

M.Sc.(Chem.) Semester - 4 (CBCS) Examination
March/April - 2025 (As Per Syllabus Year June-2019)
Modern Spectroscopy (Elective)

Time: 2:30 Hours

Marks: 70

Instructions:

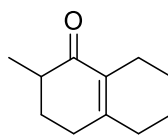
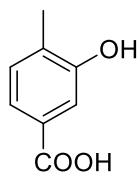
1. All questions are compulsory.
2. Figures to the right indicate marks.
3. Standard data sheet for UV, IR and NMR Spectroscopy attached with this paper

Que-1(A) Question of 4 Marks (04)

- (1) Discuss application of UV spectroscopy in details.

Que-1(B) Answer any two questions out of three. (10)

- (1) Calculate the Wavelength ($\lambda_{\max}$) of following:



- (2) Discuss Bathochromic shift and Hypsochromic shift with example.
(3) Define Spectroscopy. Classify spectroscopy based on its principles with example.

Que-2(A) Question of 4 Marks (04)

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

- a. CH_4
- b. Acetylene
- c. CO_2

Que-2(B) Answer any two questions out of three. (10)

- (1) Explain non-fundamental bands of vibrations in UV spectroscopy.
Differentiate following pairs by using IR spectroscopy:
(2) 1. o-cresol and p-cresol
2. Ethylbenzene and p-xylene
(3) Discuss instrumentation of IR spectrophotometer with schematic diagram.

Que-3(A) Question of 4 Marks. (04)

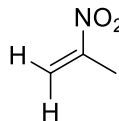
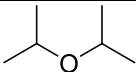
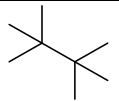
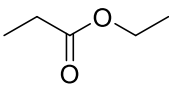
- (1) Define the following terms:
a. Base peak
b. Parent ion
c. Metastable ion
d. Rearrangement ion

Que-3(B) Answer any two questions out of three. (10)

- (1) Discuss EI, CI and FAB techniques used in Mass Spectroscopy.
(2) Explain Nitrogen and Steven's rule with examples.
(3) Discuss instrumentation of Mass Spectrophotometer with schematic diagram.

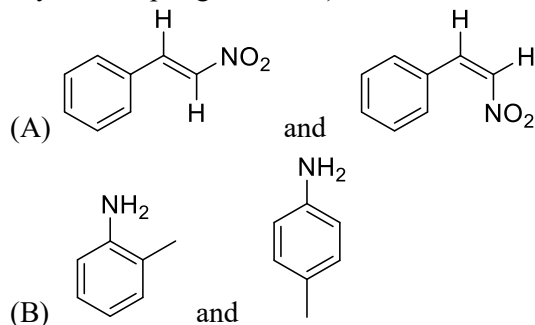
Que-4(A) Question of 4 Marks**(04)**

(1) Match the following Pairs:

Compounds	Number of ^1H NMR Signals
1. 	a. 1
2. 	b. 3
3. 	c. 4
4. 	d. 2

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

- Discuss Spin-Spin splitting and Pascal's triangle with an examples.
- Draw the structure of each of the following compounds which meets the given requirements in its PMR (^1H NMR) spectrum:
 - $\text{C}_4\text{H}_{10}\text{O}$; one singlet, one doublet and one septet
 - $\text{C}_4\text{H}_8\text{Cl}_2\text{O}$; two triplets
 - $\text{C}_3\text{H}_3\text{Cl}_5$; one doublet and one triplet
 - $\text{C}_5\text{H}_8\text{Cl}_4$; one singlet
- Define coupling constant and separate following pairs: (Give number of signals, multiplicity and coupling constants)

**Que-5(A) Question of 4 Marks****(04)**

- Enlist 2D NMR experiments.

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

- Discuss α , β and γ effects in CMR spectroscopy.
- Calculate ^{13}C NMR chemical shifts of aromatic C-atoms of Chlorobenzene and Toluene.
- Deduce the Structure of the compound from following Data:

MF: $\text{C}_9\text{H}_{10}\text{O}$

UV: strong absorption above 200 nm

IR Data: 3020, 2940, 1720, 1600, 1500, 1460, 1380, 1350, 740, 700 cm^{-1}

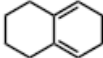
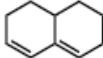
NMR Data:

a/complex/7.4 δppm /5Hb/singlet/3.5 δppm /2Hc/singlet/2.2 δppm /3H

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

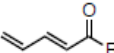
not affected by solvent

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

UV Spectroscopy

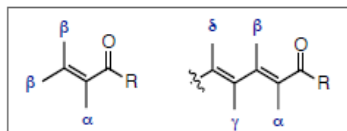
Woodward Fieser Rules for Enones

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

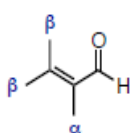
Increments:

	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		

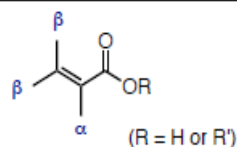


UV Spectroscopy

Woodward Fieser Rules for Other Conjugated Carbonyls



aldehydes



carboxylic acid or ester

Base Values

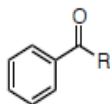
unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm

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

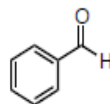
as for enones, solvent correction is also relevant

UV Spectroscopy

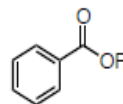
Woodward Fieser Rules for Benzoyl Derivatives



aryl ketones
(R = alkyl)



benzaldehydes



benzoic acids
and esters

base values:	246 nm	250 nm	230 nm
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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	s-vs s s	O=C-O-C stretch C=O stretch C=O stretch
RCH=CH₂	885-895 665-730 960-980 790-840	s m-s, broad s s	=C-H bend =C-H bend =C-H bend =C-H bend	Acyl Chlorides	1785-1815 1770-1800	s s	C=O stretch C=O stretch
RR'C=CH₂				Anhydrides			
cis-RCH=CHR'				R-C(O)-O-R	~1750 + ~1815	s,s	C=O symmetric
trans-RCH=CHR'				Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
RCH=CR'R''				Nitriles			
Alkynes				R-C≡N	2240-2260	m-s	C≡N stretch
R-C≡C-H	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	C≡C-N or Ar-C≡N	2220-2240	s	C≡N stretch
Alkyl halides				Amines			
R-F	1000-1350	vs	C-F stretch	R-NH₂	~3400 + ~3500 (two bands) 1580-1650	w w-m	N-H symmetric & asym. stretch N-H bend
R-Cl	750-850	s	C-Cl stretch	RR'N-H	3310-33350	w	N-H stretch
R-Br	500-680	s	C-Br stretch	Amides			
R-I	200-500	s	C-I stretch	R-C(O)-NH₂	3200-3400 and 3400-3500 (two bands) 1650-1690 1590-1655	w-m s, broad m-s	N-H symmetric & asym. stretch C=O stretch N-H bend
Alcohols	3300-3400 1035-1050 1050-1085	s, broad m-s m-s	O-H stretch C-O stretch C-O stretch	R-C(O)-NH-R	3400-3500 1640-1690 1510-1560	w-m s, broad m-s	N-H stretch C=O stretch N-H bend
C=C-CH₂-OH				R-C(O)-NR'R''	1630-1680	m-s	C=O stretch
R-CH₂-OH (1°) or C=C-CH(R)-OH	1085-1125	m-s	C-O stretch	Nitro Compounds			
RR'CH-OH (2°) or C=C-CRR'-OH				R-NO₂	~1550 and ~1370	s s	N-O symmetric & asym. stretch
RR'R''C-OH (3°)	1125-1205	m-s	C-O stretch	C=C-NO₂ or Ar-NO₂	~1525 and ~1335 (both two bands)	s s	N-O symmetric & asym. stretch
Ar-O-H	1180-1260	m-s	C-O stretch	Aromatic Compounds	3010-3100 1450-1600 (two to four bands)	m m-s sharp	Ar C-H stretch ring C=C stretch
Ethers				monosubstituted	730-770 and 690-710 (two bands)	s s	C-H bend C-H bend
R-O-R'	1085-1150	s	C-O-C stretch	o-disubstituted	735-770	s	C-H bend
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch	m-disubstituted	750-810 and 690-710	s s	C-H bend C-H bend
Aldehydes	2700-2725 1720-1740 1685-1710	m s s	H-C=O stretch C=O stretch C=O stretch	p-disubstituted	810-840	s	C-H bend
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				

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

Standard chemical shift value (ppm from TMS)

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 $\equiv$ 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 (<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