KUSHAGRA AGARWAL 2018113012

PART-A

Q1) a) **Rotational Spectrum**

we need to consider two isotopes. Let's take $^1H^{16}O$ & $^2H^{16}O$

↓ deuterium.

$$E_{Rot} = \frac{h^2}{8\pi^2 I} J(J+1)$$

where $I = \mu r^2$ → reduced mass $\left(\frac{m_1 m_2}{m_1+m_2}\right)$

$$\therefore \Delta E_{rot} = \frac{h^2}{8\pi^2 I}\left(J_1(J_1+1) - J_2(J_2+1)\right)$$

selection rule says: $|J_1 - J_2| = 1$

let's take $J_1 = J_2 + 1$

$$\Delta E_{rot} = \frac{h^2}{8\pi^2 I}\left((J_2+1)(J_2+2) - J_2(J_2+1)\right)$$

$$= \frac{h^2}{8\pi^2 I}\left((J_2+1)(2)\right) = \frac{h^2}{8\pi^2 I} \times 2 \times J_1$$

$$\boxed{\Delta E_{rot} = \left(\frac{2h^2 J_1}{8\pi^2 r^2}\right) \times \left(\frac{1}{\mu}\right)}$$

for $^1H^{16}O \rightarrow \mu = \frac{1\times 16}{1+16} = 16/17$

$^2H^{16}O \rightarrow \mu = \frac{2\times 16}{2+16} = 16/9.$

⊛ in general if 2 atoms m_1, m_2 and one replaced by isotope m_1', m_2

then $\mu_1 = \frac{m_1 m_2}{m_1+m_2}$ $\mu_2 = \frac{m_1' m_2}{m_1'+m_2}$

$\mu_1 > \mu_2$ if $\frac{m_1 m_2}{m_1+m_2} > \frac{m_1' m_2}{m_1'+m_2}$

$\Rightarrow m_1 m_1' + m_1 m_2 > m_1 m_1' + m_1' m_2$

$\Rightarrow m_1 > m_2'$

$\therefore$ $\boxed{\mu_1 > \mu_2 \text{ if } m_1 > m_2' \text{ and vice versa}}$

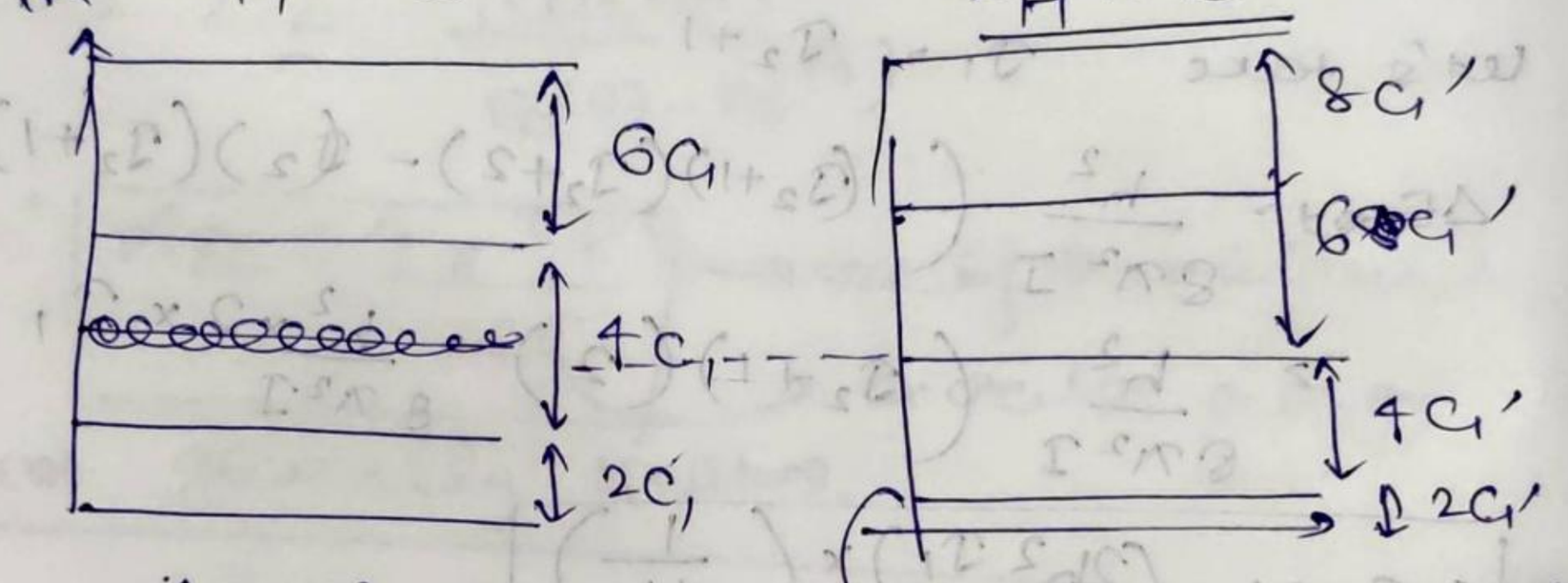
in our case $m_1' > m_1$, $\therefore \mu_2 > \mu_1$,
as can be observed (16/9 is greater than 16/17)

$$\therefore \boxed{\Delta E_{rot} = C \times \frac{1}{\mu_1}}$$

$C \rightarrow \frac{2h^2 \pi_1}{8\pi^2 r^2}$

$\therefore$ if $\mu_2 > \mu_1$,
then $\Delta E_{rot_2} < \Delta E_{rot_1}$ as inversely proportional

ΔE_{rot} represents the spacing b/w 2 levels. the gap will be lesser in $^2H^{16}O$ than in $^1H^{16}O$.



b) Vibrational Spectrum

$$\text{Energy}_{vib} = h(v + 1/2)\sqrt{k/\mu}$$

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

again very precisely illustrated logic if a molecule $m_1 m_2$ is changed to $m_1' m_2$
then $\mu_1 > \mu_2$ if $m_1 > m_1'$
and vice versa

and if $\mu_1 > \mu_2$ then $\Delta E_{vib,1} < \Delta E_{vib,2}$
(inversely proportional)

taking $^1H^{16}O$ and $^2H^{16}O$ again.

$\mu_1 = 16/17$ $\quad \mu_2 = \frac{2\times16}{18} = 16/9$.

$\mu_1 < \mu_2$ as (2.71 mass of H isotope)

$\therefore \Delta E_{vib,1} > \Delta E_{vib,2}$

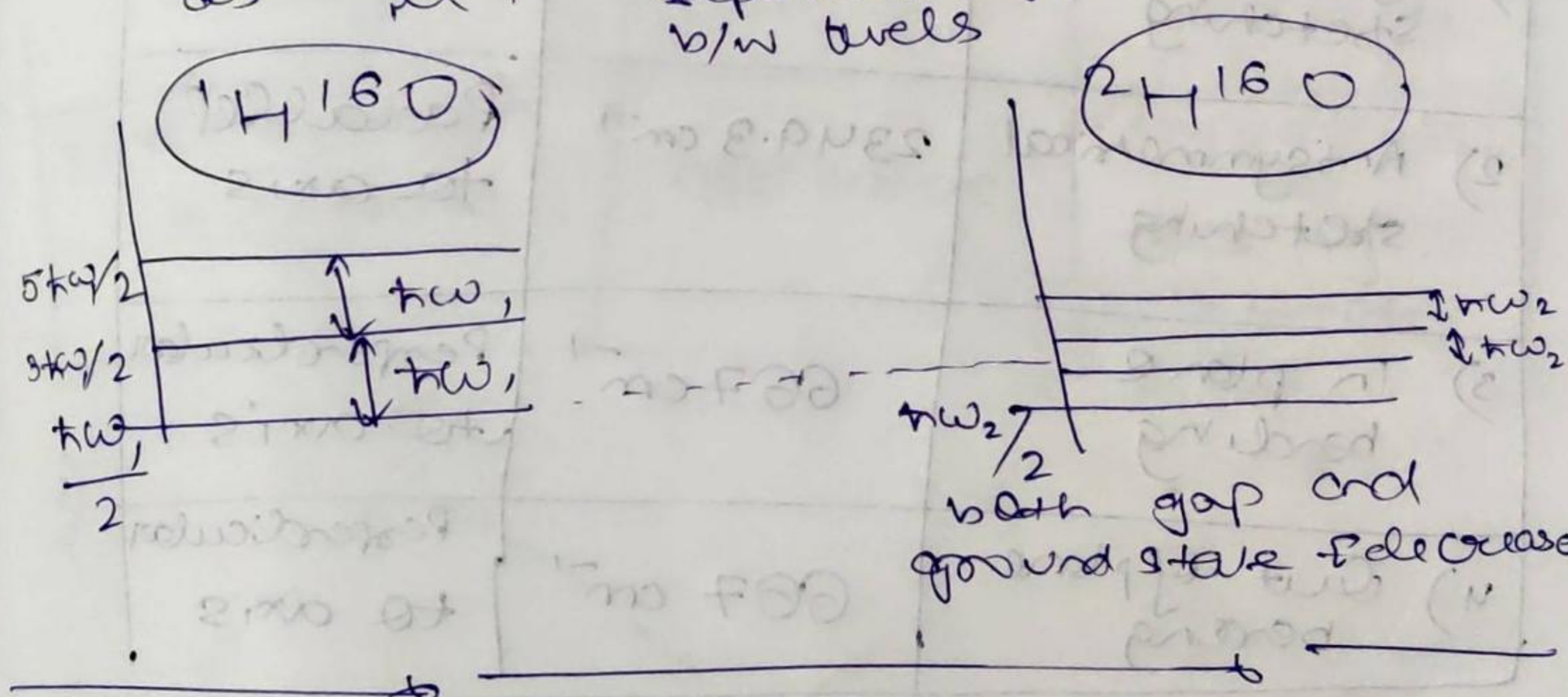
Ground state energy $= \frac{\hbar\omega}{2} = \frac{\hbar}{2}\sqrt{k/\mu}$

as $\mu \uparrow$ ground state energy $\downarrow$

also $\Delta E_{vib} = \hbar\omega(v+1 + 1/2 - v - 1/2)$

$= \hbar\sqrt{k/\mu}$

as $\mu \uparrow$ separation $\downarrow$. b/w levels



both gap and ground state decreases

iii) Electronic spectra

The ~~mass~~ reduced mass has no relation to the electronic band spectra of ~~diatomic~~ molecules. Therefore even if one ~~not~~ atom in a molecule was replaced by its isotope (leading to only mass change and no chemical property change) the electronic spectrum remains the same. Therefor for 2 molecules $^1H^{16}O$ and $^2H^{16}O$, the spectra (electronic is same)

Q2) 1) CO_2

O — C — O → axis

linear molecule.

No. of atoms : N = 3 → as it is linear

No. of modes = (3N-5)

= 3(3) - 5 = 9 - 5 = 4

We will have 4 vibrational modes for CO_2 molecule

Mode of vibration	Associated wave number	Symmetry
1) Symmetrical stretching	1340 cm^{-1}	Parallel to axis
2) Antisymmetrical stretching	2349.3 cm^{-1}	Parallel to axis
3) In plane bending	667 cm^{-1}	Perperdicular to axis
4) Out of plane bending	667 cm^{-1}	Perperdicular to axis

i) ← O — C — O →

Symmetric

2) → ← →

O — C — O

Antisymmetric

3) ↑ O — C — O ↑

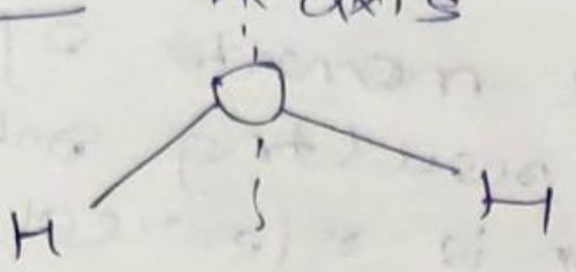
↓

In plane bending

4) O — C — O

Out of plane bending

ii) H_2O



Non linear molecule. N = 3

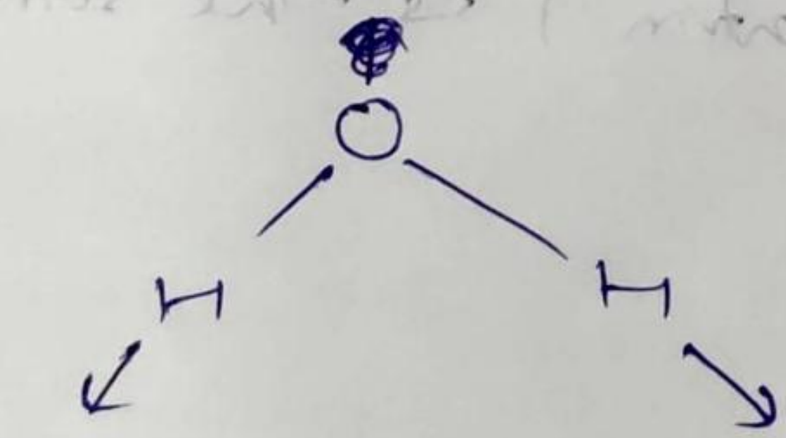
No. of modes = 3(3) − 6 = 3.

$\leftarrow (3N-6)$

CO_2 : Non linear

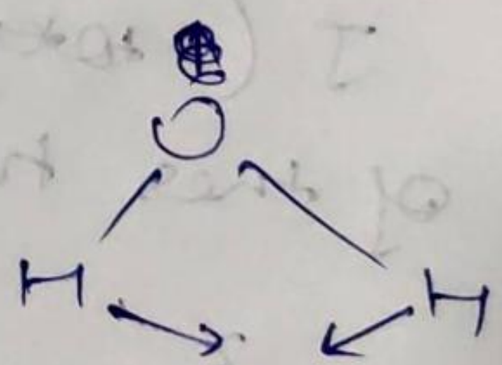
Mode of vibration	Associated wavenumber	Symmetry
1) Symmetric stretching	3651.7 cm^{-1}	Parallel to axis of Symmetry
2) Symmetric Bending	1595 cm^{-1}	Parallel to axis of Symmetry
3) Antisymmetric stretching	3755.8 cm^{-1}	Perpendicular to axis of symmetry.

1)



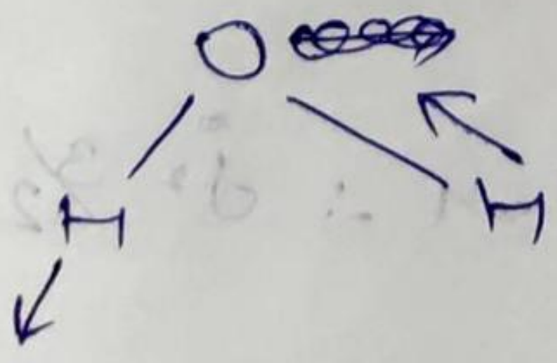
symmetric stretching

2)



symmetric bending

3)



antisymmetric stretching

8 3) Stark effect

The splitting of atomic spectral lines as a result of external electric field is called the Stark effect.

~~As the~~ The splitting of a line is not symmetric.

The splitting of the energy levels by an electric field first requires that the field polarizes the atom and then interacts with the resulting dipole moment. That dipole moment depends upon the magnitude of M_j (not its sign), ∴ the energy levels show splitting proportional to the quantum numbers $J+1$ / $J+1/2$ for integer & half integer spins respectively.

Stark effect results in the shifting as well as splitting of the spectral lines of a molecule when an external electric field is present

shifting is $\Delta V \propto (ME)^2$ (for linear molecules)

splitting causes a single state to split into multiple states (thereby making them non-degenerate)

84) L-S coupling

The coupling of angular momenta of individual electrons to a resulting orbital angular momentum and spin is referred to as LS coupling or Russell-Saunders coupling.

* gives us a good justification for the observed spectral lines for light atoms where the spin-orbit coupling is weak

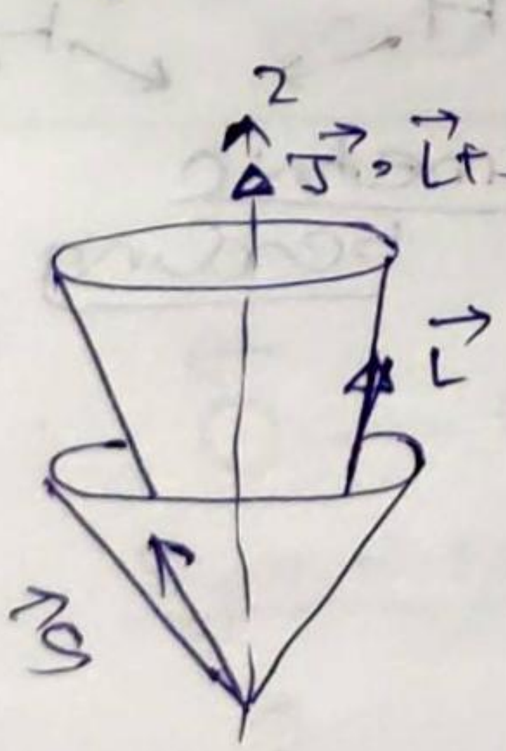
$$\vec{J} = \vec{L} + \vec{S}$$

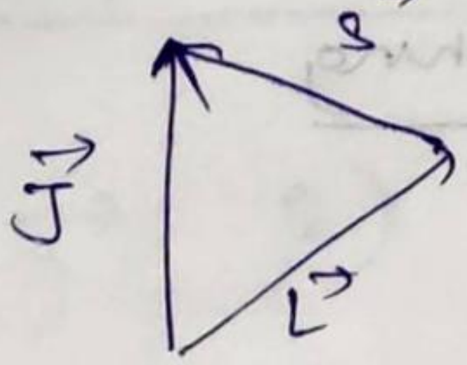
$\vec{J}$: total angular momentum
$\vec{L}$: total orbital angular momentum
$\vec{S}$: total spin angular momentum

J is formed by the coupling of individual spin angular momentums

L is formed by addition of individual electrons to produce resultant orbital angular momentum

J (total angular momentum) is the sum of these two. This





say $s = 1/2$ $l = 1 \therefore j = 3/2$

8S) Quantum Mechanical Addition of L and S:-

we know deer LS coupling that

$$J = L + S$$

$$\therefore J^2 = (L+S)^2$$

$$= L^2 + S^2 + 2LS$$

$$\therefore LS = \frac{(J^2 - L^2 - S^2)}{2}$$

we know $L_\pm |l, m_l\rangle = \hbar\left((l \pm m_l + 1)(l \mp m_l)\right)^{1/2} \times \hbar\,|l, m_l \pm 1\rangle$

$\therefore$ for eigenstates of J^2, L^2 and S^2 we can use $|j, m_j, l\rangle$

Maximal spin state is given by

$$|l+1/2,\ l+1/2,\ l\rangle = |l,\ l\rangle \otimes |\uparrow\rangle$$

spin up state

$$J_- |l,l\rangle \otimes |\uparrow\rangle = \hbar\sqrt{2l}\,|l,l-1\rangle \otimes |\uparrow\rangle + \hbar\,|l,l\rangle \otimes |\downarrow\rangle$$

Normalizing RHS,

$$|l+1/2,\ l-1/2,\ l\rangle = \sqrt{\frac{2l}{2l+1}}\,|l,l-1\rangle \otimes |\uparrow\rangle + \sqrt{\frac{1}{2l+1}}\,|l,l\rangle \otimes |\downarrow\rangle$$

∴ full expression for basis states is

$$|j=l+1/2,\ m_j,\ l\rangle = \sqrt{\frac{l+m_j+1/2}{2l+1}}\,|l,m_j-1/2\rangle \otimes |\uparrow\rangle + \sqrt{\frac{l-m_j+1/2}{2l+1}}\,|l,m_j+1/2\rangle \otimes |\downarrow\rangle$$

$$|l-1/2,\ m_j,\ l\rangle = -\sqrt{\frac{l-m_j+1/2}{2l+1}}\,|l,m_j-1/2\rangle \otimes |\uparrow\rangle + \sqrt{\frac{l+m_j+1/2}{2l+1}}\,|l,m_j+1/2\rangle \otimes |\downarrow\rangle$$

∴ in conclusion

$$|j=l\pm 1/2,\ m_j,\ l\rangle = \alpha_\pm\,|l,m_j-1/2\rangle \otimes |\uparrow\rangle + \beta_\pm\,|l,m_j+1/2\rangle \otimes |\downarrow\rangle$$

$$\langle 1/r^3 \rangle = \frac{1}{l(l+1/2)(l+1)\,n^3 a^3}$$

$$E_{so}^1 = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2} \times \left(\frac{\pm 2/2)(j(j+1)-l(l+1)_n}{(l)(l+1/2)(l+1)}\right)^{-3/4}$$

$$E_H^1 = \frac{E^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right)$$

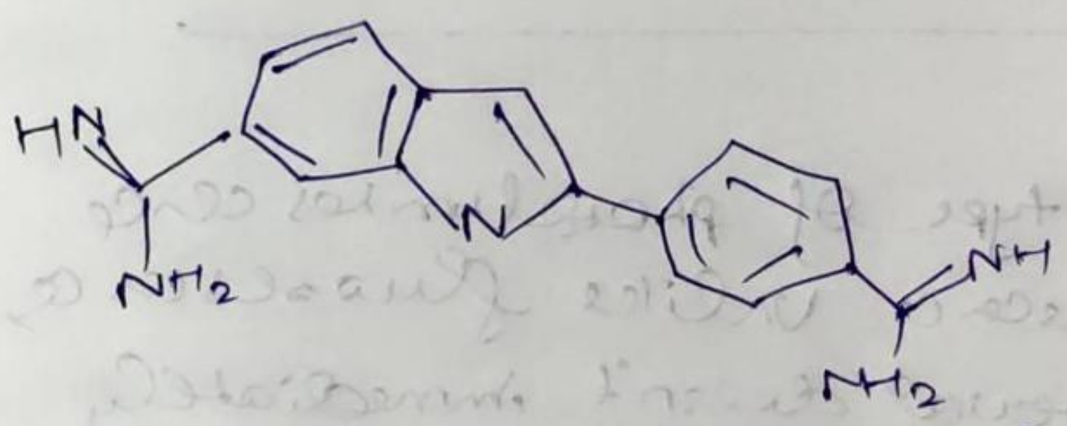
$$E_{nj} = -\frac{13.6}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - 3/4\right)\right]$$

Q6) Fluorescence

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases the emitted light has a longer wavelength (i.e. lower energy) than incident light

Molecules that exhibit fluorescence

i) DAPI (4', 6- diamidino 2-phenylindole) is a fluorescent stain that binds strongly to adenine-thymine rich regions in DNA. It is used in fluorescence microscopy. As DAPI can pass through an intact cell membrane, it can be used to stain both live and fixed cells.



DAPI structure

When bound to double stranded DNA, DAPI has an absorption maximum at wavelength of 358nm (UV) and its emission maximum is at 461nm (blue). Therefore for fluorescence microscopy, DAPI is excited with UV light and detected through a blue/cyan filter. The DNA fluorescent probe has been effectively modelled using the time dependent density functional theory coupled with IEF version of the polarizable continuum model.

ii) Benzene →

Benzene has a wavelength of fluorescence which is in the range of 270-310 nm (UV). It has ultraviolet fluorescence. In general

Benzene

for fused rings it has been found that fluorescent properties exist. On top of it electron donating groups such as NH_2, OH and OCH_3 enhance the fluorescence whereas electron withdrawing groups like COOH, $-N=N-$ tend to reduce it. Heterocyclic compounds like pyridine and pyrrole do not fluoresce significantly but when fused to an aromatic ring as in case of quinoline become fluorescent. Conjugated double bond structures in combination with aliphatic/acyclics exhibit fluorescence

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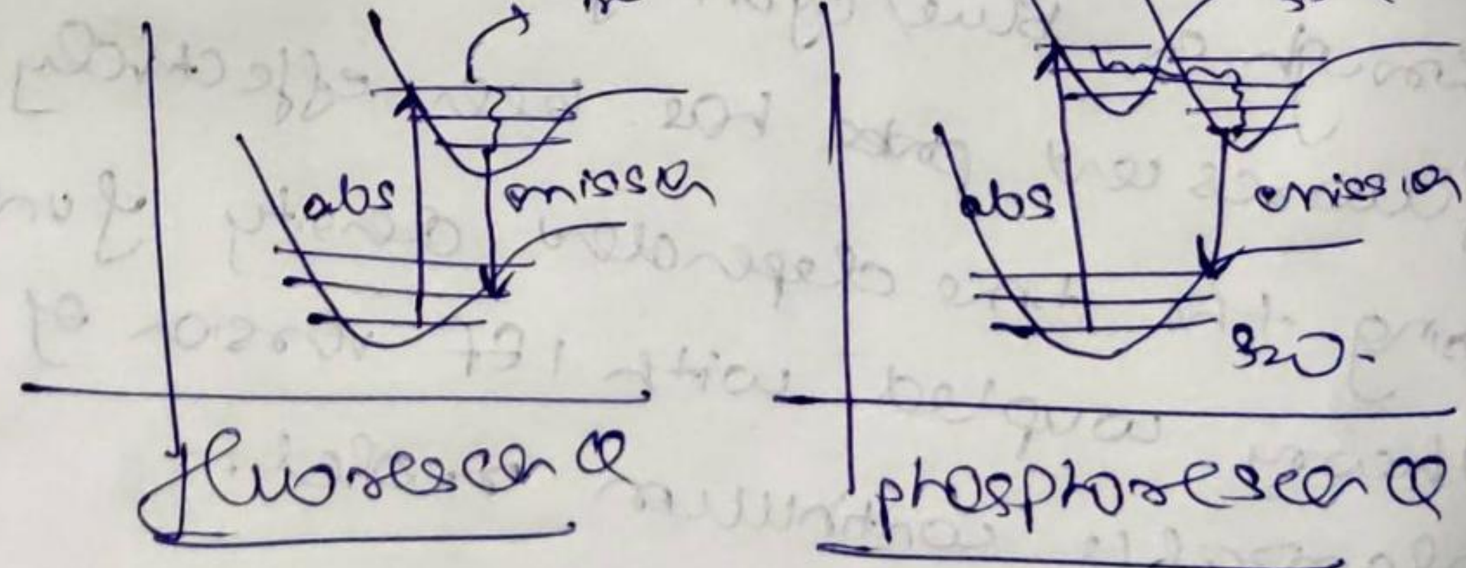
Phosphorescence

Phosphorescence is a type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material doesn't immediately re-emit the radiation it absorbs. The slower time scales of re-emission are associated with forbidden energy state transitions in quantum mechanics.

Jablonski diagrams



Molecules that show phosphorescence are:

i) Strontium Aluminate ($SrAl_2O_4$)

also ($SrO \cdot Al_2O_3$) → diagnostically useful

It is a pale yellow monoclinic crystalline powder which when activated with a suitable dopant (eg: europium, written as Eu: $SrAl_2O_4$) it acts as a photoluminescent phosphor with long persistence of phosphorescence

It is vastly superior phosphor to its predecessor copper activated zinc sulfide, it is 10 times brighter and glows for 10 times longer.

It produces green and aqua hues (green has highest brightness & aqua has longest glow).

Excitation wavelengths range from 200-450 nm

Glow intensity depends on the particle size; generally bigger the particles better the glow

ii) Zinc sulphide (ZnS)

Most copper application is the cathode ray tubes. Zinc sulphide with the addition of a few ppm of suitable activator exhibits strong phosphorescence (described by Nikola Tesla in 1893). Its current uses apart from cathode ray tubes is X-ray screens to glow in the dark products. If we use silver as an activator then the resulting colour is bright blue with maximum at 450 nm. Using manganese yields an orange red colour at around 590 nm. Copper gives long time glow. Copper doped zinc sulphide (ZnS plus Cu) is used in electroluminescent panels.

iii) Calcium sulphide (CaS) glows blood red for an hour even after the light source is removed.