation effects an increase in the electromagnetic field between particles and makes it possible to observe enhanced Raman scattering. However, SERS has been reported for non-aggregated or particularly aggregated colloids and the enhancement was comparable or even greater for some molecules. It has also been reported that different anions can strongly affect SERS spectra and the magnitude of the enhancement, without perceptibly
changing the aggregation state of the colloid [37]. This means that there is also chemical enhancement and colloids cannot be considered as SERS system with only electromagnetic enhancement.

The SERS spectrum of a substance on colloidal systems results from the adsorption of molecular species on the colloidal particles. For multicomponent samples, selective molecular adsorption on silver surfaces has been demonstrated [38]. The relative intensities of SERS features arising from the several components depend on the relative adsorptivities and the solution concentrations. The solvent plays a major role in SERS activity. The observed effect depends on the adsorbate concentration and on the volume of the solvent. Water is often the most preferred solvent because a large number of adsorbates are amenable to SERS studies, and lower analytic concentration can be detected [39].

The use of metal colloids for SERS studies is common because they are easy to prepare and easy to investigate by spectroscopic methods, electron microscopy etc. These systems are also very convenient for theoretical stimulations of SERS phenomena. In practical applications they provide the lowest detection for many molecules. A disadvantage of colloidal metals is the poor reproducibility of their properties from one preparation to another. The poor reproducibility makes control of the size, shape and surface properties of particles and aggregates extremely difficult.[40]
1.10 4 SERS SPECTRA OF CERTAIN SYSTEMS - A BRIEF REVIEW

1.10.4 1 Early investigation

The advantages of SERS as a technique for the detection and identification of molecules adsorbed at surfaces were clearly obvious from the early experimental work in this field. Initial studies by Fleischmann et al. [33], Jeanmaire and Van Duvane [41] and Albrecht and Creighton [42] demonstrated that Raman scattering from pyridine on a roughened silver electrode was enhanced drastically. From these quantitative studies it become clear that SERS was a new, sufficiently sensitive spectroscopic method for surface science, analytical applications and biophysics. These early results stimulated considerable experimental and theoretical interest in this phenomenon which resulted in a large number of publications. [33, 43-51] S.J. Greaves and W.P. Griffith studied SERS spectra from silver colloids of vanadate, phosphate and arsenate [52]. They observed strongly enhanced spectra for \((\text{VO}_4)^{3-}\), \((\text{PO}_4)^{3-}\) and \((\text{HASO}_4)^{2-}\). They also observed that deuteration has no effect on the band positions in the SERS spectra.

1.10.4 2 Biological systems

In the early 1980s, three research groups began to study SERS of biological molecules in order to obtain new structural-functional information. Koglin and Sequariss [53] initially focused on nucleic acid, components and DNA. Nabiev et al. [54] investigated amino acids, water soluble and membrane proteins and nucleic acids. Cotton [55, 56] studied a number of proteins
containing chromophores. Following these pioneering studies many others demonstrated the immense potential of this approach for solving a number of problems in biochemistry, biophysics and molecular biology. The studies included amino acids, peptides, chlorophylls and related compounds [57-59], bile pigments [60-61], eyelens pigments [62], proteins [53-56], antibodies [63-65], DNA [53-56, 66, 67] etc.

One of the important questions concerning SERS studies of biomolecules is whether the molecular structure and function is preserved after interaction with the surface. Although initial experimental results relating to this question were ambiguous, it now appears that significant structural changes (denaturation) may occur for some proteins under certain conditions, but these are not necessarily due to the interaction of the protein with the surface. It was found that after only 25 s of irradiation a significant conversion of the protein from its native low spin state to a denatured high spin state occurred. The use of a diode-array detector minimizes the time of sample exposure and also allows the detection of changes in the spectrum which are due to photodegradation. New methods are developed to minimize denaturation. One method that appears promising is to record the spectra at low temperatures [68]. A second method is to use electrode modifiers. Studies by Rospadowksi and co workers [69-78] indicated that citrate or citrate oxidation products that are present after reduction of AgNO₃ are adsorbed to the surface of the solution. This in turn prevents the protein from contacting the metal directly and thereby prevents denaturation.
In the present thesis IR, Raman and SERS spectra of sulphamic acid, ethylene diammonium phosphate, ethylene diammonium arsenate, dimethyl ethanol ammonium dihydrogen phosphate monohydrate and two biological molecules viz spermine phosphate hexahydrate and arcaine sulphate are studied.
Fig. 1.1
Energy level diagram of a diatomic molecule
Fig. 1.2
Block diagram of an absorption spectrometer

Fig. 1.3
FT-IR Spectrometer
Fig. 1.4
Cosine waves representing the Fourier transform

Fig. 1.5
Time-domain spectrum