



BBA-003-1104001

Seat No. _____

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

June / July - 2021

C-401 : Chemistry

(Advance Spectroscopic Techniques) (All Branches)

(New Course)

Faculty Code : 003

Subject Code : 1104001

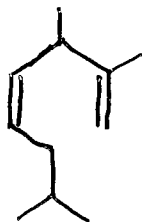
Time : $2\frac{1}{2}$ Hours]

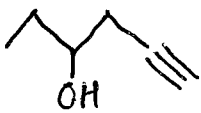
[Total Marks : 70

- Instructions :** (1) All questions carry equal marks.
(2) Attempt any five questions out of ten.

1 Answer the following : **14**

- (a) Why mass spectrometers operate at very low pressure ?
- (b) Write the full form of following techniques :
 - (i) HMBC
 - (ii) NOESY
 - (iii) HETCOR
 - (iv) DEPT
- (c) Show the possible electronic transition of acetone and benzaldehyde.
- (d) Draw the ^1H NMR spectrum of vinyl acetate and show the splitting pattern of signals.
- (e) Draw the hypothetical mass spectrum and explain the molecular ion peak.
- (f) Differentiate Raman and IR spectra.
- (g) Draw the ^{13}C NMR of following compound at 135° rotation.



- 2 Answer the following : 14
- Give the principle of Raman spectroscopy.
 - Discuss the limitations of ESR spectroscopy.
 - Give the types of UV absorption shifts.
 - Write the name of reference standard used in NMR spectroscopy in aqueous and organic solvents.
 - Write a note on COSY-2D NMR techniques.
 - Enlist the factors affecting the chemical shift value in PMR.
 - Explain nitrogen rule and their importance in the interpretation of mass spectrum.
- 3 Answer the following : 14
- Sketch the NMR spectrum of AMX and A_2B_2 system with suitable example.
 - Describe HSQC 2D NMR technique with suitable example.
- 4 Answer the following : 14
- Discuss quantum mechanical theory of Raman effect.
 - What is hyperfine splitting in ESR spectroscopy ?
- 5 Answer the following : 14
- What is mass analyzer ? Give their name and explain with diagram of quadrupole mass analyzer.
 - Explain in detail electronic ionization and chemical ionization with benefits and limitations.
- 6 Answer the following : 14
- Calculate the ^{13}C NMR chemical shift of followings :
 - $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
 - 
 - How many ^{13}C NMR signals are possible for the following compounds:
 - o-xylene
 - 1,2-dichlorobenzene
 - p- NO_2 -benzaldehyde
 - m-cyano chlorobenzene

- 7 Answer the following : 14
(a) Enlist the applications of NIR.
(b) Discuss the Popal notation in detail.
- 8 Answer the following : 14
(a) Discuss the applications of UV spectroscopy.
(b) Discuss Woodward – Fisher rules for the calculation of absorption maxima in dienes, trienes and polyenes.
- 9 Answer the following : 14
(a) Give the application of Raman spectroscopy.
(b) Draw the electronic energy level diagram and discuss electronic transitions in detail.
- 10 Answer the following : 14
(a) Discuss the ESR spectrum of H_2 .
(b) Discuss the classical theory of Raman effect.
-

Data Table for ¹³C NMR Spectroscopy

TABLE 5.1

¹³ 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 CH₃ group bound to a R₂CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₂CH 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 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 3.14 δ values for the carbons in aromatic and heterocyclic molecules (sp² and sp³ carbons listed)

benzene	naphthalene	anthracene	phenanthrene
tetralin	indane	acenaphthene	acenaphthylene
furan	thiophene	pyrrole	pyridine
tetrahydrofuran, THF	tetrahydrothiophene	pyrrolidine	piperidine
imidazole	pyrazole	GLUCOSE	
		α - OH axial β - OH equatorial	
		C ₁ C ₂ C ₃ C ₄ C ₅ C ₆	
		α - 97 75 77 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	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
CH=CH ₂	+20	+6	+6	+8	-0.5
C≡CH	+4.5	+3	+5.5	+8	-3.5
COOH	+21	+16	+3	+2	-2
COO-	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28	+2.5	+2	-0.5
CONH ₂	+22	+24	+1	+1	-2
OR	+30	+24	+6	+1	-2
CHO	+31	+24	+1	+1	-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	+36	+6	+6	-3
NR ₃ ⁺	+31	+25	+5	+5	-7
NO ₂	+63	+57	+4	+4	-3
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4
SR	+20	+20	+7	+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 3.2 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 ₂), 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 ₂ 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 ₂ 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	
S(CH ₃) ₂	+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 δ values for the carbons in carbonyl groups and some other multiple-bonded environments (solvent shifts, ± 2 ppm, are commonly observed for $C=O$)





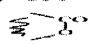
$R-CHO$	aliphatic aldehydes	200-205
$Ar-CHO$	aryl and conjugated aldehydes*	190-194
$R-CO-R'$	dialkyl ketones	205-218
$Ar-CO-R$	aryl and conjugated ketones	196-199
$Ar-CO-Ar'$		
	cyclohexanone derivatives	209-213
	cyclopentanone derivatives	214-220
	bicyclic ketones	215-219
	simple quinones	180-187
$R-COOH$	carboxylic acids and salts	166-181
$R-COO^-$		
$R-COO-R'$	aliphatic esters	169-176
$Ar-COOR$	esters with conjugation to the acid or alcohol moiety	164-169
	lactones	170-178
$-CO-O-CO-$	anhydrides, all classes	163-175
$-CON<$	amides, all classes including lactams	162-179

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

X	$X-C-C-C-C$ $\alpha \quad \beta \quad \gamma$			β -shift	γ -shift
	α -shift				
	$X-CH_2-$ 1°	$X-CH-$ R 2° or	$X-C-$ 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	-2
$-C\equiv CH$	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
$-SO_3H, -SO_2N<$	50	-	-	3	0