II Semester M.Sc. Degree Examination, July 2017
(Repeaters) (NS – 2010 – 11 Scheme)
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) Which of the following molecules would not show any rotational spectrum on irradiation by microwaves ? Give reasons.

      i) HF   ii) CO   iii) CO_2 iv) OCS

   b) What is the point group symmetry of BF_3 ? What would the point group symmetry of $BClF_2$ be ?

   c) A molecule AX_2 has three normal modes, while BX_2 has four normal modes. Suggest their possible structures.

   d) The R_0 and P_1 lines in the vibration-rotation spectrum of a diatomic molecule are separated by 8 cm^{-1}. What is the energy difference in cm^{-1} between the R_1 and P_2 lines in the same spectrum.

   e) Of the following direct product representations in O_h, pick those which contain A_{1g} as one of their components. Give reasons.

      i) $T_{2g} T_{1u}$ ii) $T_{2g}E_g$ iii) E_g^2 iv) T_{1u}^2

      v) $T_{2g}E_g$

   f) List the complete set of symmetry operations included in the point group D_{4h}. What is the order of this group ?

   g) For a diatomic molecule, make a schematic plot of the surface harmonics Y_0^0 and Y_1^0 and indicate their symmetry.

   h) For the molecule CO_2, indicate the normal mode that would be the strongest in the vibrational Raman spectrum. Give reasons.

i) Make a schematic plot of the wave function $\psi_v (v = 5)$ for a harmonic oscillator. Compare it with that of an anharmonic oscillator.

j) Make a schematic plot of the vibration-rotation spectrum of a diatomic molecule as the breakdown of the Born-Oppenheimer approximation.

k) C_2H_4 is a planar molecule (point group symmetry, D_{2h}). What is the structure of the ethylene diradical $\dot{C}H_2 - \dot{C}H_2$ and its point group symmetry ?

l) Suggest a method for studying the vibration spectrum of N_2. Give reasons.

2. a) Determine the point group symmetries of the following molecules :

   i) Chlorobenzene
   ii) O-dichlorobenzene
   iii) p-dichlorobenzene
   iv) 1, 3, 5- trichlorobenzene.

   b) Obtain the character table for the point group, C_{2h} and assign the Mulliken symbols to all the irreducible representations.

   c) If a σ_v is added to C_{2h}, what is the resultant point group ?   **(4+6+2)**

3. a) The spacing between successive lines in the microwave spectrum of CO is 3.84235 cm^{-1}. Calculate its rotational constant, moment of inertia and bond length. What is the expected spacing between successive lines in $^{13}C^{18}O$? (h $= 6.626 \times 10^{-34}$Js; N $= 6.023 \times 10^{23}$)

   b) Make a schematic drawing of the energy level diagram of an oblate symmetric top.

   c) How does the spectrum of a rigid symmetric top differ from that of a non-rigid symmetric top ?   **(6+2+4)**

4. a) Write the energy expression, draw the energy level diagram and the wave functions, give the selection rules and make a schematic plot of the vibration spectrum of a harmonic oscillator.

   b) Use perturbation theory to obtain the selection rules of an anharmonic oscillator and make a schematic plot of its vibration spectrum.

   c) Find the number of normal modes in C_2H_2. How many of these are stretching and how many bending modes ?   **(4+6+2)**

5. a) Consider a linear molecule, for l = 1, plot schematically, the orientation of the orbital angular momentum vector corresponding to the σ and π states.

   b) Obtain the spectroscopic term symbols corresponding to the $(\pi)'(\delta)'$ electronic configuration for a diatomic molecule in the triplet state. **(6+6)**

6. a) Define parallel and perpendicular vibrations for a polyatomic molecule.

   b) Consider a bent molecule AX_2. Make a schematic drawing of its normal modes and classify them as parallel and perpendicular.

   c) Obtain the vibration-rotation contours for the perpendicular of AX_2. **(2+4+6)**

7. The Character table of the C_{3v} point group is given below :

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	
E	2	−1	0	(x, y)

Find which of the following transitions is forbidden

   i) $a_1 \leftrightarrow a_1$ ii) $a_1 \leftrightarrow e$

   iii) $a_2 \leftrightarrow e$ iv) $a_1 \leftrightarrow a_2$ **12**

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