M.Sc. 3rd Semester Examination, 2019

CHEMISTRY

(*Organic/Inorganic/Physical Special*)

PAPER —CHEM-301

Full Marks : 40

Time : 2 hours

Answer **all** questions

The figures in the right-hand margin indicate marks

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

Illustrate the answers wherever necessary

GROUP – A

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

1. Considering the following parameters with reference to the fluorescence of a solution,

   (*A*) Molar absorptivity of the fluorophore.

(B) Dissolve oxygen in the medium.

(C) Intensity of light source used for excitation. The correct answer for the enchancement of fluorescence with the increase in these parameters is/are,

(i) A and B
(ii) B and C
(iii) A and C
(iv) C only

2. The first electronic absorption maximum of a polar and relatively rigid aromatic molecule appears at 310 nm but its fluorescence maximum in acetonitrile solution appears with large stokes shift at 450 nm. The most likely reason for the stokes shift is
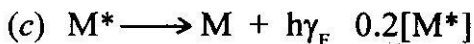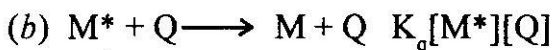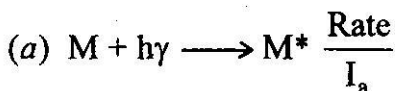
(i) Large change in molecular geometry

(ii) Increase in dipole moment of the molecule in the excited state.

(iii) Decrease in polarizibility of the molecule in the excited state.

(*iv*) Lowered interaction of the excited molecule with polar solvent.

3. Photochemistry of a molecule, M is described by the following mechanism.

(*a*) $M + h\gamma \longrightarrow M^* \quad \dfrac{Rate}{I_a}$

(*b*) $M^* + Q \longrightarrow M + Q \quad K_q[M^*][Q]$

(*c*) $M^* \longrightarrow M + h\gamma_F \quad 0.2[M^*]$

The intercept at [Q] = 0 is 2 for the inverse of fluorescence intensity (1/F) Vs. [Q] plot. The value of I_a is :

(*i*) 0.5
(*ii*) 0.25
(*iii*) 4
(*iv*) 0.8.

4. The interaction of an unpaired electron with N^{14} causes a splitting of three lines while with Mn^{55} it gives six lines. — Explain.

5. Water and alcohol are not suitable solvents for ESR studies. — Justify.

6. Energy of α-spin of electron increases linearly, whereas that of β-spin of electron decreases with the increase in external magnetic field strength. — Explain.

7. A two level pumping scheme has no practiacl significance for lasing. — Explain.

8. What are chemical LASER$_s$?

GROUP — B

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

9. Write down the characteristics of twisted intramolecular charge transfer(TICT) emission. Explain the effect of solvent polarity on TICT emission. $2 + 2$

10. The fluorescence lifetime of a molecule in a solution in 5×10^{-9}s. The sum of all the non

-radiative rate comtant (ΣK_{hr})for the decay of excited state is 1.2×10^8 s^{-1}. Calculate the fluorescence quantum yield of the molecule.   4

11. What is meant by exciplex emission. Draw the potential energy diagram for exciplex. How do you explain the broad structureless emission of exciplex ? $1 + 2 + 1$

12. The ESR frequency for a free electron is 9430MHz. Calculate the magnetic field strength at which the ESR spectrometer is working.   4

13. Showing all possible transitions, discuss the ESR spectrum of $[CH_3]^{\cdot}$ radical.   4

14. Predict the intensity distribution in the hyperfine lines of the ESR spectrum of NH_2 radical.   4

15. What are optical cavities ? How are they useful in LASER ? $2 + 2$

16. Differentiate between optical pumping and

electrical pumping scheme. How can pumping help in achieving population inversion ? 2 + 2

GROUP – C

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

17. Write down the steps involved and the rate of each steps for bi-molecular photophysical processes. Deduce Stern-Volmer equation. How do you obtain Stern-Volmer quenching constant (K_{sr}) using half quanching method. 2 + 3 + 3

18. What is meant by excited state acidity constant ? How do you obtain excited state acidity constant of β-naphthol using its absorption spectral data ?
2 + 3 + 3

19. (*i*) Explain the appearance of two lines in the ESR spectrum of Hydrogen atom.

(*ii*) Explain the ESR spectrum of *p*-benzosemi-quinone radical anion. 4 + 4

20. (*i*) Write a short note on "Hyperfine splitting" in the ESR spectrum.

(*ii*) Show the hyperfine interaction for a radical containing three equivalent ^{14}N nuclei.

(*iii*) Predict the number of lines in the ESR spectrum of the following radical

$$[^{13}CF_2D]^{\cdot}$$ 3 + 3 + 2

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