PG – 180

Second Semester M.Sc. Degree Examination, July 2017
(CBCS Scheme)
CHEMISTRY
C-204 : Spectroscopy – I

Time : 3 Hours Max. Marks : 70

***Instruction** : Answer question no. **1** and **any five** of the remaining.*

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

   a) Define the terms; axis of symmetry and centre of symmetry.

   b) Why do CO_2 and SO_2 molecules belong to different point groups ?

   c) Assign the Mulliken symbols for the following irreducible representations with justification.

	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_1	1	1	1	–1	–1
Γ_2	1	–1	1	1	–1

   d) Microwave spectra are difficult to be observed in solids and liquids. Why ?

   e) Calculate the normal modes for NO_2 and N_2O. How many stretching and bending modes are present in each of these molecules ?

   f) Is the electronic transitions between two π-orbitals allowed ? Justify your choice.

   g) Distinguish between harmonic and anharmonic oscillators with the help of their potential energy curves.

   h) Give the meaning of polarizability and depict the polarizability ellipsoid for $CHCl_3$.

   i) When a particular molecule is irradiated with Ar-laser of wavelength 514.5 nm, one of the Raman lines appears at 564.8 nm. Calculate the wave number of vibration band.

   j) How do the functions X, Y, Z transform in the point group C_{2v} ? Mention their irreducible representations.

   k) State the terms fluorescence and phosphorescence using a sketch of the energy diagram.

   l) Distinguish between overtones and combination bands.

2. a) How many irreducible representations are possible for water molecule ? Show that character systems for C_{2v} obey the properties of irreducible representations.

   b) Using the following character table, find the direct products and their irreducible components for $T_1 \times T_2$, $E \times T_1$ and $E \times E$.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	–1	–1
E	2	–1	2	0	0
T_1	3	0	–1	1	–1
T_2	3	0	–1	–1	1

(4+6=10)

3. a) Identify the symmetry elements and operations and assign the appropriate point groups for B_2H_6, $XeOF_4$ and XeF_4.

   b) Write the matrix representations of the operations of C_{2h} – point group.

   c) What is stark effect ? How does it affect the $J = 1 \rightarrow J = 2$ line in the rotational spectrum of a diatomic molecule ? **(3+3+4=10)**

4. a) Explain the effect of isotopic substitution on the rotation spectrum of carbon monoxide.

   b) Write a short note on fortrat parabolae.

   c) Explain the selection rules for symmetry and spin-forbidden transitions. **(3+3+4=10)**

5. a) How does the break down of the Born-Oppenheimer approximation affect the P and R branch lines of vibration-rotation spectrum of a diatomic molecule ?

   b) The spacing between two consecutive S-branch lines of the rotational Raman spectrum of hydrogen gas is found to be 243.2 cm^{-1}. Calculate bond length of hydrogen. (Given $h = 6.6 \times 10^{-34}$ Js, $C = 3 \times 10^{8}$ ms^{-1} and mass of H-atom $= 1.673 \times 10^{-27}$ kg). **(5+5=10)**

6. a) Explain the differences in the intensities of the Stoke's and anti-Stoke's lines in vibrational Raman spectra.

   b) State the Franck-Condon principle. How does it help in explaining the intensities of vibrational structures ? **(4+6=10)**

7. a) The force constant of CO is 1840 Nm^{-1}. Calculate oscillation frequency and wave number in cm^{-1}.

   b) Discuss briefly on vibration-rotation spectra of linear polyatomic molecule. **(4+6=10)**

8. a) Sketch schematically the normal modes of AB_3-planar molecule and comment on their IR and Raman activity.

   b) Write brief notes on :

   Mutual exclusion principle, Fermi resonance and internal conversion. **(4+6=10)**