647510 **MSC4OrE1404A** **Seat No :_____**

M.Sc.(Chem.) Semester - 4 (*CBCS*) Examination
March/April - 2026 (As Per Syllabus Year June-2019)
Modern Spectroscopy (Elective)

Time: 2:30 Hours **Marks:70**

Instructions:

1. All questions are compulsory.
2. Figures to the right indicate marks.
3. Standard data sheet for IR and NMR Spectroscopy attached with this paper

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Q.1(A) Answer the following Question. **(04)**

(1) Discuss different types of shifts observed in UV Spectroscopy with examples.

Q.1(B) Answer any two questions out of three. **(10)**

(1) Give applications of UV spectroscopy.

(2) State and Derive Lambert-Beer's Law.

(3) Draw schematic diagram of double beam UV spectrophotometer and discuss monochromator in details.

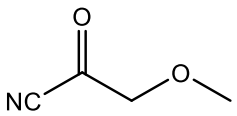
Q.2(A) Answer the following Question. **(04)**

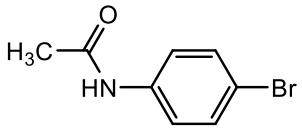
(1) Discuss various solid sample handling techniques used in IR spectroscopy.

Q.2(B) Answer any two questions out of three. **(10)**

(1) Explain fundamental modes of vibration in IR spectroscopy.

(2) Write possible IR frequencies for following examples:

i) 

ii) 

(3) Predict the total number of fundamental bands, stretching and bending vibration in following molecules:

1. NH_3
2. H_2O
3. CO_2

Q.3(A) Answer the following Question. **(04)**

(1) Discuss McLafferty rearrangement with mechanism and give 2 examples.

Q.3(B) Answer any two questions out of three. **(10)**

(1) Discuss any two ionization techniques used in Mass Spectroscopy.

(2) Discuss fragmentation pattern for 2-methylpentane.

(3) Explain Nitrogen rule and Steven's rule with examples.

Q.4(A) Answer the following Question. **(04)**

(1) Discuss Instrumentation of NMR Spectrophotometer with schematic diagram.

Q.4(B) Answer any two questions out of three. **(10)**

(1) Discuss coupling constant in details.

(2) Explain Spin-Spin splitting and Pascal's triangle with suitable example.

(3) An organic compound with MF: $C_6H_{10}O_4$ furnished the following spectral data:
UV: No significant absorption above 210 nm.
IR: 2950,1765 and 1050 cm^{-1}
PMR: δ 1.5 (3H, d), 2.2 (6H, s) and 6.9 (1H, q)
CMR (Off-resonance decoupled): One singlet at δ170, one doublet and two quartets
MS: Prominent peaks at m/e 146, 87 and 43.
Deduce the structure of the compound and explain the spectral data.

Q.5(A) Answer the following Question. **(04)**

(1) What is the principle of Fourier transform? Calculate chemical shift of n-pentane in CMR spectroscopy.

Q.5(B) Answer any two questions out of three. **(10)**

(1) Find out molecular formula and deduce the structure of compound from the given analytical data and interpret it.
MW: 158 g/mol, Elements: C-60.8%, H-8.8%.
IR: 2910, 1830, 1750, 1410, 1385, 1365, 1225 cm^{-1}
PMR: a/septet/2H/2.73 δppm, b/doublet/12H/1.20 δppm.
CMR (Proton noise decoupled): 3 Signals (δppm: 18.8, 35.6 and 173.2)

(2) Calculate the chemical shift value of carbon of following compounds:
a) 3-methylpentane b) Benzoic acid c) p-xylene

(3) Indicate the number of signals and multiplicity of Isopropyl benzene and Ethylbenzene in off-resonance decoupled ^{13}C NMR spectra.

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Standard Data Sheet for IR spectroscopy

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Alkanes and Alkyls	2850-3000	s	C-H stretch
	1450-1470	s	C-H bend
	1370-1390	m	CH_3 C-H bend
	1365 + 1395 (two bands)	m	$-CH(CH_3)_2$ or $-(CH_3)_3$ bend
	715-725	w	$-(CH_2)_n$ bend
Alkenes	3020-3140	w-m	=C-H stretch
	1640-1670	vw-m	C=C stretch
$RCH=CH_2$	910 + 990 (two bands)	m + s	=C-H bend
$RR'C=CH_2$	885-895	s	=C-H bend
cis-RCH=CHR'	665-730	m-s, broad	=C-H bend
trans-RCH=CHR'	960-980	s	=C-H bend
RCH=CR'R"	790-840	s	=C-H bend
Alkynes			
R-C≡C-H	3265-3335	s, sharp	≡C-H stretch
	2100-2140	m	C≡C stretch
	610-700	s, broad	≡C-H bend
R-C≡C-R'	2190-2260	vw-w	C≡C stretch
Alkyl halides			
R-F	1000-1350	vs	C-F stretch
R-Cl	750-850	s	C-Cl stretch
R-Br	500-680	s	C-Br stretch
R-I	200-500	s	C-I stretch
Alcohols	3300-3400	s, broad	O-H stretch
$C=C-CH_2-OH$	1035-1050	m-s	C-O stretch
$R-CH_2-OH$ (1^o) or C=C-CH(R)-OH	1050-1085	m-s	C-O stretch
RR'CH-OH (2^o) or C=C-CRR'-OH	1085-1125	m-s	C-O stretch
RR'R"C-OH (3^o)	1125-1205	m-s	C-O stretch
Ar-O-H	1180-1260	m-s	C-O stretch
Ethers			
R-O-R'	1085-1150	s	C-O-C stretch
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch
Aldehydes	2700-2725	m	H-C=O stretch
R-CH=O	1720-1740	s	C=O stretch
C=C-CH=O or Ar-CH=O	1685-1710	s	C=O stretch
Ketones			
RR'C=O	1710-1720	s	C=O stretch
C=C-C(O)-R	1665-1685	s	C=O stretch
Ar-C(O)-R	1675-1695	s	C=O stretch
four member cyclic	1770-1780	s	C=O stretch
five member cyclic	1740-1755	s	C=O stretch
six member cyclic	1710-1720	s	C=O stretch

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Carboxylic Acids	2500-3500	s, broad	O-H stretch
R-C(O)-OH	1710-1715	s, broad	C=O stretch
C=C-C(O)-OH or Ar-C(O)-OH	1680-1710	s	C=O stretch
Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310	s-vs	O=C-O-C stretch
R-C(O)-O-R	1735-1750	s	C=O stretch
C=C-C(O)-O-R or Ar-C(O)-O-R	1715-1730	s	C=O stretch
R-C(O)-O-Ar	1760-1790	s	C=O stretch
Acyl Chlorides			
R-C(O)-Cl	1785-1815	s	C=O stretch
Ar-C(O)-Cl	1770-1800	s	C=O stretch
Anhydrides			
R-C(O)-O-C(O)-R	~1750 + ~1815	s,s	C=O symmetric
Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
Nitriles			
R-C≡N	2240-2260	m-s	C≡N stretch
C=C-C≡N or Ar-C≡N	2220-2240	s	C≡N stretch
Amines			
$R-NH_2$	~3400 + ~3500 (two bands)	w	N-H symmetric & asym. stretch
	1580-1650	w-m	N-H bend
RR'N-H	3310-33350	w	N-H stretch
Amides			
$R-C(O)-NH_2$	3200-3400 and 3400-3500 (two bands)	w-m	N-H symmetric & asym. stretch
	1650-1690	s, broad	C=O stretch
	1590-1655	m-s	N-H bend
R-C(O)-NH-R	3400-3500	w-m	N-H stretch
	1640-1690	s, broad	C=O stretch
	1510-1560	m-s	N-H bend
R-C(O)-NR'R"	1630-1680	m-s	C=O stretch
Nitro Compounds			
$R-NO_2$	~1550 and ~1370	s s	N-O symmetric & asym. stretch
$C=C-NO_2$ or $Ar-NO_2$	~1525 and ~1335 (both two bands)	s s	N-O symmetric & asym. stretch
Aromatic Compounds	3010-3100	m	Ar C-H stretch
	1450-1600 (two to four bands)	m-s sharp	ring C=C stretch
monosubstituted	730-770 and 690-710 (two bands)	s s	C-H bend C-H bend
o-disubstituted	735-770	s	C-H bend
m-disubstituted	750-810 and 690-710	s s	C-H bend C-H bend
p-disubstituted	810-840	s	C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

^{13}C chemical shifts for some linear and branched-chain alkanes

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
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
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	

Olefinic carbons	
Substituent carbon C	**Correction**
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	+1.5
z *(cis)*	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+9	+6	+10	+8	−2
$HC{=}CH_2$	+20		+6		−0.5
$C{\equiv}CH$	+4.5		+5.5	+2	−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
NH_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

Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm)

Substituent	C-1	C-2 (*ortho*)	C-3 (*meta*)	C-4 (*para*)
H	0.0	0.0	0.0	0.0
CH_3	+9.3	+0.7	–0.1	–2.9
CH_3CH_2	+15.6	–0.5	0.0	–2.6
$CH(CH_3)_2$	+20.1	–2.0	0.0	–2.5
$HC{=}CH_2$	+9.1	–2.4	+0.2	–0.5
C_6H_5	+12.1	–1.8	–0.1	–1.6
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
OH	+26.6	–12.7	+1.6	–7.3
OCH_3	+31.4	–14.4	+1.0	–7.7
CHO	+8.2	+1.2	+0.6	+5.8
$COCH_3$	+7.8	–0.4	–0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	–16.0	+3.6	+0.6	+4.3
NO_2	+19.6	–5.3	+0.9	+6.0
NH_2	+19.2	–12.4	+1.3	–9.5
$NHCOCH_3$	+11.1	–9.9	+0.2	–5.6
$COOCH_3$	+2.0	+1.2	–0.1	+4.8

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