Registration Number:

Date & session:

ST. JOSEPH'S UNIVERSITY, BENGALURU - 27
M.Sc (CHEMISTRY) – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2023
(Examination conducted in November/December 2023)

CH 7422 – SPECTROSCOPY - I
(For current batch students only)

Time: 2 Hours **Max Marks: 50**

This paper contains THREE printed pages and THREE parts.
All parts of the question paper are compulsory. The character tables are provided at the end of the question paper.

Some useful constants: h = 6.626 x 10^{-34} Js ; k = 1.381x10^{-23}J/K ; c = 2.998 x 10^{10} cm/s; 1 amu = 1.66x10^{-27} kg; 1 cm^{-1} = 11.958 J/mol.

PART-A

Answer any **EIGHT** of the following questions. Each question carries **TWO** marks. [8×2 = 16]

1. Which point group does HCN belong to?
2. Explain fluorescence.
3. What are irreducible representations? Give an example.
4. Draw the two orientations for a carbon dioxide molecule which has i) maximum and ii) minimum polarizability.
5. Using a *trans*-dichloroethene prove S_2=i.
6. Calculate the energy of the rotational energy level, J=7, in cm^{-1}.
7. Calculate the number of fundamental modes of vibration of SO_2. How many bands will be observed corresponding to these vibrations in the IR spectrum of the molecule?
8. The line spacing in P and R branches of acetylene molecule is found to be 4B instead of 2B. Justify.
9. Intensity of first overtone is weaker than the fundamental vibration. Give reason.
10. Illustrate any two ways by which electronic transitions can lead to dissociation using Morse potential energy curve.

PART-B

Answer any **TWO** of the following questions. Each question carries **TWELVE** marks. [2×12 = 24]

11. a) Show that the characters of the various irreducible representation of C_{2v} point group obey the corollaries of GOT.
    b) What is plane of symmetry? Explain vertical plane, horizontal plane and dihedral plane with an example for each. **(6+6)**

12. a) Sketch the polarizability ellipsoids of H_2O molecule in vibrational Raman spectroscopy. Indicate the Raman activity of the different modes of vibration.
    b) Draw the energy level diagram for a linear polyatomic molecule undergoing perpendicular vibrations. State the selection rules and obtain an expression for $\Delta\varepsilon$ (cm^{-1}) in the Q branch. **(6+6)**

13. a) Give the energy expression for a non-rigid diatomic rotor in cm^{-1}. Outline the changes in rotational energy levels and the spectrum as the molecule changes from rigid to non-rigid rotor.
    b) Estimate equilibrium vibration frequency and anharmonicity constant of $^{35}Cl^{19}F$ given that the fundamental and first overtone are 773.3 and 1535.3 cm^{-1}, respectively.
    c) Based on Franck-Condon principle, draw the potential energy diagram and account for the intensities of vibrational – electronic spectral lines when
    i) internuclear distances are equal in upper and lower states
    ii) upper state internuclear distance is little greater than that in the lower state. **(4+4+4)**

PART-C

Answer any **TWO** of the following questions. Each question carries **FIVE** marks. [2×5 = 10]

14. a) Methane molecule belongs to T_d point group. The character table for T_d is provided at the end of this paper.
        i) What are the representations corresponding to Raman modes of vibration?
        ii) Are any modes of Raman degenerate in energy?
    b) Calculate the most intense spectral line of a rigid diatomic rotor having a series of equidistant lines spaced 41.106 cm^{-1} apart, at 45° C. **(2+3)**

15. Calculate the energy (in cm^{-1}) of the photon absorbed when CO molecule transits from the state v=0, J''=0 to v=1, J'=1. Assume that v=0 and v=1 states have same B values. Given that the equilibrium vibration frequency = 1731 cm^{-1}, anharmonicity constant = 0.00733, bond length = 0.1131 nm, m_C = 12 amu and m_O = 15.99 amu.

16. a) What will be the Mulliken symbol for the bonding molecular orbital (p_x) of ethylene in the ground state with one electron in it? Illustrate that C_2^z, C_2^y and C_2^x are anti-symmetric, anti-symmetric and symmetric, respectively for this Mulliken symbol. (Ethylene belongs to D_{2h} point group.)
    b) Justify d_{zx} and d_{x2-y2} belong to B_1 and A_1, respectively in a C_{2v} character table. **(3+2)**

**********End of questions**********

Character Tables

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

D_{2h}	E	$C_2^{(z)}$	$C_2^{(y)}$	$C_2^{(x)}$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		($2z^2- x^2 - y^2$, x^2-y^2)
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

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