IV Semester M.Sc. Examination, June 2015
(NS)
CHEMISTRY
C-404 : Spectroscopy – III
(Common to IC/PC/AC)

Time : 3 Hours
Max. Marks : 80

Instruction : *Answer Q. No.* **1** *and* **any five** *of the* **remaining**.

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

   a) How is the possibility of NO_2 being linear ruled out on the basis of IR data ?

   b) The IR spectrum of KrF_2 has bands at 233 and 588 cm^{-1}, the Raman spectrum displays a single band at 499 cm^{-1}. Give the structure of KrF_2.

   c) The C (1s) binding energy is higher in CO_2 than in CO, but the O (1s) binding energy is lower. Account for these observations ?

   d) Obtain an expression for the calculation of energy for the conversion of a molecule into its ion $(M \rightarrow M^+)$ in PES.

   e) Predict and sketch ^{31}P NMR spectrum of $HPO(OH)_2$ and $H_2PO(OH)$ assuming J_{P-OH} to be negligible.

   f) The ^{19}F NMR spectra of equimolar quantities of TiF_6^{2-} and TiF_4 in ethanol shows two peaks with intensity ratio 4 : 1. Explain with its structure.

   g) Calculate the g_1 and g_{11} values for a CuC(1) complex if the resonances occurred at 3214 and 3071 G respectively and for the reference at 3286 G. g value for the reference is 2.0037.

   h) How many ESR lines are expected in the spectrum of $^{\cdot}CD_3$ radical ? What are their relative intensities ?

   i) The Mössbauer spectrum of $Fe(CO)_5$ shows splitting but that of $K_4Fe(CN)_6$ doesn't. Why ?

   j) How many resonances are expected in the NQR spectrum of nuclei with $I = \frac{5}{2}$ when $\eta = 0$? Sketch the energy levels.

   k) The ^{35}Cl e^2Q_9 of KCl and FCl are 0.04 and –146.0 respectively. Account for this variation.

   l) What is the significance of EXAFS ?

2. a) Explain how are the following distinguished using IR spectra :

   i) S– and N– bonded thiocyanate complexes.

   ii) nitro– and nitrite complexes.

   b) What differences in the number of bands and frequencies are expected between C – O absorptions of the following : acetate ion, acetic acid, silver acetate and acetate bound to zinc as a bidentate ligand.

   c) How does the critical absorption edge arise ? Point out its significance.

   (4+5+3=12)

3. a) What is resonance Raman effect ? Discuss the advantages of resonance Raman spectrum over normal Raman spectrum.

   b) How does inverse Raman effect arise ? How does it differ from stimulated Raman effect ?

   c) Sketch the photoelectron spectrum of N_2- molecule and explain the observed pattern. **(5+3+4=12)**

4. a) The photo-ionization of F_2 by He(I) produces F_2^+. Explain why the intensity of $\upsilon = 0 \rightarrow 2$ transition is stronger than that of $0 \rightarrow 0$ transition.

   b) What is Auger process ? What information can be obtained from an Auger spectrum ?

   c) How does a photo acoustic spectrum arise ? Mention any one application. **(5+4+3=12)**

5. a) In the ^{1}H NMR spectral studies of $HIrCl_2(Et_3P)_3$ one isomer shows only one coupling constant (15 Hz) whereas the other isomer shows two coupling constants (19 and 163 Hz). Explain.

   b) What are the possible structures of ClF_3 ? How are these possibilities resolved by using ^{19}F NMR spectrum ? Explain.

   c) Predict the ^{31}P NMR spectra of fac– and mer – $[RhCl_3(PPh_3)_3]$ and explain the patterns. **(4+4+4=12)**

6. a) What is zero-field splitting ? How does it arise ? Explain its consequences in the ESR spectrum of a d^2- ion.

   b) How does anisotropy arise in 'g' values ? Explain.

   c) Calculate the magnetic field at which the resonance occurs if the 'g' value of the benzene radical anion is 2.0025 and the ESR spectrometer is operating at 9302 MHz. ($h = 6.626 \times 10^{-34}$ Js, $\beta = 9.2741 \times 10^{-24}$ J T^{-1}). **(5+4+3=12)**

7. a) How are the following distinguished by Mössbauer spectroscopy ?

   i) $SnCl_2$ and $SnCl_4$

   ii) $K_2[Fe(CN)_5 (NH_3)]$ and $FeCl_3.6H_2O$.

   b) How are recoillers emission and resonant reabsorption of γ-rays achieved in Mössbauer spectroscopy ?

   c) Outline the principles of NQR spectroscopy and explain its importance in distinguishing ionic and covalent bonds. **(4+4+4=12)**

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