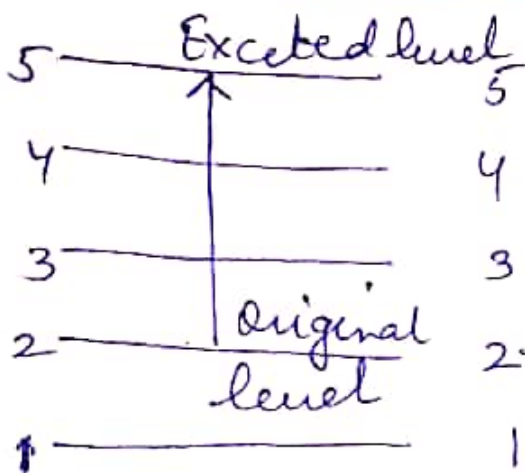


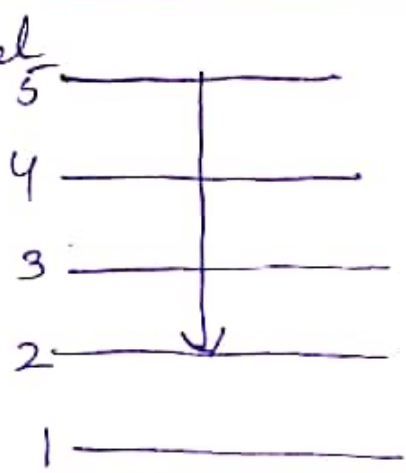
Raman Spectra

- When a substance, gaseous liquid or solid is irradiated with monochromatic light of a definite frequency ν , the light scattered at right angle to the incident light contained lines not only of the incident frequency but also of lower frequency and sometimes of higher frequency.
- The lines with lower frequency are called Stokes's lines.
- Lines with higher frequency are called anti Stokes's lines.
- Line with the same frequency as the incident ray of light is called Rayleigh line.
- The frequency difference of incident light and scattered line is constant depending upon the nature of the substance.
- If ν_i is the frequency of the incident light and ν_s that of a particular scattered line the difference $\Delta\nu = \nu_i - \nu_s$ is called Raman frequency or Raman shift.
- The frequencies are particular for a particular substance.

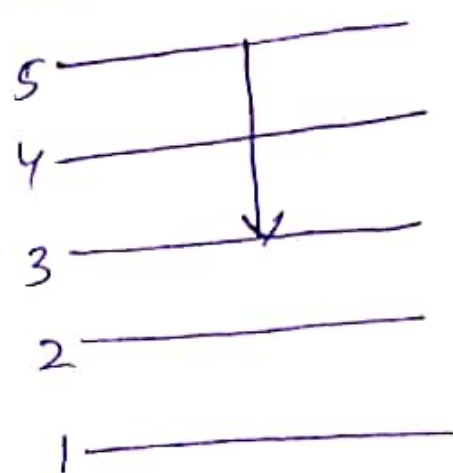
Explanation of Rayleigh's line, Stokes's lines and anti Stokes's lines in Raman spectra



Energy absorbed by molecule

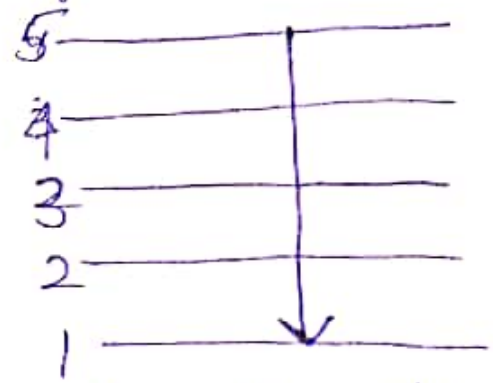


Rayleigh scattering



Formation of Stokes's lines

When a photon is incident on the molecule the energy is absorbed by molecule and it goes excited to higher energy level.



Formation of anti Stokes's line

- when if photon emit some energy as absorbed then Rayleigh & scattering.

- The excited ~~energy~~ molecule returns to a level higher than original level, hence emitting less energy than absorbed, they are Stokes's line.

- The excited molecule return to level lower than than original. More energy is emitted than absorb. Thus anti Stokes's lines appear.

(3)

Pure rotational Raman spectra expected for diatomic molecule:

Selection rule for pure rotational Raman spectra of diatomic molecule are

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

For Rayleigh ~~line~~ scattering $\Delta J = 0$,

$\Delta J = \pm 2$ for Raman lines.

Energy of a rotational level with quantum number J is

$$\bar{\nu} = BJ(J+1)$$

For transition from lower rotational level with quantum number J to a higher rotational level with quantum number $(J+1)$ energy absorbed will be

$$\Delta \bar{\nu} = BJ'(J'+1) - BJ(J+1)$$

For selection rule $\Delta J = +2$ $J' - J = 2$

$$\begin{aligned} \Delta \bar{\nu} &= B(J+2)(J+3) - BJ(J+1) \\ &= B(4J+6), \quad J \neq 0, 1, 2, 3 \end{aligned}$$

S.R $\Delta J = -2$ $J' - J = -2$

$$\begin{aligned} \Delta \bar{\nu} &= BJ'(J'+1) - B(J'+2)(J'+3) \\ &= -B(4J'+6) \quad J' = 0, 1, 2, 3 \end{aligned}$$

$$\bar{\nu} = \bar{\nu}_i \pm \Delta \bar{\nu}$$

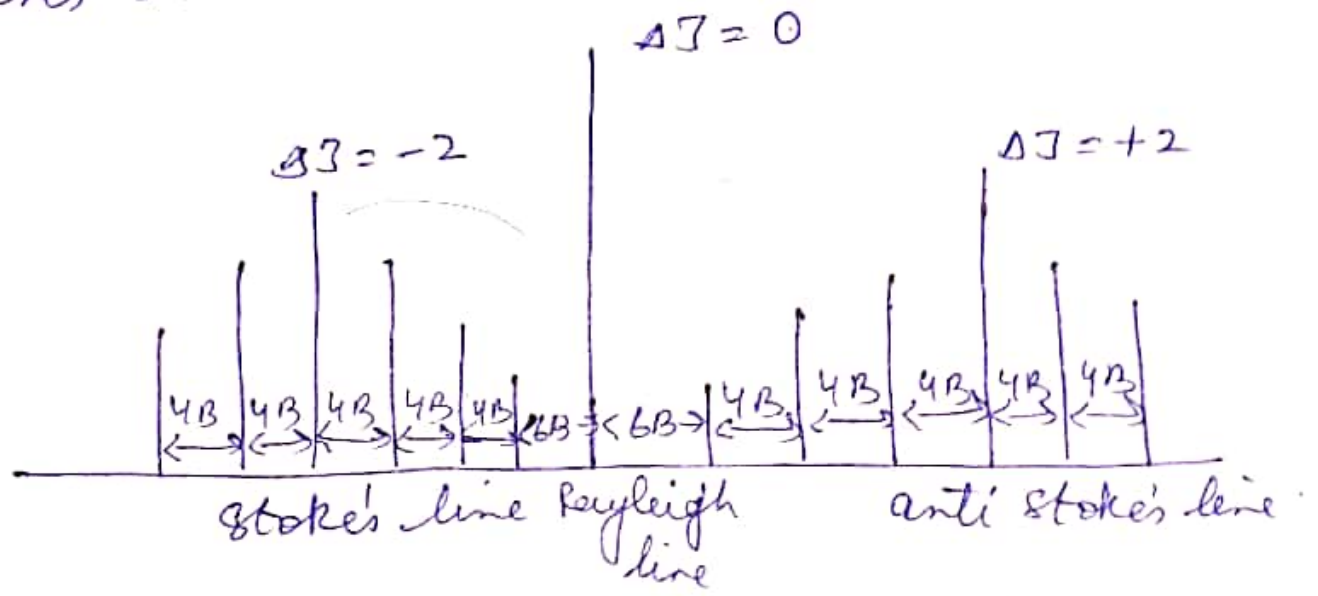
$$\boxed{\bar{\nu} = \bar{\nu}_i \pm B(4J+6)}$$

$\bar{\nu}_i$ = Rayleigh line wave number.
 + sign represent anti stokes line
 - sign represent stokes line

$J=0, \quad \bar{\nu} = \bar{\nu}_i + 6B$ — first stoke and anti stoke line

lines will be at $6B$ separation from Rayleigh line $J=1, 2, 3 \dots$

The distance between two adjacent stokes lines or anti stokes lines will be $4B$.



Rotational-Vibrational Raman spectra of Diatomic molecules

The diatomic gaseous molecules give rotational vibrational Raman spectra

Selection rule $\Delta v = \pm 1$
 $\Delta J = 0, \pm 2$

At room temp, molecules are at lowest vibrational level ($v=0$) fundamental transition is from $v=0$ to $v=1$

$\Delta J = 0, \Delta \bar{\nu} = \omega_e(1 - 2x_e)$ Q Branch

$\Delta J = +2, \Delta \bar{\nu} = \omega_e(1 - x_e) + B(4J + 6)$

S Branch

$\Delta J = -2, \Delta \bar{\nu} = \omega_e(1 - 2x_e) - B(4J + 6)$

O Branch

$\Delta \bar{\nu}_0, \Delta \bar{\nu}_S \text{ \& } \Delta \bar{\nu}_Q$ wave number of exciting radiation by $\bar{\nu}_i$, the wave numbers of the Stokes line will be.

$\bar{\nu}_Q = \bar{\nu}_i - \Delta \bar{\nu}_Q; \bar{\nu}_S = \bar{\nu}_i - \Delta \bar{\nu}_S$

$\bar{\nu}_0 = \bar{\nu}_i - \Delta \bar{\nu}_0$

$\Delta \nu = +1$ for Stokes line

$\Delta \nu = -1$ for anti Stokes line

$\nu = 0$ to $\nu = 1$ rotational vibrational Raman spectrum

