RAMAN SPECTROSCOPY

14.12 SCATTERING OF LIGHT

(*i*) **Rayleigh scattering.** When radiation is incident on a molecule, it is in general, scattered by the molecule. The dominant mode of scattering is elastic scattering. Here, the frequency of the scattered light remains the same as that of the incident radiation. This phenomenon is called Rayleigh scattering.

Rayleigh showed theoretically that the intensity of scattered light is inversely proportional to the fourth power of the wavelength *i.e.*, $I \propto \frac{1}{\lambda^4}$.

This is called Rayleigh's law of scattering. I is also proportional to the square of the volume of the particle. The blue colour of the sky is due to the greater scattering of short wavelengths by the dust suspensions in the atmosphere or by the air molecules. This type of scattering simply produces separation of wavelengths originally present in the incident light. No wavelength can be present in the scattered light which is not present in the incident light *i.e.*, no new wavelength is created. For this reason, Rayleigh scattering is called coherent scattering.

C.V. Raman (1888-1970)

(*ii*) **Raman Effect.** While studying the scattering of light, Raman found that when a beam of monochromatic light was passed through organic liquids such as benzene, toluene, etc., the scattered light contained other frequencies in addition to that of the incident light. This is called *Raman effect.*

The scattering is inelastic.

14.13 EXPERIMENTAL STUDY OF RAMAN EFFECT

Fig. 14.24 shows the apparatus used for studying Raman effect in liquids.

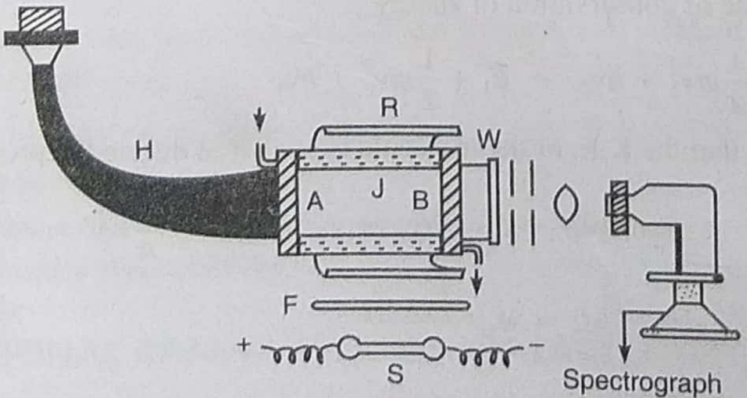

Fig. 14.24

It consists of a glass tube AB containing the pure experimental liquid free from dust and air bubbles. The tube is closed at one end by an optically plane glass plate W and at the other end it is drawn into a horn (H) and blackened on the outside. Light from a mercury arc S is passed through a filter F which allows only monochromatic radiation of $\lambda = 4358$ Å to pass through it. The tube is surrounded by a water-jacket (J) through which water is circulated to prevent overheating of the liquid. A semi-cylindrical aluminium reflector R is used to increase the intensity of illumination. The scattered light coming out of W is condensed on the slit of a spectrograph. The spectrograph must have a large light gathering power and the prism must have a large resolving power. A short focus camera is used to photograph the spectrum.

It is observed that the spectrum contains, in addition to the original wavelength (4358 Å), some lines which have wavelengths longer as well as shorter than the original wavelength.

These lines of modified wavelengths are known as *Raman lines*. The lines having wavelengths greater than that of the incident wavelength are called *Stokes lines* and those having shorter wavelengths are called *anti-Stokes lines*. The Stokes lines are found to be more intense than the anti-Stokes lines. Most of the Raman lines are strongly polarised.

The displacement of the modified spectral lines from the exciting line, when measured in wavenumbers, depends only on the scattering substance and is independent of the wavenumber of the exciting radiation. The Raman spectrum is thus characteristic of the scattering substance.

The spectrum exhibits a number of Stokes' lines, a few anti-Stokes lines and a strong unmodified line (Fig. 14.25).

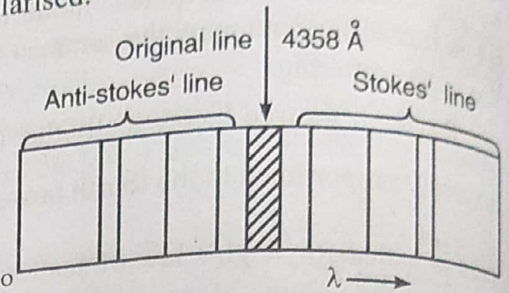

Fig. 14.25

Characteristics of Raman Lines

(1) The Stokes lines are found to be more intense than the anti-Stokes lines.

(2) The Raman lines are symmetrically displaced about the parent line.

(3) The frequency difference between the modified and parent line represents the frequency of the corresponding infrared absorption line.

14.14 QUANTUM THEORY OF RAMAN EFFECT

Raman effect is due to the interaction between a light photon and a molecule of the scatterer. Suppose a photon of frequency ν_1 is incident on a molecule and there is a collision between the two. Let m = mass of the molecule, v_1 and v_2 its velocities before and after impact, E_1 and E_2 the intrinsic energies of the molecule before and after collision. Let ν_2 be the frequency of the scattered photon. Applying the principle of conservation of energy,

$$E_2 + \frac{1}{2}mv_2^2 + h\nu_2 = E_1 + \frac{1}{2}mv_1^2 + h\nu_1 \qquad ...(1)$$

We may assume that the K.E. of the molecule is unaltered during the process. Hence,

$$E_2 + h\nu_2 = E_1 + h\nu_1 \text{ or } \nu_2 - \nu_1 = \frac{E_1 - E_2}{h}$$

or

$$\nu_2 = \nu_1 + \frac{E_1 - E_2}{h} \qquad ...(2)$$

Three cases may arise:

(1) When there is no change in the energy of the molecule, $E_1 = E_2$. Then $\nu_1 = \nu_2$. This represents the unmodified line.

(2) If $E_2 > E_1$, then, $\nu_2 < \nu_1$. This represents the Stokes line. It means that the molecule has absorbed some energy from the incident photon. Consequently the scattered photon has lower energy or longer wavelength.

(3) If $E_2 < E_1$, then, $\nu_2 > \nu_1$. This represents the anti Stokes line. It means that the molecule was previously in the excited state and it handed over some of its intrinsic energy to the incident photon. The scattered photon thus has greater energy or shorter wavelength.

Since the molecules possess quantised energy levels, we can write,

$$E_1 - E_2 = nh\nu_c \qquad ...(3)$$

where $n = 1, 2, 3$....etc, and ν_c = the characteristic frequency of the molecule.

In the simplest case $n = 1$, equation (2) reduces to

$$\nu_2 = \nu_1 \pm \nu_c \quad \text{...(4)}$$

Equation (4) shows that the frequency difference $\nu_1 - \nu_2$ between the incident and scattered photon corresponds to the characteristic frequency ν_c of the molecule.

14.15 CLASSICAL THEORY OF RAMAN EFFECT

When a molecule is placed in an electric field E, the field distorts the electronic structure and polarizes the molecule. The polarization induced (P) is proportional to the applied electric field (E).

$$P = \alpha E \quad \text{...(1)}$$

Here, α is the polarizability of the molecule.

When radiation of frequency ν_0 is allowed to fall on the molecules, each molecule experiences a varying electric field E given by

$$E = E_0 \cos 2\pi\nu_0 t \quad \text{...(2)}$$

For a vibrating molecule, the polarizability along a direction will vary about an average value α_0 with a frequency equal to the vibrational frequency. We can write

$$\alpha = \alpha_0 + \beta \cos 2\pi\nu_m t \quad \text{...(3)}$$

Here, α_0 is the equilibrium polarizability, and β is the rate of change of polarizability with the vibration. Then the induced polarization is given by

$$P = (\alpha_0 + \beta \cos 2\pi\nu_m t)(E_0 \cos 2\pi\nu_0 t) \quad \text{...(4)}$$

$\cos A \cos B = \frac{1}{2}[\cos(\alpha+\beta) + \cos(\alpha-\beta)]$

$$\therefore P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{E_0\beta}{2}[\cos 2\pi(\nu_0 + \nu_m)t + \cos 2\pi(\nu_0 - \nu_m)t] \quad \text{...(5)}$$

Thus, the induced polarization contains the three distinct frequency components ν_0, $(\nu_0 + \nu_m)$ and $(\nu_0 - \nu_m)$.

ν_0 is the frequency of incident radiation *i.e.*, Rayleigh scattering.

The last two frequencies are more and less than the frequency of incident radiation and predict the existence of Raman scattering.

No Raman line will be observed, if the change in polarizability β is zero.

Thus we have the general rule:

In order to be Raman active, a molecular rotation or vibration must cause some change in a component of the molecular polarizability.

14.16 VIBRATIONAL RAMAN SPECTRA OF DIATOMIC MOLECULES

The transition energies of the vibrational Raman spectra for a diatomic molecule can be written using the energy expression of an anharmonic oscillator [cf. Eq. (2), Section 14.6].

$$\varepsilon = \bar{\nu}_e\left(V + \frac{1}{2}\right) - \bar{\nu}_e x_e\left(V + \frac{1}{2}\right)^2 m^{-1}, \text{ for } V = 0, 1, 2.... \quad \text{...(1)}$$

Here, $\bar{\nu}_e$ is called the *equilibrium oscillation frequency* of the molecule expressed in wave numbers and is the value for small displacements. x_e is the corresponding anharmonicity constant.

The selection rule for Raman scattering is given by $\Delta V = \pm 1, \pm 2$, ...

Considering the $V = 0 \rightarrow V = 1$ transition, we have

$$\Delta\varepsilon = \bar{\nu}_e(1-2x_e)\ m^{-1} \qquad ...(2)$$

During collision, if the molecule gains energy from the exciting radiation $\bar{\nu}_0$, it gives rise to a line on the low frequency side of $\bar{\nu}_0$ which is the Stokes Raman line.

In anti-Stokes Raman, the exciting radiation gains energy from the molecule. Hence, we may write

$$\bar{\nu} = \bar{\nu}_0 \pm \bar{\nu}_e(1-2x_e) \qquad ...(3)$$

Here the minus sign represents the Stokes' lines. The plus sign refers to the anti-Stoke's lines. Since the Raman scattering of light is of low intensity, we can ignore completely all the weaker effects such as overtones and '*hot*' bands.

14.16.1. Pure Rotational Raman Spectra (Linear Molecules)

The rotational energy levels of linear molecules are given by [cf. Eq. (6), Section 14.3]

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2\ \text{cm}^{-1}\ (J = 0, 1, 2, ...)$$

But, in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D, the centrifugal distortion constant. Thus we take the simpler expression:

$$\varepsilon_J = BJ(J+1)\ \text{cm}^{-1}\ (J = 0, 1, 2, ...) \qquad ...(1)$$

to represent the energy levels.

Transitions between these levels follow the selection rule:

$$\Delta J = 0, \text{ or } \pm 2 \text{ only} \qquad ...(2)$$

We define ΔJ as ($J_{\text{upper state}} - J_{\text{lower state}}$). We can ignore the selection rule $\Delta J = -2$ since, for a pure rotational change, the upper state quantum number must necessarily be greater than that in the lower state. Further, the 'transition' $\Delta J = 0$ is trivial since this represents no change in the molecular energy and hence Rayleigh scattering only.

Combining, then, $\Delta J = +2$ with the energy levels of Eq. (1) we have:

$$\Delta\varepsilon = \varepsilon_{J' = J+2} - \varepsilon_{J'' = J}$$

$$= B(4J+6)\ \text{cm}^{-1}\ (J = 0, 1, 2, ...) \qquad ...(3)$$

The wavenumbers of the rotational Raman lines are given by

$$\bar{\nu} = \bar{\nu}_0 \pm B(4J+6)\ \text{cm}^{-1} \qquad ...(4)$$

Here, the plus sign refers to anti-Stokes' lines, the minus to Stokes' lines, and $\bar{\nu}_0$ is the wavenumber of the exciting radiation.

Stokes' and anti-Stokes' lines have comparable intensity because many rotational levels are populated and hence downward transitions are approximately as likely as upward ones.

Fig. 14.26 shows the rotational energy levels of a diatomic molecule and the rotational Raman spectrum arising from transitions between them. Spectral lines are numbered according to their lower J values.

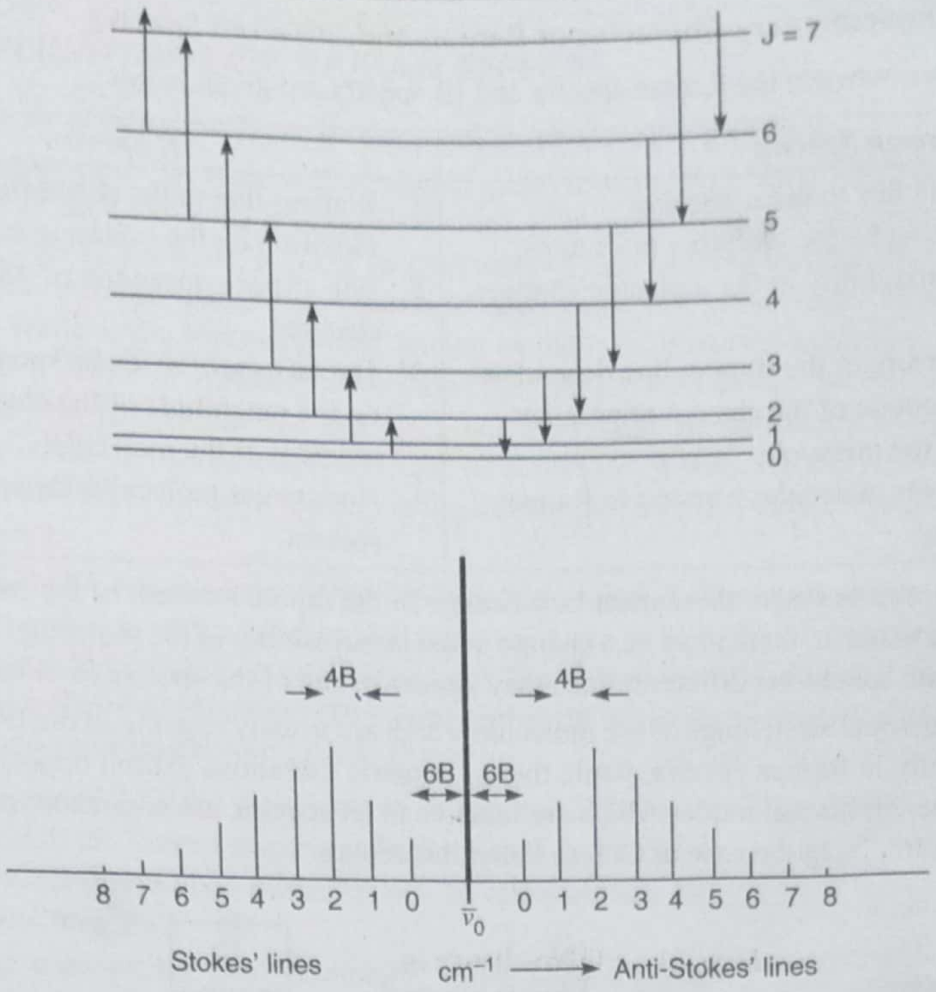

Fig. 14.26

Putting $J = 0$ in Eq. (4), we find that the separation of the first line from the exciting line is $6B$ cm^{-1}, while the separation between successive lines is $4B$ cm^{-1}.

For diatomic and light triatomic molecules, the rotational Raman spectrum will normally be resolved and we can obtain a value of B. Hence the moment of inertia and bond length for such molecules can be found.

Homonuclear diatomic molecules (for example O_2, H_2) give no infra-red or microwave spectra since they possess no dipole moment, whereas they *do* give a rotational Raman spectrum. Therefore, structure of such molecules can be obtained from Raman technique. Raman technique is thus complementary to microwave and infra-red studies.

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 and CO_2 (since the spin of oxygen is zero) 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 $J = 0, 2, 4, \ldots$ in Fig. 14.26 is also completely missing from the spectrum. In the case of H_2, and other molecules composed of nuclei with non-zero spin, the spectral lines show an alternation of intensity.

14.16.2. Complementary Character of Raman and Infra-red Spectra

The differences between the Raman spectra and IR spectra are given below:

Raman Spectra	*IR Spectra*
1. It appears due to the scattering of radiation by the vibrating molecules.	1. It arises due to the absorption of radiation by the vibrating molecules.
2. The polarizability of the molecule changes.	2. The dipole moment of the molecules changes.
3. The intensity of the Raman line depends on the magnitude of the change of polarizability of the molecule.	3. The intensity of an IR absorption band depends on the magnitude of the change in dipole moment of the molecule.
4. Homopolar molecules respond to Raman scattering.	4. Homopolar molecules cannot exhibit IR spectra.

For IR spectra to occur, there must be a change in the dipole moment of the molecule. For the Raman spectra to occur, there must be a change in the polarizability of the molecule. Since these two requirements are somewhat different, lines may appear in one of the spectra or in both.

The symmetrical stretchings of the molecule which are usually missing in the IR spectra appear very prominently in Raman spectra, while the asymmetric vibrations exhibit opposite behaviour. It follows that the vibrational modes which are inactive in IR spectra, are sometimes active in Raman spectra. For example, in the case of CO_2 (a linear molecule),

$$\underset{\text{Sym. stretching}}{O \overset{\leftarrow}{=} C \overset{\rightarrow}{=} O}\ \left\{\begin{array}{ll}\text{No change in dipole moment} & \boxed{\text{IR inactive}}\\ \text{Appreciable change in polarizability} & \boxed{\text{Raman active}}\end{array}\right.$$

$$\underset{\text{A sym. stretching}}{\vec{O} = C = \vec{O}}\ \left\{\begin{array}{ll}\text{Appreciable change in dipole moment} & \boxed{\text{IR active}}\\ \text{No change in polarizability} & \boxed{\text{Raman inactive}}\end{array}\right.$$

$$\left.\begin{array}{c}\underset{\text{In-plane bending}}{\uparrow O = C = O \uparrow}\\ \underset{\text{Out-of-plane bending}}{\overset{+}{O} = \overset{-}{C} = \overset{+}{O}}\end{array}\right\}\ \text{Both are degenerate}\ \begin{array}{l}\boxed{\text{IR active}}\\ \boxed{\text{Raman inactive}}\end{array}$$

With small molecules, the less symmetric vibrations often produce intense IR-bands, while the (more) symmetric vibrations often give rise to strong Raman bands.

According to *Rules of Mutual Exclusion*, which states that if a molecule has a centre of symmetry (e.g., centrosymmetric molecule like H_2, CO_2, C_2H_2, etc.), the Raman active vibrations are IR-inactive and *vice versa*. The molecule for which the centre of symmetry is absent, may be simultaneously Raman and IR active. It is, therefore, the stretching vibrations of homonuclear diatomic molecules (such as H_2, N_2, O_2, etc.) which are IR-inactive, are Raman active.

Thus, it may be stated that the IR and Raman spectra are complementary to each other.

14.17 APPLICATIONS OF RAMAN EFFECT

(1) Structure determination from Raman and Infra-red Spectroscopy

Triatomic molecules: Dealing with triatomic molecules (of type AB_2), the questions to be decided are: whether each molecule is linear or not and, if linear, whether it is symmetrical (B-A-B) or asymmetrical (B-B-A). From the number and intensity of the observed lines in the Raman effect in conjunction with infrared data, it is possible to draw important conclusions about molecular structure. Theory leads to the following rule, known as the *rule of mutual exclusion.* It states that *for molecules with a centre of symmetry transitions that are allowed in the infrared are forbidden in Raman spectra and vice versa.* The rule does not imply that all transitions forbidden in one must occur in the other; *i.e.*, some transitions may be forbidden in both. On the other hand certain transitions can occur both in the infra-red and in the Raman spectra in the case of molecules without a centre of symmetry.

Examples: (*a*) CO_2 has two very strong bands in its infrared absorption spectrum at 66800 and 234900 m^{-1} while only one strong band in its Raman spectrum at 138900 m^{-1}. None of these bands occur both in Raman and infrared spectra. Hence, it follows from the rule of mutual exclusion, that CO_2 molecule has a centre of symmetry. This implies that the molecule is linear and symmetric and hence it should be represented by O - C - O.

(*b*) Nitrous oxide (N_2O) has three absorption bands at 222400, 128500 and 58900 m^{-1} of which the first two appear in the Raman spectrum. Thus the molecule cannot have a centre of symmetry though linear. Hence the molecule has the unsymmetrical structure N - N - O.

In a similar manner, the bent symmetric structure of a water molecule represented by Fig. 14.27 is revealed by Raman Effect. Thus the study of Raman spectra of different substances enables one to classify them according to their molecular structure.

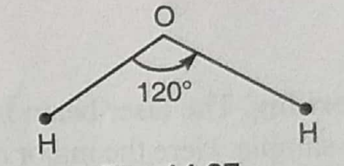

Fig. 14.27

(2) **Raman effect and molecular structure.** A qualitative identification of Raman spectrum consists in the evaluation of the wavelength of the lines, their intensities, and state of polarisation. Investigation of bond angles, bond stiffness, and other structural confirmation require Raman data in addition to infrared studies.

Diatomic molecules. From the analysis of Raman spectra of a diatomic molecule, we can have an idea about the nature of the chemical bond existing between the atoms. In a diatomic molecule, the frequency of vibration of the atoms is given by $\nu = \frac{1}{2\pi}\sqrt{\frac{F}{\mu}}$ where F is the restoring force per unit displacement and μ is the reduced mass of the molecule. It is seen that 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 upon the nature of interatomic bonds. In covalent molecules polarisability is considerably changed by the nuclear oscillations due to the nuclei. This appreciable change in polarisability gives rise to intense Raman lines. In electrovalent molecules, the binding elecrons 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 and hence no Raman lines will appear.

(3) Raman effect in crystals is complementary to X-ray crystal study and provides information about the binding forces in crystals.

(4) Various chemical effects like strength of chemical bonds, electrolytic dissociation, hydrolysis, etc., have been understood through Raman effect. Specific heat capacities of solids, brilliance of metals and their molecular structure have been explained by Raman effect.

14.18 TECHNIQUES AND INSTRUMENTATION

Raman Spectrometer

Fig. 14.28 shows the schematic diagram of a Raman spectrometer.

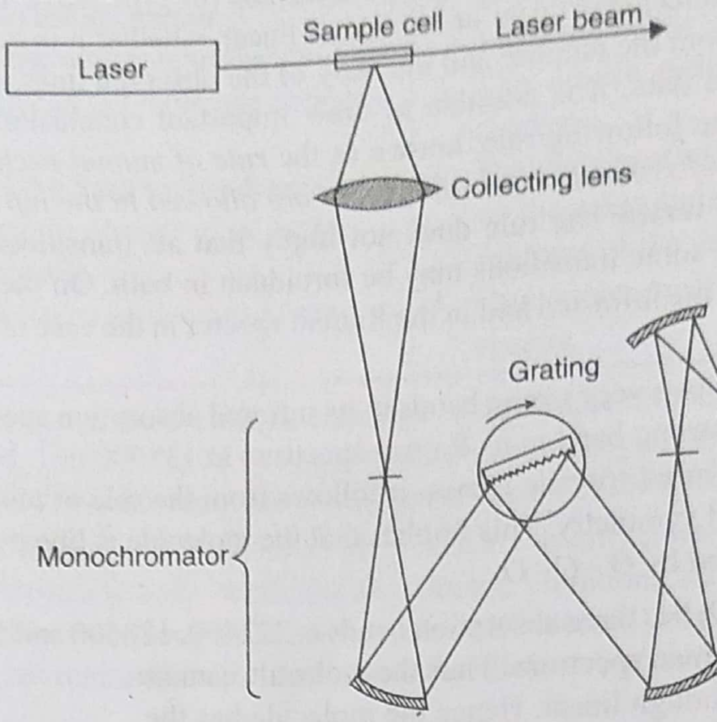

Fig. 14.28

Working. The laser beam is passed through a cell, usually a narrow glass or quartz tube filled with the sample. Here the major considerations are the effective illumination of the sample and collection of scattered radiation from the sample. Light scattered sideways from the sample is collected by a lens and passed into a grating monochromator. The signal is measured by a sensitive photomultiplier and after amplification, it is processed by a computer which plots the Raman spectrum.

We briefly discuss the components of the Raman spectrometer.

(*i*) **Source:** The highly intense, monochromatic, coherent, and directional properties of a laser allow one to obtain easily a high quality Raman spectrum. The fluorescence is expected to be low as the frequency of the radiation is less. The commonly used lasers are: He–Ne laser (632.8 nm), argon ion laser (488 and 514.5 nm) and krypton laser (647.1, 568.2, 530.8, 520.8, 482.5, 476.2 nm). In certain cases, red radiation is preferred to reduce fluorescence and decomposition of the sample.

(*ii*) **Sample illumination:** Here, the major considerations are the effective illumination of the sample and collection of scattered radiation from the sample.

Fig. 14.29 shows the arrangement for sample illumination.

- The lens L_1 focuses the laser beam into the sample.
- The lens L_2 collects the scattered radiation and focuses it to the dispersing system.
- Mirrors M_1 and M_2 together increase the intensity of the collected radiation.

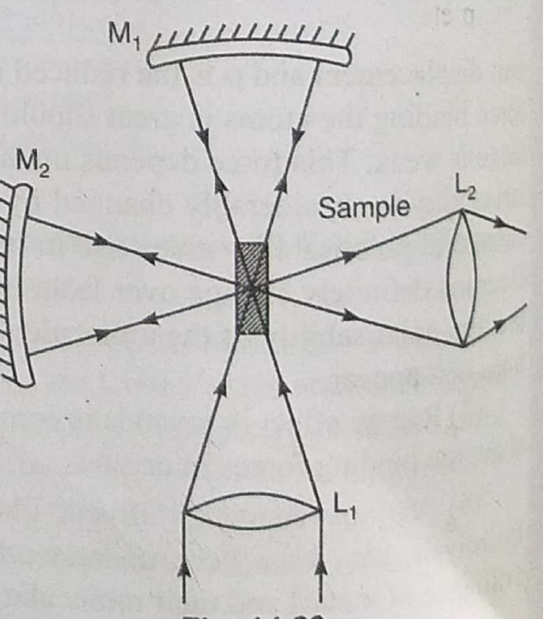

Fig. 14.29

(*iii*) **Dispersing medium:** The dispersing element allows only a narrow region to reach the detector at a time. Usually a diffraction grating is used as the dispersing element. As a single grating cannot give the required resolution, often two gratings are used in series. Then the system is called a double monochromator. For very high resolution work, a triple monochromator is preferred. Rotation of the grating allows successive regions of the spectrum to reach the detector.

(*iv*) **Detector:** A photomultiplier tube is used as the detecting device. To reduce thermal emission, it has to be cooled. The output of the photomultiplier tube is amplified and fed to the data processing system or recorder.

Advantages

For vibrational measurements, the Raman technique has several advantages over infra-red.

(1) Because both the incident and scattered radiation are at ultraviolet or visible frequencies, conventional optics and sample cells (glass, quartz, etc.) can be used, so avoiding the problems inherent in NaCl windows, atmospheric absorption, etc.

(2) Because the beam can be focused extremely finely (diameters as small as 0.1 nm are possible), very small samples can be studied. This, combined with pulsed techniques which can give very short time resolutions, enables very small quantities of transient species to be studied.

(3) Water, which has strong infra-red absorptions, is a rather weak Raman scatterer. So aqueous solutions can be studied using Raman, because the sample signal is not swamped by that of the solvent.

- In addition to liquids and solutions, Raman spectra can be obtained from gas and solid samples.

Electronic Spectra Molecules

14.19 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

14.19.1. Born-Oppenheimer Approximation

According to Born and Oppenheimer, the various forms of energies of a molecule are independent of each other.

The total energy E_{total} of a molecule is

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \qquad \text{... (1)}$$

Eq. (1) implies that the electronic, vibrational, and rotational energies of a molecule are completely independent of each other.

A change in the total energy of a molecule is

$$\Delta E_{\text{total}} = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot}} \text{ J}$$

or

$$\Delta\varepsilon_{\text{elec}} = \Delta\varepsilon_{\text{elec.}} + \Delta\varepsilon_{\text{vib.}} + \Delta\varepsilon_{\text{rot}} \text{ cm}^{-1} \qquad \text{... (2)}$$

The approximate orders of magnitude of these changes are:

$$\Delta\varepsilon_{\text{elec.}} = \Delta\varepsilon_{\text{vib.}} \times 10^3 \approx \Delta\varepsilon_{\text{rot}} \times 10^6 \qquad \text{... (3)}$$

So we see that *vibrational energy changes will produce a 'coarse structure' and* rotational changes a '*fine structure*' on the *spectra of electronic* transitions.

- Pure rotation spectra are shown only by molecules possessing a permanent electric dipole moment.
- Vibrational spectra require a change of dipole moment during its normal mode of vibration.