M Sc DEGREE (CSS) EXAMINATION, MARCH 2023

Third Semester

Faculty of Science

CORE - CH500303 - SPECTROSCOPIC METHODS IN CHEMISTRY

M Sc CHEMISTRY, M Sc ANALYTICAL CHEMISTRY, M Sc APPLIED CHEMISTRY , M Sc PHARMACEUTICAL CHEMISTRY, M Sc POLYMER CHEMISTRY

2019 ADMISSION ONWARDS

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Time: 3 Hours

Weightage: 30

Part A (Short Answer Questions)

*Answer any **eight** questions.*

Weight 1 each.

1. What is cotton effect? Give its applications

2. Explain the terms primary and secondary mass effects in vibrational spectroscopy.

3. Explain the exceptionally low carbonyl stretching frequency in 2,4,6-cycloheptatrienone

4. Distinguish between chemical equivalence and magnetic equivalence in NMR.

5. Write the theory of splitting in AB and ABC type molecules.

6. Compare the chemical shift values of homotopic, enantiotopic and diastereotopic protons.

7. What is 2D nmr? Write the theory of COSY spectra.

8. Explain the theory of MRI.

9. Briefly explain the principle and working of SIIMS, and FAB.

10. How will you identify the products in Pinacol-Pinacolone rearrangement using spectroscopic techniques?

(8×1=8 weightage)

Part B (Short Essay/Problems)

*Answer any **six** questions.*

Weight 2 each.

11. Explain why a polar solvent shifts $\pi-\pi^*$ transition to a longer wavelength and $n-\pi^*$ transitions to shorter wavelength.

12. Explain briefly on the factors effecting the IR spectra

13. Comment on different types of coupling constants in NMR.

14. Distinguish between double resonance and Off resonance in NMR

15. Deduce the structure of the molecules from the proton NMR data

    (a) $C_6H_{12}O_2$. 1HNMR data, δ 4.8(m), 2.2(t, J=7Hz), 1.6(m), 1.0(t, J=7Hz), 1.4(6H, d, J=7Hz)

    (b) $C_6H_{13}NO$. 1HNMR data, δ 2.6(6H, s), 2.3(1H, m), 1.1(6H, d, J=7Hz)

16. Explain the important features of fragmentation patterns of alcohols and phenols.

17. Ethyl butanoate in its mass spectrum shows two characteristic peaks due to odd electron ions at m/z = 88 and 60 and an abundant ion at m/z = 71. Explain the fragmentation.

18. The proton NMR spectrum of ethyl-2-butanoate (ethyl crotonate) shows the following signals at 6.95 (dq, J=16, 6.8 Hz, 1H), 5.81 (dq, J=16, 1.7 Hz, 1H), 4.13 (q, J=7 Hz, 2H), 1.88 (dd, J= 6.8, 1.7 Hz, 3H) and 1.24 (t, J=7 Hz, 3H) ppm. Assign these values to various hydrogens and predict if the double bond is cis or trans substituted.
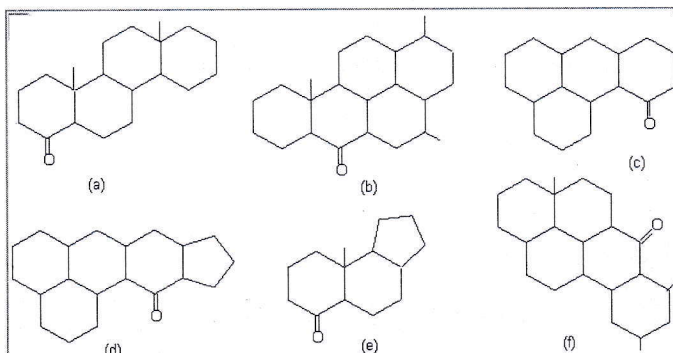
(6×2=12 weightage)

Part C (Essay Type Questions)

*Answer any **two** questions.*

*Weight **5** each.*

19. State and explain octant rule. Apply this rule and draw the octants for the following compounds and predict the sign of their optical activity.

20. What is chemical shift? Discuss the factors affecting chemical shift.

21. a) Explain Mc Lafferty rearrangement and discuss its application.

    b) Write on Nitrogen rule in Mass spectrometry

    c) Ethyl butanoate in its mass spectrum show two characteristic peaks due to odd electron ions at m/z = 88 and 60 and an abundant ion at m/z = 71. Explain the fragmentation.

22. (a) A compound with molecular formula $C_4H_8O_3$ gave the following spectral data. Deduce the structure.

IR: 1120, 1745 cm^{-1}

^{1}H NMR: δ 4.05 (2H, s), 3.8 (3H, s) and 3.5 (3H, s) ppm

(b) Acetone reacts with two molar equivalents of benzaldehyde in presence of KOH and ethanol. Propose a structure for the product. The spectral data of the product are:

^{13}C NMR : δ 125, 128, 129, 130.5, 134.5, 144 and 185 ppm

DEPT 135 –NIL

DEPT 90 - δ 125, 128, 129, 130.5 and 144 ppm

DEPT 45- δ 125, 128, 129, 130.5 and 144 ppm

(2×5=10 weightage)