

CHE 514 / CHE 515 / CHE 516

M.Sc. (IIIrd SEMESTER) EXAMINATION, 2024-25

(CBCS MODE)

CHEMISTRY



Time : Three Hours]

[Maximum Marks : 75

CHE 514 : Quantum Chemistry-II

Note: There are **three** sections (A, B and C) and Candidate has to attempt question from all questions. Marks are indicated against each section.

Section-A

1. Answer all questions : 5×3=15
- (a) Explain why the cyclobutadiene molecule is unstable ?
 - (b) What do you mean by direct product representation ?
 - (c) Differentiate between GTOs and STOs.
 - (d) Explain significance of Density Functional Theory methods.
 - (e) In centro symmetric molecule, which modes of vibrations are IR active and Raman inactive ?

Section-B

Note: Answer all questions of the following : $4 \times 5 = 20$

2. (a) Explain Force-Field method.

Or

- (b) Discuss the different postulates of the HMO theory.

3. (a) Discuss the symmetry operation and symmetry elements for a molecule.

Or

- (b) Explain CNDO and INDO method.

4. (a) Discuss the concept of aromaticity and antiaromaticity.

Or

- (b) Explain Hohenberg Kohn Theorem.

5. (a) Apply the Huckel molecular orbital theory (HMO) to calculate the π -energy levels and delocalization energy of 1, 3 butadiene.

Or

- (b) Explain Local Density Approximation (LDA) method.

Section-C

Note: Answer any two questions of the following : $2 \times 20 = 40$

6. What is electron correlation ? Explain Moller Plessey perturbation theory in detail.
7. What is basis set ? Discuss different types of basis sets with example.
8. Discuss the construction of π molecular orbitals of naphthalene.
9. Formulate the secular determinant for the benzene molecule. Utilize the HMO theory to determine the π energy levels and delocalization energy of benzene.

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CHE 515 : Chemical Applications of Symmetry & Group Theory

Note: There are **three** sections (A, B and C) and Candidate has to attempt from all sections questions. Marks are indicated against each section.

Section-A

1. Answer all questions : 5×3=15
- (a) Identify the point group in CHCl_3 and CO_3^{2-} (Planar) and also write their operation.
 - (b) Find out the subgroups in C_{2v} point group.
 - (c) Explain 'd' orbital splitting patterns of central atom (M) in ML_2 system.
 - (d) Write the matrix representation for the plane of symmetry Oxz .
 - (e) What do you understand by improper axis of rotation also write their operation.

Section-B

Note: Answer all questions of the following : 4×5=20

2. (a) Obtain matrix representation of symmetry element in a molecule of C_{2h} point group.

Or

- (b) Explain the formation of hybrid orbitals of square planar (D_{4h}) geometry involving σ -bonding.
3. (a) List the symmetry elements and general operations for the following molecules.
- (i) H_2O_2 (trans-planar)
 - (ii) IF_7
 - (iii) C_2H_6 (staggered)
 - (iv) PCl_5

Or

- (b) Derive 'd' orbital splitting patterns of central atom (M) in ML_7 system (Energy calculation are not required).
4. (a) Give the mathematical expression of the great orthogonality theorem. Explain the meaning of each term.

Or

- (b) Using the Cartesian coordinate method arrive at the number and symmetry of normal modes of B(F)Cl_2 .
5. (a) What is criteria for the formation of molecular orbital. Explain the formation of molecular orbital of AB_3 type molecule.

Or

- (b) Find out the spectroscopic terms of d^2 configuration and also explain the effect of weak crystal field on these spectroscopic terms in O_h point group.

Section-C

Note: Answer any two questions of the following : $2 \times 20 = 40$

6. Find out the fundamental vibrational modes of C_3V system of NH_3 molecule by Cartesian and internal coordinate methods. Draw the diagram of the vibrational modes. The relevant character table is given below.

C_3V	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	Z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(xz, yz)$

7. Define the term point group. Write the steps involved in systematic procedure for working out the point group of molecules or ions. Apply the rules to classify the operation of Td and Oh point group.
8. Explain the effect of weak crystal field on 'D' and 'G' spectroscopic terms in Oh and Td point group.
9. What do you understand by classes ? Explain similarity transform. Show that all the three reflection operation of C_3V point group belong to the same class, where as the two reflection operation of C_2V point group belong to different class.

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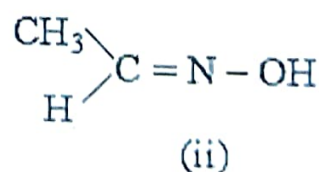
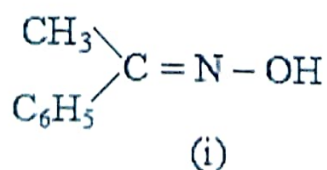
CHE 516 : Stereochemistry

Note: There are **three** sections (**A**, **B** and **C**) and Candidate has to attempt questions from all sections. Marks are indicated against each section.

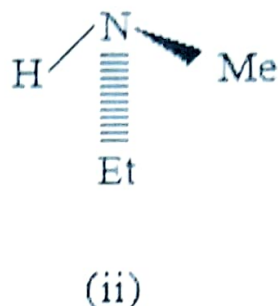
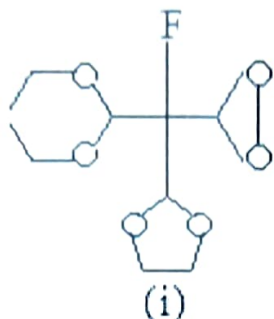
Section-A

1. Answer all questions : 5×3=15

- (a) What are homotopic atoms/groups and faces? Explain with examples.
- (b) Draw the structure of 2-Bromohexane and specify its R and S enantiomers.
- (c) What is enantiomeric excess ? Explain it with an example.
- (d) Deduce the configuration of following oximes.



- (e) Write the absolute configurations of following compounds :



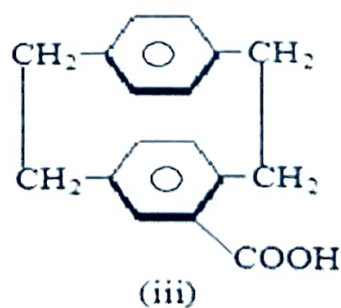
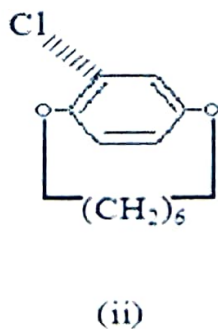
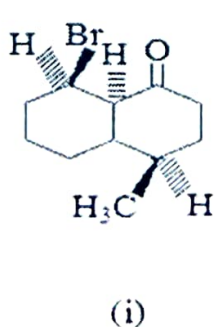
Section-B

Note: Answer all questions of the following : $4 \times 5 = 20$

2. (a) Helicity and chiral planes leads to molecular dissymmetry and give rise to optical activity. Explain.

Or

- (b) Assign absolute configuration of each chiral centres of the compound (i) and helical descriptors (P/M) of compounds (ii) & (iii).



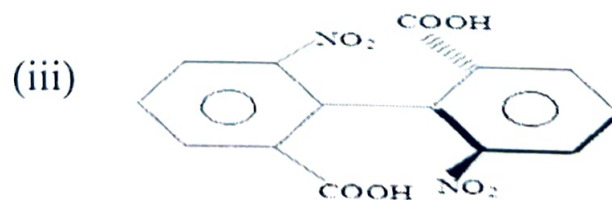
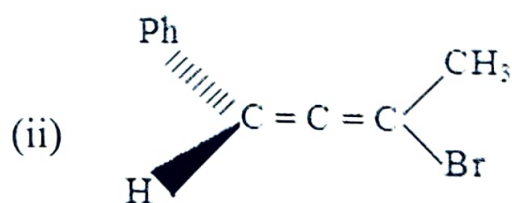
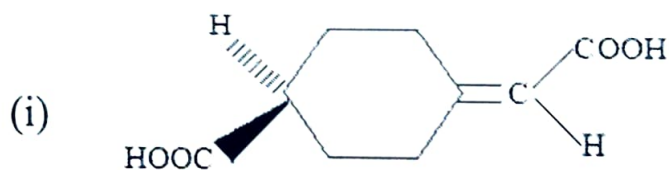
3. (a) Describe the geometrical isomerism of compounds containing nitrogen-nitrogen double bond.

Or

- (b) Explain chirality in sulphur containing compounds with at least three examples.
4. (a) Explain the stereochemistry of compounds containing phosphorus.

Or

- (b) Describe asymmetric synthesis by using a chiral catalyst.
5. (a) Designate the absolute configuration of the following compounds.



Or

- (b) Draw the conformations of 1-methyl-4-phenyl cyclohexane and discuss their stability.

Section-C

Note: Answer any two questions of the following : $2 \times 20 = 40$

6. Describe the stereochemistry of oximes. How the configurations of aldoximes and Ketoximes are deduced. Give at least two experiments in support of your answer.
7. Discuss axial chirality in allenes under the following points :
 - (a) Structure and hybridisation of allenes
 - (b) Types of allenes and its chirality
 - (c) Nomenclature of allenes
8. What are stereospecific and stereo selective reactions ? Explain in detail with suitable examples.

9. Explain any two of the following :

- (a) Nomenclature of enantiotopic and diastereotopic ligands and faces.
- (b) Necessary and sufficient condition for a biphenyl derivative to be resolvable with suitable examples.
- (c) Possible chair conformations of isomeric dimethyl cyclohexane's. Arrange them in order of their increasing stability. Which of these isomers will be optically active ?

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