

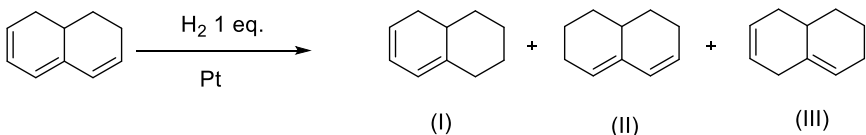
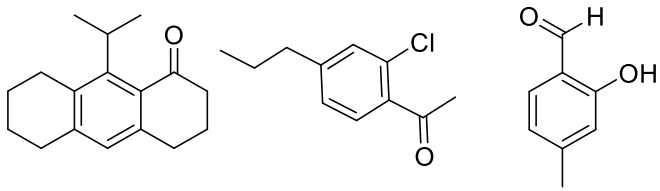
M.Sc.(Chem.) Semester - 4 (CBCS) Examination
April/May-2022 (NEW COURSE)
Modern Spectroscopy (Elective)

Time: 2:30 Hours

Marks: 70

Instructions:

1. All questions are compulsory.
2. Figures to the right indicate marks.

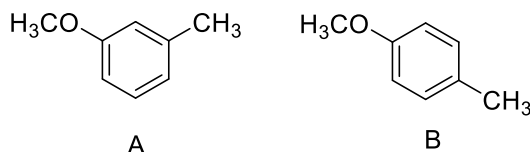
Q.1 (a)	Answer the following	4 Marks
(1)	Discuss Auxochrome and Chromophore with example.	2
(2)	Describe various applications of UV-Visible spectroscopy.	2
Q.1 (b)	Answer any two questions out of three.	10 Marks
(1)	Explain Red shift and Blue shift with one example each.	5
(2)	The following triene on partial hydrogenation gives three products, which are separated by chromatography, how can you identify the product by application of Woodward-Fischer rules?	5
		
(3)	Arrange the following compounds in decreasing order in their wavelength ($\lambda_{\max}$):	5
		
Q.2 (a)	Answer the following	Marks
(1)	Which of the following molecule is IR active? Justify your answer: (i) H_2 (ii) CO (iii) O_2 (iv) CO_2	2
(2)	How will you determine types of hydrogen bonding from IR spectroscopy?	2
Q.2 (b)	Answer any two questions out of three.	Marks
(1)	Discuss ATR technique for IR spectroscopy with its advantages.	5
(2)	Explain various factors affecting carbonyl frequency with suitable example	5
(3)	(a)What is degree of freedom? Deduce equation of vibrational degree of freedom for non-linear and linear molecules. (b) Discuss Fermi Resonance with example	5
Q.3 (a)	Answer the following	4 Marks
(1)	Draw a schematic diagram of Mass spectrometer including various components	4

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

- (1) When cyclohexanone was subjected to Mass spectroscopy with ESI-MS, peak appeared at 98, 83, 70, 55, 42. Carry out the fragmentation of molecule and deduce the structure of each fragment ion corresponding to the above peak appeared in the spectrum 5
- (2) Discuss electrospray ionization method briefly. 5
- (3) Explain McLafferty rearrangement in Mass spectroscopy with example. 5

Q.4 (a) Answer the following **4 Marks**

- (1) How will you distinguish following isomers (A & B) by PMR? 4

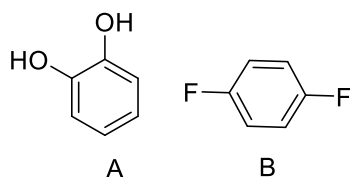


Q.4 (b) Answer any two questions out of three. **10 Marks**

- (1) What is Spin-spin coupling? Discuss AMX spectra with suitable example. 5
- (2) An unknown compound having Molecular Formula $C_7H_4N_2O_2$ showed Molecular Ion peak (M^+) at 148.12 m/z and base peak at 103.12 m/z. The FT-IR analysis showed characteristic bands at 1350 cm^{-1} , 1550 cm^{-1} , 2250 cm^{-1} . The PMR spectrum was obtained in the 400 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 7.77 (t, $J = 8.8\text{ Hz}$, 1H), 8.02 (d, $J = 8.8\text{ Hz}$, 1H), 8.51 (d, $J = 8.8\text{ Hz}$, 1H), 8.57 (s, 1H). Interpret the given spectroscopic data and deduce the structure of unknown compound. 5
- (3) An unknown compound having Molecular Formula $C_{10}H_{12}O_3$ showed Molecular Ion peak (M^+) at 180.20 m/z. The FT-IR analysis showed characteristic bands at 1750 cm^{-1} . The PMR spectrum was obtained in the 500 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 1.40 (t, 3H), 3.80 (s, 3H), 4.15 (q, 2H), 6.93 (d, $J = 8.0\text{ Hz}$, 2H), 8.01 (d, $J = 8.0\text{ Hz}$, 2H). ^{13}C NMR ($CDCl_3$): δ 15.20, 32.34, 64.23, 114.16, 122.94, 136.55, 162.63, 169.80. Interpret the given spectroscopic data and deduce the structure of unknown compound. 5

Q.5 (a) 2 Questions of 2 Marks Each. **4 Marks**

- (1) Why ^{13}C NMR is less sensitive compare to 1H NMR ?
- (2) Calculate the ^{13}C chemical shift of each aromatic carbon for following (A & B):



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

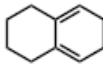
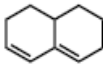
- (1) Distinguish the following 2D experiments with suitable example: 5
- (i) COSY vs TOCSY
- (ii) HMBC vs HSQC
- (2) An unknown compound having Molecular Formula $C_{12}H_{13}NO_3$ showed Molecular Ion peak (M^+) at 219.24 m/z. The FT-IR analysis showed characteristic bands at 1040 cm^{-1} , 1250 cm^{-1} , 1725 cm^{-1} and 2235 cm^{-1} . The PMR spectrum was obtained in the 400 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 1.36 (t, 3H), 1.48 (t, 3H), 4.20 (q, 2H), 4.33 (q, 2H), 6.95-6.98 (d, $J = 9.2\text{ Hz}$, 1H), 8.14-8.17 (dd, $J = 9.2 \text{ \& } 2.0\text{ Hz}$, 1H), 8.19-8.20 (d, $J = 2.0\text{ Hz}$, 1H). Interpret the given spectroscopic data and deduce the structure of unknown compound 5
- (3) An unknown compound having Molecular Formula $C_7H_{14}O_3$ showed Molecular Ion peak (M^+) at 146.19 m/z. The PMR spectrum and 2D spectrum were obtained in the 600 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed following signals and cross peaks in the 2D spectrum. Interpret the given spectroscopic data and deduce the structure of unknown compound.

δ ppm	Signal multiplicity	No. of protons	1H - 1H COSY
1.16	t	3H	Cross peak with q (3.50)
1.25	t	3H	Cross peak with q (4.15)
2.57	t	2H	Cross peak with t (3.71)
3.50	q	2H	-
3.71	t	2H	-
4.15	q	2H	-

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

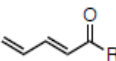
not affected by solvent

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

UV Spectroscopy

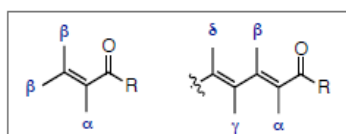
Woodward Fieser Rules for Enones

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

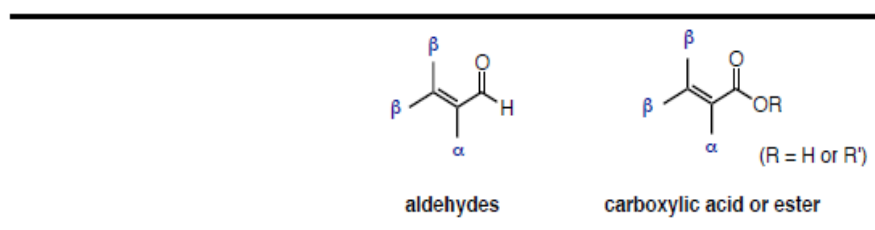
Increments:

	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



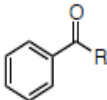
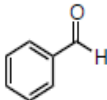
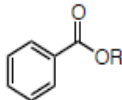
Base Values

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

			
	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 ⁻	+ 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 sharp 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)	

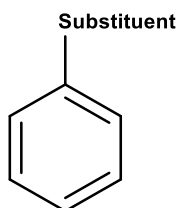
Olefinic carbons	
Substituent carbon C	Correction
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	-1.5
z (cis)	-1.1

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

Data Sheet

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
