Unit-1 :-

Atomic Spectra & Molecular Spectroscopy

Atomic Spectra
- Bohr's model App's
- L-S & J-J coupling schemes
- selection rules & Intensity rules
- Sommerfeld's orbits
- Stern & Gerlach Experiment
- Vector atom model
- Zeeman effect
- Stark Effect
- Electronic spectra of molecules & its origin

Molecular Spectroscopy
- Rotational spectrum and Inter nuclear distance.
- Raman effect
  - classical theory & Applications
  - Quantum theor
- Vibrational Spectra

Questions :-

✓ ① Describe Stern Gerlach Experiment

✓ ② Describe vector atom model and Explain Quantum numbers associated with

✓ ③ what is normal Zeeman effect How it is explained.

✓ ④ wt. is Raman effect Describe Setup use

✓ ⑤ Elementary Theory of Raman effect and determination of molecular structure.

✓ ⑥ Quantum theory of Raman effect

⑦ How do you use Rotational Spectrum to determine internuclear distances.

SAQs

✓ ① Explain origin of electonic Spectra of Molecules

② Write the applications of Raman effect

✓ ③ Saitent feautures of vector atom Model

✓ ④ Explain L-S and JJ coupling schemes

✓ ⑤ write applications of Zeeman effect

✓ ⑥ Draw backs of Bohr's theory

✓ ⑦ Explain Selection rules and Intensity rules.

✓ ⑧ write a short note on Rotational - vibrational Spectra

Relation bw Qs & SAQs

① Q ⇒ ⑦

② Q ⇒ ③ ④, ⑥ $\boxed{④⑤⑥⑧}$ ⇒ ② ✓

③ ⇒ ⑤ Q ⑦ ⇒ ①, ⑧

① Describe stern- Gerlach Experiment
We are studying about atoms.

→ Stern Gerlach expiriment studies the Behaviour of atom (silver) in a non uniform magnetic field.

principle :- The dipole in a inhomogeneous magnetifiled experiences translatory force and Torque.

→ The silver atom when passed. here the atoms energy leves split into 2 components

→ Thus this doublet structure indecates the silver atom have spin and it is Quantized.

Experimental setup:-

Silver material is kept in an oven as shown in figure.

→ The silver atoms are allowed to travel through slits S_1 & S_2. a fine beam of silver comes out from slits

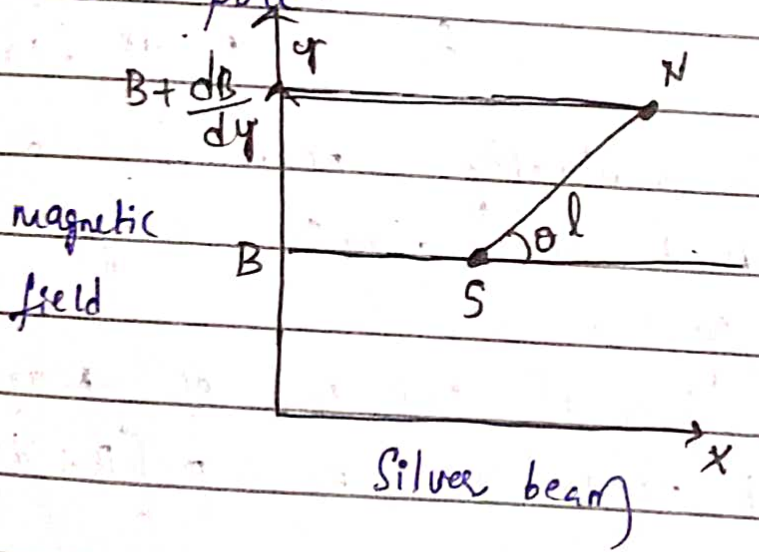
→ The silver beam is allowed to pass through non uniform magnetic field

→ The field is produced by magnetic poles M_1, M_2 one of pole will have knife edged shape and other is in a shape given in figure.

→ The silver beam is divided or deflected into 2 components in inhomogeneous field and doublect structure is observed on Screen P

Observations:-

→ magnetifield intensity increases from north pole to S pole.



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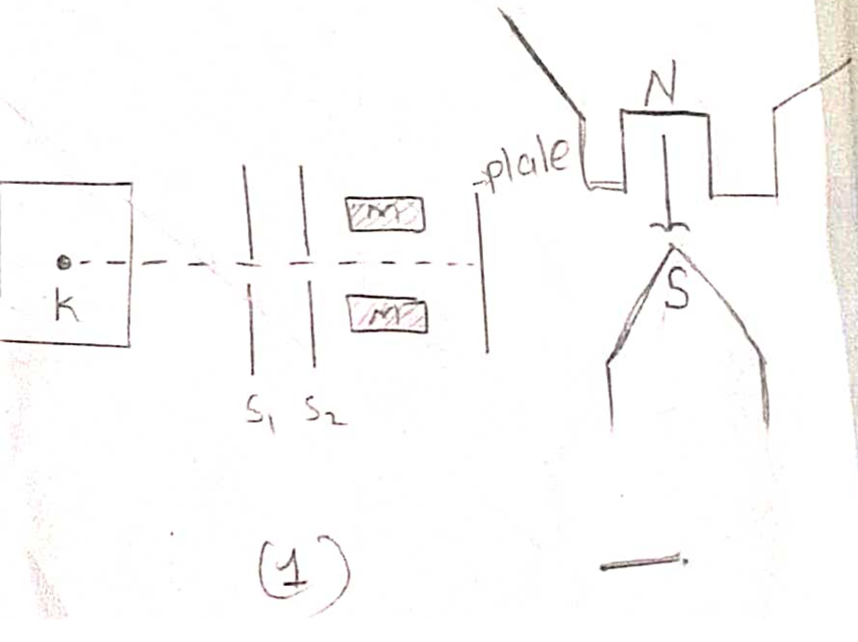
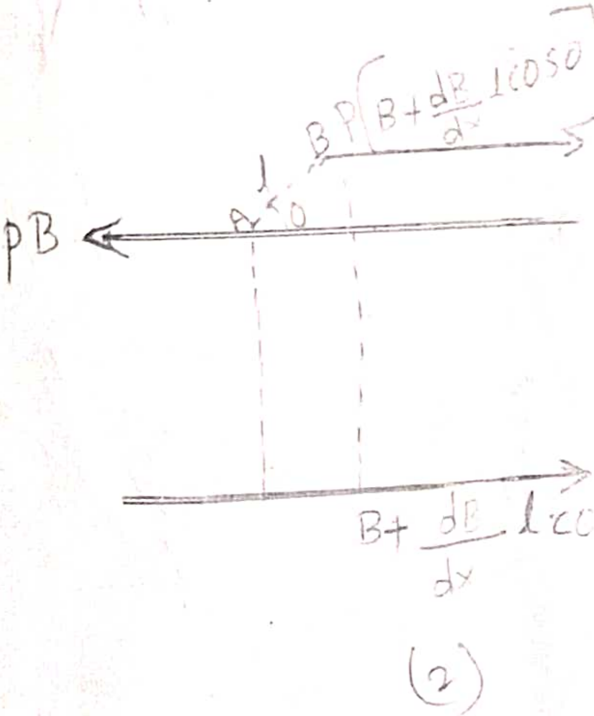
stern - Gerlach Experiment:



(1)

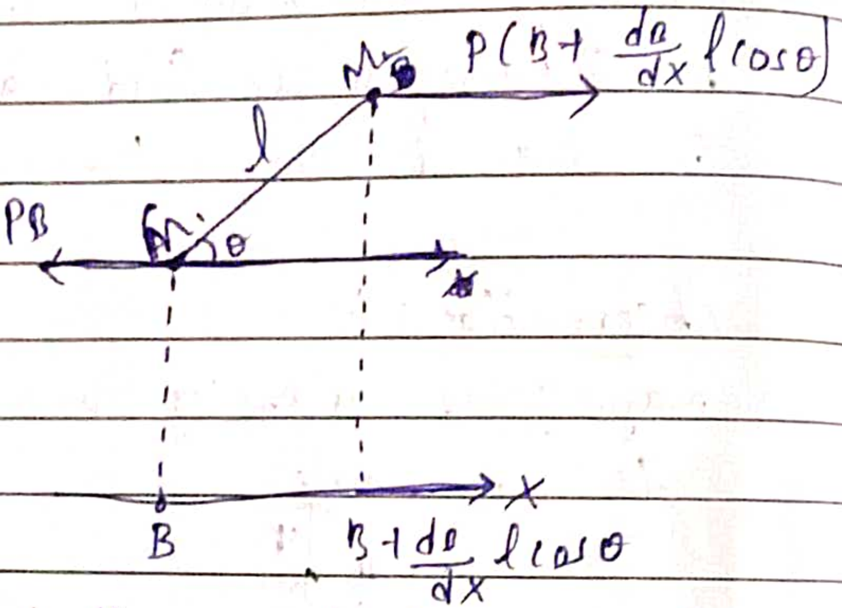


(2)

Observations:-

→ Let B be the applied field and $\frac{dB}{dx}$ is field gradient in x-direction

p = pole strength
l = length of magnet



→ Two mutually perpendicular forces will act on atomic magnet as shown in figure.

The force at one end of Magnet is pB at other end is $p\left[B+\frac{dB}{dx}l\cos\theta\right]$

→ Due to these opposite and unequal forces an external torque. $pBl\cos\theta$ acts on atomic magnet resulting in translatory motion. ~~#~~ ~~no~~ of magnet

If F_x is force on magnet

$\Rightarrow F_x$ = Force at M_2 − force at M_1.

$$F_x = \cancel{PB} \; P\left(B + \frac{dB}{dx} l\cos\theta\right) - PB$$

$$F_x = \frac{dB}{dx} p l \cos\theta \quad - ①$$

$$F_x = \frac{dB}{dx} M \cos\theta \qquad [P \times L = M]$$

Magnetic moment

If α Displacement of Silver atom along field ~~dire~~ direction

$$\alpha = dx = \frac{1}{2} a_x t^2 \qquad [a_x = \text{angular acceleration in } x \text{ direction}]$$

$$\left[t = \frac{L}{V}\right]$$

$$\alpha = \frac{1}{2}\left(\frac{F_x}{m}\right) t^2 - ②$$

[Newtons 2nd law
$F = ma$
$a = \frac{F}{m}$]

Sub ① in ②

$$\alpha = \frac{1}{2m} \frac{dB}{dx} p l \cos\theta \left(\frac{L^2}{V^2}\right)$$

$$\boxed{\alpha = \frac{1}{2}\left(\frac{M}{m}\right) \frac{dB}{dx} \frac{L^2}{V^2}}$$

[V = velocity & L = distance travelled by atom / length of magnet
m = mass $M = pl$]

∴ Stern gerlach experiment confirms spin & space quant of e^- which we study in vector atom model

② Describe vector atom model and explain quantum numbers associated with it.

A atom model is proposed to overcome defects in Bohrs model and Sommerfeld model is known as vector atom model

Vector atom model Explains 2 main concepts

i) Space Quantization.

(ii) spinn Quantization

(i) Space Quantization:-

As per Bohr's model e^{-ns} moves in circular orbit, since radius of orbit remains fixed electron has one degree of fredom here one co-ordinate is enough to describe its motion.

Bohr explained this using Quantum number (n) which is also called principal Quantum number (n)

But According to Sommer field e^{-n} motion is described by elliptical orbits hence 2 co-ordinates are required to to explain electron motion hence two Quantom numbers namely principle quantum number. (n) and Azimuthal Quantum number (k) introduced

As e^- motion is 3 dimensional atom motion is ~~considered~~ explained using 3 co-ordinted according to classical laws. ~~but~~.

There are no restrictions on orientation of orbits in atom.

But Quantum principle restricts the orientation of orbits in space. quantum law allows only certain possible orientations of orbits in space.

Therefore quntitization of orbital orientation in space is called Space quntization.

(ii) Spinning electron :-

According to Bohr and Sommerfe e^- has only orbital ~~direction~~ motion. in order to explain Certain Spectral features the spin of e^- has to be taken into account according to ulenbeck & Goud smith theory e^- will have both orbital and spin motions due to these 2 motions e^- possess orbital & Spin angular momenta

Spinning of objects results in magnetic moment since e^- posses both orbital and spin motions. it will have both spin & orbital motions resulting in magnetic and angular momenta these two moments are Quantized.

Bohrs Theory	Somerfeld theory
→ atom → center → nucleus	→ .
→ e^- $\xrightarrow[\text{around}]{\text{revolves}}$ nucleus	→
→ path orbits	→ path of orbits elliptical
→ orbital angular momentum $mvr = \frac{nh}{2\pi}$	⇒ n, K
→ Radiation of energy one orbit to another $E_2 - E_1 = h\nu$	

Quantum numbers Associated with vector atom model

Bohr explained one Principal Quantum number Sommerfeld model explained 2 i.e radial (n_r) and azimuthal Quantum numbers (K) but vector atom model is associated with 7 Quantum numbers.

imp
(i) principal Quantum number (n)
(ii) orbital QN
(iii) spin QN
(iv) Total angular momentum QN
(v) Magnetic orbital moment QN
(vi) Magnetic spin an QN
(vii) " " total angular momentum QN

(i) principal Quantum number :- (n):
It describes energy levels of electron & its distance from nucleus denoted by n = 1, 2, 3....
→ n also indicates shell of electron
n = 1, 2, 3, 4... refereed as K, L, M, N... shells
→ Max number of e^{-ns} in one shell is $2n^2$

(ii) orbital Quantum number (l) :-
it explains about shape of electron orbit denoted by l & orbital Quantum number is equal to n-1 ⇒ its values are 0, 1, 2, 3.. n-1
⇒ It also indicates subshells s, p, d, f

Date
Page

(iii) Spin Quantum number (S) :-
It describes Spin of e^- on its own axis.

→ Magnitude of Spin is always $\frac{1}{2}$.

→ $S = +\frac{1}{2}$ or $S = -\frac{1}{2}$

2 electrons with same sign of Spin are said to have parellel spins & with ~~same~~ different sign of spin are said to be opposite spins.

(iv) Total angular momentum QN :- $\vec{J}$

The sum of orbital and spin angular momentum of electron gives total angular momentum.

$$j = l + s$$

→ It is always equal to $\frac{j}{2\pi}$ where j is called total angular momentum Quantum number.

(v) Magnetic spin angular momentum :- (ms)
The projection of spin angular momentum onto direction of external magnetic field is called MSAMQN
denoted by ms

$$m_s = S\cos\theta$$

(vi) Magnetic Spin Total angular momentum QN :- m_j

The projection of Total angular momentum onto direction of external magnetic field is called msam QN denoted by m_j

$$m_j = j\cos\theta.$$

(vii) Magnetic orbital momentum Quantum number:- (m_l)

when a orbital vector is placed in an external magnetic field. it will process around axis parellel to external magnetic field direction.

→ The project of orbital angular momentum along direction of external magnetic field is called MOMQN (m_l)

$$m_l = l\cos\theta$$

③ What is zeeman effect and how is it explained.

adiation) mitting ←

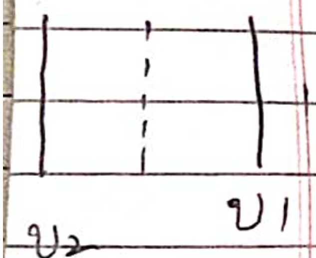
Zeeman effect :- The Splitting of Spectra lines in the process of external magnetic field is called as Zeeman effect.

That is actually the energy levels Split int multiple componets resulting in a change in atoms absorption or emission spectrum

The line can split into doublets, triplets and even more components.

Experimental Arangment :-

The experimental Sets used to observe zeeman effect is shown in figure.



It consists of 2 Magnets M_1 & M_2 a Small hole is created bw 2 poles by dividing the poles into 2 parts.

A monochromatic Light Source L is placed between 2 poles. The spectral line's can be viewed using spectrometer.

→ In the absence of magnetic field, a single line is observed, with a wavelength of λ.

→ In the presence of magnetic field we observe following things.

observations:-

when spectrum viewed in parellel direction 2 components are observed. They are circularly polarized in opposite directions

When spectrum viewed in normal directio to applied magnetic field 3 components observed. These 3 components observed ar called Lorentz components. The components are plane polarized having vibrations Perpendicular to field.

sometimes the component can split into 2; these or sometimes into more than 3 compo Based on this we have 2 types of zeeman effects

(1) Normal zeeman effect
(2) Anamalous zeeman effect.

Normal Zeeman effect :-

If the magnetic field is very strong each spectral line is split up into 2 components in parellel view & 3 components in perpendicul view.

Anamalus Zeeman effect :-

If the magnetic field is comparati weak, each line splits into more than 3 components

Frequencies of components observed in Zeeman effect and Zeeman shift

When magnetic field strong ⇒ 2/3 compots of spectral line observed.

magnetic dipole is place in external field. an increase in energy of dipole occurs.

The product of dipolemoment and magnetic field induction gives energy.

$$\Delta E = \mu_B \cdot B \quad - ①$$

$$\Delta E = \mu_B \cdot B\cos\theta \quad - ②$$

μ_B = Bohr magneton & $\mu_B = l \cdot \frac{eh}{4\pi m}$

$$\Delta E = l \cdot \frac{eh}{4\pi m} B\cos\theta .$$

According to magnetic orbital quantum number $m_l = l\cos\theta \Rightarrow \cos\theta = \frac{m_l}{l}$

$$\Delta E = \frac{eh}{4\pi} \cdot \frac{\cancel{l}}{m} B \cdot \frac{m_l}{\cancel{l}} \quad - ①$$

Let E_1 and E_2 are energies of 2 levels with quantum numbers l_1 and l_2 in absence of magnetic field

→ In the presence of magnetic field let the values of energies are E_1' and E_2' respectively

→ if m_{l_1} and m_{l_2} are magnetic orbital angular momentum Quantum number in corresponding 2 states.

$$E_1' = E_1 + m_{l_1}\left(\frac{eh}{4\pi m}\right)B \quad - ②$$

$$E_2' = E_2 + m_{l_2}\left(\frac{eh}{4\pi m}\right)B \quad - ③$$

[from ①]

eq^n ③ − ②

$$E_2' - E_1' = E_2 - E_1 + m_{l_2}\left(\frac{eh}{4\pi m}\right)B - m_{l_1}\left(\frac{eh}{4\pi m}\right)$$

$$E_2' - E_1' = (E_2 - E_1) + (m_{l_2} - m_{l_1})\left(\frac{eh}{4\pi m}\right)B \quad ④$$

We know that

$$\left.\begin{aligned} E_2' - E_1' &= h\nu \\ E_2 - E_1 &= h\nu_0 \end{aligned}\right\} ⑤$$

Sub ⑤ in ④

$$h\nu = h\nu_0 + (m_{l_2} - m_{l_1})\left(\frac{e}{4\pi m}\right)B$$

$$h\nu = h\nu_0 + \Delta m_l \left(\frac{eh}{4\pi m}\right)B \quad \left[\Delta m_l = m_{l_2} - m\right.$$

According Section rules

$$\boxed{\Delta m_l = 0, \pm 1}$$

if $\Delta m_l = 0 \Rightarrow \nu = \nu_0$

$\Delta m_l = 1 \Rightarrow \nu = \nu_0 + \left(\frac{eB}{4\pi m}\right)$

$\Delta m_l = -1 \Rightarrow \nu = \nu_0 - \frac{eB}{4\pi m}$

$$\boxed{\text{Zeeman shift} \Rightarrow \Delta\nu = \pm \frac{eB}{4\pi m}}$$

Conclusion:-

Out of 3 components observed in normal Zeeman effect.

One of them have same frequency as original

The frequencies of other 2 spectral lines vary by $\frac{eB}{4\pi m}$ known as Lorentz factor.

→ + & - of Lorentz factor in frequencies represents two components lie on opposite side. ~~with~~

Stark effect:-

The splitting of spectral lines in presence of external electric field. is called as Stark effect.

Experimental arrangement :

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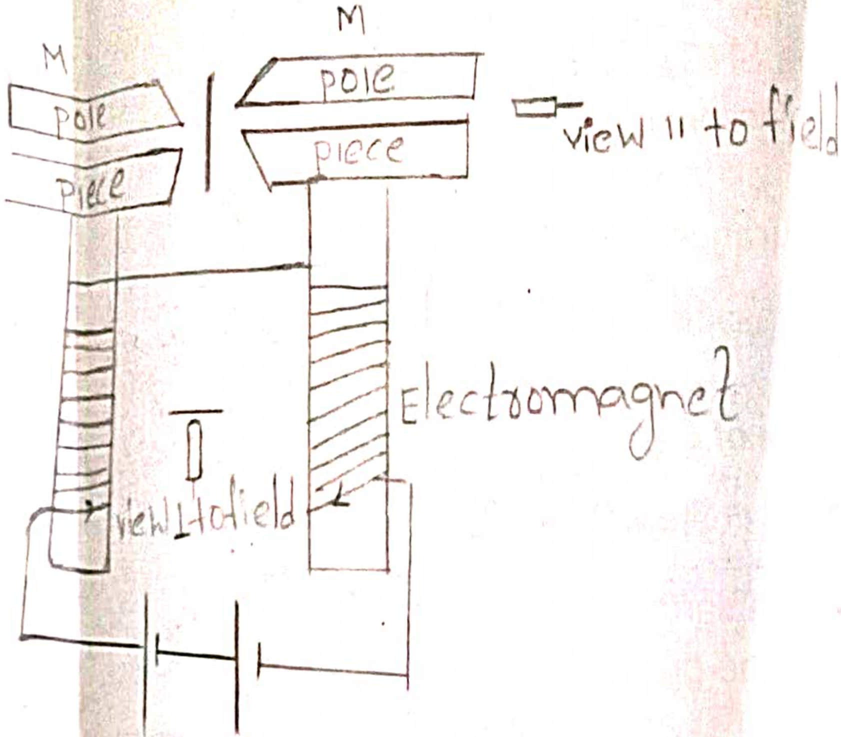


Raman Effect

1. What is RE
2. Experimental setup
3. classical theory of RE
4. Quantum Theory of RE
5. Applications of RE

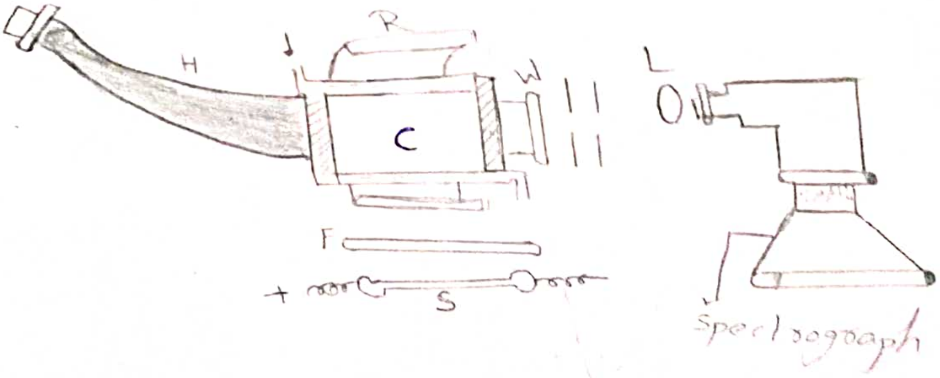
Raman Effect :-

We all know that when a light incidents on a object it gets distu

light

partic

perimental set up of Raman effect :-



④ what is Raman effect explain about Experimental Setup used in Raman Effect

We all know when light falls on object it gets Scattered

Raman observed that Spectrum of Scattered light consists of frequency greater and Smaller than those of Incident beam is known as Raman Effect

Experimental set up Raman Effect

principle or precaustion:-
We should Take care that the incident light should have single wavelength i.e monochromatic source of light so that light will have high intensity and Raman effect is can be understood better.

Set up is shown in above figure
(1) It consists of a Source 'S' filter F.
(2) cylindrical vessel 'c' called Raman tube which is filled with experimental liquid

(3) one end of tube extended like horn H (covered with black)

(4) other end acts like a window (closed with glass plate)

(8) The Scattered light is emerged out of glass window

(5) when monochromatic light is passed through liquid, it will get heated by incident light to avoid this Raman tube 'C' is Surrounded by a water bath

(6) 'R' is a Semi cylindrical reflector which enhances the intensity of light

(7) Spectograph (S)

process The light emitted from Source 'S' is allowed to pass through Filter F [It is a glass plate coated with nickel oxide]

It acts like a filter and emerges the light having wavelength 3888 A° [A° = 10^{-10}m]

→ This light will act as Source

in Raman effect, the light coming out from vessel 'c' falls on the lens 'L' and reaches the Spectra~~g~~meter.
~~graph~~
aph

The camera attached to Spectro~~meter~~graph records spectrum of outcoming Scattered light

Observations :-

The outcoming Scattered light is observed then it contains frequency in 3 ways ~~scattered light~~

(i) frequency of equal to incident light frequency

(ii) frequency of Scattered light lower than incident light

(iii) frequency of Scattered light higher than incident light.

↗ Q ⇒ 1st right wt is Raman effect.

⑤. Explain Quantum theory of Raman Effect.

In Quatum theory

When incident light is considered as array of photon having energy $h\nu$

When photon collides with moleculy of liquid 3 types of effects may takes place

(i) The molecule may defelect the photons

(ii) the molecules may import Some part of their energy to photons

(iii) The molecules may absorb Some part of energy of photons.

If E_1, V_1 and ν_1 are energy Velocity and frequency of molecule before collision and

E_2, V_2 and ν_2 are energy Velocity and frequency of molecule after collision then According to law of conservation of energy

Energy before Collision = E after Collision

$$E_1 + KE_1 + h\nu_1 = E_2 + KE_2 + h\nu_2$$

$$E_1 + \frac{1}{2}mv_1^2 + h\nu_1 = E_2 + \frac{1}{2}mv_2^2 + h\nu_2 \quad T = \text{constant}$$

$$KE = K$$

$$KE_1 = KE_2 \Rightarrow \frac{1}{2}mv_1^2 = \frac{1}{2}mv_2^2$$

$$E_1 + h\nu_1 = E_2 + h\nu_2$$

$$E_1 - E_2 = h\nu_2 - h\nu_1$$

$$E_1 - E_2 = h(\nu_2 - \nu_1)$$

(i) molecule deflect $E_1 = E_2 \Rightarrow \nu_2 - \nu_1 = 0$

$\nu_2 = \nu_1$

∴ frequency $\boxed{\nu_1 = \nu_2}$ → Rayleigh Scatting Incident light frequency = is equal to scattered light frequency

(ii) if molecule abosorbed energy from incident photon $\Rightarrow E_1 < E_2$

$\nu_2 < \nu_1$

∴ Scattery light frequency los lower incident light → Corresponding Spectrum called Stokes lines

(iii) If molecule given energy to photon $E_1 > E_2$

$\nu_2 > \nu_1$

∴ scattered light frequency is greater than incident light ⇒ corresponding spectrum is called Anti stokes lines

Acc to Quantum Theory

$$E_1 - E_2 = nh\nu_m \quad — ⑥$$

$$E_1 - E_2 = h(\nu_2 - \nu_1)$$

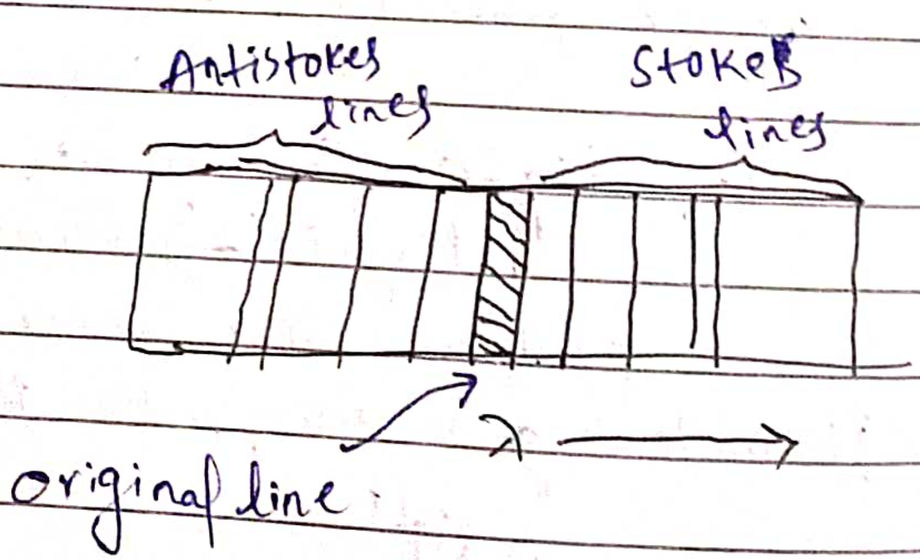
$$nh\nu_m = h(\nu_2 - \nu_1)$$

$$n\nu_m = \nu_2 - \nu_1$$

$$\boxed{\nu_2 = \nu_1 + n\nu_m}$$

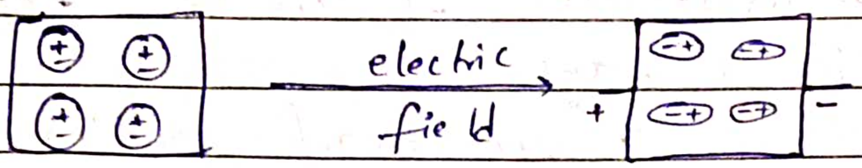
$$\boxed{\nu_2 = \nu_1 \pm n\nu_m}$$

hence difference of frequencies of Incident & Scattered light is equal to characteristic frequency of molecules (



⑥ write Elementary / classical theory of Raman effect.

Definition of REF or avoL



atoms of liquid

in presence of electrified the atoms.

When a molecule is placed in an electric field, the electrons and nuclei of Constituent atoms are attracted toward positive and negative poles respectively. This Separation of charges results in dipole moment.

the molecules gets polarized because of This dipolemoment.

Let E be electric field Intensity and μ be electric dipolemoment then

$$\mu \propto E$$

$$\mu = pE$$ [P = polarizability of molecule]

we know

$$E = E_0 \sin\omega t$$

$$\Rightarrow \mu = pE_0 \sin\omega t$$

$\mu = p E_0 \sin 2\pi\nu t$

We can consider internal motion of molecules it can be expressed in 2 ways

(i) vibrational motion and rotational motion.

(i) Vibrational motion:-

In diatomic molecule 2 nuclei of atoms vibrate along line joining the nuclei resulting in change in polarisability of molecule.

That change in polarisability (P) with displacement is given by

$$P = P_0 + \beta \frac{x}{A} \quad - ①$$

where

P_0 = polarization of molecule in equilibrium

β = change of polarisability with displacement from equilibrium posit

A = Amplitude of vibration.

According to displacement equation

of SHM.

$$x = A \sin 2\pi \nu_0 t \quad — ②$$

Sub ② in $p = p_0 + \beta \frac{x}{A}$

$$p = p_0 + \beta \sin 2\pi \nu_0 t \quad — ③$$

sub ③ in

$$\mu = pE_0 \sin 2\pi \nu t$$

we get $\mu = (p_0 + \beta \sin 2\pi \nu_0 t) E_0 \sin 2\pi \nu t$

$$\mu = p_0 E_0 \sin 2\pi \nu t + \beta E_0 \sin 2\pi \nu_0 t \cdot \sin 2\pi \nu t$$

$$\mu = p_0 E_0 \sin 2\pi \nu t + \frac{1}{2} \beta E_0 \left[\cos 2\pi(\nu - \nu_0)t + \cos 2\pi(\nu + \nu_0)t\right]$$

$\downarrow$ ④ $\qquad \downarrow$ $[2 \sin A \sin B = \cos(A - B) + \cos(A + B)]$

Therefore dipolemoment by vibrational motion vary with Applied frequency 'ν' and values lie between $\nu + \nu_0$ and $\nu - \nu_0$

The vibrational Raman shift is given by

$$\Delta \nu = \nu - (\nu - \nu_0) = \nu_0 \checkmark$$

$$\Delta \nu = (\nu + \nu_0) - \nu = \nu_0 \checkmark$$

vibrational Ramanshift.

PRS = pure rotational spectra

① How do you use Rotational Spectrum to describe internuclear distances.

Rotational / pure rotational Spectrum :-
Spectrum observed in Microwave or far Infrared region is called PRS.

pure rotational energies spectrum of Diatomic molecules

The molecules with permanent dipole moments gives pure rotational spectrum.

⇒ homonuclear diatomic molecules like H_2, O_2, N_2 cant exhibit PRS while heteronuclear diatomic molecules Such as HF, HCl HBr etc exhibit PRS

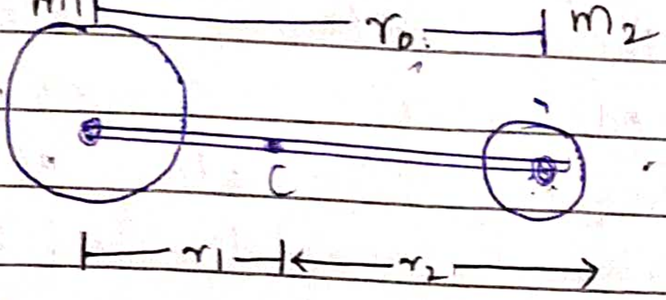
when molecules rotates because of changing dipolemoment they emit radiation during further rotation dipolemoment in fixed direction changes periodically with frequency of rotation of molecule. further in electric field of incident radiation the heterogeneous molecule ~~interac~~ absorbs energy & produce absorption spectra frequencies of This Spectral lines in RS helps to find moment of Inertia & internuclear distance of molecule.

Internuclear distance between Diatomic molecules

~~if~~ let r be the internuclear distance we can calucalate it using
$I = \mu r^2$ where ~~r~~ I = moment of Inertia
∴ for I we need Spacing Between lines B and it can be found from wave number when we know energy So lets find Energy.

The rotational energy levels & Inertia can be obtained using rigid rotator concept

Rigid Rotator :-



$r_0 = r_1 + r_2$

2 atomic mass System with 2 nuclie seperated by a definite mean distence and executes rotational motion about axis is Called rigid rotator.

Let m_1, m_2 are masses and r_0 is mean distance and 'c' is center of gravity if I is moment of Inertia & r_1, r_2 are distance of masses from axis of rotation =>

$$I = m_1 r_1^2 + m_2 r_2^2 \quad - I$$

center gravity system balance

$$m_1 r_1 = m_2 r_2 \quad - ①$$

sub ② in ①

$$m_1 r_1 = m_2 (r_0 - r_1) \qquad r_0 = r_1 + r_2$$

$$m_1 r_1 = m_2 r_0 \cancel{r_0} - m_2 r_1 \qquad r_2 = r_0 - r_1 \quad - ②$$

$$m_1 r_1 + m_2 r_1 = m_2 r_0$$

$$r_1 (m_1 + m_2) = m_2 r_0 \Rightarrow \boxed{r_1 = \frac{m_2 r_0}{m_1 + m_2}} \quad - ⑤$$

sub ③ in ①

$$m_1 (r_0 - r_2) = m_2 r_2 \qquad r_0 = r_1 + r_2$$

$$m_1 r_0 - m_1 r_2 = m_2 r_2 \qquad r_1 = r_0 - r_2 \quad ③$$

$$m_1 r_0 = m_2 r_2 + m_1 r_2$$

$$m_1 r_0 = r_2 (m_1 + m_2)$$

$$r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad - ④$$

sub ④ & ⑤ in ① I.

$$I = m_1 \left(\frac{m_2 r_0}{m_1 + m_2}\right)^2 + m_2 \left(\frac{m_1 r_0}{m_1 + m_2}\right)^2$$

$$I = \frac{m_1 m_2^2 r_0^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r_0^2}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2 [m_2 + m_1] r_0^2}{}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$\boxed{I = \mu_0 r_0^2}$$

$\mu_0 = \frac{m_1 m_1}{m_1 + m_1}$

= reduced mass

Kinetic

let ω is angular velocity of Rigid rotator.

$KE = \frac{1}{2} mv^2$

$$KE = \frac{1}{2} \overset{I}{(I)} \omega^2$$

$$= \frac{1}{2} I \omega^2$$

$\left(mvr = \frac{nh}{2\pi}\right)$

$$I\omega = J \frac{h}{2\pi}$$ [angular momentum Quantized]

J = rotational Quantum number

$$E_R = \frac{1}{2} I\omega^2 \times \frac{I}{I} = \frac{1}{2I} I^2 \omega^2$$

$$= \frac{1}{2I} \left(\frac{Jh}{2\pi}\right)^2$$

$$E_R = \frac{1}{2I} \frac{J^2 h^2}{4\pi^2}$$

$$E_R = J^2 \frac{h^2}{8\pi^2 I}$$

The schodinger eqn is given by

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

It can be expressed in polar co-ordinates of

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

$$\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)\right. + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

[illegible]

on solving q^n.

$$\therefore \quad E = J(J+1)\frac{h^2}{8\pi^2 I}. \quad [J = 0, 1, 2, \ldots$$

Determination of Inter nuclear distace :-

when molecule rised from J to $J+1$
⟹ absorption is represented by.

$$\Delta E = E_2 - E_1$$

$$\Delta E = \frac{h^2}{8\pi^2 I}(J+1)(J+2) - \frac{h^2}{8\pi^2 I}J(J+1)$$

$$\Delta E = \frac{h^2}{8\pi^2 I} \times \cancel{2}\left[(J+1)(J+2) - J(J+1)\right]$$

$$\Delta E = \frac{h^2}{8\pi^2 I}(J+1)\left[J+2-J\right]$$

$$\Delta E = \frac{h^2\, 2(J+1)}{8\pi^2 I} = 2\frac{h^2}{8\pi^2 I}(J+1)$$

Corresponding wave number of radi
is given by

$$\bar{\nu} = \frac{\Delta E}{hc} \Rightarrow \bar{\nu} = \frac{2h^2}{8\pi^2 I}\frac{(J+1)}{hc}$$

$$\bar{\nu} = \frac{2h}{8\pi^2 I c}(J+1)$$

$$\bar{\nu} = 2.B(J+1) \qquad \left[\because B = \frac{h}{8\pi^2 I c}\right.$$

~~Hen~~

In rotational Spectra of rigid diatomic molecule. The spectral lines are at equidistance.

Hence Spacing bw lines is 2B.

By rotational spectra we can find B

By using moment of Inertia & B we can calculate inter nucle distance.

Ex :- Carbon monoxide molecule.

CO ⇒ C=O is diatomic molecule.

In rotation Spectra spacing b/w lines found to be 3.844/cm.

hence $2B = 3.844$.

$$B = 1.922 \text{ cm}$$

$$\therefore \quad \cancel{I = a} \qquad B = \frac{h}{8\pi^2 I c}.$$

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

$$I = \frac{6.626\times10^{-34}}{8\,(3.14)^2 \times 3\times10^{8} \times 1.922}$$

$$I = 14.55\times10^{-47} \text{ kg}$$

$$\mu = \frac{m_O \times m_C}{m_O + m_C}\,(1.67\times10^{-27}\text{ kg}) \qquad \left[\mu_O = \frac{m_1 m_2}{m_1+m_2}\right]$$

$$\mu = \frac{16\times12}{16+12}\,(1.67\times10^{-27})\text{ kg}$$

$$\mu = 1.14\times10^{-26}\text{ kg}$$

we know $I = \mu r_b^2 \Rightarrow r_b^2 = \frac{I}{\mu}$

$$r_b^2 = \frac{I}{\mu} \Rightarrow r_b^2 = \frac{14.55\times10^{-47}}{1.14\times10^{-26}}$$

$$r_b = \left(\frac{14.55\times10^{-47}}{1.14\times10^{-26}}\right)^{1/2}$$

$$r_b = 1.13\times10^{-10}\,m$$

$$r_b = 1.13\,A^0 \Rightarrow r_b = 0.133\,nm$$

$$\boxed{r_b = 0.113\,nm}$$

1st unit

SAQ ① Draw backs of Bohr's Theory or Limitations of Bohr's Theory.

Bohr's Model doesnot explain,

① Spectra of atoms more complex than H_2 atom

② Variations in intensity of spectral lines

③ fine structure of Spectral lines

④ Splitting of Spectral lines in presence of electrical field i.e Stark effect

⑤ Spliting of Spectral lines in presence of magnetic field i.e Zeeman effect.

⑥ anything related to distribution and arrangement of electrons in atom.

② Explain L-S coupling and JJ Coupl

L-S coupling:- It is also known as Russel - Saunders coupling.

→ It is a normal coupling where all orbital angular momentum vectors 'l' of electrons combine to form a resultant vector L

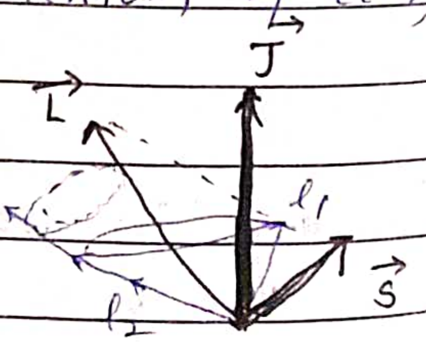
→ All angular momentum vectors S likewise combine to form a resultant vector 'S'

→ The vectors 'L' and S combine to form a vector J which represent total angular momentum of atom

$$L = l_1 + l_2 + l_3 + \dots$$

$$S = S_1 + S_2 + S_3 + \dots$$

$$J = L + S.$$



JJ coupling :-

JJ coupling.

It is observed that interaction between the spin and orbital vectors in each electron is stronger than the interaction between either spin vectors or the orbital vectors of different electors.

→ In that case JJ coupling is more suitable than L-S coupling.

In JJ coupling each e^- is considered seperately and its total angular momentum j is obtained by $j = l + s$

⇒ Total angular momentum J of atom would be vector sum of all individual j vectors of electrons

$$j_1 = l_1 + s_1$$
$$j_2 = l_2 + s_2$$
$$\vdots$$
$$\therefore J = j_1 + j_2 + j_3 + \ldots\ldots$$

$$J = \Sigma j$$

Explain

③ Selection rules and Intensity rules

According to vector atom model, forma of Spectral lines wont take place for all possible transitions but energy levels.

Emmision or absorption of Spectra lines will follow certain rules as Selection rul

Selection rules for

J	S	L
the $\bar{e}^{nic}$ Transitions take place only in way that $\Delta J = \pm 1$ or 0.	The $\bar{e}^{nic}$ transitions are only possible when $\Delta S = 0$	The $\bar{e}^{n}$ transiti takes place whe $\Delta L = \pm 1$
In a magnetic field, $\Delta m_j = 0$ or ±1	In a magnetic field $\Delta m_s = 0$	In a magnetic field Δm_l = or ±1

Intensity rules :-

(i) The intensity of Transition is strong for which L and J change in Same Sense

(~~ii~~) ~~The intensity of~~ transition is

(ii) Strong when decreasing i.e $L \rightarrow L-1$

(iii) Weak when Increasing i.e $L \rightarrow L+1$

i.e L and J change in opposite sense.

(iv) oppositely directed transition does not occur

$\Delta L = -1$	$\Delta J = -1$	Most intense
$\Delta L = -1$	$\Delta J = 0$	Less Intense
$\Delta L = +1$	$\Delta J = +1$	weaker
$\Delta L = +1$	$\Delta J = 0$	weaker
$\Delta L = -1$	$\Delta J = +1$	No transition
$\Delta L = +1$	$\Delta J = -1$	No transition

④ write Applications of Zeeman effect.

By using of Zeeman effect the specific charge $\left(\frac{e}{m_0}\right)$ of electron can be obtained. the change in frequency is given by,

$$\Delta \nu = d\nu = \frac{eB}{4\pi m_0} \quad -①$$

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

we know, $\nu = \frac{c}{\lambda}$ ⇒ Taking d on both sides

$$d\nu = c \cdot d\frac{1}{\lambda} \Rightarrow c\left(\frac{-1}{\lambda^2}\right) d\lambda$$

$$d\nu = \frac{-c}{\lambda^2} d\lambda \Rightarrow d\lambda = \frac{\lambda^2}{c} d\nu \quad \left[-ve \text{ neglect}\right]$$

$$\left[\frac{d}{dx}\frac{1}{x} = \frac{-1}{x^2}\right]$$

$$d\lambda = \frac{\lambda^2}{c} \frac{eB}{4\pi m_0}$$

Charge [illegible]

$$\boxed{\frac{e}{m_0} = \frac{4\pi c}{B} \cdot \frac{d\lambda}{\lambda^2}}$$

⑤ Write Applications of Raman effect

(i) To study molecular Structure of Cryst
and compounds

(ii) To study compositions in plastics and mixtures.

(iii) To decide about single double or triple Bond.

(iv) To study spin and statistics of Nucle

(v) To study Binding forces b/w atoms or group of atoms in Crys

(vi) To study vibrational and rotational Energy levels of homo nuclear molecul like N_2, O_2

(vii) to know number of atoms in a molecule

(ix) To know relative arrangement, relative masses and chemical bonds b/w atoms.

⑥ Explain origin of electronic Spectra of Molecules

⑦ Explain Rotational – vibrational Spectra

Molecular Spectroscopy :- It is a branch of Spectroscopy dealing with interaction of radition with molecules.

origin :- Same as atoms molecules get exited when interacted with radiation & emit spectral lines forming molecular Spectra

In general molecular spectra arise from rotation molecule because of atoms ~~of~~ vibration of its atoms and changes in their electronic configurations.

The spectrum obtained in,

Microwave / infrared region is called pure rotational spectrum	near infrared region is called vibration - Rotation Spectrum	visible / uv region is called electronic Spectrum