H-003-1104001

M. Sc. (Sem.-IV) (CBCS) Examination

April - 2023

C-401 : Advance Spectroscopic Techniques

(All branches) (New Course)

Faculty Code : 003

Subject Code : 1104001

Time : $2\frac{1}{2}$ Hours / Total Marks : **70**

Instructions : (1) All questions are compulsory.

(2) All questions carry equal marks.

1 Answer the following : (any **seven**)   **14**

(a) Write a note on halogen isotope.

(b) Write the full form of following techniques :

(1) FID

(2) DQF-COSY

(3) HSQC

(4) ROESY

(c) Give the types of UV absorption shift.

(d) Draw the ^{1}HNMR spectrum of p-ethoxy-benzoic acid and show the splitting pattern of each signal.

(e) Enlist the common detectors used in mass spectrometry and draw the hypothetical mass spectrum.

(f) Draw the ^{13}CNMR of 1-phenyl-1-pentanone at 135° rotation.

(g) Write characteristics properties of Raman Lines.

(h) How many peaks are expected of methyl radical in ESR ?

(i) Give the range of NIR and discuss the disadvantages of it.

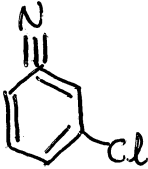(j) Why vapour of sample introduced at low temperature in mass spectrometer ?

2   Answer the following : (any **two**)   **14**

(a)   Write a note on classical theory of Raman effect.

(b)   Enlist the overall modification in NIR spectrophotometer and application of NIR.

(c)   Draw the electronic energy levels diagram and discuss electronic transitions in UV spectroscopy.

3   Answer the following :   **14**

(a)   Write a brief account on Popal Notation with suitable example.

(b)   Describe HMBC ^{2}DNMR technique and its interpretation style with suitable example.

OR

(a)   Calculate the ^{13}C value of each carbon for following compounds :

(i) $CH_2=CH-CO-O-CH_2-CH_3$

(ii)

(b)   Enlist the instrumental techniques used for the simplification of complex NMR spectrum and discuss any one in detail.

4   Answer the following :   **14**

(a)   Give the principle of mass spectrometer. Draw the schematic diagram of it and discuss its functioning.

(b)   What is first order and non-first order spectrum in NMR ? Discuss in detail.

5   Answer the following : (any **two**)   **14**

(a)   Discuss absorption due to carbonyl compounds in UV spectroscopy in detail.

(b)   Give the application of Raman spectroscopy.

(c)   Explain hyperfine splitting in ESR.

(d)   Compare and differentiate NIR and IR spectrophotometer.

TABLE 5.1

The 13C Shift Parameters in Some Linear and Branched Hydrocarbons

13C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	−2.5
δ	+0.3
ε	+0.1
1° (3°)*	−1.1
1° (4°)*	−3.4
2° (3°)*	−2.5
2° (4°)	−7.2
3° (2°)	−3.7
3° (3°)	−9.5
4° (1°)	−1.5
4° (2°)	−8.4

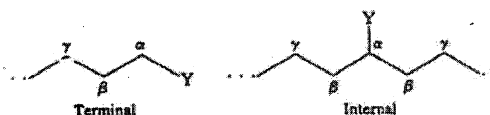*The notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₃CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₃CH group, and so on.

TABLE 5.2

The 13C 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-CH₃)	
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-CH₃)	

TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y In Alkanes. Y is Terminal or Internal* (+ downfield, − upfield)

Terminal   Internal

Y	α Terminal	α Internal	β Terminal	β Internal	γ
CH₃	+ 9	+ 6	+10	+ 8	−2
CH=CH₂	+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	
CONH₂	+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
NH₂	+29	+24	+11	+10	−5
NH₃⁺	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR₂	+42		+ 6		−3
NR₃⁺	+31		+ 5		−7
NO₂	+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 6.9

Chemical Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from benzene at 128.5 ppm downfield from TMS) (Carbon Atom of Substituent in parts per million from TMS)

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_2CH_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_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.8	−0.6	−0.4	64.5
CH_2OCCH_3 (O)	+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_6H_5	+29.0	−9.4	+1.6	−5.3	
$OCCH_3$ (O)	+22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
CH (O)	+8.2	+1.2	+0.6	+5.8	192.0
CCH_3 (O)	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
CC_6H_5 (O)	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
CCF_3 (O)	−5.6	+1.8	+0.7	+6.7	
COH (O)	+2.9	+1.3	+0.4	+4.3	168.0
$COCH_3$ (O)	+2.0	+1.2	−0.1	+4.8	51.0 (CH_3), 166.8 (C=O), 168.5
CCl (O)	+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
$NHCCH_3$ (O)	+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_2NH_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.

Table 3.16 Influence of functional group X on the chemical shift positions (δ) of nearby carbons in alkene groups and benzene rings
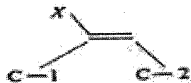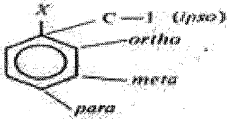
Base values: ethylene (δ 123) and benzene (δ 128)

	Alkenes		Benzenes			
	C—1	C—2	C—1 (ipso)	ortho	meta	para
—CH₃	10	−8	9	0	0	−2
R,	16	−8	15	0	0	−2
R,	23	−8	21	0	0	−2
—CH═CH₂	15	−6	9	0	0	−2
—CH≡CH	—	—	−6	4	0	0
—C₆H₅, —Ar	13	−11	13	−1	1	−1
—F	25	−34	35	−14	1	−5
—Cl	3	−6	6	0	1	−2
—Br	−8	−1	−5	3	2	−2
—I	−38	7	−32	10	3	−1
—NH₂	—	—	18	−13	1	−10
—NHR	—	—	20	−14	1	−10
—NR₂	—	—	22	−16	1	−10
—NO₂	22	−1	20	−5	1	6
—NHCOR, —NRCOR	—	—	10	−7	1	−4
—CN	−15	15	−16	4	1	6
—SH	—	—	4	1	1	−3
—OH	—	—	27	−13	1	−7
—OR	29	−39	30	−15	1	−8
—OCOR	18	−27	23	−6	1	−2
—COOH, —COOR, —CON<	4	9	2	2	0	5
—COR, —CHO	14	13	9	1	1	6
—SO₃H, —SO₂N<	—	—	16	0	0	4
—PMe₂	—	—	14	1.6	0	−1
—PAr₂	—	—	9	5	0	0

Table 3.15 Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X-\underset{\alpha}{C}-\underset{\beta}{C}-\underset{\gamma}{C}-C$$

X	α-shift			β-shift	γ-shift
	$X-CH_2-$	$X-\underset{R}{\overset{}{CH}}-$	$X-\underset{R}{\overset{R}{C}}-$		
	1° or	2° or	3°		
—CH₃	9	6	3	9	−3
— R: see table 3.11					
axial — CH₃	1	—	—	5	−6
equatorial — CH₃	6	—	—	9	0
(in cyclohexanes)					
—CH=CH₂	22	16	12	7	−2
—C≡CH	4	—	—	3	−3
—C₆H₅, —Ar	23	17	11	10	−3
—F	70	—	—	8	−7
—Cl	31	35	42	10	−5
—Br	19	28	37	11	−4
—I	−7 to 20	—	—	11	−2
—NH₂, —NHR, —NR₂	29	24	18	11	−4
—NO₂	62	—	—	3	−5
—NHCOR, —NRCOR	10	—	—	0	0
—NH₃⁺	25	—	—	7	−3
—CN	3	4	—	2	−3
—SH	2	—	—	2	−2
—OH	50	45	40	9	−3
—OR	50	24	17	10	−6
—OCOR	52	50	45	7	−6
—COOH, —COOR, —CON<	20	16	13	2	−3
—COR, —CHO	30	24	17	2	−3
—SO₃H, —SO₂N<	50	—	—	3	0

where A_n = characteristic value of the chemical shift of the observed C,
which depends upon the number of H atoms (n) attached to it

n = number of groups

α = carbon atoms in the α-position

γ = in γ and

δ = in δ positions

The characteristic values of α, γ and δ C-atoms (i.e., A_n) to be used for the calculation depend upon the number of H atoms on the observed —C and are given in Table 3.23.
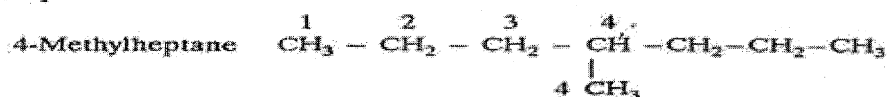
Example

4-Methylheptane

$$\overset{1}{CH_3} - \overset{2}{CH_2} - \overset{3}{CH_2} - \overset{4}{CH} - CH_2 - CH_2 - CH_3$$

$$\underset{4\ CH_3}{|}$$

TABLE 3.23

Observed C	A_n		$\longleftarrow \alpha \longrightarrow$	γ	δ
—CH₃	6.80	CH₃	0	−2.99	0.49
		CH₂	9.56		
		CH	17.83		
		C	25.48		
—CH₂—	15.34	CH₃	0.0	−2.69	0.25
		CH₂	9.75		
		CH	16.70		
		C	21.43		
—CH	23.46	CH₃	0.0	−2.07	0.0
		CH₂	6.60		
		CH	11.14		
		C	14.70		
—C—	27.77	CH₃	0.0	0.86	0.0
		CH₂	2.26		
		CH	3.96		
		C	7.35		

Note: Methyl groups in α and all groups in β have no effect. Groups in γ position have negative or only slightly positive effect.

There are 5 groups of equivalent C-atoms.

$\delta_C \quad = A_n + n\ \alpha_{32}^* + n\gamma + n\delta$ (observed δ)

$\delta_{(CH_3)}\ C_1 = 6.8 + 9.56 + (-2.99) + (2 \times 0.49) = 14.35$ (qr)   14.35 (qr)

$\delta_{(CH_2)}\ C_2 = 15.34 + 9.75 + (2 \times (-2.69)) + 0.25 = 19.96$ (tr)   19.96 (tr)

$\delta_{(CH_2)}\ C_3 = 15.34 + 9.75 + 16.70 + (-2.69) + 0.25 = 39.35$ (tr)   39.35 (tr)

$\delta_{(CH)}\ C_4 = 23.46 + (2 \times 6.60) + (-2.07) = 34.59$ (d)   34.59 (d)

Table 3.13 δ values for the carbons in alkynes (sp)

REPRESENTATIVE ALKYNES

acetylene (ethyne)   CH≡CH δ 72

R—C≡CH
  83 66

R—C≡C—R′
    82

C₆H₅—C≡CH
     83 78

C₆H₅—C≡C—R
    86

C₆H₅—C≡C—C₆H₅
      90

EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

Chemical shift (δ) = 72 + Σ(increments for carbon atoms)

C — C — C — C — C≡C — C — C — C — C

	δ	γ	β	α		α′	β′	γ′	δ′
increments	+0.5	0	+5	+7		−6	+2	−1	+0.5

base value 72

Table 3.14 δ values for the carbons in aromatic and heterocyclic molecules (sp² and sp³ carbons listed)

benzene — 128

naphthalene — 136, 128, 126

anthracene — 127, 128, 125, 132

phenanthrene — 122, 127, 129, 133, 127

tetralin — 129, 126, 137, 30, 24

indane — 144, 33, 25, 124 or 126

acenaphthene — 30, 139, 146, 119, 128, 132, 122

acenaphthylene — 129, 138, 124, 128, 128, 127

furan — 111, 144

thiophene — 127, 125

pyrrole — 108, 118

pyridine — 139, 126, 150

tetrahydrofuran, THF — 26, 68

tetrahydrothiophene — 31, 32

pyrrolidine — 26, 47

piperidine — 26, 27, 48

imidazole — 122, 136

pyrazole — 106, 135

GLUCOSE   α — OH axial
          β — OH equatorial

	C₁	C₂	C₃	C₄	C₅	C₆	
α —	97	75	77	70	77	62	38
β —	93	72	74	70	72	62	