2017

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*)

Old Syllabus

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

(Turn Over)

Group—A

1. (a) Write down the steps involved and the rate of each steps for unimolecular photophysical processes.

   Define quantum yield of fluorescence and phosphorescence.

   Assume for a photophysical process,

   $$\phi_p + \phi_f + \phi_{isc}^T \simeq 1$$

   and hence show that,

   $$K_{ISC}^T = K_p . \frac{1 - (\phi_p + \phi_f)}{\phi_p}.$$

   All the symbols have their usual significances.

   3+3+4

   (b) Write a note on E-type delayed emission. 5

2. (a) What is meant by static and dynamic quenching of fluorophore ? Give one example for each. 2+2+1

   (b) How do you obtain the static and dynamic quenching constant when both the quenching process take place simultaneously for a fluorophore. 5+5

3. What is meant by twisted Intramolecular charge transfer (TICT) emission ? Give one such example. 2+1

   Write down the characteristics of TICT emission. Explain the effect of solvent viscosity and solvent polarity on TICT emission. $4\frac{1}{2} \times 2$

   What is excimer emission ? Give one such example. 2+1

4. (a) Explain why the energy of α-spin $\left(m_s = +\frac{1}{2}\right)$ of electron increases linearly whereas that of β-spin $\left(m_s = -\frac{1}{2}\right)$ decreases with the increase in the external magnetic field. 3

   (b) Showing all possible transitions predict the ESR spectrum of methyl radical $(\dot{C}H_3)$. 4

   (c) For p-benzosemiquinone radical anion how many lines are expected in the ESR spectrum and what would be the relative intensities of these lines ? Show all possible ESR transitions for this radical anion. 1+1+2

(d) The benzene radical anion $C_6H_6^-$ has a g-value of 2.0025. At what field would you search for resonance in a spectrometer operating at 9.302 GHz ?

$$(h = 6.626 \times 10^{-34} \text{ JS})$$ 2

(e) Predict the number of lines in the ESR spectrum of the following radicals :

(i) $\left[CF_2H\right]^{\bullet}$ (ii) $\left[13CF_2H\right]^{\bullet}$
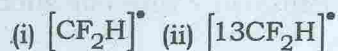
$$\left(I_{19_F} = \tfrac{1}{2},\ I_{13_C} = \tfrac{1}{2}\right).$$ 2

Group—B

5. (a) Define chemical shift (δ_H) in NMR transition.

Show that the seperation between two absorption lines for the chemical shift scale in independent of the applied magnetic field.

"Chemical shift of a given proton decreases with the increase in shielding constant" — Explain.   2+4+2

(b) Compute the NMR spectrum of a two spin system for ν_0 = 60 MHz & ν_0 = 270 MHz. Given that $\sigma_1 - \sigma_2$ = 0.24×10^{-6}, J = 8.0 Hz. Sketch the spectrum in each case.   7

6. Write down the magnetic interaction Hamiltonian and spin wave functions for A_2 spin system. Obtain the zero order energy of all the spin state and hence show the frequency of all the possible transitions.   1+2+8+4

7. (a) First order co-efficient for transition from state ψ_n to ψ_k (two level system) is given by,

$$e_k^{(1)}(t) = \frac{1}{i\hbar} \int_{t'=0}^{t'=t} e^{iw_{kn}t'} H'_{kn} dt'$$

where symbols have their usual significances and

$H'_{kn} = \langle \psi_k | H' | \psi_n \rangle$; H' is the time-dependent perturbation.

Assume H' as periodic function of time and hence deduce the expression for probability of transition from state ψ_n to state ψ_k. Comment on your result.   7+2

(b) What is Doppler broadening in spectral transition ? Deduce an expression to calculate the temperature of a gas from its spectral broadening data.

(Assume Doppler effect is the only operative mechanism for spectral broadening.)   6

8. (a) Deduce the selection rule of vibrational transition and hence show that it is the fluctuation of dipole moment during molecular vibration is responsible for vibrational transition.

Given below is the identify relation of Hermite polynomials

$$\xi H_v(\xi) = v H_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi).$$ 8

(b) Deduce the expression of Fermi-Golden rule. Comment on the final expression. 7

Group—C

9. Answer any *five* of the following : 5×5

(i) In a linear molecule A-B-C, discuss how isotopic substitution is useful for determining A-B and C-B bond distances.

(ii) Write down Franck Condon principle and discuss the quantitative basis of the principle.

(iii) What is vibronic transitions ? Discuss orbital and spin selection rule.

(iv) Short note on Stark effect.

(v) Write down the magnetic interaction Hamiltonian and the possible spin wave functions for A-X spin system.

(vi) Write a short note on P-type delayed emission.

(vii) Write down the characteristics of LASER radiation. "Inversion of population is an essential criterian for LASER" — Explain.

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(Organic Special)

Old Syllabus

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions

taking at least *two* from each group A and B.

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions

taking at least *two* from each group (A and B) and answer *five* questions from group C.

Group — A

1. (a) The NMR spectrum of AX_3 exhibits lines at $\delta = 2.1$ and 2.3 ppm (for X type protons) and $\delta = 4.1, 4.3, 4.5$ and 4.7 ppm (for A type protons), measured from TMS with an instrument operating at 200 MHz. What are the chemical shift (in ppm) of A and X protons and coupling constant (in Hz) ?   2

   (b) The uncertainty in the NMR frequency of a compound in liquid state (relaxation time = 1 s) is 0.1 Hz. What is the uncertainty in the frequency (in Hz) of same compound in solid state (relaxation time = 10^{-4} s).   2

   (c) Explain the following : The ^1H NMR spectrum of Bullualene (A) shows only one sharp singlet at 120°C but below –85°C show four complex multiplets.   3
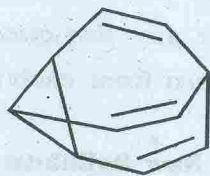
(A)

   (d) How would you distinguish between the following pairs of compounds from their ^1H NMR spectra ? Give only the distinguishing features.   2×3

   (i) Aromatic compound and Antiaromatic compound,

   (ii) Cis-Cinamic acid and Trans-Cinamic acid,

   (iii) α-D-glucopyranoside and β-D-glucopyranoside.

   (e) ^1H NMR spectrum of a mixture of benzene & acetonitrile (CH_3CN) shows two singlets of equal integration. What is the molar ratio of benzene and acetonitrile.   2

2. (a) What do you mean by first order spectra and second order spectra ?   3

   (b) Calculate the δ_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.
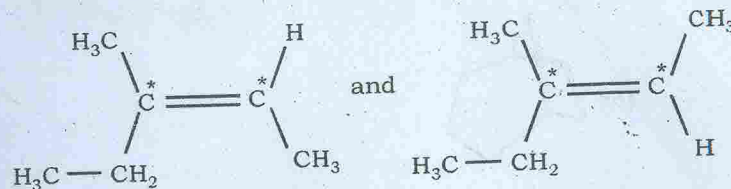
   [Additive parameters in ppm : α : +10.6, β : +7.2 ; γ : –1.5, α : –7.9, β : –1.8, γ : –1.5, Z(cis) correction : –1.1, E(trans) correction : 0, Two alkyl substituent at C1(two $C\alpha$) : –4.8 ; Base value 123.3 ppm]   3

(c) What is Karplus equation ? Draw the plot of coupling constant (J) vs dihedral angle (θ). 3

(d) Predict the number of proton NMR signals produced for (i) allyl bromide, (ii) Vinyl bromide. 2

(e) Predict the theoretical number of Proton decoupled ^{13}C NMR signal of the following compounds. 4

(i)

(ii)

(iii)

(iv)
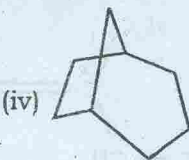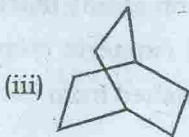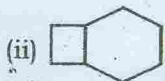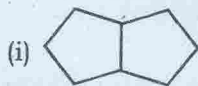
3. (a) The g-factors of ^1H and ^{13}C are 5.6 and 1.4 respectively. For the same value of the magnetic field strength, the ^1H resonates at 600 MHz. What is the resonance frequency of ^{13}C ? 2
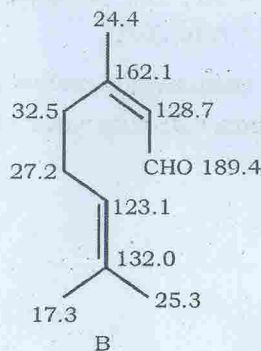
(b) The structure of the compound that matches the ^1H NMR data given below is

^1H NMR (DMSO-d_6) : δ 7.75 (dd, J = 8.8, 2.4 Hz, 1H), 7.58 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.50 (broad s, 2H), 3.8 (s, 3H).

Which of the compounds below most closely matches the ^1H NMR data ? Justify your choice. 5

(i)

(ii)

(iii)

(iv)

12
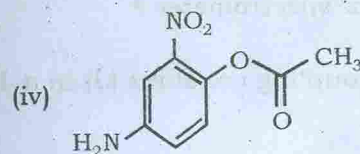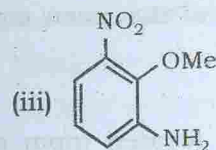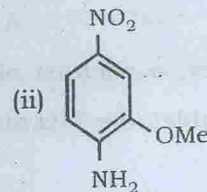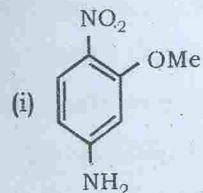
(c) Draw the expected DEPT and ATP, spectra of the compound. 4

```
        24.4
         |
       162.1
32.5      128.7
   \      /
27.2    CHO 189.4
   |
 123.1
   |
 132.0
17.3   25.3
   B
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(d) Using 60 MHz NMR spectrometer, a chemist observes the following proton signal. A doublet, J = 7Hz at δ = 4.0 ppm.

(i) What will be the frequency of the given signal in Hz unit ?

(ii) Where would this peak be located (ppm and in bertz) in a 100 MHz spectrometer ?

(iii) What would be the coupling constant (J) in a 100 MHz spectrometer ? 4

4. (a) Why a complex spectrum is simplified by using high field FT-NMR spectroscopy ? 3

(b) How will you distinguish between inter and intra-molecular hydrogen bonding on the basis of PMR spectroscopy. 2

(c) A Compound having Molecular formula $C_6H_{11}BrO_2$ exhibited the following data

^1H NMR : δ 3.59 (s, 3H) 3.32 (t, 3H), 2.25 (t, 2H), 1.85-1.75 (m, 2H), 1.73-1.62 (m, 2H)

^{13}C NMR : d 174.0, 51.0, 32.9, 32.8, 31.0, 23.0

IR : 1736 cm^{-1}

Determine the structure of the compound with justification. 5

(d) The ^1H NMR spectrum of the following compound (X) shows the following signals δ = 2.1, 3.9, 5.7, 6.8. Assign these δ values to various hydrogens, and draw the ^1H NMR of the compound indicating splitting pattern. 3

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H₃C      O
   \     ‖
    C    C
   ‖      OCH₃
   C
  / \
 H   H
   (X)
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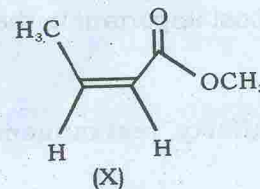
(e) 'N, N-dimethylformamide (DMF) slows three in its ^{1}H NMR spectrum at high temperature'— explain. 2

5. (a) Give three important features of the parent ion peak. 3

(b) Write the important features of the mass spectra of (i) alcohols and (ii) aliphatic carbonyl compounds. 3+3

(c) Show the mass spectral fragmentation for following compound indicating most intense peak :

(i) 2, 2-dimethylpentane (ii) n-heptane. 2+2

(d) Distinguish between isopropylbenzene and n-propylbenzene on the basis of mass spectroscopy ? 2

Group — B

6. (a) What is metastable ion ? Give some important characteristic of these peaks. 2+2

(b) Why HRMS is most important in the mass spectroscopy ? 2

(c) What is McLafferty rearrangement ? Explain with example. 3

(d) In mass spectral fragmentation, predict about the most intense peaks of the following compounds :

(i) 3-methylcyclohexene

(ii) 2-mythyl-2-hexanol

(iii) 6-methyl-3-heptanone

(iv) Phenetol ($PhOC_2H_5$). $1\frac{1}{2} \times 4$

7. How would you carry out the following conversion ?

(i) Yohimbine to pseudo-yohimbine and vice versa.

(ii) Indole alkaloid to Quinoline alkaloid.

(iii) Caryophyllene to cloven.

(iv) Quinine to Quinidine. (3+3)+3+3+3

8. Derive suitable experiment to establish the absolute configuration of the following :

(i) C_{17}-OH in yohimbine

(ii) Stereochemistry of the D/E ring junction in yohimbine.

(iii) Location of isopropyl grouping and the double bonds in abietic acid. 4+7+4

9. Answer any *three* questions of the following :   3×5

(a) Mention the biogenetic pathway for the formation of morphine from thebaine and name the enzymes involved for each step.

(b) Outline the biogenetic transformation of mevalonic acid to isopentenyl pyrophosphate (IPP). Give the respective enzyme for the steps.

(c) "Abietic acid undergoes Diels-Alder reaction with maleic anhydride via the formation of levopimaric acid." — Explain the reaction and provide evidence for the isomerisation of heteroannular cojugated diene to homoannular conjugated diene.

(d) "Pyruvic acid and D-glyceraldehyde 3-phosphate condense together in presence of thiamine pyrophosphate (TPP) and an enzyme to form 1-deoxy-D-xylulose-5-phosphate." — Provide a suitale methanism of the reaction and identify the enzyme.

(e) Elaborate the degradation sequence for the conversion of abietic acid to fluorenone. Mention the reagents and reaction conditions.

10. Answer any *three* questions of the following :   3×5

(a) Elucidate the steps involving specified reagents and reaction conditions for transforming geranylacetone to farnesol. Mechanisms of the steps are not required.

(b) Identify the products A, B and C of the following reactions and discuss the mechanism involved.

Yohimbine reacted with $Hg(OAc)_2$ to form A which is reduced with $NaBH_4$ to give exclusive product B whereas A on treatment with Zn/HOAc produces equal amount of B and C.

(c) "Thebaine on heating with conc. HCl gives morpho-thebaine whereas on warming with dil. HCl furnishes thebenine." — Explain the mechanisms of the formation of two structurally different products under the stated reaction conditions.

(d) Outline a synthesis of etorphine from thebaine. Indicate its importance as analgesic.
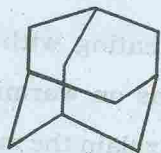
Group—C

11. Answer any *five* questions from following : 5×5

(a) What are the advantages of Fourier Transform (FT-NMR) technique over CW-NMR technique ? 5

(b) (i) The ^{13}C NMR spectrum for ethyl benzoate contains these peaks : 17.3, 61.1, 100-150 ppm (four peaks) and 166.8 ppm. Which peak belongs to which carbon atom ? 2

(ii) How many signals would you expect in the ^{13}C NMR of the following compound ? 1

(iii) Predict the approximate chemical shifts and multiplicities for the absorptions in the ^1H NMR spectrum of the following compound : 2
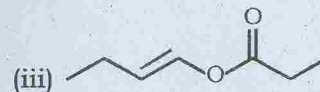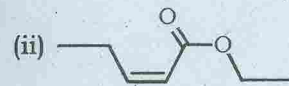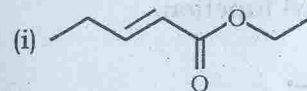
$$H_3C - \!\!\!\bigcirc\!\!\!- \overset{\overset{O}{\parallel}}{C} - O - CH_2CH_3$$
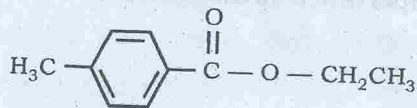
(c) An Organic compound compound of molecular formula, C7H12O2 exhibited the following data in the 1H NMR spectrum :

δ 7.10 (dt, 1H, J_1 = 16, J_2 = 7.2), 5.90 (dt, 1H, J_1 = 16, J_2 = 2), 4.1 (q, 2H, J = 7.2 Hz), 2.10 (m, 2H), 1.25 (t, 3H, J = 7.2 Hz), 0.90 (t, 3H, J = 7.2 Hz) ppm.

Which of the compound below most closely matches the ^1H NMR data ? Justify your choice. 5

(i)

(ii)

(iii)

(iv)

(d) Write down the structures of codeine and isocodeine. When each of them is reacted with PCl_5 separately, the products are different. Explain the reaction pathway for each reaction based on the different stereochemistry for the two reactants. 5

(e) Reserpine, on heating with gl. HOAc, equilibrates with isoreserpine, the latter being formed in higher proportions. Give a mechanism for this acid catalysed interconversion and provide suitable evidence in favour the suggested mechanism.   5

(f) Alkylation of Taniguchi lactone with $ICH_2CH_2OTBDPS$ is carried out in a round-about way. Elaborate the reaction sequence to obtain the alkylation at the carbon bonded to lactone carbonyl function.   5

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