



Register Number:

Date:

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

M.Sc. CHEMISTRY - II SEMESTER
SEMESTER EXAMINATION: APRIL 2019
CH 8418 – SPECTROSCOPY – II

Time- 2 ½ hours

Max. marks - 70

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

PART – A

Answer any SIX of the following questions.

6x2=12

1. Calculate the energy difference between the α and β spin states of a proton in a magnetic field of 7.046 T. The magnetogyric ratio γ for a proton is $2.67512 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$ and Planck's constant is $6.626 \times 10^{-34} \text{ J s}$.
2. When the ^1H NMR spectrum of acetone, CH_3COCH_3 , is recorded on an instrument operating at 200 MHz, a single sharp resonance at 2.1 δ is seen. i) How many hertz downfield from TMS does the acetone resonance correspond to? ii) If the ^1H NMR spectrum of acetone were recorded at 500 MHz, what would the position of the absorption be in δ units?
3. Why is FT-NMR spectroscopy preferred over continuous wave technique for ^{13}C NMR?
4. Mention the four important periods in the pulse sequence used to acquire 2D NMR spectra.
5. To record Mossbauer spectrum of a sample containing Fe, a source 'X' was used. X after nuclear transformation with 'Y' gives gamma radiation. Identify 'X' and 'Y'.
6. Draw the mass spectra of ethanol indicating the major peaks.
7. 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 13,100.
8. How can a primary amine be distinguished from secondary amine using their IR spectra?

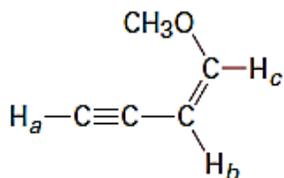
PART – B

Answer any FOUR of the following questions

4x12= 48

9. a) What is diamagnetic anisotropy? What is its influence on the chemical shift of acetylenic and aldehydic hydrogens?
b) Draw and explain the COSY spectrum of 1-nitropropane.

c) Construct tree diagrams and sketch the splitting pattern that would be observed for H_a, H_b, and H_c protons in the following compound.



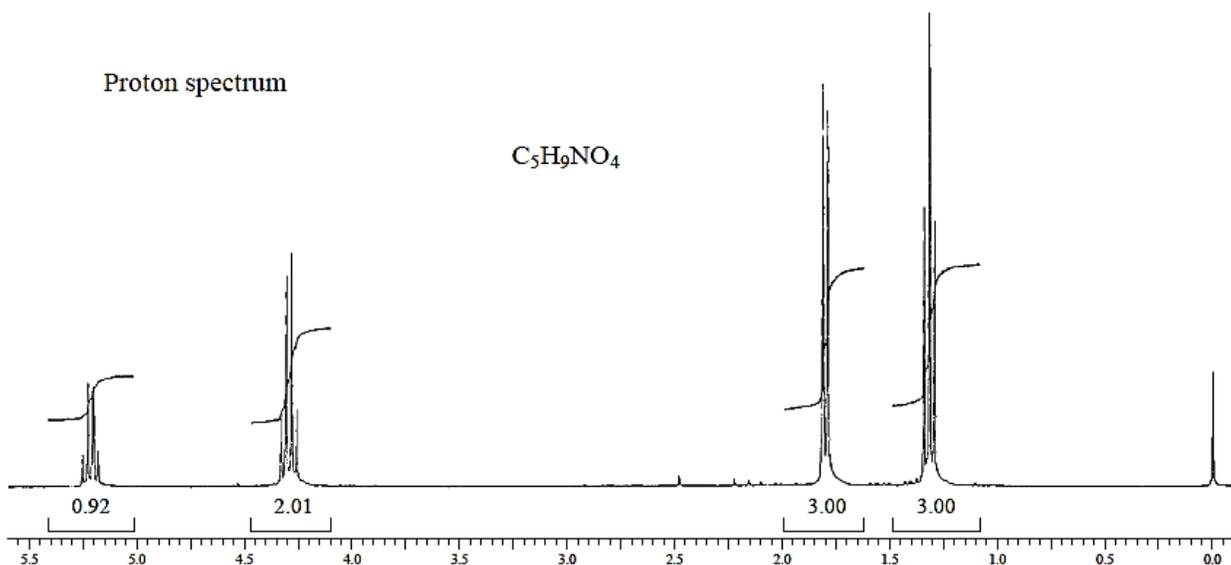
H_a (3.08 δ) H_b (4.52 δ) H_c (6.35 δ)

J_{a-b} = 3 Hz J_{a-c} = 1 Hz J_{b-c} = 7 Hz

(4+4+4)

10. a) The proton NMR spectrum is shown for a compound with formula C₅H₉NO₄. The infrared spectrum displays strong bands at 1750 and 1562 cm⁻¹ and a medium-intensity band at 1320 cm⁻¹. The normal carbon-13 and the DEPT experimental results are tabulated. Deduce the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
16	Positive	No peak
63	Negative	No peak
83	Positive	Positive
165	No peak	No peak



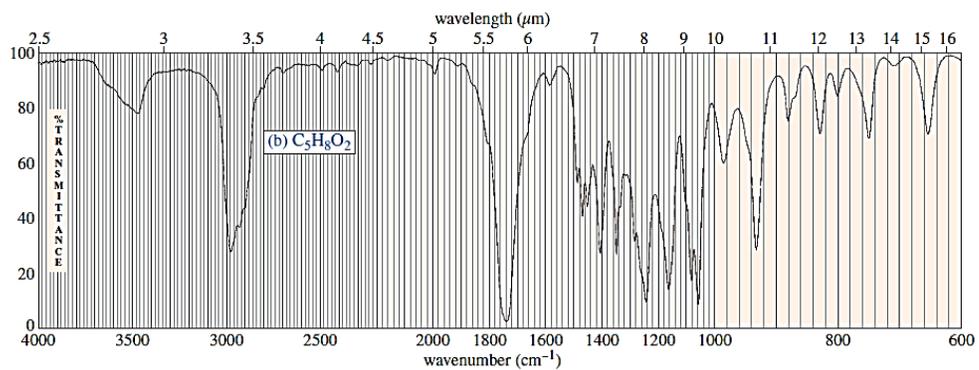
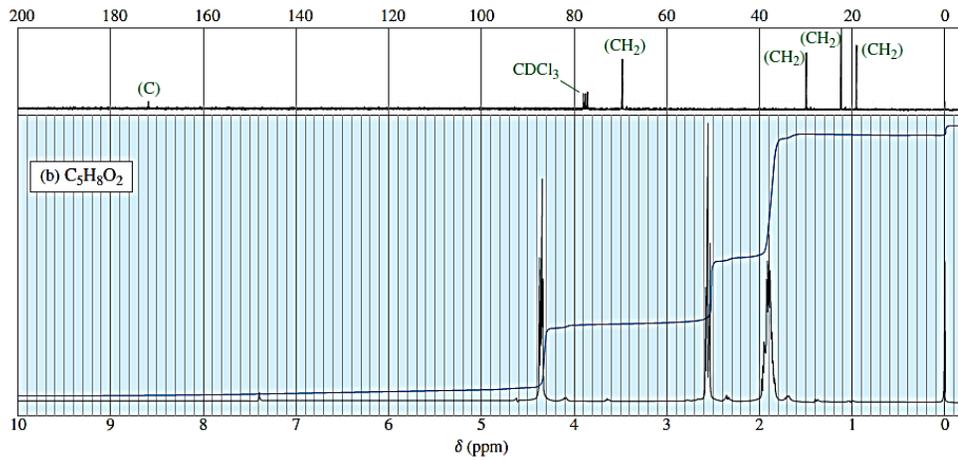
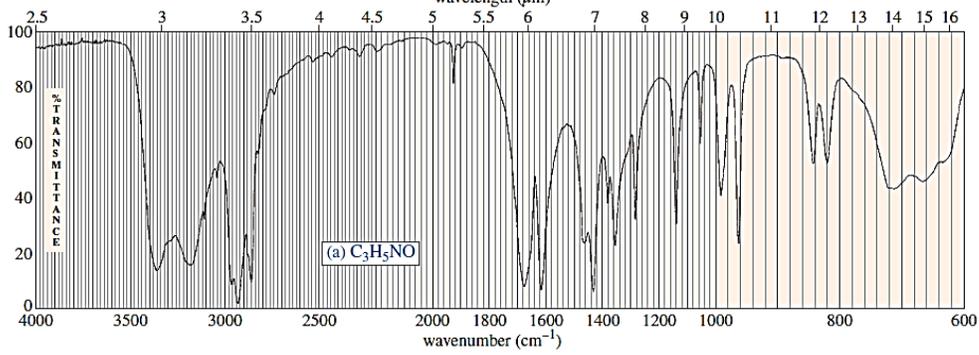
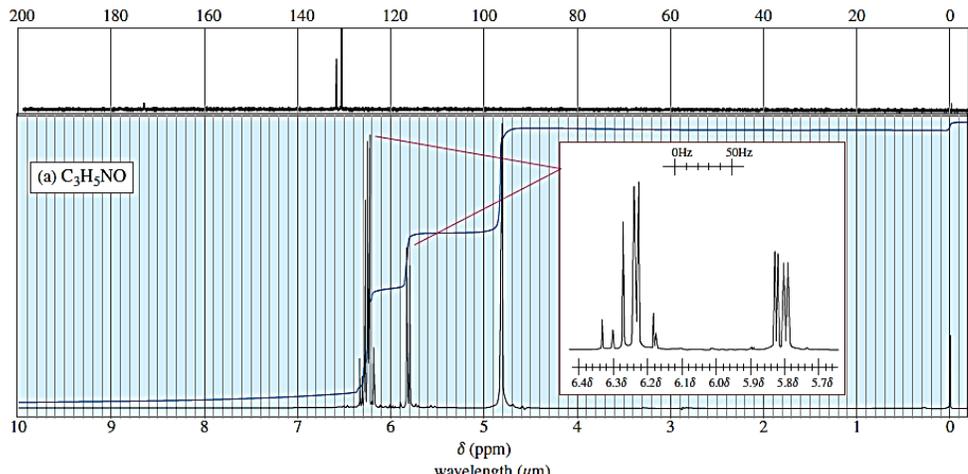
b) What is nuclear overhauser enhancement? How does cross polarization explain this effect?

(4+8)

11. a) For each set of IR and NMR spectra, determine the structure of the unknown compound. Explain how your proposed structure fits the spectra.

(i) C₃H₅NO

(ii) C₅H₈O₂



b) Give reasons for the following observations:

i) In isomeric alkenes the *trans* 3J coupling constant is always larger than the *cis* 3J coupling constant.

ii) The 1H NMR spectrum of N,N-dimethyl formamide recorded at room temperature is different from that recorded at 140 °C. (6+6)

12. a) What is an auxochrome? Mention the auxochromes which produce a bathochromic shift in alkenes and explain the mechanism involved?

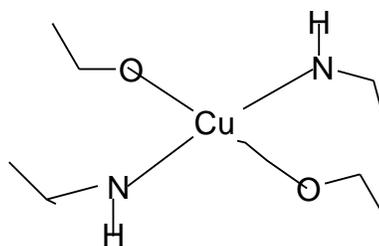
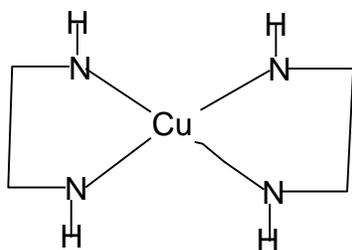
b) What is the total number of fine and hyperfine lines for octahedral Mn^{2+} ($I = 5/2$)?

Explain with the help of labelled energy level diagram. (6+6)

13. a) Calculate the number of hyperfine lines obtained for the following complexes with following considerations.

i) For Cu, $I = 3/2$

ii) Upon replacement of 'H' attached to 'N' with 'D' there is no change in number of hyperfine lines.



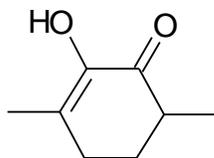
b) Explain the principal of analysis and instrumentation of mass spectrometry. (6+6)

14. a) Explain i) McLafferty and ii) Retro Diels-Alder type of fragmentation in mass spectrometry by taking a suitable example.

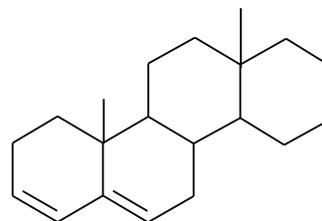
b) Explain with suitable example the effect of i) conjugation and ii) hydrogen bonding effects on the position of vibrational frequency of carbonyl bond.

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

i)



ii)



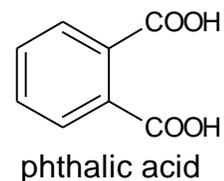
(4 + 4 + 4)

PART – C

Answer any TWO of the following questions

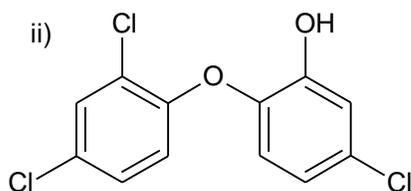
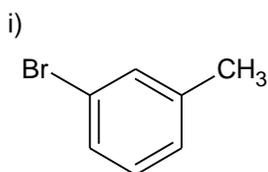
2x5=10

15. Compounds **W** and **X** are isomers; they have the molecular formula C_9H_8O . The IR spectrum of each compound shows a strong absorption band near 1715 cm^{-1} . Oxidation of either compound with hot, basic potassium permanganate followed by acidification yields



phthalic acid.
The ^1H NMR spectrum of **W** shows a multiplet at δ 7.3 and a singlet at δ 3.4. The ^1H NMR spectrum of **X** shows a multiplet at δ 7.5, a triplet at δ 3.1, and a triplet at δ 2.5. Propose structures for **W** and **X**.

16. a) How many signals are expected in the decoupled ^{13}C NMR spectrum of each of the following molecules



- b) In Mossbauer studies the sample is cooled in liquid nitrogen and the source is moved with respect to the sample. Give reasons. (3+2)

17. The absorption peak of Co – H bond in $\text{Co}(\text{CO})_4\text{H}$ is seen at 1934 cm^{-1} . Then what is the absorption frequency of Co – D bond in $\text{Co}(\text{CO})_4\text{D}$?
