

INTERNATIONAL INSTITUTE OF INFORMATION TECHNOLOGY, HYDERABAD

MIDSEM EXAM for "Chemistry Topics for Engineers"

TOTAL TIME: 90 min. Total points: 60.
Total of 10 questions.

1. [5 points] What is cyclic voltammetry? Draw a schematic voltammogram for an illustrative reversible redox reaction, explain various features and processes in it.
2. [5 points] Given that the standard potentials of Cu^{2+}/Cu and Cu^+/Cu are +0.340 V and +0.522 V respectively, find the standard EMF $E^\circ(\text{Cu}^{2+}/\text{Cu}^+)$.
3. [5 points] The transfer coefficient of a certain electrode in contact with of M^{3+} and M^{4+} in aqueous solution at 25° C is 0.42. The current density is found to be 55.0 mA cm^{-2} when the overpotential is 125 mV. What is the overpotential required for the current density of 75 mA cm^{-2} . Under normal conditions, will this be large overpotential? What is the process that will dominate (anodic or cathodic)?
4. [5 points] Suppose that a charge-transfer transition (electronic transition) in a one-dimensional system can be modelled as a process in which a Gaussian wave-function centered on $x=0$ and with 'a' makes a transition to another Gaussian wave-function centered on $x=a/2$. Evaluate the transition dipole moment.
5. [5 points] Write a short note on Franck-Condon principle.
6. [5 points] Write a short note on the principle of LASER and its action.
7. [5 points] What is fluorescence and phosphorescence? Use Jablonski diagram to illustrate various processes in them. What differentiates between them?
8. [10 points] Identify the various contributions to the intensity of NMR transition and derive the formula for intensity of such a transition. Given that for ${}^1\text{H}$ nuclei, $\gamma_N = 2.675 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$; for a sample containing 1 million protons, find the population difference between up and down spins, and thus the intensity in a 10 T machine.
9. [5 points] For the benzene radical anion, draw a schematic EPR spectrum. Explain various features in it.
10. [10 points] State the gross and specific selection rules for following spectroscopies: (a) rotational, (b) vibrational (c) rototational-vibrational (d) vibrational raman and (e) rotational raman spectroscopies. You may want to make a table.

----- END OF QUESTION PAPER ---

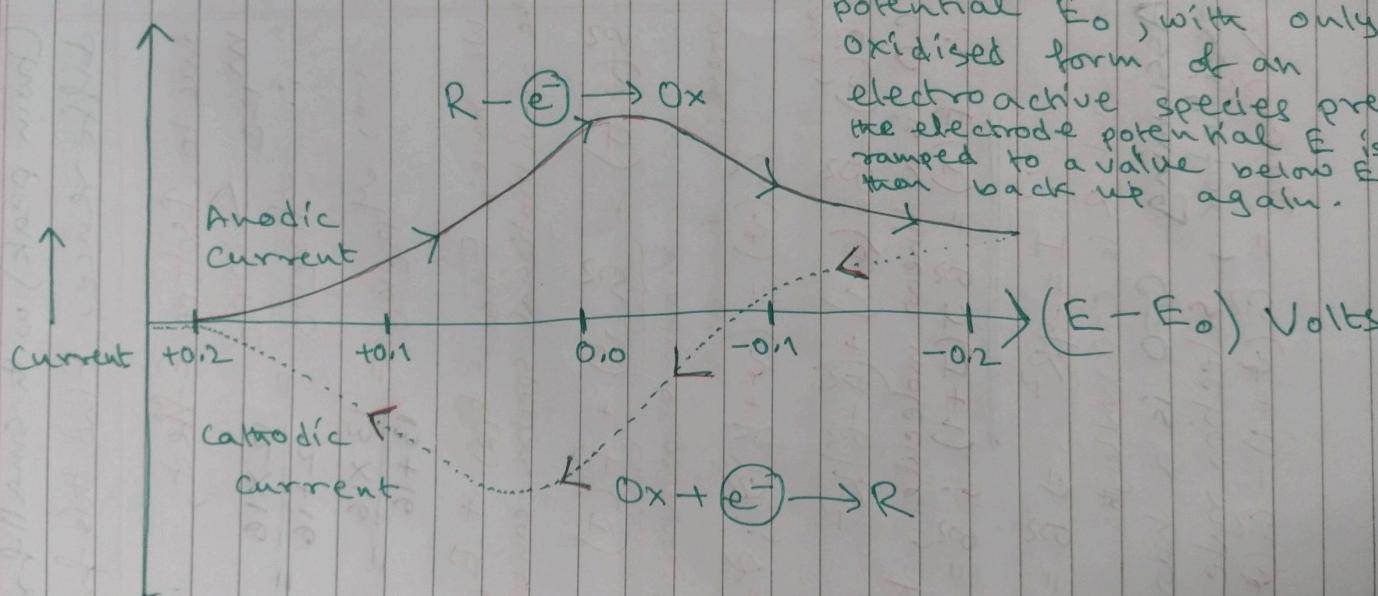
Q) What is cyclic voltammetry? Draw a schematic voltammogram for an illustrative reversible redox reaction, explain various features and processes in it.

Cyclic voltammetry is an electrochemical technique used to investigate redox reactions and electroactive species. It involves —

- 3-electrode Electrochemical Cell with a working electrode, a reference electrode and a counter electrode.
- Voltage Sweep: Linearly changing the potential at a controlled scan rate (either forward or reverse).
- Measurement of Current passing through the working electrode as the potential swept.
- Voltammogram: Plotting the data, clearly depicting peaks or plateaus that represent El.Ch. processes.
- Information Extraction: CV provides data on redox potentials, reversibility, electron transfer kinetics, and species concentration.

CV is widely used in chemistry, biochemistry, electrochemistry, materials science for studying ~~designing~~ electrochemical system reactions and materials as well as designing electrochemical systems.

Starting at a value above the standard reduction potential E_o , with only the oxidised form of an electroactive species present, the electrode potential E is ramped to a value below E_o and then back up again.



* This generates the reduction current peak (solid line) followed by the oxidation current peak (dotted line)

(Q 1)

Voltammetry definition,

Cyclic Voltammetry definition,

Keywords — Explanation

→ 3-electrode Electrochemical Cell

→ Voltage Sweep — linear (V-t) graph
(schematic)

→ Current Measurement —

reaction proceedings, Reduction-Oxidation
current peaks

→ Voltammogram —

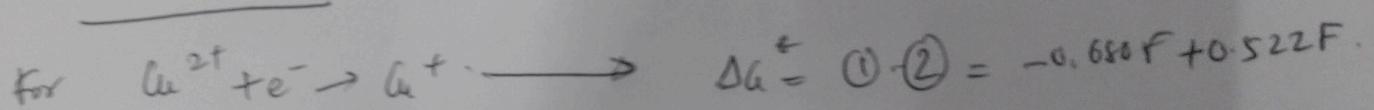
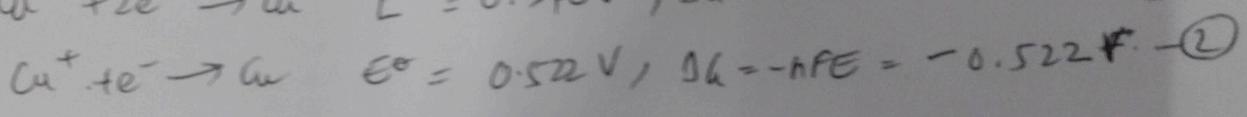
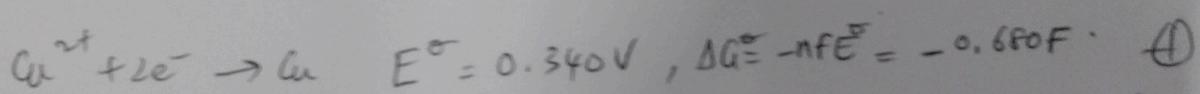
peaks / plateaus representing Elec.Chem.
process

→ Information Extraction — Uses

Schematic Voltammogram of
Reversible Redox Reaction
and

Explaining the Voltammogram
briefly ~~(Ans)~~

Q2.



$$\longrightarrow \text{Do hat } E(\text{Cu}^{2+}/\text{Cu}^+) = 0.158 \text{ V}$$

$$= \frac{\Delta G^\circ}{(-1 \text{ F})} //$$

Q3.

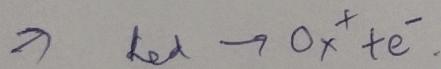
$$\alpha = 0.42 = \alpha_A = \alpha_C \quad [\text{anodic and cathodic}]$$

$$j = 55.0 \frac{\text{mA}}{\text{cm}^2}, \quad \eta = 125 \text{ mV}. \quad \text{What } \eta \text{ has } j = 75 \frac{\text{mA}}{\text{cm}^2}?$$

- ① This is large overpotential! ($\eta > 10 \text{ mV}$ typically is!).
- ② Large overpotential only anodic (or cathodic) needs to be considered, other part corresponding to cathodic (or anodic) can be neglected.

That is: $j = j_0 \left(e^{\frac{(1-\alpha)\eta F}{RT}} - e^{-\frac{\alpha\eta F}{RT}} \right)$ | has for $|\eta| > 70$ only one of the two sub-parts dominant and other negligible

Current is $+V_R$ } so process is $M^{3+} \rightleftharpoons M^{4+}$
 \Rightarrow Anodic current }



$$\Rightarrow j \approx j_0 e^{\frac{(1-\alpha)\eta F}{RT}}$$

$$\Rightarrow \frac{j_1}{j_2} = \frac{j_0 e^{\frac{(1-\alpha)\eta_1 F}{RT}}}{j_0 e^{\frac{(1-\alpha)\eta_2 F}{RT}}} = e^{\frac{(1-\alpha)F(\eta_1 - \eta_2)}{RT}}$$

$$\Rightarrow \eta_2 = \left[\frac{1}{(1-\alpha)F} \ln \left(\frac{j_1}{j_2} \right) \right] \times (-1) + \eta_1.$$

$$= \left(\frac{1}{(1-0.42)F} \right) \ln \frac{55.0}{75.0} + 125 \text{ mV}. \quad ; \quad F = \frac{F}{RT} = \frac{1}{25.69 \text{ mV}}$$

$$\eta_2 = + \frac{25.69 \text{ mV}}{0.58} \ln \left(\frac{75}{55} \right) + 125 \text{ mV.} = \boxed{138.73 \text{ mV.}} \text{ Ans.}$$

Q4: $\Psi_{\text{initial}}(x) = N_1 e^{-x^2/2a^2}$ (given)
 $\Psi_{\text{final}}(x) = N_2 e^{-(x-a/2)^2/2a^2}$ Assign same width. (given).

Transition Dipole moment = $\int dx \Psi_f^*(x) \hat{\mu} \Psi_i(x)$.
 where $\hat{\mu}$ if dipole operator. = $q \hat{x} = qx$.

$$\text{TOM} = \int_{-\infty}^{\infty} dx (N_2 e^{-(x-a/2)^2/2a^2}) (q x) (N_1 e^{-x^2/2a^2})$$

$$= q N_1 N_2 \int_{-\infty}^{\infty} dx x \cdot e^{-\frac{x^2}{2a^2} - \frac{(x-a/2)^2}{2a^2}}$$

$$x^2 + (x - \frac{a}{2})^2 = x^2 - ax + \frac{a^2}{4} = 2(x^2 - \frac{ax}{2}) + \frac{a^2}{2}$$

$$= 2 \left[\left(x - \frac{a}{4} \right)^2 - \frac{a^2}{16} \right] + \frac{a^2}{2}$$

$$= 2 \left(x - \frac{a}{4} \right)^2 + \frac{a^2}{8}$$

So $\text{TOM} = q N_1 N_2 e^{-\frac{a^2/8}{2a^2}} \int_{-\infty}^{\infty} dx x \cdot e^{-\frac{(x-a/4)^2}{a^2}}$.

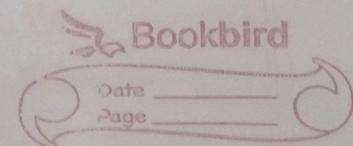
$$= q N_1 N_2 e^{-1/16} \int_{-\infty}^{\infty} dx \left(\frac{a}{4} \right) e^{-x^2/a^2} = \frac{e N_1 N_2 e^{-1/16}}{4} \sqrt{\frac{\pi}{2a}}$$

$$N_1 \int_{-\infty}^{\infty} e^{-x^2/a^2} dx = 1 \Rightarrow N_1 \sqrt{\frac{\pi}{a}} = 1, N_1 = \sqrt{\frac{a}{\pi}}$$

$$N_2 \int_{-\infty}^{\infty} e^{-(x-a/2)^2/a^2} dx = 1 \Rightarrow N_2 = \sqrt{\frac{a}{\pi}}$$

So $\text{TOM} = \frac{\sqrt{\frac{\pi}{2a}}}{a^{3/2}} e^{-1/16}$
 electric charge exponential e.

5) Write a short note on
Franck - Condon Principle.



Franck - Condon Principle → fundamental concept in QM and Spectroscopy, for studying electronic transitions in molecules.

(It describes the likelihood of electronic transitions occurring without significant changes in the nuclear positions of atoms within a molecule.)

∴ It includes —

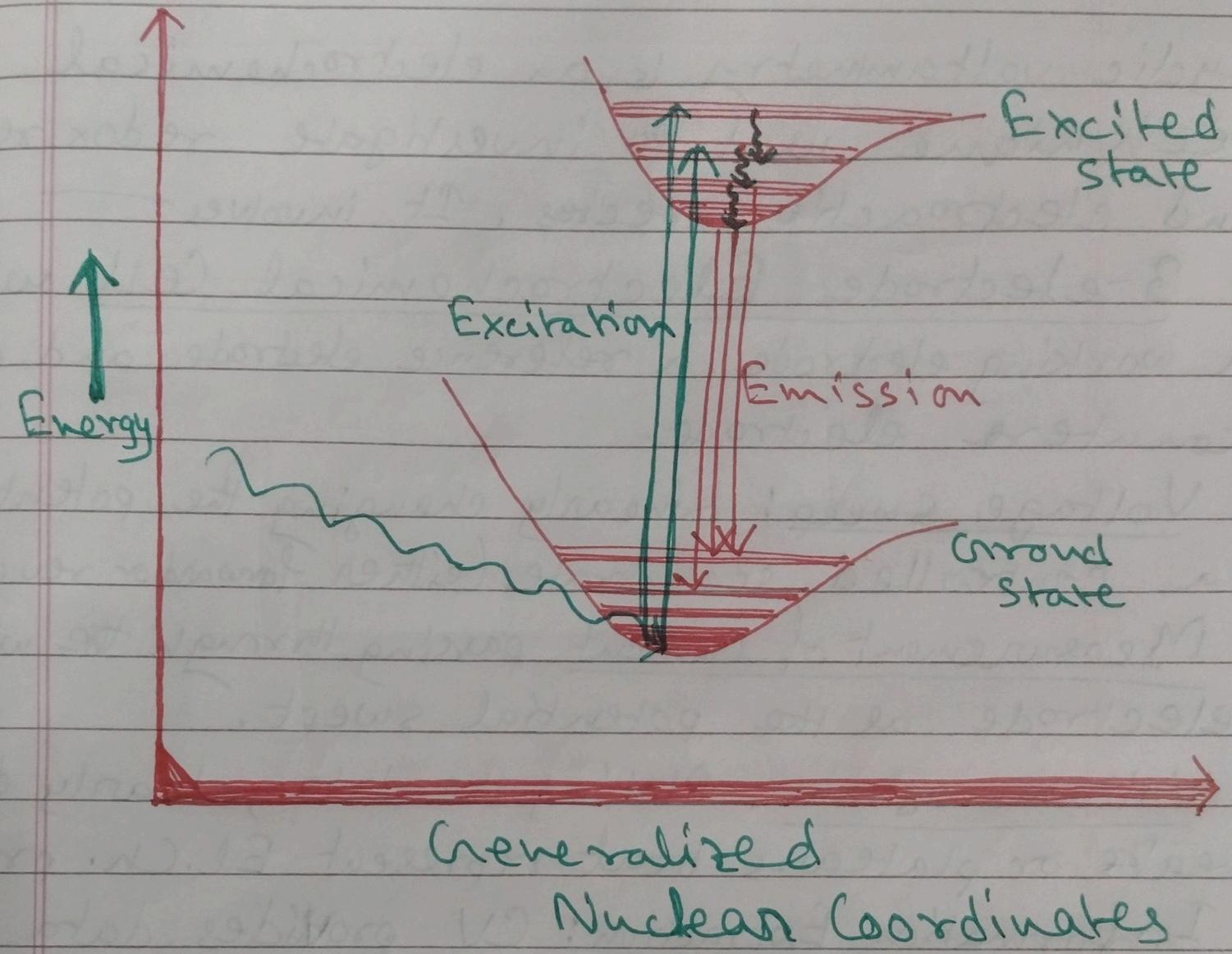
→ Electronic Transitions: molecules undergo electronic transitions, like absorption or emission of light, where electrons move between energy levels.

→ Vibrational Motion: molecules have vibrational energy levels associated with nuclear motion.

→ Franck - Condon Factor: this principle asserts that nuclear motion is negligible during electronic transitions, so the likelihood of finding the molecule in a particular vibrational state after the transition is determined by the initial vibrational state.

→ Spectroscopic Significance: it simplifies the interpretation of spectral data, explaining line intensities and shapes in electronic and vibrational spectra.

→ Applications: Spectroscopy, photo-chemistry



Q 5) Frank - Condon Principle — Probability of Electronic Transitions

Intensity of a vibrational peak —
 Electronically allowed transition —
 Absolute square of overlap integral of
 vibrational wave functions of
 initial and final states →
 frank - Condon Factor

Keywords - Explanation

Electron - Nucleus comparison

Bond Length in Electronic States

Dynamic State of Nucleus

Vertical Transition

$$|S_{(v_i)}|^2 = \left(\int \psi_{v_i}^* \psi_{v_f} d\tau_N \right)^2$$

Different Cases of Electronic Transition

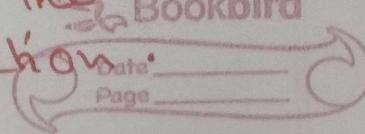
→ diagrams (schematic)

→ change in internuclear distance

* Frank - Condon Geometry

Application

b) Write a short note on the principle of LASER and its actions.



→ LASER (Light Amplification by Stimulated Emission of Radiation). generates coherent and focused light through stimulated emission in an active medium with population inversions; the principle of LASER is —

→ Population Inversions: Energize the medium to have more excited than ground state particles.

→ Stimulated Emission: Incoming photons stimulate excited particles to emit more identical photons, all in phase.

→ Amplification: multiplies photons within the medium.

→ Cavity Resonance: mirrors reflects and trap photons, causing further amplification.

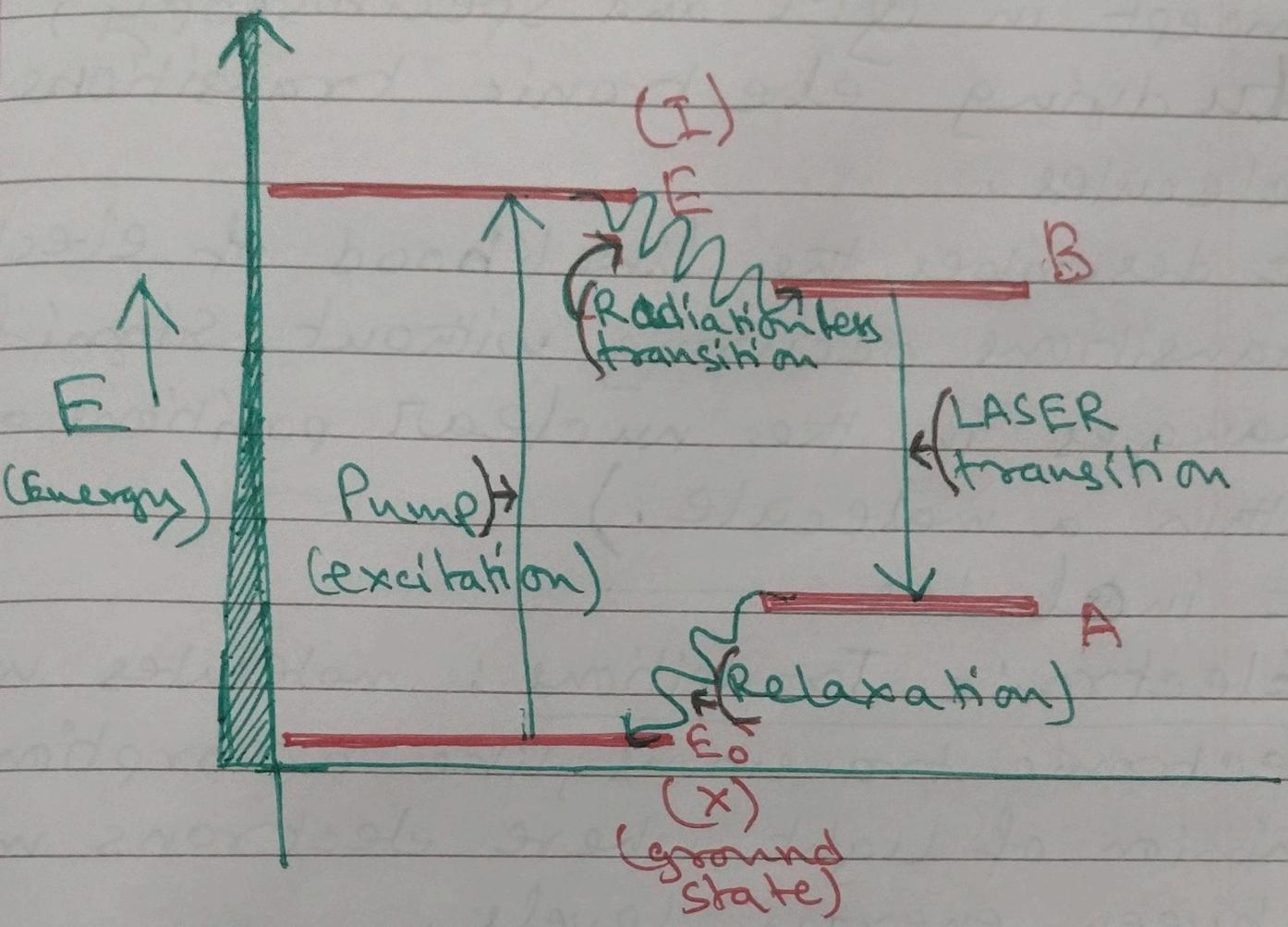
Action of LASER:-

→ Energize the Medium: pump energy into the active medium to achieve population inversion.

→ Stimulated Emission: photons entering the medium leading to rapid multiplication of identical, in-phase photons.

→ Cavity Resonance: mirrors at the ends of the cavity trap and reflect photons for further amplification.

→ Output Beam: a partially reflective mirror allowing a small portion of the light to exit as a powerful, coherent and focused beam.



Transitions involved in a four-level LASER.

Q5) LASER - full terminology, definition

- Keywords — Explanation
- Optical Pumping
- Population Inversion
- Stimulated Emission
- Metastable Excited States
- Amplification
- Cavity Resonance

Action of LASER

- Types of LASER — (Schematic diagrams)
3-level , 4-level
- Transitions Involved
- Output Beam Properties —
in-phase / coherent, focused / collimated,
high power

Application

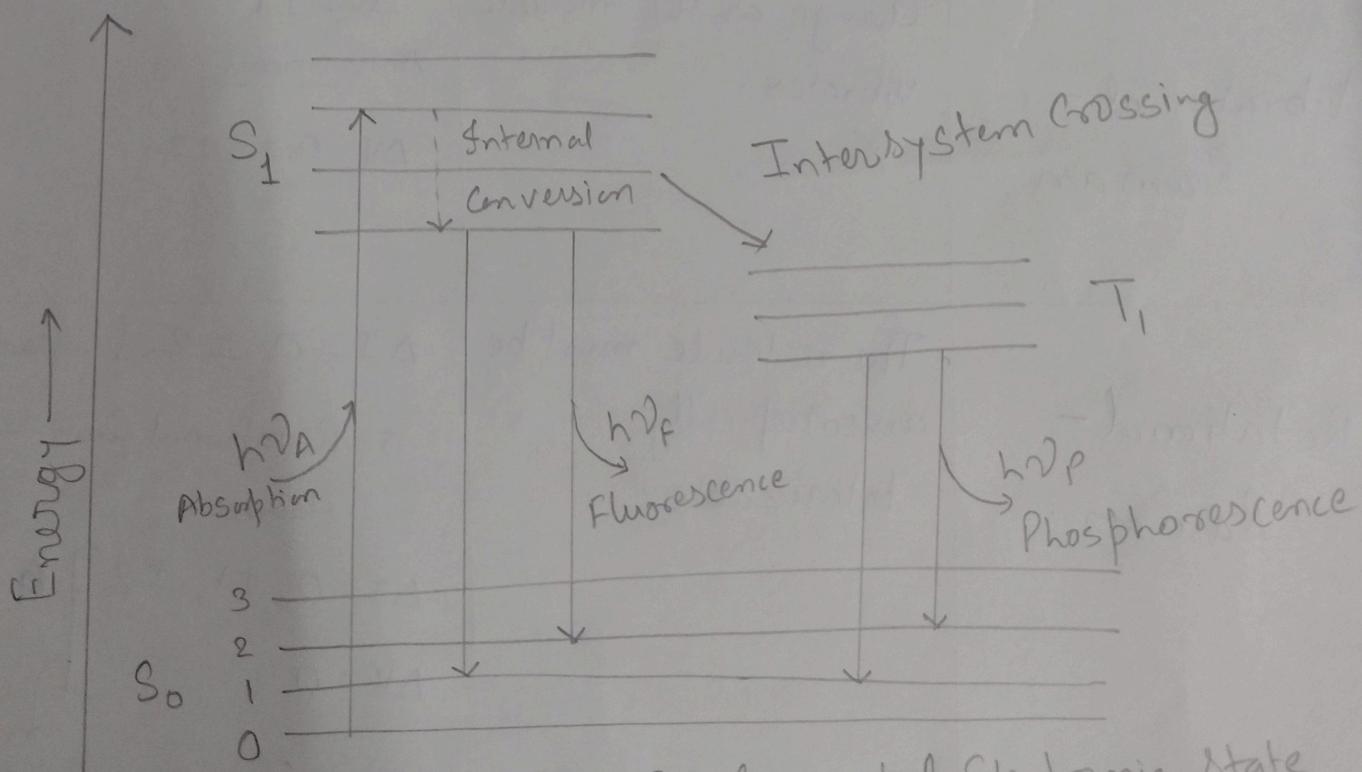
Ques:- 7

* Fluorescence: A process in which a part of energy absorbed by a substance is released in the form of light as long as stimulating radiation is continued.

The fluorescence emission took place from a singlet excited state.

(Average lifetime: from $< 10^{-10}$ to 10^{-7} sec)

* Phosphorescence: - A process in which energy of light absorbed by a substance is released relatively slowly in the form of light. The phosphorescence emission took place from triplet excited state. (Avg. lifetime: from 10^{-5} to $> 10^3$ sec).



S_0 = Fundamental Electronic State

S_0, S_1, S_2 = Singlet Electronic States

T_1, T_2 = Triplet Electronic States.

Q8.

Factor-1: NMR signal is proportional to population difference between α' and β' spin states for proton.

Since energy of spin state is given by $E = -\mu_B B$

$$E = -\vec{\mu} \cdot \vec{B} = -\mu_B B_z = -B_2 (m_e \cdot \frac{\hbar}{m}) = E_{me}$$

$$\text{So that } \Delta E = E_{\frac{1}{2}} - E_{-\frac{1}{2}} = \hbar \gamma_N B_2.$$

$$\text{So that } \frac{N_\alpha - N_\beta}{N} = \frac{\frac{N_\alpha}{N_\beta} - 1}{\frac{N_\alpha}{N_\beta} + 1}. \quad \text{Now } \frac{N_\alpha}{N_\beta} = e^{-\Delta E / kT} = \frac{e^{-\hbar \gamma_N B_2 / kT}}{e^{-\hbar \gamma_N B_2 / kT} + 1}$$

$$\frac{\hbar \gamma_N B_2}{kT} = \frac{[6.5 \times 10^{-34} \text{ Js}] (2.675 \times 10^{10} \text{ T}^{-1} \text{ s}^{-1}) \cdot (10 \text{ T})}{(2\pi)(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \\ = \cancel{0.43 \times 10^{-3}} \cdot 0.067 \times 10^{-3} \ll 1$$

$$\frac{e^x - 1}{e^x + 1} \xrightarrow{x \approx 0} \frac{x}{2} \Rightarrow \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{1}{2} \left(\frac{\hbar \gamma_N B_2}{kT} \right) =$$

$$\Rightarrow \frac{N_\alpha - N_\beta}{N} = \frac{N \hbar \gamma_N B_2}{2kT}; \text{ This is rate of absorption.}$$

Factor-2: Intensity of absorption will be proportional to magnetic field since the energy diff will stay the same.

$$\hookrightarrow \text{Intensity of signal} = \text{rate of absorption} \times \text{energy of photon.} \\ = (N_\alpha - N_\beta) \times (\hbar \gamma_N B_2). -$$

Combining Factor-1 & Factor-2, we see that

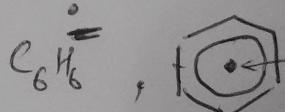
$$\text{Ans. } I = \left(\frac{N \hbar \gamma_N B_2}{2kT} \right) \times (\hbar \gamma_N B_2) = \frac{N \hbar^2 \gamma_N^2 B_2^2}{2kT}.$$

$$N = 10^6, \text{ so } N_\alpha - N_\beta = 10^6 \times \frac{\hbar \gamma_N B_2}{2kT} = 10^6 \times \frac{0.067 \times 10^{-3}}{2} \approx 33.$$

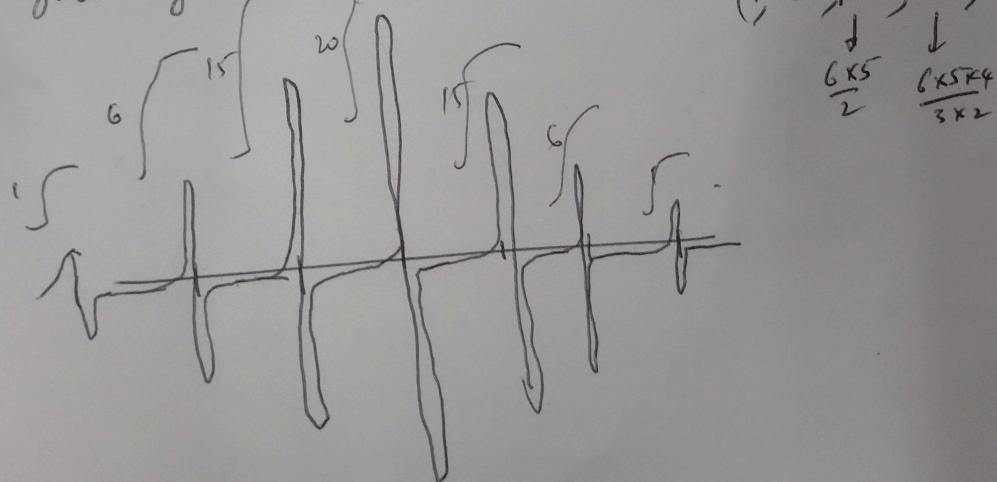
$$N_\alpha - N_\beta = 33 \text{ for } N = 10^6.$$

Note that this is very small, so signal is weak!

Q9

Benzene radical anion $C_6H_6^{\cdot-}$,  additional e^- .

This additional electron can move around all the six carbons, each having identical hydrogen. So, the hyperfine splitting is given by Pascal's triangle 6. i.e $(1, 6, 15, 20, 15, 6, 1)$.



Ques. ⑩	Spectroscopies	Gross Selection Rule	Specific Selection Rule.
①	Rotational	For a molecule to be a rotational active there must have permanent dipole moment. (Polar) Ex - CO(v), ND(v), CO ₂ (x)	$\Delta J = 0, \pm 1, \pm 2, \pm 3 \dots$ $\boxed{\Delta J = \pm 1}$ ↓ P _{SR} ↓ Q branch branch J = Rotational Quantum Number.
②	Vibrational	The dipole moment of the molecule must change when atoms are displaced relatively one another.	$\Delta V = \pm 1$ V = Vibrational Quantum Number.
③	Rotational - Vibrational	The Gross Selection rule for ro-vibrational transitions are based on changes in the vibrational Q.No (ΔV) and Rotational Q.No (ΔJ)	$\Delta J = 0, \pm 1, \Delta V = \pm 1$ J = Rotational Quantum Number
④	Vibrational - Raman	Polarizability Should Change as the molecule vibrates.	<u>Harmonic</u> $\Delta V = \pm 1$ <u>Anharmonic</u> $\Delta V = 0, \pm 1, \pm 2 \dots$
⑤	Rotational - Raman	The molecule must be anisotropically polarizable.	$\Delta J = 0, \pm 2$ (Linear) J = Rotational Quantum Number $\Delta S = 0, \pm 1, \pm 2 \dots$ $\Delta K = 0$ (Symmetric Rotors)