Referance Data :—

1. Some useful constants and conversion factors $N = 6.023 \times 10^{23}$ Mol^{-1}, $h = 6.626 \times 10^{-34}$ JS^{-1} and ergs $h = 6.623 \times 10^{27}$ ergs : $C = 3 \times 10^{10}$ cm S^{-1} or 3×10^{8} ms^{-1}. lev = 8066 cm^{-1}, 1 $A^0 = 10^{8}$ cm, lev = 1.002×10^{-12} erg. lev = 1.602×10^{-19} or 9.649×10^{4} J/ mol.

2. Some Characteristic values of the absorbtion frequencies of stretching and bending vibrations. Only approximate values are given in cm^{-1}.

3750-3000	O-H and N-H stretching
3300-2900	-C ≡ C - H, $\rangle C = \overset{H}{\overset{|}{C}}$, Ar - H (C - H stretch)
3000-2700	CH_3, CH_2, CH, $-\overset{O}{\overset{\|}{C}}-H$ (C - H stretch)
2400-2100	C ≡ C - C, C ≡ N stretching
1900-1650	$\rangle C = O$ of (acids, aldehydes, ketones, amides, esters, anhydrides) stretching.
1675-1500	$H C = C_2$ Raliphatic and aromatic, C = N - stretch.
1475-1300	C-H bending
1000-650	$\rangle C = \overset{H}{\overset{\|}{C}}$, Ar-H bending
3700-3500	Non - bonded O - H
3450-3300	Bonded O - H
3500-3300	Non - bonded N - H
3500-3100	Bonded N - H
3000-2500	Carboxylic OH
2140-2100	H - C ≡ C - H
2260-2190	R - C ≡ C - R^1

AQ – 997

Third Semester M. Sc. (Part – II) (CBCS Pattern) Examination

CHEMISTRY

Paper – IX

(Spectroscopy – I)

P. Pages : 10

Time : Three Hours] [Max. Marks : 80

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1. (a) What is rigid rotor ? Show that specing distance between adjacent rotational spectral line is 2 B cm^{-1}. 5

   (b) Explain :—

   (i) Natural line width.

   (ii) Polarization.

   (iii) Light scattering. 6

   (c) The pure rotational spectra (microwave) of HCl consist of a series of equally spaced lines separated by 20 cm^{-1}. Calculate moment of Inertia, reduced mass mol^{-1} and bond distance between atoms in molecule. (molar mass $H^1 = 1{\cdot}673 \times 10^{-27}$ kg, $^{35}Cl = 58{\cdot}06 \times 10^{-27}$ kg, NO – $6{\cdot}023 \times 10^{23}$). 5

OR

(p) What are the rigid and non-rigid (Unrigid) molecules ? Give classification of molecules on the basis of moment of inertia. 5

(q) Atom contains number of energy levels such as rotational, vibrational and electronic. Depict it diagrammatically along with energy formulation. 5

(r) Explain Stark effect and discuss its advantage and application. 6

2. (a) The Ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm.

(I) If a solution of benzonitrile in water with a concentration of 1×10^{-4} molar, is examined at a wavelength of 224 nm the absorbance is determined to be 1·30. The cell length is 1 cm, what is molar absorptivity of this absorption band ?

(II) If the same solution is examined at 271 nm, what will be the absorption reading ($\epsilon - 1000$) ? What will be the intensity ratio I_0/I ? 6

(c) Explain NOE in NMR Spectroscopy. 4

(d) An acid with molecular formula $C_{10}H_{12}O_3$. Gives signals in ^{13}C Spectrum at

Normal ^{13}C	DEPT – 135	DEPT –90
15 ppm	+ve peak	No peak
40	–ve	No peak
63	–ve	No peak
115	+ve	+ve
125	No peak	No peak
130	+ve	+ve
158	No peak	No peak
179	No peak	No peak

Deduce the structure of molecules. 4

OR

(p) Give an account of shortcoming of PMR over ^{13}C NMR. 4

(q) Explain NOESY technique with example.4

(r) An unknown compound has molecular formula of $C_6H_{10}O_2$ and the ^{13}C NMR data is

δ ppm	17·4	14·3	60	123·2	144·2	166·4
multiplicity	q	q	t	d	d	s

deduce its structure. 4

(s) What are 2D NmR Spectra ? 4

(c) Describe with suitable example the various factors which affect the magnitude of the chemical shift. 6

OR

(p) An hydrocarbon containing 90.9 % carbon shows the following four signals :—

(i) Unsymmetrical multiple = 2·82 T (5H)

(ii) Triplet 9·1 T (2H)

(iii) Triplet 8·85 T (2H)

(iv) Singlet 8·6 T (3H), what is the structure of the compounds. 6

(q) Explain the following terms in brief :—

(i) Factors affecting coupling constant 'J'.

(ii) Effect of deuterium exchange on chemical shift. 5

(r) A mixture of benzene and acetonitrile shows signals at δ 7·2 and δ 1·95 ppm respectively. Integration shows a height of 12 mm for each of these signals. Determine the mole ratio and weight ratio for each of these. 5

5. (a) Explain F^{19} nmR spectra. 4

(b) What is principle of ^{13}C NmR Spectroscopy ? 4

(b) The UV spectrum of acetone shows absorption maximum at 166, 189 and 279 nm. What type of transition is responsible for each of these bands ? 3

(c) How would the infrared spectra of the following compound differ :

$(t-C_4H_9)_2$ NH and $(C_2H_5)_3$ N 3

(d) Explain the effect of hydrogen bonding on the group frequencies of different compounds. 4

OR

(p) What type of electronic transitions are possible for each of following compounds:—

(i) Dimethyl ether (ii) Cyclohexane 4

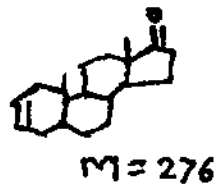
(q) Acetone absorbs light at 280, 187, 154 nm. What chromophore is responsible for each of these absorptions ? What type of transition causes each absorption ? 4

(r) Explain the following terms in detail :—

(i) Fermi Resonance (ii) Overtone band 4

(s) What is Finger Print region ? Explain importance of Finger Print region in IR spectroscopy. 4

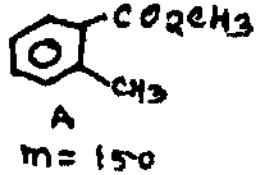
3. (a) Explain the formation of an ion at m/z 222 in the mass spectrum of the steroid shown. Name the type of Fragmentation required to form ion at 222. 4

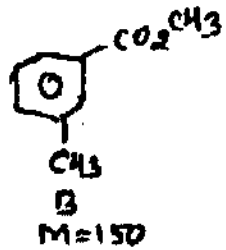


(b) Suggest the structure for the molecule which gives the following mass spectrum m/e 29, 33, 47, 48 give their fragmentation mechanism. 4

(c) What is principle of mass spectrometry ? Explain. 4

(d) What is H – Transfer rearrangement ? The mass spectrum of an ester contains an ion of m/e 118. Which of the following would be expected to yield this ion ?





4

OR

(p) What is mass spectrum ? Discuss following terms in terms of mass spectroscopy :—

(i) Molecular ion (ii) Base Peak

(iii) Metastable ions. 3

(q) Deduce the structure based on following data molecular formula $C_9H_{12}O_2$

m.s (m/2) : 150, 108, 91, 77, 65, 51, 43 4

(r) In mass spectrum of an organic compounds the ratio M : M + 1 was 100 : 24. How many Cl atoms are present ? 3

(s) Explain the following :—

(i) Nitrogen Rule.

(ii) High resolution mass spectrometry. 6

4. (a) An unknown compound gave on elemental analysis 62·1% C and 10·35% H. Its nmR Spectrum consisted of a quintet centred at 7·25 T and a triplet appeared at 5·25 T. Suggest a suitable structure for the unknown compound. 6

(b) Write in brief on spin spin coupling. 4

2260-2240 R - C ≡ N

3300 C ≡ C - H

3030 Ar - H

3040-3010 

2960-2870 Aliphatic CH_3 ; 2990-2850 - CH_2 ; 2890 C. H. 2720 Aldehydic -  - H stretch :

1710-1740.  - OH

stretch 1705-1725 R - - R 1720-1740 R - - H stretch ;

1740-170 R -  - OR (Ester); 1720-1815 R -  - X;

1680-1700; R -  - NH_2 1620-1680 h C = C g ;

1640-1690  -, 1575-1630 - N = N - ; 750 and 700 - Mono substituted benzene ; 750 - ortho ; 780-810 - Meta ; 850-800 para.

3. Characteristics IHNMR chemical shifts in δ units; CH_3 - - 0.9 ; CH_3 C-C g 1.6 ; CH_3 -  - 2.1 ; CH_3 - 2.2 ;

CH_3 - Ar 2.3 ; CH_3 - Br 2.7 ; CH_3 - Cl 3.1 ; CH_3 - O - 3.3

CH_3 -  3.3 ; - CH_2 - - 1.4 ; CH_2 - = C 2.3 ;

CH_2 -  - 2.4

CH_3 - NR_2 2.5; CH_2 - Ar, 2.7; CH_2 - Br 3.3; CH_2 - Cl 3.4

CH_2O 3.4 ; $-\overset{|}{C}H-\overset{|}{C}-$ 1.5 ; $-\overset{|}{C}H-\overset{|}{C}-C$ g 2.6 ; h CH - C - 2.5 ;

$-\overset{|}{C}H-$ Ar 3.0 ; $-\overset{|}{C}H-NR_2$ 2.9 ; $-\overset{|}{C}H-$ Br 4.1 h CHCl 4.1;

– CHO 3.7, H - N g 1 - 3 ; H - OR 1-5 ; H- C Q C - 2- 5; H - C = C g 5.5 ; H - Ar 7- 9 ; H - $\overset{\|}{C}$ - 10 ; H - O - $\overset{\|}{C}$ - 9-12

4. Characteristic 13 CNMR Chemical shifts in δ ppm –

- CH_3 - 0.30 ; - CH_2 - 10-50 ; H – $\overset{|}{C}$ – 25-60, – $\overset{|}{C}$ – Br 10-25.

$-\overset{|}{C}-Cl$ 15-30 ; $-\overset{|}{C}-OH$ 45-75 , - C Q C - 65-90 ;

H -C – C g 80-145 ; Aromatic carbons 110-170 ;

$-\overset{\|}{C}-O$ 155-180 ; $-\overset{\|}{C}-OH$ 160-185 ; $-\overset{\|}{C}-O$ 190-210 ;

H -C = 0 (carbonyl) 190-220 (singlet).