

ALL INDIA TEST SERIES CSE-2023

Candidate 's Information

PH TS-2401050

1. NAME:-Komal Punia.....
2. UPSC ROLL NO:-
3. MOBILE NO:-[REDACTED].....
4. SUBJECT:- Atomic and Molecular
5. DATE:-.....11/07/2024.....

FOR OFFICE USE ONLY:-

| Q.NO | MARKS |
|------|-------|
| 1. | 23½ ✓ |
| 2. | 33 |
| 3. | 33 |
| 4. | 30½ |
| 5. | 26 |
| 6. | |
| 7. | |
| 8. | |

Very well written

| | |
|-------------|------------|
| TOTAL MARKS | 146 250 |
|-------------|------------|

[Signature]

EXAMINER SIGNATURE

INVIGILATOR SIGNATURE

Q. 1 a)

Normal Zeeman effect refers to splitting of fine-structure lines in presence of weak magnetic field.

$$E = -\vec{\mu} \cdot \vec{B} = -\left(g_e \left(\frac{-e}{2m}\right) \cdot \vec{L} \cdot \vec{B}\right)$$

$$= g_e \frac{\mu_B}{\hbar} m_l \hbar B_z = g_e m_l \mu_B B$$

Since, energy of normal Zeeman triplet -

$$\Delta E = \pm \mu_B B \Rightarrow \Delta E = 2 \mu_B B$$

↓
Energy difference

Given,

$$\lambda = 6000 \text{ \AA} \quad \Delta \lambda = 0.1 \text{ \AA}$$

$$|\Delta E| = \frac{hc \Delta \lambda}{\lambda^2}$$

$$2 \mu_B B = \frac{hc \Delta \lambda}{\lambda^2} \Rightarrow B = \frac{hc \Delta \lambda}{\lambda^2 2 \mu_B}$$

$$B = 0.598 \text{ T}$$

required to confirm normal Zeeman triplets

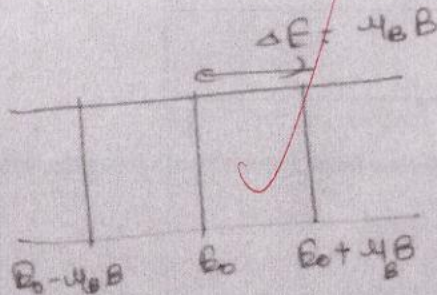


Fig: - Zeeman triplets

~~10~~

3 (b)

Splitting of energy states in presence of weak magnetic field is called Zeeman effect.

Given state: ${}^2P_{3/2}$

Magnetic moment -

$$\vec{\mu} = g_j \frac{\mu_B}{\hbar} \vec{J} \Rightarrow |\vec{\mu}| = g_j \mu_B \sqrt{J(J+1)}$$

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

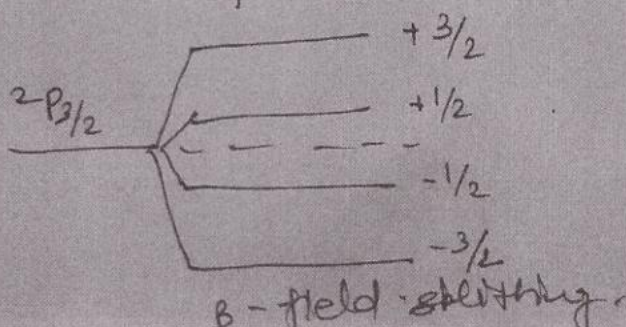
$$= 1 + \frac{3/2 \times 5/2 + 1/2 \times 3/2 - 1 \times 2}{2 \times 3/2 \times 5/2} = \underline{\underline{4/3}}$$

$$\Rightarrow |\vec{\mu}| = \frac{4}{3} \sqrt{3/2 \times 5/2} \mu_B = \sqrt{\frac{20}{3}} \mu_B$$

$$|\vec{\mu}| = \frac{2\sqrt{15}}{3} \mu_B$$

Since $\underline{j = 3/2}$ $2(2j+1) = 12 \times \frac{3}{2} + 1$
 $= 4$

So will split into 4 substates.



1(c)

LS coupling refers to magnetic interaction between orbital & spin angular momentum vectors.

d^2 state has equivalent electrons.

So using Breit's scheme -

$$l_1 = 2 \text{ \& \ } l_2 = 2 \Rightarrow L = 4, 3, 2, 1, 0$$

$$s_1 = 1/2 \text{ \& \ } s_2 = 1/2 \Rightarrow S = 0, 1$$

| m_{l_1} | 2 | 1 | 0 | -1 | -2 |
|-----------|---|----|----|----|----|
| 2 | 4 | 3 | 2 | 1 | 0 |
| 1 | 3 | 2 | 1 | 0 | -1 |
| 0 | 2 | 1 | 0 | -1 | -2 |
| -1 | 1 | 0 | -1 | -2 | -3 |
| -2 | 0 | -1 | -2 | -3 | -4 |

$$\frac{N_2}{10}$$

Diagonal terms (same m_l values so only singlet) \Rightarrow

$${}^1S_0, {}^1D_2, {}^1G_4$$

$${}^1S_{1/2}, {}^1D_{3/2}, {}^1G_{7/2}$$

Other triplet terms -

$${}^3P_{0,1,2}, {}^3F_{2,3,4}$$

प्रश्न संख्या
(Question No.)

U.P.S.C.

इस भाग में कुछ
न लिखें
(Don't write anything
in this part)

1(d)

3(e) IR spectra and Raman spectra,
in case of molecules with centre
of symmetry, show complementary
spectra according to mutual
Exclusion Principle.

CO₂ show two IR lines
which are absent in Raman
spectra \Rightarrow CO₂ has centre of
symmetry \Rightarrow CO₂ is linear.

4
10

H₂O show 3 IR lines which
overlap with Raman lines \Rightarrow
H₂O doesn't has centre of
symmetry \Rightarrow H₂O is not linear
 \Downarrow
H₂O is bent.

4.5(a)

Molecules with unpaired electrons under external magnetic field, exhibit precession of spin angular momentum due to torque experienced by \vec{B} .

When they are excited by suitable microwave excitations, leads to resonant transitions called as EPR or ESR.

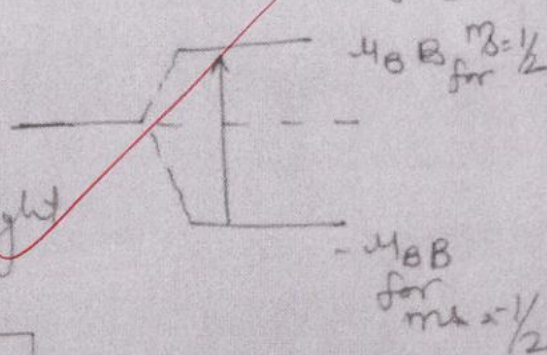
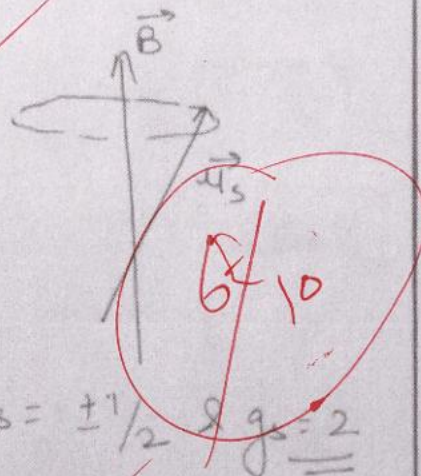
Condition of ESR

$$E = -\vec{\mu} \cdot \vec{B}$$

$$E = g \frac{\mu_B}{h} m_s B$$

for $\text{free } \Rightarrow s = 1/2 \Rightarrow m_s = \pm 1/2$ & $g = 2$

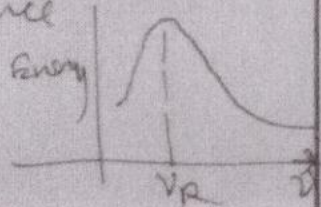
$$\Rightarrow E = \pm 4\mu_B B$$



When exciting light frequency is

$$\nu = \frac{2\mu_B B}{h}$$

resonance occurs



प्रश्न संख्या
(Question No.)

U.P.S.C.

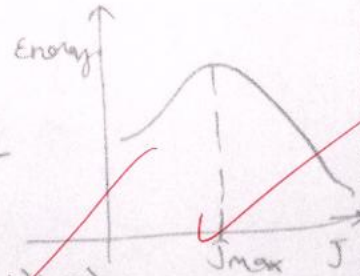
इस भाग में कुछ
न लिखें
(Don't write anything
in this part)

5 (b)

5(c) Rotational molecular transitions are given by

$$F(J) = 8J(J+1) \text{ cm}^{-1}$$

Using Maxwell-Boltzmann distribution -



~~Energy~~ $N \propto \exp\left(\frac{-8J(J+1)hc}{kT}\right)$

also considering degeneracy of states

$$N \propto (2J+1) \exp\left(\frac{-8J(J+1)hc}{kT}\right)$$

$$\left(\frac{dN}{dJ}\right)_{J=J_{\max}} = 0 \quad \& \quad \frac{d^2N}{dJ^2} < 0$$

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

where

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

$$I = 41 \text{ r}^2$$

~~6/2
10~~

$$B = 10 \text{ cm}^{-1}$$

$$J_{\max} = 4.56 - 0.5 = 4.06 \approx 4$$

as $\sqrt{\frac{kT}{2Bhc}} = 4.56$

$$\Rightarrow J_{\max} = 4$$

most populated rotational level.

Q5(d)

Hydrogen atom - $s = 1/2$

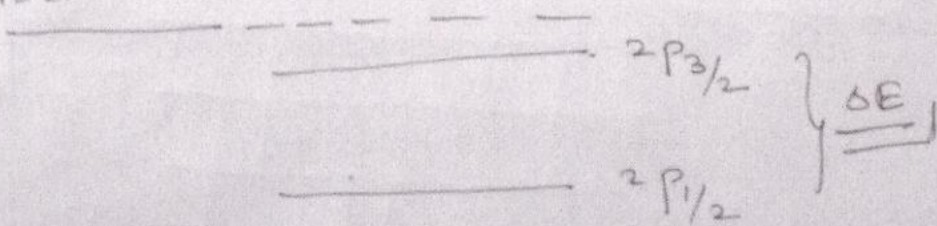
Given $n=2, l=1$ & $s=1/2$

LS coupling $|j| = |l+s|$ to $|l-s|$

$$\Rightarrow j = 3/2, 1/2$$

$\Rightarrow 2P_{3/2}$ and $2P_{1/2}$ terms.

$n=2$



LS coupling by using $\vec{L} \cdot \vec{S}$ term in Hamiltonian is

$$\Delta \bar{\nu} = \frac{\Delta E}{c} = \frac{584 Z^4}{n^3 l(l+1)} \text{ m}^{-1}$$

$Z=1, n=2, l=1$

$$\Rightarrow \Delta \bar{\nu} = \frac{584}{8 \times 1 \times 2} = 36.5 \text{ m}^{-1}$$

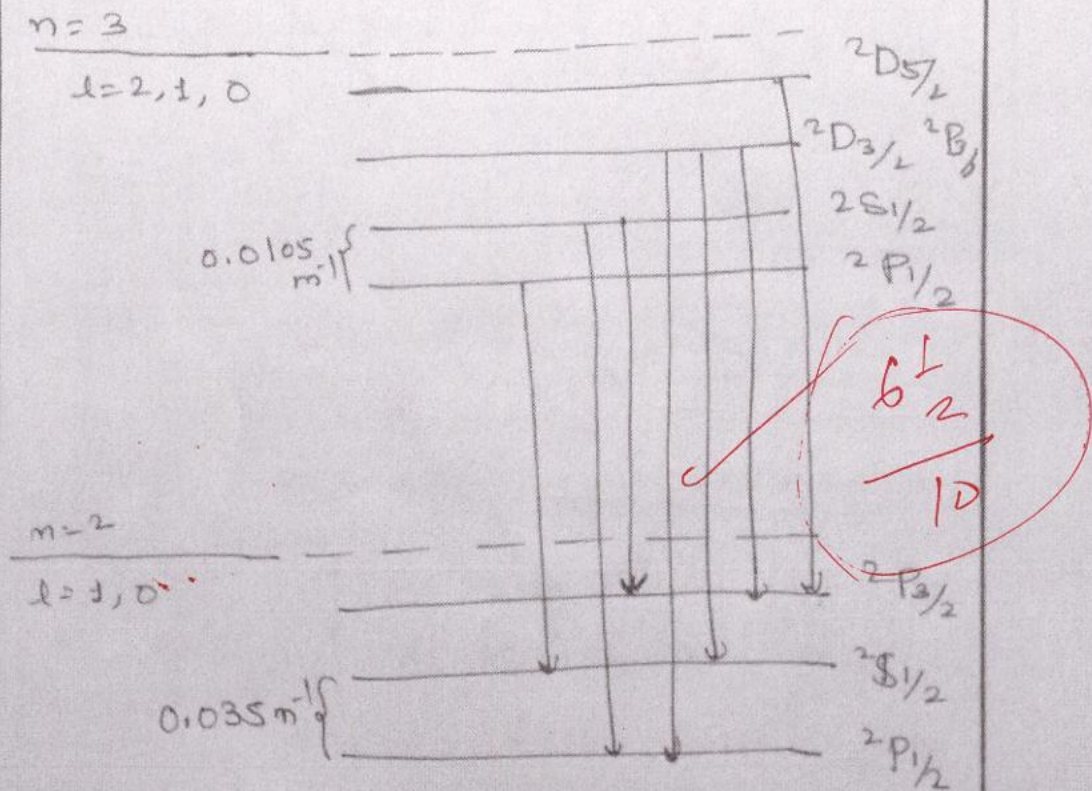
$$\Rightarrow \Delta E = 4.5 \times 10^{-5} \text{ eV}$$

$\frac{L}{b^2} = \frac{1}{10}$

5(e)

Lamb shift refers to upliftment in degeneracy of $2S_{1/2}$ and $2P_{1/2}$ levels in Hydrogen fine structure due to vacuum polarisation.

H α lines ($n=3 \rightarrow n=2$) ✓



Selection rules $\Delta l = \pm 1$
 $\Delta s = 0$

7 lines of H- α series.
or unrestricted

$\Delta j = 0, \pm 1$ by $j=0 \rightarrow j=0$

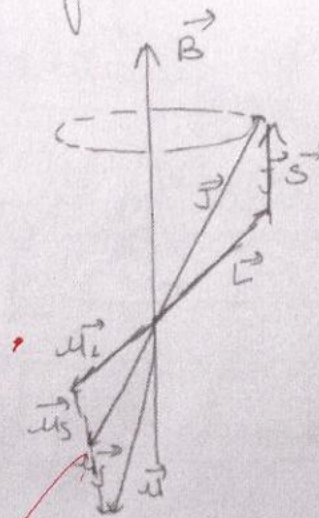
(Q.2 a)

Landé's g-factor determines the splitting of spectral lines in presence of magnetic field.

$$\vec{\mu} = -\frac{e}{2m} [g_L \vec{L} + g_S \vec{S}]$$

$$\vec{\mu} = -\frac{\mu_B}{\hbar} [\vec{L} + 2\vec{S}]$$

$$\text{as } g_L = 1 \text{ \& } g_S = 2$$



Energy $E = -\vec{\mu} \cdot \vec{B}$

$$E = \frac{\mu_B}{\hbar} [\vec{L} + 2\vec{S}] \cdot \vec{B}$$

Also, as μ_j spins around magnetic field, μ^{\perp} (perpendicular) component sums to zero in cycle & only μ_j^{\parallel} remains.

$$\text{So } \mu_j = \frac{(\vec{\mu} \cdot \vec{J}) \vec{J}}{|\vec{J}|^2}$$

$$\Rightarrow \mu_j = -\frac{\mu_B}{\hbar} [\vec{L} + 2\vec{S}] \cdot \frac{\vec{J} \cdot \vec{J}}{|\vec{J}|^2}$$

$$\Rightarrow E = \frac{\mu_B}{\hbar} \left[\frac{(\vec{J} + \vec{S}) \cdot \vec{J}}{|\vec{J}|^2} \right] J_z \cdot B \quad \text{as } \vec{J} = \vec{L} + \vec{S}$$

U.P.S.C.

$$E = \mu_B \left[1 + \frac{\vec{J} \cdot \vec{S}}{J^2} \right] m_j B$$

$$\vec{J} \cdot \vec{S} = \frac{J(J+1) + S(S+1) - L(L+1)}{2}$$

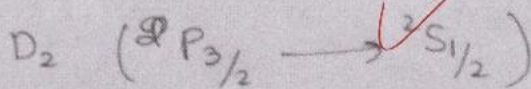
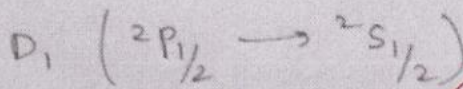
putting in E value, we get

$$E = \mu_B B g_j m_j \text{ where}$$

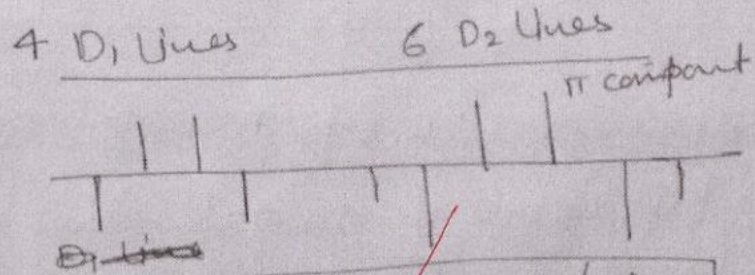
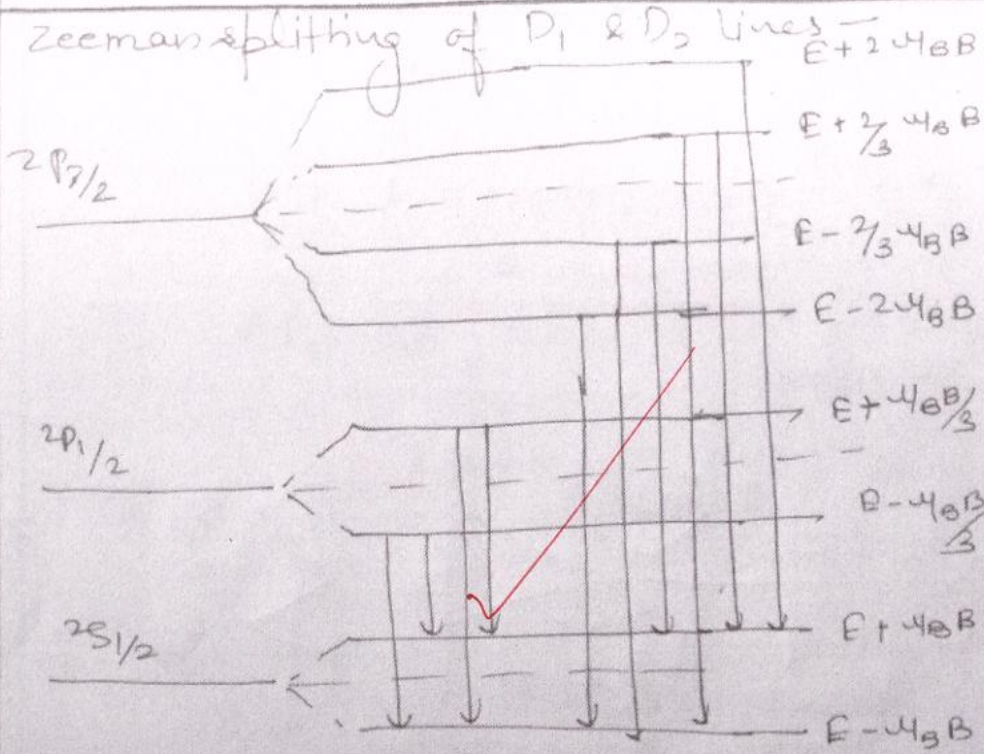
$$g_j = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Landé's g -factor.

Landé's g -factor can be used to explain Zeeman effect of Na doublet lines (D_1 & D_2).



| Term | g_j value | m_j | Energy |
|---------------|-------------|--------------------|------------------------------------------------------|
| ${}^2S_{1/2}$ | 2 | $\pm 1/2$ | $E_0 \pm \mu_B B$ |
| ${}^2P_{1/2}$ | $2/3$ | $\pm 1/2$ | $E_0 \pm \frac{\mu_B B}{3}$ |
| ${}^2P_{3/2}$ | $4/3$ | $\pm 3/2, \pm 1/2$ | $E_0 \pm \frac{2}{3} \mu_B B$ & $E_0 \pm \mu_B B$ |



selection rules - $\Delta j = 0, \pm 1$ $j=0 \not\rightarrow j=0$
 $\Delta l = \pm 1$
 $\Delta s = 0$

13/20

$\Delta \nu = \frac{eB}{4\pi m}$ Zeeman shift

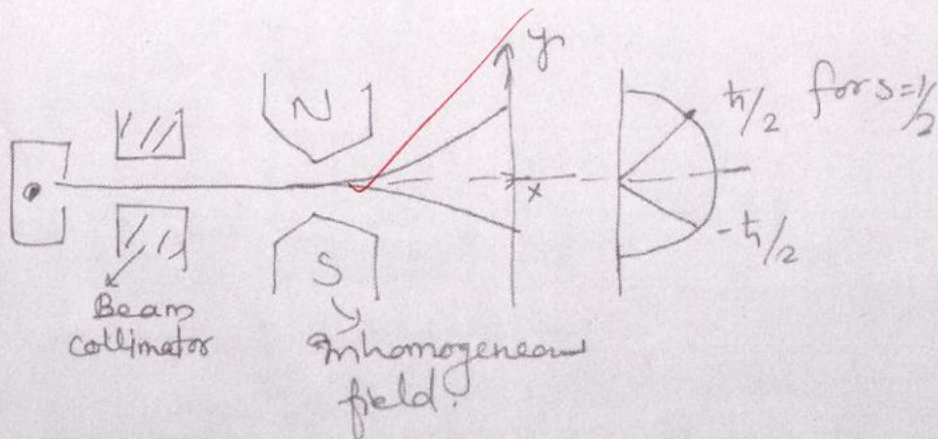
$\Rightarrow \Delta \lambda = \frac{eB}{4\pi mc} \lambda^2$

$\Rightarrow \frac{e}{m} = \frac{4\pi c \Delta \lambda}{B \lambda^2} = 1.748 \times 10^{11}$

C/100

Q.2 (b)

Strom-Gerlach experiment conclusively
proved existence of spin and
also quantisation of magnetic
moment.



~~Stern-Gerlach experimental set up -~~

- ↳ ① Beams of neutral silver atoms
- ↳ ② Inhomogeneous magnetic field.

Force due to magnetic field = $(-\vec{\mu} \cdot \vec{\nabla}) \vec{B}$

$$F_z = \mu_z \frac{\partial B_z}{\partial z}$$

$$y = \frac{1}{2} a t^2$$

$$a = \frac{F_z}{M}$$

$$t = \frac{d}{v} \text{ and } v = \sqrt{\frac{4kT}{M}}$$

$$\Rightarrow y = \frac{\mu_z \frac{\partial B_z}{\partial z} \cdot d^2}{8kT}$$

Given $\frac{\partial B}{\partial z} = 5 \frac{\text{Volt m}^{-2}}{\text{m}} = 5 \times 10^3 \frac{\text{Vm}^{-2}}{\text{m}}$

$d = 0.07 \text{ m}$

$T = 1250 \text{ K}$

$$y = \frac{9.27 \times 10^{-24} \times 5 \times 49 \times 10^{-4} \times 10^3}{8 \times 1.38 \times 10^{-23} \times 1250}$$

$y = 0.1645 \text{ cm}$

separation = $2y = 0.329 \text{ cm}^{-1}$

Existence of only two components is a proof of spin angular momentum.

10
15

(2c)

i)

Heteronuclear diatomic molecules which have a permanent dipole moment exhibit rotational energy levels.

Assuming rigid rotor, ($V(r) = 0$)

$\left[\frac{-\hbar^2}{2m} \nabla^2 \psi = E \psi \right]$ solutions give

$\left[E = \frac{J(J+1)\hbar^2}{2I} \right]$

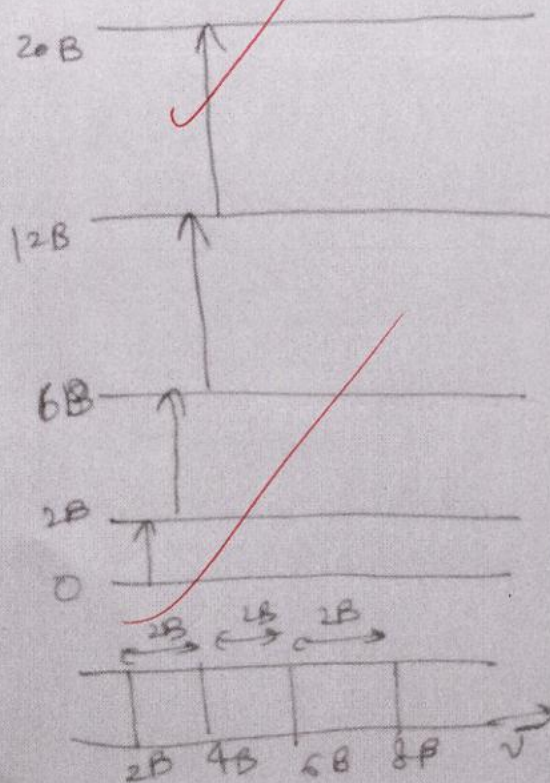
$F(J) = \frac{E}{hc} = \frac{BJ(J+1) \text{ cm}^{-1}}{\quad}$

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

Selection rules $\left[\Delta J = \pm 1 \right]$

$F(J+1) - F(J) = 2B(J+1) \text{ cm}^{-1}$

So spectrum constitute equally spaced lines with $2B$ difference.



ii) For pure rotational spectra,
necessary condition is presence
of permanent dipole moment.

So Homonuclear molecules like
H₂ & O₂ doesn't give pure
rotational spectra.

HF & NO are Heteronuclear \Rightarrow
permanent dipole moment \Rightarrow Yes
pure rotational spectra.

iii) $F(J=1) - F(J=0)$ where $F(J) = B J(J+1) \text{ cm}^{-1}$
 $= \underline{2B}$ when $B = \frac{h}{8\pi^2 I c}$

Given $2Bc = 1.153 \times 10^{11}$

$\Rightarrow \boxed{B = 1.92 \times 10^2 \text{ m}^{-1}}$

$\Rightarrow I = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 1.92 \times 10^2 \times 3 \times 10^8}$

$\boxed{I = 3.43 \times 10^{-46} \text{ kg m}^2}$

~~10/15~~

4.3 a)

Vector model of atom models the orbital and spin angular momentum

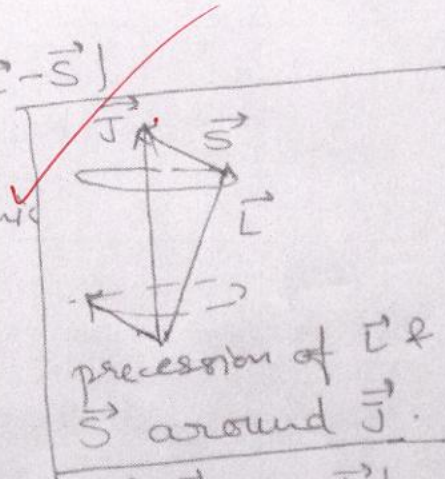
interaction as vector sum (eg.)

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

$$|\vec{J}| = |\vec{L} + \vec{S}| \text{ to } |\vec{L} - \vec{S}|$$

Also, for multielectronic atoms,

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_n$$

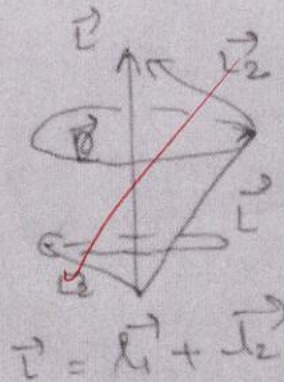
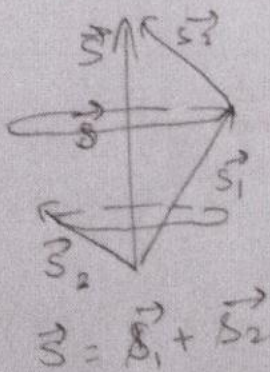


$$|\vec{L}| = |\vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_n|_{\min} \text{ to } |\vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_n|_{\max}$$

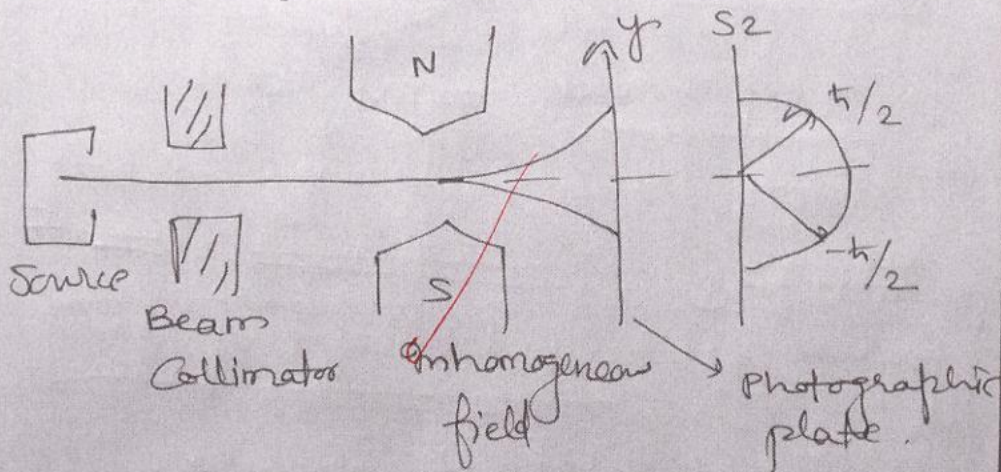
Similarly for $\vec{S} = \vec{s}_1 + \vec{s}_2 + \dots + \vec{s}_n$ i.e.

$$|\vec{S}| = |\vec{s}_1 + \vec{s}_2 + \dots + \vec{s}_n|_{\min} \text{ to } |\vec{s}_1 + \vec{s}_2 + \dots + \vec{s}_n|_{\max}$$

(eg) for 2 electrons



Strom-Gerlach experiment is about passing neutral silver atoms beam in non-homogeneous magnetic field.



Requirements -

- ① Neutral silver atom beam -
↳ charged atoms will exhibit circular motion in \vec{B} .
- ② Inhomogeneous field
↳ Homogeneous field will not exert any force hence non-deflected beam.

$$\text{Force} = (\vec{\mu} \cdot \vec{\nabla}) \vec{B} = \mu_z \frac{\partial B_z}{\partial z}$$

$$\mu_z = g_s m_s \mu_B \quad \text{for } e^-$$

$$y = \frac{1}{2} a t^2 = \frac{1}{2} \frac{\mu_z \frac{\partial B_z}{\partial z}}{m} \cdot \frac{d^2}{4KT} \times \frac{1}{m}$$

$$\Rightarrow y = g_s m_s \mu_B \frac{\partial B_z}{\partial z} \cdot \frac{d^2}{8KT}$$

from experiment, $g_s m_s = \pm 1$

$$\text{since } g_s = 2 \Rightarrow m_s = \pm \frac{1}{2} \Rightarrow \underline{\underline{S = \frac{1}{2}}}$$

Results

① ~~has~~ established concept of spin.

② Quantisation of angular momentum \rightarrow proof of vector model of atom.

③ Laid foundation of quantum mechanics.

\Rightarrow If e^- 's spin is $\frac{3}{2}$ instead of $\frac{1}{2}$ than **4** ~~embaces~~ **spots** would be obtained on screen instead of two.

$$\text{Ans for } S = \frac{3}{2} \Rightarrow m_s = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

17) In case of neutral atoms
passing through homogeneous
field, $\vec{E} = 0$ \Rightarrow No deflection
& hence no trace will be
obtained.

Hence homogeneous field is
a necessity of Stem Gerlach
exp.

Q.3 b)

Larmor precession refers to precession of angular momentum due to torque acting on it.

from figure,

$$d\phi = \frac{d\vec{J}}{|\vec{J}| \sin\theta}$$

$$\Rightarrow \frac{d\phi}{dt} = \frac{d\vec{J}/dt}{|\vec{J}| \sin\theta}$$

$$\Omega = \frac{|\vec{\tau}|}{|\vec{J}| \sin\theta} = \frac{|\vec{\mu}| B \sin\theta}{|\vec{J}| \sin\theta}$$

$$\boxed{\Omega = \frac{|\vec{\mu}| B}{|\vec{J}|}}$$

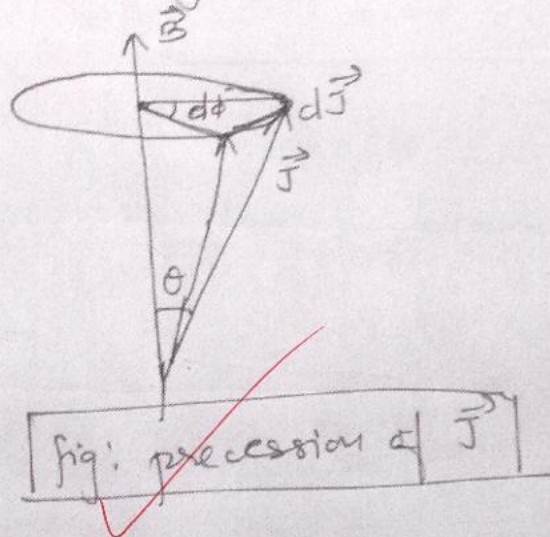
Larmor frequency.

$$|\vec{\mu}| = +g_p \frac{e}{2m} |\vec{J}| \quad \text{for proton}$$

$$g_p = 5.585$$

$$\Rightarrow \boxed{\Omega = \frac{g_p e B}{2m}}$$

$$\text{or } \boxed{\nu = \frac{eB}{4\pi m} g_p}$$



$$\nu = \frac{1.60 \times 10^{-19} \times 3 \times 5.885}{4 \times 3.14 \times 1.67 \times 10^{-27}}$$
$$= 4.26 \times 10^7 \text{ Hz} = 42.6 \text{ MHz}$$

$$\nu = 42.6 \text{ MHz}$$

10/15

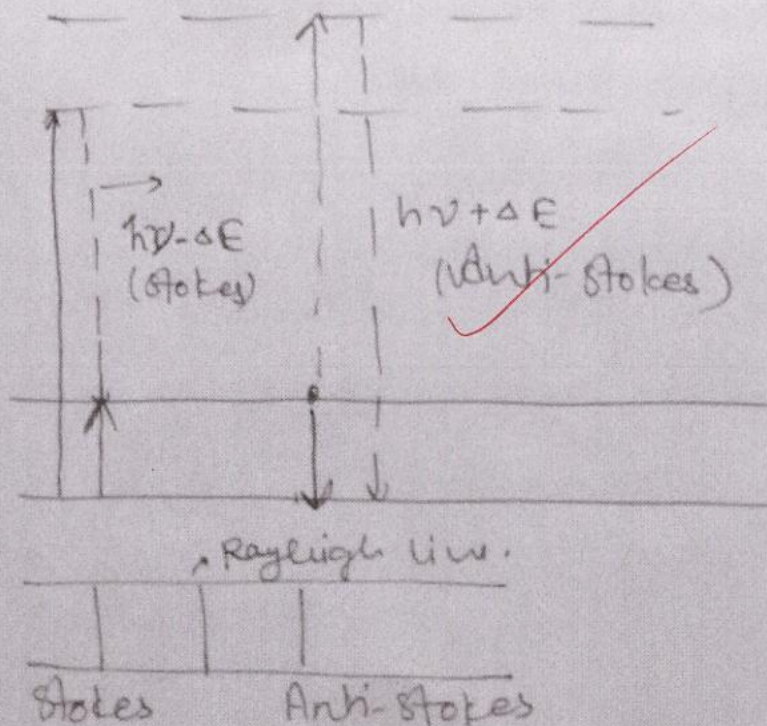
This depends only on magnetic field & not on orbit angle.

3(c)

Raman spectra constitutes both low frequency (Stokes) lines and high frequency (Anti-Stokes) lines due to internal transitions (vibrational or rotational) while scattering.

Mechanism of production of Raman lines -

Molecules undergo rotational or vibrational transitions -



→ when transition from upper to lower \Rightarrow anti-stokes line

2) (a) when transition from lower to upper \rightarrow Stokes line.

Considering rotational transitions -

$$\bar{\nu} = \bar{\nu}_0 + BJ(J+1) \text{ cm}^{-1}$$

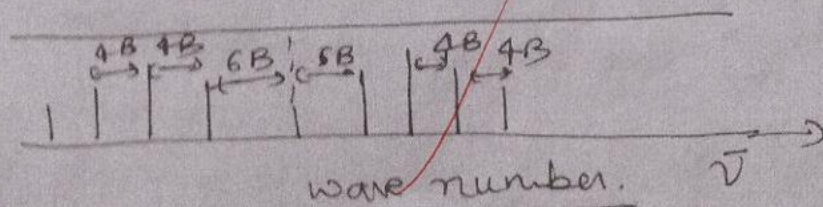
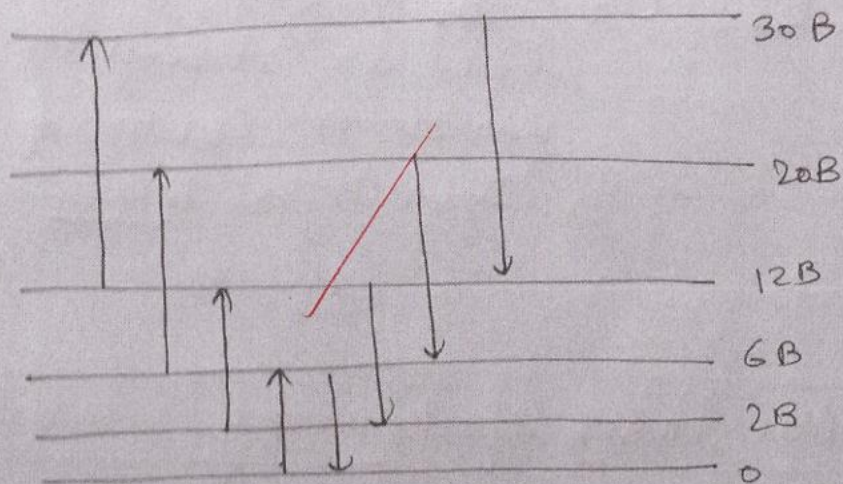
Selection rules $\Delta J = 0, \pm 2$

$$\bar{\nu} = \bar{\nu}_0 \pm B(4J+6)$$

$\Delta J = 0$ (Rayleigh line)

$\Delta J = +2$ (Anti Stokes)

$\Delta J = -2$ (Stokes)



1st line at separation of 6B &
rest at 4B.

Complementarity with IR

① According to mutual exclusion
Principle, molecules with
centre of symmetry (eg) CO_2 & CS_2
exhibits IR lines which are
missing in Raman Spectra.

② This can be used to classify
molecules as linear or bent.

(eg) CO_2 & CS_2 - 2 IR lines
which are absent in
Raman \Rightarrow Centre of
Symmetry \Rightarrow linear
structure.

Raman Laser Spectroscopy revolutionised

- ↳ ① High precision & high resolution
- ↳ ② Detection of colored salts
- ↳ ③ Non-destructive detection of molecules
- ↳ ④ Small amount of sample needed.

Given $\lambda_0 = 4358 \text{ \AA}$

$$\Rightarrow \bar{\nu}_0 = \frac{1}{\lambda_0} = 2.2946 \times 10^6 \text{ (Rayleigh Line)}$$

$$\lambda_1 = 4567 \text{ \AA} \Rightarrow \bar{\nu}_1 = 2.1896 \times 10^6 \text{ (Stokes Line)}$$

$$\Delta \bar{\nu} = \bar{\nu}_0 - \bar{\nu}_1 =$$

$$\Delta \bar{\nu} = 1049780 \text{ m}^{-1}$$

\Rightarrow

$$\bar{\nu}_{AS} = 2399578 \text{ m}^{-1}$$

Anti-Stokes Line.

$$\Rightarrow \lambda_{AS} = 4167 \text{ \AA}$$

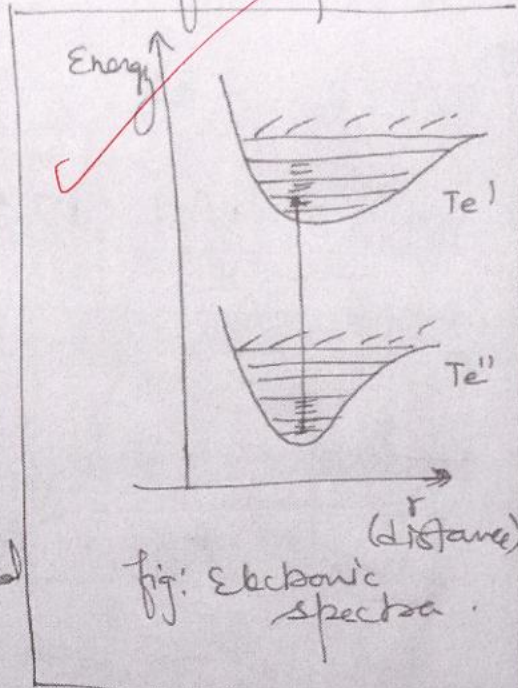
It will be less intense as it occurs due to transition from upper to lower level which are less probable than lower to upper as per M-B distribution.

~~10/15~~

Q4. (a)

Electronic spectra of diatomic molecules consists of Series, bands and progressions due to v-R gross spectra and rotational fine spectra.

$$\Delta E = T_e' - T_e'' + G_{v'} - G_{v''} + F_{J'} - F_{J''} \text{ cm}^{-1}$$



Gross spectra - VR

↳ Ignoring rotational transitions.

$$\bar{\nu} = \bar{\nu}_e + G_{v'} - G_{v''} \quad \& \quad \Delta v = \text{unrestricted}$$

$$G(v) = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \text{ cm}^{-1}$$

$v'' = 0 \rightarrow v' = 1$ transition (fundamental band)

$v'' = 0 \rightarrow v' = 2$ 1st overtone

$v'' = 1 \rightarrow v' = 2$ Hot bands.

$$\Delta \bar{\nu} = \bar{\nu}_e + (v' - v'') \bar{\nu}_e - \left[\left(v'^2 - v''^2 \right) + (v' - v'') \right] \bar{\nu}_e x_e \text{ cm}^{-1}$$

Rotational fine structure

$$\bar{\nu} = \bar{\nu}_0 + B_{v'} J'(J'+1) - B_{v''} J''(J''+1) \text{ cm}^{-1}$$

where $\bar{\nu}_0 = \bar{\omega}_e(1-2xe)$ cm^{-1} [0 \rightarrow 1 transition]

selection rules - $\Delta J = 0, \pm 1$

① $B_{v'} < B_{v''}$ (if $r' > r''$) $\&$ $B = \frac{h}{8\pi^2 I c}$

$\&$ $B_{v'} > B_{v''}$ (if $r' < r''$)

$$\bar{\nu} = \bar{\nu}_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2 \text{ cm}^{-1}$$

$m = J'' + 1$ (R-branch)

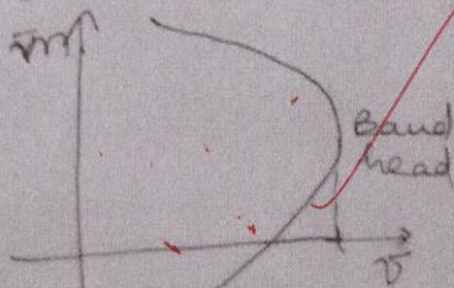
$= 1, 2, 3, 4$

R(0), R(1), R(2) - -

$\&$ $m = -J'' = -1, -2, -3$ (P-branch)

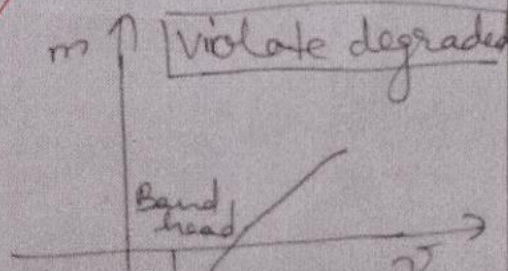
Eq. ① represents parabola whose direction depends on sign of

$(B_{v'} - B_{v''})$



\rightarrow Red degraded

if $B_{v'} - B_{v''} = -ve$



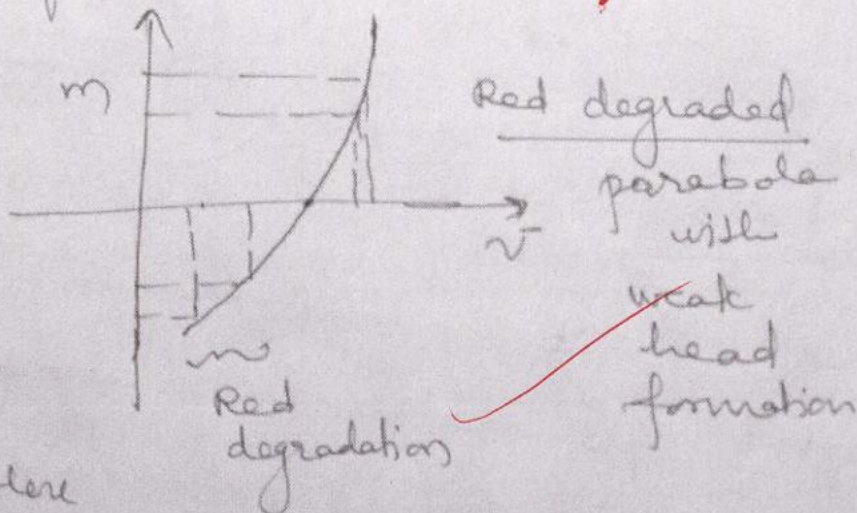
if $B_{v'} - B_{v''} = +ve$

U.P.S.C.

Electronic spectra has -

↳ Strong tendency of head formation as Bv' & Bv'' are from different electronic orbitals & vary significantly.

In V-R spectra - Bv' is slightly ^{less} ~~greater~~ than Bv'' as both are from same electronic state

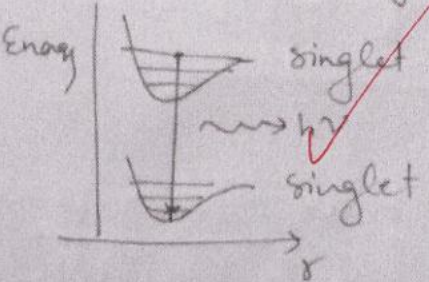
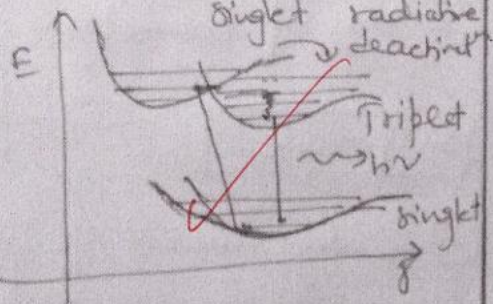


Here $(Bv' - Bv'')$ slightly -ve

13/20

Q4 (b)

Luminescence refers to transition from excited state to ground states resulting in release of photons.

| Fluorescence | Phosphorescence |
|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| 1) Transition to lower states of <u>same multiplicity</u> . | 2) Transition between states of <u>different multiplicities</u> |
|  |  |
| 2) <u>Instantaneous</u> transitions | 2) <u>Delayed emission</u> due to <u>spin forbidden</u> nature. |
| 3) No <u>internal conversion</u> occur | 2) <u>internal conversion</u> occurs due to <u>collisions</u> . |
| 4) Used in Zinc Sulfide, Strontium etc. | 5) eg. Diamond, Ruby |
| | 6) Can be used to store light for <u>few microseconds</u> . |

U.P.S.C.

Fluorescence

Raman

Mechanism -

① Transition between electronic energy levels.

② Due to quantisation of energy levels - exciting wavelengths should be equal to energy of transition.

① Scattering of light by molecules.

② Since scattering, so any exciting frequency can show Raman spectra.

Difference

① Only lines of lower wavenumber are observed.

② Emitted lines depend on excitation frequency.

① Both Stokes (lower wavenumber) & Anti-Stokes (large $\bar{\nu}$) are observed.

② Emitted lines only characteristic of material.

9/2/15

Q.4 (c)

From V-R spectra, we can determine force constant, nature of molecules, isotopic masses etc.

Given $k = 573 \text{ m}$

Energy = 450 eV (Dissociation)

$$G(v) = \left(v + \frac{1}{2}\right) \bar{\nu} - \left(v + \frac{1}{2}\right)^2 \bar{\nu} x_e \text{ cm}^{-1}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Neglecting x_e by assuming simple harmonic potential.

$$\mu = \frac{m_H m_H}{m_H + m_H} = \frac{m_H}{2}$$

$$= \frac{1.67 \times 10^{-27}}{2} = 8.35 \times 10^{-28} \text{ kg.}$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^8} \sqrt{\frac{573}{8.35 \times 10^{-28}}}$$

$$\bar{\nu} = 4.396 \times 10^5 \text{ m}^{-1}$$

$$G(v) = \left(v + \frac{1}{2}\right) \bar{\nu}$$

where

$$G(v) = \frac{E(v)}{hc}$$

~~450 x~~

$$\text{So } G(v) = \frac{540 \times 1.6 \times 10^{-19}}{hc}$$

U.P.S.C.

putting in equations -

$$\left(v + \frac{1}{2}\right) = \frac{540 \text{ eV}}{1240 \text{ eV} \times 10^{-9} \times 4.396 \times 10^5}$$

$$\Rightarrow v + \frac{1}{2} = 82.25$$

$$\Rightarrow \boxed{v = 81.75} \quad \times \quad \underline{\underline{822}}$$

So vibrational quantum number
corresponding to dissociation
energy 450 eV is $v = 81$.

