Q.P. Code : 60764

Second Semester M.Sc. Degree Examination, July 2019

(CBCS Scheme)

Chemistry

Paper C 204 – SPECTROSCOPY – I

Time : 3 Hours]   [Max. Marks : 70

Instructions to Candidates : Answer Question No. 1 and any FIVE of the remaining.

1.   Answer any **TEN** of the following questions : $(10 \times 2 = 20)$

(a)   Give any four examples of tetrahedral molecules that do not belong to Td (tetrahedral) symmetry.

(b)   Define transition moment integral and give its significance.

(c)   Represent the different vibration modes of CO_2 molecule and indicate their IR activity.

(d)   Find out the point group symmetry of the molecules

    (i) PCl_3

    (ii) PCl_5

(e)   An irreducible representation of the following character is given

	E	Cn	σd	i	σh
Γ^V	1	-1	1	-1	1

find its Mulliken symbol.

(f)   State and explain the Laporte rule for electronic transitions.

(g)   What does the symbol $^3\sum_g^+$ signify?

(h)   Spherical molecule is not microwave active. Explain.

(i)   State the law of mutual exclusion.

(j)   How do you distinguish fluorescence, phosphorescence and Raman scattering?

(k)   Using the general matrix representation for C_n write the matrix representation for C_3 and C_4 operation.

(l)   Under what conditions will the P and R branches show a band head in the rotational fine structure of an electronic spectrum?

2. (a) Derive the matrix corresponding to proper axis of rotation.

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

    (c) List the symmetry elements and assign the point groups for :

        (i)   ortho - and para - dichloro benzene

        (ii) eclipsed - and staggered ethane   (3 + 3 + 4)

3. (a) Discuss the construction of character table for NH_3 molecule.

    (b) Explain the effect of isotopic substitution in microwave spectroscopy with proper examples.   (5 + 5)

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

    (b) Calculate the intensity of the anti-stoke line in the rotational Raman spectrum relative to the intensity of the stoke line at 300 K when $\overline{W}_0 = 300$ cm^{-1} (Given K $= 1.38 \times 10^{-23}$ JK^{-1})   (5 + 5)

5. (a) Explain the quantum theory of Raman effect.

    (b) Write a note on polarization of Raman scattered photons.

    (c) Give the selection rules and make a schematic plot of the vibration-rotation IR spectrum of a perpendicular mode of symmetric top molecule.
                                                                                   (3 + 3 + 4)

6. (a) Describe the vibration-rotation Raman spectrum of a diatomic molecules and make a schematic plot of the spectrum.

    (b) Give the quantum mechanical basis of the Franck Condon principle.
                                                                                   (5 + 5)

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

    (b) Distinguish between dissociation energies D_0 and D_0'. How can they be estimated?   (5 + 5)

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

    (b) The fundamental and first overtone transitions of $^{15}N\,^{16}O$ are observed at 1876.1 cm^{-1} and 3724.2 cm^{-1} respectively. Calculate the equilibrium vibration frequency, the unharmonicity constant and zero point energy.
                                                                                   (6 + 4)