2016

M.Sc.

3rd Semester Examination

CHEMISTRY

PAPER—CEM-303

Full Marks : 40

Time : 2 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.

(*Organic + Inorganic + Physical Special*)

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

Group—A

1. (a) What happens to the absorption spectra of iodine dissolved in carbon tetrachloride, when pyridine is progressively added to it ? 2

(b) Which of the following statements are correct ? 2

(i) Maxima of the wave functions for the second vibrational energy state are at the centre and the same for the zero th vibrational level are at the edges.

(ii) Maxima of the wave functions for the second vibrational energy state are at the edges and the same for the zero th vibrational level is at the centre.

(iii) Maxima of the wave functions for the second vibrational energy state are at the centre and the same for the zero th vibrational level are at the centre.

(iv) Maxima of the wave functions for the second vibrational energy state are at the centre and the same for the zero th vibrational level are at the edges.

(c) Write down the relation between the protolytic dissociation constant of phenolic compounds in the ground and excited state with the difference in electronic transition frequencies. 2

(d) Match the following : 2

1	$S_1 \rightsquigarrow S_1$	A	$10^{11} - 10^6\ s^{-1}$
2	$S_1 \rightsquigarrow S_0$	B	$10^4 - 10^{-2}\ s^{-1}$
3	$S_1 \rightsquigarrow T_1$	C	$10^{13} - 10^{12}\ s^{-1}$
4	$T_1 \rightsquigarrow S_0$	D	$10^8\ s^{-1}$ or less

2. (a) What is an optical resonator in LASER ? 2

(b) Schematically show the energy diagram of a three level LASER. 2

(c) Why in a Ruby LASER a trace amount of Cr^{3+} ion is doped with aluminium ? 2

(d) Why are waveguides essential in IR-LASERS ? 2

3. (a) "Water and alcohol are not suitable solvents for ESR studies" — explain. 2

(b) The benzene radical anion has g = 2.0025. At what field should you search for resonance in a spectrometer operating at 29.453 GHz. 2

(c) Explain why the energy of α-spin of electron increases linearly whereas that of β-spin decreases in presence of external magnetic field. 2

(d) "The ESR signals are expected to be more instance than those of NMR signals"—comment. 2

4. (a) Why do we get two peaks for the p, d and f electrons in XPS ? 2

(b) What are "auger electrons" ? How do they differ from the normal X-ray photoelectrons ? 3

(c) Show in the spectra (not necessarily according to the scale) the sequence of the appearance of the XPS lines for Li in pure metallic form and in the form of its oxide. 3

Group—B

5. (a) Write down the relation between excited state lifetime and the rate constant involving IC, ISC. 2

(b) Which of the following exhibit excimer emission ? Pyrene, napththalene, anthracene, naphthacene, 2-mythylanthracene, 9-methylanthracene and 9, 10-diphenylanthracene. 2

(c) When Fe^{+2} salt and methylene blue are mixed together, the dye gets bleached only in the presence of light – why ? 2

(d) At 77°C, the ϕ_r and ϕ_p values of benzene are 0.2 and 0.2 respectively. Calculate the radiationless transition probabilities of benzene at the same temperature. 2

6. (a) What do you mean by coherence ? What are the different types of coherences ? 2

(b) Show that a two level pumping scheme has no practical significance for lasing. 2

(c) What is a gain in lasers ? What is the condition for a threshold gain ? 2

(d) What are optical cavities ? How are they useful in laser action ? 2

7. (a) Explain, why Mn(II) is EPR active but Cr(II) is EPR inactive. 2

(b) Using energy level diagram explain the ESR spectrum of $[NO(SO_3)_2]^{2-}$. 2

(c) What do you mean by "zero field splitting" ? 2

(d) Why are the differential plots preferred over the conventional plots in esr spectroscopy ? 2

8. (a) How would you know, a fluorescence quenching process is dynamic or static in nature ? 2

(b) Showing all possible transitions, discuss the ESR spectrum of p-benzosemiquinone radical anion. 3

(c) Explain the method of determination of the binding constant between a dye cation and polyanion by using Benesi-Hildebrand formalism. 3
