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Register number:

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

M.SC., CHEMISTRY – II SEMESTER

SEMESTER EXAMINATION – APRIL 2019

CH 8418: SPECTROSCOPY – II

Time: 2 hr 30 min.

Max marks: 70

This question paper contains four printed pages and three parts.

Part A

Answer any SIX of the following.

(6 x 2 = 12)

1. List the electronic transitions of formaldehyde and arrange them in the increasing order of energy.
2. Explain why C=O stretching shows a strong absorption while C=C shows a weak absorption.
3. What are molecular ion and isotope peaks in mass spectrometry?
4. Explain Doppler effect in Mossbauer spectra. How does it affect resonance?
5. What is DEPT technique?
6. At what frequency will ^{113}Cd nucleus resonate in a 1.5 T magnetic field given magnetogyric ratio of ^{113}Cd nucleus ($I = 1/2$) $\gamma = 5.9340 \times 10^7$?
7. What is first order spectrum in NMR?
8. Give two advantages of fourier transform NMR spectroscopy over continuous wave.

Part B

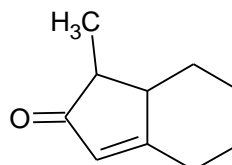
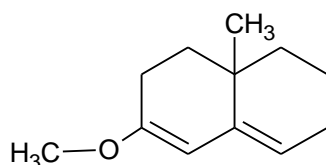
Answer any FOUR of the following.

(4 x 12 = 48)

9. a) Explain ion production in mass spectral analysis by the following methods:
i) field desorption and ii) fast atom bombardment.
b) What is hyperfine splitting? How many hyperfine lines are seen in the case of quinone and biphenyl radicals?

(6 + 6)

10. a) In Mossbauer spectra a source emitting at 3.48×10^{18} Hz had to be moved towards absorber at 2.2 mm/s for resonance. Find the shift of frequency between source and the absorber?
b) Using Woodward rules, predict the UV maximum for each of the following substances.



- c) Discuss the effect of solvent polarity on the energies of $\pi - \pi^*$ and $n - \pi^*$ transitions.

(4 + 4 + 4)

11. a) Explain with suitable example the effect of i) conjugation ii) inductive and iii) hydrogen bonding effects on the position of vibrational frequency of carbonyl bond.
 b) A given alkyl halide shows M, M + 2 and M + 4 peaks in the intensity of 1:2:1. Answer the following with proper justification. i) Identify the halogen; ii) how many halogens are present in the molecule

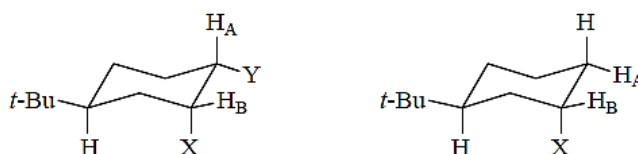
(6 + 6)

12. a) With proper reasoning, predict the structure of each compound from the given data.

- i. Molecular formula C_8H_9NO
 IR absorptions: 3328 and 1639 cm^{-1}
 1H NMR: 2.95 (singlet, 3H), 6.95 (singlet, 1H), and 7.3–7.7 (multiplet, 5H) ppm
- ii. Molecular formula $C_8H_{14}O_3$
 IR absorptions: 1810 and 1770 cm^{-1} .
 1H NMR: 1.25 (doublet, 12 H) and 2.65 (septet, 2 H) ppm

- b) Give reasons for the following:

- i) The 1H NMR spectrum of N,N-dimethyl formamide recorded at room temperature is different from that recorded at $140\text{ }^\circ\text{C}$.
 ii) The coupling constant values J_{AB} , for the compounds given below is the same.



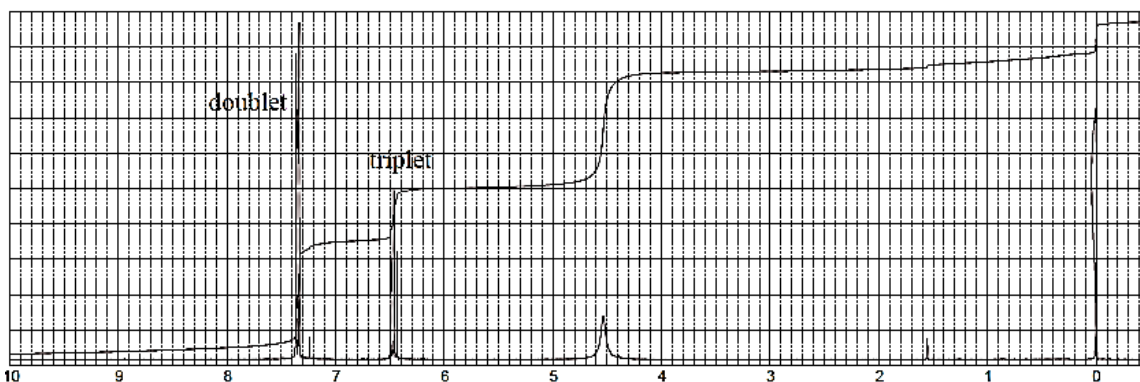
(6 + 6)

13. a) What is diamagnetic anisotropy? Why does the 1H -NMR spectrum of [18]annulene show two peaks, at 8.9 ppm and -1.8 ppm (upfield of TMS) with an integration ratio of 2:1?
 b) Distinguish chemical and magnetic equivalence using suitable examples.
 c) Draw and explain the COSY spectrum of 1-nitropropane.

(4 + 4 + 4)

14. a) Determine the structure of a compound with formula $C_6H_5Br_2N$. The proton NMR spectrum is shown. The infrared spectrum has medium bands at 3420 and 3315 cm^{-1} and a strong band at 1612 cm^{-1} . The normal carbon, DEPT-135, and DEPT-90 spectra data are tabulated.

Normal Carbon	DEPT-135	DEPT-90
109 ppm	No peak	No peak
119	Positive	Positive
132	Positive	Positive
142	No peak	No peak



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

c) Give an account of nuclear relaxation processes and their significance in NMR.

(4+4+4)

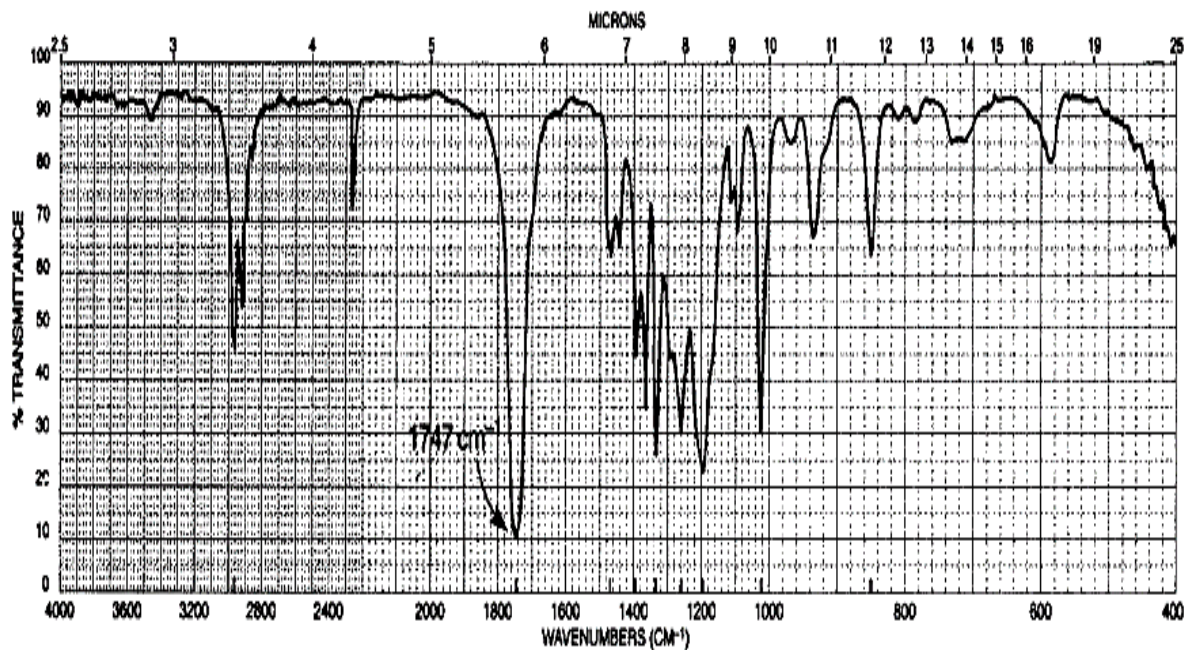
Part C

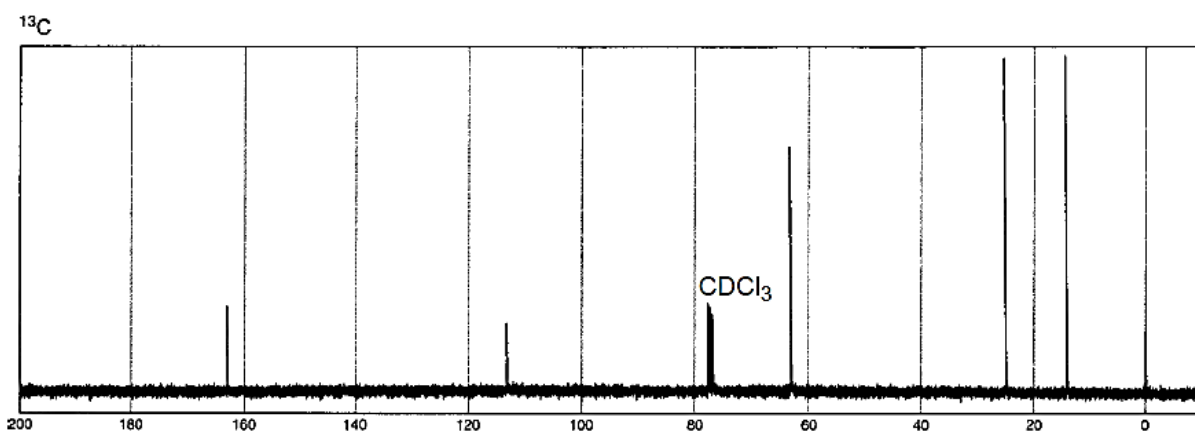
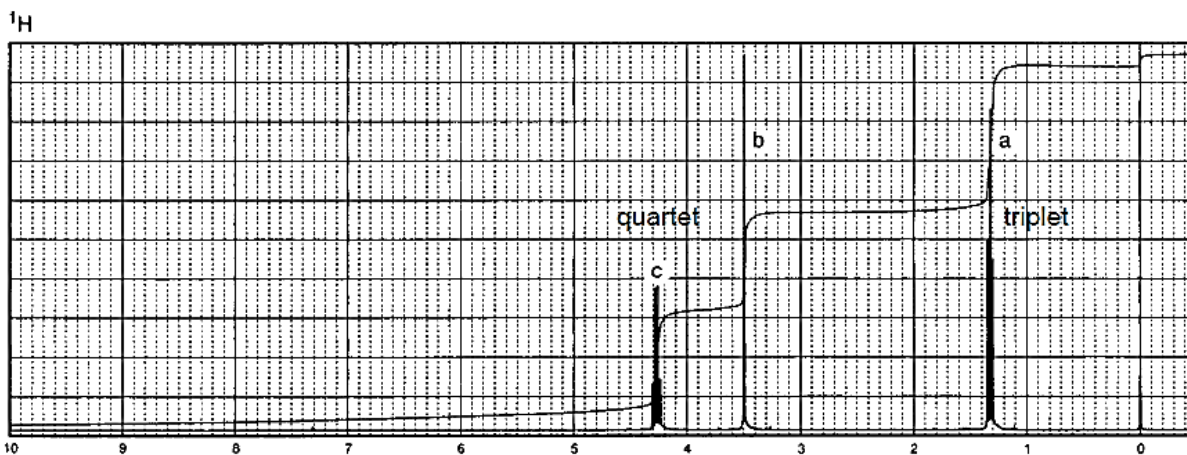
Answer any TWO of the following.

(2 x 5 = 10)

15. The g – factor of ^1H and ^{13}C are 5.6 and 1.4 respectively. For the same value of the magnetic field strength, if the ^1H resonates at 600 MHz. then what would be the resonance frequency of C-13?

16. Following are the infrared, ^1H -NMR, and ^{13}C -NMR spectra of the compound with molecular formula $\text{C}_5\text{H}_7\text{NO}_2$. Deduce the structure of the compound.

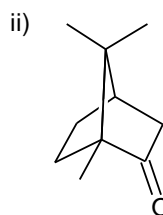
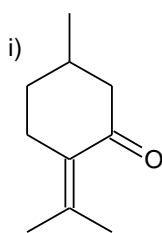




17. a) Which of the following technique can distinguish between cis and trans 1,2 dichloro ethene. Explain your choice.

i) UV-visible spectroscopy ii) Infrared spectroscopy iii) Mass spectrometry iv) EPR

b) How many signals are expected in the decoupled ¹³C NMR spectrum of each of the following molecules



(2 + 3)

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