

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 × 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 CO₂ molecule and indicate their IR activity.
- (d) Find out the point group symmetry of the molecules
 - (i) PCl₃
 - (ii) PCl₅
- (e) An irreducible representation of the following character is given

	E	C _n	σ _d	i	σ _h
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 ${}^3\Sigma_g^+$ 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 C₃ and C₄ operation.
- l) Under what conditions will the P and R branches show a band head in the rotational fine structure of an electronic spectrum?

Q.P. Code : 60764

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 $\bar{W}_0 = 300 \text{ cm}^{-1}$ (Given $K = 1.38 \times 10^{-23} \text{ JK}^{-1}$) (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 $^{14}N^{16}O$ 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)