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**ST. JOSEPH’S COLLEGE (AUTONOMOUS), BENGALURU-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 question paper contains three printed pages and three parts

**Part A**

**Answer any SIX of the following (6 x2 = 12)**

1. Why is 13C NMR 6000 times less sensitive than 1H NMR.
2. List the electronic transitions of formaldehyde and arrange them in the increasing order of energy.
3. A NMR instrument employs a magnet that provides field strength of 4.69 T. At what frequency would the hydrogen nucleus absorb in such a field? Given magnetogyric ratio of hydrogen nucleus is 2.6752 X 108 radian s--1 T-1.
4. What is meant by saturation in NMR?
5. How are the metal-carbonyl complexes identified by their IR spectral analysis?
6. Explain with an example, how tautomers can be distinguished by IR spectroscopy.
7. Sketch hyperfine esr spectra of p- hydroquinone radical.
8. How is the presence of a bromine atom in an organic compound identified by Mass spectroscopic studies.

**Part - B**

**Answer any FOUR of the following (4 x 12 = 48)**

1. a) Discuss the effect of solvent polarity on the energies of π→π\* and n→π\* transitions.

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

|  |  |
| --- | --- |
| i)  | ii) |
|  |  |

c) For the compound 3-chloropropene (CH2=CHCH2Cl), (i) Sketch the 13C NMR spectrum (totally decoupled, with a singlet for each type of carbon), showing approximate chemical shifts.(ii) Show the multiplicity expected for each signal in the off-resonance-decoupled spectrum.(iii) Sketch the spectra expected using the DEPT-90 and DEPT-135 techniques. (4+4+4)

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

b) How are off-resonance decoupled 13C spectra obtained? What are the merits and limitations of such spectra?

c) Propose a structure for compound **D** (molecular formula C9H9ClO2) consistent with the given spectroscopic data.

13C NMR signals at 30, 36, 128, 130, 133, 139, and 179 ppm

(4+4+4)

1. a) Draw the Karplus curve and explain its significance?

b) What is chemical exchange? Explain the 1H-NMR spectral features of ultra-pure and ordinary ethanol.

c) 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? (4+4+4)

1. a) Discuss in detail the characteristic IR absorption bands of aromatic hydrocarbons and alcohols.

 b) Explain the significance of g – values in electro paramagnetic spectroscopy

(6 + 6)

1. a) Account for the following mass spectral fragmentations of alcohols: (a) primary alcohols exhibit a peak at m/z = 31 (b) secondary alcohols usually give a prominent peak at m/z = 45, 59, 73 so on and (c) In tertiary alcohols the molecular ion is undetectable.

b) The excited and ground state nuclear spin values of a Mossbauer nucleus are 5/2 and 3/2 respectively. Explain using separate energy level diagrams, how these energy states are split under the influence of an electrical field gradient and magnetic field. Show the transitions involved and sketch the spectra to show the above effects. (6+6)

1. a) Define the following using a suitable example with respect to Mass spectrometry (1) Metastable ion peak and (b) FAB technique

b) Point out the consequences of coordination of a ligand to a metal on the IR absorption patterns. Explain with an example. (6+6)

**Part - C**

**Answer any TWO of the following (2 x 5 = 10)**

1. Account for the variations in the CO stretching vibrations (given within brackets) in the following compounds: acetone, **(CH3)2CO** (1715 cm-1), acetophenone, **C6H5(CO)CH3** ( 1685 cm-1), p-aminoacetophenone, **NH2C6H4(CO)CH3**(1652 cm-1) and p-nitroacetophenone, **NO2 C6H4(CO)CH3**(1693 cm-1). 5 marks.
2. Deduce the structures of compounds **A** and **B,** two of the major components of jasmine oil, from the given data.

Compound **A**: C9H10O2; IR absorptions at 3091–2895 and 1743 cm–1; 1H NMR signals at 2.06 (singlet, 3H), 5.08 (singlet, 2H), and 7.33 (broad singlet, 5H) ppm.

Compound **B**: C14H12O2; IR absorptions at 3091–2953 and 1718 cm–1; 1H NMR signals at 5.35 (singlet, 2H) and 7.26–8.15 (multiplets, 10H) ppm. (5 marks)

1. (a) Construct a splitting diagram for the Hb signal in the 1H-NMR spectrum of methyl acrylate (structure is given below) given 3Jab = 10.5 Hz and 2Jbc = 1.5 Hz . If the chemical shift of the Hb proton is centred at 5.64 ppm. What is the chemical shift value for each sub-peak, expressed in Hz ? (assume that the resonance frequency of TMS is exactly 300 MHz).



 (b) You are provided with two sets of iron octahedral complexes – set one are those of ferrous ions and the set two are of ferric ions. Further each set has two complexes one prepared with weak field ligands and the other with strong field ligands. Explain how you make use of Mossbauer studies to distinguish between the complexes in each set.

(2.5 + 2.5 marks)