* Pure Rotational Raman Spectra :—

* (1). Linear Molecules :—

The rotational energy levels for linear molecules
$= BJ(J+1) - DJ^2(J+1)^2 + \ldots\ldots\ldots \ cm^{-1}.$

now ignoring the centrifugal distortion constant.
(since, Raman spectra does not measure 'D' term with precision).

$E_J = BJ(J+1) \ cm^{-1}.$

Selection rule for the transition between these energy levels is —

$\Delta J = 0$ or ± 2.

Rotational quantum no. in Raman Spectroscopy changes the two units rather than one due to the symmetry of polarizability ellipsoid.

$\Delta J = 0$ Rayleigh line.

(since there is no change in molecular energy).

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

$\Delta E = B(J+2)(J+3) - BJ(J+1)\ cm^{-1}$.

$\Delta E = (BJ+2B)(J+3) - BJ(J+1)\ cm^{-1}$.

$\Delta E = BJ^2 + 3BJ + 2BJ + 6B - BJ^2 - BJ\ cm^{-1}$

$\Delta E = 4BJ + 6B\ cm^{-1}$

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

$\Delta J = +2$, represents the S-branch line.

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

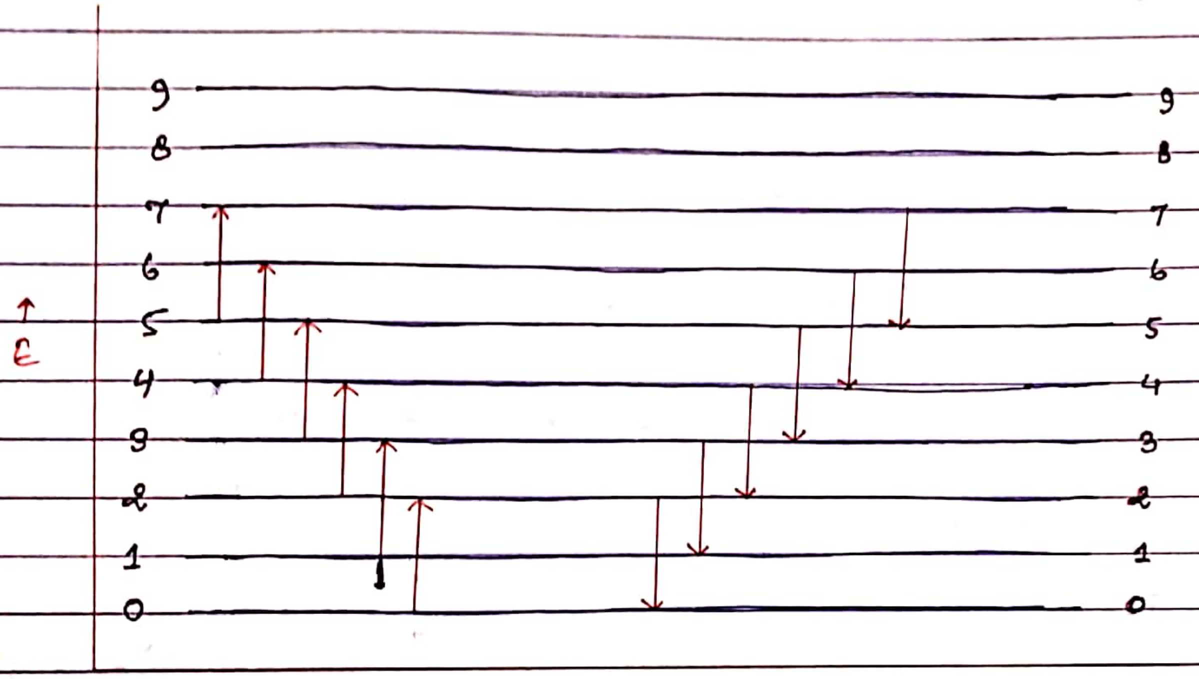
So, if a molecule gains rotational energy from their proton then a source of S-branch lines appear to the low wave number side to the exciting line. (Stoke's line) and if the molecule looses energy to the proton, the line appear to the high wave number side to the exciting line (anti-Stoke's line).

So, the wave number of corresponding spectral lines are given by—

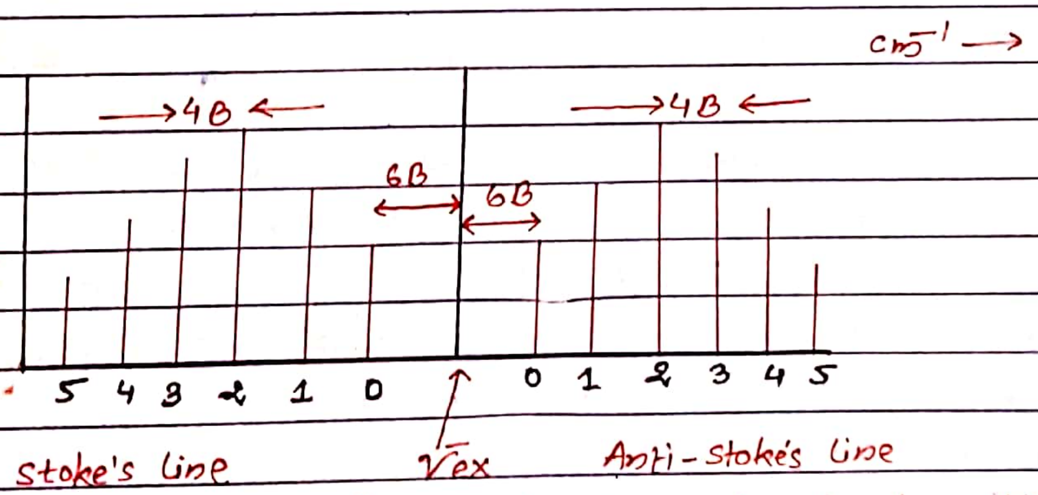
$\bar{\nu}_S = \bar{\nu}_{ex} \pm \Delta E_S$

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

where. the '+' sign refers to anti-stoke's line and the '–' sign to stoke's line.
& $\bar{\nu}_{ex}$ is the wave number of the exciting radiation.



—: Rotational energy level of a diatomic molecule :—



—: Rotational Raman Spectrum due to transitions :—

NOTE → Separation of the first line from the exciting line is $6B\ cm^{-1}$. while the separation between the successive line is $4B\ cm^{-1}$.