Enrollment No: _____Exam Seat No:_____

C.U.SHAH UNIVERSITY

Summer Examination-2022

Subject Name: Spectroscopic Techniques
Subject Code: 5SC04STC1 **Branch: M.Sc. (Chemistry)**
Semester: 4 **Date: 05/05/2022** **Time: 11:00 To 02:00** **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	Define spectroscopy	**01**
	B	What do you mean by Auxochrome?	**01**
	C	Give the wavelength range for IR region of Spectroscopy.	**01**
	D	What is called Hetero-Annular Diene? Give any one example.	**01**
	E	Give the equation showing relation between wavenumber and reduced mass.	**01**
	F	Define shielding of proton in ^{1}H-NMR spectroscopy.	**01**
	G	Write the Larmor equation of frequency for NMR.	**01**
Q-2		**Attempt all questions**	**(14)**
	A	Explain the instrumentation of UV-Visible spectroscopy.	**07**
	B	Discuss the molecular vibrations in IR spectroscopy.	**07**

OR

Q-2		**Attempt all questions**	**(14)**
	A	Write a note on various factors affecting vibrational frequency in IR spectroscopy.	**07**
	B	Explain the various transitions in UV-Visible spectroscopy.	**07**

Q-3		**Attempt all questions**	**(14)**
	A	Write a note on spin decoupling.	**05**
	B	Discuss the instrumentation of CW-NMR.	**05**
	C	Explain in short Nuclear Overhauser Effect (NOE).	**04**

OR

Q-3		**Attempt all questions**	**(14)**
	A	Give the applications of UV-Visible spectroscopy.	**05**
	B	Explain the chemical shift in ^{1}H-NMR spectroscopy.	**05**
	C	Write a note on coupling constant (*J*).	**04**

SECTION – II

Q-4		**Attempt the following questions**	**(07)**
	A	Give the name of any three deuterated solvents used in NMR spectroscopy.	**01**
	B	What do you mean by m/z in mass spectrometry?	**01**
	C	What is called equivalent protons?	**01**
	D	List out any two nuclei having nuclear spin value I = 1/2.	**01**
	E	What is the range of chemical shift for carbonyl carbon atom in ^{13}C-NMR?	**01**
	F	Draw only the ^{1}H-NMR spectrum of 1, 1-dibromoethane.	**01**
	G	What do you mean by molecular ion peak?	**01**

Q-5		**Attempt all questions**	**(14)**
	A	Explain in detail the Electron Impact Ionization Technique and Quadrupole Mass Analyzer.	**8**
	B	Write a note on Splitting of Signal, Causes and Mechanism of Splitting in ^{1}H-NMR.	**06**

OR

Q-5		**Attempt all questions**	**(14)**
	A	Discuss the Instrumentation of Mass Spectrometry.	**07**
	B	Explain the various factors affecting chemical shift in NMR spectroscopy.	**07**

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

A An Organic compound having molecular formula $C_9H_{10}O_2$ exhibit the following spectral data. Deduced the structure of the compounds. **06**

IR (cm^{-1})	UV (λ, nm)	^{1}H-NMR (δ, ppm)
1745 (s), 1225 (s), 749 (s) and 697 (s)	268, 262, 262 and 257nm	1.96 (3H, s), 5.0 (2H, s), 7.22 (5H, s)

B **04**

C **04**

OR

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

A A Pale-yellow compound is slightly acidic in nature and give the following spectral data. Deduced the structure of the compounds. **06**

IR (cm^{-1})	UV (λ, nm)	^{1}H-NMR (τ, ppm)
3460 (v), 3035 (m), 1608 (m), 1585 (m), 1510 (s), 1360 (s), 1320 (s) and 740 (m).	280	-2.1 (1H, s), Unsymmetrical pattern 2.61-2.75 τ (4H, m)

B **04**

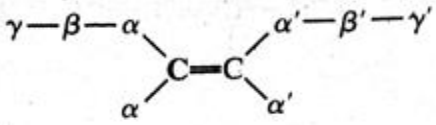
C **04**

Use the following tables for the calculation of ^{13}C-NMR Chemical shift.

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	

^{13}C SUBSTITUENT INCREMENTS FOR ALKENE (VINYL) CARBONS[a,b]



Substituent	α	β	γ	α′	β′	γ′
Carbon	10.6	7.2	−1.5	−7.9	−1.8	−1.5
$-C_6H_5$	12			−11		
−OR	29	2		−39	−1	
−OCOR	18			−27		
−COR	15			6		
−COOH	4			9		
−CN	−16			15		
−Cl	3	−1		−6	2	
−Br	−8	0		−1	2	
−I	−38			7		

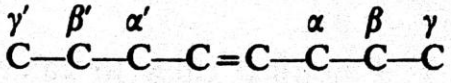
[a] *In the upper chains, if a group is in the β or γ position, the preceding atoms (α and/or β) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3 ppm).*

[b] *Calculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.*

Estimation of alkene shifts

Substitution parameters to be added to the shift of ethene δ123.3.

- On the opposite end of the double bond from the resonating carbon.
  α' (-7.9); β' (-1.8); and γ' (-1.5)
- For the same end of the double bond from the resonating carbon.
  α (10.6); β (7.2); and γ (-1.5)
- ***Z(cis)* correction - 1.1**

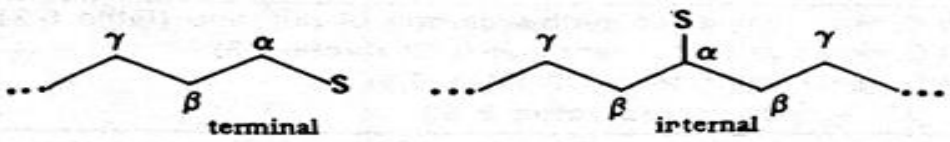


^{13}C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)[a]

Substituent Y	α (*ipso*)	o (*ortho*)	m (*meta*)	p (*para*)
$-CH_3$	9.3	0.7	−0.1	−2.9
$-CH_2CH_3$	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
$-C{\equiv}CH$	−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).*

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

corrections for branching.

^{13}C Atoms	Shift correction (ppm)	^{13}C Atoms	Shift correction (ppm)
1^0 (3^0)	-1.1	3^0 (2^0)	-3.7
1^0 (4^0)	-3.4	3^0 (3^0)	-9.5
2^0 (3^0)	-2.5	4^0 (1^0)	-1.5
2^0 (4^0)	-7.2	4^0 (2^0)	-8.4