∴ Rotational Raman Spectra :-

* (2). Symmetric Top molecules :-

Rotation about top axis in symmetric top molecules produce no change in polarizability but it changes during end-over-end rotation. Then the energy levels -

$$E_{J,K} = BJ(J+1) + (A-B)K^2 \ cm^{-1}.$$

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

$K = \pm J, \pm(J-1), \ldots\ldots$

where K is rotational quantum number. So, $\Delta K = 0$ implies that changes in the angular momen about the top axis will not give rise to Raman spectrum i.e. such rotations are Raman inactive. the selection rule $\Delta J = \pm 2$ for $K=0$ means that ΔJ cannot be ± 1 for transitions involving the ground state is $J=0$. Thus for all J values other than zero and $J = \pm 1$ transitions are allowed.

(1). $\Delta J = +1$ (R-branch line) -

$$\Delta E_R = E_{J'=J+1} - E_{J''=J}$$

Now putting the value in above expression. we get -

$$\Delta E_R = B(J+1)(J+2) - BJ(J+1)$$
$$\Delta E_R = (BJ+B)(J+2) - BJ(J+1)$$
$$\Delta E_R = BJ^2 + 2BJ + BJ + 2B - BJ^2 - BJ$$
$$\Delta E_R = 2BJ + 2B$$
$$\Delta E_R = B(2J+2)$$
$$\boxed{\Delta E_R = 2B(J+1) \ cm^{-1}}$$

where, $J = 0, 1, 2, 3, \ldots\ldots$ (but $J \neq 0$)

(2). $\Delta J = +2$ (S-branch line) :-

$$\Delta E_S = E_{J'} = J+2 - E_{J''} = J$$

$$\Delta E_S = B(J+2)(J+3) - BJ(J+1)$$

$$\Delta E_S = (BJ + 2B)(J+3) - BJ(J+1)$$

$$\Delta E_S = BJ^2 + 3BJ + 2BJ + 6B - BJ(J+1)$$

$$\Delta E_S = BJ^2 + 3BJ + 2BJ + 6B - BJ^2 - BJ$$

$$\Delta E_S = 4BJ + 6B$$

$$\boxed{\Delta E_S = B(4J+6)\ cm^{-1}}$$

where,

$J = 0, 1, 2, 3 \ldots\ldots$

Thus we have two series of lines in the Raman spectrum.

$$\bar{\nu}_R = \bar{\nu}_{ex} \pm \Delta E_R$$

$$\bar{\nu}_R = \bar{\nu}_{ex} \pm 2B(J+1)\ cm^{-1} \qquad \text{(R-Branch)}$$

$J = 1, 2, 3 \ldots\ldots$

$$\bar{\nu}_S = \bar{\nu}_{ex} \pm \Delta E_S$$

$$\bar{\nu}_S = \bar{\nu}_{ex} \pm B(4J+6)\ cm^{-1} \qquad \text{(S-Branch)}$$

$J = 0, 1, 2, 3 \ldots\ldots$

* (3). Asymmetric Top molecules :-

The polarizability ellipsoid for spherical top molecules is a spherical surface and it is evident that rotation of this ellipsoid will produce no change in polarizability. Therefore the pure rotation of spherical top molecules are completly inactive in Raman.

for example — CH_4, SiH_4, etc .....

On the other hand all rotations of asymmetric top molecules are Raman active. Thus their Raman spectra are complicated.

* Application of Pure Rotational Raman Spectra :-

The pure rotational Raman spectra provides the value B. Thus the moment of inertia and bond length of the molecule can be determined.

Homo nuclear diatomic molecules do not exhibit pure vibrational or Rotational spectra as they possesses no dipole moment But they do exhibit rotational Raman spectra and hence structural parametres which can not be determined by pure rotational spectra can be determined from the Raman spectra.