



PR-003-1104001

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

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

August - 2020

C - 401 : Advanced Spectroscopy

(All Branches)

Faculty Code : 003

Subject Code : 1104001

Time :  $2\frac{1}{2}$  Hours]

[Total Marks : 70

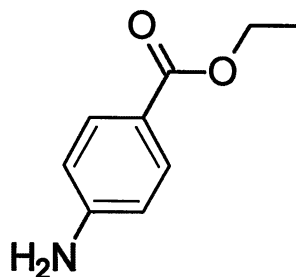
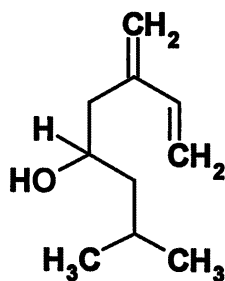
**Instruction :** All questions are compulsory and carry equal marks.

1 Answer the following : (Any Seven) 14

- Give the characteristic properties of Raman lines..
- Give the name of mass-analyzer in mass spectrometry and explain Ion-trap mass analyzer.
- Discuss types of UV absorption shift.
- Differentiate Raman and IR spectra.
- Enlist the application of NIR Spectroscopy.
- Discuss the advantage of  $^{13}\text{C}$ MR spectroscopy.
- Give the full-form of HMQC, HMBC, NOESY and TOCSY.
- Draw the  $^1\text{H}$ NMR spectrum of p-Nitro toluene with splitting of the signals.
- Enlist the factors affecting the g-value.
- Write the principle of Mass-spectroscopy.

2 Answer the following : (Any Two) 14

- Draw the DEPT-90 and 135 for the following :



- (b) Sketch the NMR spectrum of AMX and  $A_2B_2$  system with suitable example.
- (c) Describe HSQC 2D NMR technique with suitable example.

**3** Answer the following : **14**

- (a) Compare and differentiate NIR and IR spectrophotometer.
- (b) Determine the molecular formula of a compound which gives the data in its mass spectrum.

m/z	120	130	131	132	133	134	135	136	137
Rel. abundance	30	100	31	98	12	32	1.7	3.5	0.07

**OR**

- 3** (a) Draw the schematic diagram of Raman spectrophotometer and discuss it in detail.
- (b) Discuss the EPR spectrum of  $CH_3$  radical.

**4** Answer the following : **14**

- (a) Calculate  $^{13}C$ NMR chemical shifts for the following :
- (i)  $HO-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$
- (ii)  $CH=C-CH_2-CH_2-CH_2-CH_3$
- (iii) 2-Ethylexanol
- (b) Discuss the "g" value for octahedral complex with example.

**5** Answer the following : (Any Two) **14**

- (a) Discuss the (n+1) rule, its failure and solution with suitable example.
- (b) Give the application of Raman spectra.
- (c) Draw the single beam UV-spectrophotometer and functioning of it.
- (d) What are the empirical rules for calculation of absorption maxima in case of polyenes?

# Data-table for the calculation of $^{13}\text{C}$ Chemical shift

**TABLE 5.1**

$^{13}\text{C}$ Atoms	Shift (ppm) ( $\Delta$ )
$\alpha$	+9.1
$\beta$	+9.4
$\gamma$	-2.5
$\delta$	+0.3
$\epsilon$	+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

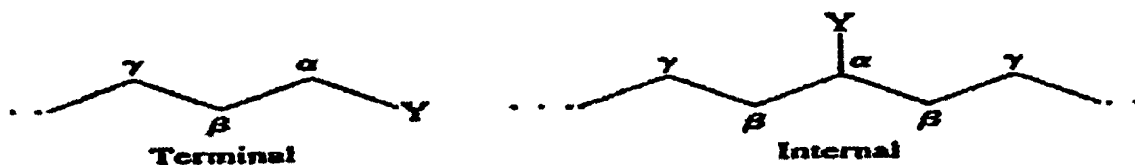
<sup>a</sup>The notations  $1^\circ (3^\circ)$  and  $1^\circ (4^\circ)$  denote a  $\text{CH}_3$  group bound to a  $\text{R}_2\text{CH}$  group and to a  $\text{R}_3\text{C}$  group, respectively. The notation  $2^\circ (3^\circ)$  denotes a  $\text{RCH}_2$  group bound to a  $\text{R}_2\text{CH}$  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- $\text{CH}_3$ )	
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- $\text{CH}_3$ )	

TABLE 5.3

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



Y	$\alpha$		$\beta$		$\gamma$
	Terminal	Internal	Terminal	Internal	
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
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 3.14  $\delta$  values for the carbons in aromatic and heterocyclic molecules ( $sp^2$  and  $sp^3$  carbons listed)


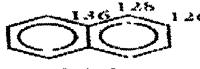



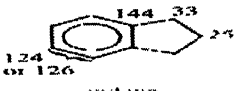
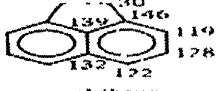

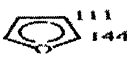
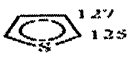
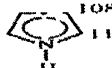
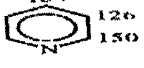
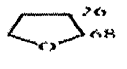
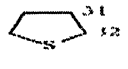
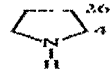

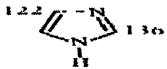
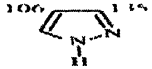
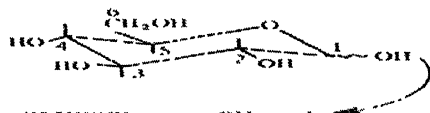
 benzene 128	 naphthalene 136 128 126	 anthracene 127 128 125	 phenanthrene 122 129 127 133																					
 tetralin 129 126 137 30 24	 indane 144 33 27 124 or 126	 acenaphthene 129 146 119 128 132 122 178	 acenaphthylene 128 138 124 128 128 127																					
 furan 111 144	 thiophene 127 125	 pyrrole 108 118	 pyridine 129 126 150																					
 tetrahydrofuran, THF 26 68	 tetrahydrothiophene 31 32	 pyrrolidine 36 47	 piperidine 26 27 48																					
 imidazole 122 136	 pyrazole 106 135	 GLUCOSE $\alpha$ - OH axial $\beta$ - OH equatorial																						
			<table border="0"> <tbody> <tr> <td></td> <td>C<sub>1</sub></td> <td>C<sub>2</sub></td> <td>C<sub>3</sub></td> <td>C<sub>4</sub></td> <td>C<sub>5</sub></td> <td>C<sub>6</sub></td> </tr> <tr> <td><math>\alpha</math></td> <td>97</td> <td>75</td> <td>77</td> <td>70</td> <td>77</td> <td>62</td> </tr> <tr> <td><math>\beta</math></td> <td>93</td> <td>72</td> <td>74</td> <td>70</td> <td>72</td> <td>62</td> </tr> </tbody> </table>		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	$\alpha$	97	75	77	70	77	62	$\beta$	93	72	74	70	72	62
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>																		
$\alpha$	97	75	77	70	77	62																		
$\beta$	93	72	74	70	72	62																		

TABLE 5.9

Chemical Shifts of the Aromatic Region Also for Monosubstituted Benzenes (ppm from Tetramethylsilane) Downloaded by Caron Atomol Substitents in part 1, 11/18/2016 10:45 AM

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)
CCl	+4.6	+2.9	+0.6	+7.0	168.5
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 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  $C=O$ )




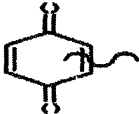
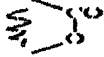
$R-CHO$ $Ar-CHO$	aliphatic aldehydes	200-205
$\text{>C=O}$ $R-CO-R'$	aryl and conjugated aldehydes* dialkyl ketones	190-194 205-218
$Ar-CO-R$ $Ar-CO-Ar$ $\text{>C=O}$	aryl and conjugated ketones	196-199
	cyclohexanone derivatives	209-213
	cyclopentanone derivatives	214-220
	bicyclic ketones	215-219
	simple quinones	180-187
$R-COOH$ $R-COO^-$	carboxylic acids and salts	166-181
$R-COO-R'$ $Ar-COOAr$ $\text{>C=O}$	aliphatic esters esters with conjugation in the acid or alcohol moiety	169-176 164-169
	lactones	170-178
$-CO-O-CO-$ $-CON-$	anhydrides, all classes amides, all classes including lactams	163-173 162-170

Table 3.17 (continued)

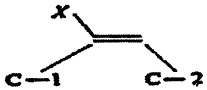
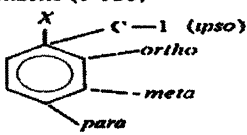
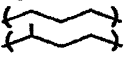

$-CO-NH-CO-$	imides	168-184
$-COCl$	acyl chlorides, all classes	167-172
$-NH-CO-NH-$	ureas	153-163
$-O-CO-O-$	carbonates	152-156
$R-C\equiv N$	nitriles	114-124
$R-N\equiv C$	isonitriles	156-158
$R-N=C=O$	isocyanates	120-130
$>C=NOH$	oximes	148-158
$>C=NNHCONH_2$	semicarbazones	158-160
$>C=N-NH-$	hydrazones	145-149
$>C=N-R$	imines	157-175

\*Note:  8 177


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

$X-\underset{\alpha}{C}-\underset{\beta}{C}-\underset{\gamma}{C}-C$							
X	----- ----- ----- ----- -----					-----	-----
	α-shift					β-shift	γ-shift
	$X-CH_2-$	$X-\underset{\substack{  \\ R}}{CH}-$	$X-\underset{\substack{  \\ R}}{C}-$	$X-\underset{\substack{  \\ R}}{C}-$	$X-\underset{\substack{  \\ R}}{C}-$		
	1°	or	2°	or	3°		
—CH <sub>3</sub>	9		6		3	9	-3
· R: see table 3.11							
axial —CH <sub>3</sub>	1					5	-6
equatorial —CH <sub>3</sub>	6				—	9	0
(in cyclohexanes)							
—CH=CH <sub>2</sub>	22		16		12	7	-2
—C≡CH	4				—	3	3
—C <sub>6</sub> H <sub>5</sub> , —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 <sub>2</sub> , —NHR, —NR <sub>2</sub>	29		24		18	11	4
—NO <sub>2</sub>	62					3	-5
—NHCOR, —NRCOR	10					0	0
—NH <sub>3</sub> <sup>+</sup>	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 <sub>2</sub> H, —SO <sub>2</sub> N<	50					3	0

**Table 3.16** Influence of functional group X on the chemical shift positions ( $\delta$ ) of nearby carbons in alkene groups and benzene rings

Base values	ethylene ( $\delta$ 123)		and	benzene ( $\delta$ 128)			
							
	Alkenes		Benzenes				
	C-1	C-2	C-1 (ipso)	ortho	meta	para	
-CH <sub>3</sub>	10	-8	9	0	0	-2	
R, 	16	-8	15	0	0	-2	
R, 	23	-8	21	0	0	-2	
-CH=CH <sub>2</sub>	15	-6	9	0	0	-2	
-CH≡CH	-	-	-6	4	0	0	
-C <sub>6</sub> H <sub>5</sub> , -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	
-NH <sub>2</sub>	.	..	18	-13	1	-10	
-NHR	..	..	20	-14	1	-10	
-NR <sub>2</sub>	..	..	22	16	1	-10	
-NO <sub>2</sub>	22	-1	20	-5	1	6	
-NHCO <sub>R</sub> , -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	
-SO <sub>3</sub> H, -SO <sub>2</sub> N<			16	0	0	4	
-PMe <sub>2</sub>	..	-	14	1.6	0	-1	
-Ph <sub>2</sub>	.	-	9	5	0	0	

**Table 3.13**  $\delta$  values for the carbons in alkynes (sp)

REPRESENTATIVE ALKYNES	
acetylene (ethyne) C <sub>2</sub> H <sub>2</sub> $\delta$ 72	
R-C≡CH 83 66	R-C≡C-R' 82
C <sub>6</sub> H <sub>5</sub> -C≡CH 85 78	C <sub>6</sub> H <sub>5</sub> -C≡C-C <sub>6</sub> H <sub>5</sub> 90
C <sub>6</sub> H <sub>5</sub> -C≡C-R 86	
EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS	
Chemical shift ( $\delta$ ) = 72 + $\Sigma$ (increments for carbon atoms)	
	
increments	+0.5 0 +5 +7 6 +2 -1 +0.5
	base value 72