CHAPTER 1

INTRODUCTION

1.1 RAMAN SCATTERING
1.1.1 Raman Effect - Classical Theory
1.1.2 Raman Effect - Quantum Theory
1.2 INFRARED ABSORPTION
1.3 NORMAL MODES OF VIBRATION
1.4 ANHARMONICITY
1.5 FERMI RESONANCE
1.6 SOLID STATE EFFECTS
1.7 HYDROGEN BONDING
1.8 POLARIZATION OF RAMAN LINES
1.9 GROUP THEORETICAL METHODS
1.10 SELECTION RULES
1.11 SINGLE CRYSTAL RAMAN SPECTRA
1.12 INSTRUMENTATION AND SAMPLE HANDLING TECHNIQUES
1.12.1 Infrared Spectrophotometer
1.12.2 Laser Raman Spectrometer
1.13 BRIEF REVIEW OF EARLIER WORKS ON MOLYBDATES

REFERENCES

FIGURES
Modern methods of spectroscopy, in the different regions of electromagnetic spectrum, have provided indispensable tools for the investigation of molecular structure. Among which, vibrational spectroscopy is undoubtedly the most powerful physical technique for the elucidation of molecular structure and for qualitative and quantitative analysis. The introduction of high intensity laser excitation sources has led to an upsurge of interest in Raman spectroscopy and to rapid development of sophisticated instrumentation. Sparking the revived interest in infrared spectroscopy is the designing and manufacturing of double beam spectrophotometers and far infrared spectrometers. Due to the complementary nature of IR and Raman spectroscopy it is interesting to compare the two techniques for studying the vibrational and rotational energies of molecules.

The vibrational spectra give an insight into the discrete motions of the atoms in a molecular system. The measured frequency shifts of Raman scattered radiation from a sample are the same as many absorption frequencies observed in the infrared and have the same origin, namely the energy differences associated with fundamental molecular vibrations. From the spectra information about molecular geometry, inter and intramolecular forces, molecular composition etc. can be obtained. Since its discovery
vibrational spectroscopy has also been important as a method for locating various functional groups or chemical bonds and for identification of compounds.

1.1 RAMAN SCATTERING

When a monochromatic radiation of wavenumber $\tilde{\nu}_0$ is incident on systems like dust free transparent gases and liquids or optically perfect transparent solids most of it is transmitted without change, but in addition some scattering of the radiation occurs. On analysing the frequency content of the scattered radiation not only the wavenumber $\tilde{\nu}_0$ associated with the incident radiation is observed but also, in general, pairs of new wavenumbers of type $\tilde{\nu}' = \tilde{\nu}_0 \pm \tilde{\nu}_m$ (Fig.1.1). In molecular systems, the wavenumber $\tilde{\nu}_m$ are found to lie principally in the ranges associated with transitions between vibrational and rotational levels. Polarization characteristics of the scattered radiation is different from those of the incident radiation. Such scattering of radiation with change of frequency is called Raman scattering.$^1$

Inelastic light scattering in molecules, predicted by Smekal$^2$ in 1923, was discovered in liquids by Raman and Krishnan$^3-5$ in 1928. Soon after this Landsberg and Mandelstam$^6$ presented the first light scattering spectrum of a crystal namely quartz and Ramdas$^7$ of ethyl ether in the vapour state. Cabannes$^8$ and Rocard$^9$ confirmed the
observations of Raman and Krishnan. Thus the phenomenon of Raman effect in gaseous, liquid and solid states was established, within a few months after the discovery.\textsuperscript{10}

1.1.1 Raman effect - Classical theory

Considering the electrical nature of matter, atoms and molecules consist of collections of oppositely charged particles whose relative positions can be altered by the application of external electric fields. This leads to an electric dipole moment being induced into the system. The ease with which a molecule or atom may be distorted by an electric field is measured by the electric polarizability. For atoms when the symmetry is spherical, the polarizability is same in all directions and can be expressed by a single scalar quantity. For molecules with a symmetry lower than spherical symmetry, the polarizability will not be same along all directions and is described by a tensor. Using the symbol $\alpha_{ij}$ to denote the components of the polarizability tensor $\alpha$, the induced dipole moment $\mu_I$, due to an external field $E$ is defined by $\mu_I = \alpha.E$ or the components of $\mu_I$ are

$$
\begin{bmatrix}
\mu_{ix} \\
\mu_{iy} \\
\mu_{iz}
\end{bmatrix}
= 
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
$$

The polarizability tensor will be symmetric and furthermore there will be a unique axis system where the polarizability
The prerequisite to the observation of Raman effect is not only the occurrence of a periodic internal motion but also the association, with this motion, of a change in the polarizability of the molecule. This change can be either in the magnitude of the polarizability tensor components or in the direction of the principal axis system, since the latter will also lead to the presence of a changing dipole.

1.1.2 Raman effect - Quantum theory

The Raman effect involves the interaction of a molecule with intense monochromatic radiation $\nu_0$, having an energy content different from that necessary to excite the molecule to a quantized upper state. This interaction, referred to as inelastic scattering results in the creation of an induced dipole given by $\mu_I = \alpha \cdot E$. In this condition the molecule is said to exist in a virtual state as opposed to a doubly quantized energy state. The existence of a molecule in a virtual state is essentially instantaneous with the molecule returning to some lower level with the polarizability tensor being diagonal, that is, the components of the induced moments will be parallel to the external field if the field lies along any one of these axes. In this case the polarizability tensor is

$$\alpha = \begin{bmatrix} \alpha_{x'x'} & 0 & 0 \\ 0 & \alpha_{y'y'} & 0 \\ 0 & 0 & \alpha_{z'z'} \end{bmatrix}$$
concurrent emission of radiation of frequency $v'$. Since the levels of the virtual state is dependent on the energy of the incident radiation and it has an infinitesimal life time, the radiation is effectively scattered rather than absorbed and re-emitted. If the final state of the molecule differs from the initial state then the scattered radiation will be shifted in frequency from the incident radiation and the scattering is inelastic. The most commonly observed cases of the Raman effect involve molecules whose initial and final states involve different rotational or vibrational energy states. In both cases the final state of the molecule and hence the frequency of the scattered radiation is determined by quantum mechanical selection rules. The net result of the Stokes ($\psi_0 > \psi'$) and anti-Stokes ($\psi_0 < \psi'$) scattering is to produce scattered radiation which has been shifted in frequency from the initial radiation by an amount equivalent to the difference between two quantized levels.\textsuperscript{11}

1.2 INFRARED ABSORPTION

When polychromatic infrared radiation is incident on a set of molecules a part of it is absorbed and a part of it passes through the sample. For infrared absorption to occur two major conditions must be fulfilled.\textsuperscript{12}

(i) The energy of the incident radiation must coincide with the energy difference between the excited and ground states of the molecule. Radiant energy will
then be absorbed by the molecule, increasing its natural vibration.

(ii) The vibration must entail a change in the electrical dipole moment.

The molecule does not absorb an infrared quantum with arbitrary energy, but only a quantum whose energy, $E = h\nu$, satisfies the Bohr frequency condition i.e., its magnitude equals the difference in the energies of two vibrational (rotational) levels of the molecule, $\Delta E$. Along with Bohr frequency condition other conditions limiting the absorption arise from the symmetry of molecules and vibrations and are contained in the selection rules. If the Bohr frequency condition, also called the resonance condition, is satisfied, then the energy of photon absorbed during interaction of radiation with the molecule results in transfer of the molecule from a lower vibrational level to a higher level. If photons of various energies are contained in IR radiation before interaction then only those absorbed in the resonance interaction will be missing after interaction.\(^{13}\) The intensity of an infrared absorption band is proportional to the square of the rate of change of dipole moment with respect to the displacement of the atoms. As defined by the quantum laws, the vibrations are not random events but can occur only at specific frequencies governed by the atomic masses and strength of chemical bonds.
\[
\bar{\nu} = \frac{1}{2 \pi c} \sqrt{\frac{k}{m}}
\]

where \( \bar{\nu} \) is the wavenumber of vibration, \( c \) is the velocity of light, \( k \) is the force constant and \( m \) is the reduced mass of atoms concerned.\(^{13}\)

1.3 NORMAL MODES OF VIBRATION

For a crystal with \( N \) primitive unit cells, each containing \( n \) atoms, there is a total of \( 3nN \) degrees of freedom arising from motion of the atoms and there can be \((3nN-6)\) nonzero solutions to the vibrational problem. At the zone centre where the factor group applies and primitive translations are treated as identity operations one considers only the \( 3n \) degrees of freedom arising from the movements of the atoms present in one primitive cell. Considering \( N \) non-interacting groups of \( n \) atoms, each group of \( n \) being the contents of one primitive cell, each cell has \((3n-6)\) vibrations, 3 translations and 3 rotations. The \((3n-6)\) vibrations are classified according to the factor group of the crystal which is identical with the point group. Each of the \( 3n \) motions of one cell couples in \( N \) different ways to give \( N \) overall modes. Both vibrations and rotations of the unit cell give rise to crystal vibrations at all positions of the Brillouin zone. For that reason there are \((3n-3)\) factor group fundamentals and pure unit cell rotations may not be factored out as they are in molecular vibrations. One factor group fundamental as
spectroscopically observed, is really the envelope of a large number of crystal modes falling within the definition. Crystal vibrations arising from \((3n-3)\) primitive cell vibrations are known as optical modes. At the exact zone centre the three translations of the unit cell clearly become the three translations of the crystal and they give rise to crystal modes known as acoustic modes since they are essentially standing sound waves present in a homogeneous medium.\(^{14}\) The number of normal modes does not necessarily correspond exactly to the number of observed absorption peaks.\(^{15}\) The number of peaks is frequently less because

(i) the symmetry of the molecule is such that no change in dipole moment results from a particular vibration.

(ii) the energies of two or more vibrations are identical or nearly identical.

(iii) the absorption intensity is too low to be observed.

(iv) the vibrational energy is in a wavelength region beyond the range of the instrument.

Modes non-existent in the gaseous and liquid states are encountered in the spectra of crystals especially in the low wavenumber region. There are the translational modes, where the unit cell building blocks (even monoatomic ions) vibrate periodically around equilibrium positions. Libration modes can be described as the turning of the polyatomic ions
or molecules around rotation axes in equilibrium positions in the unit cell. Acoustic modes (phonons) represent the propagation of certain deformations through the crystal.\textsuperscript{13}

1.4 ANHARMONICITY

The criterion for the determination of well defined equilibrium configurations of a molecule is the minimization of the electronic energy which is the potential energy for the vibrational problem. At ordinary temperatures the atoms undergo small oscillatory motions about their equilibrium positions. The vibrational potential energy in atomic displacements from equilibrium can be expressed assuming that the internal coordinates $S_t$ are linearly independent and form a complete set as

$$V_{\text{vib}} = V_0 + \sum_{t=1}^{3N-6} \left( \frac{\partial V}{\partial S_t} \right) S_t + \frac{1}{2!} \sum_{t,t'} \left( \frac{\partial^2 V}{\partial S_t \partial S_{t'}} \right) S_t S_{t'}$$

If the cubic and higher order terms are considered in this expression the molecular vibrations become anharmonic. The effects of anharmonicity are

(i) to modify the regular spacing of energy levels defined by $E_{k,v} = h \nu_k (v_k + 1/2)$, for each normal mode of vibration $k$.

(ii) to relax the selection rule $v_k \pm 1$.

$v_k = 0,1,2,...$ is the vibrational quantum number and $\nu_k$ is found to be identical to the classical frequency of
vibration of the \( k^{th} \) normal mode. Thus in real molecules, absorption features are often observed at frequencies of approximately \( 2 \nu_k, 3 \nu_k \), etc, the overtones, and at approximately, \( \nu_k + \nu_k' \), \( (l, l' = 1, 2, \ldots) \), the combinations.\(^{16}\) The intensity of the lower overtone and combination bands is directly related to the anharmonic character of the vibrations. Observed overtones are always slightly less than simple multiples of the fundamental frequencies and combinations slightly less than the sum of two fundamental frequencies. Among the combination bands the difference bands tend to be much weaker than sum bands because the intensity of difference bands depends on the population of the excited state. Further, difference bands are more likely to be met with low frequency vibrations.\(^{17}\) The absorptions due to anharmonicity are usually broad.\(^{18}\)

Another phenomenon associated with anharmonicity is the appearance of the hot bands. These are transitions in which molecules, originally in an excited state, absorb a further quantum. Thus the quantum number changes by +1, but because of anharmonicity the frequency of this transition is less than that of the fundamental. Since the appearance of hot bands depends on the population of an excited state, hot bands are usually observed with low frequency vibrations. Ternary combinations involving a total change of 3 in the quantum numbers are sometimes observed, but they are very rare.\(^{17}\)
1.5 FERMI RESONANCE

Fermi resonance is a phenomenon which occur when two vibrational levels, usually one fundamental and one overtone have nearly the same energy and are symmetrically suited. In such cases the overtone borrows intensity from the fundamental and instead of being a weak band it becomes almost, if not equally, as strong as the fundamental. The two levels repel one another and the one with greater energy moves to higher frequency and the one with the lower energy moves to lower frequency. 17

1.6 SOLID STATE EFFECTS

The symmetry of the site upon which a molecule resides is rarely the same as the molecular point group. As the site group of a molecule is a subgroup of its point group the representations of the vibrations are very easily derived by means of a correlation table. If the deviation of the molecule and its environment from the molecular point symmetry is small, the vibrational spectra of the molecule may be the spectra expected of an isolated molecule. As the deviation increases two effects may become apparent. The solid state splittings or changes in selection rules result from an interaction, usually electrostatic, of the molecule with its environment. These effects are strongest in ionic substances. Because of lower symmetry, the selection rules may change and a band may be observed which corresponds to a vibration which is forbidden in the isolated molecule. The
second result may be the splitting of degenerate vibrations.\textsuperscript{17} The nondegenerate internal vibrations can also be shifted in frequency.\textsuperscript{19}

Second effect of crystal structure results from the possibility of vibrational coupling between the two molecules in the unit cell. This type of splitting is known as correlation splitting or Davydov splitting.\textsuperscript{16} This effect may reveal itself in many ways. It causes splitting of both degenerate and nondegenerate internal vibrations. If the primitive cell has \( m \) number of molecules then the fundamental vibration can split up to a maximum of \( m \) bands.

The vibrations of one group of atoms can produce an oscillating electric field which is strong enough to couple with the field produced by the other groups. Coupling of infrared active vibrations will only be appreciable if the intensity of absorption due to these vibrations is high. High intensity is usually associated with polar bonds whose dipole moment changes considerably during vibrations. Vibrations of these bonds are most likely to couple together in the solid state. Hydrogen bonding also provides the most common route whereby vibrations of different molecules in a unit cell become coupled together.\textsuperscript{17}

1.7 HYDROGEN BONDING

Hydrogen bonding is a distinctly directional and specific interaction between a covalently bound \( \text{H} \) atom (\( \text{A-H,} \))
where A is an electronegative atom), with some tendency to
be donated, and a region of high electron density on an
electronegative atom or group of atoms, which can accept the
proton (B). The A-H bond is thereby weakened but not broken
and the properties of the acceptor group are affected. 20

(i) The absorption bands due to the A-H stretching
vibrations (fundamentals and overtones) are shifted
to lower frequencies. This is due to the weakening of
the force constant for the A-H stretching mode,
caused by the formation of the hydrogen bond. The
shifted bands are much broader than the corresponding
bands of the non-hydrogen bonded A-H group. The
integrated intensity of the fundamental band
increases. The corresponding overtones decrease
slightly in integrated intensity.

(ii) A-H deformation modes are shifted to higher
frequencies, shifts being smaller than those observed
for the A-H stretching vibrations. This is because
the formation of hydrogen bonds constrains the
deformation vibrations and therefore increases the
force constants for these modes. These shifted modes
do not show any substantial band broadening or
intensity change when H bonding occurs.

(iii) New vibrational modes corresponding to H...B
stretching and deformation are found at low
frequency in the far infrared region.
(iv) The vibrational modes of the H bond acceptor B are shifted by hydrogen bonding. These shifts may be either to lower or shorter wave lengths and are generally much smaller than those found for the donor A-H vibrations.

1.8 POLARIZATION OF RAMAN LINES

In the vibrational analysis of simple molecules, the measurement of degree of polarization of the Raman lines gives very valuable information, because it enables that band to be assigned as a totally symmetric mode and it helps to decide the geometrical arrangement of the atoms themselves. From the consideration of the polarizability ellipsoid for the molecule, that in the case where all orientations of the scattering molecules are equally probable, for Rayleigh scattering of unpolarized light

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

where \( \rho \) is the depolarization ratio which measures the degree of depolarization of the line. \( \gamma \) measures the anisotropy and may be looked upon as indicating the departure of the ellipsoid from its spherical shape and \( \alpha \) is some measure of overall size of the polarizability ellipsoid. If the ellipsoid reduces to a sphere, then by definition \( \gamma = 0 \) and from the equation \( \rho = 0 \) and Rayleigh line is termed completely polarized. Since \( \alpha \) by definition
may never be zero, $\rho$ must always be less than $6/7$. In the case of Raman lines the equation is modified as

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

where $\alpha'$ in this case can be zero. If both $\gamma'$ and $\alpha'$ are zero, then the Raman line is forbidden. If $\gamma' = 0$ and $\alpha'$ is positive, then $\rho = 0$ and the line is completely polarized. If $\alpha' = 0$ and $\gamma'$ is positive then $\rho = 6/7$ i.e., 0.86 and the line is said to be depolarized. If $0 < \rho < 6/7$, then the line is said to be polarized. The general conclusions are:

(i) Totally symmetric vibrations result in highly polarized lines, i.e., they have small value of $\rho$ ($\rho < 6/7$).

(ii) All antisymmetric vibrational modes are depolarized. If $\rho = 6/7$ the vibration is most probably antisymmetric.

(iii) Totally symmetric breathing modes of regular and octahedral molecules are completely polarized, i.e., $\rho = 0$.

(iv) Raman lines of degenerate vibrational modes are depolarized.

(v) In large unsymmetrical molecules most vibrations are polarized to some degree although vibrations of symmetric groups within such molecules can be
detected by virtue of their large degree of polarization of Raman lines.

1.9 GROUP THEORETICAL METHODS

The analysis of the effect of polarization of the incident and scattered light as well as orientation can most conveniently be carried out using group theoretical methods and it is very essential for the analysis of the vibrational spectra of crystalline materials. According to the 'free molecule' approach the assignments of fundamentals obtained from the spectra of species in the gaseous, liquid or solvated states can be applied to solid state spectra. Site group method developed by Halford recognizes that the vibrators (molecules or complexes) in crystals commonly occupy space group positions, sites, of lower point symmetry than the point group of the free vibrator. It leads to new selection rules and the lifting of degeneracies. This method is used when weak to moderate intermolecular forces prevail and when coupling between different vibrators in the crystal is negligible. But the Factor group method introduced by Bhagavantam and Venkatarayudu and elaborated by Hornig and again by Winston and Halford recognizes the coupling between equivalent molecules or complexes within a primitive unit cell, where upon different selection rules come into play. An additional advantage of the factor group method is that it provides a basis for the prediction of the
infrared and Raman spectra in the lattice mode region. In this method 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. A substantial treatise of the site group and factor group methods has been given by Fateley et al. in the Correlation method. In the correlation method, the molecular free ion symmetry is correlated to the crystal's factor group symmetry through the molecular site symmetry and the site symmetries of individual atoms are correlated to crystal's factor group.

1.10 SELECTION RULES

A molecular vibration is infrared active only if the vibration causes a change in the dipole moment $\mu$ and that the intensity of infrared band is proportional to the square of the change in dipole moment with respect to the normal coordinate $\left(\frac{\delta \mu}{\delta Q}\right)^2$. $x, y$ and $z$ components of the transition moment are

$$
\int_{-\infty}^{+\infty} \hat{\Psi_f}^* \mu_x \hat{\Psi_i} d\tau, \int_{-\infty}^{+\infty} \hat{\Psi_f}^* \mu_y \hat{\Psi_i} d\tau, \int_{-\infty}^{+\infty} \hat{\Psi_f}^* \mu_z \hat{\Psi_i} d\tau
$$

where $\hat{\Psi_i}$ is the wavefunction of the initial vibrational state and $\hat{\Psi_f}^*$ is the wave function of the final vibrational state involved in the transition. The quantities $\mu_x, \mu_y, \mu_z$ are the components of the dipole moment and $d\tau$ is the volume element. In order for the transition $\hat{\Psi_f} \leftarrow \hat{\Psi_i}$ to be
IR active at least one of the above integrals must be nonzero.\textsuperscript{29}

If a molecule has some symmetry then for certain vibrational symmetry species all these integrals may be zero as a necessary consequence of the symmetry. The band intensity which is proportional to the square of the transition moment is an observable quantity and must have the same value for all indistinguishable orientations of the molecule. That is, if the integrals are to have nonzero values then the product \( \Psi_f \mu \Psi_i \) must be totally symmetric, i.e., it must transform to the totally symmetric irreducible representation. This product will be totally symmetric only if the wave function \( \Psi_f \Psi_i \) belongs to the same species as at least one component of the dipole moment \( \mu \). Therefore, a vibrational transition between energy levels is allowed in the infrared spectrum when at least one component of the dipole moment vector has the same species as the product of the quantum mechanical wavefunctions which characterize the molecular state for the two levels involved. In order for a fundamental transition to be IR active at least one component of the dipole moment should belong to the same species as \( (\Psi_f \Psi_i) \) which is the same as that of the excited normal coordinate.\textsuperscript{29}

For a transition to be Raman active, an integral of the type
\[
\int \Psi_f^{*} \alpha_{gg} \Psi_i \text{d} \tau
\]
must be nonzero where $\alpha_{gg'}$ is one component of the polarizability, $g$ and $g'$ are $x,y$ or $z$. This leads to a selection rule for Raman activity identical to that of infrared activity but with the polarizability tensor substituted for dipole moment vector. Thus a fundamental is permitted in Raman scattering only if its species is the same as that of at least one of the components of the polarizability.

1.11 SINGLE CRYSTAL RAMAN SPECTRA

Raman technique has proved to be particularly valuable in the study of single crystals where the infrared technique has greater limitations on sample size and geometry. Single crystal Raman spectra are more informative than powder spectra since complications due to powder scattering effects and different crystalline orientations are eliminated. Polarization data allows unambiguous classification of fundamentals and lattice modes into the various symmetry classes.

The crystal orientation is set to make its $a,b,c$ axes fall in appropriate direction with respect to the direction and polarization of the incident beam. The space coordinate system is so chosen that $X,Y$ and $Z$ coincide with $a,b$ and $c$ axes respectively. The notation proposed by Porto involves four symbols which define the propagation direction of the incident radiation, the direction of the electric vector of the incident radiation,
the direction of the electric vector of the scattered radiation being examined and the direction of propagation of the scattered radiation. In the notation $c(ab)a$, the two symbols in brackets define the polarization character of the incident and scattered light while those outside the parenthesis denote the direction of propagation of incident and scattered beams respectively.

For a cubic shaped monoclinic crystal, with edges $a,b$ and $c$, $b$ is the crystal's unique or two-fold axis. When the laser beam strikes the surface of a birefringent crystal perpendicularly it is split into two components polarized at right angles. The directions of the electric vector are those of the major and minor axes of elliptic section of the indicatrix formed by the plane perpendicular to the propagation direction. If the section is very nearly circular, the interference of the two beams may result in effective depolarization of the radiation. To get exact measurements the axes of the indicatrix are to be used for the directional scattering parameters. For an orthorhombic crystal these are the crystal axes. For monoclinic crystal the unique crystal axis $b$ is coincident with one axis of the indicatrix. Thus to avoid birefringence only $a$ and $c$ may be used as propagation directions. This limit the orientations to $a(bb)c$, $a(ba)c$, $a(cb)c$ and $a(ca)c$ for a monoclinic crystal.
1.12 INSTRUMENTATION AND SAMPLE HANDLING TECHNIQUES

1.12.1 Infrared Spectrophotometer

The basic elements of an infrared spectrometer are a source of IR radiation, a monochromator unit, a detector with an amplifier and a recording device. Common commercial spectrometers employ sources yielding a continuous spectrum with IR wavelengths predominating; the individual components are separated in the monochromator. If the polychromatic source radiation passes through a sample of the compound studied, components with certain wavenumbers are absorbed to a greater or lesser degree. The radiation, attenuated by absorption enters the spectrometer monochromator unit. This beam is dispersed into the individual components and are detected. The optical-mechanical system of the spectrometers is usually constructed so that monochromatic radiation with wavenumbers linearly varying in time is incident on the detector. The recording device records the spectrum in a linear wavenumber scale. All modern double beam spectrometers employ the principle of optical zero. The source radiation is divided into two equivalent beams of which one passes through the sample and the other is used as a reference. The two beams enter the monochromator alternately, with a period determined by a rotating mirror or a chopper. The detector alternately detects signals from one and the other beam, their difference is amplified and controls insertion of an aperture into the reference beam,
so that the sample absorption is just compensated. Then identical signals fall on the detector and the instrument does not record any change; only a change in the sample absorption causes a further operation. If the aperture movement is coupled with the movement of the recorder pen, the spectrum is recorded in relative intensities or in terms of transmittance.¹³

The sample placed on a support, in a cell, is dissolved or pressed with a medium to form a pellet. In the present work the IR spectra of the samples are recorded using the KBr pellet method. A pressed disc is prepared by compressing the finely ground mixture of the sample and KBr to form transparent discs. As KBr does not absorb in the middle IR region the only absorption obtained is that due to the sample.

1.12.2 Laser Raman Spectrometer

In the present work a Spex Ramalog 1401 spectrometer equipped with a Spectra Physics model 165 Argon ion laser is used for recording the Raman spectra. The detailed optical diagram of a Raman spectrometer is given in Fig.1.2.

Raman spectra of the deuterated samples have been recorded on a Dilor Z24 Raman spectrometer.

A laser Raman system consists of four major components, (i) laser (ii) sample illuminator (iii) monochromator (iv) detector and read out electronics.
Spectra Physics 165 model Argon ion laser is capable of providing extremely stable single frequency output power and operating in the TEM\textsubscript{00} mode at any one of more than twenty spectral lines or at several lines simultaneously. Its range is from the ultraviolet wavelength of 350.7 nm to the far red 799.3 nm. Laser consists of a laser head, which contains the plasma tube solenoid and optical resonator and the model 265 exciter. Exciter contains all the necessary electronic circuits to create, sustain and monitor the ion discharge in the plasma tube, to monitor and control the output power and to supply and regulate the solenoid current. Both 514.5 nm and 488.0 nm lines are used to record the spectra in the present work.

Sample illuminator is equipped with a dielectric or aluminium coated mirror to direct the laser beam on to the sample area. The laser light expanded by a beam expander passes through a Claassen filter which is used to disperse the light from the laser and to filter out plasma lines. The radiation in the visible region is focused on to the sample by a condensing lens. Two spherical mirrors M\textsubscript{1} (above) and M\textsubscript{2} (behind) are provided to increase the energy density on the sample. These mirrors also reflect the scattered light to the collection lens system. Collection lens assembly collects the light scattered from the sample and image it on the entrance slit of the spectrometer. After the collection lens assembly a polarization analyser which can be used to
measure the depolarization ratio is used. The scrambler follows the polarization analyzer and scrambles the polarization of the light which enters the spectrometer. This corrects for the polarizing effect of the spectrometer. An optional polarization rotator may be mounted in front of the beam expander to change the polarization properties of the laser beam.

The double spectrometer is of Czerny-Turner type. The optical bridging system is arranged for additive dispersion of the collected radiation. This results in nearly doubled resolution, luminosity or signal to noise ratio compared to a single or subtractive double system.

Each monochromator consists of a holographic grating with 1800 g/mm, blazed for high efficiency over the Raman range. Grating G₁ is rotated by the scanning drive and G₂ follows through its linkage. Four slits s₁, s₂, s₃ and s₄ are bilaterally adjustable to continuously vary the width. The light entering the exit slit of the monochromator is focused on the photosensitive surface of the detector with a floating lens assembly where it is converted into electric signal. By having many dynodes in a chain, a cascade process develops until the charge arriving at the anode consists of a pulse of $10^6$ to $10^7$ electrons. A DPC-2 digital photometer amplifies it and converts the output of the photomultiplier tube into uniform pulses. This is coupled to a recorder
controller with a bidirectional stepper motor. It can drive the recorder backward and forward in synchronism with the spectrometer scanning.

A few samples studied in the present thesis are of polycrystalline nature. A capillary tube is used as an excellent container for these samples. The sample is ground to a fine powder and is partially filled in the capillary tube. It is then placed in the sampling compartment and is properly positioned. For a hygroscopic sample the ends are sealed to prevent decomposition. Once a capillary is properly aligned at the focused region of the laser it can be readily substituted by another sample in a capillary of same diameter.

For a single crystal which is not grown with suitable faces conventional grinding and polishing techniques can be used to provide such faces. Crystallographic axes can be identified using a polarization microscope. The single crystal is then fixed to a goniometer that allows simple traversal in X, Y and Z directions. The spectra are recorded in the 90 degree scattering geometry for different orientations of the optical axes to the co-ordinates a, b, c of the crystal.

Since quantum yield in Raman spectroscopy is less than one millionth of that in fluorescence, even trace impurities can cause serious difficulties. The amount of fluorescence depends on the excitation frequency and
therefore a different line may be used to reduce it, or the sample can be exposed to a 200-500 mW laser radiation for a few minutes. The choice of laser frequency is restricted in the case of a coloured material. When a high intensity exciting line is used which falls entirely within the visible absorption band of a sample, rapid absorption of the radiation may cause local overheating and decomposition. But the spectra can be obtained by the rotating technique since the relative motion between the laser focus and sample surface avoids local overheating and decomposition. Solids are amenable to this rotating technique by pressing them into ring shaped pellets.\textsuperscript{33}

A few shortcomings exist in the Raman technique. The frequency of the exciting radiation must be lower than the electronic energies of the molecule so that no absorption of the incident light occurs. If a substance is absorbing in the exciting region, it will reabsorb the Raman scattering and this will make it difficult to detect the Raman lines. After absorption, fluorescence may occur, and this will obscure the Raman spectrum. The excitation frequency of the Raman sources are selected to lie below most S-S* electronic transitions and above most fundamental vibrational frequencies. Both the solid and liquid samples must be free from dust particles or the Raman spectrum may be masked by Tyndall scattering.\textsuperscript{12}
1.13 BRIEF REVIEW OF EARLIER WORKS ON MOLYBDATES

Structurally molybdates are of interest since some of them contain tetrahedral anionic group whereas others contain octahedral anionic group. Their structure and spectroscopic properties have been extensively studied by many researchers. Normal molybdates of types $ABO_4$ and $A_2BO_6$ ($B = Mo$) may crystallize with different structures like scheelite, wolframite, spinel etc. Of the crystal structures occurring for $ABO_4$ type compounds, the scheelite type structure is the most common. It is adoptable for a large range of radii ratios and charge combinations of cations.

Molybdates with tetrahedral anionic groups

Raman and infrared spectra of molybdates of tetrahedral structure have been extensively investigated. But considerable disagreement exists in the assignment of the fundamental bending modes $v_2(E)$ and $v_4(F_2)$. From the study of the Raman spectra of aqueous solutions and the infrared spectra of nujol mulled samples of several molybdates, Busey and Keller have assigned to $v_2$ a higher frequency than $v_4$. IR spectra of molybdates having tetrahedral and octahedral structures have been recorded by Clark and Doyle and Brown et al. For the compounds containing $MoO_4^{2-}$ ion the assignment $v_2 > v_4$ is favoured. Kanesaka et al. have reported the infrared and
polarized Raman spectra of \( \alpha\text{-MnMoO}_4 \). In the IR spectra, they have observed significant differences from those of related compounds with scheelite structure, especially in the Mo-O stretching region. According to them also, a \( \nu_2 \) mode has a higher frequency than \( \nu_4 \) mode.

Weinstock et al.\(^{38}\) have attempted to suggest a definite assignment for the \( \nu_2 \) and \( \nu_4 \) vibrations of aqueous solutions of \( \text{MoO}_4^{2-} \) by calculating the relative intensities of Raman bands from approximate force fields using Long's matrix method based on Wolkenstein theory. The assignment of \( \nu_1 \) and \( \nu_3 \) modes are confirmed by the measurement of the degree of depolarization of the Raman lines. They have concluded that if two deformation vibrations in the Raman spectrum are partially resolved the weaker band should be assigned to the \( \nu_4 \) mode. In the Raman spectrum of the solution, \( \nu_4 \) and \( \nu_2 \) must nearly coincide and cannot be resolved. They have also proposed that for tetrahedral molecules or ions of the type \( \text{MX}_4 \) the \( \nu_4 / \nu_2 \) ratio increases with decreasing mass of M if M belongs to a vertical row of the periodic system. In an isoelectronic row the \( \nu_4 / \nu_2 \) ratio increases as the charge of the central atom increases.

The infrared reflection and laser Raman spectra of a few scheelite structures (tungstates and molybdates of Ca, Sr, Ba and Pb) single crystals have been reported.\(^{39}\) In this study the correlation field splitting of the \( \nu_3 \) mode has
been explained in terms of the dipole coupling. A greater frequency is assigned to the $\nu_4$ mode than to the $\nu_2$ mode. In the study of the Raman spectra of MgMoO$_4$ single crystals by Miller, vibrations other than those of MoO$_4^{2-}$ are observed. Vibrational spectra of a number of transition metal tetra-oxo-complexes have also been reported and the fundamental vibrational modes are established by Gonzalez-Vilchez and Griffith. From a comparative study of various potential functions for tetrahedrally co-ordinated species, Basile et al. have concluded that, in general, for those transition metal tetra-oxo anions having $\nu_1 > \nu_3$, $\nu_4$ has a higher frequency than $\nu_2$. Vibrational studies on the melts of molybdates and tungstates also support the assignment $\nu_4 > \nu_2$. In the IR spectral analysis of a few anhydrous molybdates Cord et al. have confirmed the tetrahedral co-ordination of molybdenum and a detailed assignment is suggested. The IR data available on molybdates of the scheelite family have been compiled by Tarte and Duyckaerts.

Double molybdates of the type KLn(MoO$_4$)$_2$ (Ln-lantanide) are an interesting group of oxy-compounds which exhibit unusual spectroscopic and optical properties. Most of the compounds exhibit luminescence making it possible to use them as laser materials. They also show polymorphism leading to a variety of structures. The IR and polarized Raman spectra of single crystals of KDy(MoO$_4$)$_3$
have been analysed by Hanuza and Fomitsvev. The spectral data indicate additional intermolecular interactions due to pair coupling of the molecular tetrahedra. This pair coupling is observed for Ky(MoO₄)₂ also by Hanuza and Labuda. Ky(MoO₄)₂ crystals doped with lanthanide ions have high gain factors and low excitation levels for use as laser active materials.

Saleem and Aruldhas have carried out the Raman and IR spectral studies of gel grown nickel and lanthanum molybdates. Based on the vibrational analysis a tetrahedral co-ordination of oxygen atoms around molybdenum atoms is suggested. IR spectra at 300 and 85 K and polarized Raman spectra (20-250 cm⁻¹) of GdTb(MoO₄)₃ and Tb₁.₈Eu₀.₂(MoO₄)₃ single crystals have been recorded and analysed by Saleem et al. An assignment for the multiphonon modes of the molybdate ion has been proposed. Based on the C₂ᵥ symmetry, Saleem et al. have carried out the group theoretical and vibrational analysis of these compounds by recording polarized Raman spectra at various temperatures in the region 250-1000 cm⁻¹ and the IR spectra. IR, Raman and optical absorption spectra of Tb₁.₈Eu₀.₂(MoO₄)₃ single crystal also have been studied by Saleem et al. From the vibrational spectra of neodymium doped NaLa(MoO₄)₂, Ramkrishnan and Aruldhas have concluded that the frequencies and intensities are not altered due to doping. They have also carried out the vibrational analysis of Tb₀.₂Dy₀.₉Gd₀.₉(MoO₄)₃.
The vibrational dynamics as well as the molecular crystal structure of Y, Dy, Ho, Er, Tm, Yb and Lu molybdates have been analysed in terms of a model including a binuclear system with a double oxygen bridge (Hanuza and Macalick).\textsuperscript{59} Hanuza et al. have also studied the electron absorption luminescence, vibrational and magnetic properties of K Dy\textsubscript{x}Y\textsubscript{1-x} (MoO\textsubscript{4})\textsubscript{2} (x=0-1) crystal over a temperature range of 13-239 K.\textsuperscript{60} Symmetry types of the characteristic modes of MoO\textsubscript{4}\textsuperscript{2-} ion are calculated and are compared with the experimental results for Pb\textsubscript{2}MoO\textsubscript{5} single crystals.\textsuperscript{61} Pinnow and Uitert\textsuperscript{62} have reported that this crystal has a large acousto-optic figure of merit and is expected to be useful for acousto-optic applications.

Triple molybdates with tetrahedral co-ordination of oxygen to molybdenum and octahedral co-ordination to the cations with high oxidation states exhibit super-ionic properties. Vibrational spectra of two triple molybdates KMgSc(MoO\textsubscript{4})\textsubscript{3} and KMgLu(MoO\textsubscript{4})\textsubscript{3} and phases of variable composition based on them have been studied by Mokhosoev et al.\textsuperscript{63} Silver lanthanide double molybdates form tetragonal crystals with a disordered scheelite type structure. The IR spectra of the compound have been reported by Perepelitsa et al.\textsuperscript{64} They have explained that the splitting of the $\nu_3(F_2)$ mode and the appearance of $\nu_1(A_1)$ mode is due to the reduction in the symmetry of MoO\textsubscript{4} tetrahedra from Td to C\textsubscript{2v}. CsLiMoO\textsubscript{4} exhibit structural phase transitions with a
similar sequence of phases. Raman spectra of CsLiMoO$_4$ single crystal have been recorded for a wide range of temperatures and a relationship is established between the changes in the spectra and the characteristics of the structure of the investigated compound.$^{65}$

Solid solutions of $M_{1-3x}^{II}Bi_{2x}MoO_4 (M^{II} = Sr^{2+}, Ba^{2+}, Pb^{2+}$ etc.; $x \leq 0.1$) have been studied extensively for catalytic activity and selectivity for the allylic oxidation of alkenes. Raman spectra of $Pb_{1-3x}Bi_{2x}MoO_4 (x \leq 0.06)$ and their $^{18}O$ substituted systems are studied by Kanesaka et al. A new band observed at 896 cm$^{-1}$ is assigned to a local mode $\nu_1$, due to a molybdate ion occupying a cation vacancy. Their observations show that a molybdate ion interacting strongly with a $Bi^{3+}$ ion and a cation vacancy is inactive for $^{18}O$ substitution.$^{66}$

**Molybdates with octahedral anionic groups**

The structure of the most simple perovskite $ABX_3$ ($X=0$ or $F$) may be described as a close cubic packing of $AX_3$ sheets, the octahedral interstices of which are occupied by small $B$ cations. The type of packing determines the linking mode of the $BO_6(MoO_6)$ octahedra. In the cubic close packing the octahedra are linked by their apexes whereas they are sharing faces in hexagonal close packing. Infrared and Raman spectra of a series of hexagonal perovskites of the type
$A_{2}B^{II}B^{VI}O_{6}$ (A = Sr, Ba, Pb, B$^{II}$ = Mg, Ni, Co, Cr, Zn, Cd, Ca, Sr, Ba, B$^{VI}$ = U, W, Mo, Te) have been reported by Liegeois-Duyckaerts and Tarte.$^{67}$ They have also studied the influence of the size and nature of cations on the symmetric $A_{1g}$ mode.

The three compounds MoO$_3$·2H$_2$O, yellow (or $\beta$-)$^{68}$ MoO$_3$·2H$_2$O and white (or $\alpha$-) MoO$_3$·H$_2$O, known as molybdic acids constitute the three stoichiometric well characterized hydrates of MoO$_3$. In $\alpha$-MoO$_3$·H$_2$O, the large splitting of Mo-O asymmetric stretching mode and the failure to obey Weinstock's intensity criteria indicate that the Mo-O co-ordination is in an intermediate state between tetrahedral and octahedral structures.$^{68}$ Infrared spectrum of H$_1$·0MoO$_3$·H$_2$O is reported as a part of its structural and thermodynamic characterization by Crouch-Baker and Dickens.$^{69}$ Philip et al.$^{70}$ have reported the vibrational spectra of MoO$_3$·2H$_2$O and have observed strong distortions in the octahedral arrangement of anions. Massa$^{71}$ has reviewed the infrared reflectivity and Raman scattering spectra of X$_0$·3MoO$_3$(X=K,Rb) single crystals. Kreusler et al.$^{72}$ have reported the infrared and Raman spectral analysis of Rb$_2$Mo$_3$O$_{10}$·H$_2$O. The analysis reveals that the anion forms a chain with hexameric units built up from MoO$_6$ octahedra. The structure and hydrogen bonding of (NH$_2$)$_2$·0.3 MoO$_3$·H$_2$O have been discussed on the basis of T.G.A., IR spectrum and X-ray study by Lasocha et al.$^{73}$ IR spectrum shows similarities to
that of rubidium compound in the region of metal-oxygen vibrations.

Multicomponent molybdate catalysts are currently used for the industrial oxidation and ammoxidation of propylene. In order to investigate the role of the host structure in multicomponent molybdate catalysts, \( \text{Cr}_2(\text{MoO}_4)_3 \) and \( \text{Al}_2(\text{MoO}_4)_3 \) have been characterized using various techniques. IR and Raman spectral analysis indicates the presence of octahedral co-ordination of molybdenum atoms to oxygen.\(^7\) Vibrational spectroscopic studies of \( \text{NiMoO}_4 \), \( \text{CoMoO}_4 \) and \( \text{FeMoO}_4 \), which crystallize in the monoclinic system, are of interest since they are known to be active and selective catalysts for the oxidation of hydrocarbons. Cobalt and nickel molybdates exhibit polymorphism. On studying the infrared and Raman spectra of these three molybdates, Saleem\(^7\) has concluded that when the \( \text{MoO}_6 \) ion loses its octahedral symmetry and sharing (edges and corners) of oxygen atoms happens, there will be appreciable changes in its normal frequencies. The structural transformation from tetrahedral to octahedral (\( \beta \) to \( \alpha \)) due to the application of slight pressure has been followed and the frequency at 700 cm\(^{-1}\) in the Raman spectrum has been identified as characteristic of the octahedral co-ordination.
Phosphomolybdates

Molybdenum-phosphorous oxides consisting of molybdenum and oxygen octahedra and phosphate tetrahedra form microporous framework structure with cations located in tunnels or between layers. The oxidation state of molybdenum in these compounds varies from +3 to +6. These molybdenum framework structures with various oxidation states are of interest as catalysts or as ion exchangers. Infrared and Raman spectra of $K(MoO_2)(PO_4)\cdot H_2O$ have been reported by Peascoe and Clearfield as a part of their structural characterisation. They have observed the existence of distorted $MoO_6$ octahedra and regular $PO_4$ tetrahedra. The 12-phosphomolybdic acid, $H_3PMo_{12}O_{40}\cdot nH_2O$, crystallizes in different systems depending upon the number of water molecules present in it. The vibrational analysis of the compound shows distortions in $MoO_6$ octahedra and $PO_4$ tetrahedra.

Isopolymolybdates

Isopolymolybdates constitute a large class of inorganic compounds. They consist of a simple cation and a condensed molybdate anion. Solution of these compounds are the starting point for molybdate and tungstate based supported catalysts for hydrodesulfurization and hydrodenitration. Supported molybdates and tungstates are also good candidates to become sulfur tolerant methanation
and water gas shift reaction catalysts. When molybdate solutions are acidified they condense and give rise to many different polymolybdates. They contain MoO$_6$ octahedra joined together in a variety of ways by sharing corners or edges or both. A detailed spectroscopic and scattering investigation of isopolymolybdate solutions as a function of concentration and pH has been made by Simon and Gulari.\textsuperscript{78} From the discrete changes in the Raman spectra they have concluded that the formation of isopolyanions is not a continuous process and only a certain species are present in the solution. The nature and species present in aqueous solutions of molybdates at different pH and high metal concentrations have been studied using Raman and IR spectroscopy by Griffith and Lesniak.\textsuperscript{79} One of the most interesting factors of the crystal chemistry of polymolybdates is the relationship between the structures which these compounds adopt when crystallized from the melt or from an aqueous solution. The possible existence of polyanions in molybdate melts is considered and the ability to predict polymolybdate structures from IR absorption spectra is critically assessed by Gatehouse and Leverett.\textsuperscript{80} Vibrational spectra of (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O is reported and an assignment for the internal vibrations of the paramolybdate anion is proposed by Escobar and Baran.\textsuperscript{81} Souaya et al.\textsuperscript{82,83} have reported the IR spectral analysis of Co, Cu and Ni amine paramolybdate complexes. They have suggested that the compounds prepared are of ion-pair type. It has been
reported that various alkylammonium polymolybdates show photochemical and photochromic properties in aqueous solution and in the solid state. Crystal structure and photochemistry of isopolymolybdate Hexakis (propyl ammonium) heptamolybdate (VI) Trihydrate and Hexakis (isopropylammonium) heptamolybdate (VI) Trihydrate have been reported by Ohashi et al.\textsuperscript{84} \((\text{C}_5\text{H}_5\text{NH})_4\text{Mo}_8\text{O}_{26}\) is an isopolymolybdate containing a ligand bound to molybdenum through a donor other than oxygen, namely \([\text{(C}_5\text{H}_5\text{N})_2\text{Mo}_8\text{O}_{26}]^{4-}\). Raman and IR spectra of this compound are reported along with those of \((\text{C}_5\text{H}_5\text{NH})_4[\text{(C}_5\text{H}_5\text{N})_2\text{Mo}_8\text{O}_{26}]\). They have observed characteristic bands of pyridinium ion and bands corresponding to a weakly co-ordinatively bound pyridine.\textsuperscript{85}

Heteropolymolybdates

Heteropolycompounds are obtained when two or more different types of anions condense together. All heteropoly compounds can form variety of crystal hydrates and the number of water molecules is often difficult to determine exactly. These compounds are widely used in analytical chemistry. Heteropolymolybdates are also used as industrial catalysts, ion exchange agents, corrosion inhibitors, precipitating agents for dye materials\textsuperscript{86} and solid electrolytes for fuel cells.\textsuperscript{87}

Raman and infrared spectra of Keggin heteropolyanion \([\text{XM}_{12}\text{O}_{40}]^{n-}\) \((X = P, Si, M = Mo, W)\) have been studied by
A comparative study of a series of heteropolyanions of molybdenum $\alpha-X M_{12}O_{40}^{n-}$ ($X = B^{III}$, $Si^{IV}$, $Ge^{IV}$, $P^{V}$, $As^{V}$ and $M=W^{VI}$, $Mo^{VI}$) have been carried out by Raman and IR spectroscopy. Grabowski et al. have reported the vibrational spectra of a few transition metal telluromolybdates and have assigned the various modes to the stretching vibrations of Mo-O bonds. A few oxy-fluoromolybdates have also been studied by IR and Raman spectroscopy. Spectra indicate that the oxygen and fluorine atoms are disordered statistically over the terminal and bridging ligand positions. Vanadomolybdophosphate heteropolycompounds are also widely used as homogeneous catalysts. Vibrational spectra of $E_9[PMo_6V_6O_{40}]\cdot mH_2O$ ($E = H$, Na) have been reported as a part of their structural studies by Klevstova et al. A number of trimolybdates, tetramolybdates, paramolybdates and pyridinium molybdates have been studied by IR spectroscopy by Schwing Weill and Arnaud - Neu.

On the basis of structural and infrared data of Mo-O bonds, several aspects of multiple bonds from oxygen to transition metals have been examined and assignment of Mo-O stretching frequencies are proposed by Cotton and Wing. A correlation is developed by Hardcastle and Wachs for relating Raman stretching frequencies for Mo-O bonds to their respective bond distances in molybdenum oxide compounds. The stretching frequencies for the perfect MoO$_4$ and MoO$_6$ structures are also predicted.
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Fig. 1.1 Quantum representation of energy interchange involved in the Raman effect.
Fig. 1.2. Schematic representation of the Raman System.

- $\text{M}^{\text{I}}, \text{M}^{\text{II}}, \text{M}_5, \text{M}_6$ - Plane Mirrors;
- $\text{M}_1, \text{M}_2, \text{M}_3, \text{M}_4, \text{M}_7, \text{M}_8$ - Concave Mirrors;
- L, L$_1$ - Condensing Lenses;
- G$_1, G_2$ - Gratings;
- S$_1$ - S$_4$ - Slits;
- S - Sample;
- PMT - Photo Multiplier Tube;
- DPC2 - Digital Photon Counter.