

C.U.SHAH UNIVERSITY

Summer Examination-2018

Subject Name: Spectroscopic Techniques

Subject Code: 5SC04STC1

Branch: M.Sc. (Chemistry)

Semester: 4

Date: 01/05/2018

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.
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SECTION – I

- Q-1 Attempt the Following questions (07)**
- Define spectroscopy (1)
 - Define Wavelength and Frequency (1)
 - Give the regions of IR spectroscopy. (1)
 - Define Chemical shift (1)
 - What do you mean by equivalent protons? (1)
 - Write the full name of COSY and HETCOR? (1)
 - Give the multiplicity and approximate chemical shift value for protons of n-propyl bromide in $^1\text{H-NMR}$ spectroscopy. (1)
- Q-2 Answer the following questions (14)**
- Explain the electronic transitions in UV-Visible spectroscopy. (7)
 - Discuss the theory of molecular vibrations. (7)

OR

- Q-2 Answer the following questions (14)**
- Explain various shifts in UV-Visible spectroscopy with proper representation. (7)
 - Explain the Instrumentation of IR spectroscopy with proper block diagram. (7)
- Q-3 Answer the following questions (14)**
- Explain instrumentation of Continuous Wave-NMR spectrometer. (7)
 - Write a note on chemical shift in $^1\text{H-NMR}$ spectroscopy. (7)

OR

- Q-3 Answer the following questions**
- Explain spin-spin coupling or splitting of signal in $^1\text{H-NMR}$. (5)
 - Explain shielding and deshielding of proton in NMR. (5)



- c. Explain coupling constant (J). (4)

SECTION – II

Q-4 Draw the structure of followings... (07)

- a. Give the general energy absorption range for ^{13}C -NMR spectroscopy. (1)
b. What do you mean by molecular ion peak? (1)
c. Why ^{13}C - ^{13}C coupling is negligible or not observed? (1)
d. What is DEPT? (1)
e. What is the ^{13}C -NMR range for carbonyl carbon atom? (1)
f. Define the term: Mass analyzer. (1)
g. What do you mean by base peak in mass spectrometry? (1)

Q-5 Answer the following questions (14)

- a. Explain the principle of mass spectrometry. (7)
b. Explain the instrumentation of mass spectrometry. (7)

OR

Q-5 Answer the following questions (7)

- a. Explain ion inlet system and quadrupole mass analyzer. (7)
b. Explain electron impact ionization and chemical ionization techniques. (7)

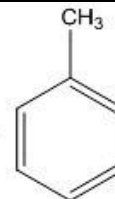
Q-6 Answer the following questions (14)

- a. Organic compound having molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$ exhibit the following spectral data. Deduce the structure of the compounds. (5)

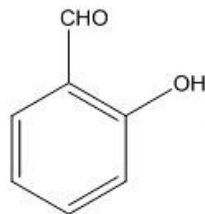
IR (cm^{-1})	UV (λ , nm)	^1H -NMR (δ , ppm)
1745, 1225, 749 and 697	268, 264, 262 and 257	1.9 (3H, Triplet), 9.0 (2H, Quartet), 7.2 (3H, Triplet), 7.0 (2H, Doublet)

- b. (5)

Calculate ^{13}C -NMR shift (δ ppm) for each carbon in $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ and



- c. (4)



Calculate the ^{13}C -NMR shift in δ ppm for each carbon in the given compound.

OR

Q-6 Answer the following questions (5)

- a. Organic compound having molar mass 134.0 g/mole exhibit the following spectral data. Deduced the structure of the compounds. (5)



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. Calculate the ¹³C-NMR shift for each C of 2-hydroxybutane and bromopropane. (5)
- c. Calculate the ¹³C-NMR shift for each C of 2,2-dimethylpropane. (4)

TABLE A 8.3
¹³C SUBSTITUENT INCREMENTS FOR ALKANES AND CYCLOALKANES (PPM)^a

Substituent Y	Terminal: Y-C _α -C _β -C _γ			Internal: C _γ -C _β -C _α -C _β -C _γ		
	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=CH	4.5	5.4	-3.5			-3.5
-C ₆ H 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

TABLE A 8.7
¹³C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)^a

Substituent Y	α (ipso)	o (ortho)	m (meta)	p (para)
-CH ₃	9.3	0.7	-0.1	-2.9
-CH ₂ CH ₃	11.7	-0.5	0	-2.6
-CH(CH ₂) 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=CH	-6.2	3.6	-0.4	-0.3
-C ₆ H 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 ₆ H 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



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
$1^\circ (3^\circ)^a$	-1.1
$1^\circ (4^\circ)^a$	-3.4
$2^\circ (3^\circ)^a$	-2.5
$2^\circ (4^\circ)$	-7.2
$3^\circ (2^\circ)$	-3.7
$3^\circ (3^\circ)$	-9.5
$4^\circ (1^\circ)$	-1.5

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 (+ left, - right)

Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
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
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

