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

M.Sc.(Chem.) Semester - 4 (*CBCS*) Examination
March/April - 2024 (NEW COURSE)
Modern Spectroscopy (Elective)

Time: 02:30 Hours **Marks: 70**

Instructions:

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

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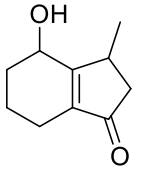
Q.1 (A) Answer the following. **(04)**

(1) Draw schematic diagram of double beam UV spectrophotometer.

(2) Calculate the Wavelength (λmax) of.



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

(1) Answer the following:

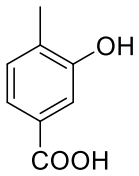
(a) Discuss Red and Blue Shift with example.

(b) Discuss Auxochorme and Chromophore with example.

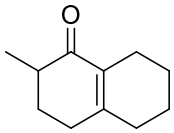
(2) State and Derive Lambert-Beer's Law.

(3) Calculate the Wavelength (λmax) of following:

(a)



(b)



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

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

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

(1) Discuss overtone, fermi-resonance and combination tones with example.

(2) Discuss instrumentation of IR spectrophotometer with schematic diagram.

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

1. CH_4
2. Acetylene
3. CO_2

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

(1) Define the following terms:

a) Base peak
b) Parent ion
c) Metastable ion
d) Rearrnagement ion

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

(1) Discuss instrumentation of Mass Spectrophotometer with schematic diagram.

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

(3) Explain Mclafferty rearrangement in Mass spectroscopy with example.

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

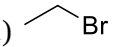
(1) Draw the structure of each of the following compounds which meets the given requirements in its PMR spectrum:

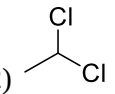
a) $C_4H_{10}O$; one singlet, one doublet and one septet
b) $C_4H_8Cl_2O$; two triplets
c) $C_3H_3Cl_5$; one doublet and one triplet
d) $C_5H_8Cl_4$; one singlet

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

(1) Discuss shelding and deshelding effect with examples.

(2) Predict Spin-Spin splitting in following examples and illustrate Pascal's triangle.

(1) 

(2) 

(3) An organic compound having MF: $C_6H_{10}O_2$ furnished the following spectral data:

IR: 3010, 2905, 1720, 1660, 1450, 1380 and 1280 cm-1
PMR: δ 1.1 (3H, t), 1.6 (3H, d), 4.2 (2H, q), 5.8 (1H, m) and 6.7 (1H, d, J = 16 Hz)
CMR: δ 14, 19, 61, 144, 146, 166

Deduce the structure of the compound and explain the spectral data

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

(1) Calculate the chemical shift value of carbon of following compounds:

a) 2-flouropentane b) 3-bromotoluene

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

(1) Deduce the structure of compound from the given analytical data and explain it.

MF: $C_{11}H_{14}O_2$
IR: 1715 cm^{-1}
PMR: δ 2.1 (3H, s), 2.6 (2H, t), 2.8 (2H, t), 3.8 (3H, s), 6.8 (2H, d, *J* = 8.5 *Hz*), 7.1 (2H, d, *J* = 8.5 *Hz*).
CMR: δ 21, 31, 34, 62, 127, 129, 136, 138, 173

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

(3) Deduce the structure of compound from the given spectral data and explain it.
MF: $C_{10}H_{10}O$
IR: 3030, 2950, 1710, 1480, 1380, 750 and 700 cm^{-1}
PMR: (a/singlet/3H/7.8 τppm), (b/doublet/1H/3.8 τppm/*J* = 16.5 *Hz)*, (c/doublet/1H/3.2 τppm/*J* =16.5 *Hz*), (d/multiplet/5H/2.2-2.8 τppm),

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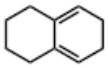
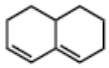
UV Spectroscopy

Woodward Fieser Rules for Dienes

	 *s-trans*	 homoannular (cisoid)	 heteroannular (transoid)
base values:	**217 nm**	**253 nm**	**214 nm**

Increments:

For each additional conjugated double bond		+ 30 nm
For each exocyclic double bond		+ 5 nm
For each alkyl group or Ring Residue		+ 5 nm
For each of the following groups:		
	- OR	+ 6 nm
	- O(C=O)R	+ 0 nm
	- Cl	+ 6 nm
	- Br	+ 6 nm
	- SR	+ 30 nm
	- NR_2	+ 60 nm
	- Ph	+ 60 nm

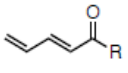
not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λmax is used.

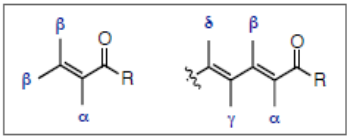
Solvent Correction	nm
H_2O	- 8
EtOH	0
$CHCl_3$	+ 1
Dioxane	+ 5
Et_2O	+ 7
Hydrocarbon	- 11

UV Spectroscopy

Woodward Fieser Rules for Enones

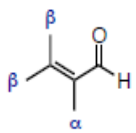
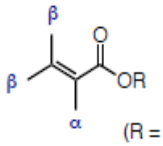
	 acyclic enone	 6-membered ring enone	 5-membered ring enone	 acyclic dienone
base values:	**215 nm**	**215 nm**	**202 nm**	**245 nm**

Increments:		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:	- OH	+ 35 nm	+ 30 nm		+ 50 nm
	- OR	+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
	- O(C=O)R	+ 6 nm	+ 6 nm		+ 6 nm
	- Cl	+ 15 nm	+ 12 nm		
	- Br	+ 25 nm	+ 30 nm		
	- SR	+ 30 nm	+ 85 nm		
	- NR_2	+ 60 nm	+ 95 nm		



UV Spectroscopy

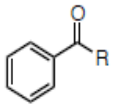
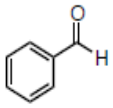
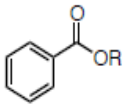
Woodward Fieser Rules for Other Conjugated Carbonyls

	 aldehydes	 (R = H or R') carboxylic acid or ester
Base Values		
unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm

as for enones, solvent correction is also relevant

UV Spectroscopy

Woodward Fieser Rules for Benzoyl Derivatives

	 aryl ketones (R = alkyl)	 benzaldehydes	 benzoic acids and esters
base values:	**246 nm**	**250 nm**	**230 nm**
Increments:	ortho	meta	para
For each alkyl group or RR	+ 3 nm	+ 3 nm	+ 10 nm for RR +7 nm
For each OH or OR (R = alkyl)	+ 7 nm	+ 7 nm	+ 25 nm
For each $O^{\ominus}$	+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:			
- Cl	+ 0 nm	+ 0 nm	+ 10 nm
- Br	+ 2 nm	+ 2 nm	+ 15 nm
- NH_2	+ 13 nm	+ 13 nm	+ 58 nm
- $NH(C=O)CH_3$	+ 20 nm	+ 20 nm	+ 45 nm
- $NHCH_3$			+ 73 nm
- $N(CH_3)_2$	+ 20 nm	+ 20 nm	+ 85 nm

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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