Total Pages—14 **PG/IIIS/CH-2103/10**

M.Sc 3rd Semester Examination 2010

CHEMISTRY

PAPER—CH-2103

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Physical Special*)

Answer any four questions taking one from each Group

GROUP—A

Answer any *one* of the following :

1. (*a*) What do you mean by prolate and oblate symmetric top ? Give one example for each.

(*b*) Constract the Hamiltonian operators for prolate and oblate symmetric top and hence obtain their energies using the eigen value equation of $\hat{L}^2$, $\hat{L}_Z$ and $\hat{L}_{Z}$ operator w.r.t the Wigner function D^J_{MK}, where J, M and K are quantum number associated with the total angular momentum, Z component of angular momentum in the lab frame and Z' component of angular momentum in the molecular frame respectively.

(*c*) Show that, the energy of prolate symmetric top increases with the increasing value of ‘*k*’, whereas this trend is opposite in case of oblate symmetric top. 2 + 6 + 2

2. First order co-efficient for transition from state *i*’ to sate ‘*f*’ is given by,

$$C_f^{(1)} = -\frac{i}{\hbar}\int_0^t e^{i\omega_{fi}t}\; V_{fi}(t)\, dt$$

where, $V_{fi}(t) = \langle f|\, H'(t)\,|i\rangle$; $H'(t)$ is the time dependent perturbing field.

(*i*) Assume $H'(t)$ as Harmonic perturbation (say $H'(t) = V(r)\cos(\omega t)$) and give a theoretical explanation for the phenomena of stimulated absorption and stimulated emission processes.

(*ii*) Assume $H'(t)$ as constant perturbation and ω_{fi} having very small value to obtain,

$$P_{i \to f} = |C_f^{(1)}|^2 = \frac{|V_{fi}|^2}{\hbar^2} \cdot t^2.$$

Comment on the above expression. 6 + 4

GROUP—B

Answer any *one* of the following :

3. (*a*) Using Einstein treatment of absorption and emission phenomenon for a two level system, show that,

$$\frac{A_{21}}{B_{21}\varrho(\gamma)} = e^{h\gamma/KT} - 1$$

where symbols have their usual significance. Inversion of population was first achieved in the microwave region of spectrum. Explain.

(*b*) Write down the characteristic features of LASER radiation. (5 + 2) + 3

4. (*a*) Inversion of population cannot be achieved in two level system. Justify.

(*b*) Write down the principle of *Q*-switching. How do you obtain a giant LASER pulse using *Q*-switching technique ? 6 + 4

GROUP—C

Answer any *one* of the following :

5. What do you mean by dynamic quenching of a fluorophore? Deduce the following form of Stern–Volmer equation :

$$\frac{\phi^{\circ}_f}{\phi_f} = 1 + K_{SV}[Q]$$

where symbols have their usual significance. Describe one method for the determination of dynamic quenching constant. 1 + 6 + 3

6. What do you mean by *E*–type and *P*–type delayed emission? Write down the different photophysical steps and their rate for *p*–type delayed emission. How do you obtain ΔE_{ST} (energy gap between the first excited singlet and triplet state) for a molecule showing *E*–type delayed emission? 3 + 2 + 5

GROUP—D

Answer any *one* of the following :

7. (*a*) Express the energy of an spin half nucleus in presence of a magnetic field applied in the *z*-direction.

(*b*) What is Larmor precession? What is the relation between the frequency of Larmor precession and the frequency of NMR transition?

(*c*) Explain, why NMR spectrum of an organic compound is taken in a deutorated solvent. 4 + 3 + 3

8. (*a*) Draw schematically the energy level of $A-X$ system (spin of A and $X = \frac{1}{2}$) in presence of a magnetic field, in presence of spin–spin interaction. Indicate the NMR transitions.

(*b*) Write the wavefunction for A_2 system (spin $= \frac{1}{2}$) and indicate the symmetric and antisymmetric one.

(*c*) Explain, what is meant by chemical shift? What is the relation between chemical shift and shielding constant? 4 + 3 + 3

(*Inorganic Special*)

Answer any **four** questions :

1. Explain why : $2\frac{1}{2}\times 4$

   (*a*) Dissolved oxygen is to be removed from the polarographic cell before an experiment.

   (*b*) Increased viscosity increases fluorescence intensity whereas increased temperature decreases it.

   (*c*) Hydrogen atom shows ESR spectrum whereas hydrogen molecule does not.

   (*d*) Limiting current curve runs parallel to the voltage axis in voltametry.

2. Write short notes on (any *two*) : 5 + 5

   (*i*) Hollow cathode lamp

   (*ii*) Photoemissive cell

   (*iii*) Nonflame AAS technique.

3. (*a*) What kind of weak interactions are involved in "molecular crystal engineering" ?

(*b*) Write down the applications of "Metal-organic frameworks".

(*c*) Discuss the band structure of "semiconductor" and "insulator".

(*d*) "Mg" is a metallic conductor while "Si" is an insulator. Explain in the light of band theory. 2 + 2 + 4 + 2

4. (*a*) Why does defect occur in a crystal ? What is a perfect crystal ?

(*b*) What do you mean by "metal excess defect" ?

(*c*) Discuss "Frenkel and Schottky" defects. 3 + 2 + 5

5. How do you estimate ? 4 + 3 + 3

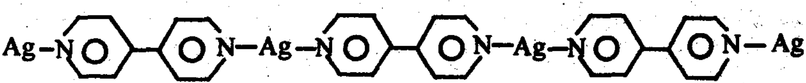
(*i*) Cadmium in blood

(*ii*) Arsenic in hair

(*iii*) Lade in petroleum.

6. (*a*) Schematically represent the formation of metallo-supramolecules and coordination polymers by convergent and divergent approach respectively.

(*b*) What do you mean by 'building block' in a coordination polymer ? Identify synthons and Tectons in the following coordination polymer.



(*c*) A molecular square is formed when M^{n+} (metal ion) is reacted with ethylene diamine and 4, 4′-bipy ligand. Write down the probable structures. What structure of the product will you expect when the same rection is performed in absence of ethylene diamine ligand.

(*d*) What is the aim of "supramolecular chemistry" ?

2 + 3 + 3 + + 2

7. (*a*) What is the basic principle of colorimetry ? How do you determine the molecular composition of a complex colorimetrically ?

(*b*) How do you estimate gold in photographic film ?

(*c*) Write short notes on "Interferences in AAS analysis". (1 + 4) + 2 + 3

(*Organic Special*)

Paper — CH-2103

Answer any **five** questions :

1. (*a*) Identify the spin systems (pople notation) constituted by the underlined protons in any *two* of the following molecules : 2 + 2

   (*i*) $ClC\underline{H}_2C\underline{H}Cl_2$

   (*ii*) $Ph\,C\underline{H}Br\,C\underline{H}_2Br$

   (*iii*) $C\underline{H}_3C\underline{H}_2C\underline{H}_2NO_2$

   (*b*) Attempt any *two* questions : 2 + 2

   (*i*) Why is "superconducting Magnet" required for recording FT NMR spectra ?

   (*ii*) Write down the structure of Eu $(DPM)_3$ and state what it is used for.

   (*iii*) What are the advantages of FT NMR over CW NMR ?

2. (*a*) (*i*) Depicting the three stable conformers, explain why the vicinal coupling constants in freely rotating carbon chains (alkyl groups) is around 7 Hz. Given, ${}^3J_{HH}$ for Hs = 3 Hz and for aute - Hs, ${}^3J_{HH}$ = 15 Hz.

(*ii*) Draw the structures of two compounds where W coupling (${}^4J_{HH}$) is present.

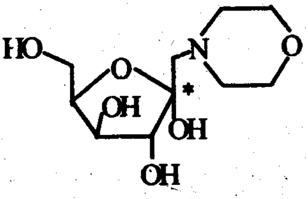
2 + 2

(*b*) (*i*) Explain "Pseudocontact Shift" in connection with the use of Lanthanide Shift Reagents.

(*ii*) Compare, using necessary calculations, the Receptivity of ^{1}H and ^{13}C nuclei in NMR spectroscopy. 2 + 2

3. (*a*) (*i*) How would you distinguish between the *Z* and *E*-isomers of $CH_3CI = CHCO_2Me$?

(*ii*) What is the usefulness of 'Rotating frame of Reference'? How can you calculate the 'repetition time' (D) in PFT NMR? 2 + 2 (*b*) (*i*) How would you calculate the expected ^{13}C chemical shift of the C^* in the following compound? Show only the break-ups; values need not be used.



(*ii*) Explain "Spin Tickling" with reference to SFORD experiment in ^{13}C NMR spectroscopy. 2 + 2

4. (*a*) Calculate $\delta^{13}C^*$ in the following compund :

$$CH_3COCH_2\overset{*}{C}H_2CO_2CH_3$$

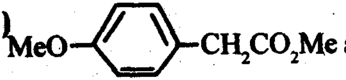
Given, shielding values: α-$CO_2 = 22 \cdot 6$ ppm and β-$CO = 3 \cdot 0$ ppm.

(*b*) Explain what is Heavy Atom Effect (^{13}C NMR). 4 + 4

5. (*a*) Distinguish between the following pairs of structural isomers (any *two*) by MS : 2 + 2

(*i*) $PhOCH_2CH_3$ and $PhCH_2OCH_3$

(*ii*)



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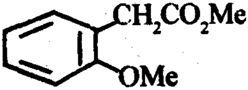

(*iii*) 2 - Hexane and 3-Hexane.

(*b*) Attempt any *four*: 1 x 4

(*i*) In CI–MS, what are the reagent ion and the pseudomolecular ion if $(CH_4 + NO)$ is used as the reagent gas ?

(*ii*) Calculate the apprarent mass (m^*) of a "metastable ion" from the masses of the parent ion (m_1) and the daughter ion (m_2).

(*iii*) If a compound contains '*n*' nuclear of chlorine or bromine atoms, how many molecular ion-peaks would be observed in its MS ?

(*iv*) What is meant by 'TOF' in MS ?

6. (*a*) (*i*) In HR EI–MS, what are the successive fields through which the ions coming out of the ionisation chamber are passed through?

(*ii*) Identify the compound which recorded peaks at m/z 128 & 126 (1:3), 91 (100%), 65.

(*iii*) Explain the formation of a peak at m/z 68 in the mass spectrum of '*Z*'-Methyl crotonate.

(*iv*) What is the common mode of fragmentation in the mass spectra of phenyl acetate, benzyl acetate and acetaniliade? 1 x 4

(*b*) (*i*) In FAB-MS, why is a matrix used?

(*ii*) What kind of molecules are subjected to a soft ionisation MS technique?

(*iii*) Define "Resolution" (*R*) as used in MS.

(*iv*) What is the full form of ESI-MS? 1 x 4

7. Identify the compound, C_8H_7OBr, which recorded the following spectral data : IR : 1641 cm^{-1}; ^{1}H NMR : δ 4·47 (2H, *s*), 7·49 (2H, *t*, J = 7 Hz) 7·61 (^{1}H, *t*, J = 7 Hz), 7·99 (2H, *d*, *J* = 7 Hz) ; ^{13}C NMR : δ 191·5 (C), 134·18 (C), 134·21 (CH), 129·17 (CH), 129·10 (CH), 31·1 (CH_2) ; ^{13}C – ^{1}H correlations : δ 31·1 to δ 4·47 ; δ 129·1 to δ 7·49 and 7·99 ; δ 134·21 to δ 7·61 ; EI–MS : m/z 200 & 198 (1 : 1), 119, 105, 77, 51. Explain all the data. Show its mass fragmentions. 8

8. Characterise the compound, $C_4H_6O_3$, from its given data. IR : 1730 cm^{-1} ; ^{1}H NMR : δ 3·85 (3 H, *s*) and δ 2·46 (3H, *s*) ; ^{13}C NMR : δ 191·8 (C), 161·3 (C), 53·2 (CH_3), 26·9 (CH_3) ; EI–MS : *m*/*z* 102 (M^+), 71, 43 ; ^{1}H–^{13}C correlations : δ 3·85 to δ 53·2 ; δ 2·46 to δ 26·9. Explain all the data. 8