

C.U.SHAH UNIVERSITY
Summer Examination-2016

Subject Name: Spectroscopic Techniques

Subject Code: 5SC04CHC3

Branch: M.Sc. (Chemistry)

Semester: 4

Date: 10/05/2016

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.

SECTION – I

Q-1 Attempt the Following questions (07)

- a. Write the fundamental NMR equation? (1)
- b. What is the basic function of Fourier Transform technique in NMR? (1)
- c. How many signals will we get for 2,2-dichloropropane in ^1H -NMR spectroscopy? (1)
- d. Assign the spin system (pople notation) for p-chloroaniline. (1)
- e. Indicate the position of the signals for the solvents CD_3CN and CDCl_3 in ^{13}C -NMR. (1)
- f. Write the important characteristic properties of DEPT-90 and DEPT-135 spectra. (1)
- g. Which Internal reference is used for samples scanned in D_2O ? (1)

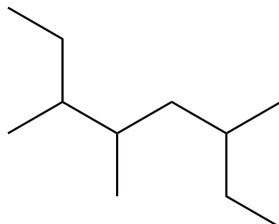
Q-2 Attempt all questions (14)

- a. Write a note on chemical shift in NMR spectroscopy. (5)
- b. Sketch the expected ^1H - ^1H COSY spectrum of aromatic region of styrene by taking approximate δ value for each signal. (5)
- c. Calculate ^{13}C -NMR shift of m-chloroaniline. (4)

OR

Q-2 Attempt all questions (14)

- a. Calculate ^{13}C -NMR shift for following compound. (5)



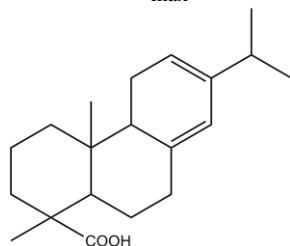
- b. What is relaxation process in NMR spectroscopy? (5)



- c. How can we differentiate between anomeric structures of D-glucose using PMR spectroscopy? (4)

Q-3 Attempt all questions (14)

- a. Define the following terms: (i) Auxochrome, (ii) Chromophore, (iii) Bathochrome, (iv) Hypsochrome, (v) Hyperchrome and (vi) Hypochrome. (6)
- b. Explain the principle of IR spectroscopy. (5)
- Calculate λ_{\max} for the following compound. (3)



OR

Q-3 Attempt all questions

- a. Write a note on coupled interaction and Fermi resonance in IR spectroscopy. (6)
- b. Discuss different characteristic electronic transitions in UV spectroscopy. (5)
- c. Write different factors affecting theoretical number of bands in IR spectroscopy. (3)

SECTION – II

Q-4 Attempt the Following questions (07)

- a. What is the fundamental IR equation? (1)
- b. How many signals will be obtained for ^{13}C -NMR spectra of benzene? (1)
- c. What is the characteristic feature of metastable peak in mass spectra? (1)
- d. State Beer-Lambert law. (1)
- e. Why do we get band in IR spectra instead of peak? (1)
- f. What is the basic functionality required for auxochrome groups? (1)
- g. What is E-band? (1)

Q-5 Attempt all questions (14)

- a. Explain the general rules for predicting prominent peaks in EI-mass spectra. (6)
- b. Explain the principle of Mass spectroscopy? (5)
- c. What is McLafferty rearrangement observed in mass spectroscopy? (3)

OR

Q-5 Attempt all questions

- a. Explain different methods for molecular formula determination in mass spectroscopy. (6)
- b. Derive the governing equation of mass spectroscopy. (5)
- c. Discuss CI method in mass spectroscopy. (3)

Q-6 Attempt all questions (14)

- a. A compound has molecular formula $\text{C}_5\text{H}_7\text{NO}_2$. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. (10)



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. An organic compounds gave the following molecular ion group peaks in the mass spectrum (4)

	M	M+1
m/z	142	143
Abundance	100	1.14

What is the molecular formula for the compound?

OR

Q-6

Attempt all Questions

- a. A compound has molecular formula C₁₀H₁₂O₂. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. (10)

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. Determine the formula of fragment from the data given (4)

m/z	69	70	71
Abundance	100	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
ϵ	+0.1
$1^\circ (3^\circ)^a$	-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
$4^\circ (2^\circ)$	-8.4

^aThe notations $1^\circ (3^\circ)$ and $1^\circ (4^\circ)$ denote a CH_3 group bound to a R_2CH group and to a R_3C group, respectively. The notation $2^\circ (3^\circ)$ 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* (+ downfield, - upfield)

Y	Terminal		Internal		
	α	β	α	γ	
CH_3	+ 9	+ 6	+10	+ 8	-2
$\text{CH}=\text{CH}_2$	+20		+ 6		-0.5
$\text{C}\equiv\text{CH}$	+ 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

*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.



TABLE 5.9

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	9.3	+0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	+15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6	
CH ₂ OH	+13.3	-0.8	-0.6	-0.4	64.5
CH ₂ OCCH ₃	+7.7	-0.0	-0.0	-0.0	20.7 (CH ₃), 66.1 (CH ₂), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH ₃	+31.4	-14.4	+1.0	-7.7	54.1
OC ₆ H ₅	+29.0	-9.4	+1.6	-5.3	
OCCH ₃	+22.4	-7.1	-0.4	-3.2	23.9 (CH ₃), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH ₃	+7.8	-0.4	-0.4	+2.8	24.6 (CH ₃), 195.7 (C=O)
CC ₆ H ₅	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF ₃	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH ₃	+2.0	+1.2	-0.1	+4.8	51.0 (CH ₃), 166.8 (C=O) 168.5
CCl	+4.6	+2.9	+0.6	+7.0	
C≡N	-16.0	+3.6	+0.6	+4.3	119.5
NH ₂	+19.2	-12.4	+1.3	-9.5	
N(CH ₃) ₂	+22.4	-15.7	+0.8	-11.8	40.3
NHCCH ₃	+11.1	-9.9	+0.2	-5.6	
NO ₂	+19.6	-5.3	+0.9	+6.0	
N=C=O	+5.7	-3.6	+1.2	-2.8	129.5
F	+35.1	-14.3	+0.9	-4.5	
Cl	+6.4	+0.2	+1.0	-2.0	
Br	-5.4	+3.4	+2.2	-1.0	
I	-32.2	+9.9	+2.6	-7.3	
CF ₃	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH ₃	+10.2	-1.8	+0.4	-3.6	15.9
SO ₂ NH ₂	+15.3	-2.9	+0.4	+3.3	
Si(CH ₃) ₃	+13.4	+4.4	-1.1	-1.1	

*See D. E. Ewing, *Org. Magn. Reson.*, 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

