

Total number of printed pages-5

14 (CHM-2) CH 204

2019

CHEMISTRY

(Spectroscopy-2)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer **any five** : 5×5=25

(a) What is the requirement for an isotopic nucleus to be NMR active? What is the fallout of this requirement on the nucleus? Explain Zeeman splitting.

1+2+2

(b) What do you mean by nuclear sensitivity in NMR spectroscopy? How do you explain higher sensitivity of ^1H as compared to ^{13}C ?

1+4

Contd.

(c) Define chemical shifts in NMR and discuss intramolecular factors which affect chemical shifts. 1+4

(d) What is resolution in NMR? Discuss conditions which need to be satisfied for high resolution NMR spectra, and how do you propose to achieve it? 1+4

(e) Define NOE. Explain with example how NOE is helpful in elucidation of Molecular structures. 1+4

(f) ^1H NMR spectrum of DMF is temperature dependent — Why? Discuss. 5

(g) What are shift reagents in NMR? Explain with example the contact and pseudocontact shifts. 2+3

2. Answer **any three** : 3×5=15.

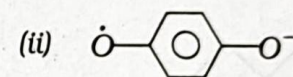
(a) What are zero field splitting and Kramer's degeneracy in ESR? Explain with example. 5

(b) Define g -value in ESR and explain its significance. What is the value of g_e ? 4+1

(c) Define hyperfine splitting in ESR. What is the significance of hyperfine splitting constant? Draw the ESR spectrum of ^1H -atom. 3+1+1

(d) Predict and discuss the ESR patterns for the following species : (**any two**) $2\frac{1}{2}\times 2$

(i) C_5H_5 (cyclopentadienyl anion radical)



(1,4-benzosemiquinone anion radical)

(iii) H_3C (methyl radical)

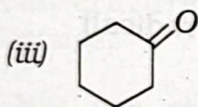
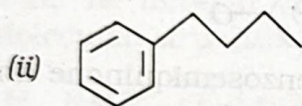
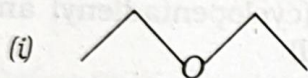
3. Answer **any three** : 3×5=15

(a) Write briefly about EI and CI as ionization techniques in mass spectrometry, and discuss about their merits and demerits. 5

(b) What is meant by molecular ion peak in mass spectrometry? Relative intensity of molecular ion peaks of aromatics is usually higher than that of alicyclics — why? How do you account for $M-1$ and $M+1$ molecular ion peaks? 2+2+1

- (c) Discuss with example the importance of (i) energy factor and (ii) stabilization factor in fragmentation processes of organic molecules. 5

- (d) Discuss the fragmentation patterns for **any two** of the following molecules : $2\frac{1}{2} \times 2 = 5$



4. Answer **any one** : $1 \times 5 = 5$

- (a) Show the nuclear decay scheme for the generation of 14.4 keV γ -radiation using radioactive cobalt source in ^{57}Fe Mössbauer spectroscopy. Comment on the lifetime of the excited nuclear states and transition energies for the nuclei suitable for studying using Mössbauer spectroscopy. 3+2

- (b) Predict the Mössbauer spectra for the following molecules : (**any two**) $2\frac{1}{2} \times 2$

