B.M.S. COLLEGE FOR WOMEN, AUTONOMOUS
BENGALURU – 560004
SEMESTER END EXAMINATION – SEPT/OCT 2023

M.Sc. in Chemistry – 2ⁿᵈ Semester

MOLECULAR SPECTROSCOPY

Course Code: MCH204T   **QP Code: 12010**
Duration: 3 Hours   **Max. Marks: 70**

Instruction: Answer Question No. 1 and any FIVE of the remaining.

1. **Answer any *TEN* questions.**   **(2X10=20)**
    a) State improper axis of symmetry with an example?
    b) Assign the point groups of
       i) cis-1,2-dichloroethylene ii) ortho-dibromobenzene
    c) Write transition moment integral.
    d) How does isotopic substitution affect the rotational constant value?
    e) What is zero point energy? Explain.
    f) A pure rotational spectrum is not obtained for CO_2 but CO is microwave active. Justify
    g) What are the advantages of FT-IR?
    h) The rotational constant for $^{12}C^{16}O$ is observed to be 1.92118 cm^{-1}. What is the value of B
       for $^{13}C^{16}O$?
    i) State mutual exclusion principle.
    j) The odd even classification of orbitals does not arise in heteronuclear diatomic molecules.
       Why?
    k) The spectroscopic term symbol for the round state of a diatomic molecule is $^3\Delta_2$. Specify
       the Λ, Σ and Ω values for this state.
    l) Define the terms vibrational relaxation and internal conversion.

2. a) Construct the group multiplication table for the symmetry operations of ammonia
      molecule?
   b) Deduce the matrix representation for the rotation of a vector with respect to Z-axis and
      evaluate the matrix for C_2 and C_3 operations.   **(5+5=10)**

3. a) Define symmetric top molecule. Obtain an expression for the rotational energy of a rigid
      symmetric top molecule.
   b) Give the selection rules and make a schematic plot of the vibration-rotation IR spectrum
      of a perpendicular mode of symmetric top molecules.   **(5+5=10)**

4. a) The fundamental and first overtone transitions of $^{14}N^{16}O$ are observed at 1876.1cm^{-1} and
      3724.2 cm^{-1} respectively. Calculate the equilibrium vibration frequency,
      anharmonicity constant and zero point energy.
    b) Discuss in detail the use of IR and Raman spectroscopic techniques in the structural
       elucidation of AX_2 molecules   **(5+5=10)**

5. a) Explain the selection rules for the electronic transition of diatomic molecule and indicate which among the following transition are optically allowed or forbidden. Give reason?

(i) $^1\Pi_g \rightarrow \, ^1\Pi_u$ (ii) $^4\Sigma_u^+ \leftrightarrow \, ^2\Sigma_u^+$ (iii) $^1\Delta_u \leftrightarrow \, ^1\Sigma_g^+$

b) Depict the electronic configuration of the ground and excited states of HCHO molecule. Explain the electronic transitions involved in it.   **(5+5=10)**

6. a) List all the symmetry operations generated by S_3 and S_4 axes.

b) Write the flow chart for the classification of point groups of molecules.

c) How does the breakdown of the Born-Oppenheimer approximation affect the P and R branch in the vibration –rotation spectrum of a diatomic molecule?   **(4+3+3=10)**

7. a) Depict the normal modes of XY_2 linear and non-linear type molecules and explain their IR activity.

b) Write a brief notes on parallel and perpendicular vibration

c) Define polarizability? Draw schematically the polarizability ellipsoid of CO_2

(4+3+3=10)

8. a) How does the Franck Condon principle help in explaining the intensities of vibrational structure?

b) Write the expression for fortrat parabola and for the band head appearing in the R-branch

c) Define a sub-group. How it differs from cyclic group? Explain with an example.

(4+3+3=10)

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