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UP\$C TEXT BOOKLET: OPTIONAL

ANSWER WRITING PROGRAMME CHEMISTRY OPTIONAL SAMPLE

1. What is ISC (inter system crossing) for an excited molecule in single state? answer using Jablonski diagram

Inter-System Crossing (ISC) in Excited Molecules – Explained Using the Jablonski Diagram

Inter-System Crossing (ISC) is a **non-radiative transition** where an excited molecule moves from one **spin state** to another (e.g., from a **singlet (S₁) to a triplet (T₁) state**) without emitting a photon. This process violates the spin selection rule ($\Delta S = 0$) but can occur due to **spin-orbit coupling** and vibronic interactions.

Key Features of ISC:

1. Spin Flip Occurs:

- The electron changes its spin orientation (e.g., from singlet (paired spins, S=0) to triplet (unpaired spins, S=1)).
- Example:
 - Singlet $(S_1) \rightarrow Triplet (T_1)$ (most common ISC).
 - Rarely, **Triplet** $(T_1) \rightarrow Singlet (S_0)$ (reverse ISC).

2. Non-Radiative Process:

• No photon is emitted or absorbed during ISC.

- Energy is lost as **vibrational heat (internal conversion to the surroundings)**.
- 3. Requires Spin-Orbit Coupling:
 - Heavy atoms (e.g., Br, I) or paramagnetic species enhance ISC by increasing spin-orbit coupling.
- 4. Competes with Fluorescence & Internal Conversion (IC):
 - $_{\odot}~$ If ISC is fast, fluorescence is reduced, and phosphorescence (from T_1) may dominate.

ISC in the Jablonski Diagram

Below is a simplified Jablonski diagram highlighting ISC:



- 1. Excitation:
 - $_{\odot}$ Molecule absorbs light, promoting an electron from $S_{0} \rightarrow S_{1} \mbox{ or } S_{2}.$

2. Internal Conversion (IC):

- \circ If in **S**₂, it rapidly relaxes to **S**₁ via IC (vibrational relaxation).
- 3. ISC ($S_1 \rightarrow T_1$):
 - Some molecules undergo ISC to **T**₁ due to spin-orbit coupling.
- 4. Emission from T₁ (Phosphorescence):
 - $_{\circ}$ The triplet state T_{1} decays slowly to $\boldsymbol{S_{0}},$ emitting phosphorescence.

Factors Affecting ISC Rate:

1. Heavy Atom Effect:

• Heavy atoms (e.g., I, Br, Pt) increase spin-orbit coupling, enhancing ISC.

2. Molecular Rigidity:

• Rigid molecules (e.g., aromatic rings) favor ISC by reducing competing fluorescence.

3. Oxygen Quenching:

 \circ Oxygen can quench triplets (T₁), reducing phosphorescence.

4. Temperature & Environment:

 \circ Lower temperatures stabilize T₁, increasing phosphorescence yield.

Key Differences Between ISC & Other Transitions:

Process	Spin Change?	Radiative?	Example Transition	Resulting Emission
Fluorescence	No (ΔS=0)	Yes	$S_1 \rightarrow S_0$	Fast emission (ns)
Phosphorescence	Yes (∆S≠0)	Yes	$T_1 \rightarrow S_0$	Slow emission (ms-s)
ISC	Yes (∆S≠0)	No	$S_1 \rightarrow T_1$	No light, heat loss

Conclusion:

- **ISC is a spin-forbidden but vibronically allowed transition** that converts singlets to triplets.
- It competes with fluorescence and leads to delayed emission (phosphorescence).
- The **Jablonski diagram** visually explains how ISC bridges singlet and triplet states.

2. Distinguish between HDPE and LDPE with reference to their mode of production and physical properties. mention any two applications for each.

Difference Between HDPE and LDPE

Property	HDPE (High-Density Polyethylene)	LDPE (Low-Density Polyethylene)	
Production Method	Produced using Ziegler-Natta or Metallocene catalysts at low pressure (10-80 atm) and temperature (70- 150°C). Linear structure with minimal branching.	Produced via free-radical polymerization at high pressure (1000-3000 atm) and temperature (200-300°C). Highly branched structure.	
Density	0.941–0.965 g/cm ³ (higher density due to tight packing)	0.910–0.925 g/cm ³ (lower density due to branching)	
Crystallinity	High (60-80%) due to linear chains	Low (40-50%) due to irregular branching	
Strength & Rigidity	Stronger, more rigid, higher tensile strength	Softer, more flexible, lower tensile strength	
Melting Point	120–140°C (higher due to crystallinity)	105–115°C (lower due to amorphous regions)	
Chemical Resistance	Excellent resistance to oils and solvents	Good resistance, but slightly less than HDPE	
Transparency	Opaque or translucent	More transparent than HDPE	
Impact Resistance	Less flexible but more puncture- resistant	More flexible but less puncture- resistant	

Applications

HDPE Applications:

- 1. Plastic Bottles (Milk, Detergents) Due to its rigidity and chemical resistance.
- 2. **Pipes & Fittings** Used in water/gas pipelines because of high strength and durability.

LDPE Applications:

- 1. Plastic Bags & Packaging Films Due to flexibility and ease of processing.
- 2. Squeeze Bottles (Honey, Cosmetics) Because of its softness and transparency.

Key Takeaways:

- **HDPE** is **stronger**, **more rigid**, **and chemically resistant**, making it suitable for containers and pipes.
- LDPE is softer, more flexible, and transparent, ideal for films and squeeze bottles.
- **3.** Distinguish between DNA and RNA with regard to their nucleotide structures, location in the cells and functions.

Differences Between DNA and RNA

Property	DNA (Deoxyribonucleic Acid)	RNA (Ribonucleic Acid)
Sugar in Nucleotide	Contains deoxyribose (lacks an -OH group at 2' carbon)	Contains ribose (has an -OH group at 2' carbon)
Nitrogenous Bases	Adenine (A), Thymine (T), Cytosine (C), Guanine (G)	Adenine (A), Uracil (U), Cytosine (C), Guanine (G) (No thymine)
Structure	Double-stranded (helix, antiparallel strands)	Single-stranded (but can fold into complex shapes like tRNA)
Stability	More stable (due to deoxyribose and hydrogen bonding)	Less stable (prone to hydrolysis due to 2'-OH group)
Location in Cell	Nucleus (eukaryotes), cytoplasm (prokaryotes)	Nucleolus, cytoplasm, ribosomes (mRNA, tRNA, rRNA)
Function	Stores genetic information (long-term)	Transfers genetic info (mRNA), protein synthesis (tRNA, rRNA), gene regulation (miRNA)

Key Differences in Nucleotide Structure

1. Sugar Backbone:

- **DNA:** Deoxyribose (missing -OH at 2' carbon \rightarrow more chemically stable).
- **RNA:** Ribose (has -OH at 2' carbon \rightarrow less stable, prone to degradation).

2. Nitrogenous Bases:

- **DNA:** Uses **thymine (T)**, which pairs with adenine (A).
- **RNA:** Uses **uracil (U)** instead of thymine (pairs with adenine).

3. Strand Formation:

- **DNA:** Double helix (two complementary strands held by H-bonds).
- **RNA:** Mostly single-stranded (but can form hairpin loops via base pairing).

Functions of DNA vs. RNA

DNA Functions:

- 1. **Genetic Blueprint:** Stores and transmits hereditary information.
- 2. **Replication:** Passes genetic info to daughter cells during cell division.

RNA Functions:

- 1. **mRNA (Messenger RNA):** Carries genetic code from DNA to ribosomes for protein synthesis.
- 2. **tRNA (Transfer RNA):** Brings amino acids to ribosomes during translation.
- 3. **rRNA (Ribosomal RNA):** Forms the ribosome's structure and catalyzes peptide bonds.
- 4. Regulatory RNAs (miRNA, siRNA): Control gene expression.

Summary

- **DNA:** Double-stranded, stable, stores genetic info (nucleus).
- **RNA:** Single-stranded, less stable, involved in protein synthesis (cytoplasm).

5. Explain the mechanism of free radical chain polymerisation of vinyl chloride using benzyl peroxide as an initiator.

Mechanism of Free Radical Polymerization of Vinyl Chloride Using Benzoyl Peroxide

The free radical polymerization of **vinyl chloride** ($CH_2=CHCI$) using **benzoyl peroxide** ($C_6H_5COO-OOCC_6H_5$) as an initiator proceeds in three main stages:

1. Initiation

 Benzoyl peroxide decomposes thermally to form phenyl radicals (C₆H₅·) and CO₂:

 $C_6H_5COO\text{-}OOCC_6H_5 {\rightarrow} \Delta 2\ C_6H_5COO\text{-}OOCC_6H_5 {\Delta} 2$

• The phenyl radical attacks the π -**bond** of vinyl chloride, forming a new radical:

2. Propagation

- The radical reacts with another vinyl chloride monomer, extending the chain:
- This process repeats, forming a long-chain **polyvinyl chloride (PVC) radical**:

3. Termination

- **Combination:** Two growing radicals combine:
- **Disproportionation:** A hydrogen atom transfers, forming two dead chains (one saturated, one unsaturated).

Key Features of PVC Formation

- Benzoyl peroxide acts as a radical initiator.
- The reaction is **highly exothermic** and requires temperature control.
- PVC chains are **atactic** (random Cl arrangement), making the polymer **amorphous and rigid**.

Applications of PVC

- Pipes & Fittings (due to rigidity).
- Electrical Insulation (good dielectric properties).
- 6. write a method of preparation of a tertiary alcohal containing two identical alkyle groups. write one method for distinguishing primary, secondary and tertiary alcohal.

Method of Preparation of a Tertiary Alcohol with Two Identical Alkyl Groups

A tertiary alcohol with **two identical alkyl groups** can be synthesized via the **Grignard reaction** using a **ketone** and an excess of a **Grignard reagent (RMgX)**.

Example: Synthesis of 2-Methyl-2-butanol (Tertiary Alcohol with Two Methyl Groups)

Reagents:

- Ketone: Acetone (CH₃-CO-CH₃)
- Grignard Reagent: Methylmagnesium bromide (CH₃MgBr)
- **Solvent:** Dry ether (anhydrous conditions)

Reaction Steps:

1. Formation of the Grignard Reagent:

 $CH_{3}Br + Mg \rightarrow Dry \ ether CH_{3}MgBr CH_{3}Br + MgDry \ ether CH_{3}MgBr$

- Nucleophilic Addition to Acetone: CH₃-CO-CH₃+CH₃MgBr→(CH₃)₃C-OMgBrCH₃-CO-CH₃+CH₃MgBr→(CH₃)₃C-OMgBr
- 3. Acidic Hydrolysis to Form Alcohol: (CH₃)₃C-OMgBr+H₃O⁺→(CH₃)₃C-OH+Mg(OH)Br(CH₃)₃C-OMgBr+H₃O⁺→(CH₃)₃C-OH+Mg(OH)Br

Final Product:

• **2-Methyl-2-propanol (tert-Butanol)** – A tertiary alcohol with **three methyl groups** (two identical alkyl groups).

Method to Distinguish Primary, Secondary, and Tertiary Alcohols

Lucas Test (Based on Reactivity with HCl/ZnCl₂)

- Principle:
 - Tertiary alcohols react **immediately** with Lucas reagent (conc. HCl + ZnCl₂) to form a cloudy **alkyl chloride layer**.
 - Secondary alcohols react within 5-10 minutes.
 - Primary alcohols **do not react at room temperature** (require heating).

Procedure:

- 1. Take **1 mL** of the alcohol in a test tube.
- 2. Add 2-3 mL of Lucas reagent (ZnCl₂ + conc. HCl).
- 3. Shake well and observe:
 - **Tertiary Alcohol: Immediate turbidity** (formation of insoluble alkyl chloride).
 - Secondary Alcohol: Turbidity appears within 5-10 minutes.
 - **Primary Alcohol: No turbidity at RT** (may react on heating).

Example Reactions:

• Tertiary Alcohol (Fastest):

 $\label{eq:charge} \begin{array}{l} (CH_3)_3C\text{-}OH\text{+}HCl \rightarrow ZnCl_2(CH_3)_3C\text{-}\\ Cl\text{+}H_2O(Instant\ cloudiness)(CH_3)_3C\text{-}OH\text{+}HClz_nCl_2(CH_3)_3C\text{-}\\ Cl\text{+}H_2O(Instant\ cloudiness) \end{array}$

- Secondary Alcohol (Slower): $(CH_3)_2CH-OH+HCl \rightarrow ZnCl_2(CH_3)_2CH-Cl+H_2O(5-10 min)(CH_3)_2CH-OH+HCl_{ZnCl_2}(CH_3)_2CH-Cl+H_2O(5-10 min)$
- Primary Alcohol (No reaction at RT):

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 $CH_3CH_2OH+HCl \rightarrow ZnCl_2No \text{ reaction (requires heat)}CH_3CH_2OH+HClz_n Cl_2No \text{ reaction (requires heat)}$

Alternative Tests:

- Oxidation Test (KMnO₄/K₂Cr₂O₇):
 - Primary \rightarrow Aldehyde \rightarrow Carboxylic acid.
 - \circ Secondary \rightarrow Ketone.
 - \circ Tertiary \rightarrow No reaction.

Summary

- **Synthesis:** Grignard reaction with a ketone gives a tertiary alcohol with identical alkyl groups.
- Lucas Test: Differentiates alcohols based on reactivity with HCl/ZnCl₂.