PG – 230

II Semester M.Sc. Degree Examination, June/July 2014
(NS) (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) Prove that in BF_3 molecule $C_3\sigma_v \neq \sigma_v C_3$.

b) Using the general matrix representation for $C_n(z)$. Write the matrix representations for C_3 and C_4 operation.

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

d) A molecule absorbs a photon of frequency 3×10^{10} Hz. Convert this frequency into wave number, wavelength and energy (J/mole) units.

e) Make a schematic plot of the rotational wave functions $Y_J^M (J = 0, 1, 2)$ a rigid diatomic molecule and classify them according to their symmetrics.

f) The rotational constant for $H^{35}Cl$ is observed to be 10.5909 cm^{-1}. What are values of B for $H^{37}Cl$ and for $^2D^{35}Cl$?

g) Given a dipole moment operator, F, which is symmetric (g), determine the transitions for which $\int \psi_1^* F \psi_2 d\tau$ remain nonzero.

h) Some of the vibration rotation bonds in the spectrum of a molecule, XYZ have no intensity at the band centre. In case of another molecules ABC all bands have absorptions at the band centre. Deduce their structures with reason.

i) Write the electronic structure of O_2. Calculate the bond order of O_2 and O_2^+.

j) How do you distinguish phosphorescence, fluorescence and Raman scattering from each other ?

k) Plot schematically the time domain signals from two spectral lines having the same frequency but different widths.

l) Define the term polarizability and depict the polarizability ellipsoid for H_2O molecule.

2. a) List the diagnostic symmetry elements and obtain the point group symmetry of the following molecules :

   i) NH_3 ii) H_2O iii) PCl_3

   iv) C_2H_4 v) C_2H_2 vi) $CHCl_3$

   b) A linear molecule AX_2 adopts two different structures of $C_{\infty v}$ and $D_{\infty b}$ symmetrics respectively. Sketch the normal modes and predict the number of IR active and Raman active normal modes in each structure. **(6+6)**

3. a) Applying the principles of symmetry, derive the Orthonormalization conditions of wave function.

   b) Using pertubation theory, obtain the selection rules governing the vibrational transitions of an anharmonic oscillator. **(6+6=12)**

4. a) The absorption spectrum of O_2 shows vibrational structure with a continuum at 56,876 cm^{-1}; the upper electronic state dissociates into one ground state atom and one excited atom (excitation energy measured from atomic spectrum is 15,875 cm^{-1}). Estimate the dissociation energy in KJ mole.
   (N = 6.023×10^{23}, h = 6.626×10^{-34}Js : C = 3×10^{8} ms^{-1}.)

   b) State and explain the selection rules for the electronic transition.

   c) Explain the importance of Frank-Condon principle for explaining the intensities of vibrational structures. **(4+4+4=12)**

5. a) Using classical mechanics obtain the centrifugal distortion constant for a diatomic rotor.

   b) Write the selection rules and make schematic plots of the vibration-rotation spectra of the parallel and perpendicular vibrations of symmetric top molecules. **(6+6=12)**

6. a) The NO_3^- ion belongs to D_{3h} symmetry. Obtain the number of IR allowed. (and their symmetries) and Raman allowed (their polarization) lines in its vibrational spectrum.

b) A_2H_2 has IR and Raman lines as in the following table.

Cm^{-1}	IR	Raman
3374	–	S (Pol)
3287	PR(s)	–
1973	–	VS (Pol)
729	PQR(s)	–
612	–	W (depol)

Give the structure of A_2H_2 and assign the lines. **(6+6=12)**

7. a) Illustrate on a Jablonski diagram the various photophysical pathways for the decay of excited states and comment an their characteristics features.

b) What is unharmonicity constant ? How does it affect the spectral lines in an IR spectrum ? **(6+6=12)**