

G-4/416/21

Roll No.

M.Sc. IV Semester Examination, 2021

CHEMISTRY

Paper IV

(Spectroscopy)

Time : 3 Hours]

[Max. Marks : 80

Note : All questions are compulsory. Question Paper comprises of 3 sections. Section A is objective type/multiple choice questions with no internal choice. Section B is short answer type with internal choice. Section C is long answer type with internal choice.

SECTION A

1×8=8

(Objective Type Questions)

Note : Attempt all the eight questions.

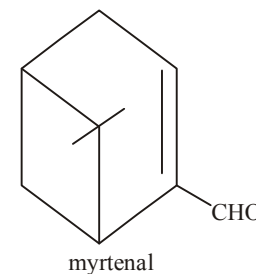
1. ^1H NMR spectrum of HD would show :

- (a) a singlet
- (b) a doublet
- (c) a triplet with intensity ration 1 : 2 : 1
- (d) a triplet with intensity ratio 1 : 1 : 1

2. In the ^1H NMR spectrum of myrtenal, the two methyl groups are expected to display signal at (chemical shift values (S) in ppm.)

P.T.O.

[2]



- (a) 1.35 (5, 3H) and 5.0 (5, 3H)
- (b) 0.74 (5, 3H) and 1.33 (5, 3H)
- (c) 1.22 (5, 6H)
- (d) 0.70 (5, 6H)

3. Number of signals that appear in the broad band decoupled ^{13}C NMR spectrum of ortho, meta and para-dichlorobenzenes, respectively are :

- (a) 3, 4 and 2
- (b) 3, 3 and 2
- (c) 4, 4 and 2
- (d) 3, 4 and 4

4. What is PAS ?

5. Find out the total numbers of fine and hyperfine EPR line for octahedral high-spin Mn (II) complex. ($I = 5/2$ for Mn)

6. Which of the following pairs match the correct V_{NO} (cm^{-1}) frequencies ?

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[3]

- (a) $\text{N} \equiv \text{O}^+$ (1) 1880
 (b) NO (2) 886
 (c) NO^- (3) 1366
 (d) NO^{-2} (4) 2273

7. In the mass spectrum of dichlorobenzene the ratio of the peaks of m/z 146, 148 and 150 is :
 : :
8. Write the correct order of isomeric shift Fe (II), Fe (III) and Fe (IV).

SECTION B

6×4=24

(Short Answer Type Questions)

Note : Answer all questions.

Unit I

1. (a) Write explanatory notes on shift reagent and spin-spin decoupling.
 (b) How is NMR spectroscopy useful in the detection of aromaticity ?

Or

Predict the number of signals and their relative intensities in the PMR spectra of the following isomers :

[4]

- (a) Acetone and propanal
 (b) Ethylbenzene and *p*-xylene
 (c) 2-pentanone and 3-pentanone

Unit II

2. Write application of photoacoustic spectroscopy.

Or

Explain a factors affecting ^{13}C chemical shifts.

Unit III

3. Explain application of ESR spectroscopy to transition metal complexes (having one unpaired electron).

Or

Write application of vibrational spectroscopy for the study of active sites of metalloproteins.

Unit IV

4. What is mass spectrum ? Explain base peak, molecules ion peak $M + 2$ peak in mass spectrum with suitable example.

Or

Write the applications of Mossbauer spectroscopy.

SECTION C

12×4=48

(Long Answer Type Questions)

Note : Answer all questions.

Unit I

1. Discuss coupling constant and Karplus relationship for the variation of coupling constant 3J with the dihedral angle α .

Or

Explain shielding effect in terms of electronegativity effects, hybridization effects, acidic and exchangeable protons and hydrogen bonding.

Unit II

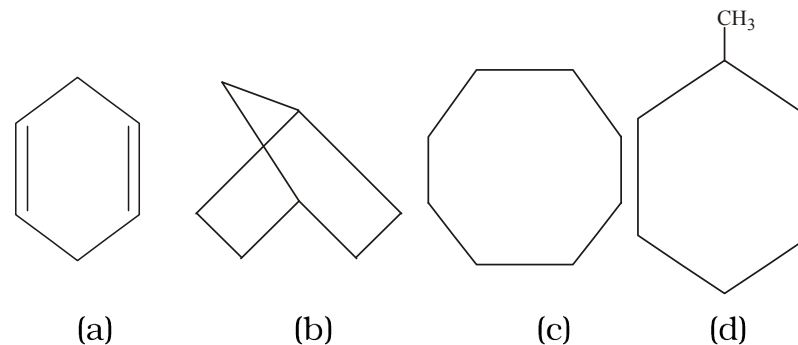
2. Write short notes on :
- The DEPT experiment,
 - The COSY technique of two-dimensional experiments,
 - Application of PAS.

Or

- (a) How many peaks do you expect in the proton-noise decoupled ^{13}C NMR spectra of the following compounds ?

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- (b) Predict the number of peaks and their multiplicity in the CMR spectra of the following compounds. Also indicate carbons with highest and the lowest chemical shifts in 5 unit from TMS, In each case,
- Acetophenone,
 - Ethyl malonate,
 - Ethyl acetate,
 - Pentane.

Unit III

3. Explain symmetry and shapes of AB_2 , AB_3 and AB_6 type molecules.

Or

- Calculate the g value if methyl radical shows ESR signal at 3290 g (0.3290 T) in spectrometer operating at 9230 MHz ($h\nu = g\beta H_0$).
- Predict the number of lines in the ESR spectrum of each of the following radicals :
 - $[\text{CF}_2\text{H}]^\bullet$,
 - $[\text{CH}_3]^\bullet$,
 - $[\text{CF}_2\text{D}]^\bullet$,
 - $[\text{CF}_2\text{H}]^\bullet$.

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Unit IV

4. Explain the following :

- (a) Metastable Ions,
- (b) McLafferty rearrangement,
- (c) Isomer shift of Mossbauer spectroscopy.

Or

Explain two parameters that are used for characterization of Mossbauer spectrum by taking example of ^{57}Fe and ^{119}Sn in different oxidation state.

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