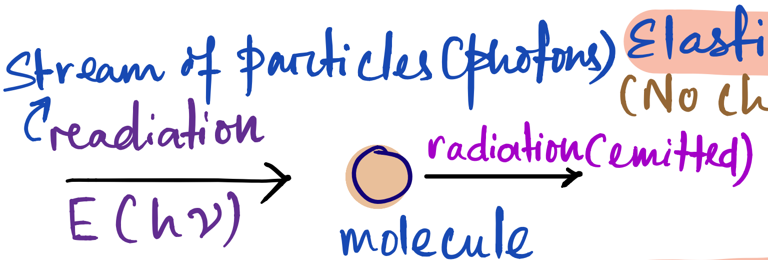
Raman Spectroscopy

Energy Source = LASER

Scattering :-

(Rayleigh Scattering)

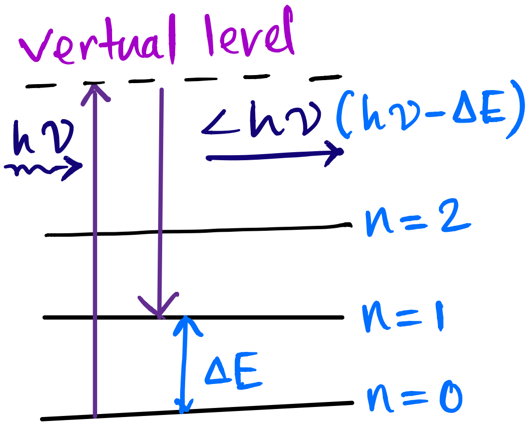


Elastic Collision
(No change in energy)

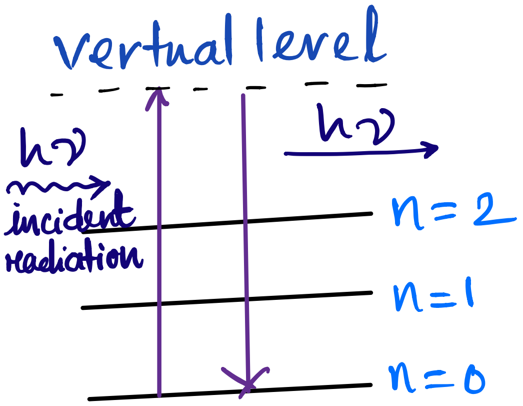
(Raman Scattering)

Inelastic Collision
(Change in Energy)

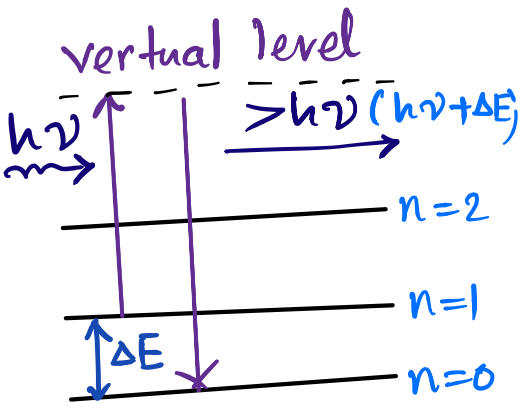
- Stokes lines
  (ν < Rayleigh lines)
- Antistokes lines
  (ν > Rayleigh lines)



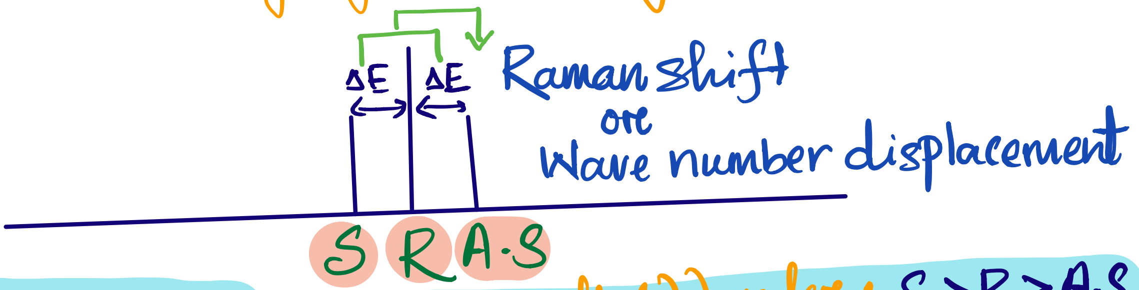
(Stokes lines)



(Rayleigh Scattering)



(Antistokes lines)



Raman shift
or
Wave number displacement

Energy order : A.S > R > S

Wavelength (λ) order : S > R > A.S

Question:

① The exciting line in an exp is 5650 Å and the stokes line is 5810 Å. Calculate the wavelength of stokes lines.

Solution: Relation, $\boxed{E \propto \nu \propto \bar{\nu}}$ $\boxed{E \propto 1/\lambda}$

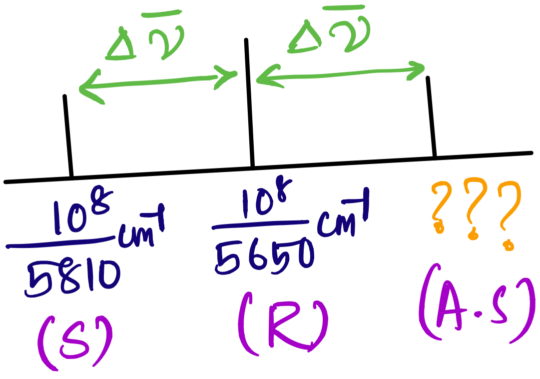
So, if the values are given in the form of wavelength (λ), first convert those into $\bar{\nu}$.

Exciting line (Rayleigh line) (λ) = 5650 Å

$$\Rightarrow \bar{\nu} = \frac{1}{5650\text{Å}} = \frac{1}{5650 \times 10^{-8}} \text{cm}^{-1} = \frac{10^8}{5650} \text{cm}^{-1}$$

Stokes lines (λ) = 5810 Å

$$\Rightarrow \bar{\nu} = \frac{1}{5810\text{Å}} = \frac{1}{5810 \times 10^{-8}} \text{cm}^{-1} = \frac{10^8}{5810} \text{cm}^{-1}$$



Now,
$$\Delta\bar{\nu} = \frac{10^8}{5650} - \frac{10^8}{5810} = \left(\frac{581 - 565}{565 \times 581}\right) 10^7$$
$$= \frac{16 \times 10^7}{565 \times 581} \text{cm}^{-1}$$

Now, $\bar{\nu}$ for Antistokes line $= \left(\frac{10^8}{5650} + \frac{16 \times 10^7}{565 \times 581}\right) \text{cm}^{-1}$

$$= \left(\frac{10^7}{565} + \frac{16 \times 10^7}{565 \times 581}\right) \text{cm}^{-1} = \frac{10^7}{565}\left(1 + \frac{16}{581}\right) \text{cm}^{-1}$$

$$= \frac{10^7}{565}\left(\frac{581 + 16}{581}\right) \text{cm}^{-1} = \frac{597 \times 10^7}{565 \times 581} \text{cm}^{-1}$$

Now, the wavelength of the Antistokes line $= \frac{1}{\bar{\nu}} = \frac{565 \times 581}{597 \times 10^{7}}$ cm

$= 549.85 \times 10^{-7}$ cm

$= 5498.5 \times 10^{-8}$ cm

② When a substance is irradiated with 4365 Å line, a Raman line attributed to the symmetrical stretching vibration found at 4814 Å. Calculate the fundamental frequency fore this vibration.

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

$\bar{\nu}$ of Raman line $= \frac{1}{4814 \times 10^{-8}} = 20772.7\ \text{cm}^{-1}$

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

$= 2136.8\ \text{cm}^{-1}$

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

$= 6.41 \times 10^{13}\ \text{s}^{-1}$

$= 6.41 \times 10^{13}$ Hz

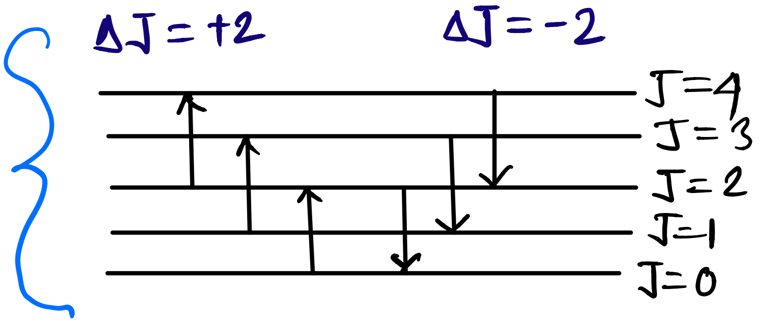
Rotational Raman Spectroscopy:

Value of $B = \frac{h}{8\pi^2 I c}$

$I = \mu r_0^2$

$E_J = BJ(J+1)$, Selection rule : $\Delta J = 0, \pm 2$

Transitions according to the Selection rule $\Delta J = \pm 2$



$\Delta J = 0$

↓

Rayleigh line

Now, for transition, $J \rightarrow (J+2)$

$$\begin{aligned}\Delta E &= E_{J+2} - E_J \\ &= B(J+2)(J+2+1) - BJ(J+1) \\ &= B(J+2)(J+3) - BJ(J+1) \\ &= B\{J^2+5J+6-J^2-J\}\end{aligned}$$

$$\Delta E = B(4J+6)$$

→ Find the ΔE value for a transition of $J(0) \rightarrow J(2)$

Solution: $\Delta E = E_{0+2} - E_0 = B\,2(2+1) - B(0)(0+1)$

$= 6B$

4B

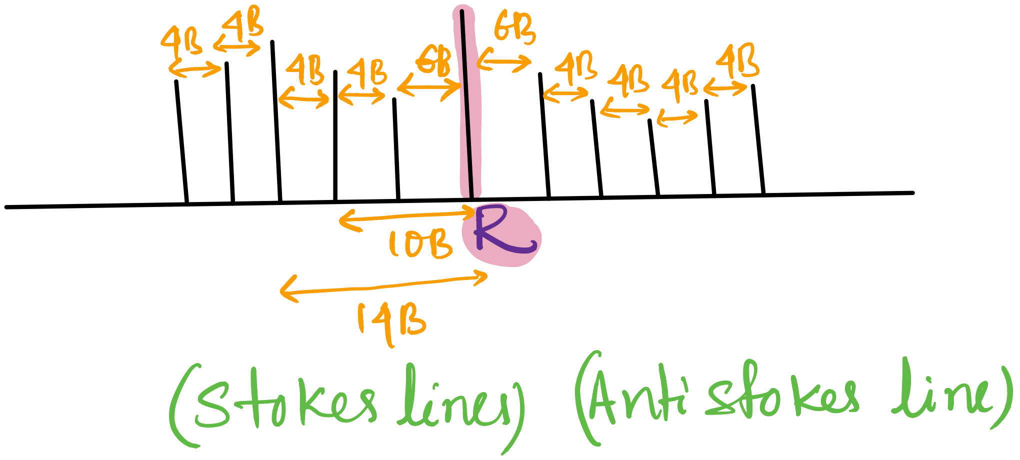
→ For, $J=1$, $1 \rightarrow 3$, $\Delta E = B(4\times1+6) = 10B$

4B

→ For, $J=2$, $2 \rightarrow 4$, $\Delta E = B(4\times2+6) = 14B$

4B

→ For, $J=3$, $3 \rightarrow 5$, $\Delta E = B(4\times3+6) = 18B$



Question for Practice

① In the raman spectra of triatomic molecule, the first three lines are at 4.86, 8.14, 11.36 cm⁻¹. Determine the rotational const. B and moment of inertia.

Solⁿ:-

$$\underbrace{4.86, \quad 8.14}_{4B}, \quad \underbrace{, \quad 11.36}_{4B} \quad cm^{-1}$$

$$4B = 8.14 - 4.86$$

$$B = 0.81\ cm^{-1}$$

Imp

$$\boxed{\begin{aligned} 1J &= kg\,m^2 s^{-2} \\ &= 10^7 g\,cm^2 s^{-2} \end{aligned}}$$

The value of $B = \frac{h}{8\pi^2 I C}$

$$\Rightarrow I = \frac{h}{8\pi^2 BC}$$

$$\Rightarrow I = \frac{6.626 \times 10^{-3}\ Js}{8 \times (3.14)^2 \times 0.81\ cm^{-1} \times 3 \times 10^{10}\ cm s^{-1}}$$

$$= 34.45 \times 10^{-40}\ g\,cm^2$$

② Bond length of H_2 molecule is 0.7417 Å. Determine the position of first three Raman lines.

(Given mass of $^1H = 1.67 \times 10^{-24} g$)

Solⁿ:- $r_0 = 0.7417\ Å$, $\quad m = 1.67 \times 10^{-24} g$

$$\mu_{H_2} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.67 \times 10^{-24} g)^2}{1.67 \times 10^{-24} g + 1.67 \times 10^{-24} g}$$

$$= 0.8365 \times 10^{-24} g$$

$$B = \frac{h}{8\pi^2 \underbrace{\mu r^2}_{I} c} = \frac{6.626 \times 10^{-34}\ Js}{8 \times (3.14)^2 \times 0.8365 \times 10^{-24} g\,(0.7417 \times 10^{-8} cm)^2 \times 3.10^{10}\ cm s^{-1}}$$

$= 60.73\ \text{cm}^{-1}$

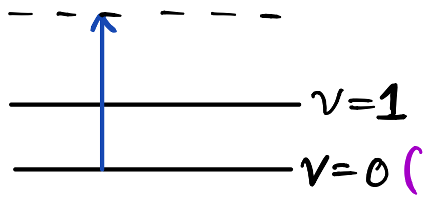
First three lines at 6B, 10B and 14B

$\downarrow$ 364.4 cm^{-1} $\downarrow$ 607.3 cm^{-1} $\downarrow$ 850.2 cm^{-1}

Vibrational Raman Spectroscopy:

$$E_\nu = (\nu + \tfrac{1}{2})\bar{\omega}_e - (\nu + \tfrac{1}{2})^2 \bar{\omega}_e x_e$$

Selection rule : $\Delta\nu = 0, \pm 1, \pm 2 \ldots\ldots$



(population is more)

most probable transition is $\nu=0 \longrightarrow \nu=1$

So, the ΔE for fundemental vibration

$$\Delta E_{\nu=0\to1} = E_1 - E_0$$
$$= (1+\tfrac{1}{2})\bar{\omega}_e - (1+\tfrac{1}{2})^2 \bar{\omega}_e x_e - \left\{(0+\tfrac{1}{2})\bar{\omega}_e - (0+\tfrac{1}{2})^2 \bar{\omega}_e x_e\right\}$$

$$\Delta E_{\nu=0\to1} = \bar{\omega}_e(1-2x_e)$$

The spectral lines given in terms of $\bar{\nu}$, so as $E \propto \bar{\nu}$

We can write, $\bar{\nu} = \bar{\nu}_0 \pm \omega_e(1-2x_e)$

$\downarrow$ initial wave no (Rayleigh line)

$+ \Rightarrow$ A.Stokes

$- \Rightarrow$ Stokes

Mutual Exclusion Principle:

* Applicable for molecule containing Centre of symmetry.
(COS)

In Case of COS molecules,

→ IR active modes will be Raman inactive

→ IR inactive modes will be Raman active

	IR	Raman
Any mode	A	I.A
Any mode	I.A	A

Q. Guess which of the table represents for CO_2 and which is for H_2 by using M.E principle.

Table-1

Modes of Vib^n	Raman	IR
# Sym. Stretching	Active	I. A
# Sym. bending	I. A	Active
# Asy. stretching	I. A	Active

Table-2

Modes of Vib^n	Raman	IR
# sym. Stretching	A	A
# Bending	A	A
# Asy. Stretch	A	A

Sol^n:- CO_2 Contains C.O.S, So it will follow M.E principle

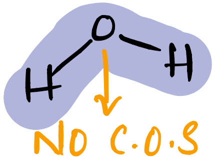
In table-1, Raman active modes are IR inactive and Raman I.A modes are IR A.

So, table-1 is accordance with the M.E Principle.

Hence, table-1 represents CO_2.

$O=C=O$,

C.O.S present



Structure determination from Raman Spectroscopy:

Important points

① If follows M.E Principle, then Molecule has C.O.S.

② → If IR active modes has PR branches, then Linear molecule.

→ If PR branches is absent, then non-Linear molecule.

Question

① A_2B_2	Raman	IR
3374 cm^{-1}	strong	—
3287 cm^{-1}	—	very strong PR
1973 cm^{-1}	very strong	—
729 cm^{-1}	—	very strong PQR
612 cm^{-1}	weak	—

Sol^n:- In the above table it's shown that, the Raman active are IR inactive and Raman I.A are IR active.

So, it follows M.E Principle.

→ The molecule A_2B_2 has C.O.S.

Now, the IR active modes has both PR and PQR branches

so, If PR branches present, then molecule is linear.

→ The molecule A_2B_2 is linear.

All the str. of Linear A_2B_2 molecule will be

① A – B – B – A (C.O.S present) ✓

② A – A – B – B (No COS present)

③ B – A – A – B (COS present) ✓

④ A – B – A – B (No COS)

⑤ B – A – B – A (No COS)

So, From the table data comparision the possible strs are either

A – B – B – A

or

B – A – A – B

② Determine the str from the given data

AB_2	IR	Raman
# 3756 cm^{-1}	very strong	——
# 3652	strong parallel	strong polarised
# 1595	very strong	——

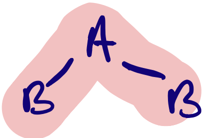
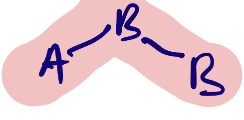
Sol^n:- From the given table it is clear that the vibrational mode at 3652 cm^{-1} is both IR and Raman active.

Hence, it's not accompany with M.E principle.

→ The molecule does not have COS.

Now, by looking closely to IR data there is no PR branches in any mode of vibration.

→ The molecule is not linear i.e, it's bent.

So, the possible strs are  or  .

③

$\bar{\nu}$ (cm^{-1})	IR	Raman
2215	vs, PR	s, depol
1250	vs, PR	vs, pol
560	s, PQR	—

vs → very sharp
s → sharp
pol → polarised
depol → depolarised

[NET 2018]

The str. of AB_2 is :

(i) Linear symmetrical ($D_{\infty h}$)
(ii) Bent symmetrical (C_{2v})
(iii) Linear asymmetrical ($C_{\infty v}$)
(iv) Bent " (C_s)

Sol^n:- From the table it is clear that it's not following M.E. principle.

→ Molecule does not have COS, i.e, asymmetrical

PR branches is present in IR

→ molecule is linear

So, the str. of AB_2 will be Linear asymmetrical and the point group will be $C_{\infty v}$.

A—B—B ($C_{\infty v}$ point group.
(Linear)
(asymmetrical)

option (iii) is the Correct ans.