

PD-372
(533) M.Sc. CHEMISTRY (THIRD SEMESTER)
Examination, Dec.-2020
Compulsory/Optional
Group- A, B and C
Paper-I

Name/Title of Paper-APPLICATIONS OF SPECTROSCOPY

Time : Three Hours]

[Maximum Marks : 80

Note : Answer from both the Sections as directed. The figures in the right-hand margin indicate marks.

Section-A

1. Answer the following questions:

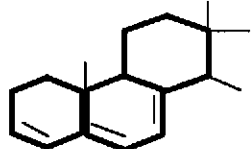
1x10=10

- (a) How many signals will be observed in the NMR spectra of N, N-dimethyl formamide at low temperature?
- (b) How many lines will be observed in the ESR spectrum of $vo(acac)_2$ at 77 K [$I(^{51}\text{V}) = \frac{7}{2}$].
- (c) Calculate the total number of vibrations in allyl bromide.
- (d) Why there is no absorption due to $n - \sigma^*$ transition in the spectrum of trimethylamine in the acidic solution?
- (e) $\text{C}=\text{O}$ stretching frequency is higher in which compound benzoic acid or m-halobenzoic acid? Why.
- (f) What would be the ratio of peak areas of the signals found in NMR of 1,3,5 trimethyl benzene.
- (g) How many lines are seen in $\text{C}-13$ NMR spectra of methyl propanoate?? Which carbon has the highest chemical shift value?
- (h) Write any two points on which $\text{C}-13$ NMR spectroscopy is different from $\text{H}-1$ NMR spectroscopy.
- (i) What is molecular ion?
- (j) Predict the functional group in the compound which shows m/e peaks at 88, 70, 55, 42, 31 (much intense) and 29.

2. Answer the following questions:-

2x5=10

- (a) Calculate the ESR frequency in a magnetic field of 25000 gauss.
- (b) Write about the different kinds of relaxation processes for a nucleus.
- (c) Find out $\lambda - \text{max}$ for the following compound-



- (d) In cyclic ketones, $\text{C}=\text{O}$ absorption increases as the size of the ring decreases. Why?
- (e) Write most probable species for the peaks at m/e 106, 91, 65 in the mass spectrum of ethyl benzene.

Section-B

Answer all question.

12x5=60

Unit-I

3. Discuss the mode of vibration, structure, shape and symmetry of AB_2 and AB_4 type molecules with examples.

OR

Discuss hyperfine interaction. Write the application of ESR to transition metal complexes.

Unit-II

4. Write notes on-

- (a) Instrumentation and sample handling in UV-visible spectroscopy
- (b) Effect of solvent on electronic transitions.

OR

Differentiate between following compounds using IR spectra:

- (a) $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$
- (b) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and $\text{CH}_3-\text{CO}-\text{N}(\text{CH}_3)_2$
- (c) o-hydroxybenzoic acid and m-hydroxy benzoic acid

Unit-III

5. Discuss the factors which affect the chemical shift in detail.

OR

What is coupling constant? Discuss germinal and vicinal coupling in detail.

Unit-IV

6. (a) Calculate ^{13}C chemical shifts in 3-Methyl pentane.

The observed chemical shifts for $\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_6$ are 11.6, 29.6, 36.7 and 18.6 δ_c respectively.

(b) Explain the factors which affect the C-13 chemical shifts.

OR

Write a note on-

- (a) Optical Rotatory Dispersion (ORD)
- (b) Octant rule for ketones.

Unit-V

7. Discuss the following: _

- (a) Melafferty reanangement
- (b.) Modes of fragmentation of organic compounds

OR

(a) Write various fragmentation modes of 1-hexanol

(b) Determine the structure of the compound whose peaks in the mass spectrum have m/e values 57(100% abundance), 41, 29 and 27.