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المرحلة الرابعة

# Chapter four: Raman Spectroscopy

## Raman Scattering:-

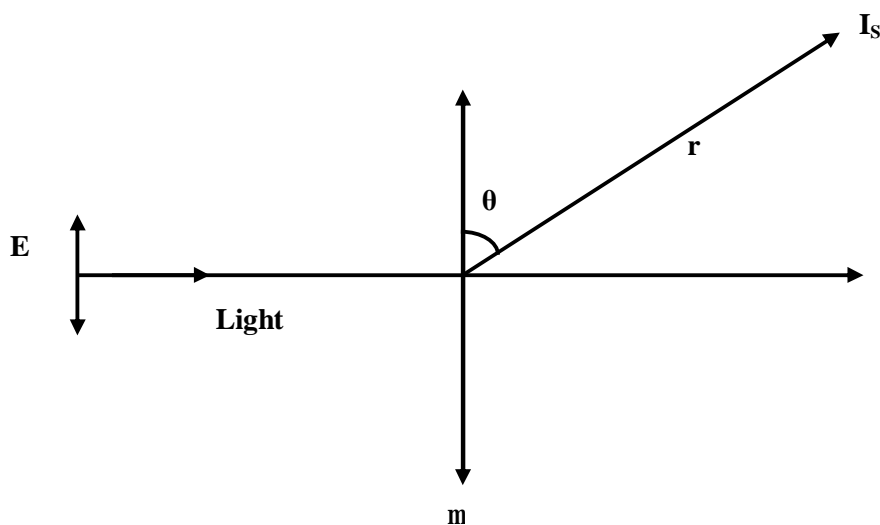
The mechanism of light scattering involves the polarization of the atom or the molecule by the electric field of the incident light.

The incident dipole moment ( $\mu$ ) will oscillate with the same frequency of the electric field of the incident light and emits scattering light with the same frequency ( $F_0$ ) or ( $\nu_0$ ). This called **Rayleigh Scattering**.

$I_s$ : Intensity of the scattered light.

$$I_s \propto \frac{\alpha^2 \sin^2 \theta}{\lambda^4 r^2} \quad \text{This relation was found by Reyleigh in 1899}$$

Where  $\alpha$ =polarizability of the moment.

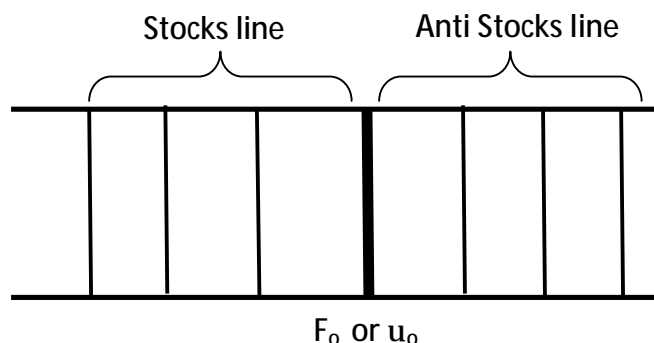


$$|\vec{\mu}| = \alpha |\vec{E}|$$

### Note:-

- 1-The maximum scattering happen at  $\theta=90$ .
- 2- The minimum scattering happen at  $\theta=0$ .

In 1929 Raman discovered that a small part of the scattered light ( $\cong 170$ ) occurs with different frequency this called Raman Scattering.



$$\Delta F = \text{Raman shift} = |F_0 - F|$$

- If ( F ) less than  $F_0$  the lines called stocks.
- If ( F ) greater than  $F_0$  the lines called anti stocks .

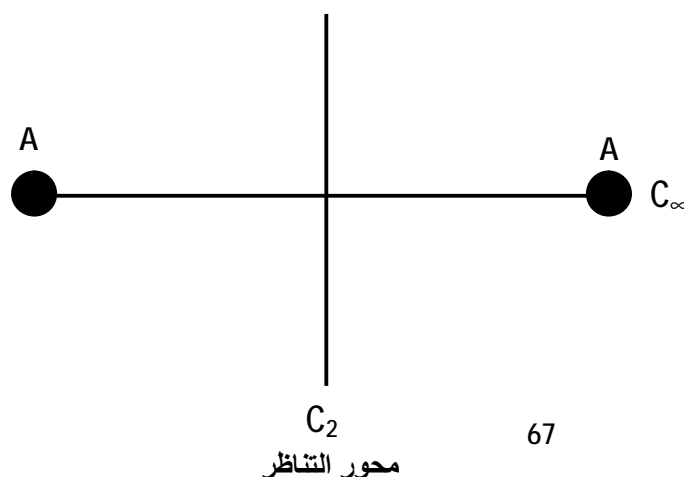
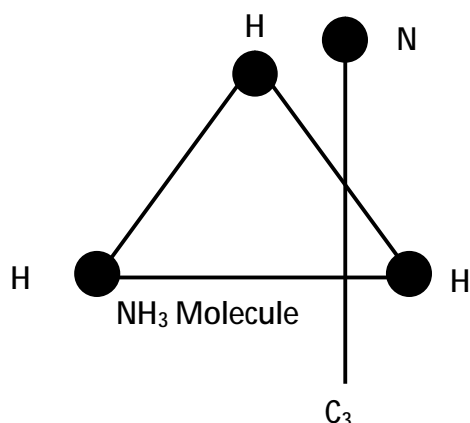
### Classical Theory of Raman scattering:-

The effect of the applied electric field is to produce a force on the positive charge in one direction and opposite force on the negative charge and they will be displace and hence induced dipole moment is induced

$$|\vec{\mu}| = \alpha |\vec{E}|$$

$\alpha$ : depend on the orientation of the molecule.

The applied electric field in generate the direction of  $\mu$  is not the same as the direction of  $E$  unless  $E$  is in the direction of the axis of symmetry of the molecule



**C<sub>3</sub>**:- Means the Number of related molecule and still the same orientation and so as few C<sub>2</sub>, C<sub>∞</sub>.

Let X, Y, Z be axis of symmetry of  
The diatomic molecule, then

$$\mu_x = \alpha E_x$$

$$\mu_y = \alpha E_y$$

$$\mu_z = \alpha E_z$$

Since X and Y axis are equivalent

Then  $\alpha_x = \alpha_y$

Let the equation of the electron field of the incident light is

$$\mathbf{E} = \mathbf{E}_0 \sin 2\pi F \cdot t$$

Due to relation, the polarizability  $\alpha$  will be given by

$$\alpha = \alpha_0 + \alpha_1 \sin[2\pi(2F_r)t]$$

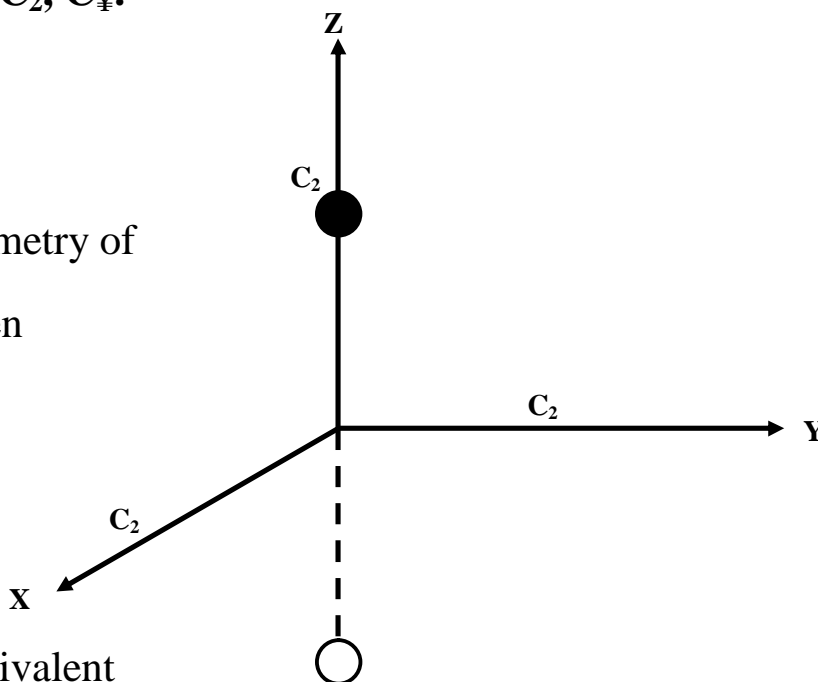
**Where**  $\alpha_0$  = average of polarizability.

$\alpha_1$  = the amplitude.

$F_r$  = Frequency of rotation.

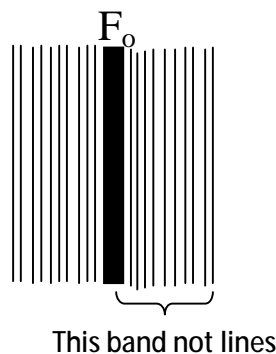
The equation of  $\mu$  (induced dipole moment) will be

$$\mu = \alpha E = [\alpha_0 + \alpha_1 \sin 2\pi(2F_r)t][E_0 \sin 2\pi F \cdot t]$$



$$= \alpha_0 E_0 \sin 2\pi F_0 t + \frac{\alpha_1 E_0}{2} [\cos 2\pi(F_0 - 2F_r)t - \cos 2\pi(F_0 + 2F_r)t]$$

Hence  $\mu$  will oscillate not only with frequency  $F_0$  but also with frequency  $F_0 \pm 2F_r$ . But according to the classical theory  $F_0$  is continuous. we expect therefore to have continuous freq. of scattered light.



For vibration  $\alpha_v = \alpha_{0v} + \alpha_{1v} \sin 2\pi F_v t$

$$\mu = \alpha E (\alpha_{0v} + \alpha_v \sin 2\pi F_v t) (E_0 \sin 2\pi F_0 t)$$

$$\mu = \alpha_{0v} E_0 \sin 2\pi F_0 t + \frac{\alpha_{1v} E_0}{2} [\cos 2\pi(F_0 - F_v)t - \cos 2\pi(F_0 + F_v)t]$$

## Quantum theory of Raman scattering:-

The scattering according to the quantum theory is due to the collision between the light photon and the molecule.

**Rayleigh scattering occurs when the collision is elastic**

$$hf_0 + A \text{ (R)} \quad hf_0 + A^*$$

**A:** molecule in ground state.

**A\*:** molecule in excited state.

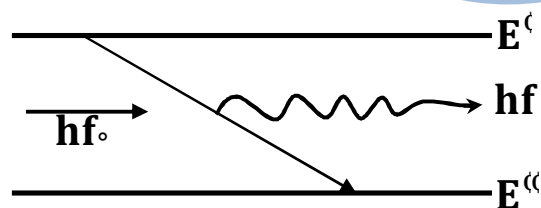
**hf<sub>0</sub>:** The energy of incident light or photon.

**Raman scattering occurs when the collision is inelastic.**

$$1- hf_0 + A^* \text{ (R)} \quad hf + A \quad f > f_0$$

$$hf_0 + E^c = hf + E^{\alpha}$$

$$f - f_0 = \frac{E^c - E^{\alpha}}{h} \quad (\text{anti stocks})$$

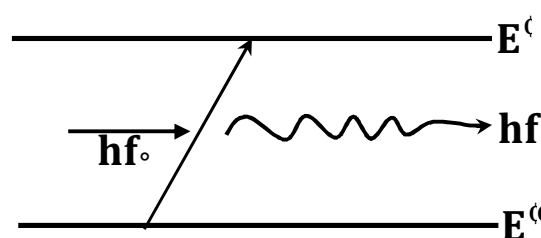


اي انه الجزيئة في حالة تهيج  $E^c$  يسقط عليها فوتون بطاقة  $hf_0$  فعندما تعود الى  $E^{\alpha}$  يكون التردد والطاقة من  $hf_0$  مضافا له فرق الطاقة بين  $E^c$  و  $E^{\alpha}$ .

$$2- \quad hf_0 + A^{\circ} \rightarrow A^* + hf \quad f < f_0$$

$$hf_0 + E^{\alpha} = hf + E^c$$

$$f - f_0 = -\frac{E^c - E^{\alpha}}{h} \quad (\text{stocks})$$



### Selecting rule for Raman scattering:-

$$R_{mn} = \int \varphi_m^* \mu \varphi_n d\tau$$

$$\mu = \alpha E = \alpha E_0 \sin 2\pi F_0 t$$

$$R = (E_0 \int \varphi_m^* \alpha \varphi_n d\tau) \sin 2\pi F_0 t$$

$$R_{mn} = E_0 \int \varphi_m^* \alpha \varphi_n d\tau$$

#### For rotation

$X_F, Y_F, Z_F$  specified axis.

$X, Y, Z$  fixed to the molecule.

Let us consider are component of the electric field

$Z_F$  axis

$$E_X = E_{Z_F} \cos(X, Z_F).$$

$$E_Y = E_{Z_F} \cos(Y, Z_F).$$

$$E_Z = E_{Z_F} \cos(Z, Z_F).$$

Since  $x, y, z$  are axis's of symmetry then

$$\mu_x = \alpha_x E_x, \quad \mu_y = \alpha_y E_y, \quad \mu_z = \alpha_z E_z$$

$$\begin{aligned} \mu_{Z_F} &= \mu_x \cos(X, Z_F) + \mu_y \cos(Y, Z_F) + \mu_z \cos(Z, Z_F) \\ &= \alpha_x E_{Z_F} \cos^2(X, Z_F) + \alpha_y E_{Z_F} \cos^2(Y, Z_F) + \alpha_z E_{Z_F} \cos^2(Z, Z_F) \quad (1) \end{aligned}$$

But  $\alpha_x = \alpha_y$  ----- (2) (symmetry)

$$\therefore \cos^2(X, Z_F) + \cos^2(Y, Z_F) + \cos^2(Z, Z_F) = 1 \text{ --- --- (3)}$$

Let  $\angle(Z, Z_F) = \theta$

\ From eq. 1,2 and 3 we get

$$\mu_{Z_F} = \{\alpha_x [\cos^2(X, Z_F) + \cos^2(Y, Z_F)] + \alpha_z \cos^2 \theta\} E_{Z_F}$$

**OR**

$$\mu_{Z_F} = \{\alpha_x [1 - \cos^2 \theta] + \alpha_z \cos^2 \theta\} E_{Z_F}$$

$$\mu_{Z_F} = \{\alpha_x + (\alpha_z - \alpha_x) \cos^2 \theta\} E_{Z_F}$$

$$\therefore \mu_{Z_F} = \alpha_{Z_F} E_{Z_F}$$

**Where**

$$\alpha_{Z_F} = \alpha_x + (\alpha_z - \alpha_x) \cos^2 \theta$$

$$R_{nm} = E_{Z_F} \int \varphi_n^* \alpha_{Z_F} \varphi_m d\tau$$

$$(\mathbf{R}_{z_f})_{J'\mu', J''\mu''} = \mathbf{E}_{Z_F} \int \mathbf{Y}_{J'\mu'}^* \{ \alpha_x + (\alpha_z - \alpha_x) \cos^2 \theta \} \mathbf{Y}_{J''\mu''} d\tau$$

$$Y = \theta \phi$$

$$\therefore R = \left\{ \alpha_x \int \mathbf{Y}_{J'\mu'}^* \mathbf{Y}_{J''\mu''} d\tau + (\alpha_z - \alpha_x) \int \mathbf{Y}_{J'\mu'}^* \cos^2 \theta \mathbf{Y}_{J''\mu''} d\tau \right\}$$

$$\mathbf{R}_{z_f} \neq 0 \text{ When } \Delta J = 0, \Delta J = \pm 2$$

$$\Delta F = \frac{\Delta E}{h} = F(J') - F(J'')$$

$$\Delta F = B_v J^c (J^c + 1) - D_e^c J^{c2} (J^c + 1)^2 - B_v^\alpha J^\alpha (J^\alpha + 1) - D_e^\alpha J^{\alpha 2} (J^\alpha + 1)^2$$

For pure rotational transition  $\nu^c = \nu^\alpha$

$$\text{We } B_{\nu^c} = B_{\nu^\alpha}$$

$$\text{For } \Delta J = \pm 2 \rightarrow J^c = J^\alpha + 2$$

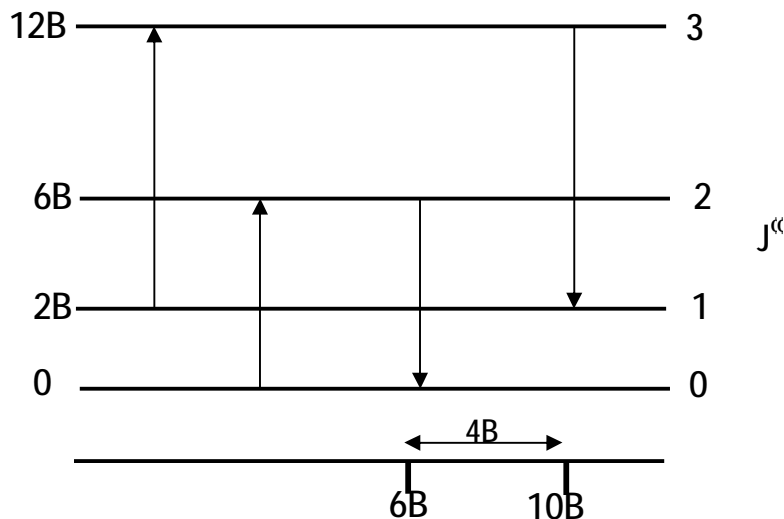
$$\Delta F = \left\{ (4B_v - 6D_e) - 8D_e^c \left( J^\alpha + \frac{3}{2} \right) \right\} \left( J^\alpha + \frac{3}{2} \right)$$

Ignoring  $D_e^c$

$$\therefore \text{Raman shift or Raman line } \Delta F = B_v (4J^\alpha + 6)$$

$$J^\alpha = 0, 1, 2, 3, \dots$$

$$\Delta F = 6B_v, 10B_v, 14B_v, \dots$$





For vibration Raman selection rules  $\Delta v=0,\pm 1$

### Example(1):-

Irradiation of carbon tetrachloride by 4358°A radiation gives Raman lines of 4400, 4419, and 4447 °A Calculate the Raman shift for each of these lines.

### Solution:-

$$\text{Frequency of the exciting line } \nu^{\circ} = \frac{1}{\lambda^{\circ}} = \frac{10^8}{4358} \text{ cm}^{-1}$$

$$\text{Raman shift of 4400 °A line} = \frac{10^8}{4358} - \frac{10^8}{4400} = 219 \text{ cm}^{-1}$$

$$\text{Raman shift of , 4419 °A line} = \frac{10^8}{4358} - \frac{10^8}{4419} = 316.8 \text{ cm}^{-1}$$

$$\text{Raman shift of 4447 °A line} = \frac{10^8}{4358} - \frac{10^8}{4447} = 459.2 \text{ cm}^{-1}$$

### H.W.(1):-

The Raman line associated with a vibrational mode which is both Raman and infrared actives is found at 4600 °A when excited by light of wave length 4358 °A calculate the wave length of the corresponding infrared band.

### Solution:-

$$\text{Frequency of the exciting line } \nu^{\circ} = \frac{1}{\lambda^{\circ}} = \frac{10^8}{4358} \text{ cm}^{-1}$$

$$\nu^{\circ} - \nu_m^{\circ} \text{ or } \nu^{\circ} - \nu = \frac{10^8}{4600} \text{ cm}^{-1}$$

$$\nu_m^{\circ} = \frac{10^8}{4358} - \frac{10^8}{4600} = 1207.2 \text{ cm}^{-1}$$

$$\lambda_m = \frac{1}{1207.2} = \mathbf{0.00082838 \text{ cm} = 82838^\circ\text{A}}$$

Since the mode is active in both infrared and Raman , the wave length of the corresponding infrared band is 82838<sup>o</sup>A.

### Example(2):-

If the band length of H<sub>2</sub> is 0.07417nm , what would be the position of the first three rotational Raman lines in the spectrum ? What is the effect of nuclear spin on the spectrum? (H' = 1.673x10<sup>-27</sup> Kg).

### Solution:-

$$\mu \text{ of the H}_2 \text{ molecule} = \frac{(1.673 \times 10^{-27})}{2} = \mathbf{0.8365 \times 10^{-27} \text{ Kg}}$$

$$\mathbf{B} = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c}$$

$$B = \frac{6.625 \times 10^{-34}}{8\pi^2 \times 0.8365 \times 10^{-27} \times (0.07417 \times 10^{-9})^2 \times 3 \times 10^8} = \mathbf{60.78 \text{ cm}^{-1}}$$

The first three lines are at  $\nu = 6B, 10B, 14B$

$$\nu = 364.73, 607, 89, 851.01 \text{ cm}^{-1}$$

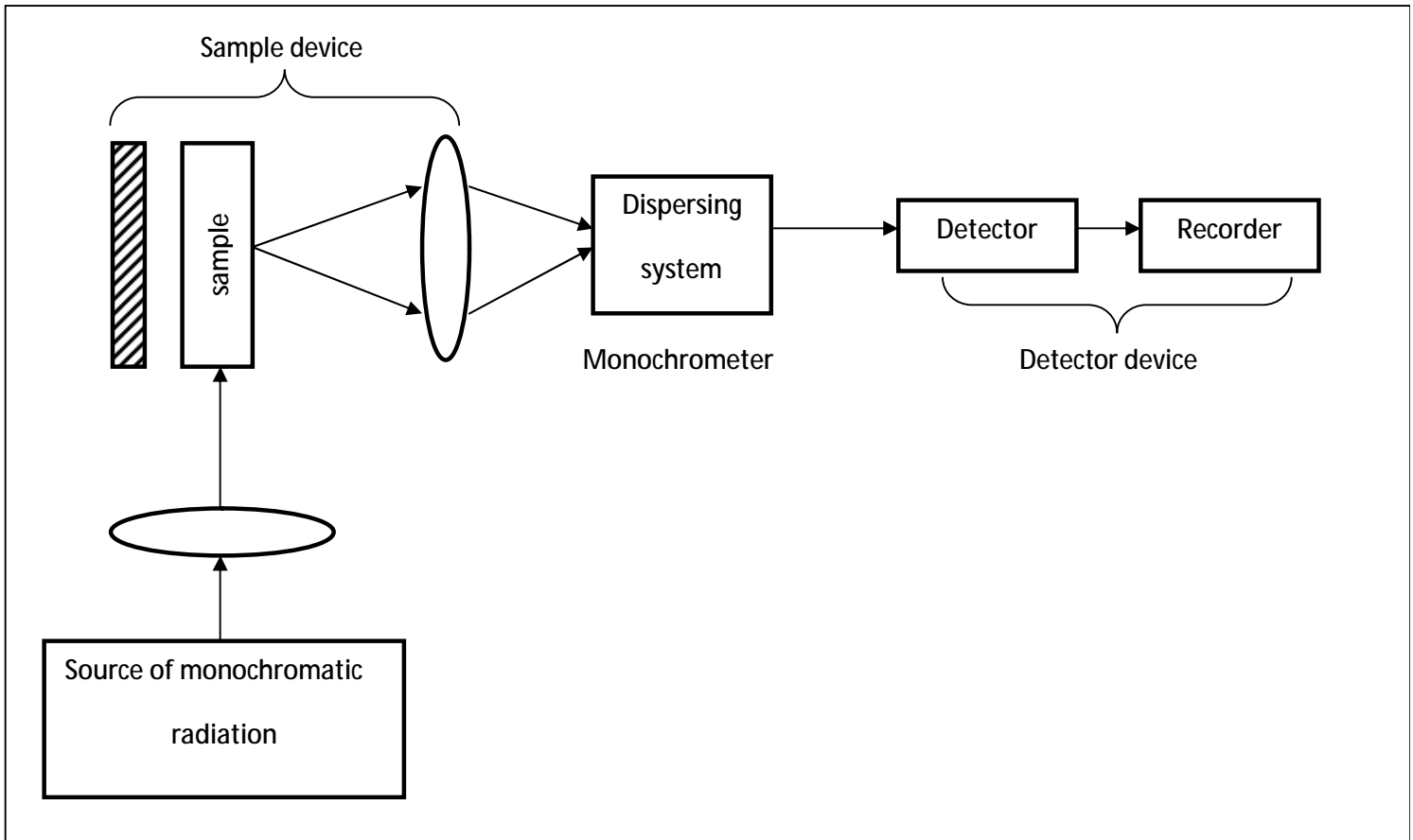
### H.W.(2):-

The first three rotational Raman lines of linear tri atomic molecules are at 4.80 , 8.14 and 11.36  $\text{cm}^{-1}$  from the exciting Raman line Estimate the rotational constant B and the moment of inertia of the molecule.

## Raman spectrometer:-

### 1- Source

- The first Raman spectrum of an organic compound was observed using sun as the source a telescope as the receiver and human eye as the detector.
- In the pre-laser days the commonly used sources were the 4358 nm (blue) and 253.6 nm (uv) emission lines of mercury vapor  
But many disadvantages for this source:-
  - i. The source is excited and the brightness is very small.
  - ii. The mercury radiation often causes the sample to fluoresce making very weak Raman lines undetected.
  - iii. In colored samples get absorbed in this high Frequency it is not possible to record their spectra.
- The highly directional and intense laser allows one to record the spectrum down up to  $10\text{ cm}^{-1}$  from the exciting line He-Ne laser ( 632.8 nm ) and argon ion laser ( 488 and 514.5nm) krypton laser 647.1nm and red radiation is preferred to reduce fluorescence.



The Schematics of Raman spectrometer

## 2- Sample device:-

A laser beam may be focused to produce a beam of much smaller diameter beam extends over a short length before beginning to again , the region in which the beam is most is caused focal cylinder whose diameter  $D$  and length  $L$  are given by

$$D = \frac{4\lambda f}{\pi d} \quad , \quad L = \frac{16\lambda f^2}{\pi d^2}$$

$\lambda$ : –wave length of radiation

$d$ :- diameter of the unfocussed laser beam .

f:- focal length of lens .

The vacuum of the focal cylinder is about  $10^{-5}$  cm<sup>3</sup>.Hg the of the focused beam is about  $10^{-3}$  times the area of the unfocussed beam is not used. In most cases the sample is placed outside laser cavity .

L<sub>1</sub> focuses laser to sample.

L<sub>2</sub> collects the scattered radiation to dispersing system.

### **3- Monochrometer:-**

Allows only a narrow wave number band to reach the detector at a time the most important property of any monochrometer is its spectral purity.

To distinguish the narrow wave number band  $\nu' \pm d\nu'$  this property depend on some factors like resolving power dispersion , slit width.

### **4- Detection device:-**

The dispersed radiation is detected photoelectrical the exit slit allows only a narrow band to reach the photo multiplier tube and the rotation grating allows the successive bands to reach the detector.

The photo of multiplier is cooled to reduce the noise.

The efficiency has 4000-8000°A.