

End Semester Questions

CH 5102; Duration: 3 hours; Marks: 100

PART A

1. Why the lanthanide emissions possess longer excited state lifetimes whereas the values for the transition metals are shorter?----- (3 marks)
2. Explain why no splitting of the ground state term symbol ($^8S_{7/2}$) is observed for Gd^{3+} ?----- (2 marks)
3. Explain antenna effect in Ln^{3+} complexes and their ----- (5 marks)
4. Calculate the room temperature magnetic moment of Er^{3+} ion. The ground state term symbol is $^4I_{15/2}$. ----- (4 marks)
5. Explain why Eu^{3+} doped samples show sharp emission peaks whereas Eu^{2+} -doped samples exhibit broad emission when excited under UV radiation. ----- (4 marks)
6. Explain the process of FRET with diagram and explain each term in the following equation----- (5 marks)

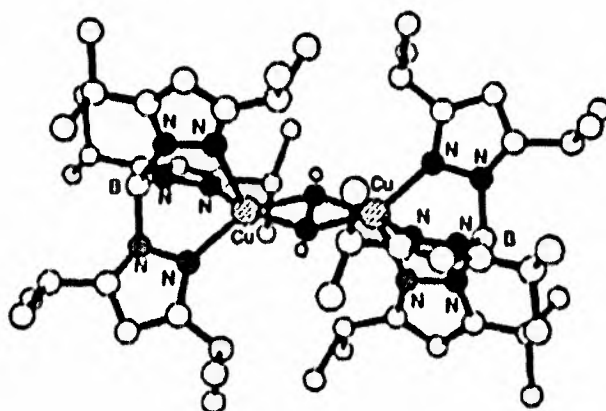
$$\eta_{et} = 1 - (\tau/\tau_0) = [1 + (R/R_0)^6]^{-1}$$

7. The fluorescence lifetime measured from the metastable state $^4F_{3/2}$ of Nd^{3+} ions in the laser crystal $(YGa_3(BO_3)_4)$ is 56 μs . If the quantum efficiency from this state is 0.24, determine the radiative lifetime and the radiative and nonradiative rates. ----- (5 marks)
8. Explain the process upconversion and down conversion with diagrams----- (4 marks)
9. Explain in brief the terms (1) cross relaxation (2) concentration quenching-- (4 marks)
10. Explain the use of a scintillator materials and the mechanism ----- (4 marks)

PART B [15 marks for each. Total= 4 X 15 = 60]

1. (a) Describe MOT of a heterodinuclear molecule NO with the help of diagram. Explain why transition metal is generally bonded to N atom in metal nitrosyl complexes.
(b) It is difficult to assign the oxidation state of metal in metal nitrosyl complexes. Provide a detailed overview.
(c) Cite an example of a transition metal nitrosyl complex that contains $\{FeNO\}^8$, $\{FeNO\}^9$, and $\{FeNO\}^{10}$ core. How they could be differentiated.
2. (a) Show different binding modes of dioxygen in transition metal complexes.
(b) The binding of Fe and $\{O_2\}$ is bent after dioxygen activation by Fe-porphyrine complex. Explain such behavior with qualitative MO & bonding scheme.

(c)



The molecule shown above, does exhibit antiferromagnetic exchange interaction with $J = -203 \text{ cm}^{-1}$. Calculate the energy difference between all the spin states in terms of $k(\text{Kelvin})$. [Note: Derive the energy expression of all the spin states. O-O bond distance is 1.42 angstrom]

(d) TEMPO exhibits an EPR spectrum with a g value of 2.006 when performed in X-band at 9.137GHz. Calculate the field where the resonance would be expected.

(e) The above mentioned molecule exhibits 3 lines hyperfine. Explain in details. Show the hyperfine transitions, explain intensity ratio. Draw the spectrum where the hyperfine coupling constant is 2mT.

3. (a) Describe the MOT of dirhodium tetracetate

(b) Show with plausible mechanism that such compound can lead to both intramolecular & intermolecular C-H amination catalysis.

(c) Describe the MOT of $\{\text{Ru}_2\}^{5+}$ core. Show that such compound is effective in C-H amination.

4. (a) What do you mean by "ZFS". Explain

(b) The $2e^-$ paramagnetic species $\text{VCl}_3(\text{THF})_3$ exhibits two line transitions. Provide your detailed overview. How do you determine an axial ZFS (D) when $E=0$ from the EPR spectroscopy of the above mentioned complex.

(c) How EPR spectroscopy is helpful in determining whether a dinuclear compound with $\{\text{V}_2\}^{9+}$ core is valence delocalized or valence localized. Show all the transitions.

(d) Why do we represent first derivative of absorption instead of absorption in EPR spectroscopy.