# V P & R P T P SCIENCE COLLEGE

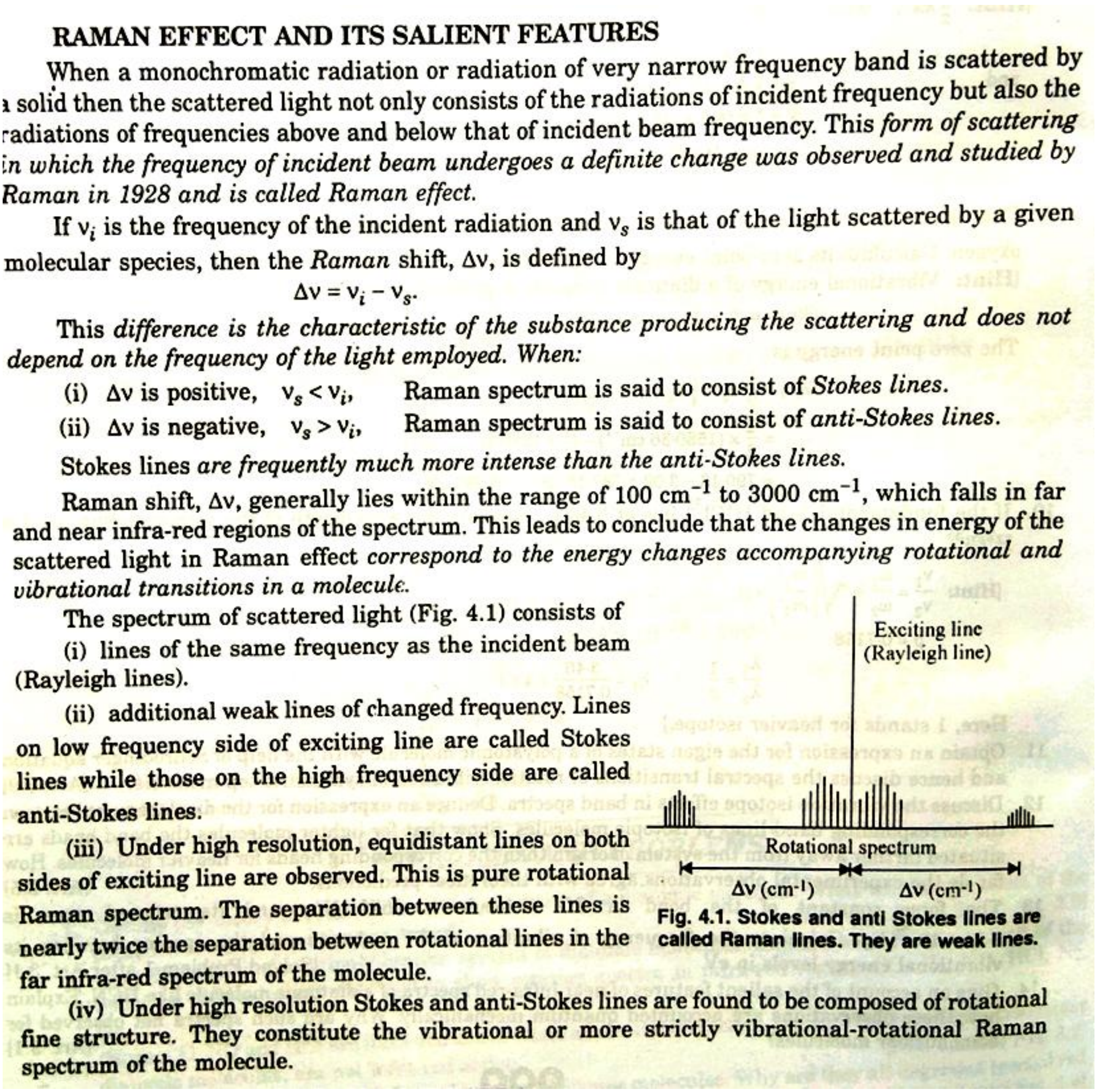
Vallabh Vidyanagar-388120

B.Sc. (Semester - 6) Subject: Physics Course: US06CPHY22

Atomic and Molecular Spectroscopy

**[STUDY MATERIAL]**

## UNIT- IV RAMAN SPECTRA



### RAMAN EFFECT AND ITS SALIENT FEATURES

When a monochromatic radiation or radiation of very narrow frequency band is scattered by a solid then the scattered light not only consists of the radiations of incident frequency but also the radiations of frequencies above and below that of incident beam frequency. This *form of scattering in which the frequency of incident beam undergoes a definite change was observed and studied by Raman in 1928 and is called Raman effect.*

If $\nu_i$ is the frequency of the incident radiation and $\nu_s$ is that of the light scattered by a given molecular species, then the *Raman* shift, $\Delta\nu$, is defined by

$$\Delta\nu = \nu_i - \nu_s.$$

This *difference is the characteristic of the substance producing the scattering and does not depend on the frequency of the light employed. When:*

(i) $\Delta\nu$ is positive, $\nu_s < \nu_i$, Raman spectrum is said to consist of *Stokes lines.*

(ii) $\Delta\nu$ is negative, $\nu_s > \nu_i$, Raman spectrum is said to consist of *anti-Stokes lines.*

Stokes lines *are frequently much more intense than the anti-Stokes lines.*

Raman shift, $\Delta\nu$, generally lies within the range of $100\ \text{cm}^{-1}$ to $3000\ \text{cm}^{-1}$, which falls in far and near infra-red regions of the spectrum. This leads to conclude that the changes in energy of the scattered light in Raman effect *correspond to the energy changes accompanying rotational and vibrational transitions in a molecule.*

The spectrum of scattered light (Fig. 4.1) consists of

(i) lines of the same frequency as the incident beam (Rayleigh lines).

(ii) additional weak lines of changed frequency. Lines on low frequency side of exciting line are called Stokes lines while those on the high frequency side are called anti-Stokes lines.

(iii) Under high resolution, equidistant lines on both sides of exciting line are observed. This is pure rotational Raman spectrum. The separation between these lines is nearly twice the separation between rotational lines in the far infra-red spectrum of the molecule.

(iv) Under high resolution Stokes and anti-Stokes lines are found to be composed of rotational fine structure. They constitute the vibrational or more strictly vibrational-rotational Raman spectrum of the molecule.

**Fig. 4.1. Stokes and anti Stokes lines are called Raman lines. They are weak lines.**

**Experimental study: The Raman Effect has been extensively studied by a great number of workers. The general technique used in these researches is to illumine the substance under investigation with an intense monochromatic source of light and photograph the scattered**

**radiation by means of a spectrograph arranged in a transverse direction. But the technical details vary according to the nature of the substance under test, i.e., liquid, solid or gas, the chief purpose being to obtain best and quick results.**

**Apparatus: The original simple arrangement of Raman was not quite efficient and required very long exposures of about hundred hours and more to obtain good records of the Raman spectrum. Hence, improvements were made as regards the container of the**

**substance, the source of radiation, filter, spectrograph, etc.**

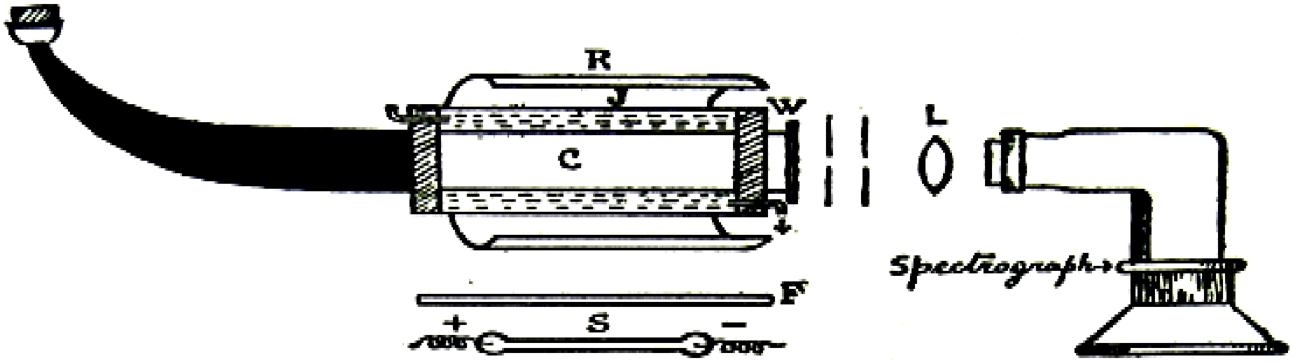


**Fig. 256. Apparatus for the study of Raman effect.**

**The apparatus shown in Fig. 256 is the one first developed by Wood, and now ordinarily used in the study of the Raman effect in liquids.**

**The *container* C of the liquid to be investigated, called the *Raman tube*, consists of a glass tube of about 1 to 2 cms. in diameter and 10 to 15 cms. long, one end of which is drawn out into the shape of a horn and blackened outside to provide a suitable background, the other end being closed with an optically plane glass plate constituting the window W through which the scattered light emerges. The container is surrounded by a water jacket J in which cold water is circulated to prevent overheating of the liquid due to the proximity of the exciting arc.**

**An ideal *source* S would be light from a helium discharge tube filtered by nickel oxide glass, giving a strictly monochromatic line of wavelength 3888 A°. But on account of the many technical difficulties involved in the construction and manipulation of this source, it is not widely used. The source ordinarily employed is the mercury arc, the next best available, from which it is possible to get single wavelengths by the use of suitable filters. Thus, for instance, to obtain the 4358 line, slightly acidulated quinine sulphate solution contained in a novial glass vessel is used as filter, which cuts off all the other lines except 4358 A°. To get the 4046 line a solution of iodine in carbon tetrachloride contained in a novial glass cell is found to be a very satisfactory filter. The filter solution may be arranged either to surround the Raman tube or in front of the arc. The mercury arc is placed as close to the Raman tube as possible, which results in large intensity of the incident light. A semi-cylindrical aluminium reflector R enhances the intensity of illumination still further.**

**The chief features of a *spectrograph*, suited for the study of the Raman spectra, are (1) large light-gathering power, (2) special prisms of high resolving power and (3) a short-focus camera. A lens L in front of the plane window W directs the scattered radiation upon the slit of the spectrograph which is carefully aligned along the axis of the Raman tube and screened from the direct rays of the arc. The**

intense Raman lines of a liquid such as $CCl_4$ can be photographed in about an hour with a small spectrograph, but the recording of the complete spectrum may require up to ten or fifteen hours, depending largely on the intensity of the incident light, the speed of the spectrograph and the intrinsic brilliance of the Raman lines. It may be noted that instruments of high resolving power such as gratings are not used with advantage, on account of the poor luminosity which necessitates long exposures.

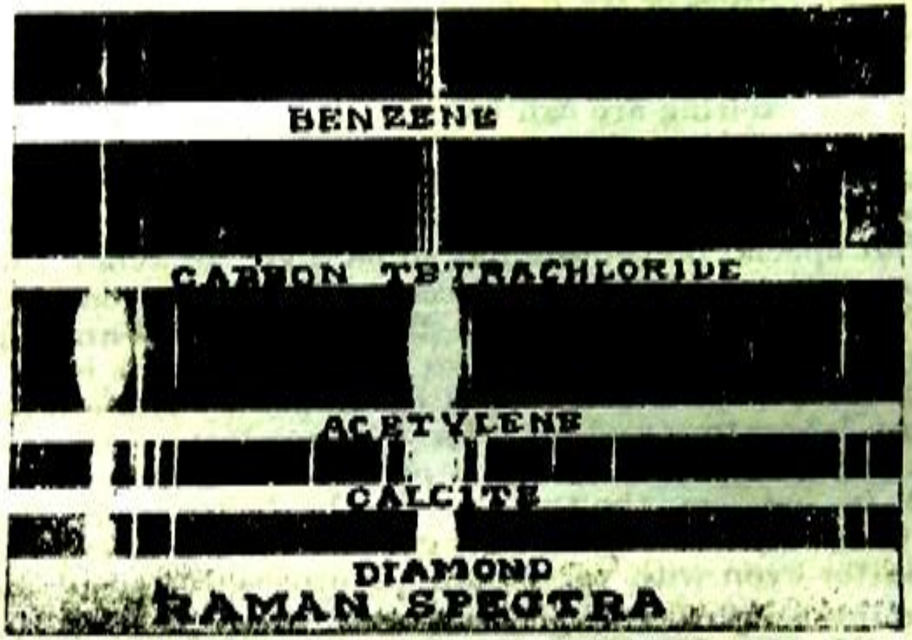
*Certain modifications in the experimental arrangements are necessary for the excitation of the Raman effect in solids and gases.* In the case of substances which are available as *large and transparent solid blocks*, like gypsum, quartz, etc., a container is not required and the light from the exciting arc can be directly focused on the material with a large condensing lens. With solids which are in the form of *loose crystals* or *powder*, the Raman effect can be obtained, as was first shown by Baer and Menzies, by reflecting light from crystal surfaces. But special precaution has to be taken to avoid the masking effect due to a large amount of direct light coming out of the container by repeated reflection at the crystal faces and entering the spectrograph. To achieve this, two techniques have been used, *one* the use of complimentary filters as developed by Ananthakrishnan at the Raman laboratory and *the other* a special type of spectrograph with two parts, each part having a prism and two lenses with a common slit in between the two, devised by Billroth, Kohlrausch and Reitz in Germany. Both give very good results with crystal powders, and the latter even with very small quantities of the substance.

The intensity of the light scattered from *gases* is very weak, but this difficulty has been overcome by intense illumination of the gas under high pressure and the use of spectrographs of great light-gathering power. Wood employed a very long tube of HCl gas and obtained its Raman spectrum at atmospheric pressure using a specially made mercury arc, which was placed in contact with the gas tube, hollow, cylindrical reflectors enclosing both of them. The illumination produced in this way was very intense as the light from the arc was returned back and forth between the walls of the reflectors. Rasetti was the first to develop the technique of exciting Raman effect in gases under high pressure, which shortened considerably the time of exposure. He used a thick-walled quartz tube, 20 cms. long and 2·2 cms., internal diameter, which could withstand pressures of 10 to 15 atmospheres. With the 2537 line of the mercury arc as the exciting radiation, he was able to obtain the Raman spectra of several gases under pressure. Bhagavantam

Dr. S. Bhagavantam

has constructed a Raman tube for gases which can stand pressures up to 50 atmospheres. It is made of transparent silica and enclosed in an outer steel tube for protection. He has been able to obtain with his apparatus good photographs of Raman spectra of gases in about 40 to 50 hours' time of exposure using the 3650, 4046 and 4358 mercury lines.

**Results.** An idea of the type of Raman spectra produced by solids, liquids and gases may be formed by inspecting the photographs obtained with benzene, carbon tetrachloride (liquids), acetylene (gas), calcite and diamond (solids), given above. It is seen that a number of new lines and bands, exhibiting a variety of characters of intensity, width, polarisation and fine structure are recorded on either side of the exciting radiation. There is also some unresolved continuous radiation, which generally appears as wings extending slightly unsymmetrically on either side of the parent line. This continuous spectrum shows great variations in intensity with different substances. Each line in the incident spectrum, if of sufficient intensity, gives rise to its own set of lines or bands and associated continuous spectrum. We shall now outline the main results obtained from researches made on the effect with such photographic records.



Raman spectra of different substances (Bhagavantam)

**Raman effect in liquids.** About a hundred liquids, so far examined, show the phenomenon in an unmistakable manner. The frequency shifts of the Raman lines produced with benzene correspond to an infra-red wavelength 3·27 $\mu$, in which region benzene exhibits a strong band in its absorption spectrum. A close examination, however, of the infra-red absorption spectrum and the Raman spectrum of benzene shows that none of the Raman lines are represented in infra-red absorption and *vice-versa*. An interesting feature with

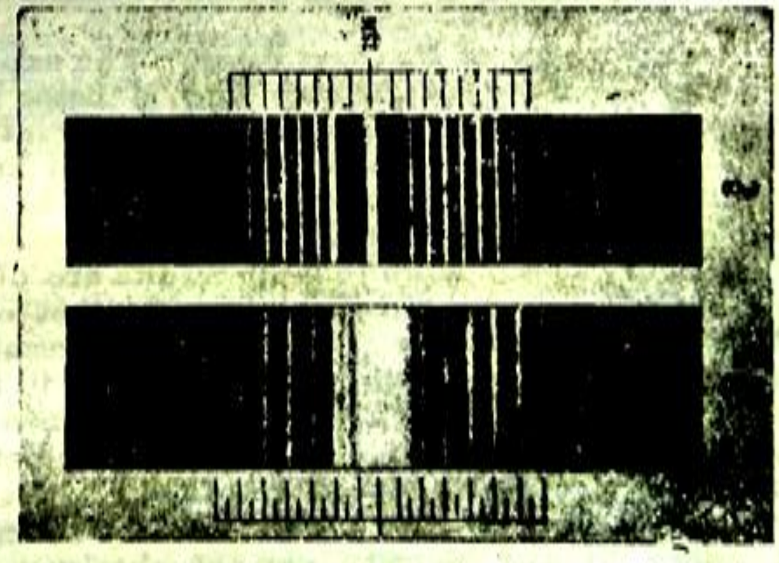
$CCl_4$ is the triad of Stokes' and anti-Stokes' lines equally spaced on either side of the exciting 4358 line.

With very well purified water Dadieu and Kohlrausch found two broad bands instead of sharp lines at about $\lambda = 3\mu$.

Solutions of salts in water give the Raman spectra characteristic of the salts and the water. Ganesan and Venkateswaran found that the bands due to water in aqueous solutions of $H_2SO_4$, HCl and $HNO_3$ acids become sharper with increasing concentration. The similarities exhibited by solutions of carbonates of different metallic radicals and the similarity of the sulphates and nitrates appear to support the view that the characteristic frequencies are those of the ionised acid radical.

**Raman effect in gases.** The Raman spectrum of HCl gas obtained by Wood and those of CO and $CO_2$ by Rasetti were the first observations made with gases. Then many other gases such as hydrogen, oxygen, nitrogen, ammonia, NO, $N_2O$, $CS_2$, etc., were studied. The frequency shift of the Raman line of HCl gas corresponds to $\lambda = 3{\cdot}466\mu$, which is almost exactly the wavelength of the central missing line of tha infra-red absorption band of HCl. Carbon monoxide gives a Raman line whose frequency shift is equal to the frequency of its infra-red band, while $CO_2$ gives a line whose shift is equal to the frequency difference of two of its infra-red bands.

Oxygen, hydrogen and nitrogen give a pattern of equally-spaced lines. The intensities of the individual lines alternate in the case of nitrogen and hydrogen, while with oxygen the alternate lines are absent, as seen in the adjacent figure, where the Raman spectra of oxygen and nitrogen, obtained by Rasetti, are reproduced. These peculiarities in intensity of alternate lines have led to very significant conclusions as regards molecular structure and nuclear spin. McLennan carried out a series of experiments on the Raman effect with liquid oxygen, nitrogen, hydrogen and nitrous oxide. His results with liquid oxygen suggested that the normal mode of vibration of the molecule is the one involved in the production of the four Raman lines observed, while those for liquid hydrogen supported the view that hydrogen at low temperatures must be regarded as a mixture of two distinct types of molecules known as the *para* and *ortho* hydrogen. The Raman spectrum of $CO_2$ which is similar to that of



Raman effect in oxygen and nitrogen (Rasetti) oxygen indicates a symmetric structure for its molecule, while that of $N_2O$ where there is no alternation in intensity of the lines suggests an unsymmetric molecular structure. Rasetti has observed a Raman line with NO whose frequency shift is 121 cm.$^{-1}$, which has been classified as having an electronic origin.

**Raman effect in solids.** On account of the numerous experimental difficulties, comparatively a few solids only have been studied so far. Mandelstam, Landsberg, Baer and Menzies were the pioneer workers in this branch of Raman effect Other investigators were Schaefer, Matossi and Aderhold, Miss Osborne, Cabannes and Canals, Nedungadi and Bhagavantam. The substances analysed are gypsum, quartz, calcite, sodium nitrate, potassium nitrate, ammonium phosphate, ammonium chloride, diamond and a few others. The Raman lines obtained with crystals are sharp, becoming diffuse with rise of temperature. In calcite ($CaCO_3$) two lines which are nearest to the parent line have been definitely identified with the oscillations of the crystal lattice, while the others are due to the vibrations of the $CO_3$ groups. With gypsum ($CaSO_4$, $2H_2O$) which contains two molecules of water of crystallisation, Krishnan found, in addition to the wavelengths which could be attributed to the $SO_4$ radical, three sharp lines at $\lambda = 2\cdot8\mu$, $2\cdot9\mu$ and $3\cdot0\mu$, which are evidently due to the water of crystallisation and are practically in the same position as the components of the band observed with water. Diamond exhibits a strong and sharp line of a comparatively large frequency shift, which has to be ascribed to a lattice oscillation. In solid benzene, the intense continuous spectrum obtained with liquid benzene is replaced by bands.

**Intensity of Raman lines.** The experimental determination of the intensity of Raman line is beset with many difficulties on account of their extreme weakness. The intensity of a Raman line, when expressed as a fraction of the parent line, is usually a few hundredths in liquids and a few thousandths in gases. No accurate data are available as regards the absolute intensities of Raman lines in liquids or gases. More reliable results are obtained in the determination of relative intensities of a given set of Raman lines excited by a given parent line. To obtain good results, photographic plates which have great and uniform sensitivity in the region of investigation should be used. The densities obtained for the lines under comparison are measured with a microphotometer. On each plate, a set of calibration spectra are recorded, with the help of which density curves for each wavelength can be drawn, and the intensities corresponding to any density can be obtained from such curves. The measured intensities should be corrected for various causes of error, such as absorption in the body of the substance in the Raman tube, the oblique refraction at the prism surfaces in the spectrograph, etc.

In spite of the numerous experimental difficulties, results of fundamental importance have been obtained. Very faint Raman lines as well as very intense ones are met with, *e.g.*, the band in NaCl recorded by Rasetti and the anti-Stokes' line in diamond obtained by Bhagavantam are very faint, while the principal Raman line of diamond at 1332 and the line in benzene having a frequency shift of 992 are very intense. These variations in intensity as we pass from line to line and from substance to substance are of great significance in the study of molecular structure and chemical constitution.

Since the intensity of scattering increases with the fourth power of the frequency, it is advantageous to use, where the absorption of the substance under investigation permits, light of as short a wavelength as possible. Hence the ultra-violet mercury resonance line 2537 A° is often used. The Stokes' lines are always more intense than the corresponding anti-Stokes' lines. The anti-Stokes' lines grow more intense and, in addition, all the Raman lines move inward towards the parent line as the temperature is increased.

**Polarisation of Raman lines.** Just as the Raman lines vary greatly in their intensities, so also their states of polarisation. The fact that different lines are differently polarised is probably connected with their relative intensity.

The experimental arrangement used for determining the polarisation of Raman lines is essentially the same as that described on page 796 but with the following modifications. The light from the source is concentrated by means of a condenser into the substance contained in the Raman tube. A suitably oriented double image prism whose function is to separate the vertical and horizontal components in the scattered light is placed in front of the slit of the spectrograph, so that two images, one above the other, are formed on the slit, which are simultaneously photographed.

The state of polarisation of a Raman line is measured by a quantity known as the *depolarisation factor* which is simply the ratio of the intensities of the horizontal and vertical components when the incident light is vertically polarised. This ratio is readily obtained from the traces photographed as described above, by one of the usual methods employed for comparing the intensities of two beams of the same wavelength. In order to get fairly accurate values of the depolarisation factor, the following precautions should be taken : (*i*) crystalline quartz should not be used for condenser, spectrographs or windows, since its optical activity complicates the phenomenon of polarisation ; (*ii*) the window of the Raman tube through which the scattered light emerges should be strain-free and plane, (*iii*) errors arising from oblique refraction at the prism surfaces, want of transversality in the incident beam and slit width should be eliminated.

Cabannes found that the Raman lines in crystals, such as quartz, are differently polarised, the intensity and depolarisation of the lines depending upon the orientation of the crystal. Menzies has investigated the polarisation of the Raman lines in liquids, such as $CCl_4$, in directions perpendicular and obliquely forward to the incident beam and has shown that many of the observed facts could be accounted for by considering the initial and final directions of vibra tions in the molecule involved to be parallel in the case of polarised lines, perpendicular in that of unpolarised lines and at an oblique angle for partially polarised lines. The following are some of the important results obtained :—

(*a*) The depolarisation factor varies from 0 to 0·86 for the vibrational Raman lines, while it has a constant value of 0·86 for the rotational lines.

(*b*) With circularly polarised incident light, part of the Raman line is circularly polarised in the reverse direction and part circularly polarised in the same direction as that of the incident light. Highly depolarised rotational lines exhibit reverse circular polarisation.

(*c*) Sharp and strong lines are ordinarily characterised by low depolarisation factors, while diffuse and weak ones by high depolarisation factors.

(*d*) Corresponding lines in molecules having similar structures have nearly the same depolarisation factors. This is to be expected as the polarisation of a Raman line is mainly decided by the symmetry of the oscillation.

**Nature of the Raman effect.** From the many and varied experimental data, it is clear that the Raman effect is a molecular phenomenon. In the case of free molecules scattering light, three different kinds of Raman effect can therefore be distinguished, *viz.*, a rotational effect, a vibrational effect and an electronic effect. A mixed "rotation-vibration" effect can also take place under certain circumstances. Solids can exhibit yet another type of Raman effect in which the crystal lattice as a whole takes the place of the molecule.

Since the rotational energies involved are small relative to the vibrational energies, the pure rotational Raman lines lie correspondingly closer to the parent line and are often masked by the intense light of the parent line on the photographic plate. They are obtained separately only in the case of certain light gases, such as hydrogen, deuterium, oxygen, nitrogen, etc. In heavier gases, the lines are much closer and instruments of greater resolving power are required to separate them.

Most of the observed Raman lines and bands with moderate or large frequency shifts are due to the vibrational effect, corresponding to various normal modes of vibration of the molecule or the crystal lattice. The fainter lines may be due partly to overtones or combination tones. The lines arising from an oscillating crystal lattice are characteristic of only the solid state and are not present in liquids or gases.

Raman lines due to the electronic effect are rarely observed, as in the single case of NO obtained by Rasetti.

Analysis of the continuous spectrum under high dispersion reveals that it cannot be separated from the parent line and that its intensity is maximum near the parent line. Although it is difficult to decide upon the exact nature and origin of the continuous spectrum in all cases, very probably it is due to an unresolved rotational effect. In the solid state, it is replaced by broad bands, while in the gaseous state by separate lines, which may be ascribed to the rotation of the molecule. In certain cases the broad bands which replace the continuous spectrum have been identified with the oscillations of the crystal lattice.

## Relation between the Raman and Infrared absorption spectra:

| Raman Sepctra | Fluorescence Spectra |
|---|---|
| 1. Spectral lines have frequencies greater and lesser than the incident frequency. | Line frequency is always less than the incident frequency. |
| 2. Frequencies of Raman lines are determined not by the scatterer but by incident frequencies. | Frequencies of the fluorescence lines are determined by the nature of the scatterer. |
| 3. Raman lines are strongly polarised. | Lines are not polarised. |
| 4. Raman lines are weak in intensity due to which concentrated solutions are preferred as samples to give enough intensity. | The intensity of fluorescence lines is considerable and samples at concentrations as low as 1 part in $10^9$ are used. |

Though Raman shift falls in far and near infra-red regions of the spectrum but Raman spectra are quite different from infra-red spectra as pointed out below:

| Raman Sepctra | Fluorescence Spectra |
|---|---|
| 1. It arises due to scattering of light by the vibrating molecules. | It arises due to absorption of light by vibrating molecules. |
| 2. It is the polarizability of the molecule which determines whether the Raman spectra will be observed or not. | The molecule must possess permanent dipole moment to exhibit spectra. |
| 3. For Raman lines, being of weaker intensity, concentrated solutions as samples are preferred. Water can be used as solvent. | Generally dilute solutions are preferred and water, being opaque, cannot be used as solvent. |

**Importance of the Raman effect.** Over and above the great theoretical interest attached to it as a further confirmation of the quantum theory of radiation, the Raman effect is of immense practical importance on account of its many useful applications in Physics and Chemistry. The universal nature of the phenomenon, the relative simplicity of the experimental technique as compared with that of infra-red measurements, the ease with which the effect can be controlled, making it appear as a part of the visible spectrum, which can be chosen at will (its position depending only on the choice of the incident frequency) and the complementary character of the spectra obtained with reference to those of infra-red absorption (the former containing lines which are forbidden in the latter) make the Raman effect a very convenient and powerful tool of research in problems concerning the intimate structure of matter, chiefly as regards the constitution of molecules, their number, arrangement and motion, in gaseous, liquid and solid states. We shall here summarise some of the important applications which have led to sure and significant results.

## APPLICATIONS OF THE RAMAN EFFECT IN PHYSICS

(*i*) **Molecular structure.** The Raman effect has been put to very great use in the study of the structure of molecules. Raman spectra are, in general, determined by those factors which affect most the nature of vibration, *viz.*, the number of atoms in the molecule, the masses of the atoms and the strength of the chemical bonds between the atoms.

Taking a *diatomic molecule*, its natural frequency of vibration is given by $\nu_0 = (1/2\pi)\sqrt{F/\mu}$, where F is the restoring force per unit displacement and $\mu$ the resultant mass. This means that (*a*) there is only one vibration frequency in diatomic molecules, (*b*) a molecule containing light atoms should have a higher frequency than one containing heavier atoms and (*c*) a molecule in which the force binding the atoms is great should have higher characteristic frequency than one in which the force is weak. This force depends on the nature and strength of the inter-atomic bonds. Thus a diatomic molecule with a double bond should have a higher frequency than one containing only a single bond. The Raman lines are also expected to appear with great intensity when the bond is of the covalent type (homopolar or electrically non-polar molecules) while the reverse is the case when the bond is of the electrovalent type (polar or heteropolar molecules). The reason for this is to be found in the fact that the Raman lines essentially depend upon the symmetry of the molecules and the extent to which the polarisability is affected by the oscillations. In covalent molecules the binding electrons remain common to the nuclei, so that the polarisability of the molecule is considerably modified by nuclear oscillations and this variation in polarisability gives rise to Raman lines. In electrovalent molecules the binding electrons definitely change over from one nucleus to the other in the formation of the molecule so that the polarisability of the molecule is little affected by nuclear oscillations, which means no Raman lines will occur.

Considering *polyatomic molecules* which are constituted by more than two atoms, the Raman spectra will naturally be much more complex. First of all, more than one characteristic frequency is to be expected : *e.g.*, triatomic molecules will, in general, have three such frequencies. Secondly, the arrangement of atoms, such as symmetrical or unsymmetrical, linear or non-linear symmetry, etc., is an additional factor by which the intensity of the Raman lines is essentially determined. Hence, from the number and intensity of the observed lines in the Raman effect, in conjunction with infra-red data, it is possible to draw important conclusions about molecular structure. Theory leads to the following important rule, known as *the rule of mutual exclusion.* For molecules with a centre of symmetry, transitions that are allowed in the infra-red are forbidden in the Raman spectrum and *vice versa.* This rule implies that for molecules without a centre of symmetry there are transitions that can occur both in the infra-red and the Raman effect. It does not, however, imply that all transitions that are forbidden in one must occur in the other. For, some transitions may be forbidden in both.

The following examples may serve to illustrate these remarks.

**Diatomic molecules.** Some of the diatomic molecules studied are $H_2$, $D_2$, $N_2$, $O_2$, HCl, HBr and HI. The first four are homonuclear molecules, *i.e.*, constituted with identical atoms, while the last three heteronuclear molecules, *i.e.*, made up of non-identical atoms. In all these cases there is only one vibration frequency and its value obtained from Raman spectra is given below. The restoring force per unit displacement F in each case, calculated with the help of the relation $\nu_0 = (1/2\pi)\sqrt{F/\mu}$, is also given.

| | $H_2$ | $D_2$ | $N_2$ | $O_2$ | HCl | HBr | HI |
|---|---|---|---|---|---|---|---|
| $\nu_0$ (cm.$^{-1}$) | 4156 | 2993 | 2331 | 1556 | 2880 | 2558 | 2233 |
| $F \times 10^{-5}$ | 5·1 | 5·3 | 22·4 | 11·4 | 4·8 | 3·8 | 2·9 |

It is readily seen from such a tabulation that (1) the heavier the molecule the lower is the vibration frequency and (2) the values of F, which is a measure of the binding strength, may be roughly classified in the ratio of 3 : 2 : 1, thereby indicating the existence of three different types of bonds, triple, double and single, between the atoms in the molecule.

**Triatomic molecules.** Among the several triatomic molecules analysed, we shall consider here only three, *viz.*, $CO_2$, $N_2O$ and $H_2O$ as typical cases illustrating some special points of interest in molecular structure.

*Carbon dioxide* ($CO_2$) is one of the most frequently and thoroughly studied molecules. It has two very strong bands in its infra-red absorption spectrum at 668 and 2349 cm.$^{-1}$, while only one strong band in its Raman spectrum at 1389 cm.$^{-1}$. As none of these occurs both in the Raman and infra-red spectrum, it follows from the rule of mutual exclusion that the molecule of $CO_2$ must have a centre of symmetry. For triatomic molecules this implies that the molecule is linear and symmetric. Hence the molecular structure of $CO_2$ is O—C—O. This symmetric structure is confirmed by the rotational Raman spectrum of $CO_2$, which consists only of alternate (odd) levels, like that of $O_2$. The three bands stated above, two in the infra-red spectrum and one in the Raman spectrum, represent the three fundamental frequencies of $CO_2$. Carbon disulphide ($CS_2$) also belongs to this class.

*Nitrous oxide* ($N_2O$). This molecule has the same number of electrons as $CO_2$ and one might therefore expect it to have a linear symmetric structure. But analysis of the infra-red and Raman spectra of $N_2O$ shows clearly that this molecule, although linear, is not symmetrical. The three fundamental frequencies of $N_2O$ are 2224, 1285 and 589 cm.$^{-1}$. All the three appear in the infra-red absorption and two of them, *viz.*, 2224 and 1285, appear in the Raman spectrum. 589 has, however, not been recorded, due to weak intensity. At any rate, the two Raman lines appear also in the infra-red, which argues to the absence of the centre of symmetry in the molecule. For, if there was a centre of symmetry, only one fundamental should appear in the Raman spectrum and this fundamental should not appear in the infra-red, according to the rule of mutual exclusion. Hence the molecule has the unsymmetrical structure N — N -- O. This conclusion is confirmed by the rotational Raman spectrum of $N_2O$, which consists of both (odd and even) sets of lines without any alternation in intensity. Other molecules of this type are HCN, ClCN, BrCN, ICN, etc.

*Water* ($H_2O$). The observation of a strong pure rotational spectrum and its structure, as well as that of the rotation-vibration spectrum lead unambiguously to the conclusion that $H_2O$, though symmetrical, is not linear but bent (Fig. 257). According to theory, all triatomic molecules of bent symmetrical structure should give rise to three Raman lines all of which are represented in the infra-red spectrum. There are two very strong bands at 1595 and 3756 cm.$^{-1}$ in the infra-red absorption spectrum, which are very probably two of the three fundamental frequencies. There is also evidence to show that the bend in the system is 120°. In the Raman spectrum, two frequencies have been recorded at 1665 and 3605 cm.$^{-1}$, which correspond roughly with the infra-red frequencies. There is some difficulty in recording the Raman lines of $H_2O$, which are very weak, due evidently to the fact that the moments of the light hydrogen atoms do not cause appreciable variation in the polarisability tensor. Water gives some other extra bands which have to be ascribed to polymerised molecules—$(H_2O)_2$ and $(H_2O)_3$. $D_2O$, $S_2O$ and $H_2S$ have similar bent symmetrical structures.

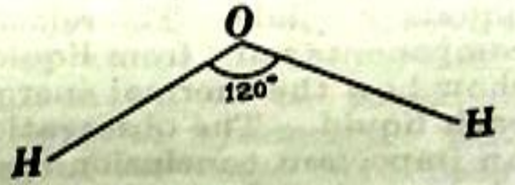


Fig. 257.

Thus the study of Raman spectra of different substances enables one to classify them according to their molecular structure.

*(ii)* **Nature of the liquid state.** Considering the gaseous state, it can be readily shown that the translatory motions of the molecules are such that the Rayleigh scattering will be spread out in accordance with Maxwell's law. On the other hand, for the solid state, Brillouin, disregarding molecular structure and replacing the solid by a homogeneous elastic continuum, so that the translatory motions may be resolved into a system of elastic waves traversing the medium in all directions, arrived at an expression showing that the scattered light should merely consist of two displaced components depending upon the velocity of the waves and the angle of

scattering. Now, as regards the intermediate liquid state, Raman and Ragavendra Rao, in their study of the Raman spectra of a number of liquids, found that while Brillouin's theory was verified, a central line brighter than the displaced components was seen. With increase of temperature the central line grew in intensity at the expense of the neighbouring Brillouin components which themselves broadened out and tended to merge into the central line. The two Brillouin components were found to be completely polarised in transverse scattering, while the central line was also nearly fully polarised in non-polar liquids. In strongly associated liquids, like formic acid, the central line showed appreciable depolarisation, while in viscous liquids the Brillouin components were faint.

The experimental finding of the Brillouin components is characteristic of the elastic continuous medium. The presence of the central line, however, which is not to be expected in Brillouin's theory, can be accounted for solely on the basis of random type of movements, as in a gas. The central component is always brighter and this readily follows from the fact that gaseous Rayleigh scattering is always much more intense than the corresponding scattering from liquids or solids. The relative intensities of the central and Brillouin components vary from liquid to liquid and this may be taken to show how the thermal energy is shared between the two types in each liquid. The observations of Raman spectra have thus led to an important conclusion regarding the liquid state, *viz.*, that it is characterised by both types of thermal energy, one in which it is organised in the manner of elastic waves and the other in which it is akin to random types. In other words, the thermal motion of liquid molecules, which goes to make up its heat content, is neither wholly disorganised as in the case of the molecules of a gas, nor wholly organised in the form of elastic waves as in a solid.

***(iii)* Crystal physics.** The analysis of crystal structure by X-ray diffraction methods concerns itself with the determination of the position and arrangement of the atoms or molecules which scatter the X-rays. It does not tell us anything about the forces binding the atoms or molecules together in the lattice, which determine the physical properties of the crystal, and hence of the solid state, since most solids are crystalline in structure.

The Raman effect offers us a new method of studying crystals, which, in a sense, is complementary to X-ray diffraction. For, it furnishes us with just the kind of information that X-rays do not give concerning the strength and nature of the forces which hold the crystal together. Furthermore, this information is of a precise character, as the Raman lines are very sharp and can be measured very accurately. The frequencies deduced from the Raman spectra and the known positions and masses of the atoms in crystals enable us to determine the binding forces in the crystals.

Although the study of Raman effect in crystals has been initiated only recently and has not much advanced till now, yet some important results have already been obtained. The case of diamond, studied by Ramasamy and Bhagavantam, shows clearly that it is not necessary for a crystal to contain molecules in order that it should exhibit Raman effect, for diamond is a non-polar substance in which it is impossible to identify any particular group of atoms as forming an ion or molecule. The Raman spectra of a series of crystalline nitrates analysed by Krishnamoorthi and Gerlach established that the frequency characteristics of the $NO_3$ ions are notably influenced by the presence of the kations. This suggests that the assumption of complete ionisation in the solid crystal may be invalid.

The Raman effect in crystals has been studied also with reference to two other fundamental problems in crystal physics, *viz.*, the existence of a "*mosaic*" *structure* and *thermal agitation* in crystals. From the Raman spectra of crystals, the existence of discrete monochromatic infra-red frequencies has been clearly demonstrated. In a quantitative study of the phenomenon, Raman has shown that a crystal has, in general, $(24p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies, where $p$ is the number of interpenetrating atomic lattices of the crystal. Of this number $(3p - 3)$ modes may be ascribed as oscillations of the $p$ interpenetrating lattices, while the remaining $21p$ modes are oscillations with respect to each other of various important planes of atoms in the crystal. The number of monochromatic frequencies is shown to be considerably reduced when the crystal has a high degree of symmetry. But the number of frequencies and the geometry of the modes have been fully worked out from considerations of symmetry. For instance, diamond has been shown to have eight fundamental frequencies, rocksalt nine, and fluorspar fourteen. The fine structure of the infra-red spectrum of crystals actually observed is readily and adequately accounted for on the basis of the above-mentioned analysis.

(*iv*) **Nuclear physics.** The Raman effect has been applied also in the study of certain aspects of nuclear physics, such as the *spin*, *statistics* as well as the *isotopic* constitution of the nucleus. The rotational Raman lines of homonuclear diatomic molecules like $H_2$, $D_2$, $O_2$, $N_2$, etc., characterised by their alternating intensities, have been most fruitful in giving precise results. Thus, for instance, in the case of *hydrogen*, the Raman lines arising from odd rotational levels are three times more intense than those coming from transitions between even levels, which can be shown to be due to the fact that the hydrogen nucleus has a spin of half a unit, obeying Fermi-Dirac statistics and that the statistical weight of the odd rotational levels is three times that of the even rotational levels. With *deuterium*, the stronger of the alternating Raman lines correspond to transitions between even levels and their intensities are twice that of the weaker ones arising from odd levels. These observed data lead to the results that the deuterium nucleus has a spin of one unit, conforming to Bose-Einstein statistics, and that the statistical weight of the even levels is twice that of the odd levels. In the case of *oxygen* the entire rotational spectrum consists of lines arising from transitions between odd levels only, while those from even levels are completely missing, which means that the nuclear spin of oxygen is zero. With *nitrogen* the intensities of the Raman lines alternate, the more intense lines corresponding to transitions between even levels, unlike hydrogen but similar to deuterium. This leads to the conclusion that the nitrogen nucleus has a spin of one unit and obeys Bose-Einstein statistics. These results are in complete agreement with those derived by other methods.

The substitution of an isotopic atom for the original one in the molecule is expected to alter the symmetry of the molecule and the effective mass. Many isotopic molecules have been studied from this standpoint and it has been found that the phenomenon of alternating intensities in the rotational Raman lines, well exhibited by the spectra of $H_2$ and $D_2$, is absent in the spectrum of HD showing that the substitution of D for H has destroyed the symmetry.

## CLASSICAL THEORY OF RAMAN EFFECT

If an atom or molecule is placed in an electric field, the electrons and nuclei are displaced—electrons being attracted to the positive pole whereas nuclei to negative pole. An induced dipole moment is produced in the molecule due to the displacement of nuclei and electrons; and the molecule is said to be polarised. If $F$ is the strength of the electric field and $\mu$ is the magnitude of induced dipole moment, then

$$\mu = \alpha F, \qquad \ldots(1)$$

where $\alpha$ is the *polarizability* of the molecule. The strength, $F$, of the electronic field of an electromagnetic wave of frequency, $\nu$, can be expressed as

$$F = F_0 \sin 2\pi\nu t. \qquad \ldots(2)$$

where $F_0$ is the equilibrium value of field strength. From equation (1),

$$\mu = \alpha F_0 \sin 2\pi\nu t, \qquad \ldots(3)$$

implying that interaction of radiation of frequency $\nu$ induces in the atom or molecule a dipole moment which oscillates with the same frequency $\nu$. By classical theory, this oscillating dipole should scatter (emit) radiation of the identical frequency $\nu$, *i.e.*, incident and scattered frequencies will be equal—a case of Rayleigh scattering.

While arriving at equation (3), no internal motion, *e.g.*, vibration and rotation of the molecule has been considered. Let us consider first the effect of vibration. Suppose the molecule is diatomic; then as the *two nuclei vibrate along the line joining them, the polarizability of the molecule will vary.* The variation in polarizability $\alpha$, with small displacement $x$ from equilibrium position is given by

$$\alpha = \alpha_0 + \beta \frac{x}{A}, \qquad \ldots(4)$$

where $\alpha_0$ is equilibrium polarizability, $\beta$ is the rate of variation of the polarizability with displacement and $A$ is the vibrational amplitude.

If the molecule executes simple harmonic motion, the displacement, $x$, can be represented by

$$x = A \sin 2\pi\nu_v t,$$

where $\nu_v$ is the frequency of vibration of the molecule. Therefore,

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_v t, \qquad \ldots(5)$$

which when substituted in equation (3), gives

$$\begin{aligned}\mu &= \alpha_0 F_0 \sin 2\pi\nu t + \beta F_0 \sin 2\pi\nu t \sin 2\pi\nu_v t \\ &= \alpha F_0 \sin 2\pi\nu t + \tfrac{1}{2}\beta F_0[\cos 2\pi(\nu - \nu_v)t - \cos 2\pi(\nu + \nu_v)t]. \qquad \ldots(6)\end{aligned}$$

Thus induced dipole moment oscillates with frequencies ν (equal to the frequency of incident radiation, *i.e.*, Rayleigh scattering), $(\nu + \nu_\upsilon)$ and $(\nu - \nu_\upsilon)$. The last two frequencies are more and less than the frequency of incident radiation and predict the existence of Raman scattering. The vibrational *Raman shift* will be

$$= (\nu + \nu_\upsilon) - \nu = \nu_\upsilon,$$

*equal to the frequency of vibration of the diatomic molecule.*

Now we consider the effect of rotation of molecule on polarizability. During the course of rotation, the orientation of a molecule with respect to the electric field of radiation changes, and therefore if the *molecule is not optically isotropic, i.e.,* it exhibits different polarizabilities in different directions, then its polarization will vary with time. Expressing variation of α by an equation identical to equation (5), we get

$$\alpha = \alpha_0 + \beta' \sin 2\pi(2\nu_r)t, \quad \ldots(7)$$

where $\nu_r$ is the frequency of rotation. Since a rotation through π angle will bring the diatomic molecule in a position in which its polarizability is the same as initially, the rate at which the polarizability changes is twice as great as the rotation. Therefore, instead of $\nu_r$, $2\nu_r$ has been put in above equation.

Substituting equation (7) in equation (3), we get

$$\mu = \alpha_0 F_0 \sin 2\pi\nu t + \beta' F_0 \sin 2\pi\nu t \sin 4\pi\nu_r t$$

$$= \alpha_0 F_0 \sin 2\pi\nu t + \tfrac{1}{2}\beta' F_0[\cos 2\pi(\nu - 2\nu_r)t - \cos 2\pi(\nu + 2\nu_r)t] \quad \ldots(8)$$

For above expression, we find that the frequencies of Raman lines will be $(\nu + 2\nu_r)$ and $(\nu - 2\nu_r)$, ν. The rotational *Raman shift* should thus be

$$= (\nu + 2\nu_r) - \nu = 2\nu_r,$$

*equal to twice the frequency of rotation of molecule.*

From above discussion, it is obvious that:

(i) In the spectrum of scattered light one obtains vibrational Raman lines at distances $\nu_\upsilon$ on either side of Rayleigh line (exciting line), ν, and also rotational Raman lines at distances $2\nu_r$ on either side of ν. It is thus clear that the molecule need not have a permanent dipole moment for its Raman spectrum to appear. Hence, besides heteronuclear molecules like HCl, the homonuclear molecules like $H_2$, $N_2$, $O_2$ also show Raman spectra although they do not show infra-red spectra.

(ii) According to the classical theory, Raman lines on the two sides of the Rayleigh line must be of the same intensity but this is not so. Raman lines on the high frequency side (anti-Stokes) are too weak to be observed. Therefore classical theory is met with this objection.

## 4.3. QUANTUM THEORY OF RAMAN EFFECT

In scattering, due to the absorption of the incident radiation by scattering molecules, they are raised to a higher energy state. Now if they return to their original state, then frequency of radiation emitted is same as that of incident light: but if they return to a higher or lower vibrational or rotational level, the frequency of scattered radiation is less or greater than that of the incident radiation—the amount of this difference is equivalent to the difference in vibrational or rotational energy states. Let us consider a molecule in its initial (lower) state $E''$ and is exposed to incident radiation of frequency $\nu_i$ cm$^{-1}$. The absorption of this incident radiation would raise this molecule to a level in which its energy is $(E'' + hc\nu_i)$. Now suppose it returns to a level of energy $E'$ lying above the level $E''$, by losing energy $hc\nu_s$ and emitting (scattered) radiation having observed frequency $\nu_s$. It follows then

$$E'' + hc\nu_i - hc\nu_s = E'.$$

$$\therefore \qquad E' - E'' = hc(\nu_i - \nu_s)$$

$$= hc\,\Delta\nu, \qquad \text{...(1)}$$

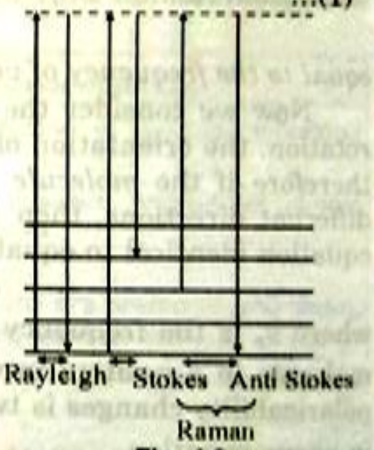


**Fig. 4.3.**

which shows, as said earlier, that Raman shift $\Delta\nu$ is equal to the difference in energy of the two levels represented by $E'$ and $E''$. It is obvious that sign of $\Delta\nu$ depends upon $(E' - E'')$. If $E' > E''$ or in other words, if the molecule is initially in lower state when it absorbs energy of incident light, Stokes lines of Raman spectrum (for which $\Delta\nu$ should be positive) are produced; but if the molecule is initially in upper state $E'$ and then returns to the lower state $E''$ after emission of scattered Raman radiation, then $\Delta\nu$ is negative and hence Raman spectrum will consist of anti-Stokes lines.

The transitions are illustrated in Fig. 4.3.

It should be noted that frequency shifts of Raman lines, their intensity and polarization are characteristics of the scattering substance. Classically, stokes and antistokes lines should have equal intensity. However, experiments confirm that stokes lines are more intense. Quantum mechanically it is because such transitions are more probable and hence more intense. Further, the dotted level shown in the energy level diagram is not a stationary level. It is a virtual level. Since energy is not preserved in a virtual level, the photon immediately returns to lower stationary level after emitting a photon. Fluorescence effect basically differs from Raman effect in the sense that in fluorescence there is always a transition to stable state.

### Probability of Energy Transition in Raman Effect: Occurrence of Ramal Spectrum

We know that if an atom or molecule is placed in an electric field, of strength $F$ (say), the electrons and nuclei are displaced in such a manner as to induce a dipole moment of magnitude $\mu$ (say in the atom or molecule), then :

$$\mu = \alpha F, \qquad \text{...(1)}$$

where $\alpha$ is the *polarizability of the molecule*. Now when the two nuclei (in a diatomic molecule) vibrate along the line joining them, polarizability of the molecule will vary. For small displacement $x$ from the equilibrium position, it is possible to represent the variation of polarizability $\alpha$ with the displacement by

$$\alpha = \alpha_0 + \beta \frac{x}{A}, \qquad \text{...(2)}$$

where $\alpha_0$ is the equilibrium polarizability, $\beta$ is the rate of variation of polarizability with displacement and $A$ is the vibrational amplitude.

Writing $\mu_x = \alpha_{xx} F_x$ from eq. (1) in equation (17) of § 2.1 the $x$-component of the matrix element which determines the transition probability can be written as

$$P_{mn}(x) = \int \psi_m^* (\alpha_{xx} F_x) \psi_n \, d\tau, \qquad \ldots(3)$$

where $\alpha_{xx}$ is the polarizability in the $x$-direction when the field $F_x$ acts in the same direction. Accounting for the variation of $\alpha_{xx}$ in the course of an oscillation from equation (2), we write

$$\alpha_{xx} = \alpha_{xx}^0 + \beta_{xx} \frac{x}{A}.$$

Therefore equation (3) is

$$P_{mn}(x) = F_x \alpha_{xx}^0 \int \psi_m^* \psi_n \, d\tau + \frac{F_x}{A} \beta_{xx} \int \psi_m^* \, x \psi_n \, d\tau \qquad \ldots(4)$$

We conclude from equation (4) that:

(i) The first term on the right hand side of equation (4) is zero except when $m = n$ (because the vibrational eigenfunctions are orthogonal). This term, therefore, gives rise to a transition which does not involve a vibrational or other transition or in other words, *this term simply gives the probability of Rayleigh scattering.*

(ii) For Raman scattering, $m \neq n$ and hence first term vanishes. Therefore for Raman lines to appear, the second term must differ from zero. Obviously, if $\beta_{xx}$ be zero, second term also vanishes and hence no Raman scattering. It means that *polarizability must change during the course of molecular vibration if Raman effect is to be exhibited.*

(iii) From equation (3), we also conclude that for Raman effect to appear, it is necessary that even in the case of molecular rotation, the polarizability either in $x$, $y$ or $z$ direction must vary in the course of rotation because only then there can be any probability of transition.

*Thus we conclude that it is necessary for the molecule to be polarizable to different extents in different directions if it is to exhibit Raman scattering.* The polarizability of a molecule can be considered as made up of three components in directions at right angles to each other, which gives the dimensions of the so called *polarization ellipsoid*. If during the course of molecular vibration, any of the three dimensions of polarization ellipsoid changes (which is equivalent to saying that polarizability in any of the three directions changes), the vibration will give rise to Raman effect. Further, if the ellipsoid is spherical, rotation will not affect the polarizability and hence for rotational Raman effect the ellipsoid should not be spherical. For a *diatomic molecule whether homonuclear or not (that is, whether it possesses permanent dipole moment or not) the polarization ellipsoid will not be spherical and will also change its dimensions in the course of molecular vibration and hence all such molecules will exhibit both rotational and vibrational Raman spectra.*

**Vibrational Raman Spectra :**

The vibrational Raman spectrum arises due to transition of molecule from one vibrational energy state to the other of the same electronic state. Quantum mechanically if $\beta_{xx}$ in equation (4) is not zero, the molecule will exhibit Raman scattering. By the study of the matrix element $P_{mn}(x)$ of the polarizability, it is found that in the case of harmonic oscillator the same selection rule holds for Raman-effect as for the infra-red spectrum, namely

$$\upsilon = \pm 1$$

showing that a transition can take place only to the adjacent vibrational state, *i.e.*, from one level to the next upper (Stokes) or to the next lower (anti-Stokes) level. Thus Raman spectrum consists of one Stokes and one anti-Stokes line which are shifted by an amount,

$$|\Delta\nu| = G(\upsilon + 1) - G(\upsilon) = \omega$$

to either side of the original line. At ordinary temperatures, most of the molecules are in their lowest vibrational states, *i.e.*, $\upsilon = 0$; hence the majority of transitions will be of the type $\upsilon = 0$ to $\upsilon = 1$. A small number of molecules will initially occupy the $\upsilon = 1$ level which may undergo the

Writing $\mu_x = \alpha_{xx} F_x$ from eq. (1) in equation (17) of § 2.1 the $x$-component of the matrix element which determines the transition probability can be written as

$$P_{mn}(x) = \int \psi_m^* (\alpha_{xx} F_x) \psi_n \, d\tau, \qquad \ldots(3)$$

where $\alpha_{xx}$ is the polarizability in the $x$-direction when the field $F_x$ acts in the same direction. Accounting for the variation of $\alpha_{xx}$ in the course of an oscillation from equation (2), we write

$$\alpha_{xx} = \alpha_{xx}^0 + \beta_{xx} \frac{x}{A} .$$

Therefore equation (3) is

$$P_{mn}(x) = F_x \alpha_{xx}^0 \int \psi_m^* \psi_n \, d\tau + \frac{F_x}{A} \beta_{xx} \int \psi_m^* \, x \psi_n \, d\tau \qquad \ldots(4)$$

We conclude from equation (4) that:

(i) The first term on the right hand side of equation (4) is zero except when $m = n$ (because the vibrational eigenfunctions are orthogonal). This term, therefore, gives rise to a transition which does not involve a vibrational or other transition or in other words, *this term simply gives the probability of Rayleigh scattering.*

(ii) For Raman scattering, $m \neq n$ and hence first term vanishes. Therefore for Raman lines to appear, the second term must differ from zero. Obviously, if $\beta_{xx}$ be zero, second term also vanishes and hence no Raman scattering. It means that *polarizability must change during the course of molecular vibration if Raman effect is to be exhibited.*

(iii) From equation (3), we also conclude that for Raman effect to appear, it is necessary that even in the case of molecular rotation, the polarizability either in $x$, $y$ or $z$ direction must vary in the course of rotation because only then there can be any probability of transition.

*Thus we conclude that it is necessary for the molecule to be polarizable to different extents in different directions if it is to exhibit Raman scattering.* The polarizability of a molecule can be considered as made up of three components in directions at right angles to each other, which gives the dimensions of the so called *polarization ellipsoid*. If during the course of molecular vibration, any of the three dimensions of polarization ellipsoid changes (which is equivalent to saying that polarizability in any of the three directions changes), the vibration will give rise to Raman effect. Further, if the ellipsoid is spherical, rotation will not affect the polarizability and hence for rotational Raman effect the ellipsoid should not be spherical. For a *diatomic molecule whether homonuclear or not (that is, whether it possesses permanent dipole moment or not) the polarization ellipsoid will not be spherical and will also change its dimensions in the course of molecular vibration and hence all such molecules will exhibit both rotational and vibrational Raman spectra.*

### Vibrational Raman Spectra :

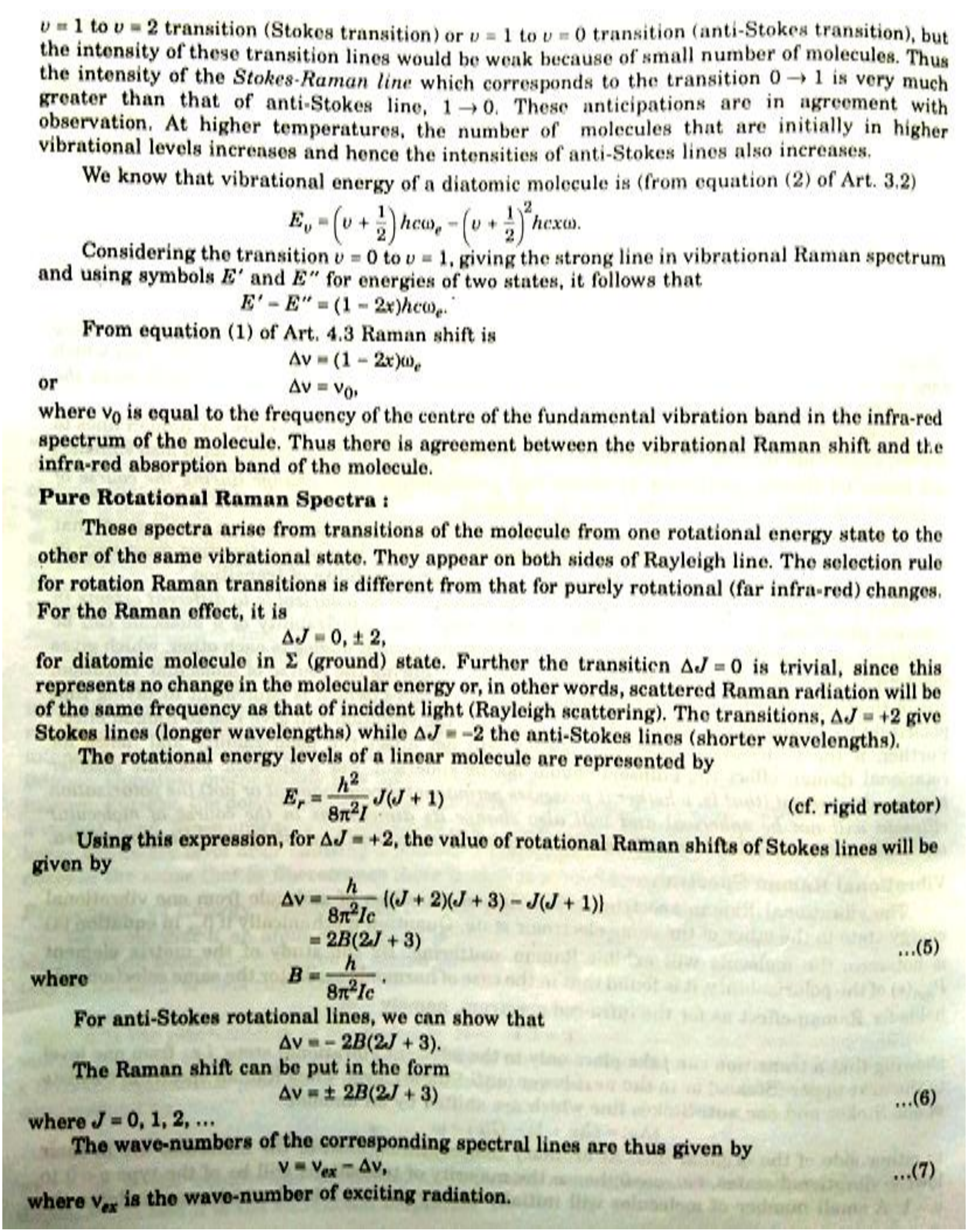
The vibrational Raman spectrum arises due to transition of molecule from one vibrational energy state to the other of the same electronic state. Quantum mechanically if $\beta_{xx}$ in equation (4) is not zero, the molecule will exhibit Raman scattering. By the study of the matrix element $P_{mn}(x)$ of the polarizability, it is found that in the case of harmonic oscillator the same selection rule holds for Raman-effect as for the infra-red spectrum, namely

$$\upsilon = \pm 1$$

showing that a transition can take place only to the adjacent vibrational state, *i.e.*, from one level to the next upper (Stokes) or to the next lower (anti-Stokes) level. Thus Raman spectrum consists of one Stokes and one anti-Stokes line which are shifted by an amount.

$$|\Delta \nu| = G(\upsilon + 1) - G(\upsilon) = \omega$$

to either side of the original line. At ordinary temperatures, most of the molecules are in their lowest vibrational states, *i.e.*, $\upsilon = 0$; hence the majority of transitions will be of the type $\upsilon = 0$ to $\upsilon = 1$. A small number of molecules will initially occupy the $\upsilon = 1$ level which may undergo the



$v = 1$ to $v = 2$ transition (Stokes transition) or $v = 1$ to $v = 0$ transition (anti-Stokes transition), but the intensity of these transition lines would be weak because of small number of molecules. Thus the intensity of the *Stokes-Raman line* which corresponds to the transition $0 \rightarrow 1$ is very much greater than that of anti-Stokes line, $1 \rightarrow 0$. These anticipations are in agreement with observation. At higher temperatures, the number of molecules that are initially in higher vibrational levels increases and hence the intensities of anti-Stokes lines also increases.

We know that vibrational energy of a diatomic molecule is (from equation (2) of Art. 3.2)

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_e - \left(v + \frac{1}{2}\right)^2 hcx\omega.$$

Considering the transition $v = 0$ to $v = 1$, giving the strong line in vibrational Raman spectrum and using symbols $E'$ and $E''$ for energies of two states, it follows that

$$E' - E'' = (1 - 2x)hc\omega_e.$$

From equation (1) of Art. 4.3 Raman shift is

$$\Delta\nu = (1 - 2x)\omega_e$$

or

$$\Delta\nu = \nu_0,$$

where $\nu_0$ is equal to the frequency of the centre of the fundamental vibration band in the infra-red spectrum of the molecule. Thus there is agreement between the vibrational Raman shift and the infra-red absorption band of the molecule.

**Pure Rotational Raman Spectra :**

These spectra arise from transitions of the molecule from one rotational energy state to the other of the same vibrational state. They appear on both sides of Rayleigh line. The selection rule for rotation Raman transitions is different from that for purely rotational (far infra-red) changes. For the Raman effect, it is

$$\Delta J = 0, \pm 2,$$

for diatomic molecule in $\Sigma$ (ground) state. Further the transition $\Delta J = 0$ is trivial, since this represents no change in the molecular energy or, in other words, scattered Raman radiation will be of the same frequency as that of incident light (Rayleigh scattering). The transitions, $\Delta J = +2$ give Stokes lines (longer wavelengths) while $\Delta J = -2$ the anti-Stokes lines (shorter wavelengths).

The rotational energy levels of a linear molecule are represented by

$$E_r = \frac{h^2}{8\pi^2 I} J(J + 1) \qquad \text{(cf. rigid rotator)}$$

Using this expression, for $\Delta J = +2$, the value of rotational Raman shifts of Stokes lines will be given by

$$\Delta\nu = \frac{h}{8\pi^2 Ic} \{(J + 2)(J + 3) - J(J + 1)\}$$
$$= 2B(2J + 3) \qquad \text{...(5)}$$

where

$$B = \frac{h}{8\pi^2 Ic}.$$

For anti-Stokes rotational lines, we can show that

$$\Delta\nu = -2B(2J + 3).$$

The Raman shift can be put in the form

$$\Delta\nu = \pm 2B(2J + 3) \qquad \text{...(6)}$$

where $J = 0, 1, 2, \ldots$

The wave-numbers of the corresponding spectral lines are thus given by

$$\nu = \nu_{ex} - \Delta\nu, \qquad \text{...(7)}$$

where $\nu_{ex}$ is the wave-number of exciting radiation.

In Fig. 4.4 allowed transitions and the Raman spectrum arising out are shown. It can be seen that frequency separation of successive lines is $4B$ (remember it is $2B$ cm$^{-1}$ in far infra-red spectra), while on putting $J = 0$ in equation (7), we find that the separation of the first line from the exciting lines is $6B$ cm$^{-1}$.

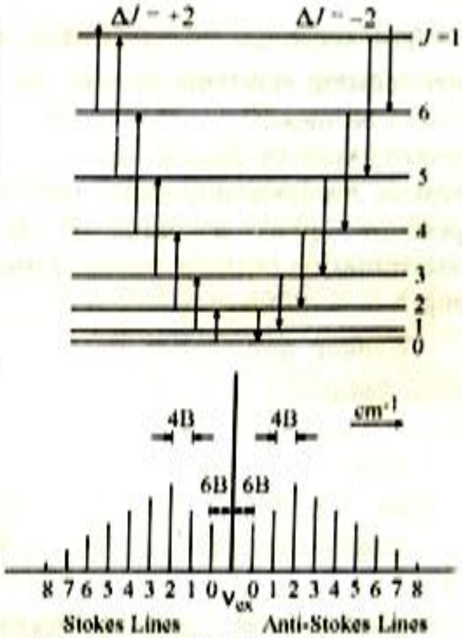


**Fig. 4.4. The rotational levels of a diatomic molecule and the rotational Raman Spectra.**

**Discussion :**

(i) For diatomic and light triatomic molecules the rotational spectrum will normally be resolved. The value of $B$ can then be obtained and hence the moment of inertia and bond length for such molecules can be found.

(ii) Important to note is that whereas the homonuclear diatomic molecules (*e.g.* $O_2$, $H_2$, $D_2$, $N_2$) give no infrared or microwave spectra, they do exhibit rotational Raman spectra. Therefore structure of such molecules can be obtained from Raman technique.

(iii) If a molecule has a centre of symmetry (*e.g.* $H_2$, $O_2$, $CO_2$), then the effects of nuclear spin will be observed in both the Raman and infra-red spectra. Thus for $O_2$, $CO_2$ *every alternate rotational level is absent;* for example, in the case of $O_2$, every level with *even* $J$ values is missing and thus every transition labelled $J = 0, 2, 4$ in Fig. 4.4 will be missing from the spectrum.

**Vibration-Rotation Raman Spectra :**

It is possible, theoretically (such spectra are rarely resolved except in the case of diatomic molecules), for vibrational and rotational transitions to occur simultaneously in a Raman transition, the selection rules are identical with those for separate transitions, *i.e.*, $\Delta v = \pm 1$ and $\Delta J = 0, \pm 2$.

For a diatomic molecule vibration-rotation energy levels are given by

$$E_{rv} = hc\left[\omega_e\left(v + \frac{1}{2}\right) - \omega_e x\left(v + \frac{1}{2}\right)^2\right] + BhcJ(J+1)\ \text{cm}^{-1}$$

(where $v = 0, 1, 2, \ldots; j = 0, 1, 2, \ldots$)

or in terms of frequency,

$$\nu = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x\left(v + \frac{1}{2}\right)^2 + BJ(J+1). \qquad \ldots(8)$$

Applying selection rules, stated earlier, we have

$$\Delta J = 0: \quad \Delta\nu(Q) = \nu_0\ \text{cm}^{-1} \quad (\text{for all } J) \qquad \ldots(9)$$

$$\left.\begin{array}{lll} \Delta J = +2: & \Delta\nu(S) = \nu_0 + B(4J+6) & (J = 0, 1, 2, \ldots) \\ \Delta J = -2 & \Delta\nu(O) = \nu_0 - B(4J+6) & (J = 2, 3, 4, \ldots) \end{array}\right\} \qquad \ldots(10)$$

where $\nu_0$ is written for $\omega_e\,(1 - 2x)$ and $O$, $Q$ and $S$ refer to the $O$ branch lines, $Q$ branch lines and $S$ branch lines respectively.

Stokes lines will occur at wavenumber given by

$$\nu(Q) = \nu_{ex} - \Delta\nu(Q) = \nu_{ex} - \nu_0\ \text{cm}^{-1} \quad (\text{for all } J)$$

$$\nu(O) = \nu_{ex} - \nu_0 + B(4J+6)\ \text{cm}^{-1} \quad (J = 2, 3, 4, \ldots)$$

$$\nu(S) = \nu_{ex} - \nu_0 - B(4J+6)\ \text{cm}^{-1} \quad (J = 0, 1, 2, \ldots).$$

The spectrum is sketched in Fig.4. 5 with pure rotation spectrum at one side.

It is to be noted here that unlike near infra-red spectra, here in Raman spectrum $Q$ branch is present. Analysis of $O$ and $S$ branches in Raman spectrum gives a value of $B$ and hence determination of the moment of inertia and bond length is possible.

Weaker anti-Stokes line will occur at the same distance from, but to high frequency side, of the exciting line.

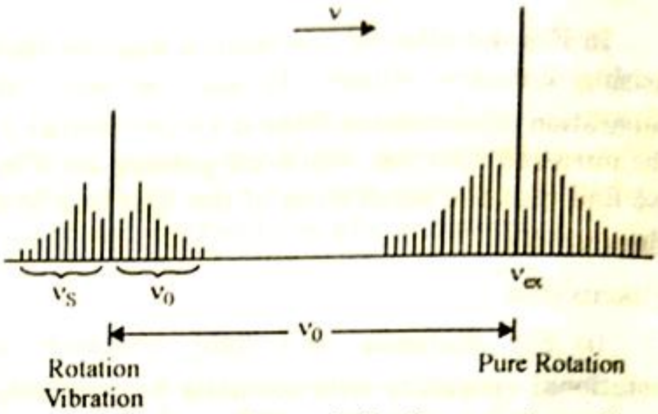


**Fig. 4.5. Pure rotation and vibration spectrum of a diatomic molecule.**

**Problem.** *With exciting line* 4358 Å, *a sample gives Stokes lines at* 4458 Å. *Deduce the wavelength of anti-Stokes line.*

**Refer to the equation (7), art. 4.3, the wave number of corresponding spectral lines are given by**

$$\nu = \nu_{ex} - \Delta\nu$$

**with** $$\Delta\nu = \pm 2B(2J + 3);$$

**the plus sign stands for Stokes lines and minus for anti-Stokes line. Thus we have**

$$\nu_{ex} = 2{\cdot}2999 \times 10^6 \text{ m}^{-1}$$

$$\nu_s = 2{\cdot}2431 \times 10^6 \text{ m}^{-1}$$

$$\Delta\nu = 0{\cdot}0568 \times 10^6 \text{ m}^{-1}$$

$$\nu_s = 2{\cdot}3567 \times 10^6 \text{ m}^{-1}$$

$$\lambda_{as} = 0{\cdot}42432 \times 10^{-6} \text{ m} = 4243{\cdot}2 \text{ Å}.$$