PG – 707

II Semester M.Sc. Degree Examination, June 2016
(N.S.) (2010-11 & Onwards)
CHEMISTRY
C – 204 : Spectroscopy – I

Time : 3 Hours Max. Marks : 80

Instruction : *Answer question* ***1*** *and* ***any five*** *of the remaining.*

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

a) A diatomic molecule has a fundamental vibration at 3000 cm^{-1}. Express this energy in Hz, nm and kJ/mole units.

b) Identify the diagnostic symmetry elements and determine the point group symmetry of the following molecules :
   i) BF_3
   ii) $ClBF_2$.

c) What is the point group symmetry of CH_4 ? List the number of rotation axes of different orders in this point group.

d) In the vibration – rotation spectrum of a diatomic molecule, the energy difference between the R_1 and P_2 lines is found to be 16 cm^{-1}. What is the rotational constant of the molecule ?

e) Calculate the dimensions of the following reducible representations :
   i) E_g^2
   ii) $T_{2g} + T_{1u} + A_{1g}$.

f) Calculate the number of normal modes of C_2H_2. How many of these are stretching and how many are bending modes ?

g) The spacing between successive lines in the Rotational Raman spectrum of a diatomic molecule is 12 cm^{-1}. What is the Raman shift of the first stoke line ?

h) State with reasons which among the following molecules would not have a K quantum number :
   i) NH_3 ii) BF_3 iii) CH_3Cl iv) HBFCl

i) The spectroscopic term symbol for the ground state of a diatomic molecule is ${}^3\Delta_2$. Specify the Λ, Σ and Ω values for this state.

j) Give the electronic structure and bond order of O_2 and O_2^+.

k) State the rule of mutual exclusion. Does it apply to a molecule of C_{2h} symmetry ? Give reasons.

l) What do the Mulliken Symbols B_{1g} and A_{2u} signify ?

2. a) A linear molecule AX_2 adopts two different structures of $C_{\infty v}$ and $D_{\infty h}$ symmetries respectively. Sketch the normal modes and predict the number of IR active and Raman active normal modes in each structure.

b) List the diagnostic symmetry elements and obtain the point group symmetry of the following molecules.
i) H_2O ii) NH_3 iii) PCl_3 iv) C_2H_4 v) C_2H_2 vi) $CHCl_3$. **(6+6)**

3. a) Define a cyclic group. From first principles obtain the character table of the pure rotation group C_5.

b) Which point group is obtained if
i) a horizontal plane is added to C_5 and
ii) a horizontal plane and a set of vertical planes are added to C_5. List the complete set of symmetry operations in each case. **(6+6)**

4. a) Obtain an expression for the rotational energy of a symmetric top molecule.

b) Give the selection rules and make a schematic plot of the Rotational Raman spectrum of a symmetric top molecule.

c) A diatomic molecule has a rotational constant 1 cm^{-1}. What is the intensity of the $J = 5 \rightarrow J = 6$ transition, relative to that of the $J = 4 \rightarrow J = 5$ transition ? **(4+5+3)**

5. a) Describe the vibrations of a polyatomic molecule using normal coordinates and predict the various possible vibrational transitions.

b) For a linear molecule, plot schematically the orientation of the orbital angular momentum vector of the $l = 2$ state corresponding to the σ, π and δ molecular. orbitals. **(6+6)**

6. a) Give the electronic structure and the term symbol for the ground state and first three excited states of singlet H_2 and predict its electronic absorption spectrum.

   b) The equilibrium vibration frequency of HCl is 2990 cm^{-1} and the anharmonicity constant is 0.0174. Calculate the vibrational quantum number at the dissociation limit. From this, evaluate D_e and D_o in kJ/mole. **(6+6)**

7. a) Write the expression for the probability of $\psi_l \rightarrow \psi_m$ transition and explain all the terms (do not derive).

   b) In a certain molecule both initial and ground states transform according to the irreducible representation E_g, and the dipole moment operator is totally symmetric (A_{1g}). Explain whether the transition is symmetry allowed or for- bidden with reasons.

   c) In (b) above, how does the result change if the dipole moment operator is of E_u symmetry ? **(4+6+2)**