

# Raman Spectroscopy.

# Energy source used in Raman Spectroscopy.

**LASER**

# Scattering -

① Elastic collision - (no change in ene. after collision).

Stream of particles (photon)  $\rightarrow$

$(E)$   
 $(h\nu)$

$\bigcirc$   
molecule.

No change in energy  $(E)$ .

$\Rightarrow$  Rayleigh Scattering.

② Inelastic collision - (change in ene. after collision)  
(may decrease or increase)

$\Rightarrow$  Raman Scattering.

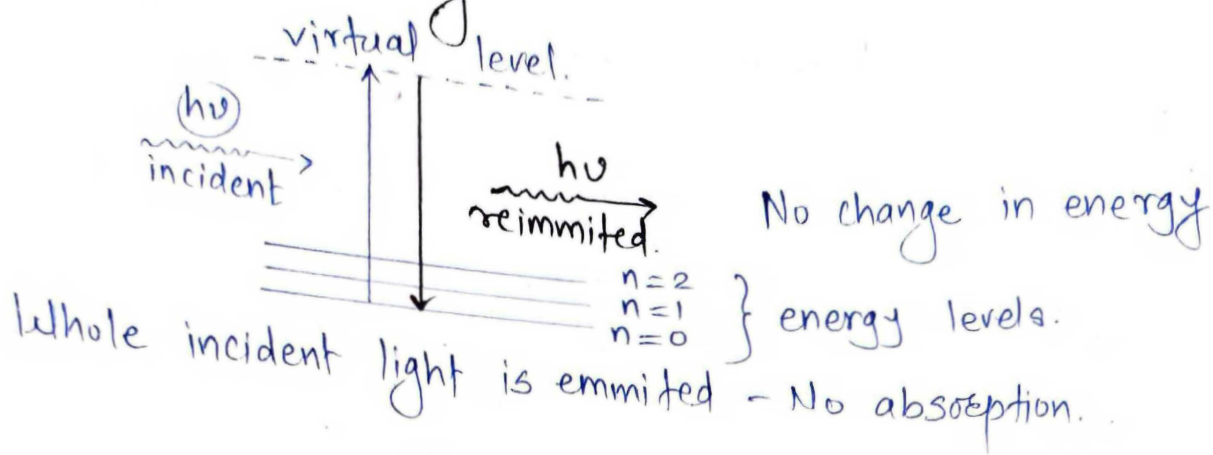
Stokes lines

$(\nu < \text{Rayleigh})$

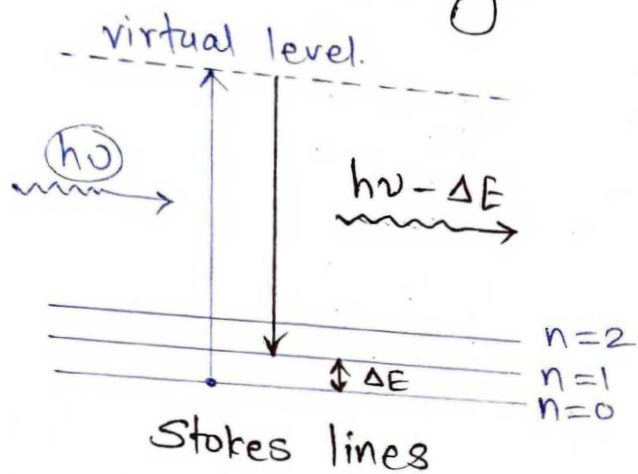
Anti-stokes lines.

$(\nu > \text{Rayleigh})$

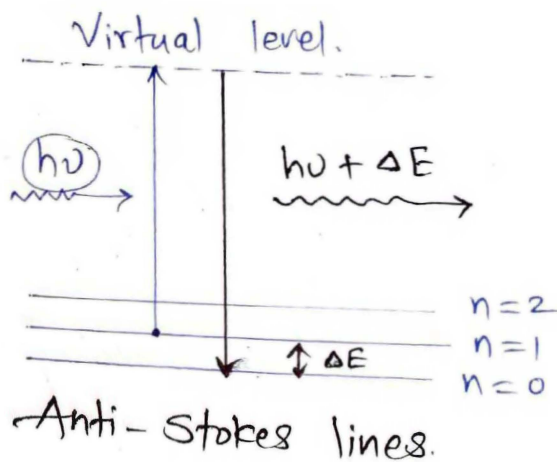
# # Rayleigh Scattering -



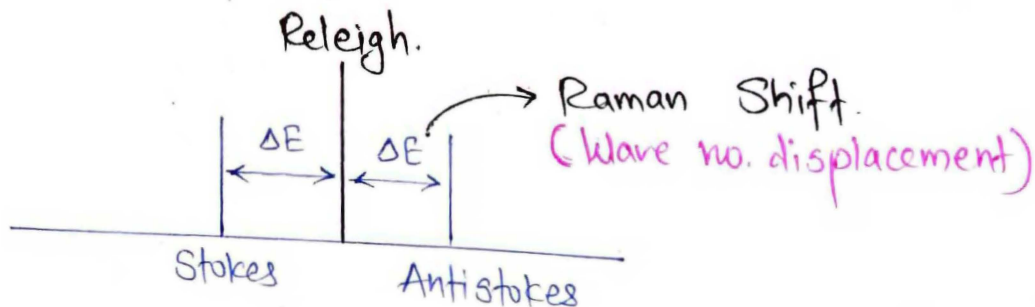
# # Raman Scattering -



Energy of molecule increases.  
Energy of incident radiation decreases.



Energy of molecule decreases.  
Energy of incident radiation increases.



Order of energy -  $AS > R > S$

wave length -  $S > R > AS$

# These three cases are for same molecule.

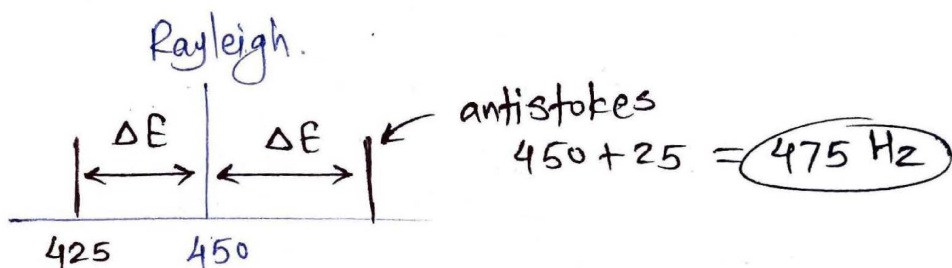
By change in the incident radiation, there will be no change in wave number displacement.

i.e.  $\Delta E$  must remain constant, irrespective of  $(h\nu)$ .

Ex. Que. At frequency  $450 \text{ Hz}$  of incident radiation, there is a Stokes line at  $425 \text{ Hz}$ .

What should be value of anti-Stokes line if freq. of incident radiation is  $550 \text{ Hz}$ .

Ans. -



$$\Delta E = 450 - 425 = 25$$

Ans - 475 Hz

# Units -

$$E = h\nu$$

Joules                  Hz or  $s^{-1}$

$$E = h \frac{c}{\lambda}$$

$$c = \text{ms}^{-1} \text{ or } \text{cm s}^{-1}$$

$$\lambda = \text{cm or m or nm or } \text{Å}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

$$= \frac{1}{\text{cm}}$$

$$\bar{\nu} = \text{cm}^{-1}$$

↑  
wave number.

$$E = h\nu = h \frac{c}{\lambda} = hc\bar{\nu}$$

#

$$E = h\nu = h \cdot \frac{c}{\lambda} = hc\bar{\nu}$$

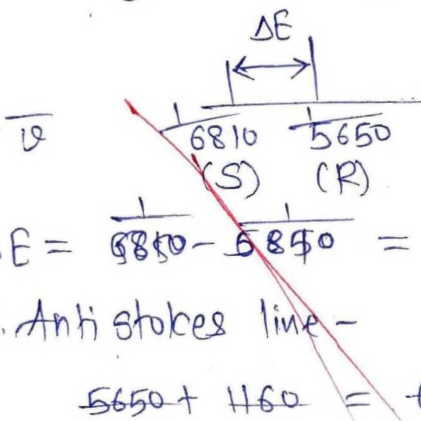
$$E \propto \nu \propto c \propto \bar{\nu}$$

$$E \propto \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

Que. The exciting line in an exp. is  $5650 \text{ \AA}$  and Stokes line is  $6810 \text{ \AA}$ . Calculate wavelength of anti-stokes line.  $5810$  (Ans.  $5498.5 \text{ \AA}$ )

Ans. (Exciting line  $\equiv$  Rayleigh salt. value.)



$$\Delta E = \frac{1}{6810} - \frac{1}{5650} = 1160 \text{ \AA} \cdot \frac{6810 - 5650}{6810 \times 5650} \text{ \AA}^{-1}$$

$\therefore$  Anti Stokes line -

$$5650 + 1160 = 6810$$

$$\frac{1}{5650} + \frac{6810 - 5650}{6810 \times 5650} = \frac{6810 + 1160}{5650 \times 6810} = \frac{6970}{5650 \times 6810}$$

$$\text{wavelength} = \frac{5650 \times 6810}{6970}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

Rayleigh line -  $\lambda_R = 5650 \text{ \AA}$

$$\bar{\nu}_R = \frac{1}{\lambda} = \frac{1}{5650 \text{ \AA}} = \frac{1}{5650 \times 10^{-8} \text{ cm}} = \frac{10^8}{5650} \text{ cm}^{-1}$$

Stokes line -  $\lambda_S = 6810 \text{ \AA}$

$$\bar{\nu}_S = \frac{1}{\lambda} = \frac{10^8}{6810} \text{ cm}^{-1}$$

$$\Delta E = \bar{\nu}_R - \bar{\nu}_S = \left[ \frac{10^8}{5650} - \frac{10^8}{6810} \right] \text{ cm}^{-1}$$

$$\text{Anti Stokes line} = \bar{\nu}_R + \Delta E = \left( \frac{10^8}{5650} + \frac{10^8}{6810} - \frac{10^8}{6810} \right)$$

Ans. -

$$\text{For exciting line, } \bar{\nu}_R = \frac{1}{5650 \times 10^{-8} \text{ cm}} \\ = 17699.1 \text{ cm}^{-1}$$

$$\text{For Stokes line, } \bar{\nu}_S = \frac{1}{5810 \times 10^{-8} \text{ cm}} \\ = 17211.7 \text{ cm}^{-1}$$

$$\text{Displacement } \Delta \bar{\nu} = 17699.1 - 17211.7 \\ = 487.4 \text{ cm}^{-1}$$

$$\text{Wave no. of antistokes line} = \bar{\nu}_R + \Delta \bar{\nu} \\ = 17699.1 + 487.4 \\ = 18186.5 \text{ cm}^{-1}$$

$$\text{Corresponding } \lambda = \frac{1}{18186.5} = 5498.5 \times 10^{-8} \text{ cm}$$

$$\lambda = 5498.5 \text{ \AA}$$

Que. When a substance is irradiated with  $4365 \text{ \AA}$  line, a raman line attributed to the symmetrical stretching vibration is found at  $4814 \text{ \AA}$ . Calculate the fundamental frequency for the vibration  
( $\text{A} = 6.41 \times 10^{13} \text{ Hz}$ )

Ans -

$$\text{Exciting line, } \bar{\nu} = \frac{1}{4365 \times 10^{-8}} = 22909.5 \text{ cm}^{-1}$$

$$\text{Wave no. of Raman line} = \frac{1}{4814 \times 10^{-8}} = 20772.7 \text{ cm}^{-1}$$

$$\text{Displacement, } \Delta \bar{\nu} = 22909.5 - 20772.7 \\ = 2136.8 \text{ cm}^{-1}$$

$$\text{Corresponding frequency} = 2136.8 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm s}^{-1} \\ = 6.41 \times 10^{13} \text{ s}^{-1} \\ = 6.41 \times 10^{13} \text{ Hz}$$

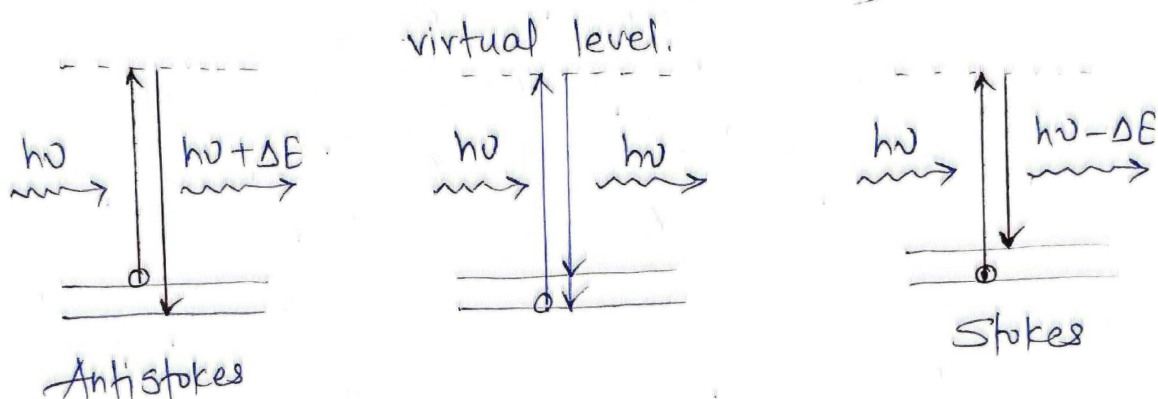
# # Rotational Raman Spectroscopy -

$$E = BJ(J+1)$$

Selection rule = 0,  $\pm 2$

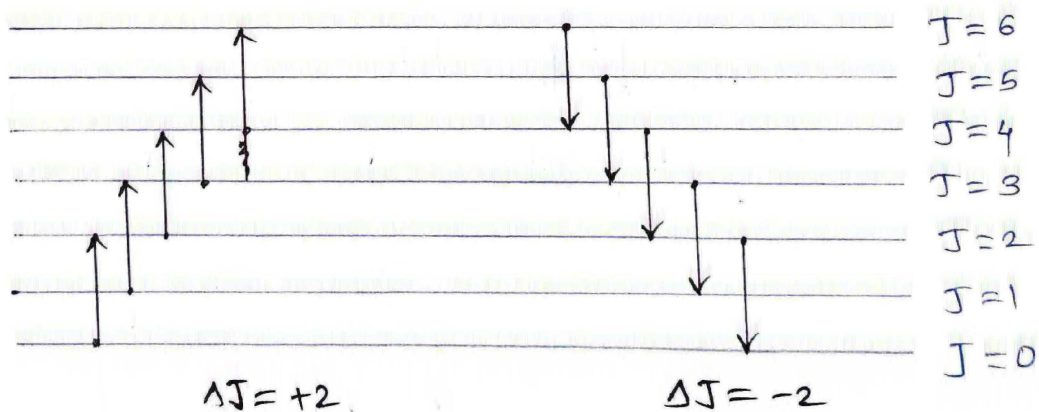
(# By absorption of energy, molecule goes to the excited state.

This doesn't mean it jumps up  $\rightarrow$  goes to higher level. This means molecules starts rotating faster and also faster vibrations than before.)



# Selection rule -

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



$\Delta J = 0$   $\Rightarrow$  Rayleigh line.   
 consider.

#  $\Delta J = +2$

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

$$= B(J+2)(J+2+1) - BJ(J+1)$$

$$= B[(J+2)(J+3) - J(J+1)]$$

$$= B[J^2 + 2J + 3J + 6 - J^2 - J]$$

$$\Delta E = B[4J + 6]$$

#

Transition -

$0 \rightarrow 2$	$\Delta E = 6B$	$\leftarrow$	$4B$	} difference
$1 \rightarrow 3$	$\Delta E = 10B$	$\leftarrow$	$4B$	
$2 \rightarrow 4$	$\Delta E = 14B$	$\leftarrow$	$4B$	
$3 \rightarrow 5$	$\Delta E = 18B$	$\leftarrow$	$4B$	

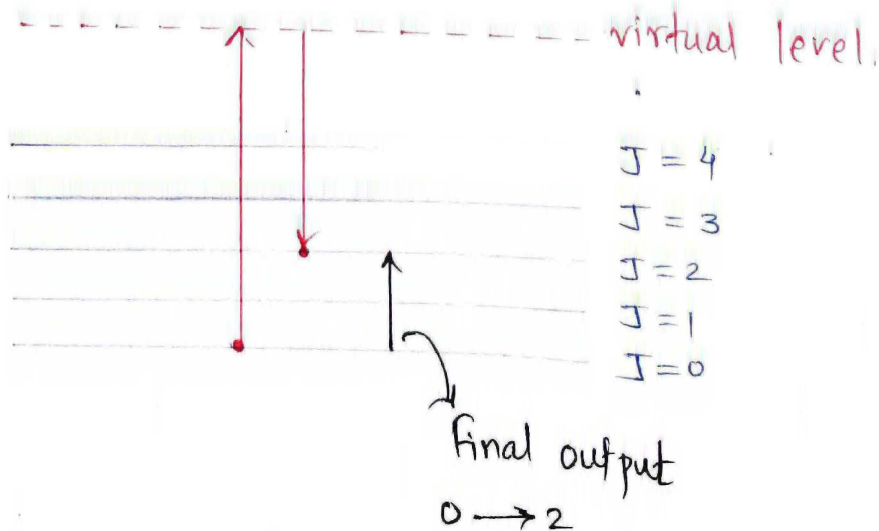
#  $\Delta J = -2$

We know that difference in Stokes lines is equal to difference in anti-stokes lines.

# Spectra -

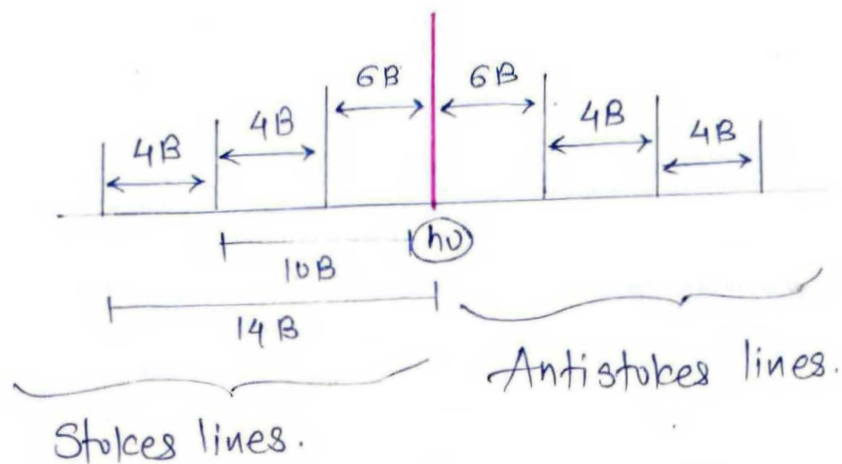
Actual meaning of transition -

$0 \rightarrow 2$





## # Spectra-



# For transition  $0 \rightarrow 2$ ,

From  $J=0$ , molecule goes to virtual level and comes back to  $J=2$ .

$\Rightarrow$  Energy of molecule increased. (absorbed)

$\Rightarrow$  This increased ~~inter~~ energy comes from photon.  
Hence, ene. of photon decreases.

$\Rightarrow$  Stokes line.

$$h\nu - \Delta E$$

# For transition  $2 \rightarrow 0$ ,

From  $J=2$ , molecule goes to virtual level and comes back to  $J=0$ .

$\Rightarrow$  Energy of molecule decreased. (released).

$\Rightarrow$  This released ene goes to the photon.

Hence, ene. of photon increases.

$$h\nu + \Delta E$$

$\Rightarrow$  Anti-Stokes line.

Que. In the Raman Spectra of triatomic molecule, the first three lines are at  $4.86, 8.14, 11.36 \text{ cm}^{-1}$ . Determine the rotational constant  $B$  and moment of inertia.

Ans. - (Raman lines  $\equiv$  Stokes & Anti-stokes lines)

Difference betn two lines in Raman spectra,  $= 4B$

$$\text{First line} = 4.86 \text{ cm}^{-1}$$

$$\text{Second line} = 8.14 \text{ cm}^{-1}$$

$$\text{Third line} = 11.36 \text{ cm}^{-1}$$

$$8.14 - 4.86 = 4B$$

$$3.28 = 4B$$

$$B = \frac{3.28}{4}$$

$$\boxed{B = 0.82 \text{ cm}^{-1}}$$

$$\text{Now, } I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34} \text{ (J s)}}{8 \times \left(\frac{4}{3}\right)^2 \times 0.82 \text{ (cm}^{-1}) \times 3 \times 10^{10} \text{ (m s}^{-1})}$$

$$= 0.1893 \times 10^{-24}$$

$$= 0.03414 \times 10^{-24} \text{ J s}^2 \times 10^7 \text{ g cm}^2$$

$$= 34.14 \times 10^{-40} \text{ g cm}^2$$

$$I = \mu r_0^2$$

$$\text{unit} - \text{g cm}^2 / \text{kg m}^2$$

Conversion -  $\text{J s}^2 \rightarrow \text{g cm}^2$

$$\text{J} \rightarrow \text{ene. (work)} = f \times d.$$

$$\hookrightarrow \text{J} = \text{mass} \times \text{acc.} \times d.$$

$$= (\text{kg}) (\text{m. s}^{-2}) (\text{m})$$

$$= \text{kg. m}^2. \text{s}^{-2}$$

$$\text{Now, } \text{J, s}^2 = \text{kg. m}^2. \cancel{\text{s}^{-2}}. \text{s}^2 = \text{kg. m}^2 = (1000 \text{g}) (100 \text{cm})^2$$

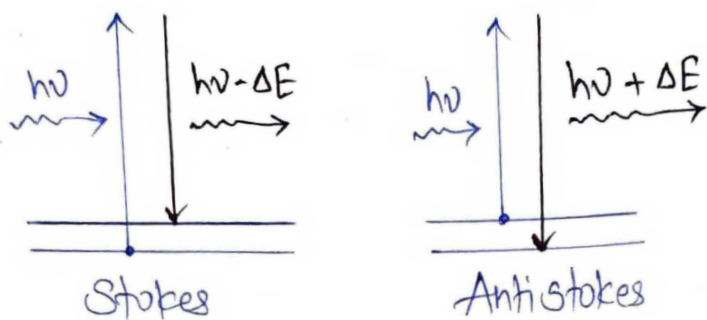
$$= 10^{3+4} \text{ g cm}^2$$



# # Vibrational Raman Spectroscopy -

$$E_v = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e$$

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



#  $v=0 \rightarrow v=1$

$$\Delta E = \bar{\omega}_e (1 - 2x_e)$$

↑ Fundamental freq

# Spectra in terms of wave number -

Wave no. for Rayleigh line =  $\bar{\nu}_0$

For Anti-Stokes lines

$$\bar{\nu}_{AS} = \bar{\nu}_0 + \bar{\omega}_e (1 - 2x_e)$$

for Stokes lines

$$\bar{\nu}_S = \bar{\nu}_0 - \bar{\omega}_e (1 - 2x_e)$$

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

+  $\Rightarrow$  AS.

-  $\Rightarrow$  S.

$\bar{\nu} = \bar{\nu}_0 \Rightarrow$  Rayleigh Scattering

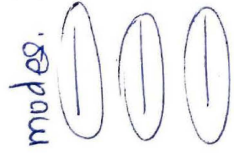
# # Rule of Mutual Exclusion Principle -

⇒ Applicable for molecules containing  $\text{CO}_2$ .

ex.  $\text{CO}_2$

\* IR active mode will be Raman Inactive  
and IR inactive mode will be Raman active.

Ex.

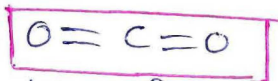


IR	Raman	IR	Raman
A	I	A	I
I	A	I	A
A	I	(A)	(A)

$\underbrace{\hspace{10em}}_{\text{CO}_2 \checkmark}$        $\underbrace{\hspace{10em}}_{\text{CO}_2 \times}$

4) Analyse the given data & identify to which molecule it belongs -  $H_2O$  or  $CO_2$ .

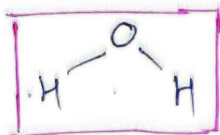
① Modes of vibration	Raman	IR
Symm. stretching	Active	Inactive
Symm. bending	Inactive	Active
Asymm. stretching	Inactive	Active



$CO_2$  has centre of symmetry.

∴ Follows rule of mutual exclusion.

② Modes of vibration	Raman	IR
Symm. stretching	A	A
Bending	A	A
Asymm. stretching	A	A



No centre of symm. present.

# Determine the structure of molecule from data given.

①  $A_2B_2$

	Raman	IR	
3374 $\text{cm}^{-1}$	strong	-	
3287 $\text{cm}^{-1}$	-	very strong	PR contour $\rightarrow$ Linear
1973 $\text{cm}^{-1}$	very strong	-	(11) $\rightarrow \Delta J = \pm 1$
729 $\text{cm}^{-1}$	-	very strong	PCR
612 $\text{cm}^{-1}$	weak	-	(1) $\rightarrow \Delta J = 0, \pm 1$

$\Rightarrow$  Rule of mutual exclusion following.  
 $\therefore$  cos present.

$\Rightarrow$  PR branch  $\Rightarrow$  Linear molecule

$\Rightarrow$  Linear molecule with cos.

$\checkmark$  A-B-B-A } Possible structures.  
 $\checkmark$  B-A-A-B }

②  $AB_2$

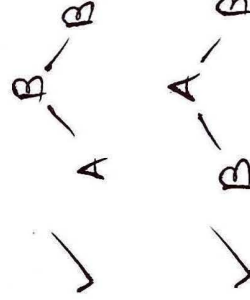
$cm^{-1}$	IR	Raman
3756	very strong	-
3652	strong parallel	strong polarised
1595	very strong	-

⇒ Rule of mutual exclusion not followed.  
COs absent.

⇒ Non-linear molecule.

Since, PR, ~~PR~~ Branches not mentioned.

⇒ Non-linear molecule without COs.



} Possible structures.