

# C.U.SHAH UNIVERSITY

## Summer Examination-2019

**Subject Name: Spectroscopic Techniques**

**Subject Code: 5SC04STC1**

**Branch: M.Sc. (Chemistry)**

**Semester: 4**

**Date: 22/04/2019**

**Time: 02:30 To 05:30**

**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)**
- a. What is called spectroscopy? **01**
  - b. Define chromophore **01**
  - c. Give the wavelength range for UV-Visible Spectroscopy. **01**
  - d. What is called homoannular diene? **01**
  - e. Give the relation of wavenumber and force constant for IR spectroscopy. **01**
  - f. What do you mean by COSY? **01**
  - g. Draw the  $^1\text{H-NMR}$  spectrum of 1, 1, 2-tribromomethane. **01**
- Q-2 Attempt all questions (14)**
- a. Explain the sampling techniques in IR spectroscopy. **07**
  - b. Explain the various shifts in UV-Visible spectroscopy. **07**
- OR**
- Q-2 Attempt all questions (14)**
- a. Write a note on various factors affecting vibrational frequency. **07**
  - b. Explain the various types of transitions in UV-Visible spectroscopy. **07**
- Q-3 Attempt all questions (14)**
- a. Draw and Explain CW-NMR Instrumentation. **07**
  - b. Explain the chemical shift in  $^1\text{H-NMR}$  spectroscopy. **07**

**OR**



- Q-3 Attempt all questions (14)**
- a. Write a note on splitting of signal and mechanism of splitting in  $^1\text{H-NMR}$ . **05**
- b. Explain the relaxation processes in  $^1\text{H-NMR}$  **05**
- c. Explain coupling constant (J). **04**

**SECTION – II**

- Q-4 Attempt the following questions (07)**
- a. Give the general chemical shift range for  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy. **01**
- b. What do you mean by molecular ion peak? **01**
- c. Why  $^{13}\text{C-}^{13}\text{C}$  coupling is negligible or not observed? **01**
- d. Give two-two examples of nuclei having nuclear spin value  $I = \frac{1}{2}$  and  $I = 1.0$ . **01**
- e. What is the range of chemical shift in  $^{13}\text{C-NMR}$  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. Discuss the instrumentation of mass spectrometry. **07**

**OR**

- Q-5 Attempt all questions (14)**
- a. Write a note on magnetic sector 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  $\text{C}_9\text{H}_{10}\text{O}_2$  exhibit the following spectral data. Deduced the structure of the compounds. **05**

IR ( $\text{cm}^{-1}$ )	UV ( $\lambda$ , nm)	$^1\text{H-NMR}$ ( $\delta$ , ppm)
3031 (v), 2941 (w), 1608, 1504 (w), 1060 (s) and 830 (s)	274	2.35 (3H, singlet), 3.82 (3H, singlet), 7.30-7.85 (4H, doublet)

- b. **05**
- c. **04**

**OR**



Q-6

Attempt all questions

(14)

- a. Organic compound having molar mass 160.0 g/mole exhibit following spectral data. Deduced the structure of the compounds.

05

IR (cm <sup>-1</sup> )	UV (λ, nm)	<sup>1</sup> H-NMR (δ, ppm)
2857-2941, 1742, 1460, 1056, 1260.	212	7.5 (2H, singlet), 8.71 (6H, triplet), 5.84 (4H, Quartet)

b.

05

c.

04

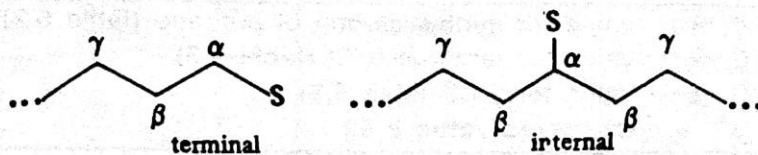
Use the following tables for the calculation of <sup>13</sup>C-NMR Chemical shift.

**Table 5.2 :** <sup>13</sup>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 <sub>3</sub> )	
2,3-dimethylbutane	19.5	34.3			
2,2,3-trimethylbutane	27.4	33.1	38.3	16.1	



**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 <sub>3</sub>	+9	+6	+10	+8	-2
CH=CH <sub>2</sub>	+20	—	+6	—	-0.5
C≡CH	+4.5	—	+5.5	—	-3.5
COOH	+21	+16	+3	+2	-2
COO <sup>-</sup>	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28	—	+2	—
CONH <sub>2</sub>	+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 <sub>2</sub>	+29	+24	+11	+10	-5
NH <sub>3</sub> <sup>+</sup>	+26	+24	+8	+6	-5
NHR	+37	+31	+8	+6	-4
NR <sub>2</sub>	+42	—	+6	—	-3
NR <sub>3</sub> <sup>+</sup>	+31	—	+5	—	-7
NO <sub>2</sub>	+63	+57	+4	+4	—
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4

Source: Adapted from E.W. Wehli and T. Wirthlin, Interpretation of Carbon-13 NMR spectra. London:







**<sup>13</sup>C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)<sup>a</sup>**

Substituent Y	$\alpha$ ( <i>ipso</i> )	<i>o</i> ( <i>ortho</i> )	<i>m</i> ( <i>meta</i> )	<i>p</i> ( <i>para</i> )
-CH <sub>3</sub>	9.3	0.7	-0.1	-2.9
-CH <sub>2</sub> CH <sub>3</sub>	11.7	-0.5	0	-2.6
-CH(CH <sub>2</sub> ) <sub>2</sub>	20.1	-2.0	-0.3	-2.5
-C(CH <sub>3</sub> ) <sub>3</sub>	18.6	-3.4	-0.4	-3.1
-CH=CH <sub>2</sub>	9.1	-2.4	0.2	-0.5
-C $\equiv$ CH	-6.2	3.6	-0.4	-0.3
-C <sub>6</sub> H <sub>5</sub>	8.1	-1.1	-0.5	-1.1
-CHO	8.2	1.2	0.6	5.8
-COCH <sub>3</sub>	8.9	-0.1	-0.1	4.4
-COC <sub>6</sub> H <sub>5</sub>	9.1	1.5	-0.2	3.8
-COOH	2.1	1.6	-0.1	5.2
-COOCH <sub>3</sub>	2.0	1.2	-0.1	4.3
-CN	-16.0	3.6	0.6	4.3
-NH <sub>2</sub>	18.2	-13.4	0.8	-10.0
-N(CH <sub>3</sub> ) <sub>2</sub>	16.0	-15.7	0.8	-10.5
-NHCOCH <sub>3</sub>	9.7	-8.1	0.2	-4.4
-NO <sub>2</sub>	19.6	-4.9	0.9	6.0
-OH	28.8	-12.7	1.6	-7.3
-OCH <sub>3</sub>	33.5	-14.4	1.0	-7.7
-OCOCH <sub>3</sub>	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

<sup>a</sup>Add these increments to the base value for benzene-ring carbons (128.5 ppm).

**corrections for branching.**

<sup>13</sup> C Atoms	Shift correction (ppm)	<sup>13</sup> C Atoms	Shift correction (ppm)
1 <sup>o</sup> (3 <sup>o</sup> )	-1.1	3 <sup>o</sup> (2 <sup>o</sup> )	-3.7
1 <sup>o</sup> (4 <sup>o</sup> )	-3.4	3 <sup>o</sup> (3 <sup>o</sup> )	-9.5
2 <sup>o</sup> (3 <sup>o</sup> )	-2.5	4 <sup>o</sup> (1 <sup>o</sup> )	-1.5
2 <sup>o</sup> (4 <sup>o</sup> )	-7.2	4 <sup>o</sup> (2 <sup>o</sup> )	-8.4

