



DCI-003-1104001

Seat No. \_\_\_\_\_

M. Sc. (Sem. IV) Examination

July - 2022

C-401 : Advanced Spectroscopy (All Branches)

Faculty Code : 003

Subject Code : 1104001

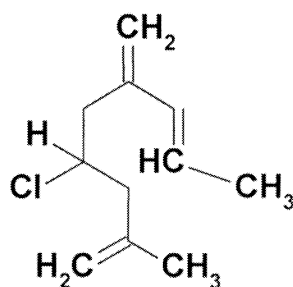
Time : 2:30 Hours]

[Total Marks : 70

**Instruction:** All questions are compulsory and carry equal marks.

1 Answer the following. (any seven) 14

- (a) Write the principle of Mass spectrometry.
- (b) Write the full form of following techniques:  
(1) HMBC (2) INDIQUITE (3) NOESY (4) DEPT
- (c) Write the advantage of double beam UV-Instrument.
- (d) Draw the  $^1\text{H}$ NMR spectrum of p-Methyl-benzoic acid and show the splitting pattern of signals.
- (e) Explain McLafferty rearrangement with suitable example.
- (f) Draw the  $^{13}\text{C}$ NMR of following compound at  $135^\circ$  rotation.



- (g) Give the characteristic properties of Raman lines.
- (h) How many peaks are expected in methyl radical?
- (i) Enlist the detector used in NIR-spectrophotometer.
- (j) Enlist the techniques used for ionization in Mass spectrometry.

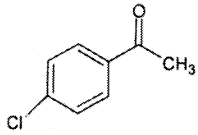
- 2 Answer the following. (any two) 14
- Discuss the classical theory of Raman effect in detail.
  - Discuss the advantages and application of NIR.
  - Draw the schematic diagram of single beam UV spectrophotometer and discuss its main components in details.
- 3 Answer the following: 14
- Sketch the NMR spectrum of AA'BB' and AMX system with suitable example.
  - Describe HETCOR 2D NMR technique with suitable example.
- OR**
- 3 Answer the following: 14
- Calculate the  $^{13}\text{C}$  Value for following Compounds.
- $$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$$
- 
- Give a brief account on following :
    - Relaxation Process
    - Chemical Shift in NMR Spectroscopy
- 4 Answer the following: 14
- Enlist the Mass analyzer and explain TOF mass analyzer in detail with diagram.
  - Enlist different types of coupling in PMR spectroscopy and explain any two with suitable example.
- 5 Answer the following. (any two) 14
- Draw the electronic energy levels diagram and discuss electronic transition in UV spectrophotometer.
  - Discuss quantum mechanical theory of Raman effect.
  - Discuss accurate molecular weight determination method with suitable example in mass spectrometry.
  - Explain hyperfine splitting in ESR.

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 <sub>3</sub>	9.3	+0.7	-0.1	-2.9	21.3
CH <sub>2</sub> CH <sub>3</sub>	+15.6	-0.5	0.0	-2.6	29.2 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH <sub>3</sub> )
C(CH <sub>3</sub> ) <sub>3</sub>	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH <sub>3</sub> )
CH=CH <sub>2</sub>	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH <sub>2</sub> )
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C <sub>6</sub> H <sub>5</sub>	+12.1	-1.8	-0.1	-1.6	
CH <sub>2</sub> OH	+13.3	-0.8	-0.6	-0.4	64.5
CH <sub>2</sub> OCCH <sub>3</sub>	+7.7	-0.0	-0.0	-0.0	20.7 (CH <sub>2</sub> ), 66.1 (CH), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1
OC <sub>2</sub> H <sub>5</sub>	+29.0	-9.4	+1.6	-5.3	
OCCH <sub>3</sub>	+22.4	-7.1	-0.4	-3.2	23.9 (CH <sub>3</sub> ), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH <sub>3</sub>	+7.8	-0.4	-0.4	+2.8	24.6 (CH <sub>3</sub> ), 195.7 (C=O)
CC <sub>2</sub> H <sub>5</sub>	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF <sub>3</sub>	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH <sub>3</sub>	+2.0	+1.2	-0.1	+4.8	51.0 (CH <sub>3</sub> ), 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 <sub>2</sub>	+19.2	-12.4	+1.3	-9.5	
N(CH <sub>3</sub> ) <sub>2</sub>	+22.4	-15.7	+0.8	-11.8	40.3
NHCCH <sub>3</sub>	+11.1	-9.9	+0.2	-5.6	
NO <sub>2</sub>	+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 <sub>3</sub>	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH <sub>3</sub>	+10.2	-1.8	+0.4	-3.6	15.9
SO <sub>2</sub> NH <sub>2</sub>	+15.3	-2.9	+0.4	+3.3	
Si(CH <sub>3</sub> ) <sub>3</sub>	+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 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 <sub>3</sub>	9.3	+0.7	-0.1	-2.9	21.3
CH <sub>2</sub> CH <sub>3</sub>	+15.6	-0.5	0.0	-2.6	29.2 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH <sub>3</sub> )
C(CH <sub>3</sub> ) <sub>3</sub>	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH <sub>3</sub> )
CH=CH <sub>2</sub>	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH <sub>2</sub> )
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C <sub>6</sub> H <sub>5</sub>	+12.1	-1.8	-0.1	-1.6	
CH <sub>2</sub> OH	+13.3	-0.8	-0.6	-0.4	64.5
CH <sub>2</sub> OCCH <sub>3</sub>	+7.7	-0.0	-0.0	-0.0	20.7 (CH <sub>2</sub> ), 66.1 (CH <sub>2</sub> ), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1
OC <sub>2</sub> H <sub>5</sub>	+29.0	-9.4	+1.6	-5.3	
OCCH <sub>3</sub>	+22.4	-7.1	-0.4	-3.2	23.9 (CH <sub>2</sub> ), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH <sub>3</sub>	+7.8	-0.4	-0.4	+2.8	24.6 (CH <sub>3</sub> ), 195.7 (C=O)
CC <sub>2</sub> H <sub>5</sub>	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF <sub>3</sub>	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH <sub>3</sub>	+2.0	+1.2	-0.1	+4.8	51.0 (CH <sub>2</sub> ), 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 <sub>2</sub>	+19.2	-12.4	+1.3	-9.5	
N(CH <sub>3</sub> ) <sub>2</sub>	+22.4	-15.7	+0.8	-11.8	40.3
NHCCH <sub>3</sub>	+11.1	-9.9	+0.2	-5.6	
NO <sub>2</sub>	+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 <sub>3</sub>	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH <sub>3</sub>	+10.2	-1.8	+0.4	-3.5	15.9
SO <sub>2</sub> NH <sub>2</sub>	+15.3	-2.9	+0.4	+3.3	
Si(CH <sub>3</sub> ) <sub>3</sub>	+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 3.17  $\delta$  values for the carbons in carbonyl groups and some other multiple-bonded environments (solvent shifts,  $\pm 2$  ppm, are commonly observed for  $C=O$ )




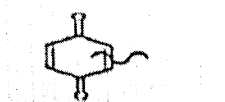
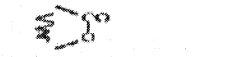
$R-CHO$ $Ar-CHO$	aliphatic aldehydes	200-208
$\text{---}CHO$ $R-CO-R'$	aryl and conjugated aldehydes* dialkyl ketones	190-194 205-218
$Ar-CO-R$ $Ar-CO-Ar$ $\text{---}CO\text{---}$	aryl and conjugated ketones	196-199
	cyclohexanone derivatives	209-213'
	cyclopentanone derivatives	214-220
	bicyclic ketones	218-219
	simple quinones	180-187
$R-COOH$ $R-COO^-$	carboxylic acids and salts	168-181
$R-COO-R'$ $Ar-COO-Ar$ $\text{---}COO\text{---}$	aliphatic esters esters with conjugation in the acid or alcohol moiety	169-176 164-169
	isotones	170-176
$\text{---}CO-O-CO\text{---}$ $\text{---}CON\text{---}$	anhydrides, all classes amides, all classes including lactams	165-175 163-179

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

$X-C-C-C-C$   
 $\alpha \quad \beta \quad \gamma$

X	$\alpha$ -shift			$\beta$ -shift	$\gamma$ -shift
	$X-CH_2-$ 1°	$X-CH-$ R 2° or	$X-\overset{\overset{R}{ }}{C}-$ R 3°		
$-CH_3$	9	6	3	9	-3
$-R$ : see table 3.11					
axial $-CH_3$	1	-	-	5	-6
equatorial $-CH_3$	6	-	-	9	0
(in cyclohexanes)					
$-CH=CH_2$	22	16	12	7	-1
$-C\equiv CH$	4	-	-	3	-3
$-C_6H_5, -Ar$	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
$-NH_2, -NHR, -NR_2$	29	24	18	11	-4
$-NO_2$	62	-	-	3	-5
$-NHCOR, -NRCOR$	10	-	-	0	0
$-NH_3^+$	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
$-SO_2H, -SO_2N<$	50	-	-	3	0

# Data Table for <sup>13</sup>C NMR Spectroscopy

TABLE 5.1

<sup>13</sup> C Atoms	Shift (ppm) (Δ)
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 CH<sub>3</sub> group bound to a R<sub>2</sub>CH group and to a R<sub>3</sub>C group, respectively. The notation 2° (3°) denotes a RCH<sub>2</sub> group bound to a R<sub>2</sub>CH group, and so on.

TABLE 5.2

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 <sub>3</sub> )	
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 <sub>3</sub> )	

Table 3.14 δ values for the carbons in aromatic and heterocyclic molecules (sp<sup>2</sup> and sp<sup>3</sup> carbons listed)

benzene	naphthalene	anthracene	phenanthrene					
tetraлин	indane	acenaphthene	acenaphthylene					
furan	thiophene	pyrrole	pyridine					
tetrahydrofuran, THF	tetrahydrothiophene	pyrrolidine	piperidine					
imidazole	pyrazole	GLUCOSE						
		α - OH axial β - OH equatorial						
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	
		α -	97	75	27	70	77	62
		β -	93	72	74	70	72	62

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	
	Terminal	Internal	Terminal	Internal
CH <sub>3</sub>	+ 9	+ 6	+10	+ 8
CH=CH <sub>2</sub>	+20		+ 6	
C≡CH	+ 4.5		+ 5.5	
COOH	+21	+16	+ 3	+ 2
COO <sup>-</sup>	+23	+20	+ 3	+ 3
COOR	+20	+17	+ 3	+ 2
COCl	+33	+28	+ 3	+ 2
CONH <sub>2</sub>	+22	+ 2.5		
CONH <sub>2</sub>	+22	+24	+ 1	+ 1
CONR <sub>2</sub>	+30			
CHO	+31		0	
Phenyl	+23	+17	+ 9	+ 7
OH	+58	+41	+10	+ 8
OR	+58	+51	+7	+ 3
OCOR	+51	+45	+ 6	+ 5
NH <sub>2</sub>	+29	+24	+11	+10
NHR	+26	+24	+ 8	+ 6
NRR <sub>2</sub>	+37	+31	+ 8	+ 6
NR <sub>2</sub>	+42		+ 6	
NR <sub>2</sub>	+31		+ 5	
NO <sub>2</sub>		+57	+ 4	+ 4
CN	+ 4	+ 1	+ 3	+ 3
SH	+11	+11	+12	+11
SR	+20		+ 7	
F	+68	+63	+ 9	+ 6
Cl	+31	+32	+11	+10
Br	+20	+25	+11	+10
I	- 6	+ 4	+11	+12

\*Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift values compiled from Table 5.1. Source: F. W. Wehrli, A. P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., London: Heyden, 1981.

