MBS-003-010401

Seat No. _____

M. Sc. (Sem. IV) (CBCS) Examination

April / May- 2018

C-401 : Spectroscopy

(All Branches) (Old Course)

Faculty Code : 003
Subject Code : 010401

Time : $2\frac{1}{2}$ Hours] [Total Marks : **70**

Instruction : All questions are compulsory and carry equal marks.

1 Answer the following : (any **seven**) **14**

(a) Enlist the methods of simplification of complex NMR spectra.

(b) Sketch the ^{13}CNMR spectrum of ethyl phenyl acetate with labelling.

(c) Sketch the electronic energy levels with various transitions in UV Spectroscopy.

(d) What is a mass spectrum? Enlist various detectors used in MS technique.

(e) The IR spectrum of methyl salicylate shows absorption bands at 3300, 3050, 2990, 1700, 1590 and 1540 cm^{-1}. Assign these bands.

(f) State the nitrogen and ring rules.

(g) When and who formulated a set of empirical rules for calculating or predicting λ_{max} in conjugated dienes and trienes?

(h) Identify salicylic acid and m-hydroxybenzoic acid by IR technique.

(i) Give an account of chemical ionization technique.

(j) Draw schematic diagram of IR spectrometer.

2 Answer the followings : (any **two**) **14**

(a) Give an account of Mc. Lafferty rearrangement with suitable example.

(b) Determine the structure of the compound whos peaks at m/e values 124, 122, 81, 79, 43(Base Peak), 41, 29 and 27 in the mass spectrum.

(c) Draw block diagram of mass spectrometer with labeling and functioning of each components.

(d) Using the mass spectrum data of 1-propanol shown below answer the questions follow its fragmentation :

m/z	27	31	42	59	60
Relative intensity	10.4	100	12.4	15.9	10.3

(a) Draw a structure of most likely molecular ion formed and provide its m/z value.

(b) Draw a structure of the ion responsible for the base peak at m/z = 31. Provide a reaction mechanism of the fragmentation of the molecular ion that will lead to that ion.

(c) Likewise draw a likely structure for the ion that produced the next most intense signals.

(d) Why does peak at m/z = 15 have such a low relative intensity?

3 Answer the following : **14**

(a) Calculate the ^{13}CNMR chemical shifts aromatic C-atoms of 2,4-dinitrophenol and 2,6-dimehtylphenol. Take base value as 128.5 ppm Following incremental shifts of aromatic C-atoms are given below :

Substituent	C-1(ipso)	C-2	C-3	C-4
OH	+26.6	-12.7	+1.6	-7.3
NO_2	+19.6	-5.3	+0.9	+6
CH_3	+9.3	+0.7	-0.1	-2.9

(b) Sketch the ^{1}HNMR spectrum of butanal and assign each of the protons with multiplicity and coupling constants.

(c) Discuss the effects of solvents on UV transitions and also enlist the applications of UV spectroscopy.

4 Answer the following : (Any **two**) **14**

(a) An organic compound containing carbon, hydrogen and oxygen gave following spectral data ;
Mass (m/z):45, 91 (BP), 186(M^+); UV (λ_{max}):229 and 257 nm; IR (cm^{-1}): 1710; ^{1}H NMR (δ): 7.2 (s, 5H), 3.5 (s, 2H), Deduce the structure of the compound and also predict ^{13}CNMR signals.

(b) Sketch the ^{1}HNMR of AMX system with suitable example and explain it briefly.

(c) Distinguish following isomeric compounds by IR spectroscopy:

(i) $CH_3CH_2C = CH$ and $CH_3–C = C–CH_3$

(ii) $CH_3–CH_2–OH$ and.$CH_3–O–CH_3$

(iii) $(CH_3)_3–N$ and $CH_3–CH_2–NHCH_3$

(iv) $R–NH_2$ and $R–CONH_2$

5 Answer the following : (any **three**) **14**

(a) Write a Note on Nuclear Over Hauser effect

(b) Give an account of FAB techniques and give its merits and demerits.

(c) A compound having molecular formula $C_{10}H_{14}$ gave two signals in its ^{1}HNMR spectrum at 0.88 δ (s, 9H) and 7.28 δ (s, 5H). Assign the structure of the compound and also predict ^{13}CNMR chemical shifts and principal mass fragments.

(d) Discuss sample handling techniques in IR spectroscopy.
