PG – 360

II Semester M.Sc. Examination, June 2015
(CBCS)
CHEMISTRY
C204 : Spectroscopy – I

Time : 3 Hours | Max. Marks : 70

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

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

   a) A molecule has two mutually perpendicular planes of reflection. What is the axis lying on the line of intersection of the two planes ?

   b) Identify the point group symmetry of trans-ML_4X_2. List the complete set of operations of this point group.

   c) For a diatomic molecule, make a schematic plot of the axial components of the orbital angular momentum vector with $l = 2$. What are the symbols used to represent the MOs generated by these axial components of $\vec{l}$?

   d) Obtain the possible term symbols for a diatomic molecule having the configuration $(\pi)(\delta)$.

   e) CO_2 belongs to the point group $D_{\infty h}$ and N_2O has $C_{\infty v}$ symmetry. Explain with reasons, which of these obeys the rule of mutual exclusion in their vibration spectra.

   f) The energy difference between the first stoke and the first anti-stoke line in the pure rotational Raman spectrum of a diatomic molecule is 24 cm^{-1}. What is the B value ?

   g) Schematically sketch the bending modes of linear AB_2 molecule. What happens to these modes when AB_2 is bent ?

   h) Plot schematically the potential energy curve of a diatomic molecule. Compare it with the harmonic potential and indicate the limits where the two do not match.

i) Consider two diatomic molecules X_2 and Y_2. The equilibrium bond length of X_2^+ is shorter than the equilibrium bond length X_2. In the other, both Y_2 and Y_2^+ have the same equilibrium bond length. What do you conclude about the nature of the HOMO in X_2 and Y_2 ?

j) Write any one form of an anharmonic potential for a diatomic molecule and explain all the terms.

k) A symmetric top has the rotational constants A=C=1 ; B=3. On distortion C varies gradually until A=1 and B=C=3. Identify the prolate and oblate limits. What is the nature of the top in the intermediate value A=1, B=2 and C=3 ?

l) A molecule vibrates with a frequency of 1000 cm^{-1}. Express this energy in kJ/mole.

2. a) The spacing between the successive lines in the microwave spectrum of CO is 3.84235 cm^{-1}. Obtain the bond length of CO. ($h = 6.626 \times 10^{-34}$ Js ; $c = 3 \times 10^{10}$ m s^{-1} ; $m_H = 1.67 \times 10^{-27}$ kgs).

b) Write the expression for the rotational energy of

i) a rigid symmetric top and

ii) the non-rigid symmetric top.

Make schematic plots of the microwave spectra of the two by giving the selection rules. **(5+5)**

3. a) The fundamental and first overtone transitions of $^{14}N^{16}O$ appear at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Evaluate the equilibrium vibration frequency, the anharmonicity constant and the zero point energy. What is the value of the vibrational quantum number at the dissociation limit ?

b) Define the parallel and perpendicular vibrational modes of a polyatomic molecule. Obtain the energies of the vibration-rotation transitions of the perpendicular mode of symmetric top and plot the schematic spectrum. **(5+5)**

4. Consider a molecule with C_{3v} symmetry. Consider the transitions :

i) $a_1 \leftrightarrow a_2$

ii) $a_1 \leftrightarrow e$

iii) $a_2 \leftrightarrow e$ and

iv) $e \leftrightarrow e$.

Which of these transitions are allowed when

a) the dipole moment changes along z and

b) the dipole changes in the x-y plane ?

Given below is the character table for C_{3v}. **10**

	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	–1	
E	2	–1	0	(x, y)

5. a) Draw the localized MOs of HCHO and obtain the energy level diagram. Give the electronic configuration of the ground state and three excited states of HCHO.

   b) Based on the character table of the C_{2v} point group given below, obtain the symmetries of the ground state and three excited states of HCHO and predict the allowed transitions. **(5+5)**

C_{2v}	E	C_2	σ_v	σ'_v (molecular plane)	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y

6. a) Draw the structures of

   i) trans-planar H_2O_2,

   ii) cis-planar H_2O_2 and

   iii) trans non-planar H_2O_2

   In each case determine the point group symmetry and make a complete list of the operations in each of the respective point group.

   b) State the great orthogonality theorem and give its applications. **(5+5)**

7. a) A diatomic molecule AB and its excited state (AB)* have the same equilibrium bond length. Make a schematic plot of its vibrational coarse structure.

   b) Draw the MO diagram of H_2. Give the electron configuration of the ground state and first three excited states of singlet H_2 and obtain the corresponding term symbols. **(4+6)**

8. a) Describe the classical theory of Raman effect.

   b) Explain the origin of O and S branches in the vibration-rotation Raman spectrum of a diatomic molecule. **(4+6)**
