Enrollment No: _____ Exam Seat No:_____

C.U.SHAH UNIVERSITY

Summer Examination-2017

Subject Name : Spectroscopic Techniques

Subject Code : 5SC04CHC3 **Branch: M.Sc.(Chemistry)**

Semester : 4 **Date : 18/04/2017** **Time : 10:30 To 01:30** **Marks : 70**

Instructions:

(1) Use of Programmable calculator and any other electronic instrument is prohibited.
(2) Instructions written on main answer book are strictly to be obeyed.
(3) Draw neat diagrams and figures (if necessary) at right places.
(4) Assume suitable data if needed.

SECTION – I

Q-1 **Attempt the following questions** **(07)**

a. What is the characteristic feature of meta stable peak in mass spectra? **(1)**
b. Write the fundamental NMR equation? **(1)**
c. Write the important characteristic properties of DEPT. **(1)**
d. Indicate the position and multiplicity of the signals for the solvents CD_3CN and DMSO-d_6 in ^{13}C-NMR. **(2)**
e. Why do we get broad peak in NMR spectra of proton of amine? **(2)**

Q-2 **Attempt all questions** **(14)**

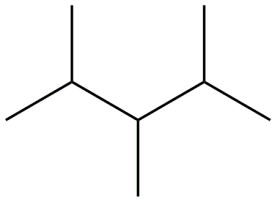
a. Explain different method for simplification of NMR spectra. **(7)**
b. Explain principle of NMR spectroscopy. **(7)**

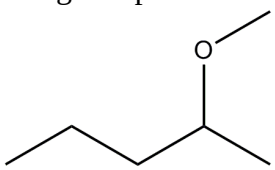
OR

Q-2 **Attempt all questions** **(14)**

a. Sketch the following 2D-NMR spectra by taking approximate δ value for each signal: **(7)**
(i) ^{1}H-^{13}C HETCOR spectrum of 2-butanol and
(ii) ^{1}H-^{1}H COSY spectrum of aromatic region of styrene.

b. Calculate ^{13}C-NMR shift for following compound: **(7)**





Q-3 **Attempt all questions** **(14)**

a. Discuss instrumentation of Mass Spectrophotometer. **(7)**
b. Explain the general rules for predicting prominent peaks in EI-Mass spectra. **(7)**

OR

Q-3 **Attempt all questions**

a. What is the principle of Mass spectroscopy? Derive the governing equation of mass spectroscopy. **(7)**

b. What is Mclafferty rearrangement observed in mass spectroscopy? Discuss CI method in mass spectroscopy. **(7)**

SECTION – II

Q-4 **Attempt the following questions** **(07)**

a. Define Auxochrome. **(1)**

b. Define Hypochrome. **(1)**

c. Define Bathochrome. **(1)**

d. Define Hypsochrome. **(1)**

e. State Beer-Lambert law. **(1)**

f. Why do we get band in IR spectra instead of peak? **(1)**

g. What is the fundamental IR equation? **(1)**

Q-5 **Attempt all questions** **(14)**

Discuss IR spectra of CO_2. **(7)**

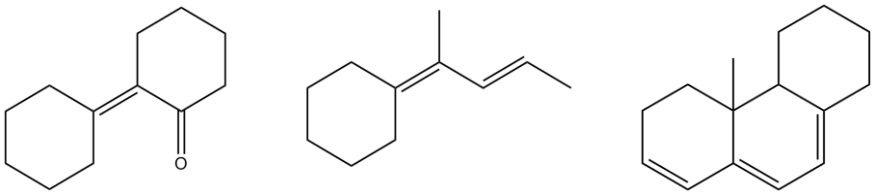
Explain principle of IR spectroscopy. **(7)**

OR

Q-5 **Attempt all questions**

a. Discuss different characteristic electronic transition in UV spectroscopy. **(7)**

b. Calculate λ_{max} for the following compound. **(7)**



Q-6 **Attempt all questions** **(14)**

a. A compound has molecular formula $C_{10}H_{12}O_2$.It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(6)**

^{1}H NMR			^{13}C NMR		
δ (ppm)	Multiplicity	No. of protons	δ (ppm)	DEPT-90	DEPT-135
2.1	Singlet	3H	29.0		Positive
3.6	Singlet	2H	50.0		Negative
3.8	Singlet	3H	55.0		Positive
6.9	Doublet	2H	114.0	Positive	Positive
7.1	Doublet	2H	127.0		
			130.0	Positive	Positive
Mass: (m/z) 164(M^+), 149, 133, 121, 107, 43			159.0		
IR: (cm^{-1}) 1711, 3000, 2950, 1500, 1600, 820			207.0		

b. A compound has molecular formula C_8H_{10}. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(4)**

^{1}H NMR		
δ (ppm)	Multiplicity	No. of protons
7.1	Singlet	5H
2.6	Quartet	2H
1.2	Triplet	3H
IR: (cm^{-1}) 3070, 2970, 1610, 1498, 692		

c. A compound has molecular formula C_8H_8O.It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(4)**

^{1}H NMR		
δ (ppm)	Multiplicity	No. of protons
7.9	Complex	2H
7.5	Complex	3H
2.5	Singlet	3H
IR: (cm^{-1}) 3070, 1685, 1582, 1450, 688		

OR

Q-6 **Attempt all Questions**

a. A compound has molecular formula $C_5H_7NO_2$.It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(6)**

^{1}H NMR			^{13}C NMR
δ (ppm)	Multiplicity	No. of protons	δ (ppm)
4.3	Quartet	2H	14.0
3.5	Singlet	2H	25.0
1.3	Triplet	3H	63.0
			113.0
IR: (cm^{-1}) 2260, 1747, 2150, 1200			163.0

b. A compound has molecular formula $C_8H_8O_2$.It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(4)**

^{1}H NMR		
δ (ppm)	Multiplicity	No. of protons
3.8	Singlet	3H
7-8	Complex	4H
8	Singlet	1H
IR: (cm^{-1}) 2940, 2700, 1700, 1515, 834		

c. A compound has molecular formula $C_{15}H_{14}O$.It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **(4)**

^{1}H NMR		
δ (ppm)	Multiplicity	No. of protons
3.5	Singlet	2H
7.2	Multiplet	5H
IR: (cm^{-1}) 3093, 2925, 1725, 1587, 1455		

TABLE 5.1

The ^{13}C Shift Parameters in Some Linear and Branched Hydrocarbons

^{13}C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	−2.5
δ	+0.3
ϵ	+0.1
1° (3°)[a]	−1.1
1° (4°)[a]	−3.4
2° (3°)[a]	−2.5
2° (4°)	−7.2
3° (2°)	−3.7
3° (3°)	−9.5
4° (1°)	−1.5
4° (2°)	−8.4

[a]The notations 1° (3°) and 1° (4°) denote a CH_3 group bound to a R_3CH group and to a R_3C group, respectively. The notation 2° (3°) denotes a RCH_2 group bound to a R_2CH group, and so on.

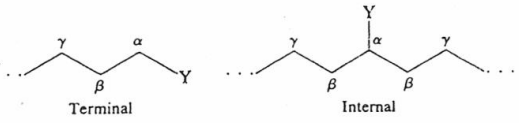
TABLE 5.2

The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a] (+ downfield, − upfield)



	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+ 9	+ 6	+10	+ 8	−2
$CH{=}CH_2$	+20		+ 6		−0.5
$C{\equiv}CH$	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+ 3	+ 2	−2
COO^-	+25	+20	+ 5	+ 3	−2
COOR	+20	+17	+ 3	+ 2	−2
COCl	+33	+28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3^+	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3^+	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

[a]Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift value calculated from Table 5.1.

Source: F.W. Wehrli, A.P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*. 2nd ed., London: Heyden, 1983.