PG – 819

Fourth Semester M.Sc. Degree Examination, June 2016
(NS)
CHEMISTRY
C-404 : Spectroscopy – III
(Common to IC/PC/AC)

Time : 3 Hours Max. Marks : 80

***Instruction** : Answer question no. **1** and **any five** of the remaining.*

1. Answer **any ten** of the following : **(10×2=20)**

   a) How many bending and stretching modes are present in a non-linear triatomic molecule ?

   b) The ammine stretching frequencies of the metal complexes are lower than those of the free ammine. Give reasons.

   c) The ^{31}P NMR spectrum of P_4S_3 consists of two peaks with intensity ratios of three to one. Explain with its structure.

   d) What is the energy of electron ejected from a carbon (1s) orbital of binding energy of 294 eV by Al-Kα radiation having photon energy of 1586 eV ?

   e) In tetracyano complexes of divalent Ni, Pd and Pt, the stretching frequency of nickel is expected to be the lowest. Why ?

   f) NQR spectra cannot be obtained for liquids and gases. Justify.

   g) ESR spectra are commonly presented as derivative curves. Why ?

   h) What is Doppler Effect ? Mention its significance.

   i) Distinguish between different oxidation states of tin by Mossbauer spectroscopy.

   j) The ^{19}F NMR spectrum of NF_3 exhibits a sharp single peak at –205 °C but a sharp triplet at +20 °C. Give reasons. (I of ^{14}N = 1).

   k) List the different lasers and their advantages in Raman spectroscopy.

   l) Distinguish between normal and resonance Raman scattering.

2. a) The ^{31}P NMR spectrum of solid phase PCl_5 consists of two sharp peaks, whereas in solution state it has only single peak. Explain.

   b) Predict and interpret the high resolution ^{11}B NMR spectra of B_5H_9 and B_5H_{11}.

   c) Sketch ^{19}F NMR spectra of ClF_3 and BrF_5 and deduce their structures.

(4+4+4=12)

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3. a) Discuss the factors affecting the magnitude of 'g' values in ESR spectroscopy.
   b) Discuss about the EPR spectrum of bis-salicyladimine copper (II) complex.
   c) Draw and explain ESR spectrum of methyl radical. **(5+4+3=12)**

4. a) Explain the terms 'zero-field splitting' and 'Kramer's degeneracy' with examples.
   b) Calculate the energies of all the quadrupolar energy states for a nucleus whose 'I' value is 5/2 in an axially symmetric field. Deduce the transitions in terms of eQq.
   c) Give a comprehensive note on the origin of EXAFS and its applications. **(4+4+4=12)**

5. a) Discuss the Mossbauer spectra of $Fe(CO)_5$, $K_3[Fe(CN)_6]$ and $Na_2[Fe(CN)_5NO]$.
   b) Indicate the changes that occur in the IR spectra of carbonato and thiocyanato groups upon coordination to metal ions. **(6+6=12)**

6. a) Explain the effect of spin-orbit coupling on the photoelectron spectra of CH_3X and HCl.
   b) Sketch the photoelectron spectrum of XeF_2 and explain its main features.
   c) Write a comprehensive note on Koopman's theorem. **(4+4+4=12)**

7. a) Explain how nitro and nitrito coordination can be studied by IR spectroscopy.
   b) Discuss with suitable examples the usefulness of vibrational spectra in the structural elucidation of carbonyl and nitrosyl complexes.
   c) What is Auger effect ? Depict and interpret the Auger spectrum of sulfur in sodium thiosulfate. **(4+4+4=12)**