Q.P. Code : 60773

Third Semester M.Sc. Degree Examination, January/February 2020

(CBCS Scheme)

Chemistry

Paper C 303 — SPECTROSCOPY — II

(For Analytical, Inorganic and Physical branches)

Time : 3 Hours] *[Max. Marks : 70*

Instructions to Candidates : Answer question No. 1 and any five of the remaining.

1. Answer any **TEN** of the following questions : **(10 × 2 = 20)**

   (a) With the help of a neat diagram indicate the allowed electronic transitions in organic molecules.

   (b) Write the mathematical expression of Hooke's law and elaborate the terms.

   (c) What are Fermi resonance bands? How are they formed?

   (d) How will you distinguish the following pair using IR spectroscopy?

   (e) Mention the different types of relaxation processes in NMR spectroscopy.

   (f) Differentiate terms germinal and vicinal coupling of protons with suitable examples.

   (g) Illustrate the usefulness of SFORD in 13C NMR spectroscopy.

   (h) How are the isomers of dichlorobenzenes differentiated by CMR spectroscopy?

   (i) Give the mathematical relationship of metastable ions with parent and daughter ions.

   (j) Define nitrogen rule. Give its significance in mass spectroscopy.

   (k) Illustrate the usefulness of CI technique in mass spectrometry.

   (l) Chlorobenzene gives peaks at M^+ and $M^{+}+2$ values in the ratio 3 : 1. Why?

2. (a) Enumerate the Woodward-Fieser rules for conjugated dienes with the help of any two examples.

(b) Discuss the complementarity of IR and Raman spectroscopy's. **(5 + 5 = 10)**

3. (a) What are the factors which influence chemical shifts in ^1H NMR spectroscopy?

(b) Write a note on Nuclear Overhauser Effect and its applications. **(5 + 5 = 10)**

4. (a) How the following are identified using CMR spectroscopy?

(i) CH_3-CH_3

(ii) $CH_2=CH_2$

(iii) CH_3OH

(iv) $(CH_3)_3-OH$

(b) Explain proton decoupled and off-resonance decoupled CMR spectra using suitable examples. Mention their merits and demerits. **(4 + 6 = 10)**

5. (a) What are Lanthamide shift reagents? Highlight their utility in simplifying complex ^1H NMR spectra.

(b) Illustrate the usefulness of Tandem mass spectroscopy (MS/MS). **(5 + 5 = 10)**

6. (a) Account for the peaks observed in the mass spectrum of the following compounds :

(i) $CH_3(CH_2)_4CH_2Br$; m/z = 135, 137 and 85

(ii) $(CH_3)_2CH-O-(CH_2)_4CH_3$; m/z = 115 and 71.

(b) What is Mclafferty rearrangement? Explain its mechanism with suitable examples. **(5 + 5 = 10)**

7. (a) Explain with suitable examples how the inter and intra molecular hydrogen bonding is distinguished using IR spectroscopy.

(b) Write a note on Karplus equation-curve and its applications. **(5 + 5 = 10)**

8. (a) Distinguish between First-order and Non-first order splitting in ^1H NMR spectroscopy citing appropriate examples.

(b) Deduce the structure of a organic compound with the help of following data and assign the values :

Molecular formula : C_8H_9NO ;

UV-Vis (λmax) : 316 nm ;

IR (cm^{-1}) : 3396, 3334, 3038, 1662, 1594 and 1283 ;

^1H NMR (δ, ppm) : AA'BB' quartet centring at 7.10 (4H), 4.79 (br, 2H) and 2.44 (s, 3H) ;

^{13}C NMR (δ, ppm) : 196.5, 151.5, 130.8, 127.7, 113.7 and 26.1

Mass (m/z) : 135, 120 (bp), 92, 65 and 43. **(5 + 5 = 10)**
