Register Number:
Date:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27

M.Sc. CHEMISTRY - II SEMESTER

SEMESTER EXAMINATION: APRIL 2017

CH 8415 – SPECTROSCOPIC METHODS OF ANALYSIS – II

Time- 2 ½ hours Max. marks-70

This paper contains *three* printed pages and *three* parts

PART – A

Answer any SIX of the following questions. **6x2=12**

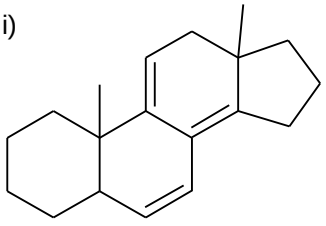
1. The UV spectrum of acetone shows absorption maxima at 166, 189 and 279 nm. With justification indicate what type of transition is responsible for each of these bands?
2. What is the field strength (in tesla) needed to generate a ^{1}H frequency of 500 MHz, given the magnetogyric ratio for the hydrogen nucleus = 42.576 MHz T^{-1}.
3. What is a pulse sequence in NMR?
4. What are the allowed nuclear spin states for the following atoms: ^{14}N, ^{13}C?
5. How do you distinguish between hydrido and aqua metal complexes by IR spectral analysis?
6. How can the *para* and *meta* disubstituted benzenes be distinguished by IR spectral analysis?
7. Expand DPPH and mention its application.
8. Explain EI technique in mass spectral analysis.

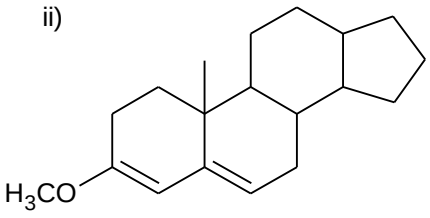
PART – B

Answer any FOUR of the following questions **4x12= 48**

9. a) What changes would you expect in the UV spectra of (i) phenol if the spectrum is recorded at pH=12 and at pH=4 (ii) aniline if the spectrum is recorded at pH=2 and pH=10.

   b) Using Woodward rules, predict the UV maximum for each of the following substances

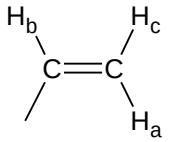
   i) 

   ii) 

   c) What is nuclear overhauser effect? How is it useful in ^{13}C NMR spectroscopy?

   (4+4+4)

10. a) Using the 2nI+1 rule, draw tree diagrams to show both number of lines and relative intensities for the H_a, H_b and H_c protons in the following molecule. Determine where to measure coupling constants (J values) and the notation for the coupling constants.



where $J_{HH(trans)}$ = 16 Hz, $J_{HH(cis)}$ = 8Hz, $J_{HH(gem)}$ = 2Hz

b) Sketch the ^{1}H NMR spectrum of N,N-dimethylformamide at (i) room temperature and (ii) 140°C. Account for the difference in the spectra.

c) Deduce the structure of the compound with molecular formula $C_9H_{11}Br$ from the following data: δ 2.15 (2H, quintet, J= 7 Hz); δ 2.75 (2H, triplet, J= 7 Hz); δ 3.38 (2H, triplet, J= 7 Hz); δ 7.22 (5H, singlet, J= 7 Hz). (4+4+4)

11. a) Draw and explain the COSY spectrum of 2-nitropropane.

b) Propose a structure for an aromatic hydrocarbon, $C_{11}H_{16}$, that has the followingn^{13}C NMR spectra data:

Broadband decoupled: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

DEPT-90: 125.5, 127.5, 130.3 δ

DEPT-135: positive peaks at 29.5, 125.5, 127.5, 130.3 δ ; negative peak at 50.2 δ

c) Draw the Karplus curve and explain its significance. (4+4+4)

12. a) Explain the steps involved in the interpretation of IR spectra of an unknown compound.

b) Explain isotropic hyperfine splitting patterns in methyl free radical and account for the signal intensity ratios. (6+6)

13. a) Sketch a labeled Mass spectrometer and explain its working principle.

b) Explain briefly the small changes in energy required for absorption in Mossbauer studies that results due to the following factors (i) chemical environment and (ii) quadrupole interactions. (6+6)

14. a) A monosubstituted aromatic ketone shows peaks in its mass spectrum at m/e values 162, 134 (McLafferty ion) 120, 91 and 65. Deduce the structure of the compound with proper explanation.

b) Explain IR absorption region of different carbonyl compounds. With suitable examples, discuss any two structural parameters that affect this absorption.

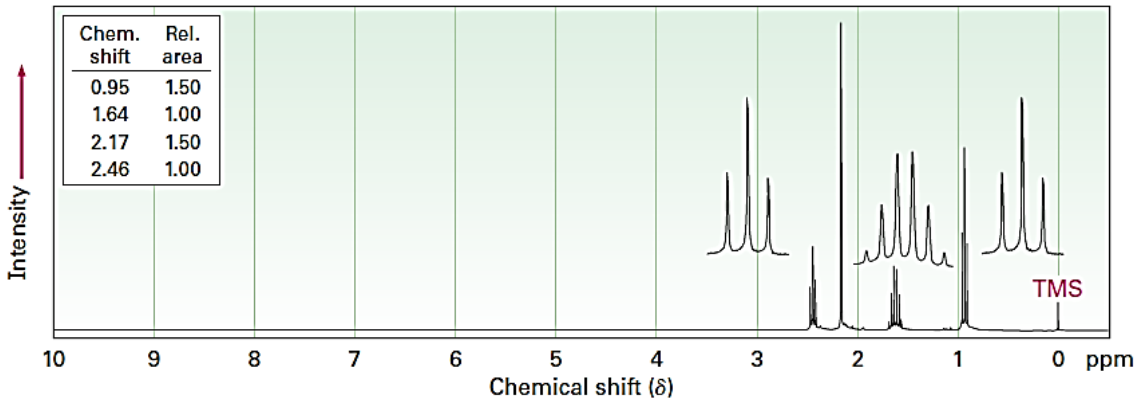
(6+6)

PART – C

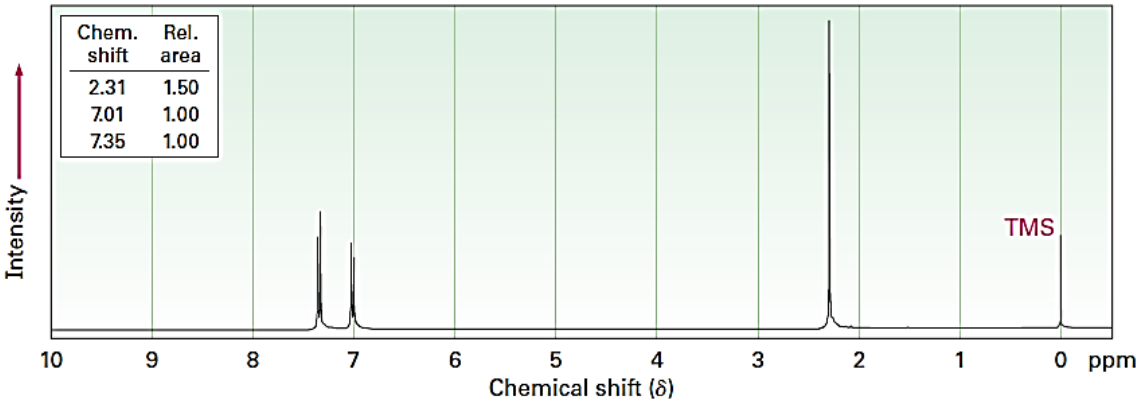
Answer any TWO of the following questions **2x5=10**

15. Propose structures for the two compounds whose 1H NMR spectra are shown.

a) $C_5H_{10}O$



b) C_7H_7Br



(2.5 +2.5)

16. a) Transition metal ions usually exhibit 'g' values different from that of a free electron. Explain.

b) The methine proton in 1,1-dichloroethane appears as a quartet at 5.8 ppm on a 80 MHz NMR spectrometer with J = 6 Hz. Calculate the position of each of the subpeaks in the quartet in Hz. (2.5 +2.5)

17. Deduce the structure of the unknown from the following spectral data.

Mass spectra: m/z values given in brackets: $M^{\cdot+}$(102), base peak(29) and another prominent peak (57).

Infrared bands at: 1740 cm^{-1} and 1200 cm^{-1}

^{1}H-NMR data: δ 4.1 (2H) q; δ 2.4 (2H) q; δ 1.1 (3H) t; δ 1.2 (3H) t,

^{13}C NMR data: δ = 174, 60, 29, 15, 10

UV band: at 205 nm.