M. Sc. (Chemistry) Examination, 2023

(4th Semester)

Paper: XV–I

[Inorganic Chemistry Special]

Time : Two Hours Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

Unit: I-4151

Answer ***all*** the questions.

1. a) How would you determine the structure of $P_3N_3Cl_4F_2$ by NMR spectroscopy?

   b) $[PtBrCl(PR_3)_2]$ ($R=CH_3$) exists in two isomers. How would you identify each of them using NMR spectral measurement? ($I=\frac{1}{2}$ for both ^{31}P and ^{195}Pt)

   c) Compare the ^{19}F NMR of WF_6L (L= pyridine) and $W_2O_2F_9^-$.

   d) Draw the nuclear quadrupole energy level diagram with nuclear spin I=5/2 in an axially symmetric and non-axially symmetric field. Identify the possible NQR transition(s).

   e) Why do we carry out NQR studies normally on a solid crystal? 2+2+2+3+1

2. a) What do you mean by recoilless nuclear transition?

What are the conditions to satisfy for the recoilless nuclear transition?

b) The s-electron density directly controls the isomer shifts – Explain.

c) With proper explanation compare the Mössbauer spectra of deoxyhemoglobin (δ = 0.89 mm/s, Quadrupolar splitting = 2.23 mm/s) and oxyhemoglobin (δ = 0.23 mm/s, Quadrupolar splitting = 2.12 mm/s).

d) What do you mean by hyperfine interaction in the ESR? How can you determine hyperfine coupling constant for H-atom if you know the frequency of two possible transitions? Discuss with schematic energy level diagram. $2\frac{1}{2}+2+2+3\frac{1}{2}$

Unit: I-4152

Answer ***all*** the questions.

3. a) What is the first act of any photochemical and photophysical process? Write down the possible mode of deactivation of the excited state? 2

b) Show schematically where light can act as a reactant and also be obtained as a product. 2

c) What do you mean by Light Emission Sensitizers (LES)? Show schematically how LES function. What are the essential criteria of an ideal LES? 2

d) $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) displays intense emission at room temperature while $[Ru(tpy)_3]^{2+}$ (tpy=2,2':6',2"-terpyridine) does not. Suggest a plausible explanation for the observation. 2

e) $[Ru(bpy)_3](PF_6)_2$ is photochemically inert in water but $[Ru(bpy)_3](Cl)_2$ is photochemically labile in dichloromethane at room temperature. Suggest a probable reason for the experimental finding and predict the final product that can be obtained from $[Ru(bpy)_3](Cl)_2$ in dicholromethane. 2

4. a) What are the essential criteria of any molecular species to perform as Photochemical Molecular Device? Is there any difference between photochemical molecular device and photochemical molecular machine? 2

b) Taking a suitable example, illustrate the function of molecular wire. 3

c) Demonstrate the function of molecular plug/socket by taking advantage of supramolecular interaction. 3

d) What do you mean by “top-down” and “bottom-up” approaches for the construction of nanoscale molecular devices? What strategy would be appropriate for the fabrication of molecular device below the dimension of 100 nm? 2