

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

Time: 02:30 Hours

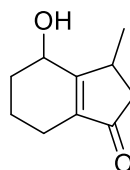
Marks: 70

Instructions:

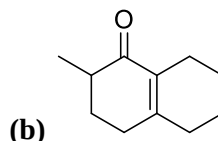
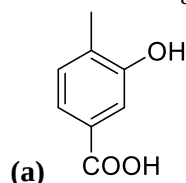
1. All questions are compulsory.
2. Figures to the right indicate marks.
3. Standard data sheet for UV, IR and NMR Spectroscopy attached with this paper

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

- (1) Draw schematic diagram of double beam UV spectrophotometer.
- (2) Calculate the Wavelength ($\lambda_{\max}$) 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 Auxochrome and Chromophore with example.
- (2) State and Derive Lambert-Beer's Law.
- (3) Calculate the Wavelength ($\lambda_{\max}$) of following:

**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) Rearrangement ion

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

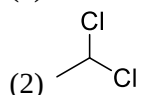
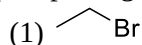
- (1) Discuss instrumentation of Mass Spectrophotometer with schematic diagram.
- (2) Discuss any two ionization techniques used in Mass Spectroscopy.
- (3) Explain McLafferty rearrangement in Mass spectroscopy with example.

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:
- $C_4H_{10}O$; one singlet, one doublet and one septet
 - $C_4H_8Cl_2O$; two triplets
 - $C_3H_3Cl_5$; one doublet and one triplet
 - $C_5H_8Cl_4$; one singlet

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

- (1) Discuss shielding and deshielding effect with examples.
- (2) Predict Spin-Spin splitting in following examples and illustrate Pascal's triangle.



- (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:
- 2-fluoropentane
 - 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).

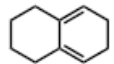
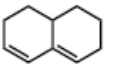
CMR: δ 21, 31, 34, 62, 127, 129, 136, 138, 173

- (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 τ ppm), (b/doublet/1H/3.8 τ ppm/ $J = 16.5$ Hz), (c/doublet/1H/3.2 τ ppm/ $J = 16.5$ Hz), (d/multiplet/5H/2.2-2.8 τ ppm),

Standard Data Sheet for UV spectroscopy

UV Spectroscopy

Woodward Fieser Rules for Dienes

			
	<i>s-trans</i>	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

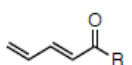
not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λ_{max} is used.

UV Spectroscopy

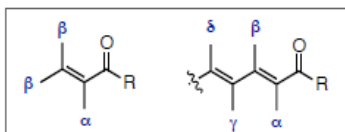
Woodward Fieser Rules for Enones

Solvent Correction	nm
H ₂ O	- 8
EtOH	0
CHCl ₃	+ 1
Dioxane	+ 5
Et ₂ O	+ 7
Hydrocarbon	- 11

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

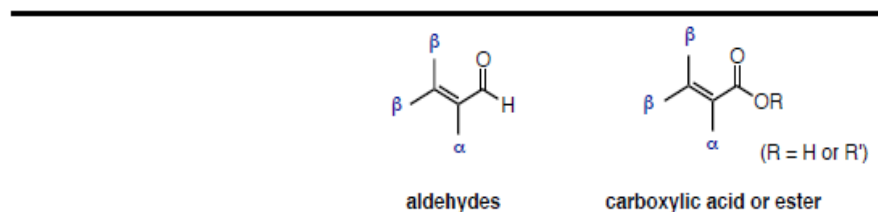
Increments:

	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



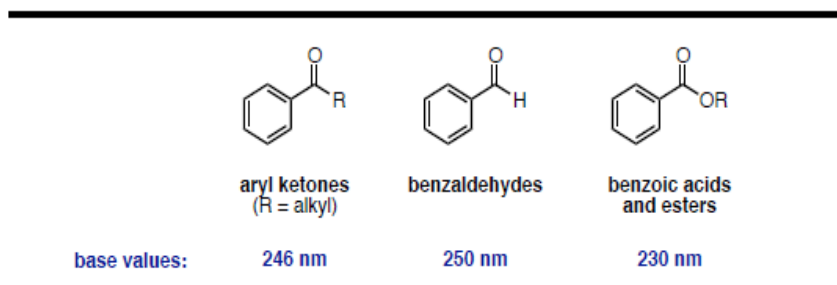
Base Values

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



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^-	+ 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	Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment
Alkanes and Alkyls	2850-3000 1450-1470 1370-1390 1365 + 1395 (two bands) 715-725	s s m m w	C-H stretch C-H bend CH ₃ C-H bend -CH(CH ₃) ₂ or -(CH ₃) ₃ bend -(CH ₂) _n bend	Carboxylic Acids	2500-3500 1710-1715 1680-1710	s, broad s, broad s	O-H stretch C=O stretch C=O stretch
Alkenes	3020-3140 1640-1670 910 + 990 (two bands)	w-m vw-m m + s	=C-H stretch C=C stretch =C-H bend	Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310 1735-1750 1715-1730 1760-1790	s-vs s s s	O=C-O-C stretch C=O stretch C=O stretch C=O stretch
Alkynes	3265-3335 2100-2140 610-700 2190-2260	s, sharp m s, broad vw-w	≡C-H stretch C≡C stretch ≡C-H bend C≡C stretch	Acyl Chlorides	1785-1815 1770-1800	s s	C=O stretch C=O stretch
Alkyl halides	1000-1350 750-850 500-680 200-500	vs s s s	C-F stretch C-Cl stretch C-Br stretch C-I stretch	Anhydrides	~1750 + ~1815 ~1720 + ~1775 (both two bands)	s,s s,s	C=O symmetric & asym. stretch
Alcohols	3300-3400 1035-1050 1050-1085 1085-1125 1125-1205 1180-1260	s, broad m-s m-s m-s m-s m-s	O-H stretch C-O stretch C-O stretch C-O stretch C-O stretch C-O stretch	Nitriles	2240-2260 2220-2240	m-s s	C≡N stretch C≡N stretch
Ethers	1085-1150 1020-1075 and 1200-1275 (two band)	s m-s	C-O-C stretch =C-O-C sym. & asym. stretch	Amines	~3400 + ~3500 (two bands) 1580-1650 3310-33350	w w-m w	N-H symmetric & asym. stretch N-H bend N-H stretch
Aldehydes	2700-2725 1720-1740 1685-1710	m s s	H-C=O stretch C=O stretch C=O stretch	Amides	3200-3400 and 3400-3500 (two bands) 1650-1690 1590-1655 3400-3500 1640-1690 1510-1560 1630-1680	w-m s, broad m-s w-m s, broad m-s m-s	N-H symmetric & asym. stretch C=O stretch N-H bend N-H stretch C=O stretch N-H bend C=O stretch
Ketones	1710-1720 1665-1685 1675-1695 1770-1780 1740-1755 1710-1720	s s s s s s	C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch	Nitro Compounds	~1550 and ~1370 ~1525 and ~1335 (both two bands)	s s s s	N-O symmetric & asym. stretch N-O symmetric & asym. stretch
				Aromatic Compounds	3010-3100 1450-1600 (two to four bands) 730-770 and 690-710 (two bands) 735-770 750-810 and 690-710 810-840	m m-s s s s s	Ar C-H stretch ring C=C stretch C-H bend C-H bend C-H bend C-H bend C-H bend

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

Standard chemical shift value (ppm from TMS)

¹³C 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 Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
HC=CH ₂	+20		+6		-0.5
C≡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 (<i>ortho</i>)	C-3 (<i>meta</i>)	C-4 (<i>para</i>)
H	0.0	0.0	0.0	0.0
CH ₃	+9.3	+0.7	-0.1	-2.9
CH ₃ CH 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 ₆ H 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
