

2015

M.Sc. Part-II Examination

CHEMISTRY

PAPER—VII

Full Marks : 75

Time : 3 Hours

*The figures in the margin indicate full marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

*Illustrate the answers wherever necessary.*

**(Physical Special)**

Answer any five questions  
taking at least two from each group.

**Group—A**

1. (a) Spectroscopic transition probability ( $W_{n \rightarrow k}$ ) from state,  $n$  to state,  $k$  under a weak perturbing potential ( $H'$ ) is given by,

$$W_{n \rightarrow k} = \frac{1}{\hbar^2} \left| \int_{t'=0}^{t'=t} e^{iW_{kn}t'} H'_{kn} dt' \right|^2$$

Where  $W_{kn} = 2\pi\nu_{kn}$  and all other symbols have their usual significances. Use  $H'_{kn}$  as a periodic function of time to obtain the transition probability  $W_{n \rightarrow k}$ . Interpret your result. 8

- (b) Deduce the selection rule for vibrational transition (use Harmonic Oscillator model) and also show that there must be some fluctuation of dipole moment during molecular vibration of a molecule to show Infrared activity.

Given below the recursion formula for Hermite polynomials.

$$\xi H'_v(\xi) = v H_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi) \quad 7$$

2. (a) What is meant by static and dynamic quenching of a fluorophore? Deduce the following form of Stern-Volmer equation,

$$\frac{\tau_0}{\tau} = 1 + K_{sv}[Q]$$

Where  $\tau_0$  &  $\tau$  are the fluorescence lifetime of the fluorophore in the absence and presence of quencher (Q).

How do you obtain  $K_{sv}$  from half quenching method? 2+4+2

- (b) How do you obtain both static and dynamic quenching constant when both the quenching take place simultaneously? 7
3. (a) Write down the steps involved and the rate of each steps for Unimolecular photophysical processes and hence deduce, 2+5

$$\frac{\phi_P}{\phi_f} = \left( \frac{K_{ISC}}{K_f} \right) \left( \frac{K_p}{K_{ISC}^T + K_p} \right)$$

Where symbols have their usual significances. 2+5

- (b) Write short notes on E-type and P-type delayed emission. 4+4

4. (a) Write down the characteristic features of LASER radiation.

"Population inversion is an essential criteria for a system to show Lasing activity" — Explain. 2+2

- (b) "Inversion of population cannot be achieved for a two level system" — Justify or criticize the statement. 7
- (c) Write short note on Mode-locking of LASER. 4

### Group—B

5. (a) Write down the spin wave functions and the magnetic interaction Hamiltonian of an isolated proton. Obtain the expression of its energy and the frequency of transition. 5
- (b) Deduce the expression of precessional frequency of a magnetic nuclei in presence of an applied magnetic field,  $B_0$ . 4
- (c) Write a short note on spin-lattice relaxation. 6
6. (a) What is meant by excited state acidity constant of an organic acid ?  
How do you obtain excited state acidity constant of an organic acid using Fröster cycle ? 2+7
- (b) What is meant by stimulated Raman Scattering ? Give a schematic energy level diagram to explain the stimulated Raman Scattering. 2+4

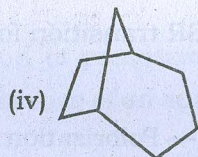
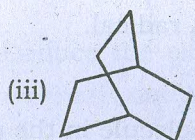
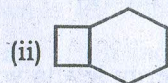
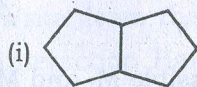
7. (a) Write down the magnetic interaction Hamiltonian and spin wave functions of Hydrogen atom. Obtain the expression for zero order energy and energy with first order correction using Fermi contact term as perturbing term to its Hamiltonian. Find the frequencies of all possible transition for both zero order and first order correction to energy. 2+3+3+2
- (b) Draw the energy levels with possible  $M_I$  and  $M_S$  values for  $^1\text{CH}_3$  radical. State the selection rule and show the possible ESR transition for  $^1\text{CH}_3$  radical. 5
8. (a) Prove that — Polarization of a molecule in the presence of an electro static field is the measurement of change in volume. 2
- (b) Derive the combined equation of Debye and Lorentz-Lorentz. 6
- (c) What is Curie Temperature ? 1
- (d) What are ferro magnetism and antiferrow magnetism ? 3+3

**(Organic Special)**

Answer any *five* questions taking at least *two* from each group.

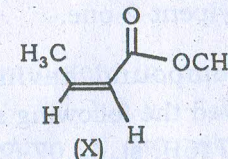
**Group — A**

1. (a) Predict the theoretical number of Proton decoupled  $^{13}\text{C}$  NMR signal of the following compounds. 4



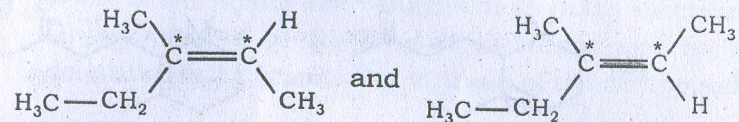
- (b) How will you distinguish between inter and intra-molecular hydrogen bonding on the basis of PMR spectroscopy. 2
- (c) What is spin-lattice relaxation? What factors influence the of Spin-lattice Relaxation time in NMR spectroscopy? 3
- (d) A compound having molecular formula  $\text{C}_9\text{H}_{11}\text{Br}$  showed the following signals in  $^1\text{H}$  NMR data :  
 $\delta 2.25$  (2H, m),  $\delta 2.75$  (2H, t),  $\delta 3.38$  (2H, t),  $\delta 7.22$  (5H, s)  
 Determine the structure of the compound with justification. 6

2. (a) Arrange the chemical shift of different types of proton in the following compound and indicate splitting pattern. 2



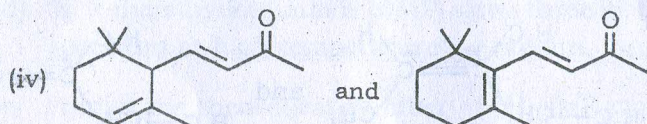
- (b) Why a complex spectrum is simplified by using high field FT-NMR spectroscopy? 3
- (c) 'Magnetic equivalence nuclei are chemical shift equivalence but the reverse is not true' — explain with suitable example. 3
- (d) Why the sensitivity of  $^{13}\text{C}$  NMR signal is very low? 2
- (e) Explain the basic theory of FT-NMR spectroscopy? 5
3. (a) What do you mean by first order spectra and second order spectra? 3
- (b) What is Karplus equation? Draw the plot of coupling constant (J) vs dihedral angle ( $\theta$ ). 3
- (c) 5-Methylcyclopenta-1, 3-diene shows a singlet for methyl group in its  $^1\text{H}$  NMR spectrum. 2

- (d) 'N, N-dimethylformamide (DMF) slows three in its  $^1\text{H}$  NMR spectrum at high temperature' — explain. 2
- (e) Predict the theoretical number of  $^1\text{H}$  NMR signal for 3-chloro-4-methylpent-2-one. 1
- (f) An organic compound having molecular formula  $\text{C}_{10}\text{H}_{13}\text{Cl}$  showed the following spectral data.  
 $^1\text{H}$  NMR :  $\delta$ 1.57 (6H, s),  $\delta$ 3.07 (2H, s),  $\delta$ 7.27 (5H, s).  
 Determine the structure of the compound with justification. 4
4. (a) An organic compound having molecular formula  $\text{C}_7\text{H}_{12}\text{O}_4$  showed the following spectral data.  
 $^1\text{H}$  NMR :  $\delta$ 1.29 (6H, t,  $J = 7.2$  Hz),  $\delta$ 2.5 (2H, s),  $\delta$ 4.16 (4H, q,  $J = 7.2$  Hz).  
 IR ( $\text{cm}^{-1}$ ) : 2941-2857 (m), 1742(S), 1460(m), 1220(s), 1056(s).  
 Determine the structure of the compound with justification. 5
- (b) A compound having molecular formula  $\text{C}_4\text{H}_6\text{O}$  showed the following signals in  $^1\text{H}$  NMR data.  
 $\delta$ 6.20 (1H),  $\delta$ 6.0 (1H),  $\delta$ 5.8 (1H),  $\delta$ 2.2 (3H)  
 Determine the structure of the compound and assign these  $\delta$  values to various hydrogen of the compound. 4
- (c) Calculate the  $\delta_{\text{C}}$  values of the carbon atoms marked with asterisk of the following pairs of isomeric compounds and show how they can be distinguished from each other. 2



[ Additive parameters in ppm :  $\alpha$  : +10.6,  $\beta$  : +7.2;  $\gamma$  : -1.5,  $\alpha$  : -7.9,  $\beta$  : -1.8,  $\gamma$  : -1.5, Z(cis) correction : -1.1, E(trans) correction : 0, Two alkyl substituent at C1 (two  $\text{C}\alpha$ ) : -4.8 ; Base value 123.3 ppm ]

- (d) An organic compound having molecular formula  $\text{C}_9\text{H}_{10}\text{O}_2$  showed the following spectral data.  
 $^1\text{H}$  NMR :  $\delta$ 1.96 (3H, s),  $\delta$ 5.00 (2H, s),  $\delta$ 7.22 (5H, broad singlet).  
 IR ( $\text{cm}^{-1}$ ) : 2941-2857(m), 1745(S), 1225(s), 749(m), 697(s)  
 Determine the structure of the compound with justification. 4
5. (a) How would you distinguish between the following pairs of isomeric compounds from their mass spectral fragmentations? 2x4
- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_3$
- (ii) n-propyl benzene and isopropyl benzene
- (iii)



- (b) What is parent ion peak and base peak? 2
- (c) What is the most characteristic feature of the mass spectra of compound containing one (i) one bromine atom and (ii) one chlorine atom. 2
- (d) What is metastable ion? Give some important characteristic of these peaks. 1+2

### Group — B

6. (a) In mass spectral fragmentation, predict about the most intense peaks of the following compounds :  $1\frac{1}{2} \times 6$
- 2-methyl-2-butanol
  - 6-methyl-3-heptanone
  - n-butyl cyclohexane
  - 4-methylcyclohexene
  - Anthracene
  - butyl amine
- (b) Fill in the blank :
- In case of primary alcohols ( $M$  = molecular mass), base peak will be observed at  $m/e$  \_\_\_\_\_ and another prominent peak with high relative abundance will be at  $m/e$  \_\_\_\_\_.

- (c) What is McLafferty rearrangement in mass spectrum? Give example of it. Why it is important in the determination of molecular formula of the compound. 3
- (d) Give important features of HRMs techniques. 1
7. (a) Alkylation of Indole at  $C_2$ -occurs via migration from  $C_3$ . — Justify the statement with an experimental observation.
- (b) How can you carryout the synthesis of tryptamine from *ortho* nitrotoluene?
- (c) How can you carryout the transformation :  
Yohimbine  $\longrightarrow$  yohimbineoxiindole & vice versa. 5×3
8. (a) Although structurally altogether different Indole & quinine alkaloids originates from same biogenetic precursor. — Justify the statement with a scheme.
- (b) How can you show that all cinchona alkaloids have same stereochemistry at  $C_3$  and  $C_4$  and hence deduce their absolute configuration?
- (c) How can you establish D/E ring junction of yohimbine is *trans* and hence establish the absolute configuration of  $C_{15}$  &  $C_{20}$  centre? 5×3

9. (a) Give biosynthetic conversion of (any *three*) : 3×4

- (i) Geranyl-pyrophosphate to squalene.
- (ii) Lanosterol from squalene.
- (iii) Pregnenolone to progesterone.
- (iv) Coumarin from cinnamic acid.

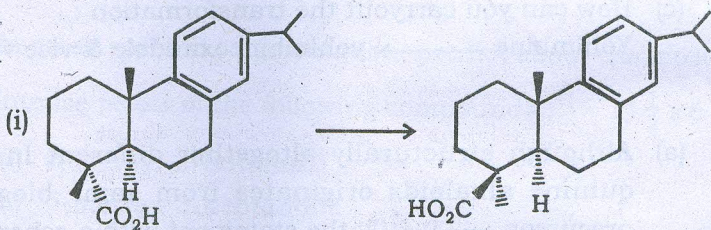
(b) Give synthesis with mechanism of all steps for coumarin from piniol. 3

10. (a) Delineate the following biogenetic conversions :

(i) Acetyl coenzyme to IPP. 4

(ii) FPP to squalene. 4

(b) Explain the following conversions :



(ii)

