Reg. No ..... Name **17P3645**

MSc DEGREE END SEMESTER EXAMINATION- OCTOBER-NOVEMBER 2017

SEMESTER 3 : CHEMISTRY

COURSE : **16P3CHET12 ; SPECTROSCOPIC METHODS IN CHEMISTRY**

(For Regular - 2016 admission)

Time : Three Hours Max. Marks: 75

Section A

Answer any 10 (2 marks each)

1. How will you distinguish between p ? p? and n ? p? transitions? Apply the effect of solvation to illustrate this.
2. Calculate the ?max of the following compound.

3. Explain the consequence of Field effect in IR spectroscopy citing a suitable example.
4. How can you differentiate between *p*-aminoacetophenone and acetophenone using IR spectroscopy?
5. The frequency of the OH stretch in phenol is lowered by 80 cm^{-1} when the spectrum is recorded in benzene compared to that in Carbon tetrachloride. Explain.
6. The aldehydic proton in 2-hydroxybenzaldehyde show a chemical shift value of d10.4 in the proton NMR spectrum. Give reason.
7. Pedict the chemical shift values of the olefinic protons in phenyl vinyl ether.
8. Predict the proton NMR spectrum of vinylmethylether
9. Predict the chemical shift values and spliting pattern in the proton NMR spectrum of 2-propylacetate.
10. Explain rule of thirteen in mass spectrometry.
11. Propose a suitable structure of a molecule having molecular ion peak at *m/z* 87 and another at 44 u.
12. A 4-carbon compound showed two correlations in ^{1}H-^{1}H cosy and two correlations in ^{1}H-^{13}C cosy. There are two negative signals in DEPT-135. The EI mass spectrum showed ions of m/z 69.0578 and 43. Identify the structure.

13. An organic compoud shows only two signals in both ^{1}H and ^{13}C NMR spectrum, one of the signals give a positive signal in DEPT-135. The chemical shift values in the proton NMR are 2.2 and 11.5. The EI mass spectrum shows ion of m/z 60. Identify the compound.

10 x 2 (20)

Section B
Answer any 5 (5 marks each)

14. Deduce axialhaloketone rule using Octant rule.
15. How do you distinguish between $C_{33}H_{77}$+ and $C_{22}H_{55}N$+?
16. Why the protons of benzene are highly deshielded ? Predict the proton NMR spectrum of ethyl benzene.
17. Discuss AMX coupling system in proton NMR taking styrene as example.
18. Distinguish between H-H cosy and H-C cosy spectra. Draw the two types of cosy spectra of 1-bromopropane.
19. Predict the proton and carbon-13 NMR spectra of propanal. Sketch the homo cosy spectrum of the compound.
20. Give a brief note on LC-MS. What are its advantages?
21. An organic compound with molecular formula C_4H_6 shows two signals in ^{13}C NMR spectrum. In the DEPT-135 experiment one of the signals is negative. The proton NMR spectrum shows three signals, at delta 5.1(dd, J=11, J=2), 5.3 (dd, J=16, J=2), 6.3 (m). Elucidate the structure and assign the values. What is the type of splitting pattern.

5 x 5 (25)

Section C
Answer any 2 (15 marks each)

22. Discuss in detail the factors affecting IR absorptions of Organic compounds citing suitable examples.
23. Explain the various types of 2-bond and 3-bond spin-spin couplings observed in proton NMR spectroscopy. Give an example for each type. What are the coupling constants in each case. The olefinic protons of an isomer of cinnamic acid comes to resonance at 1947.5, 1963.1 & 2325.4, 2341.0. Calculate the coupling constant and identify the isomer.
24. Outline the principle involved the ion production in various types of mass spectrometers. Compare and contrast the important features.
25. An organic compound having molecular formula $C_{11}H_{14}O_2$, showed the following spectral data: Proton NMR: d 7.3, 5.1, 2.4, 1.1. Carbon NMR: d 18, 34, 66, 135, 127, 128, 129, 178. DEPT-135 spectrum shows 5 positive signals and one negative signal. EI mass spectrum showed ions of m/z 178, 91, 71. IR 3060, 2940, 1730, 1200, identify the structure and explain the data. Sketch the predicted hetero cosy spectrum.

2 x 15 (30)