PG/IIIS/CEM/301/23

M.Sc. 3rd Semester Examination, 2023

CHEMISTRY

(*Phy./Org./Inorg. Spl.*)

PAPER – CEM-301

Full Marks : 50

Time : 2 hours

The figures in the right hand margin indicate marks

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

GROUP – A

Answer any *four* questions of the following : 2×4

1. When a 30.4 nm radiation is used to produce the photoelectron spectrum of benzene, the highest energy photoelectrons have the kinetic energy of 31.5 eV. Find the ionization energy of the highest occupied molecular orbital of benzene.

2. In addition to the use of microwave radiation, it is essential to apply external magnetic field for recording EPR spectrum of a sample. Comment.

3. State and explain the rate of the primary step of a photophysical process.

4. What is meant by static quenching of fluorophore ? Give one example.

5. What are optical cavities in LASERS ?

6. Why are the explosives easily detectable by NQR spectroscopy ?

GROUP – B

Answer any *four* questions of the following : 4×4

7. (*i*) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of $[NH_2]^{\bullet}$ radical.

(*ii*) Water and alcohol are not suitable solvents for ESR studies. Comment. 3 + 1

8. Explain the appearance of two lines in the atomic photoelectron spectrum of Ar. 4

9. Deduce the following form of Stern-Volmer equation,

$$\frac{\tau_f^0}{\tau_f} = 1 + K_{sv}[Q]$$ 4

(Symbols have their usual significance)

10. Write down the characteristics of exciplex emission.
'Exciplex emission is broad, structureless and red shifted"–Explain. 1 + 3

11. Explain the construction and function of a He-Ne LASER. 4

12. Compare and contrast active and passive mode locking. 4

GROUP – C

Answer any *two* questions of the following : 8×2

13. (*i*) Photoelectron spectrum of molecular nitrogen exhibits three vibrationally structured photo-ionizations at about 15.6, 17.0 and 18.8eV and a detail of the spectrum is given below. Predict the nature of different molecular orbitals of N_2 molecules. (Vibrational frequency for the ground state of N_2 is 2345 cm^{-1}).

	Ionization at 15.6 eV	Ionization at 17.0 eV	Ionization at 18.8 eV
Most intense peak	adiabatic ionization	vertical ionization (v=0 to v=1)	adiabatic ionization
Vibrational spacing	2150 cm^{-1}	1810 cm^{-1}	2390 cm^{-1}

(*ii*) Explain the appearance of three lines in the ESR spectrum of di-*t*-butyl nitroxide radical. 5 + 3

(*Continued*)

14. (*i*) Showing "crystal field splitting" and weak "zero-field splitting" predict the expected EPR spectrum of octahedral Cr(III) complex.

(*ii*) Photoelectron spectrum of solid NaN_3 exhibits two peaks with intensity ratio 2:1.-Explain.

(*iii*) Photoelectron spectrum of H_2 molecule consists of a vibronic band system with first peak at 15.45 eV and the spectrum extended up to 18.0 eV. On the other hand, photoelectron spectrum of He exhibits only a single peak at 24.59 eV. From these spectral data explain which of the two isoelectronic H_2 and He should have greater ionization energy and why ? 4 + 2 + 2

15. Write down the steps and the rate of each step for unimolecular photophysical process.

Assume, $\varphi_f + \varphi_P + \varphi_{ISC}^T \cong 1$ for any unimolecular photophysical process and hence deduce the following expression,

$$K_{ISC} = \frac{1}{\tau f}\left(\frac{1-\varphi f}{\varphi f}\right)$$

(Symbols have their usual significance) 2 + 6

16. What is an optical resonator in LASER ? Schematically show the energy diagram of a three level LASER. Why in a Ruby LASER a trace amount of Cr^{3+} ion is doped with aluminium ? Why are waveguides essential in IR-LASERS ? 2 + 2 + 2 + 2

[Internal Assessment — 10 Marks]