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DGG-003-010401 Seat No. _____

M. Sc. (Sem. IV) (CBCS) Examination

April / May – 2015

C - 401 : Spectroscopy

(All Branches)

Faculty Code : 003
Subject Code : 010401

Time : $2\frac{1}{2}$ Hours] [Total Marks : **70**

Instruction: All questions carry equal marks

1. Answer the following (Any Seven):
   a. Give the full form of the following terms: DEPT, NOE, FAB, EI, CI.

      Also enlist at least five deuterated solvents.

   b. When and who formulated the empirical rules for the calculations of λ_{max} in conjugated diene and triene systems. Also give the wavelength ranges for far and near UV regions.

   c. What are mass spectrum and base peak? What information can be derived from a given mass spectrum? List common detectors used in mass spectroscopy.

   d. State the wavelength ranges for near and far infrared regions. What information can be deduced from a given IR spectrum? Also state applications of IR spectroscopy.

   e. Give the possible structures of isomeric ethers having molecular formula $C_4H_{10}O$. How many signals will be observed in ^{13}CNMR spectrum of each of the compound?

   f. State the factors affecting chemical shifts. By which processes ^{13}CNMR spectra can be simplified?

   g. An organic compound having MF $C_4H_{10}O$ shows one doublet, one triplet, and two quartets in its off resonance proton decoupled ^{13}CNMR spectrum. Deduce the structure of the compound. Also predict its ^{1}HNMR signals with splitting pattern.

   h. Fill in the blanks:
      i. From DEPT spectrum one can distinguish ---------,-------- and ------ groups.
      ii. IR spectroscopy is also known as --------- spectroscopy. The IR region below 1500cm^{-1} is known as ----- region.
      iii. Protons attached to adjacent atoms are called as ------ and they are separated by ------- bonds.
      iv. Among all transitions -------- transition requires least energy, while --------transition requires high energy ------- bonds stronger bonds.

i. Select the appropriate answer:

i. Proton decoupled ^{13}C NMR spectra of o, m, p – xylene exhibit ---------- signals.

A 3, 4, 5
B 4, 5, 3
C 5, 4, 3
D 3, 5, 4

ii. The region extending from 200 to 380 nm is called .....

A. Near UV
B. Quartz
C. Both A and B
D. Visible

iii. Vibrational frequencies are affected by ----

A Coupled vibrations
B Fermi resonance
C Hydrogen bonding
D Inductive and mesomeric effects

iv. Which one of the following compounds shows 5 ^{13}CNMR signals?

A. 1,4-Dihydroxy benzene
B. 1,3-Dihydroxy benzene
C. 1,2-Dihydroxy benzene
D. None of the above

j. The mass spectrum of ethyl benzene has shown peaks at m/e 106, 91, 65, give the structure of the probable species. Also state the number of ^{13}CNMR and ^{1}HNMR signals with their multiplicities.

2. Answer the following:
   a. Discuss IR, ^{1}H and ^{13}CNMR, and mass spectral analysis of isopentyl acetate.
   b. Discuss sample handling techniques in IR spectroscopy.
3. Write notes on following (Any Two):
   a. UV transitions
   b. Mass spectrometer
   c. ^{13}CNMR chemical shifts
   d. Double beam IR spectrometer
4. Answer the following:

   a. Distinguish following pairs of compounds by ^{1}HNMR spectroscopy.

   A 1,2-Dimethoxyethane and 1,1-dimethoxyethane
   B cis-1-chloropropene and trans-1-chloropropene
   C CH_3COCH_3 and CH_3COOCH_3

   b. Explain mass fragmentation of following:

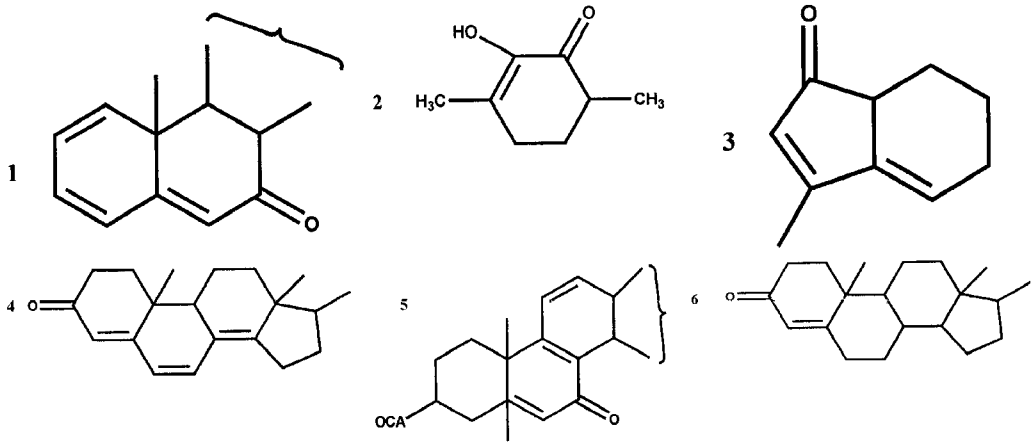
   A. Methyl butyrate
   B. Methyl benzoate
   C. Acetophenone

c. How will you distinguish methylpropionate and ethyl acetate by ^{1}HNMR spectroscopy? Also predict ^{13}CNMR signals of these compounds.

OR

4. Answer the following:

a. For below compounds calculate λmax using Woodward-Fisher rules.



Following data are given:

1. Parent α, β-unsaturated six or more or acyclic ketone = 215nm
2. Parent α, β-unsaturated five ring ketone = 202 nm
3. Each exocyclic double bond = 15 nm
4. A double bond extending conjugation = 30 nm
5. Homodiene component = 39 nm
6. Each alkyl group or ring residue at α position= 10 nm, β position = 12 nm, Y or δ and higher = 18 nm
7. OH group α = 35 nm, β = 30 nm, Y= , δ or higher = 50 nm

b. A liquid compound of molecular formula $C_9H_{10}O_2$ gave following spectral data:

IR (Cm^{-1}): 1720(s), 1602(m), 1581(m), 1270(s), 1105(s)
^{1}H NMR (δ): 1.29 (t), 4.35 (q), 7.40 (m), 8.81 (m)

Establish the structure of the compound and also predict the principal ions in its mass spectrum and number of ^{13}CNMR proton coupled signals with their mul
tiplicities.

5. Answer the following:

a. (i) Outline the mode of fragmentation leading to the ions causing peaks in the mass spectrum of the following compounds:

A. Pentanoic acid at m/e 60
B. Phenetole ($C_6H_5OC_2H_5$) at m/e 94
C. Dimethylamine at m/e 30

(ii) In the mass spectrum of an unsaturated hydrocarbon, the molecular ion M^+ peak has relative intensity 70.0, the M+1 4.7 and the base peak a relative intensity of 100. How many carbon atoms are there in the hydrocarbon per molecule.

OR

a. An organic compound of molecular formula $C_5H_{11}Cl$ gave following ^{1}HNMR signals:

Chemical shift, ppm	1.0	1.5	1.8
Multiplicity	Triplet	Singlet	Quartet
No. of protons	3	6	2

Deduce the structure of the compound and also give characteristic IR absorption peaks and number of proton coupled ^{13}CNMR peaks.

b. Distinguish following pairs of the compounds by IR and ^{1}HNMR spectroscopy:
A. CH_3COOH and $HCOOCH_3$
B. $ClCH_2CH_2CH_2COOH$ and $CH_3OCH_2CH_2COCl$
C. CH_3CH_2CHO and $CH_2{=}CHCH_2OH$

c. Calculate the chemical shifts of 3-methylpentane and n-hexane. Following data are given below:

13C atoms	Shift A, ppm
α	9.1
β	9.4
γ	-2.5
δ	0.3
ε	0.1
1°(3°)	-1.1
1°(4°)	-3.4

13C atoms	Shift A, ppm
2°(3°)	-2.5
2°(4°)	-7.2
3°(2°)	-3.7
3°(3°)	-9.5
4°(1°)	-1.5
4°(2°)	-8.4