Enrollment No: _____ Exam Seat No: _____

C. U. SHAH UNIVERSITY

Winter Examination-2018

Subject Name: Spectroscopic Techniques

Subject Code: 5SC04STC1 **Branch: M.Sc. (Chemistry)**

Semester: 4 **Date: 23/10/2018** **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 called non-equivalent protons? **01**
b) Define: Wave number and Frequency **01**
c) Give the wavelength range for UV-Visible Spectroscopy. **01**
d) Define: Chemical shift **01**
e) Define: Spectroscopy **01**
f) What do you mean by COSY and HETCOSY? **01**
g) Draw the ^{1}H-NMR spectrum of 1, 1-dibromoethane. **01**

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

a) Explain the various shifts in UV-Visible spectroscopy. **07**
b) Explain the theory of molecular vibrations. **07**

OR

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

a) Explain the electronic transitions in UV-Visible Spectroscopy. **07**
b) Explain the Instrumentation of UV-Visible Spectroscopy. **07**

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

a) Explain CW-NMR [Continuous Wave] instrumentation in NMR spectroscopy. **07**
b) Explain the chemical shift in ^{1}H-NMR spectroscopy. **07**

OR

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

a) Write a note on spin-spin coupling or splitting of signal in ^{1}H-NMR. **05**

b) Explain the shielding and deshielding of proton in NMR. **05**

c) Explain coupling constant (*J*). **04**

SECTION – II

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

a) Give the general energy absorption range for ^{13}C-NMR spectroscopy. **01**

b) What do you meant by molecular ion peak? **01**

c) Why ^{13}C-^{13}C coupling is neglible or not observed? **01**

d) What is called DEPT-NMR? **01**

e) What is the ^{13}C-NMR range for carbonyl carbon atom? **01**

f) Define the term: Mass analyzer. **01**

g) What is called base peak in mass spectrometry? **01**

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

a) Explain the principle of mass spectrometry. **07**

b) Explain the instrumentation of mass spectrometry. **07**

OR

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

a) Explain ion inlet system and quadrupole mass analyzer. **07**

b) Explain electron impact ionization and chemical ionization techniques. **07**

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

a) Organic compound having molecular formula $C_9H_{10}O_2$ exhibit the following spectral data. Deduced the structure of the compounds. **05**

IR (cm^{-1})	UV (λ, nm)	^{1}H-NMR (δ, ppm)
1745, 1225, 749 and 697	268, 264, 262 and 257	1.9 (3H, Triplet), 9.0 (2H, Quartet), 7.2 (3H, Triplet), 7.0 (2H, Doublet)

b) **05**

c) **04**

OR

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

a) Organic compound having molar mass 134.0 g/mole exhibit the following spectral data. Deduced the structure of the compounds. **05**

IR (cm^{-1})	UV (λ, nm)	^{1}H-NMR (δ, ppm)
3031, 2941, 1725, 1608, 1060 and 830	274	7.6 (4H, Doublet), 6.18 (3H, Singlet), 3.25 (3H, Singlet)

b) **05**

c) **04**

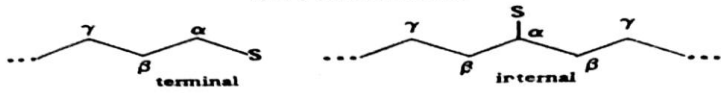
Important tables for calculations:

Tables for ^{13}C-NMR shift for hydrocarbon, Branched hydrocarbon, functional hydrocarbons and substituted benzene ring.

corrections for

^{13}C Atoms	Shift correction (ppm)	^{13}C Atoms	Shift correction (ppm)
1° (3°)	-1.1	3° (2°)	-3.7
1° (4°)	-3.4	3° (3°)	-9.5
2° (3°)	-2.5	4° (1°)	-1.5
2° (4°)	-7.2	4° (2°)	-8.4

Table 5.3* : *Increments (ppm) for Substituents (S) On Replacement of H in Alkanes with a Substituent (S)*



Substituent S	α		β		γ
	terminal	internal	terminal	internal	
F	+68	+63	+9	+6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	−6	+4	+11	+12	−1
CH_3	+9	+6	+10	+8	−2
$CH{=}CH_2$	+20	—	+6	—	−0.5
C≡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

Data taken from F.W. Wehrli and T. Wirthlin, Interpretation of Carbon-13 NMR spectra. London. Heyden 1976.

*These corrections are to be made in the Shift value of a carbon calculated from eq. I Scheme 5.3 or eq. II Scheme 5.3 or in the Values of Table 5.1.

Table 5.2 : *^{13}C Shifts for Selected Linear and Branched-Chain Alkanes (ppm from TMS)*

	C—1	C—2	C—3	C—4	C—5
methane	−2.6				
ethane	5.7				
propane	15.8	16.0	15.8		
butane	13.4	25.2	25.2	13.4	
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
isobutane	24.5	25.0			
isopentane	22.2	31.1	32.0	11.7	
neopentane	31.7	28.1			
3-methylpentane	11.3	29.3	36.7	(18.6, 3—CH_3)	
2,3-dimethylbutane	19.5	34.3			
2,2,3-trimethylbutane	27.4	33.1	38.3	16.1	

TABLE A8.7
^{13}C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)[a]

Substituent Y	*a* (*ipso*)	*o* (*ortho*)	*m* (*meta*)	*p* (*para*)
$-CH_3$	9.3	0.7	−0.1	−2.9
$-CH_2CH_3$	11.7	−0.5	0	−2.6
$-CH(CH_3)_2$	20.1	−2.0	−0.3	−2.5
$-C(CH_3)_3$	18.6	−3.4	−0.4	−3.1
$-CH=CH_2$	9.1	−2.4	0.2	−0.5
$-C\equiv CH$	−6.2	3.6	−0.4	−0.3
$-C_6H_5$	8.1	−1.1	−0.5	−1.1
$-CHO$	8.2	1.2	0.6	5.8
$-COCH_3$	8.9	−0.1	−0.1	4.4
$-COC_6H_5$	9.1	1.5	−0.2	3.8
$-COOH$	2.1	1.6	−0.1	5.2
$-COOCH_3$	2.0	1.2	−0.1	4.3
$-CN$	−16.0	3.6	0.6	4.3
$-NH_2$	18.2	−13.4	0.8	−10.0
$-N(CH_3)_2$	16.0	−15.7	0.8	−10.5
$-NHCOCH_3$	9.7	−8.1	0.2	−4.4
$-NO_2$	19.6	−4.9	0.9	6.0
$-OH$	28.8	−12.7	1.6	−7.3
$-OCH_3$	33.5	−14.4	1.0	−7.7
$-OCOCH_3$	22.4	−7.1	−0.4	−3.2
$-F$	33.6	−13.0	1.6	−4.5
$-Cl$	5.3	0.4	1.4	−1.9
$-Br$	−5.4	3.4	2.2	−1.0
$-I$	−31.2	8.9	1.6	−1.1

[a] *Add these increments to the base value for benzene-ring carbons (128.5 ppm).*

^{13}C SUBSTITUENT INCREMENTS FOR ALKANES AND CYCLOALKANES (PPM)[a]

	Terminal: $Y-C_\alpha-C_\beta-C_\gamma$			*Internal*: $C_\gamma-C_\beta-\underset{\displaystyle Y}{C_\alpha}-C_\beta-C_\gamma$		
Substituent Y	α	β	γ	α	β	γ
$-D$	−0.4	−0.1	0			
$-CH_3$	9	10	−2	6	8	−2
$-CH=CH_2$	19.5	6.9	−2.1			−0.5
$-C\equiv CH$	4.5	5.4	−3.5			−3.5
$-C_6H_5$	22.1	9.3	−2.6	17	7	−2
$-CHO$	29.9	−0.6	−2.7			
$-COCH_3$	30	1	−2	24	1	−2
$-COOH$	20.1	2	−2.8	16	2	−2
$-COOR$	22.6	2	−2.8	17	2	−2
$-CONH_2$	22	2.5	−3.2			−0.5
$-CN$	3.1	2.4	−3.3	1	3	−3
$-NH_2$	29	11	−5	24	10	−5
$-NHR$	37	8	−4	31	6	−4
$-NR_2$	42	6	−3			−3
$-NO_2$	61.6	3.1	−4.6	57	4	
$-OH$	48	10	−6.2	41	8	−5
$-OR$	58	8	−4	51	5	−4
$-OCOCH_3$	56.5	6.5	−6.0	45	5	−3
$-F$	70.1	7.8	−6.8	63	6	−4
$-Cl$	31	10	−5.1	32	10	−4
$-Br$	20	11	−3	25	10	−3
$-I$	−7.2	10.9	−1.5	4	12	−1

[a] *Add these increments to the values given in Table A8.1.*