



Register No.

Date:

**ST. JOSEPH'S COLLEGE (AUTONOMOUS) BANGALORE – 560 027**  
**M.Sc. CHEMISTRY – II SEMESTER**  
SEMESTER EXAMINATION: APRIL 2018  
**CH 8415: SPECTROSCOPIC METHODS OF ANALYSIS – II**

Time: 2 ½ hours.

Max marks: 70

This question paper contains three printed pages and three parts

**Part A**

Answer any SIX of the following

(6x2 = 12)

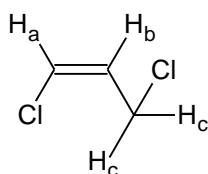
1. What is pulse sequence in NMR?
2. What is the energy difference between the two spin states of  $^1\text{H}$  in a magnetic field of 5.87 T given the magnetogyric ratio of hydrogen nucleus =  $267.512 \times 10^6 \text{ rad T}^{-1} \text{ s}^{-1}$ ?
3. What is the Dirac vector model that explains spin-spin coupling in NMR?
4. A sample of 2,5-dimethyl-2,4-hexadiene in methanol in a 1.00 cm cell shows an absorbance of 0.65 at 242.5 nm. What is the concentration of the diene? The molar absorptivity at this wavelength is 13100.
5. Give the diagnostic bond stretching vibrations of phenol?
6. How are the following hydrocarbons distinguished from their IR spectral analysis: alkanes and alkenes.
7. Predict the number of lines and sketch a representative epr spectra of  $[\text{VO}(\text{glycolate})_2]^{-2}$ ? ( $I_V = 7/2$ )
8. The relative intensities of M and M+2 peaks in  $\text{CH}_3\text{Br}$  are in the ratio of 1:1. Explain.

**Part - B**

Answer any FOUR of the following

(4x12 = 48)

9. a) Draw and explain the COSY spectrum of 1-nitropropane.  
b) Propose a structure for a compound with molecular formula  $\text{C}_7\text{H}_{12}\text{O}_2$ , which has the following  $^{13}\text{C}$  NMR spectra data:  
Broadband-decoupled  $^{13}\text{C}$  NMR: 19.1, 28.0, 70.5, 129.0, 129.8, 165.8  $\delta$   
DEPT-90: 28.0, 129.8  $\delta$   
DEPT-135: positive peaks at 19.1, 28.0, 129.8  $\delta$ ; negative peaks at 70.5, 129.0  $\delta$   
c) Draw a splitting tree diagram for the  $\text{H}_b$  proton in the following molecule, given  $J_{ab} = 10 \text{ Hz}$  and  $J_{bc} = 4 \text{ Hz}$ .



(4+4+4)

10. a) Explain the origin of nuclear overhauser enhancement based on cross polarization theory.

b) Give reasons for the following:

i) The proton spectrum of ultrapure dimethylamine,  $(\text{CH}_3)_2\text{NH}$ , differs from the spectrum of this compound to which  $\text{D}_2\text{O}$  has been added.

ii) Fourier transform NMR spectroscopy is preferred over continuous wave as a technique for  $^{13}\text{C}$  NMR.

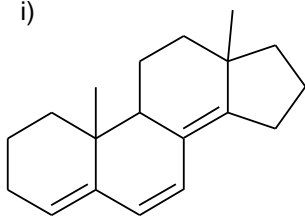
iii) The chair form of cyclohexane has protons in two distinct environments, axial and equatorial. However, the proton NMR of cyclohexane when run on a 100-MHz instrument at  $23^\circ\text{C}$ , only one signal for the compound is observed. (6+6)

11. a) Write the Karplus equation. Draw the Karplus curve and explain its significance.

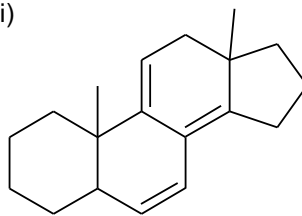
b) Explain the effect of pH on the electronic absorption bands of phenol and aniline?

c) Using the Woodward-Fieser rules for dienes, predict the UV maximum for each of the following compounds.

i)



ii)



(4+4+4)

12. a) Describe in detail the various factors affecting the carbonyl stretching frequency.

b) Define hyperfine splitting and explain this concept by taking methyl radical as an example. (6+6)

13. a) Explain (i) McLafferty and (ii) Retro-Diels Alder type of fragmentations in MS by taking an example each. Identify the  $m/z$  value of the prominent detectable ion fragment in each case.

b) Write a note on isomer shift in Mossbauer studies. Discuss any two factors affecting isomer shift. (6+6)

14. a) Explain the principle of analysis and instrumentation of mass spectrometry.

b) Describe the IR spectral features of (i) aqua and (ii) hydroxy complexes. State how they are differentiated from each other from their IR spectra. (6+6)

### Part - C

Answer any TWO of the following

(2x5 = 10)

15. Sketch and explain a typical IR spectrum of 2-hydroxy-N-methylaniline ( $\text{OH}-\text{C}_6\text{H}_4-\text{NH}(\text{CH}_3)$ ). Annotate the peaks. Pay attention to the bands – intensity and width.

16. Identify each of the following compounds on the basis of the IR and  $^1\text{H}$  NMR information provided. Match the data with the protons in the structure of the compound.

a)  $\text{C}_{10}\text{H}_{16}\text{O}_6$ : IR:  $1740\text{ cm}^{-1}$

NMR:  $\delta$  1.3 ppm (triplet, 9H)

$\delta$  4.2 ppm (quartet, 6H)

$\delta$  4.4 ppm (singlet, 1H)

b)  $\text{C}_4\text{H}_7\text{NO}$ : IR:  $2240\text{ cm}^{-1}$

$3400\text{ cm}^{-1}$  (broad)

NMR:  $\delta$  1.65 ppm (singlet, 6H)

$\delta$  3.70 ppm (singlet, 1H)

(2.5+2.5)

17. a) Consider a quartet signal in a  $^1\text{H}$ -NMR spectrum obtained on a 300 MHz instrument. The chemical shift is recorded as 1.7562 ppm, and the coupling constant is  $J = 7.6\text{ Hz}$ . What is the chemical shift, expressed to the nearest 0.1 Hz, of the furthest downfield sub-peak in the quartet?

b) The relative isomer shift values of  $\text{Fe(II)} > \text{Fe(III)} > \text{Fe(IV)}$ . Explain. (2.5+2.5)

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