

# ATOMIC & MOLECULAR PHYSICS

①

## TOPICS

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### ATOMIC PHYSICS

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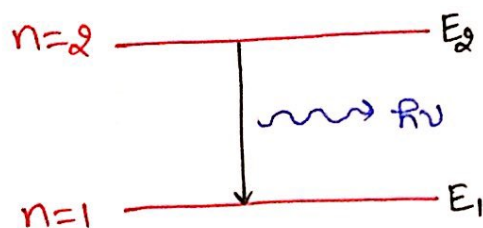
### MOLECULAR PHYSICS

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→ Bohr's Theory of H-like atom:

Bohr's quantization condition:  $L = mvr = n\hbar$  —①

Frequency of Radiation:



$$\Delta E = h\nu$$

$$\nu = \frac{E_2 - E_1}{h}$$

electrostatic force = centripetal force

$$\frac{ze^2}{4\pi\epsilon_0 r_n^2} = \frac{mv_n^2}{r_n}$$

$$\frac{ze^2}{4\pi\epsilon_0 r_n^2} = \frac{m}{r_n} \times \frac{n^2 \hbar^2}{4\pi^2 m^2 r_n^2} \quad \text{by eqn ①}$$

$$r_n = \frac{n^2 \hbar^2 \epsilon_0}{\pi m z e^2}$$

→ Radius of nth order.

$$r_n = \frac{n^2}{z} a_0$$

$a_0 = 0.529 \text{ \AA}$  → Bohr's Radius

velocity of nth orbit: 

$$v_n = \frac{ze^2}{2\epsilon_0 n \hbar}$$

$$v_1 = 2.18 \times 10^6 \text{ m/s}$$

→ largest possible  
velocity for  $e^-$  in  
H-atom

(3)

$$E_n = K.E + P.E$$

$$E_n = \frac{1}{2} m \left( \frac{Ze^2}{8n\epsilon_0 \hbar} \right)^2 - \frac{Ze^2}{4\pi\epsilon_0} \left( \frac{\pi m Ze^2}{m^2 \hbar^2 \epsilon_0} \right)$$

$$E_n = - \frac{m Z^2 e^4}{8 \epsilon_0^2 n^2 \hbar^2} = - \frac{Z^2 \hbar c}{n^2} R_\infty$$

$$R_\infty = \frac{m e^4}{8 \epsilon_0^2 \hbar^3} = 1.097 \times 10^7 \text{ m}^{-1}$$

↑ Redburg constant. (for  $\infty$  nuclear mass)

$$E_n = - \frac{13.6 Z^2}{n^2}$$

Total energy (-ve) indicates that  $e^-$  is bound to nucleus.

Finite Nuclear mass correction:

$$\text{Reduced mass: } \mu = \frac{m_{\text{nucleus}} m_{e^-}}{m_{\text{nucleus}} + m_{e^-}}$$

$$m_{\text{nucleus}} (\text{H-atom}) = m_p = 1836 m_e$$

$$\mu = \frac{1836 m_e \times m_e}{1836 m_e + m_e} = \frac{1836}{1837} m_e$$

$$\mu_H < m_e$$

→ For  $\infty$  nuclear mass:  $\mu_H = m_e$



For finite nuclear mass:

(9)

→  $r_n \propto \frac{1}{M}$  i.e. larger Radius

→  $v_n = \text{unchanged}$

→  $R_H \propto M$  i.e. smaller Rydberg constant

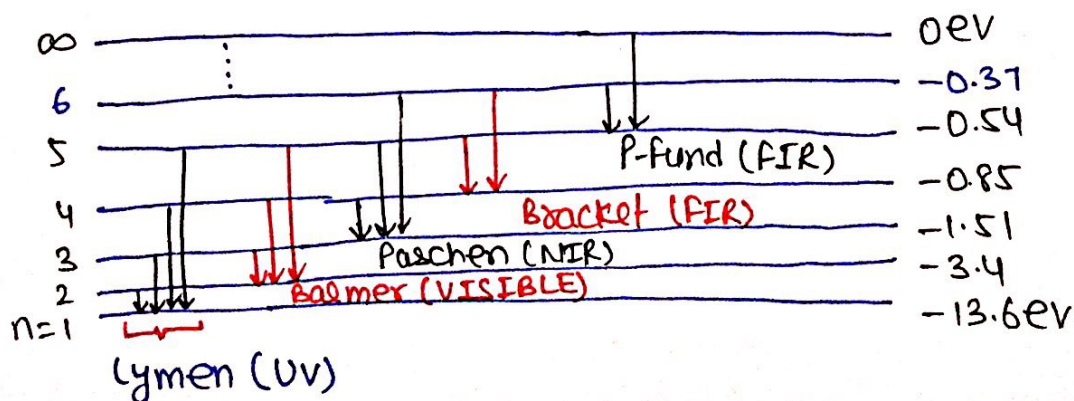
| ${}_1\text{H}^1$   | ${}_1\text{H}^2$   | ${}_1\text{H}^3$   |
|--------------------|--------------------|--------------------|
| Hydrogen           | Deuterium          | Tritium            |
| $m_n = m_p$        | $m_n = 2m_p$       | $m_n = 3m_p$       |
| $M_H = 0.9994 m_e$ | $M_D = 0.9997 m_e$ | $M_T = 0.9998 m_e$ |

→  $M_T > M_D > M_H \Rightarrow R_T > R_D > R_H$

Positronium atom:  $M_{\text{Pos.}} = \frac{m_e}{2}$

Muonic atom:  $M_{\text{muonic}} = 186.83 m_e$

### Hydrogen Spectrum:





(5)

$$\text{freq.}(\nu) = \frac{c}{\lambda} = c\bar{\nu} \quad \bar{\nu} \rightarrow \text{wave number}$$

$$\bar{\nu} = \frac{1}{\lambda} = R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\lambda = \frac{12400}{E_g(\text{eV})} \text{ \AA}$$

1) Lyman Series: ( $n_f = 1$ )

$$\rightarrow \lambda_{\min} = 912 \text{ \AA} \quad n(\infty) \text{ to } n=1$$

$$\lambda_{\max} = 1215 \text{ \AA} \quad n=2 \text{ to } n=1$$

$\rightarrow$  observed in absorption spectrum.

2) Balmer Series: ( $n_f = 2$ )

$$\frac{1}{\lambda} = R_{\infty} \left( \frac{1}{2^2} - \frac{1}{n_i^2} \right) Z^2$$

$Z=1$  for H-atom

$$n=3 \text{ to } n=2 \rightarrow H_{\alpha} \text{ line}$$

$$n=4 \text{ to } n=2 \rightarrow H_{\beta} \text{ line}$$

Ionization Energy:

$$E_{\text{ion}}(\text{H}) = E_{\infty} - E_1 = 0 - (-13.6) \text{ eV} = 13.6 \text{ eV}$$

$$E_{\text{ion}}(\text{Pos}) = H \times E_{\text{ion}}(\text{H})$$

$$= \frac{1}{2} \times 13.6 = 6.8 \text{ eV}$$

Excitation energy: energy required to make the  $e^-$  capable of jump to higher energy state.

(6)

1st excitation energy of H-atom:

$$E_1(H) = E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$$

For Positronium:  $E_1(P) = \mu \times E_1(H) = 5.1 \text{ eV}$

Binding energy: minimum energy required to remove a  $e^-$  from atom.

$$B.E = -E_n$$

$$B.E(H) = -(-13.6) = 13.6 \text{ eV}.$$

Ionization Potential:

$$I.P = \frac{I.E(\text{eV})}{e}$$

For  $\text{Li}^{2+}$ :  $I.E = (3)^2 \times 1 \times 13.6 = 122.4 \text{ eV}$

$$I.P = \frac{122.4 \text{ eV}}{e} = 122.4 \text{ Volts}.$$

Excitation Potential:

$$(E.P)_1 = \frac{(E_2 - E_1)}{e} = \frac{10.2 \text{ eV}}{e} = 10.2 \text{ Volts}.$$

Relation b/w Energy, Frequency,  $\lambda$  & wave number:

|                                                                        |    |                         |                                 |    |                                               |
|------------------------------------------------------------------------|----|-------------------------|---------------------------------|----|-----------------------------------------------|
| $E = h\nu = R \frac{c}{\lambda} = hc\bar{\nu} = \frac{h}{2\pi} \omega$ |    |                         |                                 |    | <del><math>\frac{h}{2\pi} \omega</math></del> |
| ↑                                                                      | ↑  | ↑                       | ↑                               | ↑  | ↑                                             |
| eV, J, cal                                                             | Hz | $\text{\AA}, \text{nm}$ | $\text{m}^{-1}, \text{cm}^{-1}$ | Hz | <del>Hz</del>                                 |

## Relative Population of two levels:

⑦

$n=2$  —————  $E_2$

$n=1$  —————  $E_1$

$$N \propto e^{-E/k_B T}$$

Boltzmann law

Ratio of number of atoms:

$$\frac{N_2}{N_1} = \exp\left(-\frac{(E_2 - E_1)}{k_B T}\right) \times \frac{g_2}{g_1}$$

$g \rightarrow$  degeneracy of level

## Frequency of Revolution of electron:

$$DE = R \nu$$

$$\nu = \frac{E_i - E_j}{R} = \frac{me^2}{8\epsilon_0^2 R^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^2$$

$$F = \frac{2 R \alpha c}{n^3}$$

## Failures:

- can't explain: fine structure, anomalous zeeman effect, rate & selection rule of transition.
- can't applicable on more than  $1e^+$  system.

Summary:



Ques 1 Given that the ground state energy of H-atom is  $-13.6 \text{ eV}$ , the ground state energy of the positronium (which is bound state of an electron & positron) is: (2)

- a)  $6.8 \text{ eV}$    b)  $-6.8 \text{ eV}$    c)  $-13.6 \text{ eV}$    d)  $-27.2 \text{ eV}$

Sol<sup>n</sup>o-

$$\mu_p = \frac{m_{e^+} \times m_{e^-}}{m_{e^+} + m_{e^-}} = \frac{1}{2} m_e \quad m_{e^+} \approx m_{e^-}$$

$$E_1^{(p)} = \frac{1}{\mu} \times E_1^{(H)} = \frac{1}{2} (-13.6) \text{ eV}$$

$$= -6.8 \text{ eV} \quad \boxed{B}$$

Ques 2 A muon ( $\mu^-$ ) from cosmic rays is trapped by a proton to form a  $\mu$ -like atom. Given that a muon is approximately 200 times heavier than  $e^-$ , the longest wavelength of the spectral line (in the analogue of the Lyman series) of such an atom will be:

- a)  $5.62 \text{ \AA}$    b)  $6.67 \text{ \AA}$    c)  $3.75 \text{ \AA}$    d)  $13.3 \text{ \AA}$
- $\uparrow \lambda_{\max} = 1215 \text{ \AA}$

Sol<sup>n</sup>o- 
$$\mu = \frac{m_p \cdot m_\mu}{m_p + m_\mu} = \frac{1836 m_e \times 200}{(1836 + 200) m_e} \approx 181 m_e$$

$$\lambda_\mu = \frac{1}{\mu} \times \lambda_H = \frac{1}{181} \times 1215 = 6.71 \text{ \AA} \quad \boxed{B}$$

Ques 3 The electronic energy levels in a H-atom are given by  $E_n = -(13.6/n^2)$  eV. If a selective excitation to the  $n=100$  level is to be made using a laser, the maximum allowed frequency line width of the laser is:

- a) 6.5 MHz    b) 6.5 GHz    c) 6.5 Hz    d) 6.5 kHz

Sol<sup>n</sup>o - energy separation =  $\Delta E$

$$E = -\frac{13.6}{n^2}$$

$$\Delta E = + \frac{13.6 \times 2}{n^3}$$

$$h \Delta \nu = (27.2/n^3) \text{ eV}$$

$$\Delta \nu = \frac{27.2 \times 1.6 \times 10^{-19}}{(100)^3 \times 6.63 \times 10^{-34}}$$

$$\Delta \nu = 659 \times 10^9 \text{ Hz}$$

$$\Delta \nu = 6.59 \text{ GHz}$$

[B]

Ques 4 If the B.E's of the  $e^-$  in the K & L shells of Silver atom are 25.4 keV & 3.34 eV. Then the K.E of Auger  $e^-$  will be:

- a) 22 keV    b) 9.3 keV    c) 10.5 keV    d) 18.7 keV

Sol<sup>n</sup>o - Auger  $e^- \rightarrow$  secondary  $e^-$

$$\text{K.E of Auger } e^- = \text{energy of } e^- \text{ in K-shell} - 2 (\text{energy of L shell } e^-)$$

$$= 25.4 - 6.68 = 18.72 \text{ keV} \quad [D]$$



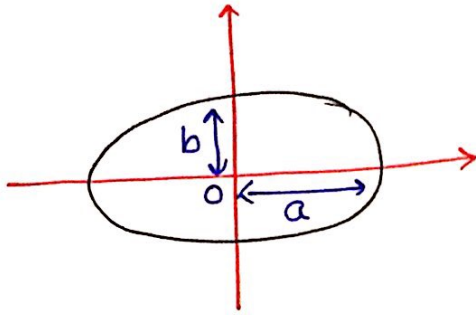
## → Sommerfeld Model:

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He made two modification in Bohr's model:

### 1) correction of elliptical model:

Quantum condition:  $\boxed{\frac{b}{a} = \frac{k}{n}}$



$n \rightarrow$  Principal quantum number

$$n = 1, 2, 3, \dots$$

$$n = n_r + k$$

$n_r \rightarrow$  radial Q.No,  $n_r = 0, 1, 2, \dots$

$k \rightarrow$  azimuthal Q.No :  $k = 1, 2, 3, \dots$

For  $n=1$ :  $n_r=0, k=1$

$$\frac{b}{a} = \frac{1}{1} \Rightarrow a=b \rightarrow \text{circular orbit.}$$

For  $n=2$ :

$$n_r=0, k=2 \Rightarrow a=b \rightarrow \text{circular}$$

$$n_r=1, k=1 \Rightarrow a=2b \rightarrow \text{elliptical}$$

### 2) Relativistic Approach:

$$\text{Relativistic K.E} = \frac{1}{2} m_0 v^2 + \frac{3}{8} m_0 \frac{v^4}{c^2} + \dots$$

$$\text{Energy} = -\frac{R_{\infty} h c z^2}{n^2} - \frac{R_{\infty} h c \alpha^2 z^4}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right)$$



$\alpha \rightarrow$  fine structure constant

$$V_1 = \alpha c = \frac{1}{137} c$$

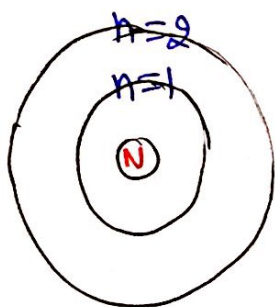
$\rightarrow$  This theory successful in explaining the fine structure of H-like atoms.

$\rightarrow$  Quantum Numbers:

Describes value of conserved quantities.

1) Principal Quantum number:

Represents orbit or shell



$n = 1, 2, 3, \dots$   
 $\uparrow \uparrow \uparrow$   
 K L M  $\dots$  shells

introduced by Sommerfeld.

$E_n \propto n^2$  as  $n \uparrow \Rightarrow E_n$  also  $\uparrow$ .

2) Orbital or azimuthal quantum number:

Represents shape of orbital

$l = 0, 1, 2, \dots, (n-1)$

$\uparrow \uparrow \uparrow$

s p d  $\dots$  subshells

3) magnetic quantum number:

$m_l = -l, -l+1, \dots, l$

total:  $(2l+1)$  values.

Represents state of atom (or electron)

(12)

$E_n \rightarrow$  for  $1e^-$  system

$E_{n,l} \rightarrow$  for multi  $e^-$  system.

4) magnetic spin quantum number:

Represents the orientation of  $e^-$  in a state.

$$m_s = \pm 1/2 \text{ for } e^-.$$

Note:

$\rightarrow$  Degeneracy of level:

1) without spin:  $g = n^2$

2) with spin:  $g = 2n^2$

$\rightarrow$  Number of  $e^-$ s in a shell =  $2n^2$

$\rightarrow$  Number of  $e^-$ s in a subshell =  $2(2l+1)$

Ques! Find the number of states available for  $e^-$  for  $n=2$  in H-atom?

sol<sup>n</sup>:- For  $n=2$ :

$$l \begin{cases} \rightarrow 0 : m_l = 0 \\ \rightarrow 1 : m_l = -1, 0, 1 \end{cases}$$

$$\psi_{nlm} = \psi_{200}, \psi_{210}, \psi_{21-1}, \psi_{211} \rightarrow \textcircled{4} \text{ Ans}$$

energy of all states:

$$E_n = \frac{-13.6}{n^2} = \frac{-13.6}{4} = -3.4 \text{ eV}$$

→ Orbital Angular Momentum:

orbital magnetic dipole moment:  $\mu_l = \sqrt{l(l+1)} \mu_B$

Bohr's magneton:  $\mu_B = \frac{e\hbar}{4\pi m} = 9.27 \times 10^{-24} \text{ A-m}^2$

Larmor frequency:  $f = \frac{eB}{4\pi m}$

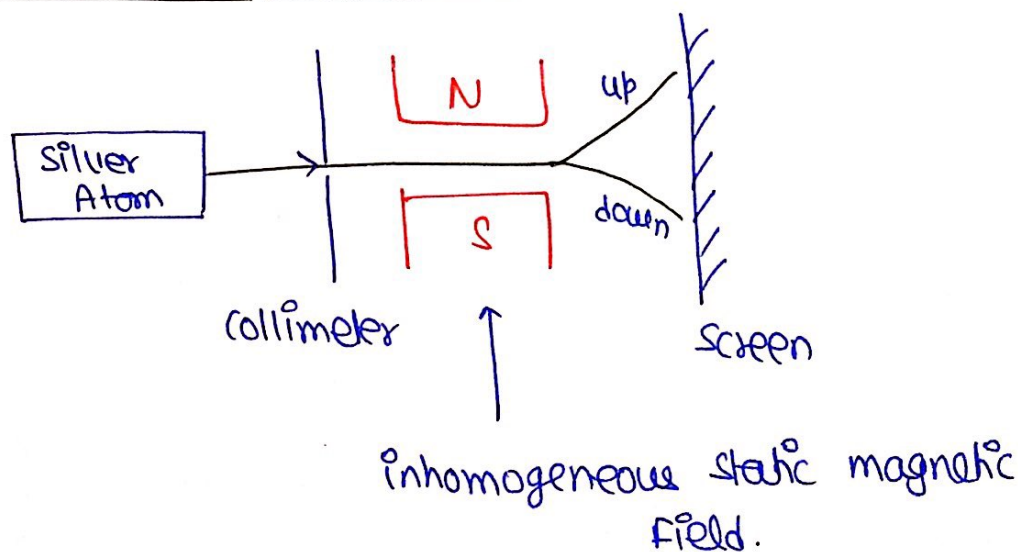
space quantization of angular momentum:

$$L_z = |\vec{L}| \cos\theta$$

$$\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m_l \hbar}{\sqrt{l(l+1)} \hbar}$$

$$\boxed{\cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$$

→ Stern-Gerlach Experiment:



it provides experimental evidence of  $e^-$  spin,  
demonstrate vector atom model & space quantization



spin magnetic dipole moment:  $M_s = g_s \sqrt{s(s+1)} \frac{e\hbar}{4\pi m}$  (14)

Space quantization of spin angular momentum:

$$\cos\theta = \frac{m_s}{\sqrt{s(s+1)}}$$

Note: spin & orbital motion of an electron are independent of each other.

→ Vector Model of an Atom:

Spin-orbit coupling:  $\vec{J} = |\vec{L} + \vec{S}| \dots |\vec{L} + \vec{S}|$

$$\vec{J} = \vec{L} + \vec{S} \quad \text{--- (1)}$$

magnetic dipole moment:  $M_J = g_J \sqrt{j(j+1)} \frac{e\hbar}{4\pi m}$

Lande g-factor:

$$g_J = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

For pure orbital motion ( $s=0$ ):  $g_L = 1$

For spin motion ( $l=0$ ):  $g_S = 2$

angle b/w different motions:

$$J^2 = L^2 + S^2 + 2(\vec{L} \cdot \vec{S})$$

$$J^2 = L^2 + S^2 + 2LS \cos\theta_{LS}$$

$$\cos \theta_{LS} = \frac{J(J+1) - L(L+1) - S(S+1)}{2\sqrt{L(L+1)}\sqrt{S(S+1)}}$$

similarly,

$$\cos \theta_{LJ} = \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)}\sqrt{L(L+1)}}$$

$$\cos \theta_{SJ} = \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}\sqrt{S(S+1)}}$$

Fine Structure symbol:

$$n \cdot \overset{(S+1)}{L} J$$

→ spectroscopic term

selection Rule:

$$\Delta J = 0 \pm 1; \Delta L = \pm 1; \Delta S = 0$$

→ vector coupling model for many electron system:

optical  $e^\ominus$  are responsible for coupling

e.g.  $6C = 1s^2 2s^2 2p^2 \rightarrow$  optical  $e^\ominus$

1) If atoms are lighter: (L-S coupling)

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \quad \& \quad \vec{L} = \vec{L}_1 + \vec{L}_2$$

$$\vec{J} = \vec{L} + \vec{S}$$

2) If atoms are heavier: (j-j coupling)

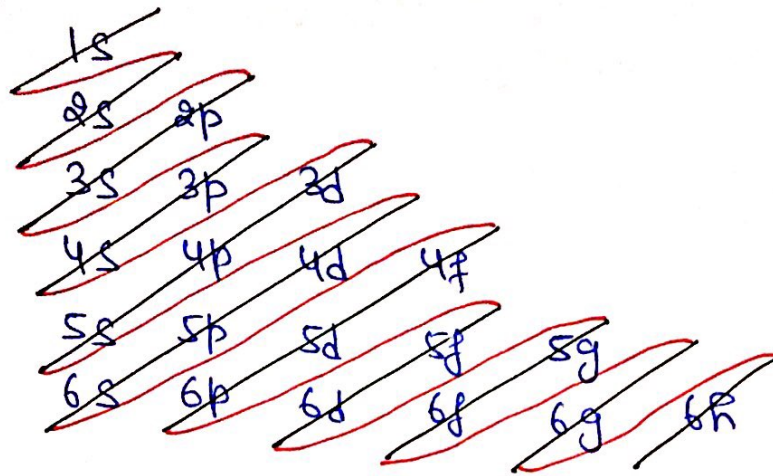
$$j_1 = l_1 + s_1 \quad \& \quad j_2 = l_2 + s_2$$

$$\vec{J} = \vec{j}_1 + \vec{j}_2$$



## Aufbau Principle:

(16)



$$\Delta J = 0, \pm 1$$

$$\Delta l = 0, \pm 1$$

$$\Delta S = 0$$

↑  
Dipole selection  
Rule for  
multi  $e^-$  system

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s . . . . .

equivalent terms:  $s^2, p^2, d^2, \dots$

non-equivalent terms:  $sp, sd, ss, pp, \dots$  etc.

## Hunds Rule for composing energy:

- largest S-term: has lowest energy
- largest L-term: has lowest energy
- For J-term:

less than  $1/2$  filled: lowest J has lowest energy

greater than  $1/2$  filled: largest J has lowest energy.

## Degeneracy:

→ Deg. of spectroscopic term =  $(2J+1)$

→ Deg. of ionic configuration =  $\frac{(4l+2)!}{(4l+2-N)! N!}$

→ Deg. =  $n_{C_r}$

$n \rightarrow$  total  $e^-$   
 $r \rightarrow$  optical  $e^-$

$(4l+2-N)! N!$

$N \rightarrow$  optical  $e^-$



Ques! How much does the total angular momentum quantum number  $J$  changes in the transition of  $\text{Cr}(3d^6)$  atom as it ionizes to  $\text{Cr}^{2+}(3d^4)$ ? (17)

- a) increases by 2                      b) decreases by 2  
c) decreases by 4                      d) doesn't change.

Sol<sup>n</sup>:

$\text{Cr}(3d^6)$ :

|       |                      |            |            |            |            |
|-------|----------------------|------------|------------|------------|------------|
| $m_l$ | -2                   | -1         | 0          | 1          | 2          |
|       | $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |
| $m_s$ | 0                    | $1/2$      | $1/2$      | $1/2$      | $1/2$      |

$$\sum m_l = -2 \Rightarrow L = 2$$

$$\sum m_s = 2 \Rightarrow S = 2$$

$J = 0, 1, 2, 3, 4$        $L = 2$  i.e. D-orbital  
 $S = 2$ :  $2S+1 = 5$

Spectroscopic terms:  $^5D_{0,1,2,3,4}$

By Hund's Rule: ground state for greater than  $1/2$  filled is Highest  $J$  value.

$^5D_4$  → ground state term.

$\text{Cr}^{2+}(3d^4)$ :

|       |            |            |            |            |  |
|-------|------------|------------|------------|------------|--|
| $m_l$ | -2         | -1         | 0          | 1          |  |
|       | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |  |
| $m_s$ | $1/2$      | $1/2$      | $1/2$      | $1/2$      |  |

→ less than half filled.

$$\sum m_l = -2 \Rightarrow L = 2$$

$$\sum m_s = 2 \Rightarrow S = 2$$

$$J = 0, 1, 2, 3, 4$$

By Hund's Rule:  $^5D_0$  → ground state term.

$5D_4$  to  $5D_0$

J decreases by 4.

[C]

(18)

Ques 2 The LS configurations of the ground state of  $^{12}\text{Mg}$ ,  $^{13}\text{Al}$ ,  $^{17}\text{Cl}$  &  $^{18}\text{Ar}$  are respectively:

a)  $3s_1, 2p_{1/2}, 2p_{1/2}$  &  $1s_0$

b)  $3s_1, 2p_{3/2}, 2p_{3/2}$  &  $3s_1$

c)  $1s_0, 2p_{1/2}, 2p_{3/2}$  &  $1s_0$

d)  $1s_0, 2p_{3/2}, 2p_{1/2}$  &  $3s_1$

Sol<sup>no</sup> -  $^{12}\text{Mg}$ :  $1s^2 2s^2 2p^6$   $(3s^2)$

↑ exactly fulfilled

ground state =  $(1s_0)$

$^{18}\text{Ar}$ :  $1s^2 2s^2 2p^6 3s^2$   $(3p^6)$

ground state =  $(1s_0)$

now check option.

[C]

Ques 3 The ground state electronic configuration of  $^{22}\text{Ti}$  is  $[\text{Ar}] 3d^2 4s^2$ . which state, in the standard spectroscopic notation, is not possible in this configuration?

a)  $1F_3$  b)  $1s_0$  c)  $1D_2$  d)  $3p_0$

Sol<sup>no</sup> -  $[\text{Ar}] (3d^2) 4s^2$

↳ equivalent term.

$l_1=2, l_2=2, s_1=1/2, s_2=1/2$

$$L = 0, 1, 2, 3, 4$$

$$S = 0, 1$$

| S | L | Spectroscopic terms |
|---|---|---------------------|
| 0 | 0 | $1S_0$ ✓            |
|   | 2 | $1D_2$ ✓            |
|   | 4 | $1G_4$              |

  
 (even-even)

for equivalent  $e^-$ s

| S | L | Spectroscopic terms     |
|---|---|-------------------------|
| 1 | 1 | $3P_0, 3P_1, 3P_2$<br>✓ |
|   | 3 | $3F_2, 3F_3, 3F_4$      |

  
 (odd-odd)

A

Ques 4 In the L-S coupling scheme, the terms arising from two non-equivalent p- $e^-$ s are:

a)  $3S, 1P, 3P, 1D, 3D$

b)  $1S, 3S, 1P, 1D$

c)  $1S, 3S, 3P, 3D$

d)  $1S, 3S, 1P, 3P, 1D, 3D$

sol<sup>n</sup>:-

$\underbrace{p\ p}_\uparrow$

$$l_1 = 1, l_2 = 1 \Rightarrow L = 0, 1, 2$$

$$s_1 = 1/2, s_2 = 1/2 \Rightarrow S = 0, 1$$

non-equivalent



| S | L | J       | Spectroscopic terms         |
|---|---|---------|-----------------------------|
| 0 | 0 | 0       | $1s_0 \rightarrow 1s$       |
|   | 1 | 1       | $1p_1 \rightarrow 1p$       |
|   | 2 | 2       | $1d_2 \rightarrow 1d$       |
| 1 | 0 | 1       | $3s_1 \rightarrow 3s$       |
|   | 1 | 0, 1, 2 | $3p_{0,1,2} \rightarrow 3p$ |
|   | 2 | 1, 2, 3 | $3d_{1,2,3} \rightarrow 3d$ |

Ques 5 Find the ground state spectroscopic terms of  $sc=21$ . Also find the degeneracy of  $sc$ ?

Soln<sup>o</sup>-  $sc: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 (3d^1)$

$$l=2, S=1/2$$

$$J = \boxed{3/2}, 5/2$$

↑ ground state.

less than  
 $1/2$  filled

$$2D_{3/2, 5/2}$$

Hund's Rule:

$$\boxed{2D_{3/2}}$$

↑ ground state.

$$\text{Deg. of } sc = \text{Deg of } D_{3/2} + \text{Deg. of } D_{5/2}$$

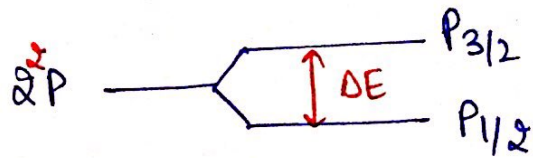
$$= (2 \times \frac{3}{2} + 1) + (2 \times \frac{5}{2} + 1) = \boxed{10}$$

alternate:

$$\text{Deg.} = \frac{(4l+2)!}{(4l+2-N)!N!} = \frac{(4 \times 2 + 2)!}{(4 \times 2 + 2 - 1)!1!} = \frac{10!}{9!} = \boxed{10}$$

→ Term separation in Doublet for  $1e^-$  system:

(21)



$$\text{term shift} = -\frac{\Delta E}{Rc} \text{ cm}^{-1}$$

$$\Delta T = \frac{5.84 z^4}{n^3 l(l+1)} \text{ cm}^{-1}$$

Ques 1 If the fine structure splitting between the  $2^2P_{3/2}$  and  $2^2P_{1/2}$  levels in the hydrogen atom is  $0.4 \text{ cm}^{-1}$ , the corresponding splitting in  $\text{Li}^{2+}$  will approximately be: DEC-2017

- a)  $1.2 \text{ cm}^{-1}$     b)  $10.8 \text{ cm}^{-1}$     c)  $32.4 \text{ cm}^{-1}$     d)  $36.8 \text{ cm}^{-1}$

Sol<sup>n</sup>:-

$$\Delta T \propto z^4$$

$$\Delta T_H = 0.4 \text{ cm}^{-1}$$

$$\Delta T_{\text{Li}^{2+}} = (z)^4 \times \Delta T_H$$

$$= (3)^4 \times 0.4$$

$$= 81 \times 0.4 \Rightarrow 32.4 \text{ cm}^{-1}$$

C

## Lande Interval Rule (Term separation in Doublet ⓀⓀ)

for multielectron system).

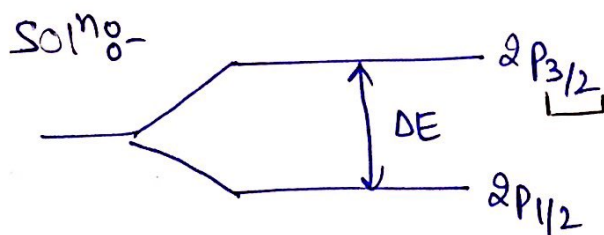
spin orbit interaction energy :  $E_J = A(\vec{L} \cdot \vec{S})$

$$E(J+1) - E(J) = a\hbar^2 \underbrace{(J+1)}_{\substack{\uparrow \\ \text{Higher } J\text{-value.}}}$$

$$\Delta E \propto (J+1)$$

Ques 1 The spin orbit interaction in an atom is given by  $H = a\vec{L} \cdot \vec{S}$ , where  $L$  &  $S$  denotes the orbital & spin angular momentum, respectively of electron. The splitting between the levels  $^2P_{3/2}$  &  $^2P_{1/2}$  is:

- a)  $\frac{3}{2}a\hbar^2$    b)  $\frac{1}{2}a\hbar^2$    c)  $3a\hbar^2$    d)  $\frac{5}{2}a\hbar^2$



Highest Q. No  
 $\Rightarrow (J+1) = 3/2$

$$\Delta E = a\hbar^2 (J+1)$$

$$\Delta E = a\hbar^2 \left(\frac{3}{2}\right)$$

A

Ques 2 The separations between the adjacent levels of a normal multiplet are found to be  $22 \text{ cm}^{-1}$

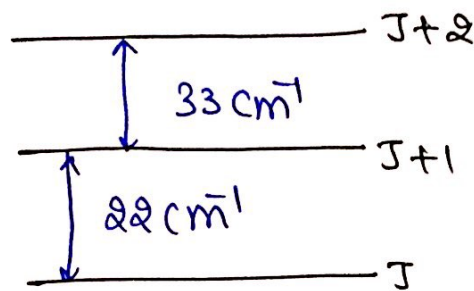


4  $33 \text{ cm}^{-1}$ . Assume that the multiplet is described well by the L-S coupling scheme & the Landé's Rule, namely  $E(J) - E(J-1) = AJ$ , where  $A$  is a constant. The term notations for this multiplet is:

- a)  $^3P_{0,1,2}$     b)  $^3F_{2,3,4}$     c)  $^3H_{3,4,5}$     d)  $^3D_{1,2,3}$

Sol<sup>n</sup>g- Landé's Rule:  $E(J) - E(J-1) = AJ$

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$$\Delta E_1 = E(J+1) - E(J) = A(J+1) = 22 \text{ cm}^{-1}$$

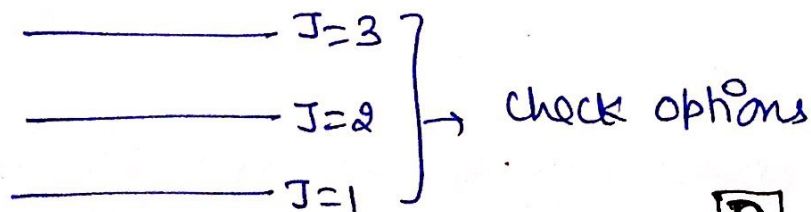
$$\Delta E_2 = E(J+2) - E(J+1) = A(J+2) = 33 \text{ cm}^{-1}$$

Divide above two eq<sup>n</sup>s.

$$\frac{A(J+1)}{A(J+2)} = \frac{22}{33}$$

$$(J+1)3 = 2(J+2)$$

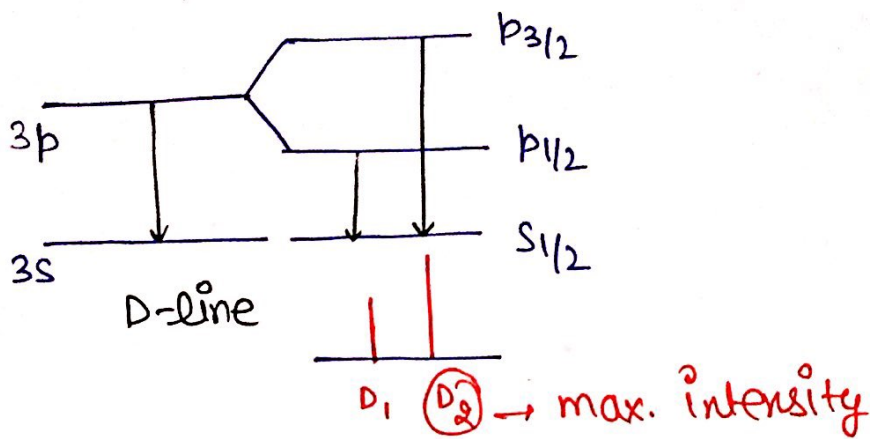
$$3J+3 = 2J+4 \Rightarrow J=1$$



**D**

## Intensity Ratio:

(24)



selection rule:  $\Delta J = \Delta L = -1$  **strongest**  
 $\Delta J = \Delta L = 1$  **strong**  
 $\Delta J = 0, \Delta L = \pm 1$  **weak**

- The sum of intensities, of those lines of a multiplet which comes from a common initial level is proportional to quantum weight  $(2J+1)$  of that level.
- The sum of intensities, of those lines which ends at a common level is proportional to quantum weight of that level.

e.g. 
$$\frac{I_{D_2}}{I_{D_1}} = \frac{(2 \times \frac{3}{2} + 1)}{(2 \times \frac{1}{2} + 1)} = \frac{4}{2} = 2$$

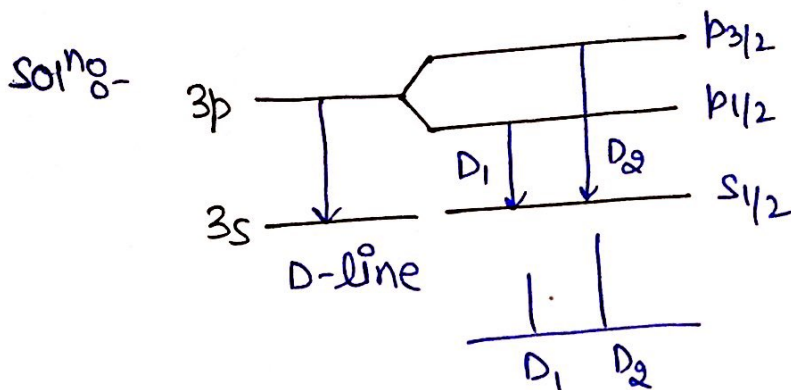
Note:

$$\frac{I_{D_2}}{I_{D_1}} = \frac{g_2}{g_1} = \frac{N_2}{N_1}$$

 \*\*\*

Ques 1 The ratio of intensities of the  $D_1$  &  $D_2$  lines of sodium at High temperature: (25)

- a) 1:1    b) 2:3    c) 1:3    d) 1:2

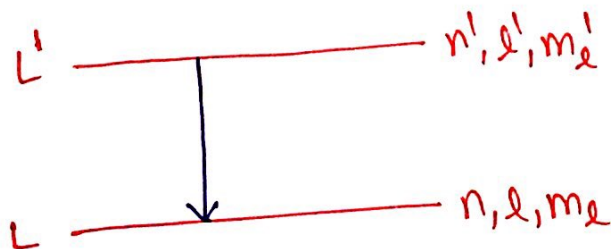


$$\frac{I_{D_1}}{I_{D_2}} = \frac{(2J_1 + 1)}{(2J_2 + 1)} = \frac{(2 \times \frac{1}{2} + 1)}{(2 \times \frac{3}{2} + 1)} = \frac{2}{4} = \frac{1}{2}$$

$$\Rightarrow 1:2$$



→ Electric Dipole Transition Rule:



Parity must be changed.

$\Delta n = n' - n$  should be an integer

$\Delta l = l' - l = \pm 1$  Parity must be changed

$\Delta m = m_l' - m_l = 0, \pm 1$

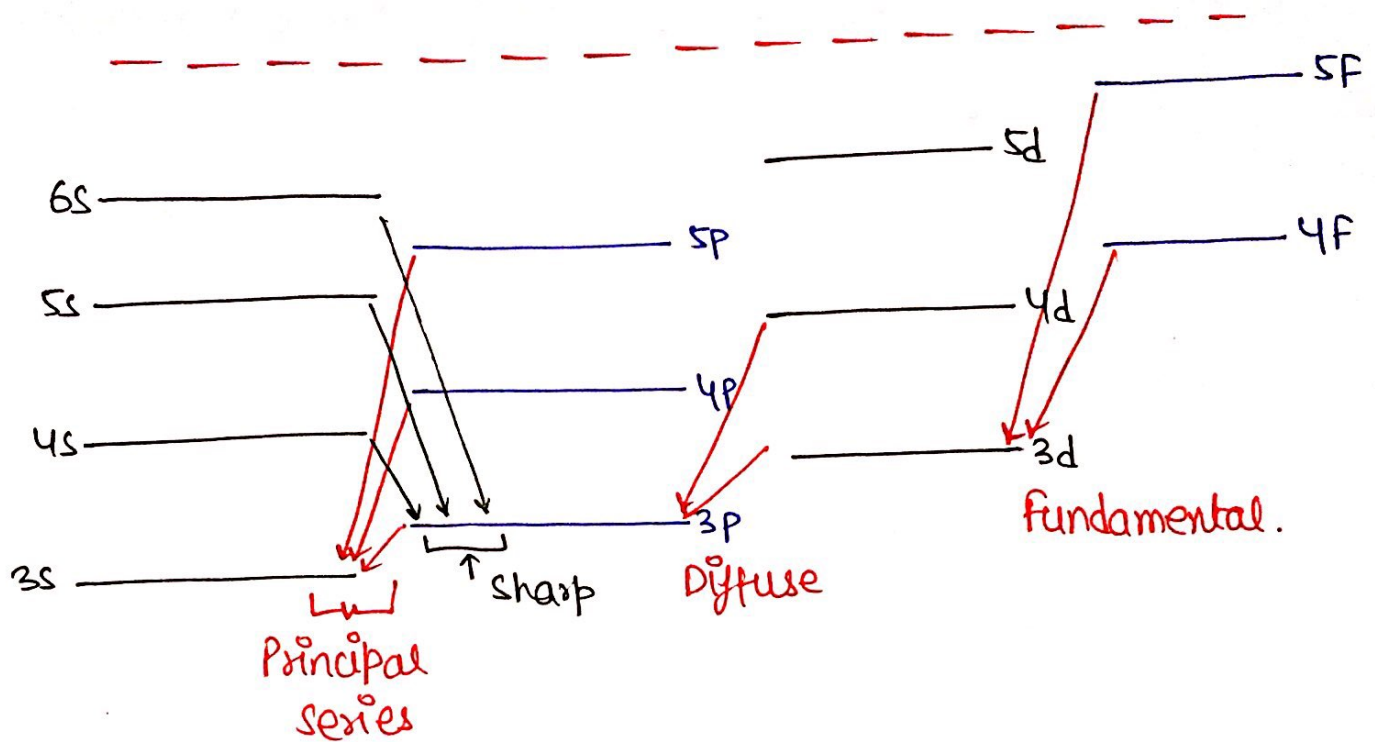
$\Delta L = L' - L = \pm 1$



→ Alkali Atom Spectra (spectra of many e<sup>-</sup>s atom)

Energy of alkali atom depends on Principal quantum number & orbital quantum number.

i.e  $E_{n,l}$  for e.g Na atom.



Observations:

- 1) Discrete Spectra.
- 2) Convergence limit of **Sharp & Diffuse** are same
- 3) energy lines of:
  - Principal & sharp → Doublet
  - diffuse & Fundamental → Triplet
- 4) Four series are observed in emission spectrum of Sodium (Na)

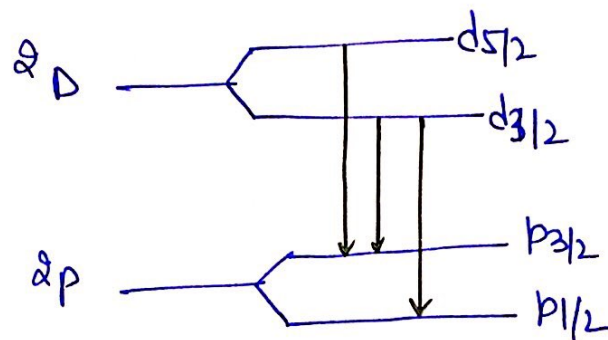
5) In absorption spectrum of sodium only principal series is obtained.

Selection Rule:  $\Delta l = \pm 1$

Ques 1 when an electron transition takes place from  $2p \rightarrow 2p$

find number of lines emitted & convergent series?

Soln:-



$\Delta l = \pm 1$

$D \rightarrow P$  Doublet series

number of lines = 3 Ans.

## ZEEMAN EFFECT

Effect of external magnetic field ( $\vec{B}$ ) on fine structure lines.

1) Normal Zeeman effect (NZE):

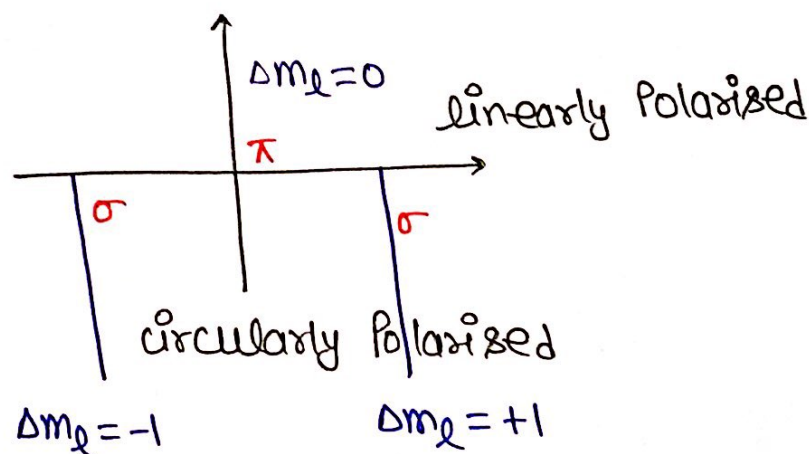
Spin:  $\vec{S}=0$  (singlet state)

$$\vec{J} = \vec{L} + \vec{S} = \vec{L} \quad (\because \vec{S}=0)$$

magnetic field: weak/strong

→ line splits into 2 or 3 components.

→ Selection Rule:  $\Delta m_l = 0, \pm 1$



light emitted along (or ||) to  $\vec{B}$ : circularly

light emitted ⊥ to  $\vec{B}$ : linearly Polarised.

→ separation blue consecutive lines.

$$\Delta\nu = g_l \frac{eB}{4\pi m} h^2$$

$$\Delta\lambda = \frac{\lambda^2}{c} \left( g_l \frac{eB}{4\pi m} \right)$$

→ first level splitting occurs then line splitting.



Ques 1 The spectral line corresponding to an atomic transition from  $J=1$  to  $J=0$  states splits in a magnetic field of 1 K gauss into three components separated by  $1.6 \times 10^{-3} \text{ \AA}$ . If the zero field spectral line corresponds to  $1849 \text{ \AA}$ , what is the  $g$ -factor corresponding to ~~1849 \text{ \AA}~~ the  $J=1$  state?

- a) 2      b)  $3/2$       c) 1      d)  $1/2$

Soln<sup>g</sup>-

$$\Delta\lambda = \frac{\lambda^2}{c} \left( g \frac{\mu_B B}{h} \right)$$

$$g = \left( \frac{hc}{\mu_B} \right) \frac{\Delta\lambda}{\lambda^2 B}$$

$$\frac{hc}{h} \approx 2 \times 10^4 \text{ cm}$$

↑ given

$$g = \frac{2 \times 10^4 \times 1.6 \times 10^{-3} \times 10^8}{(1.849 \times 10^{-5})^2 \times 10^3}$$

$$(g \approx 1)$$

[c]

alternate:

given: 2 line splits into 3 components

i.e. (NZE)  $\Rightarrow$   $g = 1$   $\therefore S = 0$

Ques 2 An atomic transition  $1p \rightarrow 1s$  in a magnetic field 1 T shows Zeeman splitting. Given that the Bohr magneton  $\mu_B = 9.27 \times 10^{-27} \text{ J/T}$ , and the wavelength corresponding to the transition is

250 nm, the separation in zeeman spectral lines is approximately: (30)

a) 0.01 nm    b) 0.1 nm    c) 1.0 nm    d) 10 nm

Sol<sup>n</sup>o- 
$$\Delta\lambda = \frac{\lambda^2}{c} \left( g_L \frac{eB}{4\pi m} \right) \times \frac{h}{R}$$

$$\Delta\lambda = \frac{\lambda^2}{c} (g_L \mu_B) \frac{B}{R}$$

$$\Delta\lambda = \frac{(250 \times 10^{-9})^2}{3 \times 10^8} \left( 1.927 \times 10^{-27} \frac{\text{J}}{\text{T}} \right) \cdot \frac{1 \text{ T}}{6.63 \times 10^{-34}}$$

$$\Delta\lambda \approx 0.01 \text{ nm} \quad \boxed{\text{A}}$$

Que 3 In a normal zeeman effect experiment using a magnetic field of strength 0.3 T, the splitting between the components of a 660 nm spectral line is:

a) 12 pm    b) 10 pm    c) 8 pm    d) 6 pm

Sol<sup>n</sup>o- 
$$\Delta\lambda = \frac{\lambda^2}{c} \left( g_L \frac{eB}{4\pi m} \right) \quad g_L = 1$$

$$= \frac{(660 \times 10^{-9})^2 \times 1.6 \times 10^{-19} \times 0.3}{4 \times 3.14 \times 3 \times 10^8 \times 9.1 \times 10^{-31}}$$

$$\Delta\lambda = 6.09 \times 10^{-12} \text{ m}$$

$$= 6 \text{ pm} \quad \boxed{\text{D}}$$



Ques 4 The Zeeman shift of the energy of a state with quantum number  $L, S, J$  &  $m_J$  is:

$$\Delta E = \frac{m_J \mu_B B}{J(J+1)} (\langle L \cdot J \rangle + g_s \langle S \cdot J \rangle)$$

where  $B$  is the applied magnetic field,  $g_s$  is the  $g$ -factor for the spin &  $\mu_B / h = 1.4 \text{ MHz-G}^{-1}$ , where  $h$  is Planck constant. The approximate frequency shift of the  $s=0, L=1$  &  $m_J=1$  state, at a magnetic field of  $1 \text{ G}$ , is:

DEC-2017

- a)  $10 \text{ MHz}$    b)  $1.4 \text{ MHz}$    c)  $5 \text{ MHz}$    d)  $2.8 \text{ MHz}$

Soln<sup>o</sup> -

$$\Delta E = \frac{eB}{4\pi m} \times \frac{h}{h} = \left( \frac{eh}{4\pi m} \right) \times \frac{B}{h}$$

$$\Delta E = \frac{\mu_B}{h} \times B$$

$$= 1.4 \frac{\text{MHz}}{\text{G}} \times 1 \text{ G}$$

$$= 1.4 \text{ MHz}$$

B



## → Anomalous Zeeman effect:

$S \neq 0$  (multiplet state)

magnetic field:  $\vec{B}$  = weak

line splits into 4 or more components

selection Rule:  $\Delta m_J = 0, \pm 1$

state of Polarization:

1) when viewed  $\perp$  to  $\vec{B}$ : Plane Polarized

$\Delta m_J = \pm 1 \rightarrow$  Plane Polarized  $\perp$  to  $\vec{B}$

$\Delta m_J = 0 \rightarrow$  Plane Polarized  $\parallel$  to  $\vec{B}$

2) when viewed  $\parallel$  to  $\vec{B}$ :

$\Delta m_J = \pm 1 \rightarrow$  circularly Polarized

$\Delta m_J = 0 \rightarrow$  Forbidden.

energy shift:

$$\Delta v = g_J \frac{eB}{4\pi m} h$$

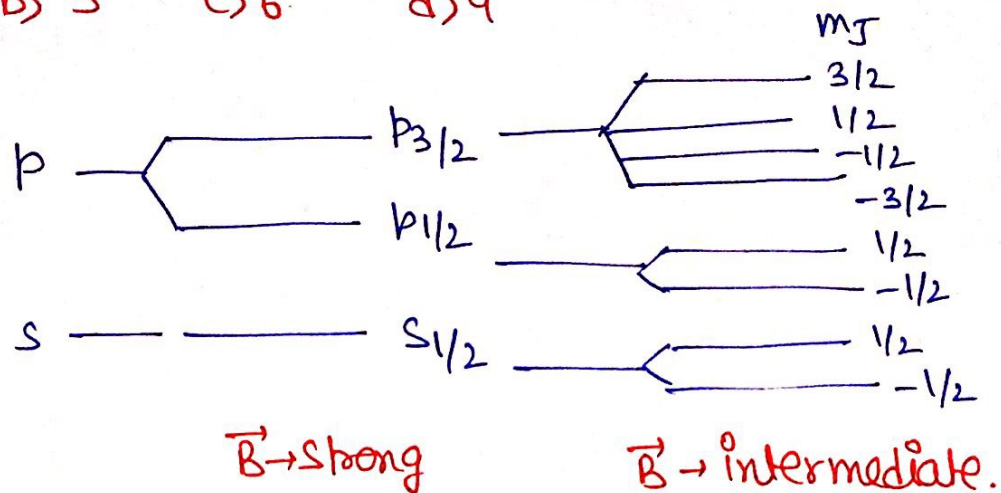
$$\Delta \lambda = \frac{\lambda^2}{c} \left( g_J \frac{eB}{4\pi m} \right)$$

Ques 1 A spectral line due to a transition from an state p to an state s splits into three zeeman lines in the presence of strong magnetic field. At intermediate field strengths the number

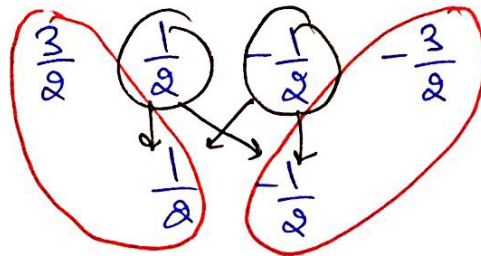
of spectral lines is:

- a) 10    b) 3    c) 6    d) 9

$\text{So } l^{n_0-}$

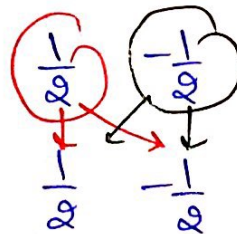


$p_{3/2} \rightarrow s_{1/2} :$



no. of lines:  $2(1) + 2(2) = 6$

$p_{1/2} \rightarrow s_{1/2}$



no. of lines:  $2(2) = 4$

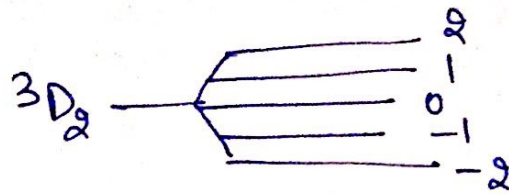
Total spectral lines =  $4 + 6 = 10$  A

Ques 2 An atomic spectral line is observed to split into 9 components due to Zeeman shift. If the upper state of atom is  $3p_2$ , then the lower state will be:

- a)  $3F_2$     b)  $3F_1$     c)  $3P_1$     d)  $3P_2$

Soln<sub>o</sub>-

(34)

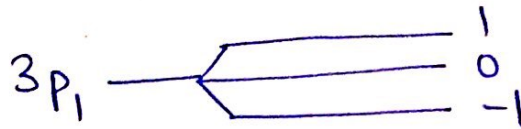


$$2S+1=3$$

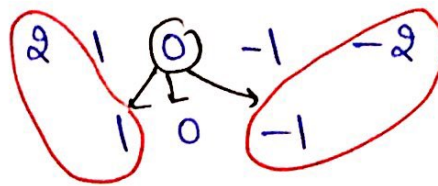
$$S=1$$

↑ AZE

$$\Delta m_j = 0, \pm 1$$



$m_j$ :



Spectral lines:  $2(1) + 2(2) + 1(3) = 9$

[C]

$$(3\hat{F}_1) \rightarrow S=1, L=3$$

$$J=2, 3, 4$$

$(3\hat{F}_1)$  invalid state.



→ Paschen Back effect (PBE)

$S \neq 0$  &  $\vec{B}$ : strong

number of lines: 2 or 3

$$\omega_L = g_L \frac{eB}{2m} = \frac{eB}{2m}$$

$$\omega_S = g_S \frac{eB}{2m} = 2 \left( \frac{eB}{2m} \right)$$

energy shift:  $\Delta E = (m_L + 2m_S) \mu_B B$

selection Rule:  $\Delta m_L = 0, \pm 1$   
 $\Delta m_S = 0$

maximum PB level:  $(2S+1)(2L+1)$

example: splitting of sodium - p line in the presence of strong magnetic field?

Sol<sup>no</sup>- Na (D-line):  $3p \rightarrow 3s$

3p:  $l=1, s=1/2$

↓

↓

$m_L = 1, 0, -1$

$m_S = 1/2, -1/2$

3s:  $l=0, s=1/2$

↓

↓

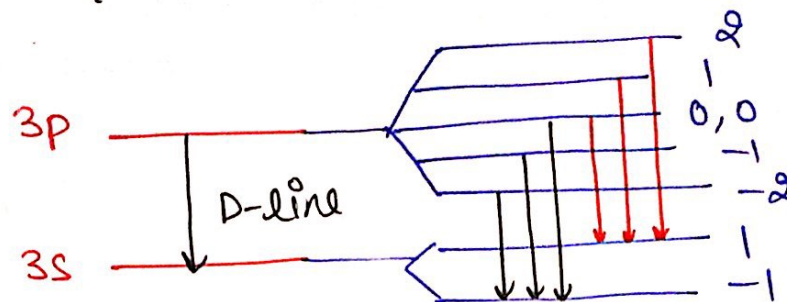
$m_L = 0$

$m_S = \pm 1/2$

| $m_L$ | $m_S$ | $m_L + 2m_S$ |
|-------|-------|--------------|
| 1     | $1/2$ | 2            |
| 0     |       | 1            |
| -1    |       | 0            |

| $m_L$ | $m_S$  | $m_L + 2m_S$ |
|-------|--------|--------------|
| 1     | $-1/2$ | 0            |
| 0     |        | -1           |
| -1    |        | -2           |

| $m_l$ | $m_s$  | $m_l + 2m_s$ |
|-------|--------|--------------|
| 0     | $1/2$  | 1            |
| 0     | $-1/2$ | -1           |



$\vec{B} = \text{strong.}$

\*\*\* Note: magnetic field completely removes the degeneracy of any level.

→ Stark effect:

splitting of atomic energy levels in the presence of external electric field.

1) linear Stark effect:

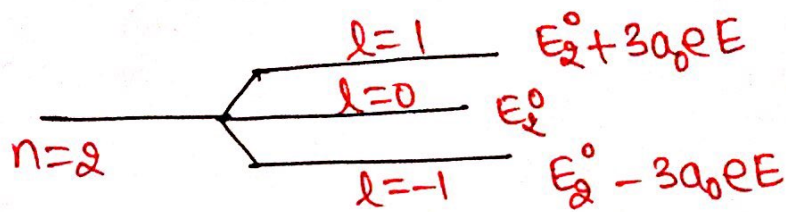
→ weak field effect

→ Selection Rule:  $\Delta m_j = 0, \pm 1$

→ energy shift:  $\Delta E \propto \text{Electric Field}$

→ no linear Stark effect in ground state of Hydrogen atom.

→ For 1st excited state of H-atom.



$E=0$

$E \neq 0$

2) quadratic Stark Effect:

→ Strong field effect

→ Selection Rule:  $\Delta m_l = 0, \pm 1$

$$\Delta m_s = 0$$

→ In ground state of H-atom

$$(\Delta E)_{\text{ground}}^{(H)} = -\frac{1}{2} \alpha E^2$$

↑  
Polarization.

Note:

\*\*\* → no linear effect in ground as well as excited states of alkali atoms (Li, Na, K etc.)

∴ Energy of alkali atoms depends on  $n$  &  $l$  i.e.  $E_{n,l}$

Here,  $l$  is non-degenerate.

\*\*\* → Electric field removes degeneracy partially.



## → Hyperfine splitting:

(38)

cause: very weak interaction.

$$\vec{F} = \vec{L} + \vec{S} + \vec{I}$$

$\vec{I} \rightarrow$  nuclear interaction.

$$|\vec{I}| = \sqrt{I(I+1)} \hbar$$

$$I_z = m_I \hbar$$

$$|M_I| = g_I \sqrt{I(I+1)} \mu_N$$

$$\mu_N = \frac{e\hbar}{4\pi m_p}$$

similarly,

$$|\vec{F}| = \sqrt{F(F+1)} \hbar$$

$$\vec{F} = \vec{J} + \vec{I}$$

$$\cos \theta_{IJ} = \frac{F(F+1) - J(J+1) - I(I+1)}{2\sqrt{J(J+1)}\sqrt{I(I+1)}}$$

total number of hyperfine levels =  $(2J+1)$  OR  $(2I+1)$

which is ever is lower.

selection Rule:  $\Delta F = 0, \pm 1$

Degeneracy:  $g = (2F+1)$

Symbol:  $\begin{matrix} 2S+1 & P \\ n & F & L & J \end{matrix}$

Term Separation:

$$\Delta E_F = a \hbar^2 \text{ (Higher F value)}$$

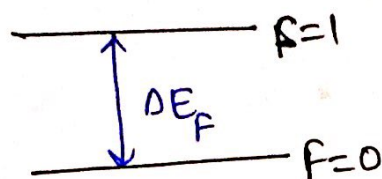


Ques 1 If the hyperfine interaction in an atom is given by  $H = a \vec{S}_e \cdot \vec{S}_p$  where  $\vec{S}_e$  &  $\vec{S}_p$  denote the  $e^-$  & proton spins, respectively, the splitting between  $3s_1$  &  $3s_0$  state is:

- a)  $\frac{ak^2}{\sqrt{2}}$     b)  $ak^2$     c)  $\frac{ak^2}{2}$     d)  $2ak^2$

DEC-2011, 2014

Soln<sup>o</sup> -



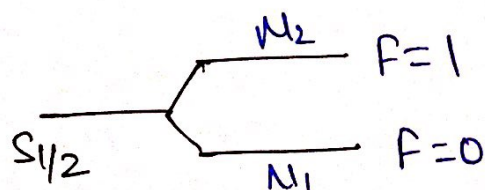
$$\Delta E_F = ak^2 (\text{Higher } F \text{ value})$$

$$= 1 \cdot ak^2 \quad \boxed{B}$$

Ques 2 The total spin of a H-atom is due to the contribution of spins of the  $e^-$  & the proton. In the high temperature limit, the ratio of number of atoms in the spin-1 state to the number of spin 0 state is:

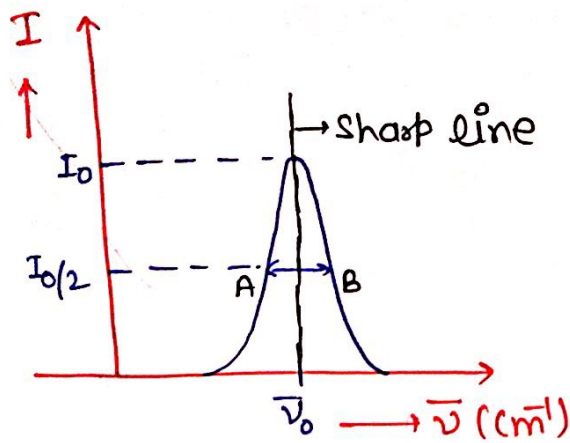
- a) 2    b) 3    c) 1/2    d) 1/3

Soln<sup>o</sup> -



$$\frac{N_2}{N_1} = \frac{g_2}{g_1} = \frac{(2F_2+1)}{(2F_1+1)} = \frac{(2 \times 1 + 1)}{(2 \times 0 + 1)} = 3 \quad \boxed{C}$$

## → Broadening In Spectral line:



Broadening is opposite to sharpness.

$$\Delta \bar{\nu} = \bar{\nu}_B - \bar{\nu}_A = \text{FWHM}$$

### 1) Natural Broadening:

arises due to finite lifetime of an energy level.

$$\Delta E \Delta t \geq \hbar/2$$

$\Delta E \Delta t \approx \hbar$  (For Reasonable approximation)

$$\Delta E = \frac{\hbar}{2\pi \Delta t} \quad \& \quad \Delta t = \frac{\hbar}{2\pi \Delta E}$$

$$\Delta t = \begin{cases} 10^{-3} & \text{for metastable state} \\ 10^{-8} & \text{normal excited state} \end{cases}$$

$$\Delta E = \hbar \Delta \nu \Rightarrow \boxed{\Delta \nu = \frac{1}{2\pi \Delta t}} \quad \&$$

$$\nu = \frac{c}{\lambda} \Rightarrow \Delta \nu = -\frac{c}{\lambda^2} \Delta \lambda$$

$$\Delta \lambda = \frac{-\lambda^2}{2\pi c \Delta t}$$



## 2) Doppler Broadening:

arises due to doppler effect.

$$\nu = \nu_0 \left(1 \pm \frac{v}{c}\right)$$

+ sign: source & observer moving towards each other i.e distance decreases  
(BLUE SHIFT)

- sign: source & observer moving away from each other (RED SHIFT)

$$\rightarrow \Delta \nu_D = (7.16 \times 10^{-7}) \nu_0 \sqrt{\frac{T}{m}} \text{ Hz}$$

$T \rightarrow$  temperature of source

$$\rightarrow \Delta \lambda_D = - (7.16 \times 10^{-7}) \lambda_0 \sqrt{\frac{T}{m}}$$

$$\rightarrow \Delta E_D = (7.16 \times 10^{-7}) E_0 \sqrt{\frac{T}{m}}$$

## 3) Collision Broadening:

Due to high pressure collision will be more frequent, photons of different energies are emitted & line will be broadened.

$$\Delta \nu_C = \frac{1}{2} n d^2 \sqrt{\frac{3k_B T}{m}}$$

$d \rightarrow$  diameter of an atom

$n \rightarrow$  density of gas

Ques 1 Two monochromatic sources  $L_1$  and  $L_2$  emit light at 600 & 700 nm, respectively. If the frequency bandwidths are  $10^1$  &  $10^3$  GHz, then the ratio of line width of  $L_1$  &  $L_2$  is approximate:

- a) 100:1    b) 1:85    c) 75:1    d) 1:75

Soln:-

$$\lambda_1 = 600 \text{ nm} \quad \Delta \nu_1 = 10^1 \text{ GHz}$$

$$\lambda_2 = 700 \text{ nm} \quad \Delta \nu_2 = 10^3 \text{ GHz}$$

$$\nu = \frac{c}{\lambda} \Rightarrow \Delta \nu = -\frac{c}{\lambda^2} \Delta \lambda \Rightarrow \Delta \lambda = -\frac{\lambda^2}{c} \Delta \nu$$

$$\frac{\Delta \lambda_1}{\Delta \lambda_2} = \frac{\Delta \nu_1}{\Delta \nu_2} \left( \frac{\lambda_1}{\lambda_2} \right)^2$$

$$= \frac{10^1}{10^3} \left( \frac{600}{700} \right)^2 = \frac{3600}{49} \approx \frac{75}{1} \quad \boxed{c}$$

Ques 2 The intensity distribution of a red LED on an absorbing layer of material is a Gaussian centered at the wavelength  $\lambda_0 = 660 \text{ nm}$  & width = 20 nm. If the absorption coefficient varies with wavelength as  $\alpha_0 - K(\lambda - \lambda_0)$  where  $\alpha_0$  &  $K$  are the constants, the light emerging from the observer will as as Blue shifted retaining the gaussian intensity distribution.

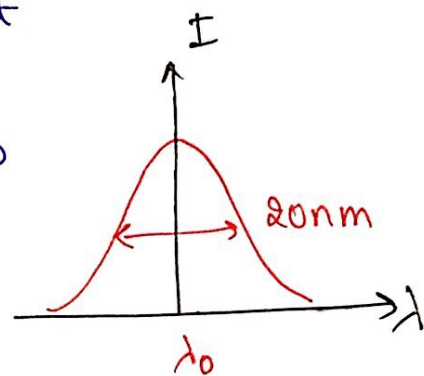


- 43
- b) Blue shifted with a symmetric intensity distribution
  - c) Red shifted retaining the gaussian intensity distribution
  - d) Red shifted with an asymmetric intensity distribution.

Sol<sup>n</sup> -  $I_t = I_i e^{-\alpha t}$  transmitted intensity

$$I_t = I_i e^{-\alpha_0 t + K(\lambda - \lambda_0)t}$$

after passing through LED  
: gaussian shape  
is disturbed.



i.e asymmetric distribution

$I_t$  includes a factor  $e^{K(\lambda - \lambda_0)t}$

which means that wavelength higher than  $\lambda_0$  will have higher intensity.

⇒ Peak will shift to higher wavelength

i.e RED shift

D



→ X-Ray spectra: (Inverse Photoelectric Effect) (44)

X-Ray are em waves of very short wave-length ( $\lambda \sim 1\text{\AA}$ )

1) Continuous X-Ray spectra:

- Inverse Photo electric effect.
- emitted due to continuous deceleration of electrons in the metal target.
- shortest wave length of radiation:

$$\lambda_{\text{swl}} = \frac{hc}{E(\text{ev})} = \frac{12400}{E(\text{ev})} \text{\AA}$$

$$\lambda_{\text{swl}} = \frac{12400}{V} \text{\AA} \quad V \rightarrow \text{tube voltage}$$

2) Characteristic X-Ray spectra:

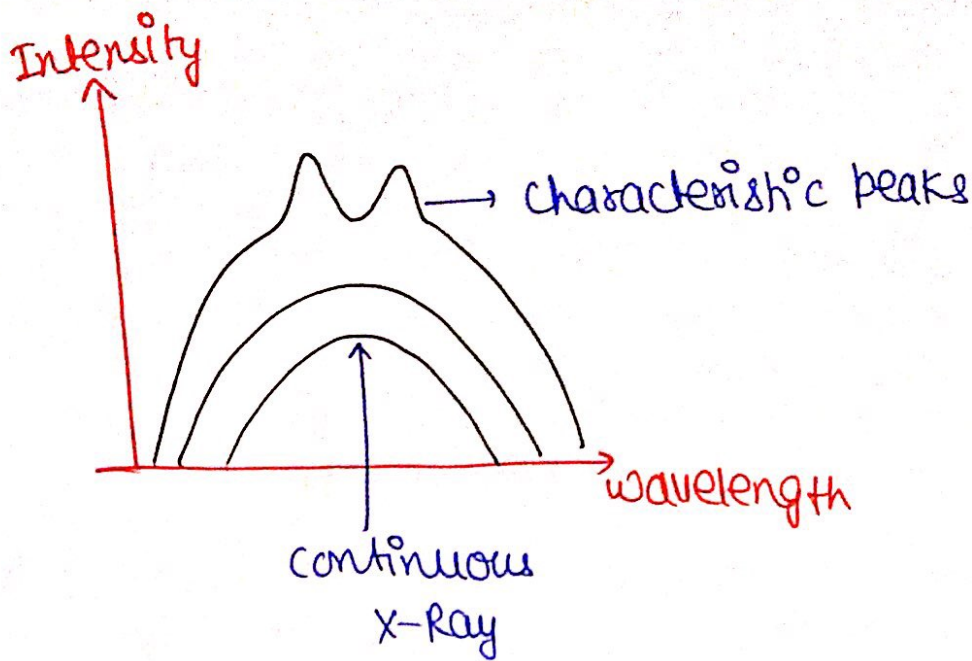
- emitted X-Ray photon is characteristic X-Ray photon because it is characteristic of target metal at anode.

$$\rightarrow \frac{1}{\lambda} = R_{\infty} (Z-\sigma)^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$\sigma = 1$  for K-shell

$\sigma = 7.4$  for L-shell

↑  
scattering constant



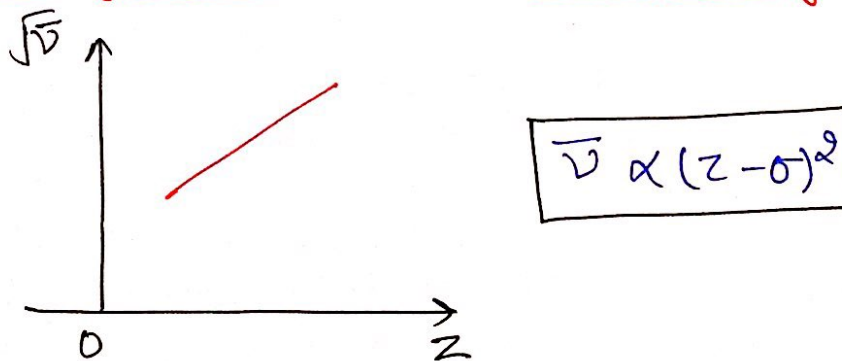
Intensity & wavelength depends on:

- continuous X-Ray: tube voltage
- characteristic X-Ray: material (target)

selection Rule for ch. X-Ray:

$$\begin{aligned} \Delta J &= 0, \pm 1 \\ \Delta L &= \pm 1 \\ \Delta S &= 0 \end{aligned}$$

Moseley law for characteristic X-Ray:



it signifies that atomic number is more fundamental than mass number.



Heteronuclear:  $\text{HCl}, \text{HBr}, \text{CO}, \dots$  MW-active

Homonuclear:  $\text{H}_2, \text{N}_2, \text{O}_2, \dots$  MW-inactive

Polyatomic:  $\text{CH}_4, \text{SF}_6, \text{P}_2\text{O}_5, \dots$  MW-inactive

### 1) Pure Rotational Spectra:

→ Shown by **Heteronuclear molecules** because they have permanent dipole moment.

→ observed in **absorption spectrum** only.

→ energy associated with rotational spectra:

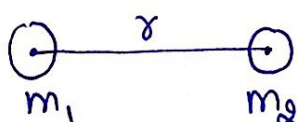
$$\Delta E_{\text{Rot.}} \sim 10^{-3} \text{ eV} = 1 \text{ meV}$$

→ Rotational spectra is a phenomenon of **micro wave region** of em radiation

$$\text{FIR} \approx 10^2 - 10^3 \text{ Hz}$$

$$\text{H-wave} \approx 10^3 - 10^4 \text{ Hz}$$

### Diatomic molecule as a Rigid Rotator:



Bond length ( $\xi$ ) will be fixed.

Reduced mass =

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

moment of inertia:

$$I = \mu \xi^2$$

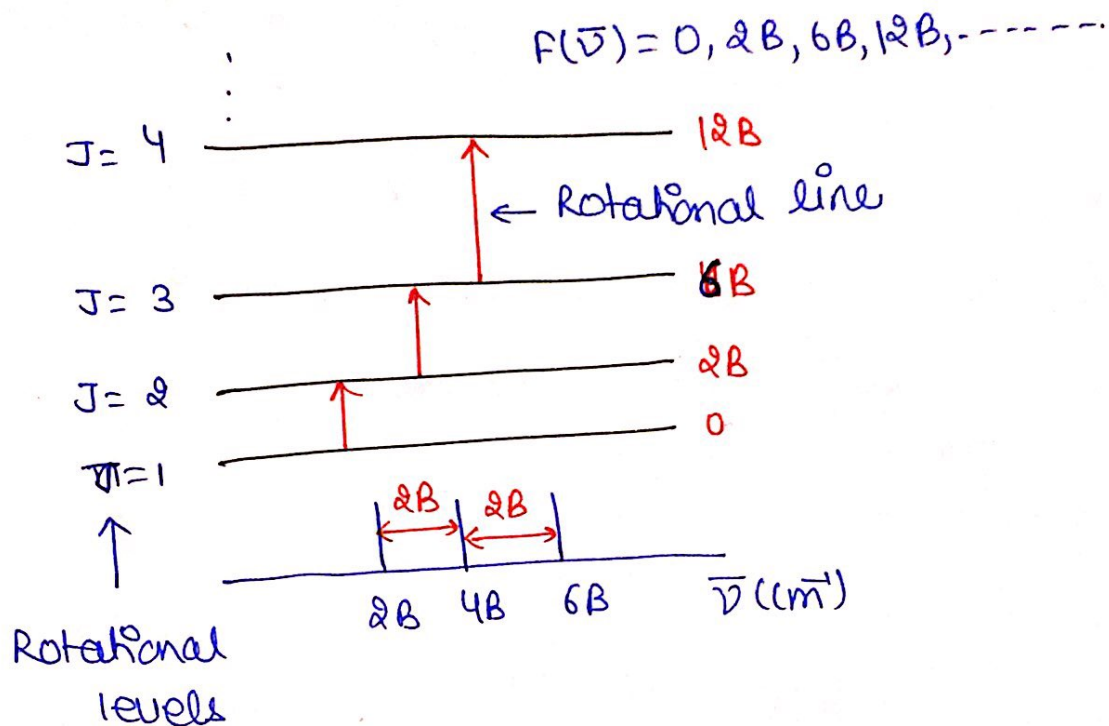


energy of Rigid Rotator:  $E_J = \frac{\hbar^2}{2I} J(J+1)$  (7)

energy in terms of wave number:  $F(\bar{\nu}) = B J(J+1)$

$$B = \frac{h}{8\pi^2 I c} \rightarrow \text{Rotational constant}$$

selection Rule:  $\Delta J = \pm 1$



→ Rotational lines are equidistant but Rotational levels are not.

→ wave number of emitted or absorbed radiation:

$$\Delta \bar{\nu} = 2B \times \text{highest Q.No.}$$

→ angular speed of molecule:

$$|\vec{J}| = I\omega \quad \& \quad |\vec{J}| = \hbar \sqrt{J(J+1)}$$

$$\omega = \frac{\hbar}{I} \sqrt{J(J+1)}$$

$$\omega = 2\pi\nu_{\text{rot}}$$

$$\nu_{\text{rot}} = \frac{h}{4\pi^2 I} J(J+1) \rightarrow \text{Rotational Frequency}$$

→ most Populated level:

Ratio of number of atoms in  $J^{\text{th}}$  level to the ground level is

$$\frac{N_J}{N_0} = (2J+1) e^{-\Delta E/k_B T}$$

For most populated level:  $\frac{dN_J}{dJ} = 0$

$$N_J = N_0 (2J+1) e^{-BJ(J+1)/k_B T}$$

Diatomic molecule as non-Rigid Rotator:

Here, Bond length doesn't remain fixed, As two atoms experience a centrifugal force.

$$F(\tilde{\nu}) = BJ(J+1) - \underbrace{DJ^2(J+1)^2}_{\substack{\uparrow \\ \text{Due to centrifugal force}}} \rightarrow \text{energy in terms of wave no.}$$

Due to centrifugal force

$D \ll B$  &  $D \rightarrow$  centrifugal distortion constant  
i.e. energy is slightly decreases.

→ Rotational lines are not equispaced.



wave number of emitted or absorbed line:

(49)

$$J \rightarrow J+1$$

$$\Delta \bar{\nu} = 2B(J+1) - 4D(J+1)^3$$

Isotopic effect in rotational spectra:

many elements are composed of isotopes  
like  $\text{HCl} - \text{DCl} - \text{TCl}$

$$M_{\text{HCl}} < M_{\text{DCl}} < M_{\text{TCl}} \quad \text{H}^i \neq \text{H}$$

$$\rightarrow B \propto \frac{1}{M} \Rightarrow B^i < B$$

$$\rightarrow F(\bar{\nu}^i) < F(\bar{\nu}) \quad \& \quad E_J^i < E_J$$

example of  $\mu$ -wave active molecule:

$\text{HCl}$ ,  $\text{CO}$ ,  $\text{OCS}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HD}$ ,  $\text{MnCl}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{NH}_3$ ,  
 $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  etc.

Because they have permanent dipole moment.

Ques! The first absorption spectrum of  $^{12}\text{C}^{16}\text{O}$  is at  $3.842 \text{ cm}^{-1}$  while that of  $^{13}\text{C}^{16}\text{O}$  is at  $3.673 \text{ cm}^{-1}$ .  
The ratio of their moments of inertia is:

a) 1.851    b) 1.286    c) 1.046    d) 1.038

Sol<sup>n</sup>o-

$$B = \frac{h}{8\pi^2 I c} \Rightarrow B \propto \frac{1}{I}$$

$$\frac{B_{^{12}\text{C}^{16}\text{O}}}{B_{^{13}\text{C}^{16}\text{O}}} = \frac{I_{^{13}\text{C}^{16}\text{O}}}{I_{^{12}\text{C}^{16}\text{O}}} = \frac{3.842}{3.673} = 1.046$$

[C]



Ques 2 Consider the Hydrogen-deuterium molecule HD.

If the mean distance between the atoms is  $0.08 \text{ nm}$  and the mass of Hydrogen atom is  $938 \text{ MeV}/c^2$ , then the energy difference  $\Delta E$  between the two lowest rotational states is approximately:

- a)  $10^1 \text{ eV}$     b)  $10^2 \text{ eV}$     c)  $2 \times 10^2 \text{ eV}$     d)  $10^3 \text{ eV}$

Sol<sup>n</sup>:- Reduced mass of HD

$$\mu = \frac{1 \times 2}{1+2} \text{ amu} = \frac{2}{3} \times 1.6 \times 10^{-27}$$

$$r = 0.08 \times 10^{-9} \text{ m}$$

$$\Delta E = E(J+1) - E(J) \quad \text{For lowest state: } J=0$$

$$= \frac{\hbar^2}{2I} [1(1+1) - 0(0+1)] = \frac{\hbar^2}{2I} \times 2$$

$$\Delta E = \frac{(1.05)^2 \times 10^{-68}}{\frac{2}{3} \times 1.67 \times 10^{-27} \times (0.08)^2 \times 10^{-18} \times 1.6 \times 10^{-19}} \text{ eV}$$

$$\Delta E \approx 0.96 \times 10^{-2} \text{ eV} \quad \boxed{B}$$

## 2) vibrational spectra:

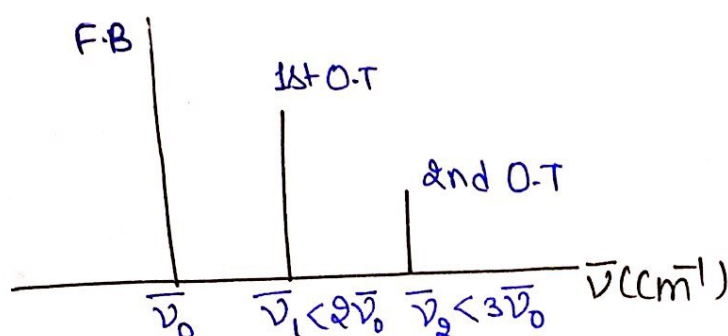
(41)

- arises from **vibrational motion** of a molecule.
- vibrational spectra is the phenomenon of **IR region** of em wave spectrum.

$$\text{NIR: } 10^0 \leq \lambda \leq 10^3 \mu\text{m}$$

- energy associated with the vibrational spectra

$$\Delta E_{\text{vib}} \sim 10^1 \text{ eV}$$



- The lowest wave number band has maximum intensity, and known as **Fundamental Band**.
- The wave number of 1st O.T is slightly less than twice of wave no. of F.B

→ vibrational energy:  $E_v = (v + \frac{1}{2}) h \omega = (v + \frac{1}{2}) h \nu_{\text{osc}}$

$$v = 0, 1, 2, \dots$$

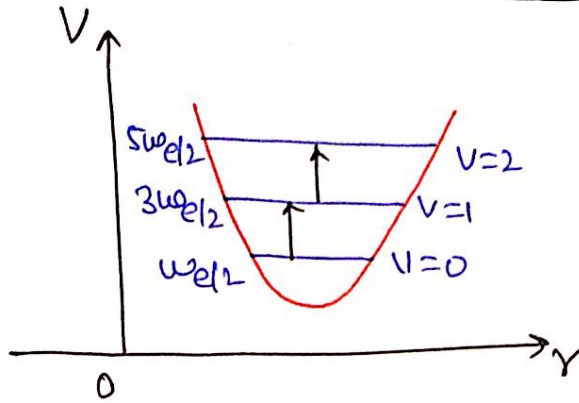
$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \rightarrow \text{vibrational frequency}$$

→ selection Rule:  $\Delta v = \pm 1$

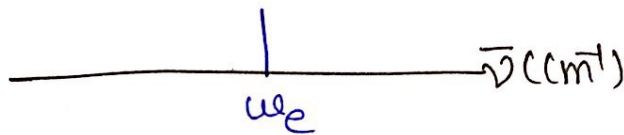
→ vibrational energy in terms of wave number:

$$F(\bar{\nu}_v) = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \frac{\nu_{osc}}{c} = \left(v + \frac{1}{2}\right) \omega_e$$

$$\omega_e = \nu_{osc}/c$$



in diatomic molecule  
single IR Band  
appears at  $\omega_e(\text{cm}^{-1})$

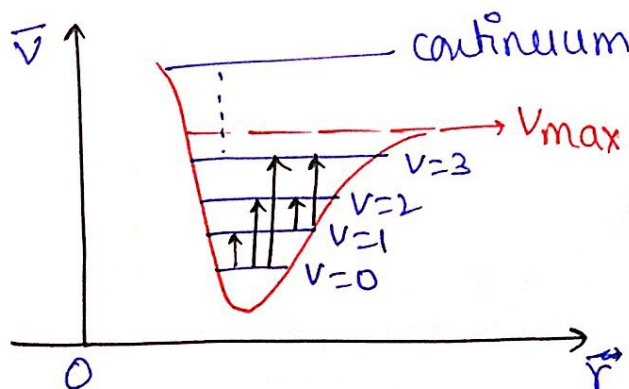


Diatomic molecule as anharmonic oscillator:

$$E(\bar{\nu}) = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e$$

$x_e \rightarrow$  anharmonicity constant

$\omega_e x_e \rightarrow$  anharmonicity term



$V_{max}$ : dissociation of  
molecule takes  
place at this  
level.



$$\bar{\nu}_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$

$$\bar{\nu}_1 = \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e$$

$$\bar{\nu}_2 = \frac{5}{2}\omega_e - \frac{25}{4}\omega_e x_e$$

$$\bar{\nu}_3 = \frac{7}{2}\omega_e - \frac{49}{4}\omega_e x_e$$

$$\Delta\bar{\nu} = \omega_e - 2\omega_e x_e$$

$$\Delta\bar{\nu} = \omega_e - 4\omega_e x_e$$

$$\Delta\bar{\nu} = \omega_e - 6\omega_e x_e$$

Selection Rule:  $\Delta V = \pm 1, \pm 2, \pm 3, \dots$

Bands in anharmonic oscillator:

1) Fundamental Band: ( $V=0 \rightarrow V=1$ )

$$\Delta\bar{\nu}_{0 \rightarrow 1} = \omega_e - 2\omega_e x_e$$

most intense Band at room temperature.

2) First overtone Band: ( $V=0 \rightarrow V=2$ )

$$\Delta\bar{\nu}_{0 \rightarrow 2} = 2\omega_e - 6\omega_e x_e$$

3) Second overtone Band: ( $V=0 \rightarrow V=3$ )

$$\Delta\bar{\nu}_{0 \rightarrow 3} = 3\omega_e - 12\omega_e x_e \quad (\text{GATE-2018})$$

4) Hot Band:  $V=1 \rightarrow V=2$

$$\Delta\bar{\nu}_{1 \rightarrow 2} = \omega_e - 4\omega_e x_e$$

Isotope effect in vibrational level:

like:  $^{12}\text{C}^{16}\text{O}$ ,  $^{13}\text{C}^{16}\text{O}$ ,  $^{13}\text{C}^{17}\text{O}$

$$\nu_{08e} \propto \frac{1}{\sqrt{\mu}}$$

$$\mu^i > \mu$$

$$\nu_{08c}^i < \nu_{08c}$$

## Diatomic molecule as a vibrating-rotator:

(54)

$$\text{Total energy} = E_{\text{rot}} + E_{\text{vib.}}$$

→ energy in terms of wave no.

$$\bar{\nu} = \frac{E}{hc} = BJ(J+1) + \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2\omega_e x_e$$

→ Selection Rule:

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

$$\Delta J = \pm 1$$

→ Branches of vibrational-rotational spectrum:

$$\text{P-Branch : } \Delta J = -1$$

$$\text{Q-Branch : } \Delta J = 0$$

$$\text{R-Branch : } \Delta J = +1$$

$$\rightarrow |\Delta \bar{\nu}| = \bar{\nu}_{R_0} - \bar{\nu}_{P_1} = 4B$$

$$|\Delta \bar{\nu}| = \bar{\nu}_{Q_0} - \bar{\nu}_{P_1} = 2B$$

Que! If the leading anharmonic correction to the energy of the  $n$ th vibrational level of a diatomic molecule is  $-\chi_e \left(n + \frac{1}{2}\right)^2 h\nu_e$  with  $\chi_e = 0.001$ , the total number of energy levels possible is approx.

a) 500      b) 1000      c) 250      d) 750

Sol<sup>n</sup>g. energy of anharmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right) h\nu_e - \chi_e \left(n + \frac{1}{2}\right)^2 h\nu_e$$



now,  $\frac{dE_n}{dn} = 0$

$$h\nu - 2x_e \left(n + \frac{1}{2}\right) h\nu = 0$$

$$2x_e \left(n + \frac{1}{2}\right) h\nu = h\nu$$

$$\left(n + \frac{1}{2}\right) = \frac{1}{2x_e}$$

$$n_{\max} = \frac{1}{2x_e} - \frac{1}{2} = \frac{1}{2 \times 0.001} - \frac{1}{2}$$

$$n_{\max} = 499.5 \quad \boxed{A}$$

Que 2 A diatomic molecule has vibrational states with energies  $E_v = h\nu \left(v + \frac{1}{2}\right)$  and rotational states with energies  $E_J = BJ(J+1)$ , where  $v$  &  $J$  are non-negative integers. Consider the transitions in which both the initial & final states are restricted to  $v \leq 1$  to  $J \leq 2$  and subject to the selection rules  $\Delta v = \pm 1$  &  $\Delta J = \pm 1$ . Then the largest allowed energy of transition is:

a)  $h\nu - 3B$     b)  $h\nu - B$     c)  $h\nu + 4B$     d)  $2h\nu + B$

Sol<sup>n</sup>:-  $E = h\nu \left(v + \frac{1}{2}\right) + BJ(J+1)$

$$\begin{aligned} E_{in} &= h\nu \left(1 + \frac{1}{2}\right) + B \cdot 2(2+1) \\ &= \frac{3h\nu}{2} + 6B \end{aligned}$$

For largest energy:  
 $v=1$   
 $J=2$



$$E_{\text{final}} = \hbar\omega\left(0 + \frac{1}{2}\right) + B(1+1)$$

using selection Rule:  $\Delta V = \pm 1$   
 $\Delta J = \pm 1$

$$E_{\text{final}} = \frac{1}{2}\hbar\omega + 2B$$

$$\Delta E = \hbar\omega + 4B \quad \boxed{C}$$

### 3) Raman Spectra:

- Discovered by C.V. Raman
- observed in UV/visible monochromatic radiation.
- shown by all kind of molecules.
- in Raman scattering, 3 different lines are observed on wave number scale.



$\bar{\nu}_0 \rightarrow$  UV/visible Region

$\Delta\bar{\nu} \rightarrow$  IR Region

- Raman shift:  $\Delta\bar{\nu} \propto$  substance  
 $\propto$  incident Radiation

→ Position of line depends on both substance & incident radiation.

$$I_{\text{anti-stokes}} < I_{\text{stokes}} < I_{\text{Rayleigh}}$$

### Rotational Raman spectra:

→ Shown by homonuclear molecules like  $H_2, N_2$  etc.

→ Selection rule:  $\Delta J = 0, \pm 2$

→ Rotational Raman shift:

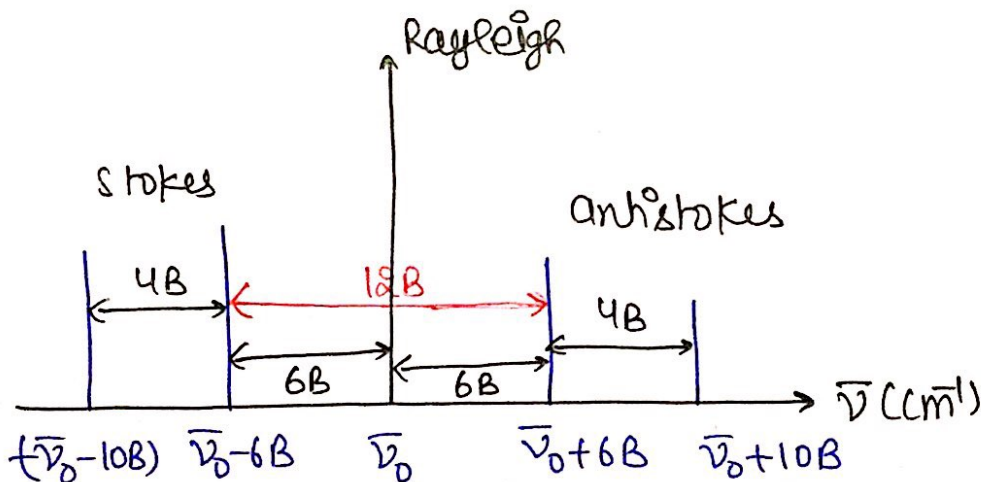
$$\bar{\nu}_{\text{Rot}}^{\text{Raman}} = \bar{\nu}_0 \pm [\bar{\nu}_{J+2} - \bar{\nu}_J]$$

$$= \bar{\nu}_0 \pm 4B \left[ J + \frac{3}{2} \right]$$

$$|\Delta \bar{\nu}_{\text{Rot}}^{\text{Raman}}| = 4B \left[ J + \frac{3}{2} \right]$$



Rotational Raman shift.



→ Distance b/w two consecutive Stokes (or anti-Stokes) line =  $4B$

→ Distance b/w 1st Stokes & 1st anti-Stokes line =  $12B$

## Vibrational Raman Spectrum:

(58)

→ Selection Rule:  $\Delta V = \pm 1$  harmonic  
 $\Delta V = \pm 1, \pm 2, \dots$  anharmonic

$$\left| \Delta \bar{\nu}_{\text{vib}}^{\text{Raman}} \right|_{F.B} = \omega_e \quad \text{harmonic}$$
$$= \omega_e - 2\omega_e x_e \quad \text{anharmonic}$$

→ vibrational raman spectrum will be shown by molecule like:  $\text{SF}_6, \text{CH}_4, \text{CCl}_4, \text{Si}, \text{SiH}_4$  etc.

## Intensity Ratio:

$$\frac{I_{\text{Stokes}}}{I_{\text{AntiStokes}}} = e^{\frac{h(\Delta \bar{\nu})C}{k_B T}}$$

Ques 1 A laser operating at 500 nm is used to excite a molecule. If the Stokes line is observed at  $770 \text{ cm}^{-1}$ , the approximate positions of the ~~stokes~~ Stokes & the antiStokes lines are:

- a) 481.5 nm & 520 nm      b) 481.5 nm & 500 nm  
c) 500 nm & 520 nm      d) 500 nm & 600 cm

Sol<sup>n</sup>:-  $\lambda_0 (\text{Rayleigh}) = 500 \text{ nm}$

$$\bar{\nu}_{\text{Ray}} = \frac{1}{\lambda_0} = \frac{1}{500 \times 10^{-9}} = \frac{10^7}{500} \text{ cm}^{-1}$$
$$= 2 \times 10^4 \text{ cm}^{-1}$$



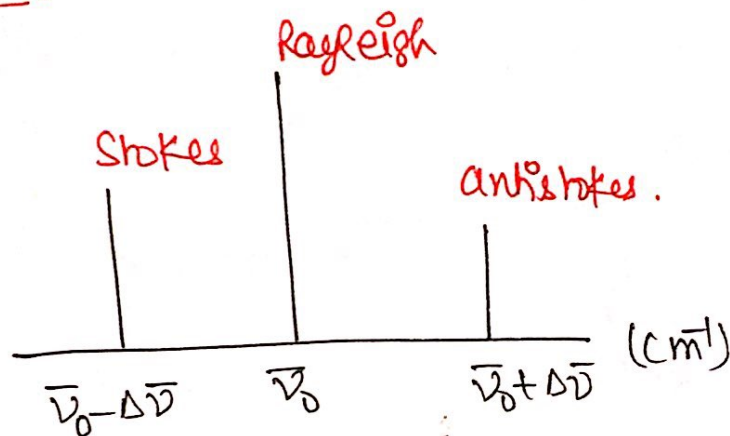
$$\bar{\nu}_{\text{Raman}}^{\text{Stokes}} = (20,000 - 770) \text{ cm}^{-1}$$

$$\bar{\nu}_{\text{anti-stokes}} = (20,000 + 770) \text{ cm}^{-1}$$

$$\lambda_{\text{Stokes}} = \frac{1}{19230} \times 10^7 \text{ nm} = 520 \text{ nm}$$

$$\lambda_{\text{anti}} = \frac{1}{20770} \times 10^7 \text{ nm} = 481.5 \text{ nm.} \quad \boxed{\text{A}}$$

alternate:



$$\bar{\nu}_{\text{anti}} > \bar{\nu}_{\text{Ray}} > \bar{\nu}_{\text{Stokes}}$$

$$\lambda_{\text{anti}} < \lambda_{\text{Ray}} < \lambda_{\text{Stokes}}$$

$$\lambda_{\text{anti}} < 500 \text{ nm} < \lambda_{\text{Stokes}} \rightarrow \text{only option}$$

$\boxed{\text{A}}$  satisfy this condition.

## Fundamental modes:

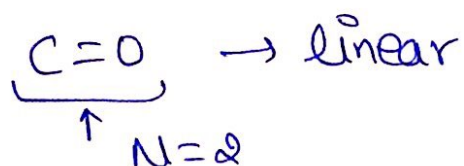
Rotational modes  $\begin{cases} \text{linear molecule: } 2 \\ \text{non-linear: } 3 \end{cases}$

vibrational modes  $\begin{cases} \text{linear: } 3N-5 \\ \text{Non-linear: } 3N-6 \end{cases}$

stretching  $\begin{cases} \text{linear: } (N-1) \\ \text{non-linear: } (N-1) \end{cases}$

Bending  $\begin{cases} \text{linear: } 2N-4 \\ \text{Non-linear: } 2N-5 \end{cases}$

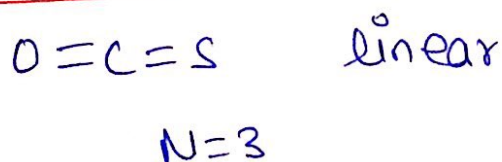
### ① CO molecule:



Rotational modes: for linear = ②

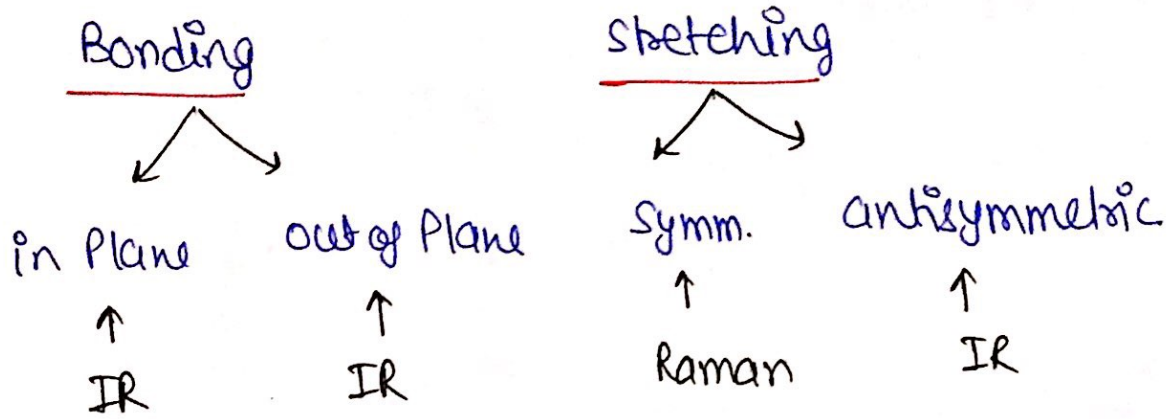
vibrational modes:  $3N-5 = 3 \times 2 - 5 = ①$

### ② OCS molecule:



Rot<sup>n</sup> modes: 2

vib. modes:  $3N-5 = 4$   $\begin{cases} 2 \text{ Bending} \\ 2 \text{ stretching} \end{cases}$



### Rule of mutual exclusion:

Those molecules (linear) which are having centre of inversion the I.R active modes are Raman inactive & vice-versa.

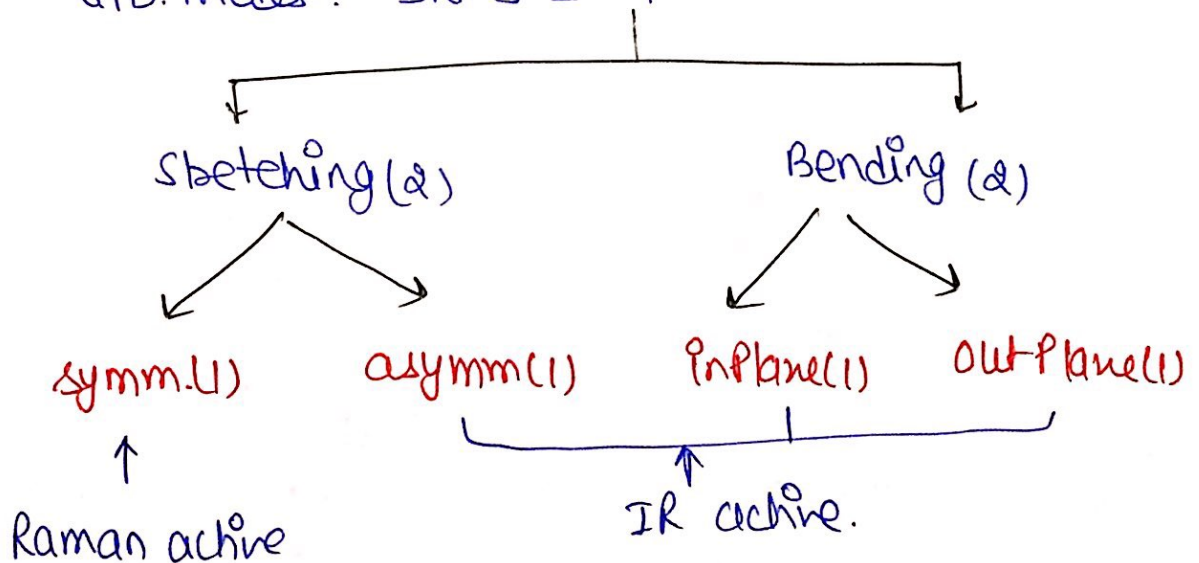
example:  $\text{CO}_2$



$$N=3$$

Rotational modes = 2

$$\text{vib. modes: } 3N-5 = 4$$

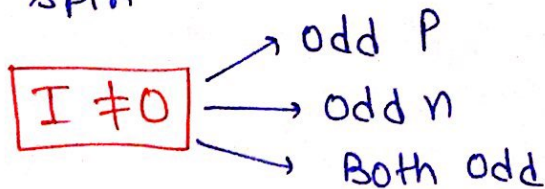




#### 4) NMR spectra:

NMR  $\rightarrow$  Nuclear magnetic Resonance

$\rightarrow$  shown by nuclei which has non-zero nuclear spin



$\rightarrow$  Phenomenon of RFR of em spectrum.

example:  ${}^{13}_6\text{C}$ ,  ${}^{17}_8\text{O}$ ,  ${}^1_1\text{H}$ ,  ${}^{35}_{17}\text{Cl}$  etc.

RFR (  $60 \times 10^6 - 600 \times 10^6 \text{ Hz}$  )

#### 5) ESR | EPR spectra:

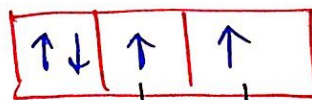
ESR: Electron spin Resonance

EPR: Electron paramagnetic Resonance

$\rightarrow$  found in those atoms or molecules which have unpaired  $e^-$ s.



example:  ${}_8\text{O} : 1s^2 2s^2 2p^4$



$\uparrow$  unpaired  $e^-$ s

$\rightarrow$  Phenomenon of  $\mu$ -wave region of em spectrum.

## 6) Electronic Spectra:

Frank-Condon Principle: according to this principle, an electronic transition takes place so rapidly that vibrating molecule doesn't change its internuclear distance during the transition.

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{electronic}}$$

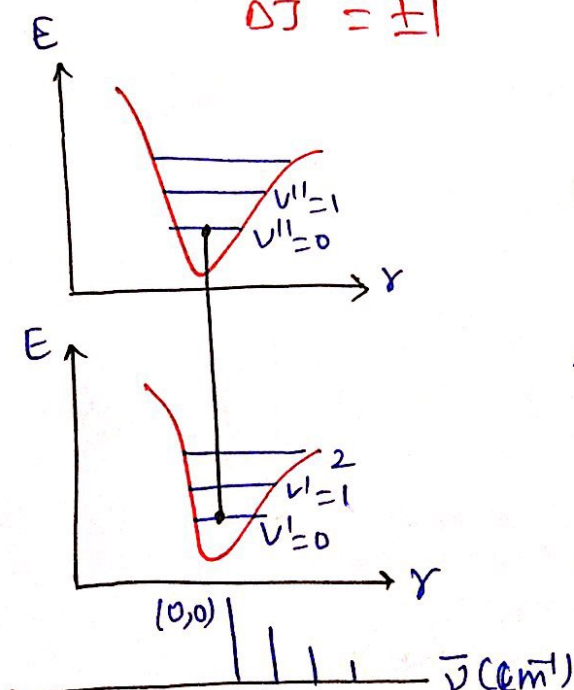
|                        |                        |                 |
|------------------------|------------------------|-----------------|
| $\uparrow$             | $\uparrow$             | $\uparrow$      |
| $\sim 10^3 \text{ eV}$ | $\sim 10^1 \text{ eV}$ | $10 \text{ eV}$ |
| (MW)                   | (IR)                   | (UV/VISIBLE)    |

- observed in both emission & absorption
- shown by all kinds of molecule
- Selection Rule:

$$\Delta n = \pm 1, \pm 2, \pm 3, \dots$$

$$\Delta V = 0, \pm 1, \pm 2, \dots$$

$$\Delta J = \pm 1$$

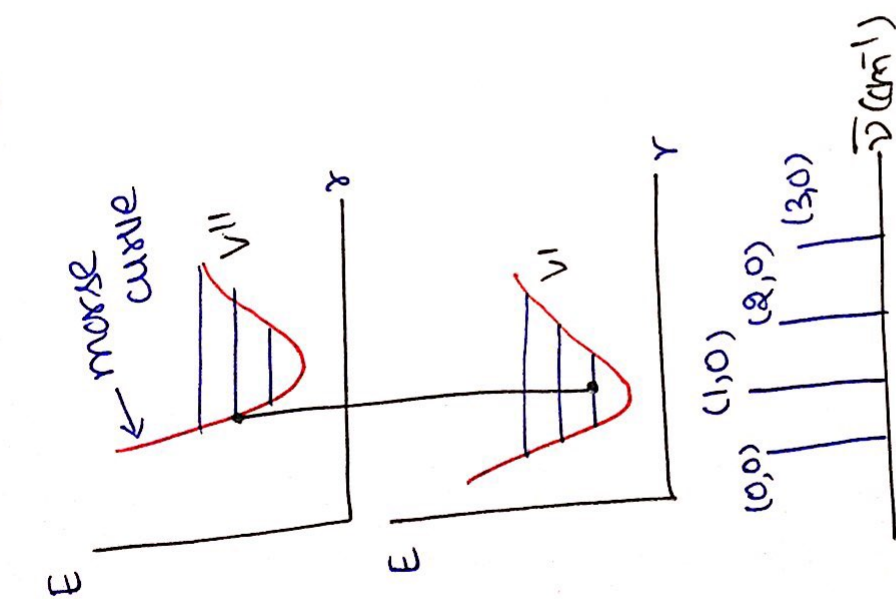


when upper & lower electronic state

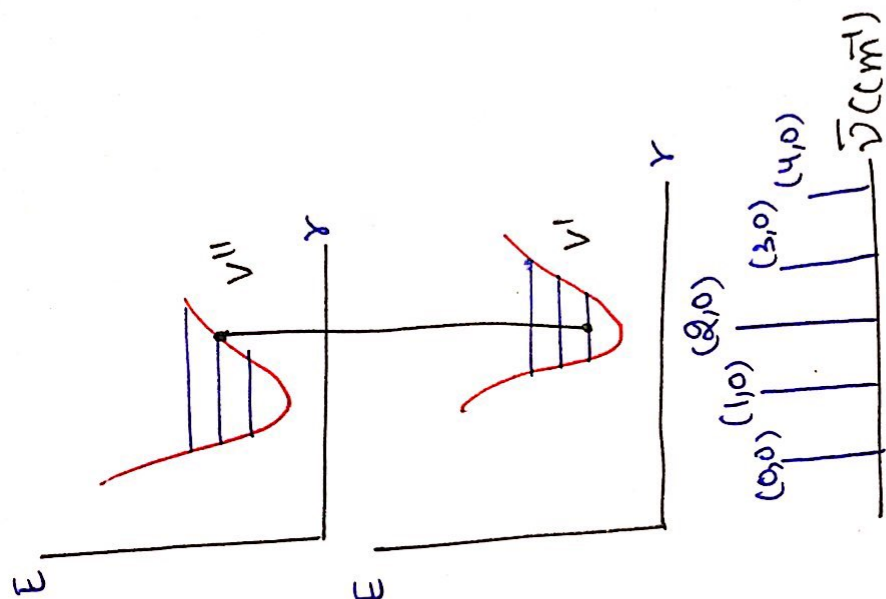
have potential energy minimum at same value of  $r$ .

example:  $O_2$  molecule.

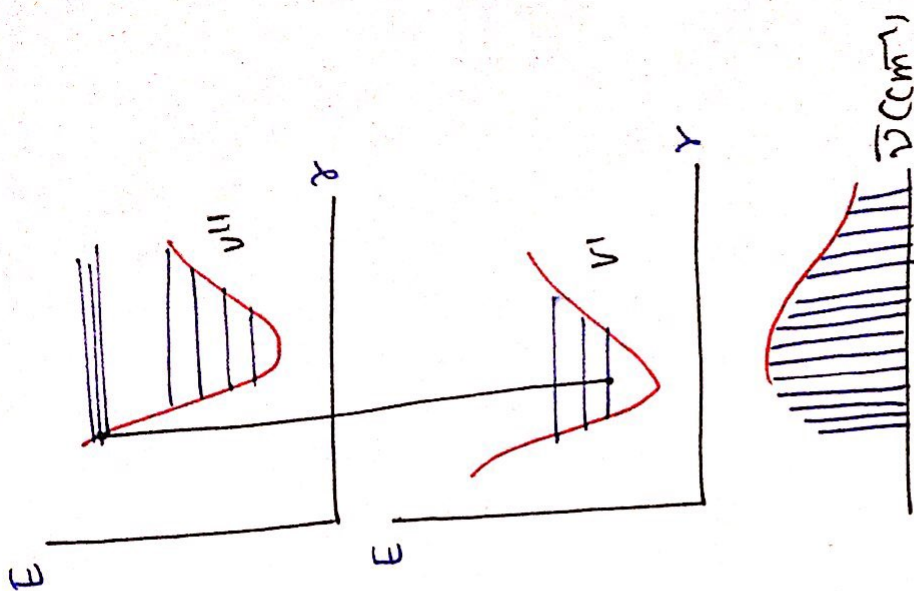




when potential energy of upper is minimum is at higher value of  $r$  than lower state



when potential energy is minimum of upper level at lower value of  $r$  than lower state

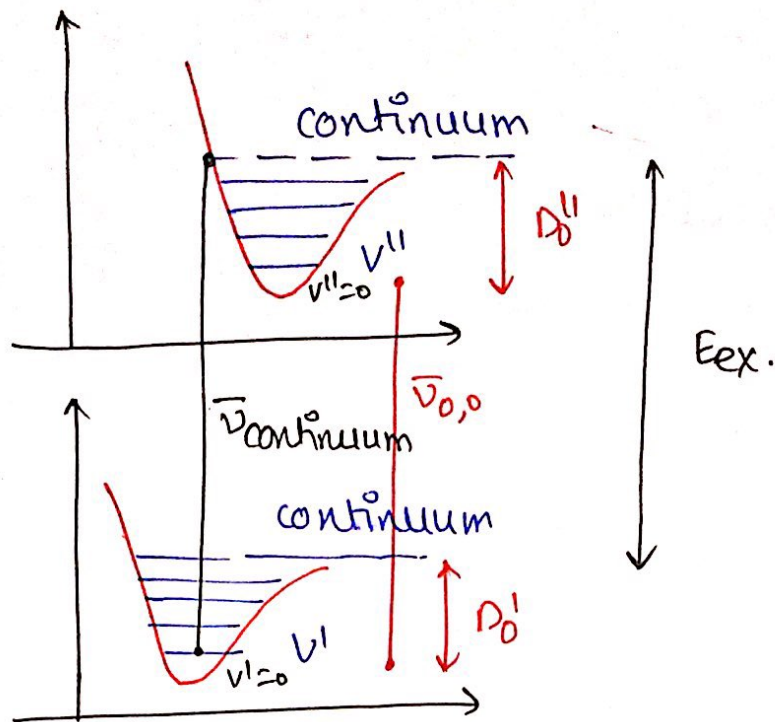


when upper electronic state is having very large inter-nuclear distance.

example: CO molecule.



## Dissociation energy:



$D_0 \rightarrow$  Dissociation energy

$E_{ex} \rightarrow$  Difference in dissociation energy of upper & lower electronic state.

$$\bar{\nu}_{\text{continuum}} = D_0' + E_{ex} = \bar{\nu}_{0,0} + D_0''$$

$$D_0'' = D_0' + E_{ex} - \bar{\nu}_{0,0}$$