2018

CHEMISTRY

CHM 104

SPECTROSCOPY-I

Full Marks : 80

Time: 3 Hours

The figures in the margin indicates full marks for the questions

1. Answer the following questions **2×10=20**

a) Why Raman spectroscopy is preferred over XRD?

b) Explain how Heisenberg's uncertainty principle influences the width of spectral line.

c) The microwave spectrum of a molecule gives two rotational constant. Which type of molecule is it? Explain

d) The carbonyl group stretching vibration gives rise to a strong absorption in the IR region but the absorption due to C=C group in an alkene is normally weak. Why?

e) What is the ground state term symbol of O_2 and H_2?

f) Explain redox spectrum.

g) Why the spectra due to d-d transitions are more intense in case of tetrahedral complexes than octahedral complexes?

h) What are shielding and deshielding in NMR spectroscopy? Discuss with examples.

i) At what range (δ value) the benzene protons can be expected to appear in ^{1}H NMR spectrum and the C=C carbons are expected to appear in ^{13}C NMR spectrum? 1+1

j) How many ^{1}H and ^{13}C NMR signals will be observed from $CH_3CH_2CH_2COCH_2ClCH_2$?

2. Answer the following questions **3×8=24**

a) Find the bond length and energy of rotational spectra in 5th excited state of HI, where the lines are equally spaced and separated by 20.8 cm^{-1}.

b) Calculate the relative population of the 3rd and 4th state of HCl molecules at 298K. [B=2.14 x 10^{-22} J].

c) Explain why heavier species show a smaller separation than a lighter species.

d) What is the effect of solvent on the electronic spectra?

e) Differentiate fluorescence from phosphorescence.

f) An aqueous solution of $[Cr(H_2O)_6]^{3+}$ is pale violet but an aqueous solution of CrO_4^{-2} is bright yellow. Explain this difference.

g) Complexes containing metal-metal bonds are intensely coloured. Rationalize this fact.

3. Answer the following questions **4×9=36**

a) Consider the molecule PCl_5, H_2O, NH_3, $CHCl_3$, CH_2Cl_2, H_2, CO, HF and BF_3.

i. What kind of rotor are they?

ii. Will they show pure rotational spectra?

b) Calculate the force constant for the HCl bond from the fact that the fundamental vibrational frequency is 8.667 X 10^{13} s^{-1} and compare with DCl.

c) State the limitations of Classical Raman spectroscopy.

d) How many vibrational modes are IR active and Raman active for the following molecules?

i. Acetylene

ii. Water

iii. Carbon dioxide

iv. Carbon tetrachloride

e) Molecular shape changes upon electronic excitation. Give evidence.

f) What is Zero field splitting? Write the consequences of it.

g) Explain why benzene protons appear at a downfield compared to those of alkene and acetylene.

h) Draw the hyperfine structure of

ii. Methyl radical.

iii. $VO(acac)_2$

i) Draw the electronic spectrum for

i. $[Ti(H_2O)_6]^{3+}$

ii. $[V(H_2O)_6]^{3+}$

****