M.Sc. (Part-II) Semester-III (C.B.C.S.) Examination

CHEMISTRY (New)

(Spectroscopy-I)

Paper—IX

Time : Three Hours] [Maximum Marks : 80

Note :— (1) **ALL** questions are compulsory.
(2) All questions carry equal marks.
(3) Reference data is provided.

1. (a) Explain the Franck-Condon principle. 5

(b) Discuss in brief Fourier transformation spectroscopy. 5

(c) Explain the terms in context with radiation :

(i) Refraction

(ii) Scattering

(iii) Polarisation. 6

OR

(p) Discuss the application of microwave spectroscopy. 5

(q) Explain the effect of isotopic substitution on rotational spectrum of a diatomic molecule and draw the spectrum. 6

(r) Write the factors affecting the reactivity of nanoparticles and its use in medicine. 5

2. (a) Explain effect of hydrogen bonding and solvent on vibrational frequency. 5

(b) Comment on :

(i) Effect of conjugation in I.R.

(ii) Effect of ring strain on I.R.

Explain with suitable example. 6

(c) Compound having molecular formula C_8H_8O shows following spectral data :

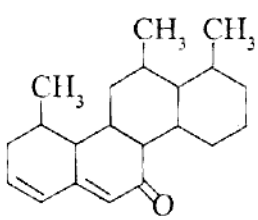
U.V. λ_{max} = 270 nm (ϵ 10,000)

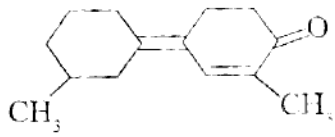
I.R. = 3090, 2960, 1735, 1500-1600, 840 cm^{-1}.

Deduce the structure. 5

OR

(p) Calculate λ_{max} for the following compounds :

(i) 

(ii)  6

(q) Write the factors that influence the $>C = O$ (carbonyl) stretching vibrations. 4

(r) How will you distinguish between the following pairs of compound using I.R.

(i) O-hydroxybenzaldehyde and P-hydroxybenzaldehyde,

(ii) Cyclohexenone and Cyclohexanone and

(iii) CH_3-CH_2-OH and CH_3-O-CH_3. 6

3. (a) What is the principle of Mass spectrometry ? Discuss different types of ions produced in Mass spectrometer. 5

(b) The compound with molecular formula $C_4H_{10}O$ shows I.R. stretch at 3540 cm^{-1} and give mass fragmentation as molecular ion M^+ m/2 = 74 and other prominent peaks appear at 59 and 45 m/2. Assign the structure. 5

(c) Write the McLafferty rearrangement in the following molecules :

(i) Methylbutanoate

(ii) 2-pentanone. 6

OR

(p) Write notes on :

(i) Retro-Diels-Alder fragmentation

(ii) Meta stable ion. 6

(q) Give the fragmentation pattern of the following molecules in mass spectrometry :

(i) 2-Butanol, (ii) Acetophenone. 4

(r) What is the most characteristic feature of the mass spectra of compounds containing one bromine atom ? Explain with suitable example and draw its mass spectrum. 6

4. (a) Indicate the number of ^{13}C NMR signals in the proton decoupled spectrum and assign the multiplicity for each signal in the off resonance decoupled spectrum for the following compounds :

(i) Toluene

(ii) 1, 4-Dibromobenzene

(iii) Propanol. 6

(b) Explain the terms :

(i) Shielding and deshielding in NMR

(ii) Variation of 'T' with dihedral angle. 5

(c) An organic compound with M.F. $C_6H_{12}O_2$ showed the following spectral data :

I.R.—2950, 1740, 1200 cm^{-1}

^1H NMR—δ 1.2 (9H, s), δ 4.2 (3H, s)

^{13}C NMR—δ 27, 61, 82, 176 ppm. 5

OR

(p) What is Karplus equation ? Discuss its application. 5

(q) How will you differentiate between ortho, meta and para-xylene on the basis of their proton decoupled ^{13}C NMR spectra and write its chemical shift values. 5

(r) Deduce the structure of the compound having M.F. $C_3H_6Cl_2$ showed the following spectral data :

I.R.—2940, 1265, 690 cm^{-1}

^1H NMR—δ 3.5 (2H, d), δ 3.3 (1H, m)

δ 1.25 (3H, d) 6

5. (a) Draw the proton decoupled DEPT-45, DEPT-90 and DEPT-135 of the compound Ethyl 2-nitropropanoate using following ^{13}C NMR values : δ 14, δ 16, δ 63, δ 82 and δ 165 ppm. 4

(b) Explain in brief :

(i) Nuclear overhauser effect (NOE)

(ii) Lanthanide shift reagent. 6

(c) Explain COSY and HETCOR technique with suitable example. 6

OR

(p) Write notes on the following :

(i) Magnetic Resonance Imaging (MRI)

(ii) Deuterium exchange

(iii) How will you distinguish between (E)-2-bromo-2-butene and (Z)-2-bromo-2-butene using NOESY spectrum ? 6

(q) Explain the DEPT technique in ^{13}C NMR spectroscopy with suitable example. 5

(r) The ^1H-NMR spectrum of 4-vinyl pyridine has following spectral data : δ 8.4 (d, 1H), δ 7.1 (d, 1H), δ 6.5 (dd, 1H), δ 5.8 (dd, 1H) and 5.3 (dd, 1H). Prepare a sketch of the ^1H-COSY spectrum for this molecule showing expected diagonal and off diagonal peaks. 5

REFRENCE ANALYTICAL & SPECTRAL DATA

Some useful constant and conversion factors:

$N = 6.023 \times 10^{23}$ mol^{-1}	$h = 6.626 \times 10^{-34}$ JS	$C = 3 \times 10^{8}$ ms^{-1}	$1\ eV = 8066\ cm^{-1}$
$1\ A^{0} = 10^{-10}$ m	$1\ eV = 1.602 \times 10^{-12}$ erg	$1eV = 1.602 \times 10^{-19}$ $Jmol^{-1}$	$1eV = 9.694 \times 10^{4}$ $Jmol^{-1}$

Conversion Factor Table:

Unit	*Erg*	*Joule*	*Lit atm*	*eV*	*Calories*
1 erg	1	10^{-7}	9.8687×10^{-10}	6.242×10^{11}	2.389×10^{-8}

Some Characteristic values of IR absorption frequencies of stretching and bending vibrations. (Only approximate values are given in cm^{-1})

IR absorption frequencies in cm^{-1}	*Bond causing absorption*
3750-3000	O-H & N-H stretching
1675-1500	HC=C_2R (Aliphatic and Aromatic), -C=N stretching
2400-2100	-C≡C, -C≡N stretching
1000-650	CH=CH, Ar-H bending
3450-3300	Bonded OH
3500-3100	Bonded NH
2140-2100	H-C≡C-H
2260-2240	R-C≡N
3030	Ar-H
2990-2850	Aliphatic - CH_2
2720	-C-H stretch ‖ O
1705-1725	R-C-R stretch ‖ O
1740-1760	R-C-OR (Ester) ‖ O
1680-1700	R-C-NH_2 ‖ O
1640-1690	H-C=N
750 & 700	Mono substituted benzene
780-810	*meta* substituted benzene

IR absorption frequencies in cm^{-1}	*Bond causing absorption*
3300-2900	-C≡C-H, -CHO (C-H stretch)
1900-1650	-C=O of Acid, Aldehydes, Ketones, Amides, Esters, Anhydrides stretching
1475-1300	-C-H bending
3700-3500	Non bonded O-H
3500-3300	Non bonded N-H
3000-2500	C=Carboxylic OH
2260-2190	R-C≡C-R'
3300	-C≡C-H
2960-2870	Aliphatic - CH_3
2890	Aliphatic -CH
1710-1740	-C-OH stretch ‖ O
1720-1740	R-C-H stretch ‖ O
1720-1815	R-C-X ‖ O
1620-1680	-HC=CH-
1575-1630	-N=N-
750	*ortho* substituted benzene
850-800	*para* substituted benzene

Characteristic ^1H NMR chemical shift in δ ppm unit:

Proton type	*chemical shift in δ unit*	*Proton type*	*chemical shift in δ unit*
$-CH_3$	0.9	CH_3-CH-	1.6
$-C(=O)-CH_3$	2.1	$-CH_2-\underset{\vert}{C}-$	1.4
CH_3-N	2.2	$Ar-CH_3$	2.3
CH_3-Br	2.7	CH_3-Cl	3.1
CH_3-O	3.3	CH_3-N^+	3.3
$CH_2-C=C-$	2.3	CH_3-NR_2	2.5
$-CH_2-Ar$	2.7	$-CH_2-Br$	3.3
$-CH_2-Cl$	3.4	$-CH_2-O$	3.4
$-CH-\underset{\vert}{C}-$	1.5	$H-\underset{\vert}{C}-Ar$	3.0
$H-\underset{\vert}{C}-Br$	4.1	$H-\underset{\vert}{C}-Cl$	4.1
-CHO	3.7	H-N-	1.3
H-OR	1.5	H-C=C	2.5
H-C=CR	5.5	H-Ar	7-9
$-C(=O)-H$	10	$-C(=O)-OH$	9-12

Coupling Constant *J*

*J*ortho = 7.5 Hz	*J*meta = 1.4 Hz	*J*para = 0.7 Hz	*J*trans = 12-24 Hz
*J*cis = 3-19 Hz	*J*ax-ax = 8-13 Hz	*J*ax-eq = 1-6 Hz	*J*eq-eq = 0-5 Hz

Characteristic ^{13}C NMR chemical shift in δ ppm unit:

^{13}Carbon type	*chemical shift in δ unit*	*^{13}Carbon type*	*chemical shift in δ unit*
$-CH_3$	0 - 30	CH_2	10 - 50
$-CH-\underset{\vert}{C}-$	25 - 60	$-\underset{\vert}{C}-OH$	45 - 75
$-\underset{\vert}{C}-Br$	10 - 25	$-\underset{\vert}{C}-Cl$	15 - 30
$-C(=O)-$	155 - 180	$-C(=O)-OH$	160 - 185
H-C=O (carbonyl)	190 – 220 (singlet)	Aromatic carbons	110 - 170
H-C=C-	80 - 145		