(61)

SARDAR PATEL UNIVERSITY
M.Sc. Semester – IV (Inorganic Chemistry) Examination
Thursday, 29th November 2012

PS04CINC01: Spectroscopy-II

Time: 10:30 am to 01:30 pm   Total Marks: 70

Note: Right hand figures indicate marks.

Q. 1   Select the correct answer in the following.   08

1. In IR, the C-H stretching absorption of alkyne is observed at

    a. ~2150 cm^{-1} c. ~1000cm^{-1}
    b. ~3300cm^{-1} d. ~1300cm^{-1}

2. In UV spectra the n $\longrightarrow$ σ* transition is shown by

    a. Ketones   c. Alcohols
    b. Alkanes   d. Olefins

3. In the instrument with 1.4 Tesla magnetic field the proton will resonate at

    a. 60 MHz   c. 100 MHz
    b. 90 MHz   d. 300 MHz

4. In the PMR spectrum, mesitylene(1,3,5-trimethyl benzene) will give

    a. 2 signals   c. 4 signalls
    b. 3 signals   d. 6 signals

5. In ^{13}C NMR, phenanthrene will give

    a. 14 signals   c. 5 signals
    b. 6 signals   d. 7 signals

6. The solvent CDCl$_3$ in ^{13}C NMR spectrum will give

    a. a doublet at 100 δ   c. a singlet at 180 δ
    b. a triplet at 77 δ   d. a singlet at 40 δ

7. In mass spectra, the metastable ion peak is observed

    a. as diffused peak at non integral m/z value   c. as two lines with equal intensity
    b. at heighest m/z value   d. at M-15 position

8. In HETCOR spectra, the connectivity observed between ^1H and ^{13}C is

    a. ^2J
    b. ^3J
                                    c. ^2J and ^3J
                                    d. ^1J

Q. 2   Answer the following (**Any Seven**).   14

1. Explain Fermi resonance observed in IR spectroscopy.

2. With suitable example explain the terms chromophores and auxochromes.

3. The symmetrical stretching vibration in H_2O is IR active whereas the same is inactive in CO_2. Explain.

4. Sketch the expected PMR spectrum for ethyl acetate by taking approximate δ value for each signal.

5. Assign the spin systems (Pople notations) for 1-nitropropane and p-chloro nitrobenzene.

6. How will you differentiate o-, m- and p- xylenes on the basis of proton decoupled ^{13}C NMR spectra.

7. Write the important characteristic properties of DEPT-90 and DEPT-135 spectra.

8. With suitable example explain Mclafferty rearrangement observed in mass spectroscopy.

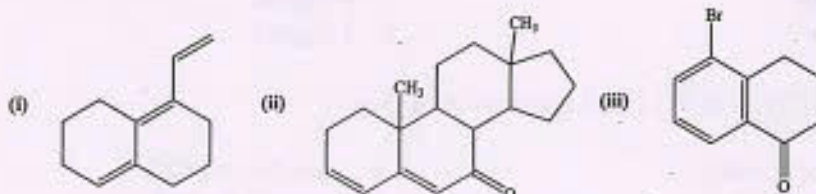9. Sketch the ^1H-^1H COSY spectrum for ethyl benzene by taking approximate δ value for each signal.

Q. 3   **A.** Answer the following.   06
      (i) State and explain the Beer-Lambert law.
      (ii) Discuss in detail the characteristic IR absorptions in aldehydes and esters.

      B. Calculate λ_{max} for the following molecules.   06

(i)   (ii)   (iii)

OR

      B. Answer the following.   06

(i) How can you differentiate o-hydroxy acetophenone and p-hydroxy acetophenone on the basis of their IR sprctra?

(ii) In IR, s-trans benzal acetone absorbs at 1674 cm^{-1} while s-cis benzal acetone absorbs at 1699 cm^{-1}. Explain.

(iii) Draw the relative energy level diagram for the following electronic transitions.
      $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$

Q. 4 A. (i) What is coupling constant in PMR? Explain vicinal and germinal couplings in detail. **03**

(ii) List the important methods for the simplifications of PMR spectra. Discuss the use of shift reagents in detail. **03**

B. (i) A compound with molecular formula $C_6H_{12}O_2$ shows the following signals in PMR spectrum. Assign the structure. **03**
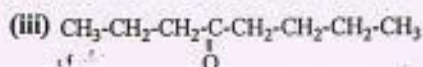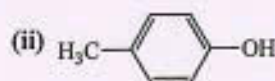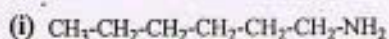
Signal position(δ)	Multiplicity	Protons
0.9	Doublet	6H
1.9	Multiplet	1H
2.1	Singlet	3H
3.85	Doublet	2H

(ii) What is nuclear overhauser effect? How will you distinguish following compounds using NOE-PMR spectra? **03**

(i)   (ii)

OR
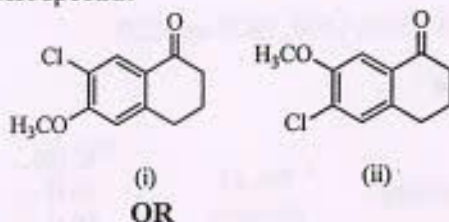
B. (i) Sketch the expected PMR spectrum for 3-methyl-2-pentanone by taking approximate δ value for each signal. **03**

(ii) What is chemical shift equivalent? Dimethylformamide, in its PMR spectrum shows two separate signals for two methyl groups at room temperature but it shows only one signal for two methyl groups at 123 °C. Explain. **03**

Q. 5 A. Do the ^{13}C NMR chemical shift calculations for the following molecules. **06**

(i) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

(ii)

(iii) $CH_3\text{-}CH_2\text{-}CH_2\text{-}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
           $\overset{\|}{O}$

B. (i) Sketch the proton coupled and proton decoupled ^{13}C NMR spectra for p-methoxy benzaldehyde by taking approximate chemical shift value for each signal. **03**

(ii) Indicate the position and multiplicity of the signals for the following solvents in ^{13}C NMR. **03**

(a) Acetone-d$_6$ (b) DMSO-d$_6$ (c) Benzene-d$_6$

OR

B. (i) A bicyclic hydrocarbon with molecular formula C_8H_{14} shows only two peaks in proton decoupled ^{13}C spectrum. The DEPT spectra indicated that those signals are for CH and CH_2. Assign the structure to the compound.　　03

(ii) Sketch the ^1H-^{13}C HETCOR spectrum for 2-butanol by taking approximate δ value for each signal.　　03

Q. 6 A. Do the mass fragmentation for the following molecules.
　(a) 2-methyl-2-pentanol　(b) 2-pentanone　(c) 3-pentanone　　06

B. (i) Discuss FAB and MALDI techniques used in mass spectroscopy.　　03

(ii) What is metastable ion peak in mass spectroscopy? A parent ion with mass 91, results a daughter ion of mass 65, calculate the position of the meta stable ion peak.　　03

OR

B. A compound has molecular formula $C_{10}H_{12}O_2$. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound.　　06

IR (cm^{-1}) : 1711, 3000, 2950, 1500, 1600 and 820.

PMR :

δ	Multiplicity	No. of protons
2.1	Singlet	3H
3.6	Singlet	2H
3.8	Singlet	3H
6.9	Doublet	2H
7.1	Doublet	2H

^{13}C NMR :

^{13}C (δ)	DEPT-90	DEPT-135
30.0	-	positive
50.0	-	Negative
55.0	-	positive
114.0	positive	positive
127.0	-	-
130.0	positive	positive
159.0	-	-
207.0	-	-

Mass:
m/e : 164(M$^+$), 149, 133, 121, 107, 43

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CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton		Chemical shift, ppm δ
Cyclopropane		0.2
Primary	RCH_3	0.9
Secondary	R_2CH_2	1.3
Tertiary	R_3CH	1.5
Vinylic	$C=C-H$	4.6–5.9
Acetylenic	$C≡C-H$	2–3
Aromatic	$Ar-H$	6–8.5
Benzylic	$Ar-C-H$	2.2–3
Allylic	$C=C-CH_3$	1.7
Fluorides	$HC-F$	4–4.5
Chlorides	$HC-Cl$	3–4
Bromides	$HC-Br$	2.5–4
Iodides	$HC-I$	2–4
Alcohols	$HC-OH$	3.4–4
Ethers	$HC-OR$	3.3–4
Esters	$RCOO-CH$	3.7–4.1
Esters	$HC-COOR$	2–2.2
Acids	$HC-COOH$	2–2.6
Carbonyl compounds	$HC-C=O$	2–2.7
Aldehydic	$R-CHO$	9–10
Hydroxylic	$R-OH$	1–5.5
Phenolic	$Ar-OH$	4–12
Enolic	$C=C-OH$	15–17
Carboxylic	$RCOOH$	10.5–12
Amino	RNH_2	1–5

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkanes	2850-2960 1350-1470
C-H	Alkenes	3020-3080 (m) 675-1000
C-H	Aromatic rings	3000-3100 (m) 675-870
C-H	Alkynes	3300
C=C	Alkenes	1640-1680 (v)
C≡C	Alkynes	2100-2260 (v)
C=C	Aromatic rings	1500, 1600 (v)
C-O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O-H	Monomeric alcohols ,phenols	3610-3640 (v)
	Hydrogen bonded alcohols, phenols	3200-3600 (broad)
	Carboxylic acids	2500-3000 (broad)
N-H	Amines	3300-3500 (m)
C-N	Amines	1180-1360
C≡N	Nitriles	2210-2260 (v)
-NO$_2$	Nitro compounds	1515-1560 1345-1385

Characteristic absorption for dienes

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
N(Alk)$_2$	+60
Solvent correction*	+0
	λ_{calc} = Total

Characteristic absorption for substituted benzene derivatives

ArCOR/ArCHO/ArCO$_2$H/ArCO$_2$R		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C$_6$H$_5$		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, (ArCO$_2$H and ArCO$_2$R)		230
Increment for each substituent on Ar:		
—Alkyl or ring residue	o-, m-	+3
	p-	+10
—OH, —OCH$_3$, —OAlk	o-, m-	+7
	p-	+25
—O⁻ (oxyanion)	o-	+11
	m-	+20
	p-	+78[b]
—Cl	o-, m-	+0
	p-	+10
—Br	o-, m-	+2
	p-	+15
—NH$_2$	o-, m-	+13
	p-	+58
—NHCOCH$_3$	o-, m-	+20
	p-	+45
—NHCH$_3$	p-	+73
—N(CH$_3$)$_2$	o-, m-	+20
	p-	+85

Characteristic absorption for α, β-unsaturated carbonyl compounds

Enone   and   Dienone
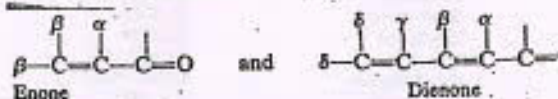
Base values		(nm)
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195

Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
—NR$_2$	β	+95
Exocyclic double bond		+5
Homodiene component*		+39

¹³C shifts for terminal and internal systems
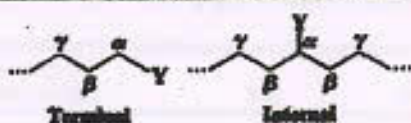
Y	α Terminal	α Internal	β Terminal	β Internal	γ
CH₃	+ 9	+ 6	+10	+ 8	-2
CH=CH₂	+20		+ 6		-0.5
C≡CH	+ 45		+ 5.5		-3.5
COOH	+21	+16	+ 5	+ 2	-2
COO⁻	+25	+20	+ 5	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH₂	+22		+ 2.5		-0.5
COR	+30	+24	+ 1	+ 1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+ 9	+ 7	-2
OH	+48	+41	+10	+ 8	-5
OR	+58	+51	+ 8	+ 5	-4
OCOR	+51	+45	+ 6	+ 5	-3
NH₂	+29	+24	+11	+10	-5
NH₃⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR₂	+42		+ 6		-3
NR₃⁺	+31		+ 5		-7
NO₂	+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

¹³C Shifts for some linear and branched chain alkanes

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
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
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH₃)	

^{13}C shifts for substituted benzenes
Base value for benzene is 128.5 ppm

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	+9.3	+0.7	-0.1	-2.9	21.3
CH_2CH_3	+15.6	-0.5	0.0	-2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH_3)
$CH=CH_2$	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH_2)
$C\equiv CH$	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	-1.8	-0.1	-1.6	
CH_2OH	+13.3	-0.8	-0.6	-0.4	64.5
CH_2OCCH_3 (O)	+7.7	-0.0	-0.0	-0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH_3	+31.4	-14.4	+1.0	-7.7	54.1
OC_6H_5	+29.0	-9.4	+1.6	-5.3	
$OCCH_3$ (O)	+22.4	-7.1	-0.4	-3.2	23.9 (CH_3), 169.7 (C=O)
CH (O)	+8.2	+1.2	+0.6	+5.8	192.0
CCH_3 (O)	+7.8	-0.4	-0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
CC_6H_5 (O)	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF_3 (O)	-5.6	+1.8	+0.7	+6.7	
COH (O)	+2.9	+1.3	+0.4	+4.3	168.0
$COCH_3$ (O)	+2.0	+1.2	-0.1	+4.8	51.0 (CH_3), 166.8 (C=O), 168.5
CCl (O)	+4.6	+2.9	+0.6	+7.0	
CNH_2 (O)	+5.0	-1.2	0.0	+3.4	
$C\equiv N$	-16.0	+3.6	+0.6	+4.3	119.5
NH_2	+19.2	-12.4	+1.3	-9.5	
$N(CH_3)_2$	+22.4	-15.7	+0.8	-11.8	40.3
$NHCCH_3$ (O)	+11.1	-9.9	+0.2	-5.6	
NO_2	+19.6	-5.3	+0.9	+6.0	
$N=C=O$	+5.7	-3.6	+1.2	-2.8	129.5
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	
CF_3	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH_3	+10.2	-1.8	+0.4	-3.6	15.9
SO_2NH_2	+15.3	-2.9	+0.4	+3.3	
$Si(CH_3)_3$	+13.4	+4.4	-1.1	-1.1	

Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X-\underset{\alpha}{C}-\underset{\beta}{C}-\underset{\gamma}{C}-C$$

X	α-shift			β-shift	γ-shift
	$X-CH_2-$	$X-\underset{R}{CH}-$	$X-\underset{R}{\overset{R}{C}}-$		
	$1°$ or	$2°$ or	$3°$		
$-CH_3$	9	6	3	9	-3
$-$R: see table 3.11					
axial$-CH_3$	1	$-$	$-$	5	-6
equatorial$-CH_3$	6	$-$	$-$	9	0
(in cyclohexanes)					
$-CH=CH_2$	22	16	12	7	-2
$-C\equiv CH$	4	$-$	$-$	3	-3
$-C_6H_5$, $-Ar$	23	17	11	10	-3
$-F$	70	$-$	$-$	8	-7
$-Cl$	31	35	42	10	-5
$-Br$	19	28	37	11	-4
$-I$	-7 to 20	$-$	$-$	11	-2
$-NH_2$, $-NHR$, $-NR_2$	29	24	18	11	-4
$-NO_2$	62	$-$	$-$	3	-5
$-NHCOR$, $-NRCOR$	10	$-$	$-$	0	0
$-NH_3^+$	25	$-$	$-$	7	-3
$-CN$	3	4	$-$	2	-3
$-SH$	2	$-$	$-$	2	-2
$-OH$	50	45	40	9	-3
$-OR$	50	24	17	10	-6
$-OCOR$	52	50	45	7	-6
$-COOH$, $-COOR$, $-CON<$	20	16	13	2	-3
$-COR$, $-CHO$	30	24	17	2	-3
$-SO_3H$, $-SO_2N<$	50	$-$	$-$	3	0

Influence of functional group X on the chemical shift positions (δ) of nearby carbons in alkene groups and benzene rings

Base values: ethylene (δ 123) and benzene (δ 128)
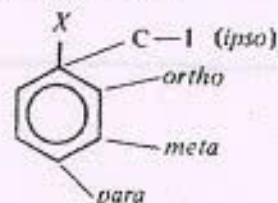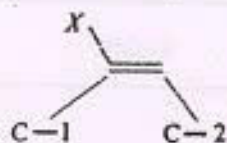
	Alkenes		Benzenes			
	C—1	C—2	C—1 (ipso)	ortho	meta	para
—CH$_3$	10	−8	9	0	0	−2
R,	16	−8	15	0	0	−2
R,	23	−8	21	0	0	−2
—CH=CH$_2$	15	−6	9	0	0	−2
—CH≡CH	—	—	−6	4	0	0
—C$_6$H$_5$, —Ar	13	−11	13	−1	1	−1
—F	25	−34	35	−14	1	−5
—Cl	3	−6	6	0	1	−2
—Br	−8	−1	−5	3	2	−2
—I	−38	7	−32	10	3	−1
—NH$_2$	—	—	18	−13	1	−10
—NHR	—	—	20	−14	1	−10
—NR$_2$	—	—	22	−16	1	−10
—NO$_2$	22	−1	20	−5	1	6
—NHCOR, —NRCOR	—	—	10	−7	1	−4
—CN	−15	15	−16	4	1	6
—SH	—	—	4	1	1	−3
—OH	—	—	27	−13	1	−7
—OR	29	−39	30	−15	1	−8
—OCOR	18	−27	23	−6	1	−2
—COOH, —COOR, —CON<	4	9	2	2	0	5
—COR, —CHO	14	13	9	1	1	6
—SO$_3$H, —SO$_2$N<	—	—	16	0	0	4
—PMe$_2$	—	—	14	1.6	0	−1
—PAr$_2$	—	—	9	5	0	0